

CRYSTAL14

User's Manual

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Introduction

The CRYSTAL package performs *ab initio* calculations of the ground state energy, energy gradient, electronic wave function and properties of periodic systems. Hartree-Fock or Kohn-Sham Hamiltonians (that adopt an Exchange-Correlation potential following the postulates of Density-Functional theory) can be used. Systems periodic in 0 (molecules, 0D), 1 (polymers, 1D), 2 (slabs, 2D), and 3 dimensions (crystals, 3D) are treated on an equal footing. In each case the fundamental approximation made is the expansion of the single particle wave functions ('Crystalline Orbital', CO) as a linear combination of Bloch functions (BF) defined in terms of local functions (hereafter indicated as 'Atomic Orbitals', AOs). See Chapter 13.

The local functions are, in turn, linear combinations of Gaussian type functions (GTF) whose exponents and coefficients are defined by input (section 1.2). Functions of symmetry s , p , d and f can be used (see page 22). Also available are sp shells (s and p shells, sharing the same set of exponents). The use of sp shells can give rise to considerable savings in CPU time.

The program can automatically handle space symmetry: 230 space groups, 80 layer groups, 99 rod groups, 45 point groups are available (Appendix A). In the case of polymers it can treat helical structures (translation followed by a rotation around the periodic axis).

Point symmetries *compatible with translation symmetry* are provided for molecules.

Input tools allow the generation of slabs (2D system) or clusters (0D system) from a 3D crystalline structure, the elastic distortion of the lattice, the creation of a super-cell with a defect and a large variety of structure editing. See Section 2.1

Specific input options allow generation of special 1D (nanotubes) and 0D (fullerenes) structures from 2D ones.

Previous releases of the software in 1988 (CRYSTAL88, [49]), 1992 (CRYSTAL92, [52]), 1996 (CRYSTAL95, [53]), 1998 (CRYSTAL98, [156]), 2003 (CRYSTAL03, [157]), 2006 (CRYSTAL06, [55]) and 2010 (CRYSTAL09, [54]) have been used in a wide variety of research with notable applications in studies of stability of minerals, oxide surface chemistry, and defects in ionic materials. See "Applications" in

<http://www.crystal.unito.it>

The CRYSTAL package has been developed over a number of years. For basic theory and algorithms see "Theory" in:

<http://www.crystal.unito.it/theorframe.html>

The required citation for this work is:

R. Dovesi, V.R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civaleri, K. Doll, N.M. Harrison, I.J. Bush, Ph. D'Arco, M. Llunell, M. Causà, Y. Noël
CRYSTAL14 User's Manual, University of Torino, Torino, 2014

CRYSTAL14 output will display the references relevant to the property computed, when citation is required.

Updated information on the CRYSTAL code as well as tutorials to learn basic and advanced CRYSTAL usage are in:

<http://www.crystal.unito.it/news.html>

CRYSTAL14 Program Features

New features with respect to CRYSTAL09 are in *italics*.

Hamiltonian

- **Hartree-Fock Theory**
 - Restricted
 - Unrestricted
- **Density Functional Theory**
 - Semilocal functionals: local [L], gradient-corrected [G] and *meta-GGA (tau-dependent* [T]
 - Hybrid HF-DFT functionals
 - * Global Hybrids: B3PW, B3LYP (using the VWN5 functional), PBE0, PBESOL0, B1WC, WC1LYP, B97H
 - * *Range-Separated Hybrids*:
 - *Screened-Coulomb (SC)*: HSE06, HSEsol
 - *Middle-range Corrected (MC)*: HISS
 - *Long-range Corrected (LC)*: LC- ω PBE, LC- ω PBEsol, ω B97, ω B97-X, RSHXLDA
 - *Minnesota semilocal and hybrid functionals (mGGA)*:
 - * *M05 family*: M05, M05-2X
 - * *M06 family*: M06, M06-2X, M06-HF, M06-L
 - *Double Hybrid functionals*: B2-PLYP, B2GP-PLYP, mPW2-PLYP
 - User-defined hybrid functionals
- Numerical-grid based numerical quadrature scheme
- London-type empirical correction for dispersion interactions (DFT-D2 scheme)

Energy derivatives

- **Analytical first derivatives with respect to the nuclear coordinates and cell parameters**
 - Hartree-Fock and Density Functional methods
 - All-electron and Effective Core Potentials
- *Analytical derivatives, up to fourth order, with respect to an applied electric field (CPHF/CPKS)*
 - *Dielectric tensor*
 - *(Hyper)-polarizabilities*

Type of calculation

- **Single-point energy calculation**
- **Geometry optimizations**
 - Uses a quasi-Newton algorithm
 - Optimizes in symmetry-adapted cartesian coordinates

- Optimizes in redundant coordinates
 - * *New internal coordinates handling and algorithm for back-transformation*
- Full geometry optimization (cell parameters and atom coordinates)
- Freezes atoms during optimization
- Constant volume or pressure constrained geometry optimization (3D only/ i_i)
- Transition state search
- **Harmonic vibrational frequencies**
 - Harmonic vibrational frequencies at Gamma point
 - Phonon dispersion using a direct approach (efficient supercell scheme)
 - *Phonon band structure and DOSs*
 - *Calculation of Atomic Displacement Parameters and Debye-Waller factors*
 - IR intensities through localized Wannier functions and Berry phase
 - *IR and Raman intensities through CPHF/CPKS analytical approach*
 - *Simulated reflectance, IR and Raman spectra*
 - Exploration of the energy and geometry along selected normal modes
- **Anharmonic frequencies for X-H bonds**
- *Automated calculation of the elastic tensor of crystalline systems*
 - *Generalized to 1D and 2D systems*
 - *Calculation of directional seismic wave velocities*
 - *Calculation of isotropic polycrystalline aggregates elastic properties via Voigt-Reuss-Hill scheme*
- **Automated E vs V calculation for Equation of State (3D only)**
 - *New EoSs: Vinet, Poirer-Tarantola and polynomial*
 - *Automated calculation of pressure dependence of volume and bulk modulus*
- *Automated calculation of piezoelectric and photoelastic tensors*
 - *Direct and converse piezoelectricity (using the Berry phase approach)*
 - *Elasto-optic tensor through the CPHF/CPKS scheme*
 - *Electric field frequency dependence of photoelastic properties*
- *Improved tools to model solid solutions*
 - *Generation of configurations*
 - *Automated algorithm for computing the energy (with or without geometry optimization) of selected configurations*

Basis set

- **Gaussian type functions basis sets**
 - s, p, d, and *f* GTFs
 - Standard Pople Basis Sets
 - * STO-nG n=2-6 (H-Xe), 3-21G (H-Xe), 6-21G (H-Ar)
 - * polarization and diffuse function extensions
 - *Internal library of basis sets with simplified input*

- User-specified basis sets supported

- **Pseudopotential Basis Sets**

- Available sets are:
 - * Hay-Wadt large core
 - * Hay-Wadt small core
- User-defined pseudopotential basis sets supported

Periodic systems

- **Periodicity**

- Consistent treatment of all periodic systems
- 3D - Crystalline solids (230 space groups)
- 2D - Films and surfaces (80 layer groups)
- 1D - Polymers
 - * space group derived symmetry (75 rod groups)
 - * helical symmetry (up to order 48)
- 1D - *Nanotubes (with any number of symmetry operators)*
- 0D - Molecules (32 point groups)

- **Automated geometry editing**

- 3D to 2D - slab parallel to a selected crystalline face (hkl)
- 3D to 0D - cluster from a perfect crystal (H saturated)
- 3D to 0D - extraction of molecules from a molecular crystal
- 3D to n3D - supercell creation
- 2D to 1D - building nanotubes from a single-layer slab model
- 2D to 0D - *building fullerenes from a single-layer slab model*
- 3D to 1D, 0D - *building nanorods and nanoparticles from a perfect crystal*
- 2D to 0D - *construction of Wulff's polyhedron from surface energies*
- Several geometry manipulations (reduction of symmetry; insertion, displacement, substitution, deletion of atoms)

Wave function analysis and properties

- **Band structure**

- **Density of states**

- Band projected DOSS
- AO projected DOSS

- **All Electron Charge Density - Spin Density**

- Density maps
- Mulliken population analysis
- Density analytical derivatives

- **Atomic multipoles**

- **Electric field**

- **Electric field gradient**
- **Static structure factors and dynamic structure factors including Debye-Waller factor**
- **Electron Momentum Density and Compton profiles**
 - *Electron momentum density maps*
 - *Automated anisotropy maps*
 - *Partitioning according to Wannier functions*
- **Electrostatic potential and its derivatives**
 - Quantum and classical electrostatic potential and its derivatives
 - Electrostatic potential maps
- **Fermi contact**
- **Localized Wannier Functions (Boys method)**
- *Mossbauer effect (isotropic effect and quadrupole interaction)*
- **Dielectric properties**
 - Spontaneous polarization
 - * Berry Phase
 - * Localized Wannier Functions
 - Dielectric constant
 - * Coupled Perturbed HF(KS) scheme
 - * Finite-field approximation
 - *High-order static electric susceptibilities (2nd- and 3rd-order)*
- *Topological analysis of the electron charge density via the TOPOND package, fully integrated in the program*

Software performance

- **Memory management: dynamic allocation**
- **Full parallelization of the code**
 - parallel SCF and gradients for both HF and DFT methods
 - Replicated data version (MPI)
 - Massive parallel version (MPI) (distributed memory) (*Improved version: lower memory usage and better scaling*)
 - *Parallel (replicated data) version of the “properties” module*
 - *New parallelization strategy on IRREPs*
- *Enhanced exploitation of the point-group symmetry*

Interfaces

- *Internal interface to CRYSCOR (serial version) for electronic structure calculation of 1D, 2D and 3D periodic non conducting systems at the L-MP2 correlated level and Double-Hybrid functionals*
- *Internal interface to TOPOND for topological analysis of the electron charge density*

WARNING: CRYSTAL14 new defaults

In CRYSTAL14, some default computational parameters have changed with respect to the Crystal09 version of the program.

A list of the changes is reported below:

SCF Parameters

- A Fock (Kohn-Sham) matrix mixing of 30 % between subsequent SCF cycles is now active by default (see keyword **FMIXING**);
- A full direct approach for the computation of the integrals (keyword **SCFDIR**) is now used as a default. Use keyword **NODIRECT** for switching this option off;
- The thresholds governing the bipolar approximation have changed from 14 10 to 18 14. See keyword **BIPOLA** for details;

Geometry optimization

- A full geometry optimization (atomic coordinates and lattice parameters) is now performed as a default option when the **OPTGEOM** keyword is used. The sub-keyword **ATOMONLY** switches back to an atomic positions only optimization;
- The **FINALRUN** = 4 option is now set by default (before it was 0). See page 126 for details;

Density Functional Theory

- The size of the default numerical integration grid has changed. Now it corresponds to the **XLGRID** option. The option **OLDGRID** has been added to set back the old grid size;
- **By default, an unlocked energy shifting of 0.6 hartree is applied to separate apart occupied from virtual orbitals, which corresponds to option **LEVSHIFT** with parameters 6 0.**

Frequencies calculation

- Eckart conditions for cleaning the Hessian matrix as regards translational and rotational vibration modes are now activated by default. See page 145 for details;

Note that:

- Total energies and CPU times can change with respect to CRYSTAL09. See Appendix G (346) for changes in total energies for the CRYSTAL test cases.
- The keyword **OLDREF09**, to be inserted in the geometry input block, switches back all new defaults to the old settings.

Conventions

In the description of the input data which follows, the following notation is adopted:

| | | | |
|---|--|--|----|
| - | • | new record | |
| - | * | free format record | |
| - | An | alphanumeric datum (first n characters meaningful) | |
| - | atom label | sequence number of a given atom in the primitive cell, as printed in the output file after reading of the geometry input | |
| - | symmops | symmetry operators | |
| - | \square , [] | default values. | |
| - | <i>italic</i> | optional input | |
| - | _____ <i>optional input records follow</i> _____ | | II |
| - | _____ additional input records follow _____ | | II |

Arrays are read in with a simplified implied DO loop instruction of Fortran 77:

$(dlist, i=m1,m2)$

where: $dlist$ is an input list; i is the name of an integer variable, whose value ranges from $m1$ to $m2$.

Example (page 35): $LB(L), L=1, NL$

NL integer data are read in and stored in the first NL position of the array LB .

All the keywords are entered with an A format (case insensitive); the keywords must not end with blanks.

conventional atomic number (usually called **NAT**) is used to associate a given basis set with an atom. The real atomic number is the remainder of the division $NAT/100$. See page 21. The same conventional atomic number must be given in geometry input and in basis set input.

Acknowledgments

Embodied in the present code are elements of programs distributed by other groups.

In particular: the atomic SCF package of Roos et al. [150], the GAUSS70 gaussian integral package and STO-nG basis set due to Hehre et al. [97], the code of Burzlaff and Hountas for space group analysis [28], Saunders' ATMOL gaussian integral package [118], the XCFun DFT library of exchange-correlation functionals [58].

We take this opportunity to thank these authors. Our modifications of their programs have sometimes been considerable. Responsibility for any erroneous use of these programs therefore remains with the present authors.

We are in debt with Cesare Pisani, who first conceived the CRYSTAL project in 1976, for his constant support of and interest in the development of the new version of the CRYSTAL program.

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Contribution to test and validate the new features is recognized to: Agnes Mahmoud, Simone Salustro, Gustavo Sophia, Marco Lorenz.

Specific contribution to coding is indicated in the banner of the new options.

Getting Started

Instructions to download, install, and run the code are available in the web site:

<http://www.crystal.unito.it> → documentation

Program errors

A very large number of tests have been performed by researchers of a few laboratories, that had access to a test copy of CRYSTAL09. We tried to check as many options as possible, but not all the possible combinations of options have been checked. We have no doubts that errors remain.

The authors would greatly appreciate comments, suggestions and criticisms by the users of CRYSTAL; in case of *errors* the user is kindly requested to contact the authors, sending a copy of both input and output by E-mail to the Torino group (crystal@unito.it).

Chapter 1

Wave-function Calculation: Basic Input Route

1.1 Geometry and symmetry information

The first record of the geometry definition must contain one of the keywords:

| | | |
|-----------------|---|---------|
| CRYSTAL | 3D system | page 15 |
| SLAB | 2D system | page 15 |
| POLYMER | 1D system | page 15 |
| HELIX | 1D system - roto translational symmetry | page 16 |
| MOLECULE | 0D system | page 15 |
| EXTERNAL | geometry from external file | page 16 |
| DLVINPUT | geometry from DLV [164] Graphical User Interface. | page 16 |

Four input schemes are used.

The first is for crystalline systems (3D), and is specified by the keyword **CRYSTAL**.

The second is for slabs (2D), polymers (1D) and molecules (0D) as specified by the keywords **SLAB**, **POLYMER** or **MOLECULE** respectively.

The third scheme (keyword **HELIX**) defines a 1D system with roto-translational symmetry (helix).

In the fourth scheme, with keyword **EXTERNAL** (page 16) or **DLVINPUT**, the unit cell, atomic positions and symmetry operators may be provided directly from an external file (see Appendix D, page 326). Such an input file can be prepared by the keyword **EXTPRT** (*crystal* input block 1, page 41; *properties*).

Sample input decks for a number of structures are provided in section 11.1, page 248.

Geometry input for crystalline compounds. Keyword: CRYSTAL

| rec | variable | value | meaning |
|-----|--|---|--|
| • * | IFLAG | 0 | convention for space group identification (Appendix A.1, page 293): space group sequential number(1-230) |
| | | 1 | Hermann-Mauguin alphanumeric code |
| | IFHR | | type of cell: for rhombohedral groups, subset of trigonal ones, only (meaningless for non-rhombohedral crystals): |
| | | 0 | hexagonal cell. Lattice parameters a, c |
| • * | IFSO | 1 | rhombohedral cell. Lattice parameters a, α |
| | | 0 | setting for the origin of the crystal reference frame: origin derived from the symbol of the space group: where there are two settings, the second setting of the International Tables is chosen. |
| | 1 | standard shift of the origin: when two settings are allowed, the first setting is chosen | |
| | >1 | non-standard shift of the origin given as input (see test22) | |
| • * | IGR | | space group identification code (following IFLAG value): space group sequence number (IFLAG=0) |
| | or A AGR | | space group alphanumeric symbol (IFLAG=1) <i>if IFSO > 1 insert</i> _____ II |
| • * | IX,IY,IZ | | non-standard shift of the origin coordinates (x,y,z) in fractions of the crystallographic cell lattice vectors times 24 (to obtain integer values). _____ II |
| • * | a,[b],[c], [α],[β] [γ] | | minimal set of crystallographic cell parameters: translation vector[s] length [Ångstrom], crystallographic angle[s] (degrees) |
| | | | number of atoms in the asymmetric unit. _____ insert NATR records _____ II |
| • * | NAT | | “conventional” atomic number. The conventional atomic number, NAT, is used to associate a given basis set with an atom. The real atomic number is the remainder of the division NAT100 |
| | X,Y,Z | | atom coordinates in fractional units of crystallographic lattice vec- tors _____ optional keywords terminated by END/ENDGEOM or STOP _____ II |

Geometry input for molecules, polymers and slabs. Keywords: SLAB, POLYMER, MOLECULE

When the geometrical structure of 2D, 1D and 0D systems has to be defined, attention should be paid in the input of the atom coordinates, that are expressed in different units, fractional (direction with translational symmetry) or Ångstrom (non periodic direction).

| translational symmetry | unit of measure of coordinates | | |
|---------------------------|--------------------------------|----------|----------|
| | X | Y | Z |
| 3D | fraction | fraction | fraction |
| 2D | fraction | fraction | Ångstrom |
| 1D | fraction | Ångstrom | Ångstrom |
| 0D | Ångstrom | Ångstrom | Ångstrom |

| rec | variable | meaning | |
|-----|------------------------|---|----|
| • * | IGR | point, rod or layer group of the system: 0D - molecules (Appendix A.4, page 300) 1D - polymers (Appendix A.3, page 297) 2D - slabs (Appendix A.2, page 296) | |
| | | <i>if polymer or slab, insert</i> | II |
| • * | a,[b], [γ] | minimal set of lattice vector(s)- length in Ångstrom (b for rectangular lattices only) \widehat{AB} angle (degrees) - triclinic lattices only | |
| • * | NATR | number of non-equivalent atoms in the asymmetric unit | |
| | | <i>insert NATR records</i> | II |
| • * | NAT X,Y,Z | conventional atomic number 3 atoms coordinates. Unit of measure: 0D - molecules: x,y,z in Ångstrom 1D - polymers : y,z in Ångstrom, x in fractional units of crystallographic cell translation vector 2D - slabs : z in Ångstrom, x, y in fractional units of crystallographic cell translation vectors | |
| | | <i>optional keywords terminated by END or STOP</i> | II |

Geometry input for polymers with roto translational symmetry.

Keyword: HELIX

| rec | variable | meaning | |
|-----|--------------|---|----|
| • * | N1 | order of rototranslational axis | |
| • * | N2 | to define the rototranslational vector | |
| • * | a_0 | lattice parameter of 1D cell - length in Ångstrom | |
| • * | NATR | number of non-equivalent atoms in the asymmetric unit | |
| | | <i>insert NATR records</i> | II |
| • * | NAT X,Y,Z | conventional atomic number 3 atoms coordinates. Unit of measure: 1D - polymers : y,z in Ångstrom, x in fractional units of crystallographic cell translation vector | |
| | | <i>optional keywords terminated by END or STOP</i> | II |

A helix structure is generated: each atom of the irreducible part is rotated by an angle $\beta = n \cdot 360/N1$ degrees and translated by a vector $\vec{t} = n \cdot a_0 \frac{N2}{N1}$ with $n = 1, \dots, (N1 - 1)$.

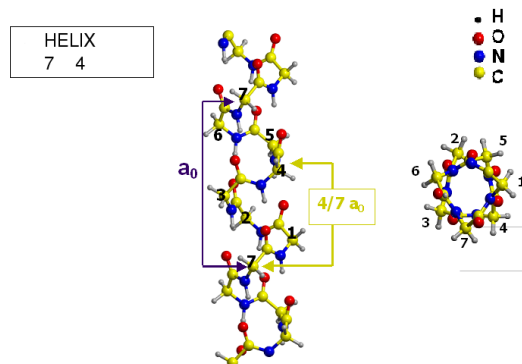
As an example let's consider the α -helix conformer of polyglycine whose structure is sketched in Figure 1.1.

The helix structure is characterized by seven glycine residues per cell. The order of the roto-translational axis is therefore seven, $N1 = 7$. In order to establish the value of $N2$, look for instance at the atom labeled 7 in the Figure. The top view of the helix shows that upon rotation by $\beta = 360/7$ degrees, atom 7 moves to atom 4; the side view clarifies that this movement implies a translational vector $\vec{t} = a_0 \frac{4}{7}$: therefore $N2 = 4$.

Geometry input from external geometry editor. Keywords: EXTERNAL, DLVINPUT

The fourth input scheme works for molecules, polymers, slabs and crystals. The complete geometry input data are read from file fort.34. The unit cell, atomic positions and symmetry operators are provided directly according to the format described in Appendix D, page

Figure 1.1: Side view (left) and top view (right) of an α -helix conformer of polyglycine



326. Coordinates in Ångstrom. Such an input file is written when **OPTGEOM** route for geometry optimization is chosen, and can be prepared by the keyword **EXTPRT** (program *crystal*, input block 1, page 41; program *properties*), or by the the visualization software DLV (<http://www.cse.scitech.ac.uk/cmog/DLV/>).

The geometry defined by **EXTERNAL** can be modified by inserting any geometry editing keyword (page 28) into the input stream after **EXTERNAL**.

Comments on geometry input

1. All coordinates in Ångstrom. In geometry editing, after the basic geometry definition, the unit of measure of coordinates may be modified by entering the keywords **FRACTION** (page 45) or **BOHR** (page 36).
2. The geometry of a system is defined by the crystal structure ([83], Chapter 1 of ref. [139]). Reference is made to the International Tables for Crystallography [91] for all definitions. The crystal structure is determined by the space group, by the shape and size of the unit cell and by the relative positions of the atoms in the asymmetric unit.
3. The lattice parameters represent the length of the edges of the cell (a, b, c) and the angles between the edges ($\alpha = \widehat{b c}$; $\beta = \widehat{a c}$; $\gamma = \widehat{a b}$). They determine the cell volume and shape.
4. Minimal set of lattice parameters to be defined in input:

| | | |
|--------------|-------------------|---|
| cubic | | a |
| hexagonal | | a, c |
| trigonal | hexagonal cell | a, c |
| | rhombohedral cell | a, α |
| tetragonal | | a, c |
| orthorhombic | | a, b, c |
| monoclinic | | a, b, c, β (b unique) |
| | | a, b, c, γ (c unique) |
| | | a, b, c, α (a unique - non standard) |
| triclinic | | $a, b, c, \alpha, \beta, \gamma$ |

5. The asymmetric unit is the largest subset of atoms contained in the unit-cell, where no atom pair related by a symmetry operator can be found. Usually several equivalent subsets of this kind may be chosen so that the asymmetric unit needs not be unique. The asymmetric unit of a space group is a part of space from which, by application of all symmetry operations of the space group, the whole of space is filled exactly.

6. The *crystallographic*, or *conventional cell*, is used as the standard option in input. It may be non-primitive, which means it may not coincide with the cell of minimum volume (*primitive cell*), which contains just one lattice point. The matrices which transform the conventional (as given in input) to the primitive cell (used by **CRYSTAL**) are given in Appendix A.5, page 301, and are taken from Table 5.1 of the International Tables for Crystallography [91].

Examples. A cell belonging to the face-centred cubic Bravais lattice has a volume four times larger than that of the corresponding primitive cell, and contains four lattice points (see page 65, keyword **SUPERCEL**). A unit cell belonging to the hexagonal Bravais lattice has a volume three times larger than that of the rhombohedral primitive cell (R Bravais lattice), and contains three lattice points.

7. The use of the International Tables to identify the symmetry groups requires some practice. The examples given below may serve as a guide. The printout of geometry information (equivalent atoms, fractional and Cartesian atomic coordinates etc.) allows a check on the correctness of the group selected. To obtain a complete neighborhood analysis for all the non-equivalent atoms, a complete input deck must be read in (blocks 1-3), and the keyword **TESTPDIM** inserted in block 3, to stop execution after the symmetry analysis.
8. Different settings of the origin may correspond to a different number of symmetry operators with translational components.

Example: bulk silicon - Space group 227 - 1 irreducible atom per cell.

| setting of the origin | Si coordinates | symmops with translational component | multiplicity |
|-----------------------|----------------|--------------------------------------|--------------|
| 2nd (default) | 1/8 1/8 1/8 | 36 | 2 |
| 1st | 0. 0. 0. | 24 | 2 |

NB With different settings, the same position can have different multiplicity. For instance, in space group 227 (diamond, silicon) the position (0., 0., 0.) has multiplicity 2 in 1st setting, and multiplicity 4 in 2nd setting.

Second setting is the default choice in **CRYSTAL**.

The choice is important when generating a supercell, as the first step is the removal of the symmops with translational component. The keyword **ORIGIN** (input block 1, page 56) translates the origin in order to minimize the number of symmops with translational component.

9. When coordinates are obtained from experimental data or from geometry optimization with semi-classical methods, atoms in special positions, or related by symmetry are not correctly identified, as the number of significative digits is lower than the one used by the program *crystal* to recognize equivalence or special positions. In that case the coordinates must be edited by hand (see FAQ at www.crystal.unito.it).
10. The symbol of the space group for crystals (IFLAG=1) is given precisely as it appears in the International Tables, *with the first letter in column one* and a blank separating operators referring to different symmetry directions. The symbols to be used for the groups 221-230 correspond to the convention adopted in editions of the International Tables prior to 1983: the 3 axis is used instead of $\bar{3}$. See Appendix A.1, page 293.

Examples:

| Group number | input symbol | |
|-------------------|---|---|
| 137 (tetragonal) | P ₁ 42/N ₁ M ₁ C | |
| 10 (monoclinic) | P ₁ 1 ₁ 2/M ₁ 1 | (unique axis <i>b</i> , standard setting) |
| | P ₁ 1 ₁ 1 ₁ 2/M | (unique axis <i>c</i>) |
| | P ₁ 2/M ₁ 1 ₁ 1 | (unique axis <i>a</i>) |
| 25 (orthorhombic) | P ₁ M ₁ M ₁ 2 | (standard setting) |

P₁2₁M₁M
P₁M₁2₁M

11. In the monoclinic and orthorhombic cases, if the group is identified by its number (3-74), the conventional setting for the unique axis is adopted. The explicit symbol must be used in order to define an alternative setting.
12. For the centred lattices (F, I, C, A, B and R) the input cell parameters refer to the centred conventional cell; the fractional coordinates of the input list of atoms are in a vector basis relative to the centred conventional cell.
13. Rhombohedral space groups are a subset of trigonal ones. The Hermann-Mauguin symbol must begin by 'R'. For instance, space groups 156-159 are trigonal, but not rhombohedral (their Hermann-Mauguin symbols begin by "P"). Rhombohedral space groups (146-148-155-160-161-166-167) may have an hexagonal cell ($a=b$; c ; $\alpha, \beta = 90^\circ$; $\gamma = 120^\circ$: input parameters a, c) or a rhombohedral cell ($a=b=c$; $\alpha = \beta = \gamma$: input parameters = a, α). See input datum IFHR.
14. It is sufficient to supply the coordinates of only *one* of a group of atoms equivalent under centring translations (eg: for space group Fm3m only the parameters of the face-centred cubic cell, and the coordinates of one of the four atoms at $(0,0,0)$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ are required).
The coordinates of only one atom among the set of atoms linked by centring translations are printed. The vector basis is relative to the centred conventional cell. However when Cartesian components of the direct lattice vectors are printed, they are those of the primitive cell.
15. The conventional atomic number NAT is used to associate a given basis set with an atom (see Basis Set input, Section 1.2, page 20). The real atomic number is given by the remainder of the division of the conventional atomic number by 100 (Example: NAT=237, Z=37; NAT=128, Z=28). Atoms with the same atomic number, but in non-equivalent positions, can be associated with different basis sets, by using different conventional atomic numbers: e.g. 6, 106, 1006 (all electron basis set for carbon atom); 206, 306 (core pseudo-potential for carbon atom, Section 2.2, page 72).
If the remainder of the division is 0, a "ghost" atom is identified, to which no nuclear charge corresponds (it may have electronic charge). This option may be used for enriching the basis set by adding bond basis function [9], or to allow build up of charge density on a vacancy. A given atom may be transformed into a ghost after the basis set definition (input block 2, keyword **GHOSTS**, page 71).
16. The keyword **SLABCUT** (Geometry editing input, page 61) allows the creation of a slab (2D) of given thickness from the 3D perfect lattice. See for comparison test4-test24; test5-test25; test6-test26; test7- test27.
17. For slabs (2D), when two settings of the origin are indicated in the International Tables for Crystallography, setting number 2 is chosen. The setting can not be modified.
18. Conventional orientation of slabs and polymers: Polymers are oriented along the x axis. Slabs are parallel to the xy plane.
19. The keywords **MOLECULE** (for molecular crystals only; page 49) and **CLUSTER** (for any n-D structure; page 38) allow the creation of a non-periodic system (molecule(s) or cluster) from a periodic one.

1.2 Basis set

Two different methods are available to input basis set data:

- Standard route
- Basis set input by keywords

1.2.1 Standard route

| rec | variable | value | meaning | |
|-----|----------|----------------------------------|--|--|
| • * | NAT | n | conventional atomic 3 number | |
| | | <200> 1000 | all-electron basis set (Carbon, all electron BS: 6, 106, 1006) | |
| | | >200 | valence electron basis set (Carbon, ECP BS: 206, 306) . ECP (Effective Core Pseudopotential) must be defined (page 72) | |
| | NSHL | =99 | end of basis set input section | |
| | | n | number of shells | |
| | | 0 | end of basis set input (when NAT=99) | |
| | | | <i>if NAT > 200 insert ECP input (page 72)</i> _____II | |
| | | | NSHL sets of records - for each shell _____II | |
| • * | ITYB | | type of basis set to be used for the specified shell: | |
| | | 0 | general BS, given as input | |
| | | 1 | Pople standard STO-nG (Z=1-54) | |
| | | 2 | Pople standard 3(6)-21G (Z=1-54(18)) Standard polarization functions are included. | |
| | LAT | | | shell type: |
| | | 0 | 1 s AO (S shell) | |
| | | 1 | 1 s + 3 p AOs (SP shell) | |
| | | 2 | 3 p AOs (P shell) | |
| | | 3 | 5 d AOs (D shell) | |
| | NG | 4 | 7 f AOs (F shell) | |
| | | | | Number of primitive Gaussian Type Functions (GTF) in the contraction for the basis functions (AO) in the shell |
| | | 1≤NG≤10 | for ITYB=0 and LAT ≤ 2 | |
| | | 1≤NG≤6 | for ITYB=0 and LAT = 3 | |
| | | 2≤NG≤6 | for ITYB=1 | |
| | | 6 | 6-21G core shell | |
| 3 | | 3-21G core shell | | |
| CHE | 2 | n-21G inner valence shell | | |
| | 1 | n-21G outer valence shell | | |
| | CHE | | formal electron charge attributed to the shell | |
| | SCAL | | scale factor (if ITYB=1 and SCAL=0., the standard Pople scale factor is used for a STO-nG basis set. | |
| | | | <i>if ITYB=0 (general basis set insert NG records)</i> _____II | |
| • * | EXP | | exponent of the normalized primitive GTF | |
| | | COE1 | contraction coefficient of the normalized primitive GTF: | |
| | | LAT=0,1 → s function coefficient | | |
| | | LAT=2 → p function coefficient | | |
| | | LAT=3 → d function coefficient | | |
| | | LAT=4 → f function coefficient | | |
| | COE2 | LAT=1 → p function coefficient | | |
| | | | _____ optional keywords terminated by END/ENDB or STOP _____II | |

The choice of basis set is the most critical step in performing *ab initio* calculations of periodic systems, with Hartree-Fock or Kohn-Sham Hamiltonians. Optimization criteria are discussed in Chapter 9.2. When an effective core pseudo-potential is used, the basis set **must** be optimized with reference to that potential (Section 2.2, page 72).

1. A basis set (BS) must be given for each atom with different conventional atomic number defined in the crystal structure input. If atoms are removed (geometry input, keyword **ATOMREMO**, page 35), the corresponding basis set input can remain in the input stream. The keyword **GHOSTS** (page 71) removes the atom, leaving the associated basis set.
2. The basis set for each atom has NSHL shells, whose constituent AO basis functions are built from a linear combination ('contraction') of individually normalized primitive Gaussian-type functions (GTF) (Chapter 13, page 275).
3. A conventional *atomic number* NAT links the basis set with the atoms defined in the crystal structure. The atomic number Z is given by the remainder of the division of the conventional atomic number by 100 (Example: NAT=108, Z=8, all electron; NAT=228, Z=28, ECP). See point 5 below.
4. A conventional atomic number 0 defines ghost atoms, that is points in space with an associated basis set, but lacking a nuclear charge (vacancy). See test 28.
5. Atoms with equal conventional atomic number are associated with the same basis set.

NAT < 200 > 1000: all electron basis set. A maximum of two different basis sets may be given for the same chemical species in different positions: NAT=Z, NAT=Z+100, NAT=Z+1000.

NAT > 200: valence electron basis set. A maximum of two different BS may be given for the same chemical species in positions not symmetry-related: NAT=Z+200, NAT=Z+300. A core pseudo-potential must be defined. See Section 2.2, page 72, for information on core pseudo-potentials.

Suppose we have four non-equivalent carbon atoms in the unit cell. Conventional atomic numbers 6 106 1006 206 306 mean that carbon atoms (real atomic number 6) unrelated by symmetry are to be associated with different basis sets: the first three (6, 106, 1006) all-electron, the second two (206, 306) valence only, with pseudo-potential.

6. The basis set input ends with the card:

```
99      0      conventional atomic number 99, 0 shell.
```

Optional keywords may follow.

In summary:

1. *CRYSTAL* can use the following all electrons basis sets:
 - a) general basis sets, including *s*, *p*, *d*, *f* functions (given in input);
 - b) standard Pople basis sets [98] (internally stored as in Gaussian 94 [77]).
STOnG, Z=1 to 54
6-21G, Z=1 to 18
3-21G, Z=1 to 54

The standard basis sets b) are stored as internal data in the *CRYSTAL* code. They are all electron basis sets, and can not be combined with ECP.

2. **Warning** The standard scale factor is used for STO-nG basis set when the input datum SCAL is 0.0 in basis set input. *All the atoms of the same row are attributed the same Pople STO-nG basis set when the input scale factor SCAL is 1.*
3. Standard polarization functions can be added to 6(3)-21G basis sets of atoms up to Z=18, by inserting a record describing the polarization shell (ITYB=2, LAT=2, p functions on hydrogen, or LAT=3, d functions on 2-nd row atoms; see test 12).

| H | | Polarization functions exponents | | | | | | He |
|-------|-------|----------------------------------|------|------|------|------|------|-----|
| 1.1 | | | | | | | | 1.1 |
| ----- | | ----- | | | | | | |
| Li | Be | B | C | N | O | F | Ne | |
| 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | -- | |
| ----- | | ----- | | | | | | |
| Na | Mg | Al | Si | P | S | Cl | Ar | |
| 0.175 | 0.175 | 0.325 | 0.45 | 0.55 | 0.65 | 0.75 | 0.85 | |
| ----- | | | | | | | | |

The formal electron charge attributed to a polarization function must be zero.

4. The shell types available are :

| shell code | shell type | n. | order of internal storage |
|------------|------------|----|--|
| 0 | S | 1 | s |
| 1 | SP | 4 | s, x, y, z |
| 2 | P | 3 | x, y, z |
| 3 | D | 5 | $2z^2 - x^2 - y^2, xz, yz, x^2 - y^2, xy$ |
| 4 | F | 7 | $(2z^2 - 3x^2 - 3y^2)z, (4z^2 - x^2 - y^2)x, (4z^2 - x^2 - y^2)y, (x^2 - y^2)z, xyz, (x^2 - 3y^2)x, (3x^2 - y^2)y$ |

When symmetry adaptation of Bloch functions is active (default; NOSYMADA in block3 to remove it), if F functions are used, all lower order functions must be present (D , P , S).

The order of internal storage of the AO basis functions is an information necessary to read certain quantities calculated by the program *properties*. See Chapter 9: Mulliken population analysis (**PPAN**, page 109), electrostatic multipoles (**POLI**, page 231), projected density of states (**DOSS**, page 207) and to provide an input for some options (**EIGSHIFT**, input block 3, page 94).

5. Spherical harmonics d-shells consisting of 5 AOs are used.

6. Spherical harmonics f-shells consisting of 7 AOs are used.

7. The formal shell charges CHE, the number of electrons attributed to each shell, are assigned to the AO following the rules:

| shell code | shell type | max CHE | rule to assign the shell charges |
|------------|------------|---------|---|
| 0 | S | 2. | CHE for s functions |
| 1 | SP | 8. | if CHE>2, 2 for s and (CHE-2) for p functions, if CHE≤2, CHE for s function |
| 2 | P | 6. | CHE for p functions |
| 3 | D | 10. | CHE for d functions |
| 4 | F | 14. | CHE for f functions - it may be ≠ 0 in CRYSTAL09. |

8. A maximum of one open shell for each of the s , p and or d atomic symmetries is allowed in the electronic configuration defined in the input. The atomic energy expression is not correct for all possible double open shell couplings of the form $p^m d^n$. Either m must equal 3 or n must equal 5 for a correct energy expression in such cases. A warning will be printed if this is the case. However, the resultant wave function (which is a superposition of atomic densities) will usually provide a reasonable starting point for the periodic density matrix.

9. When extended basis sets are used, all the functions corresponding to symmetries (angular quantum numbers) occupied in the isolated atom are added to the atomic basis set for atomic wave function calculations, even if the formal charge attributed to that shell is zero. Polarization functions are not included in the atomic basis set; *their input occupation number should be zero.*

10. The formal shell charges are used only to define the electronic configuration of the atoms to compute the atomic wave function. The initial density matrix in the SCF step may be a superposition of atomic (or ionic) density matrices (default option, **GUESSPAT**, page 104). When a different guess is required (**GUESSP**), the shell charges are not used, but checked for electron neutrality when the basis set is entered.
11. F shells functions are not used to compute the “atomic” wave function, to build an atomic density matrix SCF guess. If F shells are occupied by n_f electrons, the “atomic” wave function is computed for an ion (F electrons are removed), and the diagonal elements of the atomic density matrix are then set to $n_f/7$. The keyword **FDOCCUP** (input block 3, page 97) allows modification of f orbitals occupation.
12. Each atom in the cell may have an ionic configuration, when the sum of formal shell charges (CHE) is different from the nuclear charge. When the number of electrons in the cell, that is the sum of the shell charges CHE of all the atoms, is different from the sum of nuclear charges, the reference cell is non-neutral. This is not allowed for periodic systems, and in that case the program stops. In order to remove this constraint, it is necessary to introduce a uniform charged background of opposite sign to neutralize the system [48]. This is obtained by entering the keyword **CHARGED** (page 69) after the standard basis set input. The value of total energy must be carefully checked.
13. It may be useful to allow atoms with the same basis set to have different electronic configurations (e.g, for an oxygen vacancy in MgO one could use the same basis set for all the oxygens, but begin with different electronic configuration for those around the vacancy). The formal shell charges attributed in the basis set input may be modified for selected atoms by inserting the keyword **CHEMOD** (input block 2, page 69).
14. The energies given by an atomic wave function calculation with a crystalline basis set should not be used as a reference to calculate the formation energies of crystals. The external shells should first be re-optimized in the isolated atom by adding a low-exponent Gaussian function, in order to provide an adequate description of the tails of the isolated atom charge density [34] (keyword **ATOMHF**, input block 3, page 79).

Optimized basis sets for periodic systems used in published papers are available in:

<http://www.crystal.unito.it>

1.2.2 Basis set input by keywords

A few predefined basis set data can be retrieved by simply typing a keyword. For the moment being the set of available basis sets includes (available atomic numbers in parentheses):

- Pople’s STO-3G minimal basis set (1–53)
- Pople’s STO-6G minimal basis set (1–36)
- POB double- ζ valence + polarization basis set for solid state systems (1–35, 49, 74)
- POB double- ζ valence basis set + a double set of polarization functions for solid state systems (1–35, 49, 83)
- POB triple- ζ valence + polarization basis set for solid state systems (1–35, 49, 83)

Features and performance of Peintinger-Oliveira-Bredow (POB) basis sets are illustrated in Ref. [113].

In order to enable basis set input by keywords, the following keyword must replace the final keyword, **END**, of the structure input (input block 1):

BASISSET

This card must be followed by the selection of a basis set type. The following sets are presently available:

| Basis set label | Basis set type |
|------------------|--|
| CUSTOM | Standard input basis set: insert cards as illustrated in section 1.2.1 |
| STO-3G | Pople's standard minimal basis set (3 Gaussian function contractions) [98] |
| STO-6G | Pople's standard minimal basis set (6 Gaussian function contractions) [98] |
| POB-DZVP | POB Double- ζ + polarization basis set [113] |
| POB-DZVPP | POB Double- ζ + double set of polarization functions [113] |
| POB-TZVP | POB Triple- ζ + polarization basis set [113] |

Input example for rock-salt:

```
NaCl Fm-3m ICSD 240598
CRYSTAL
0 0 0
225
5.6401
2
11 0.0 0.0 0.0
17 0.5 0.5 0.5
BASISSET
POB-TZVP
DFT
EXCHANGE
PWGGA
CORRELAT
PWGGA
HYBRID
20
CHUNKS
200
END
TOLINTEG
7 7 7 7 14
SHRINK
8 8
END
```


1.3 Computational parameters, hamiltonian, SCF control

Default values are set for all computational parameters. Default choices may be modified through keywords. Default choices:

| | default | keyword to modify | page |
|--|------------------|-------------------|------|
| hamiltonian: | RHF | UHF (SPIN) | 116 |
| tolerances for coulomb and exchange sums : | 6 6 6 6 12 | TOLINTEG | 115 |
| Pole order for multipolar expansion: | 4 | POLEORDR | 108 |
| Max number of SCF cycles: | 50 | MAXCYCLE | 106 |
| Convergence on total energy: | 10 ⁻⁶ | TOLDEE | 115 |

For periodic systems, 1D, 2D, 3D, the only *mandatory input information* is the shrinking factor, IS, to generate a commensurate grid of \mathbf{k} points in reciprocal space, according to Pack-Monkhorst method [119]. The Hamiltonian matrix computed in direct space, $H_{\mathbf{g}}$, is Fourier transformed for each \mathbf{k} value, and diagonalized, to obtain eigenvectors and eigenvalues:

$$H_{\mathbf{k}} = \sum_{\mathbf{g}} H_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{k}}$$

$$H_{\mathbf{k}} A_{\mathbf{k}} = S_{\mathbf{k}} A_{\mathbf{k}} E_{\mathbf{k}}$$

A second shrinking factor, ISP, defines the sampling of \mathbf{k} points, "Gilat net" [85, 84], used for the calculation of the density matrix and the determination of Fermi energy in the case of conductors (bands not fully occupied).

The two shrinking factors are entered after the keyword **SHRINK** (page 110).

In 3D crystals, the sampling points belong to a lattice (called the Pack-Monkhorst net), with basis vectors:

b1/is1, b2/is2, b3/is3 is1=is2=is3=IS, unless otherwise stated

where b1, b2, b3 are the reciprocal lattice vectors, and is1, is2, is3 are integers "shrinking factors".

In 2D crystals, IS3 is set equal to 1; in 1D crystals both IS2 and IS3 are set equal to 1.

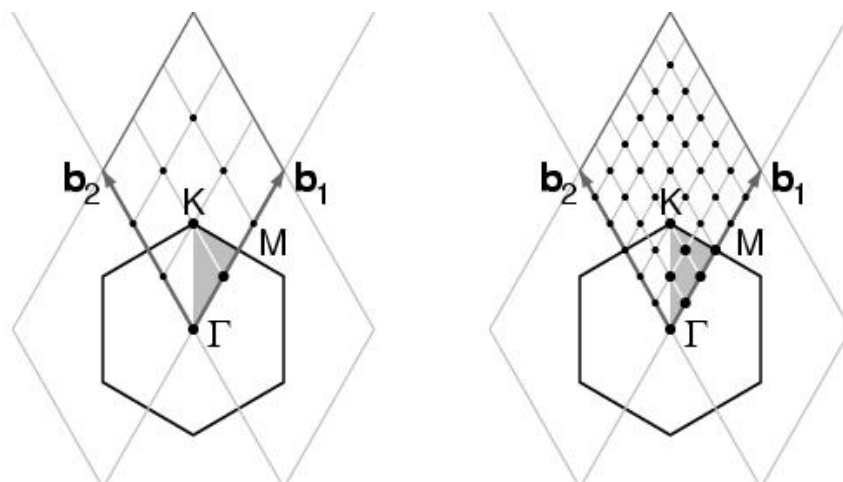
Only points k_i of the Pack-Monkhorst net belonging to the irreducible part of the Brillouin Zone (IBZ) are considered, with associated a geometrical weight, w_i . The choice of the reciprocal space integration parameters to compute the Fermi energy is a delicate step for metals. See Section 13.7, page 281.

Two parameters control the accuracy of reciprocal space integration for Fermi energy calculation and density matrix reconstruction:

IS **shrinking factor of reciprocal lattice vectors.** The value of IS determines the number of \mathbf{k} points at which the Fock/KS matrix is diagonalized.

In high symmetry systems, it is convenient to assign IS *magic* values such that all low multiplicity (high symmetry) points belong to the Monkhorst lattice. Although this choice does not correspond to maximum efficiency, it gives a safer estimate of the integral.

The \mathbf{k} -points net is automatically made anisotropic for 1D and 2D systems.



The figure presents the reciprocal lattice cell of 2D graphite (rhombus), the first Brillouin zone (hexagon), the irreducible part of Brillouin zone (in grey), and the coordinates of the \mathbf{k}_i points according to a Pack-Monkhorst sampling, with shrinking factor 3 and 6.

ISP **shrinking factor of reciprocal lattice vectors in the Gilat net** (see [142], Chapter II.6). ISP is used in the calculation of the Fermi energy and density matrix. **Its value can be equal to IS for insulating systems and equal to 2*IS for conducting systems.**

ISP跟non-conductors无关，但non-conductors可能会在SCF初期形成导电结构，故ISP必须被定义

The value assigned to ISP is irrelevant for non-conductors. However, a non-conductor may give rise to a conducting structure at the initial stages of the SCF cycle (very often with DFT hamiltonians), owing, for instance, to a very unbalanced initial guess of the density matrix. The ISP parameter must therefore be defined in all cases.

Note. The value used in the calculation is $ISP = IS * NINT(MAX(ISP, IS) / IS)$

In the following table the number of sampling points in the IBZ and in BZ is given for a fcc lattice (space group 225, 48 symmetry operators) and hcp lattice (space group 194, 24 symmetry operators). The CRYSTAL code allows 413 k points in the Pack-Monkhorst net, and 2920 in the Gilat net.

| IS | points in IBZ | points in IBZ | points BZ |
|----|---------------|---------------|-----------|
| | fcc | hcp | |
| 6 | 16 | 28 | 112 |
| 8 | 29 | 50 | 260 |
| 12 | 72 | 133 | 868 |
| 16 | 145 | 270 | 2052 |
| 18 | 195 | 370 | 2920 |
| 24 | 413 | 793 | 6916 |
| 32 | 897 | 1734 | 16388 |
| 36 | 1240 | 2413 | 23332 |
| 48 | 2769 | 5425 | 55300 |

1. When an anisotropic net is user defined (IS=0), the ISP input value is taken as ISP1 (shrinking factor of Gilat net along first reciprocal lattice) and ISP2 and ISP3 are set to: $ISP2 = (ISP * IS2) / IS1$, $ISP3 = (ISP * IS3) / IS1$.
2. User defined anisotropic net is not compatible with SABF (Symmetry Adapted Bloch Functions). See **NOSYMADA**, page 108.

Some tools for accelerating convergence are given through the keywords **LEVSHIFT** (page 105 and tests 29, 30, 31, 32, 38), **FMIXING** (page 99), **SMEAR** (page 112), **BROYDEN**

(page 82) and **ANDERSON** (page 79).

At each SCF cycle the total atomic charges, following a Mulliken population analysis scheme, and the total energy are printed.

The default value of the parameters to control the exit from the SCF cycle ($\Delta E < 10^{-6}$ hartree, maximum number of SCF cycles: 50) may be modified entering the keywords:

TOLDEE (tolerance on change in total energy) page 115

TOLDEP (tolerance on SQM in density matrix elements) page ??

MAXCYCLE (maximum number of cycles) page 106

Spin-polarized system

By default the orbital occupancies are controlled according to the 'Aufbau' principle.

To obtain a spin polarized solution an open shell Hamiltonian must be defined (block3, **UHF** or **DFT/SPIN**). A spin-polarized solution may then be computed after definition of the (α - β) electron occupancy. This can be performed by the keywords **SPINLOCK** (page 114) and **BETALOCK** (page 80).

Chapter 2

Wave-function Calculation - Advanced Input Route

2.1 Geometry editing

The following keywords allow editing of the crystal structure, printing of extended information, generation of input data for visualization programs. Processing of the input block 1 only (geometry input) is allowed by the keyword **TEST[GEOM]**.

Each keyword operates on the geometry active when the keyword is entered. For instance, when a 2D structure is generated from a 3D one through the keyword **SLABCUT**, all subsequent geometry editing operates on the 2D structure. When a dimer is extracted from a molecular crystal through the keyword **MOLECULE**, all subsequent editing refers to a system without translational symmetry.

The keywords can be entered in any order: particular attention should be paid to the action of the keywords **KEEPSYMM** 2.1 and **BREAKSYM** 2.1, that allow maintaining or breaking the symmetry while editing the structure.

These keywords behave as a switch, and require no further data. Under control of the **BREAKSYM** keyword (the default), subsequent modifications of the geometry are allowed to alter (reduce: the number of symmetry operators cannot be increased) the point-group symmetry. The new group is a subgroup of the original group and is automatically obtained by **CRYSTAL**. However if a **KEEPSYMM** keyword is presented, the program will endeavor to maintain the number of symmetry operators, by requiring that atoms which are symmetry related remain so after a geometry editing (keywords: **ATOMSUBS**, **ATOMINSE**, **ATOMDISP**, **ATOMREMO**).

The space group of the system may be modified after editing. For 3D systems, the file **FINDSYM.DAT** may be written (keyword **FINDSYM**). This file is input to the program *findsym* (<http://physics.byu.edu/stokesh/isotropy.html>), that finds the space-group symmetry of a crystal, given the coordinates of the atoms.

Geometry keywords

| Symmetry information | | | |
|----------------------|--|----|---|
| ATOMSYMM | printing of point symmetry at the atomic positions | 36 | – |
| MAKESAED | printing of symmetry allowed elastic distortions (SAED) | 47 | – |
| PRSYMDIR | printing of displacement directions allowed by symmetry. | 59 | – |
| SYMMDIR | printing of symmetry allowed geom opt directions | 67 | – |
| SYMMOPS | printing of point symmetry operators | 67 | – |
| Tensor | print tensor of physical properties up to order 4 | 67 | I |

| | | | |
|--|---|----|---|
| Symmetry information and control | | | |
| BREAKELAS | symmetry breaking according to a general distortion | 37 | I |
| BREAKSYM | allow symmetry reduction following geometry modifications | 37 | - |
| KEEPSYMM | maintain symmetry following geometry modifications | 47 | - |
| MODISYMM | removal of selected symmetry operators | 48 | I |
| PURIFY | cleans atomic positions so that they are fully consistent with the group | 59 | - |
| SYMMREMO | removal of all symmetry operators | 67 | - |
| TRASREMO | removal of symmetry operators with translational components | 68 | - |
| Modifications without reduction of symmetry | | | |
| ATOMORDE | reordering of atoms in molecular crystals | 34 | - |
| NOSHIFT | no shift of the origin to minimize the number of symmops with translational components before generating supercell | 56 | - |
| ORIGIN | shift of the origin to minimize the number of symmetry operators with translational components | 56 | - |
| PRIMITIV | crystallographic cell forced to be the primitive cell | 58 | - |
| ROTCRY | rotation of the crystal with respect to the reference system cell | 60 | I |
| Atoms and cell manipulation - possible symmetry reduction (BREAKSYM) | | | |
| ATOMDISP | displacement of atoms | 34 | I |
| ATOMINSE | addition of atoms | 34 | I |
| ATOMREMO | removal of atoms | 35 | I |
| ATOMROT | rotation of groups of atoms | 35 | I |
| ATOMSUBS | substitution of atoms | 36 | I |
| ELASTIC | distortion of the lattice | 40 | I |
| POINTCHG | point charges input | 58 | I |
| SCELCONF | generation of supercell for configuration counting | 63 | I |
| SCELPHONO | generation of supercell for phonon dispersion | 63 | I |
| SUPERCEL | generation of supercell - input refers to primitive cell | 64 | I |
| SUPERCON | generation of supercell - input refers to conventional cell | 64 | I |
| USESAED | given symmetry allowed elastic distortions, reads δ | 68 | I |
| From crystals to slabs (3D→2D) | | | |
| SLABINFO | definition of a new cell, with $xy \parallel$ to a given plane | 62 | I |
| SLABCUT | generation of a slab parallel to a given plane (3D→2D) | 61 | I |
| From slabs to nanotubes (2D→1D) | | | |
| NANOTUBE | building a nanotube from a slab | 52 | I |
| SWCNT | building a nanotube from an hexagonal slab | 66 | I |
| From periodic structures to clusters | | | |
| CLUSTER | cutting of a cluster from a periodic structure (3D→0D) | 38 | I |
| CLUSTSIZE | maximum number of atoms in a cluster | 47 | I |
| FULLE | building a fullerene from an hexagonal slab (2D→0D) | 45 | I |
| HYDROSUB | border atoms substituted with hydrogens (0D→0D) | 47 | I |
| Molecular crystals | | | |

| | | | |
|--|---|----|---|
| MOLECULE | extraction of a set of molecules from a molecular crystal (3D→0D) | 49 | I |
| MOLEXP | variation of lattice parameters at constant symmetry and molecular geometry (3D→3D) | 49 | I |
| MOLSPLIT | periodic structure of non interacting molecules (3D→3D) | 49 | – |
| RAYCOV | modification of atomic covalent radii | 59 | I |
| BSSE correction | | | |
| MOLEBSSE | counterpoise method for molecules (molecular crystals only) (3D→0D) | 48 | I |
| ATOMBSSE | counterpoise method for atoms (3D→0D) | 34 | I |
| Systematic analysis of crystal planes | | | |
| PLANES | Prints the possible crystal planes | 58 | I |
| Gibbs-Wulff construction | | | |
| WULFF | Building the Gibbs-Wulff polyhedron | 68 | I |
| From crystals to nanorods (3D→1D) | | | |
| NANORODS | Building a nanorod from a crystal | 51 | I |
| From crystals to nanocrystals (3D→0D) | | | |
| NANOCRYSTAL | building a nanocrystal from a crystal | 50 | I |
| Auxiliary and control keywords | | | |
| ANGSTROM | sets input units to Ångstrom | 33 | – |
| BOHR | sets input units to bohr | 36 | – |
| BOHRANGS | input bohr to Å conversion factor (0.5291772083 default value) | 36 | I |
| BOHRCR98 | bohr to Å conversion factor is set to 0.529177 (CRY98 value) | – | |
| END/ENDG | terminate processing of geometry input | | – |
| FRACTION | sets input units to fractional | 45 | – |
| LATVEC | maximum number of classified lattice vectors | ?? | I |
| MAXNEIGHB | maximum number of equidistant neighbours from an atom | 47 | I |
| NEIGHBOR | number of neighbours in geometry analysis | 56 | I |
| PRINTCHG | printing of point charges coordinates in geometry output | 58 | |
| PRINTOUT | setting of printing options by keywords | 59 | – |
| SETINF | setting of inf array options | 61 | I |
| SETPRINT | setting of printing options | 61 | I |
| STOP | execution stops immediately | 62 | – |
| TESTGEOM | stop after checking the geometry input | 68 | – |
| Output of data on external units | | | |
| COORDPRT | coordinates of all the atoms in the cell | 40 | – |
| EXTPRT | write file in CRYSTAL geometry input format | 41 | – |
| FINDSYM | write file in FINDSYM input format | 44 | – |
| STRUCPRT | cell parameters and coordinates of all the atoms in the cell | 62 | – |
| External electric field - modified Hamiltonian | | | |
| FIELD | electric field applied along a periodic direction | 42 | I |
| FIELDCON | electric field applied along a non periodic direction | 44 | I |
| Geometry optimization - see index for keywords full list | | | |

| | | | |
|--|---|-----|---|
| OPTGEOM | Geometry optimization input block - closed by END | 118 | I |
| Type of optimization (default: atom coordinates) | | | |
| FULLOPTG | full geometry optimization | | - |
| CELLONLY | cell parameters optimization | | - |
| INTREDUN | optimization in redundant internal coordinates | 128 | - |
| ITATOCEL | iterative optimization (atom/cell) | | - |
| CVOLOPT | full geometry optimization at constant volume | 133 | - |
| Initial Hessian | | | |
| HESSIDEN | initial guess for the Hessian - identity matrix | | - |
| HESSMOD1 | initial guess for the Hessian - model 1 (default) | | - |
| HESSMOD2 | initial guess for the Hessian - model 2 | | - |
| HESSNUM | initial guess for the Hessian - numerical estimate | | - |
| Convergence criteria modification | | | |
| TOLDEG | RMS of the gradient [0.0003] | | I |
| TOLDEX | RMS of the displacement [0.0012] | | I |
| TOLDEE | energy difference between two steps [10^{-7}] | | I |
| MAXCYCLE | max number of optimization steps | | I |
| Optimization control | | | |
| FRAGMENT | partial geometry optimization | 135 | I |
| RESTART | data from previous run | | - |
| FINALRUN | Wf single point with optimized geometry | | I |
| Gradient calculation control | | | |
| NUMGRATO | numerical atoms first derivatives | 127 | - |
| NUMGRCEL | numerical cell first derivatives | 127 | - |
| NUMGRALL | numerical atoms and cell first derivatives | 127 | - |
| External stress | | | |
| EXTSTRESS | apply external stress | 137 | I |
| EXTPRESS | apply external hydrostatic pressure | 137 | I |
| Printing options | | | |
| PRINTFORCES | atomic gradients | | - |
| PRINTHESS | Hessian | | - |
| PRINTOPT | optimization procedure | | - |
| PRINT | verbose printing | | - |
| Vibrational Frequencies - see index for keywords full list | | | |
| FREQCALC | Harmonic Γ -frequencies calculation input - closed by END | 142 | I |
| Normal modes analysis | | | |
| ANALYSIS | | 144 | - |
| COMBMODE | TO combination modes and overtones | 145 | I |

| | | | |
|--|---|-----|---|
| MODES | printing eigenvectors [default] | 147 | - |
| SCANMODE | scan geometry along selected modes | 154 | I |
| LO/TO splitting | | | |
| DIELISO | isotropic dielectric tensor | 145 | I |
| DIELTENS | anisotropic dielectric tensor | 145 | I |
| Vibrational spectrum simulation | | | |
| INTENS | intensities calculation active | 150 | - |
| INTCPHF | IR (and Raman) intensities via CPHF | 152 | I |
| INTLOC | IR intensities through Wannier functions | 151 | - |
| INTPOL | IR intensities through Berry phase [default] | 152 | - |
| INTRAMAN | Raman intensities calculation | 152 | I |
| IRSPEC | IR spectrum production | 158 | I |
| RAMSPEC | Raman spectrum production | 160 | I |
| Calculation control | | | |
| ECKART | Hessian freed by translations and rotations [default] | 145 | I |
| FRAGMENT | partial frequency calculation | 146 | I |
| ISOTOPES | isotopic substitution | 146 | I |
| NORMBORN | normalized Born tensor | 147 | - |
| NUMBERIV | technique to compute numerical 2nd derivatives | 148 | I |
| PRINT | verbose printing | | - |
| RESTART | data from previous run | | - |
| STEPSIZE | set size of cartesian displacements [0.003 Å] | 148 | I |
| TEST[FREQ] | frequency test run | | - |
| USESMM | full-symmetry exploitation at each point [default] | | - |
| <i>A posteriori</i> corrections | | | |
| SCANPES | anharmonic correction | ?? | I |
| ANSCAN | scan a mode and apply anharmonic corrections | ?? | I |
| Phonon dispersion | | | |
| DISPERSION | frequencies calculated at $\vec{k} \neq \Gamma$ points | 161 | - |
| Thermodynamics | | | |
| ADP | anisotropic displacement parameters | 148 | I |
| PRESSURE | set pressure range | 148 | I |
| TEMPERAT | set temperature range | | I |
| ANHARM | Anharmonic frequencies calculation input block - closed by END | 165 | I |
| ISOTOPES | isotopic substitution | 166 | I |
| KEEPSYMM | displace all symmetry equivalent atoms | ?? | - |
| NOGUESS | | 166 | - |
| POINTS26 | X-H distance varied 26 times around the equilibrium | 166 | - |
| PRINT | verbose printing | | - |
| TEST[ANHA] | test run | | - |
| Configurations counting and characterization | | | |
| CONFCNT | configurations counting and cluster expansion | 174 | I |
| CONFRAND | symmetry-adapted uniform at random Monte Carlo | 176 | I |
| RUNCONFS | single-point calculations and geometry optimizations | 177 | I |
| CPHF - Coupled Perturbed Hartree-Fock 168 | | | |
| ELASTCON - Second order elastic constants 183 | | | |
| EOS - Equation of state 168 | | | |

Geometry input optional keywords

ANGLES

This option prints the angle the \widehat{AXB} , where X is one of the irreducible (that is, non symmetry equivalent) atoms of the unit cell, and A and B belong to its m-th and n-th stars of neighbors.

| rec | variable | meaning |
|-----|----------|--|
| • * | NATIR | number of X atoms to be considered; they are the first NATIR in the list of irreducible atoms (flag "T" printed) generated by CRYSTAL |
| * | NSHEL | number of stars of neighbors of X to be considered; all the angles \widehat{AXB} , where A and B belong to the first NSHEL neighbors of X, are printed out |

Though the keyword **ANGLES** can be entered in geometry input, full input deck must be supplied (block 1-2-3), in order to obtain information on bond angles, when neighbors analysis is printed.

Example. Bulk Silicon. There is 1 irreducible atom, and the first star of neighbors contain 4 atoms: (from CRYSTAL output):

```
COORDINATES OF THE EQUIVALENT ATOMS (FRACTIONAL UNITS)

N  ATOM  ATOM  Z      X      Y      Z
  IRR  EQUIV
1  1      1  14 SI  1.250000E-01  1.250000E-01  1.250000E-01
2  1      2  14 SI -1.250000E-01 -1.250000E-01 - 1.250000E-01
  - - - - -
N NUMBER OF NEIGHBORS AT DISTANCE R

STAR ATOM  N R/ANG  R/AU  NEIGHBORS (ATOM LABELS AND CELL INDICES)
1  1 SI  4 2.3469  4.4351  2 SI  0 0 0  2 SI  1 0 0  2 SI  0 1 0
                               2 SI  0 0 1
```

The number of angles having the irreducible Silicon as vertex is: $(4)*(4-1)/2 = 6$

ANGLES (DEGREES) ARE INDICATED AS A-X-B(I), I=1,L

```
at A cell  at X at B cell  angle at B cell  angle at B cell  angle
          AXB              AXB              AXB
2 SI( 0 0 0) 1 SI 2 SI( 1 0 0) 109.47 2 SI( 0 1 0) 109.47 2 SI( 0 0 1) 109.47
2 SI( 1 0 0) 1 SI 2 SI( 0 1 0) 109.47 2 SI( 0 0 1) 109.47
2 SI( 0 1 0) 1 SI 2 SI( 0 0 1) 109.47
```

If it is required to consider 6 stars of neighbors to compute all the angles having the irreducible Silicon as vertex, the number of angles computed will be:

$$(4+12+12+6+12+24)*(4+12+12+6+12+24-1)/2 = 2415$$

ANGSTROM - unit of measure

The unit of length in geometry editing is set to Ångstrom, (default value).

ANHARM - Anharmonic calculation of frequencies of X-H (X-D) bond stretching

See Chapter 4, page 165.

ATOMBSSE - counterpoise for closed shell atoms and ions

| rec | variable | meaning |
|-----|----------|---|
| • * | IAT | <i>label</i> of the atom in the reference cell |
| | NSTAR | maximum number of stars of neighbors included in the calculation. |
| | RMAX | maximum distance explored searching the neighbors of the atom. |

A cluster is defined including the selected atom and the basis functions belonging to the NSTAR sets of neighbors, when their distance R from the central atom is smaller than RMAX. The atomic wave function is not computed by the atomic package, but by the standard CRYSTAL route for 0D, 1 atom system. **UHF** and **SPINLOCK** must be used to define a reasonable orbital occupancy. It is suggested to compute the atomic wave function using a program properly handling the electronic configuration of open shell atoms.

Use keyword **CLUSTER** (47) to extend the number of atoms in the cluster if requested.

Warning. The system is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.3, page 25).

ATOMDISP

| rec | variable | meaning |
|-----|----------|--|
| • * | NDISP | number of atoms to be displaced _____ insert NDISP records _____ II |
| • * | LB | <i>label</i> of the atom to be moved |
| | DX,DY,DZ | increments of the coordinates in the primitive cell [Å]. |

Selected atoms are displaced in the primitive cell. The point symmetry of the system may be altered (default value **BREAKSYM**, page 37). To displace all the atoms symmetry related, **KEEPSYMM** must be inserted before **ATOMDISP**.

Increments are in Ångstrom, unless otherwise requested (keyword **BOHR**, **FRACTION**, page 33). See tests 17, 20, 37.

ATOMINSE

| rec | variable | meaning |
|-----|----------|--|
| • * | NINS | number of atoms to be added _____ insert NINS records _____ II |
| • * | NA | conventional atomic number |
| | X,Y,Z | coordinates [Å] of the inserted atom. Coordinates refer to the primitive cell. |

New atoms are added to the primitive cell. Coordinates are in Ångstrom, unless otherwise requested (keyword **BOHR**, **FRACTION**, page 33). Remember that the original symmetry of the system is maintained, applying the symmetry operators to the added atoms if the keyword **KEEPSYMM** (page 37) was previously entered. The default is **BREAKSYM** (page 37). Attention should be paid to the neutrality of the cell (see **CHARGED**, page 69). See tests 16, 35, 36.

ATOMORDE

After processing the standard geometry input, the symmetry equivalent atoms in the reference cell are grouped. They may be reordered, following a chemical bond criterion. This simplifies the interpretation of the output when the results of bulk molecular crystals are compared with those of the isolated molecule. See option **MOLECULE** (page 49) and **MOLSPLIT** (page 49). No input data are required.

For molecular crystals only.

ATOMREMO

| rec | variable | meaning |
|-----|--------------|------------------------------|
| • * | NL | number of atoms to remove |
| • * | LB(L),L=1,NL | label of the atoms to remove |

Selected atoms, and related basis set, are removed from the primitive cell (see test 16). A vacancy is created in the lattice. The symmetry can be maintained (**KEEPSYMM**), by removing all the atoms symmetry-related to the selected one, or reduced (**BREAKSYM**, default). Attention should be paid to the neutrality of the cell (see **CHARGED**, page 69). NB. The keyword **GHOSTS** (basis set input, page 71) allows removal of selected atoms, leaving the related basis set.

ATOMROT

| rec | variable | value | meaning |
|-----|--------------|------------|--|
| • * | NA | 0 | all the atoms of the cell are rotated and/or translated |
| | | >0 | only NA selected atoms are rotated and/or translated. |
| | | <0 | the atom with label NA belongs to the molecule to be rotated. The program selects all the atoms of the molecule on the base of the sum of their atomic radii (Table on page 59). |
| | | | <i>if NA > 0, insert NA data</i> _____ II |
| • * | LB(I),I=1,NA | | label of the atoms to be rotated and/or translated. |
| • * | ITR | >0 | translation performed. The selected NA atoms are translated by $-\mathbf{r}$, where \mathbf{r} is the position of the ITR-th atom. ITR is at the origin after the translation. |
| | | ≤ 0 | a general translation is performed. See below. |
| | | =999 | no translation. |
| | IRO | > 0 | a rotation around a given axis is performed. See below. |
| | | < 0 | a general rotation is performed. See below. |
| | | =999 | no rotation. |
| | | | <i>if ITR<0 insert</i> _____ II |
| • * | X,Y,Z | | Cartesian components of the translation vector [\AA] |
| | | | <i>if ITR=0 insert</i> _____ II |
| • * | N1,N2 | | label of the atoms defining the axis. |
| | DR | | translation along the axis defined by the atoms N1 and N2, in the direction $N1 \rightarrow N2$ [\AA]. |
| | | | <i>if IRO<0 insert</i> _____ II |
| • * | A,B,G | | Euler rotation angles (degree). |
| | IPAR | | defines the origin of the Cartesian system for the rotation |
| | | 0 | the origin is the barycentre of the NAT atoms |
| | | >0 | the origin is the atom of label IPAR |
| | | | <i>if IRO>0 insert</i> _____ II |
| • * | N1,N2 | | label of the atoms that define the axis for the rotation |
| | ALPHA | $\neq 0$. | rotation angle around the N1–N2 axis (degrees) |
| | | 0. | the selected atoms are rotated anti-clockwise in order to orientate the N1–N2 axis parallel to the z axis. |

This option allows to rotate and/or translate the specified atoms. When the rotation of a molecule is required ($NA < 0$), the value of the atomic radii must be checked, in order to obtain a correct definition of the molecule. It is useful to study the conformation of a molecule in a zeolite cavity, or the interaction of a molecule (methane) with a surface (MgO).

The translation of the selected group of atoms can be defined in three different ways:

1. Cartesian components of the translation vector ($ITR < 0$);
2. modulus of the translation vector along an axis defined by two atoms ($ITR = 0$);

3. sequence number of the atom to be translated to the origin. All the selected atoms are subjected to the same translation ($ITR > 0$).

The rotation can be performed in three different ways:

1. by defining the Euler rotation angles α, β, γ and the origin of the rotating system ($IRO < 0$). The axes of the rotating system are parallel to the axes of the Cartesian reference system. (The rotation is given by: $R^{\alpha z} R^{\beta x} R^{\gamma z}$, where R are the rotation matrices).
2. by defining the rotation angle α around an axis defined by two atoms A and B. The origin is at A, the positive direction A→B.
3. by defining a z' axis (identified by two atoms A and B). The selected atoms are rotated, in such a way that the A–B z' axis becomes parallel to the z Cartesian axis. The origin is at A and the positive rotation anti clockwise ($IRO > 0, \alpha = 0$).

The selected atoms are rotated according to the defined rules, the cell orientation and the cartesian reference frame are not modified. The symmetry of the system is checked after the rotation, as the new geometry may have a different symmetry.

See tests 15, rotation of the NH_3 molecule in a zeolite cavity, and 16, rotation of the H_2O molecule in the zeolite cavity.

ATOMSUBS

| rec | variable | meaning |
|-----|----------|--|
| • * | NSOST | number of atoms to be substituted |
| | | insert NSOST records _____ II |
| • * | LB | <i>label</i> of the atom to substitute |
| | NA(LB) | conventional atomic number of the new atom |

Selected atoms are substituted in the primitive cell (see test 17, 34, 37). The symmetry can be maintained (**KEEPSYMM**), by substituting all the atoms symmetry-related to the selected one, or reduced (**BREAKSYM**, default). Attention should be paid to the neutrality of the cell: a non-neutral cell will cause an error message, unless allowed by entering the keyword **CHARGED**, page 69.

ATOMSYMM

The point group associated with each atomic position and the set of symmetry related atoms are printed. No input data are required. This option is useful to find the internal coordinates to be relaxed when the unit cell is deformed (see **ELASTIC**, page 40).

BOHR

The keyword **BOHR** sets the unit of distance to bohr. When the unit of measure is modified, the new convention is active for all subsequent geometry editing.

The conversion factor Ångstrom/bohr is 0.5291772083 (CODATA 1998). This value can be modified by entering the keyword **BOHRANGS** and the desired value in the record following. The keyword **BOHRCR98** sets the conversion factor to 0.529177, as in the program CRYSTAL98.

CRYSTAL88 default value was 0.529167).

BOHRANGS

| rec | variable | meaning |
|-----|----------|---------------------------------|
| • * | BOHR | conversion factor Ångstrom/bohr |

The conversion factor Ångstrom/bohr can be user-defined.

In CRYSTAL88 the default value was 0.529167.

In CRYSTAL98 the default value was 0.529177.

BOHRCR98

The conversion factor Ångstrom/bohr is set to 0.529177, as in CRYSTAL98. No input data required.

BREAKSYM

Under control of the **BREAKSYM** keyword (the default), subsequent modifications of the geometry are allowed to alter (reduce: the number of symmetry operators cannot be increased) the point-group symmetry. The new group is a subgroup of the original group and is automatically obtained by **CRYSTAL**.

The symmetry may be broken by attributing different spin (**ATOMSPIN**, block34, page 80) to atoms symmetry related by geometry.

Example: When a CO molecule is vertically adsorbed on a (001) 3-layer MgO slab, (D_{4h} symmetry), the symmetry is reduced to C_{4v} , if the **BREAKSYM** keyword is active. The symmetry operators related to the σ_h plane are removed. However, if **KEEPSYMM** is active, then additional atoms will be added to the underside of the slab so as to maintain the σ_h plane (see page 34, keyword **ATOMINSE**).

BREAKELAS (for 3D systems only)

This keyword breaks the symmetry of 3D systems according to a general distortion (3x3 adimensional matrix, not necessarily symmetric):

| rec | variable | value | meaning |
|-----|-------------|-------|---------------------------|
| • * | D11 D12 D13 | | first row of the matrix. |
| • * | D21 D22 D23 | | second row of the matrix. |
| • * | D31 D32 D33 | | third row of the matrix. |

BREAKELAS can be used when the symmetry must be reduced to apply an external stress (see EXTSTRESS, OPTGEOM input block, page 137) not compatible with the present symmetry.

BREAKELAS reduces the symmetry according to the distortion defined in input, but **does not perform a distortion of the lattice**.

Another possibility is when you compute elastic constants, and you want to fix a reference geometry with FIXINDEX. If your reference geometry has a symmetry higher than the distorted one, then you had to break the symmetry by applying e.g. a tiny elastic distortion with ELASTIC. By using BREAKELAS you can reduce the symmetry without distortion of the lattice.

Example - Geometry optimization of MgO bulk, cubic, with an applied uniaxial stress modifying the symmetry of the cell.

```
TEST11 - MGO BULK
CRYSTAL
0 0 0
  225
4.21
2
  12 0.   0.   0.
   8 0.5  0.5  0.5
BREAKELAS   the number of symmops is reduced, from 48 to 16
0.001 0. 0. the cell has a tetragonal symmetry now
0. 0. 0.
0. 0. 0.
OPTGEOM
FULLOPTG
EXTSTRESS
```

```

0.001 0. 0.
0. 0. 0.
0. 0. 0.
ENDOPT

```

When EXTSTRESS is requested, the code automatically checks if the required distortion is possible or not (if the symmetry had not been broken properly beforehand, an error message comes).

CLUSTER - a cluster (0D) from a periodic system

The **CLUSTER** option allows one to cut a finite molecular cluster of atoms from a periodic lattice. The size of the cluster (which is centred on a specified 'seed point' A) can be controlled either by including all atoms within a sphere of a given radius centred on A, or by specifying a maximum number of symmetry-related stars of atoms to be included.

The cluster includes the atoms B (belonging to different cells of the direct lattice) satisfying the following criteria:

1. those which belong to one of the first N (input data) stars of neighbours of the *seed* point of the cluster.

and

2. those at a distance R_{AB} from the seed point which is smaller than RMAX (input datum).

The resulting cluster may not reproduce exactly the desired arrangement of atoms, particularly in crystals with complex structures such as zeolites, and so it is possible to specify border modifications to be made after definition of the core cluster.

Specification of the core cluster:

| rec | variable | value | meaning |
|--|----------|-------|--|
| • * | X, Y, Z | | coordinates of the centre of the cluster [Å] (the seed point) |
| | NST | | maximum number of stars of neighbours explored in defining the core cluster |
| | RMAX | | radius of a sphere centred at X,Y,Z containing the atoms of the core cluster |
| • * | NNA | ≠ 0 | print nearest neighbour analysis of cluster atoms (according to a radius criterion) |
| | NCN | 0 | testing of coordination number during hydrogen saturation carried out only for Si (coordination number 4), Al (4) and O(2) |
| | N | | N user-defined coordination numbers are to be defined |
| <i>if NNA ≠ 0 insert 1 record</i> _____II | | | |
| • * | RNNA | | radius of sphere in which to search for neighbours of a given atom in order to print the nearest neighbour analysis |
| <i>if NCN ≠ 0 insert NCN records</i> _____II | | | |
| • * | L | | conventional atomic number of atom |
| | MCONN(L) | | coordination number of the atom with conventional atomic number L. MCONN=0, coordination not tested |

Border modification:

| rec | variable | value | meaning | |
|-----|----------|-------|---|----|
| • * | NMO | | number of border atoms to be modified | |
| | | | <i>if NMO > 0 insert NMO records</i> | II |
| • * | IPAD | | <i>label of the atom to be modified (cluster sequence)</i> | |
| | NVIC | | number of stars of neighbours of atom IPAD to be added to the cluster | |
| | IPAR | = 0 | no hydrogen saturation | |
| | | ≠ 0 | cluster border saturated with hydrogen atoms | |
| | BOND | | bond length Hydrogen-IPAD atom (direction unchanged). | |
| | | | <i>if NMO < 0 insert</i> | II |
| • * | IMIN | | <i>label of the first atom to be saturated (cluster sequence)</i> | |
| | IMAX | | <i>label of the last atom to be saturated (cluster sequence)</i> | |
| | NVIC | | number of stars of neighbours of each atom to be added to the cluster | |
| | IPAR | = 0 | no hydrogen saturation | |
| | | ≠ 0 | cluster border saturated with hydrogen atoms | |
| | BOND | | H-cluster atom bond length (direction unchanged). | |

The two kinds of possible modification of the core cluster are (a) addition of further stars of neighbours to specified border atoms, and (b) saturation of the border atoms with hydrogen. This latter option can be essential in minimizing border electric field effects in calculations for covalently-bonded systems.

(Substitution of atoms with hydrogen is obtained by **HYDROSUB**).

The hydrogen saturation procedure is carried out in the following way. First, a coordination number for each atom is assumed (by default 4 for Si, 4 for Al and 2 for O, but these may be modified in the input deck for any atomic number). The actual number of neighbours of each specified border atom is then determined (according to a covalent radius criterion) and compared with the assumed connectivity. If these two numbers differ, additional neighbours are added. If these atoms are not neighbours of any other existing cluster atoms, they are converted to hydrogen, otherwise further atoms are added until the connectivity allows complete hydrogen saturation whilst maintaining correct coordination numbers.

The *label* of the IPAD atoms refers to the generated cluster, *not* to the original unit cell. The preparation of the input thus requires two runs:

1. run using the **CLUSTER** option with NMO=0, in order to generate the sequence number of the atoms in the core cluster. The keyword **TESTGEOM** should be inserted in the geometry input block. Setting NNA ≠ 0 in the input will print a coordination analysis of all core cluster atoms, including all neighbours within a distance RNNa (which should be set slightly greater than the maximum nearest neighbour bond length). This can be useful in deciding what border modifications are necessary.
2. run using the **CLUSTER** option with NMO ≠ 0, to perform desired border modifications.

Note that the standard CRYSTAL geometry editing options may also be used to modify the cluster (for example by adding or deleting atoms) placing these keywords after the specification of the **CLUSTER** input.

Use keyword **CLUSTER** (47) to extend the number of atoms in the cluster if requested.

Warning. The system is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.3, page 25). See test 16.

CLUSTSIZE - maximum size of a cluster

| rec | variable | meaning |
|-----|----------|---|
| • * | NATOCU | maximum number of atoms allowed in creating a cluster |

This keyword sets a new limit to the maximum number of atoms allowed in a cluster created by keywords **CLUSTER**, **ATOMBSSE** and **MOLEBSSE**. Default value is equal to the number of atoms in the unit cell.

CONFCONT - Mapping of CRYSTAL calculations to model Hamiltonians

See Chapter 6.1, page 174.

COORPRT

Geometry information is printed: cell parameters, fractional coordinates of all atoms in the reference cell, symmetry operators.

A formatted file, "fort.33", is written. See Appendix D, page 324. No input data are required. The file "fort.33" has the right format for the program **MOLDEN** [161] which can be downloaded from:

www.cmbi.ru.nl/molden/molden.html

CPHF - performs the Coupled Perturbed HF/KS calculation up to the second order

See Chapter 5, page 168.

ELASTCON - Calculation of elastic constants

See Chapter 8, page 183.

ELASTIC

An elastic deformation of the lattice may be defined in terms of the Z or ϵ strain tensors defined in section 13.9, page 284.

| rec | variable | value | meaning |
|-----|-------------|---------|--|
| • * | IDEF | ± 1 | deformation through equation 13.49, Z matrix. |
| | | ± 2 | deformation through equation 13.48: ϵ matrix. |
| | | > 0 | volume conserving deformation (equation 13.50). |
| | | < 0 | not volume conserving (equation 13.49 or 13.48). |
| • * | D11 D12 D13 | | first row of the matrix. |
| • * | D21 D22 D23 | | second row of the matrix. |
| • * | D31 D32 D33 | | third row of the matrix. |

The elastic constant is $V^{-1} \frac{\partial^2 E}{\partial \epsilon_i^2} |_{\epsilon_i=0}$, where V is the volume of the primitive unit cell.

The symmetry of the system is defined by the symmetry operators in the new crystallographic cell. The keyword **MAKESAED** gives information on symmetry allowed elastic distortions. The calculation of the elastic constants with **CRYSTAL** requires the following sequence of steps:

1. select the ϵ_{ij} matrix elements to be changed (for example, $\epsilon_4 \equiv \epsilon_{23} + \epsilon_{32}$), and set the others ϵ_j to zero;
2. perform calculations with different values of the selected matrix element(s) ϵ_i : 0.02, 0.01, 0.001, -0.001, -0.01, -0.02, for example, and for each value compute the total energy E ;
3. perform a polynomial fit of E as a function of ϵ_i .

ϵ is adimensional, Z in Å (default) or in bohr (page 33). The suggested value for IDEF is -2 (deformation through equation 13.48, *not* volume conserving). The examples refer to this setting.

Example

Geometry input deck to compute one of the energy points used for the evaluation of the C_{44} (page 287) elastic constants of Li_2O [51].

| | | |
|---------------|--|---|
| CRYSTAL | | |
| 0 0 0 | | 3D code |
| 225 | | 3D space group number |
| 4.5733 | | lattice parameter (Å) |
| 2 | | 2 non equivalent atoms in the primitive cell |
| 8 0.0 0.0 0.0 | | Z=8, Oxygen; x, y, z |
| 3 .25 .25 .25 | | Z=3, Lithium; x, y, z |
| ATOMSYMM | | printing of the point group at the atomic positions |
| ELASTIC | | |
| -2 | | deformation not volume conserving through equation 13.48 |
| 0. 0.03 0.03 | | ϵ matrix input by rows |
| 0.03 0. 0.03 | | |
| 0.03 0.03 0. | | |
| ATOMSYMM | | printing of the point group at the atomic positions after the deformation |
| | | |

A rhombohedral deformation is obtained, through the ϵ matrix. The printout gives information on the crystallographic and the primitive cell, before and after the deformation:

LATTICE PARAMETERS (ANGSTROMS AND DEGREES) OF

- (1) ORIGINAL PRIMITIVE CELL
- (2) ORIGINAL CRYSTALLOGRAPHIC CELL
- (3) DEFORMED PRIMITIVE CELL
- (4) DEFORMED CRYSTALLOGRAPHIC CELL

| | A | B | C | ALPHA | BETA | GAMMA | VOLUME |
|-----|----------|----------|----------|-----------|-----------|-----------|-----------|
| (1) | 3.233811 | 3.233811 | 3.233811 | 60.000000 | 60.000000 | 60.000000 | 23.912726 |
| (2) | 4.573300 | 4.573300 | 4.573300 | 90.000000 | 90.000000 | 90.000000 | 95.650903 |
| (3) | 3.333650 | 3.333650 | 3.333650 | 56.130247 | 56.130247 | 56.130247 | 23.849453 |
| (4) | 4.577414 | 4.577414 | 4.577414 | 86.514808 | 86.514808 | 86.514808 | 95.397811 |

After the deformation of the lattice, the point symmetry of the Li atoms is C_{3v} , where the C_3 axis is along the (x,x,x) direction. The Li atoms can be shifted along the principal diagonal, direction (x,x,x) of the primitive cell without altering the point symmetry, as shown by the printing of the point group symmetry obtained by the keyword **ATOMSYMM** (page 36).

See test20 for complete input deck, including shift of the Li atoms.

See test38 ($KCoF_3$).

END

Terminate processing of block 1, geometry definition, input. Execution continues. Subsequent input records are processed, if required.

Processing of geometry input block stops when the first three characters of the string are "END". Any character can follow: ENDGEOM, ENDGINP, etc etc.

EXTPRT

A formatted input deck with explicit structural/symmetry information is written in file "fort.34". If the keyword is entered many times, the data are overwritten. The last geometry is recorded. The file may be used as crystal geometry input to CRYSTAL through the **EXTERNAL** keyword.

For instance, to enter the final optimized geometry, or a geometry obtained by editing operations who modified the original space group or periodicity.

When geometry optimization is performed, the name of the file is "optc(a)xxx", being xxx the number of the cycle, and it is automatically written at each cycle.

Please refer to the standard script for running CRYSTAL09 to handle input/output file names. See Appendix D, page 319.

No input data are required.

FIELD - Electric field along a periodic direction

| rec | variable | value | meaning |
|-----|---------------|-------|--|
| • * | E0MAX | | electric field intensity E_0 (in atomic units) |
| • * | DIRE(I),I=1,3 | | crystallographic (Miller) indices of the plane perpendicular to the electric field |
| • * | SMFACT | | supercell expansion factor |
| * * | IORTO | 0 | non-orthogonal supercell |
| | | 1 | orthogonal supercell |
| • * | MUL | | number of term in Fourier expansion for triangular electric potential |
| * * | ISYM | +1 | triangular potential is symmetric with respect to the $z = 0$ plane |
| | | -1 | triangular potential is anti-symmetric with respect to the $z = 0$ plane |

This option can be used with polymers, slabs and crystals and permits to apply an electric field along a periodic direction of the system.

The effect of a periodic electric field (\vec{E}) is taken into account according to a perturbation scheme. The Hamiltonian (Fock or Kohn-Sham) can be written as::

$$\hat{H} = \hat{H}_0 + \hat{H}_1(\vec{E}) \quad (2.1)$$

where \hat{H}_0 is the unperturbed Hamiltonian and $\hat{H}_1(\vec{E})$ the electric potential term.

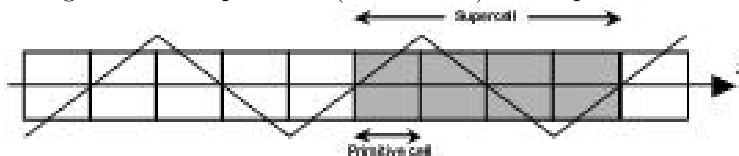
During the SCF procedure crystalline orbitals are relaxed under the effect of the field, leading to a perturbed wave function and charge density.

The applied electric field has a square-wave form, that corresponds to a triangular ("sawtooth") electric potential.

Due to the form of the potential, a single unit cell must contain both positive and negative part of the square wave electric field. Then, in order to maintain translational invariance of the system a new, expanded, unit cell is automatically created by adopting a supercell approach (see keywords **SUPERCEL/SUPERCON**, page 64).

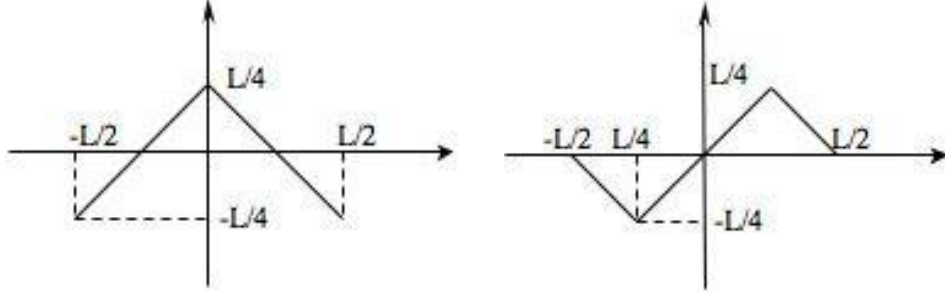
This procedure consists in two automatic steps: the re-orientation of the c lattice parameter along the chosen field direction and the multiplication of this lattice vector according to the supercell expansion factor ($\vec{C} = \text{SMFACT} \cdot \vec{c}$, see fig. 2.1). By varying this parameter is possible to control the period of the electric potential and therefore the length of the constant region of the electric field.

Figure 2.1: Triangular electric potential ("sawtooth") in a supercell with $SMFACT = 4$.



Then, for computational reasons, an automatic rotation of the crystal in the cartesian reference system is performed by aligning \vec{C} (and therefore \vec{E}) along the z cartesian direction (see keyword **ROTCRY**, page 60). After these transformations the field is along the z direction,

Figure 2.2: Left: symmetric triangular electric potential (ISIM = 1). Right anti-symmetric triangular electric potential (ISYM=-1).



and the perturbation $\hat{H}_1(\vec{E})$ takes the form:

$$\hat{H}_1^\pm(E_z) = V(z) = -qE_0 \cdot f^\pm(z) \quad (2.2)$$

where the f^+ (f^-) function is expanded as a Fourier series and is chosen according to the symmetry of the supercell in the direction of the applied field as follows:

$$f^+(z) = \frac{2C}{\pi^2} \sum_{k=0}^{+\infty} \frac{1}{(2k+1)^2} \cos\left(\frac{2\pi(2k+1)z}{C}\right) \quad (2.3)$$

$$f^-(z) = \frac{2C}{\pi^2} \sum_{k=0}^{+\infty} \frac{(-1)^k}{(2k+1)^2} \sin\left(\frac{2\pi(2k+1)z}{C}\right) \quad (2.4)$$

1. In order to evaluate the dielectric constant of a material in the direction of the applied field it is necessary to run a PROPERTIES calculation with the keyword **DIEL** (see page 205). In this way the perturbed wave function is used for the calculation of ϵ , following a macroscopic average scheme, as described in references [78], [41].
2. The field is along the z axis for 3D-crystal calculations; it is along the x for 1D-polymer and 2D-slab calculations.
3. In calculations of the dielectric constant, more accurate results can be achieved by increasing the SMFACT value. This will lead to systems characterized by a high number of atoms with large computational costs. The option IORTO = 0 allows to consider non-orthogonal supercells, characterized by the same dielectric properties of orthogonal cells, but with a lower number of atoms.
4. In 3D-crystals, the electric potential takes a triangular form to maintain translational symmetry and electric neutrality of cell. The symmetry of triangular potential has two options:
 - a) ISYM=+1, triangular potential is symmetric with respect to the center of the supercell, along the z axis. Use this option if there is a symmetry plane orthogonal to the z axis.
 - b) ISYM=-1, triangular potential is anti-symmetric. This option can be used when the supercell does not have a symmetry plane orthogonal to z axis.
5. MUL, the number of terms in the Fourier expansion, can take values between 1 and 60. MUL=40 is sufficient to adequately reproduce the triangular shape of the potential.

- High E0MAX values are inconsistent with perturbation method, the choice of E0MAX depends on the dielectric susceptibility of the system and on the gap width. For small gap cases, use of eigenvalue level shifting technique is recommended (keyword **LEVSHIFT**, page 105).
- When an external field is applied, the system can become conducting during the SCF procedure. In order to avoid convergence problems, it is advisable to set the shrinking factor of the Gilat net ISP equal to $2 \times IS$, where IS is the Monkhorst net shrinking factor (see SCF input, page 110).

Conversion factors for electric field:

$$1 \text{ AU} = 1.71527\text{E}+07 \text{ ESU}\cdot\text{CM}^{-2} = 5.72152\text{E}+01 \text{ C}\cdot\text{M}^{-2} = 5.14226\text{E}+11 \text{ V}\cdot\text{M}^{-1}$$

FIELDCON - Electric field along non-periodic direction

| rec | variable | meaning |
|-----|------------|---|
| • * | E(I),I=N,3 | field components along x,y,z directions |

For a brief theoretical introduction see keyword FIELD.

This option can be used with molecules, polymers, slabs and permits to apply an electric field along a non-periodic direction of the system.

- For molecules (N=1) three components of the field must be supplied, as the field can be directed along any direction.
- For polymers (N=2) two components (y,z) of the field must be defined; the x component of the field must be zero because the default orientation of polymers is along the x axis.
- For slabs (N=3) just one component (z) of the field have to be defined; the x,y components must be zero because the default orientation of slabs is in x-y plan.

Conversion factors for electric field:

$$1 \text{ AU} = 1.71527\text{E}+07 \text{ ESU}\cdot\text{CM}^{-2} = 5.72152\text{E}+01 \text{ C}\cdot\text{M}^{-2} = 5.14226\text{E}+11 \text{ V}\cdot\text{M}^{-1}$$

This option can evaluate the dielectric response of the molecule, polymer or slab in a direction of non periodicity (see option FIELD for a field along a periodicity direction).

Consider the following expansion of the total energy of the system as a function of the applied field:

$$E(F_0) = E_0 - \mu F_0 - \frac{1}{2!} \alpha F_0^2 - \frac{1}{3!} \beta F_0^3 - \frac{1}{4!} \gamma F_0^4 - \dots \quad (2.5)$$

By fitting the E vs F_0 data the μ , α , β and γ values can be derived. See <http://www.crystal.unito.it> → tutorials → Static dielectric constants..

FINDSYM

Geometry information is written in file FINDSYM.DAT, according to the input format of the program FINDSYM.

<http://stokes.byu.edu/findsym.html>

FINDSYM: Identify the space group of a crystal, given the positions of the atoms in a unit cell. When geometry editing modifies the basic input space group, the symmetry of the system is identified by the symmetry operators only. The program *FINDSYM* allows identification of the space group.

FRACTION

The keyword **FRACTION** means input coordinates given as fraction of the lattice parameter in subsequent input, along the direction of translational symmetry:

x,y,z crystals (3D)
 x,y slabs (2D; z in Ångstrom or bohr)
 x polymers (1D; y,z in Ångstrom or bohr)

no action for 0D. When the unit of measure is modified, the new convention is active for all subsequent geometry editing.

FREQCALC - Harmonic frequencies at Γ

See Chapter 4, page 142.

FULLE - Building a fullerene from a slab

Fullerenes are molecular cage-like structures. An effective way of constructing them exploiting all the possible symmetry is by starting from a 2D periodic flat structure.

In this flat lattice, the vector $\mathbf{R}=n_1\vec{a}_1+n_2\vec{a}_2$ (where \vec{a}_1 and \vec{a}_2 are the slab cell vectors) permits to define the side of a triangular face of the fullerene. Then, the indices $(n1,n2)$ completely define the faces of the fullerene, and are used in the literature to characterise this type of systems. The case of a (2,2) carbon fullerene is given in figure 2.3 as an example.

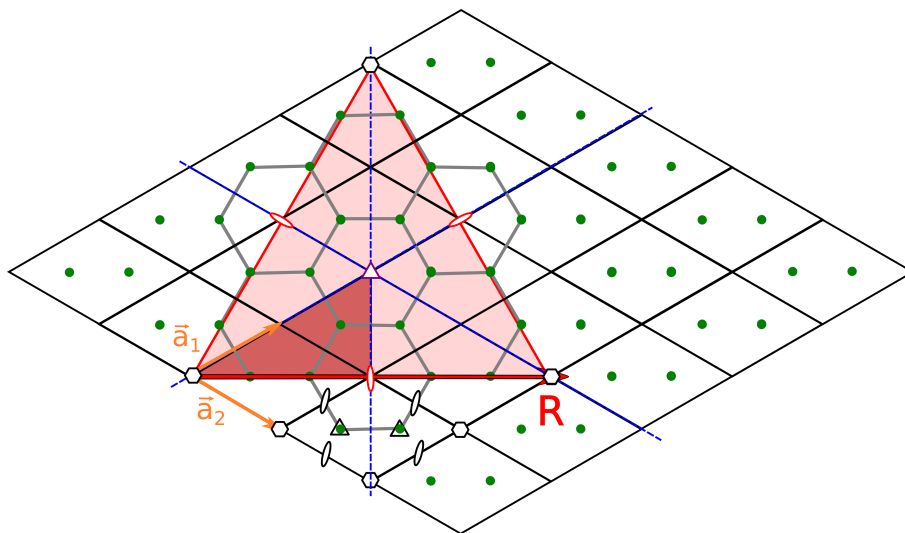


Figure 2.3: Building the (2,2) fullerene from graphene.

Once the face is defined, the second key information is the type of polyhedron to be constructed, and the corresponding point symmetry. CRYSTAL currently permits the automatic construction of the following combinations:

- Icosahedron: I, I_h ;
- Octahedron: T, T_d, T_h, O, O_h ;
- Tetrahedron: T, T_d .

The **FULLE** keyword can only be used starting from hexagonal 2D lattices.
 For further details and explanatory animations, please refer to the tutorial page:

<http://www.crystal.unito.it> → tutorials → Fullerene systems

Users of the fullerene construction options are kindly requested to cite the following paper[?]:

Y. Noël, M. De La Pierre, C.M. Zicovich-Wilson, R. Orlando and R. Dovesi, *Phys. Chem. Chem. Phys.*, **16**, 13390 (2014). *Structural, electronic and energetic properties of giant icosahedral fullerenes up to C6000: insights from an ab initio hybrid DFT study.*

| rec | variable | value | meaning |
|-----|------------|-------------------------------------|--|
| • * | n_1, n_2 | | components of the R vector in terms of the basis vectors \vec{a}_1 and \vec{a}_2 of the hexagonal unit cell |
| • * | PG | T TD TH O OH I IH | point group for the fullerene |
| • * | POLY | TETRA OCTA ICOSA | type of polyhedron |

FULLEJMOL - Graphical visualisation of fullerenes with Jmol

A file named FULLEJMOL.DAT containing the fullerene structure is generated. This file can be directly used by the 3D structure viewer Jmol (www.jmol.org). This keyword must appear in the geometry block *before* all the keywords related to fullerene construction.

FULLESPHE - Spherical fullerenes

| rec | variable | meaning |
|-----|----------|------------------------------|
| • * | RSPHE | distance from the origin [Å] |

All the atoms of the fullerene are moved to the same radius RSPHE; this is the distance from the origin of the cartesian framework. RSPHE is in Ångstrom, unless otherwise requested (keyword **BOHR**, page 33). The symmetry of the fullerene is preserved. This option permits to construct spherical fullerenes.

This keyword can be used when building fullerenes from a slab (**FULLE** keyword, page 45), when generating a fullerene from molecular point groups with **MOLECULE**, page 15 (additional **RADFULLE** keyword required, page 59), or when recovering a fullerene geometry from an external file with **EXTERNAL**, page 16 (additional **RADFULLE** keyword required). **FULLESPHE** must always be inserted after the **FULLE** or **RADFULLE** keywords.

HYDROSUB - substitution with hydrogen atoms

| rec | variable | meaning |
|-----|----------|---|
| • * | NSOST | number of atoms to be substituted with hydrogen |
| | | insert NSOST records _____ II |
| • * | LA | <i>label</i> of the atom to substitute |
| | LB | <i>label</i> of the atom linked to LA |
| | BH | bond length B-Hydrogen |

Selected atoms are substituted with hydrogens, and the bond length is modified. To be used after **CLUSTER**.

KEEPSYMM

In any subsequent editing of the geometry, the program will endeavour to maintain the number of symmetry operators, by requiring that atoms which are symmetry related remain so after geometry editing (keywords: **ATOMSUBS**, **ATOMINSE**, **ATOMDISP**, **ATOMREMO**) or the basis set (keywords **CHEMOD**, **GHOSTS**).

Example: When a CO molecule is vertically adsorbed on a (001) 3-layer MgO slab, (D_{4h} symmetry) (see page 34, keyword **ATOMINSE**), the symmetry is reduced to C_{4v} , if the **BREAKSYM** keyword is active. The symmetry operators related to the σ_h plane are removed. However, if **KEEPSYMM** is active, then additional atoms will be added to the underside of the slab so as to maintain the σ_h plane.

LATVEC - maximum size of the cluster of classified lattice vectors

| rec | variable | meaning |
|-----|-----------|--|
| • * | MAXGSIIZE | maximum number of lattice vectors to be classified |

A very accurate CRYSTAL calculation may require the evaluation of interactions between atoms in very distant cells (when using very severe computational conditions). If the list of lattice vectors which were classified by default is incomplete with respect to the requirement, an error message appears. In this case it is necessary to extend MAXGSIIZE beyond its default value (3500).

MAKESAED

Symmetry allowed elastic distortions are printed. No input data required.

MAXNEIGHB - maximum number of equidistant neighbours of an atom

| rec | variable | meaning |
|-----|----------|---|
| • * | MAXNEIG | maximum number of atoms allowed in creating a cluster |

When printing of atom neighbouring relationship is requested (**NEIGHBOR**, page 56) for several orders of vicinity the number of equidistant atoms from a given atom in the unit cell can be large. If such a number exceeds 48 (default value), the program stops with an error message. Use of this keyword allows increasing the value of MAXNEIG.

MODISYMM

| rec | variable | meaning |
|-----|-----------------|---|
| • * | N | number of atoms to be attached a flag |
| • * | LA,LF(LA),L=1,N | atom <i>labels</i> and flags (n couples of integers in 1 record). |

The point symmetry of the lattice is lowered by attributing a different "flag" to atoms related by geometrical symmetry. The symmetry operators linking the two atoms are removed and the new symmetry of the system is analyzed. For instance, when studying spin-polarized systems, it may be necessary to apply different spins to atoms which are related by geometrical symmetry.

MOLDRAW

The last version of the program *MOLDRAW* reads *crystal* standard output, and can generate a movie from an optimization run. See:

<http://www.moldraw.unito.it>.

MOLEBSSE - counterpoise for molecular crystals

| rec | variable | meaning |
|-----|----------|--|
| • * | NMOL | number of molecules to be isolated |
| II | _____ | insert NMOL records _____ II |
| • * | ISEED | <i>label</i> of one atom in the n-th molecule |
| | J,K,L | integer coordinates (direct lattice) of the primitive cell containing the ISEED atom |
| • * | NSTAR | maximum number of stars of neighbours included in the calculation |
| | RMAX | maximum distance explored searching the neighbours of the atoms belonging to the molecule(s) |

The counterpoise method [24] is applied to correct the Basis Set Superposition Error in molecular crystals. A molecular calculation is performed, with a basis set including the basis functions of the selected molecules and the neighbouring atoms. The program automatically finds all the atoms of the molecule(s) containing atom(s) ISEED (keyword **MOLECULE**, page 49). The molecule is reconstructed on the basis of the covalent radii reported in Table on page 59. They can be modified by running the option **RAYCOV**, if the reconstruction of the molecule fails. The radius of the hydrogen atom is very critical when intermolecular hydrogen bonds are present.

All the functions of the neighbouring atoms in the crystal are added to the basis set of the selected molecule(s) such that both the following criteria are obeyed:

1. the atom is within a distance R lower than RMAX from at least one atom in the molecule

and

2. the atom is within the NSTAR-th nearest neighbours of at least one atom in the molecule.

For molecular crystals only.

Use keyword **CLUSTER** (47) to extend the number of atoms in the cluster if requested.

Warning Do not use with ECP

Warning. The system obtained is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.3, page 25). See test 19.

MOLECULE - Extraction of n molecules from a molecular crystal

| rec | variable | meaning |
|-----|----------|--|
| • * | NMOL | number of molecules to be isolated |
| II | | insert NMOL records _____ II |
| • * | ISEED | label of one atom in the n th molecule |
| | J,K,L | integer coordinates (direct lattice) of the primitive cell containing the ISEED atom |

The option **MOLECULE** isolates one (or more) molecules from a molecular crystal on the basis of chemical connectivity, defined by the sum of the covalent radii (Table on page 59).

The covalent radii can be modified by running the option **RAYCOV**, if the reconstruction of the molecule fails. The covalent radius of the hydrogen atom is very critical when intermolecular hydrogen bonds are present.

The input order of the atoms (atoms symmetry related are grouped) is modified, according to the chemical connectivity. The same order of the atoms in the bulk crystal is obtained by entering the keyword **ATOMORDE** (see Section 2.1, page 34). The total number of electrons attributed to the molecule is the sum of the shell charges attributed in the basis set input (input block 2, Section 1.2, page 20) to the atoms selected for the molecule.

The keyword **GAUSS98**, entered in input block 2 (basis set input), writes an input deck to run Gaussian 98 (see page 71)

For molecular crystals only.

Warning. The system is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.3, page 25).

Test 18 - Oxalic acid. In the 3D unit cell there are four water and two oxalic acid molecules. The input of test 18 refers to a cluster containing a central oxalic acid molecule surrounded by four water molecules.

MOLEXP - Variation of lattice parameters at constant symmetry and molecular geometry

| rec | variable | meaning |
|-----|------------------------------------|--|
| • * | $\delta a, [\delta b], [\delta c]$ | increments of the minimal set of crystallographic cell parameters: |
| | $[\delta \alpha], [\delta \beta]$ | translation vectors length [Ångstrom], |
| | $[\delta \gamma]$ | crystallographic angles (degrees) |

The cell parameters (the minimum set, see page 17) are modified, according to the increments given in input. The volume of the cell is then modified. The symmetry of the lattice and the geometry (bond lengths and bond angles) of the molecules within the cell is kept. The fractional coordinates of the barycentre of the molecules are kept constant, the cartesian coordinates redefined according to the modification of the lattice parameters. Optimization of the geometry with reference to the compactness of the lattice is allowed, keeping constant the geometry of the molecules. When there are very short hydrogen bonds linking the molecules in the lattice, it may be necessary a modification of the atomic radii to allow proper identification of the molecules (see option **RAYCOV**, page 59)

MOLSPLIT - Periodic lattice of non-interacting molecules

In order to compare bulk and molecular properties, it can be useful to build a density matrix as a superposition of the density matrices of the isolated molecules, arranged in the same

geometry as in the crystal. The keyword **MOLSPLIT** (no additional input required) performs an expansion of the lattice, in such a way that the molecules of the crystal are at an "infinite" distance from each other. The crystal coordinates are scaled so that the distances inside the molecule are fixed, and the distances among the molecules are expanded by a factor 100, to avoid molecule-molecule interactions. *The 3D translational symmetry is not changed.* Reciprocal lattice information is required in the **scf** input (Section 1.3, page 25).

A standard wave function calculation of the expanded crystal is performed. The density matrix refers to the non-interacting subsystems. Before running *properties*, the lattice is automatically contracted to the bulk situation given in input. If a charge density or electrostatic potential map is computed (**ECHG**, **POTM** options), it corresponds to the superposition of the charge densities of the isolated molecules in the bulk geometry.

This option must be used only for molecular crystals only (no charged fragments).

Warning: the DFT grid is not designed for the expanded lattice yet. Large memory allocation may be necessary.

See test 21.

NANOCRYSTAL (NANO)

| rec | variable | meaning |
|-----|-------------------|---|
| • * | <i>h1, k1, l1</i> | crystallographic (Miller) indices of the first plane parallel to the first nanocrystal face |
| • * | <i>h2, k2, l2</i> | crystallographic (Miller) indices of the second plane parallel to the second nanocrystal face |
| • * | <i>h3, k3, l3</i> | crystallographic (Miller) indices of the third plane parallel to the third nanocrystal face |
| • * | ISUP1 | label of the surface layer of the first nanocrystal face |
| | NL1 | number of atomic layers parallel to the first nanocrystal face |
| • * | ISUP2 | label of the surface layer of the second nanocrystal face |
| | NL2 | number of atomic layers parallel to the second nanocrystal face |
| • * | ISUP3 | label of the surface layer of the third nanocrystal face |
| | NL3 | number of atomic layers parallel to the third nanocrystal face |
| • * | NCUT | number of further cutting operations |

The **NANOCRYSTAL** option is used to create a nanocrystal of given dimension, where three faces are parallel to given planes of the crystal. The other three faces are parallel to the first set.

Before the editing operated by **NCUT** directives, the nanocrystal is just a supercell of the 3D structure, with faces lying on the three crystallographic planes.

A new 3D crystal unit cell is defined, with three faces parallel to the given planes. The new 3D cell is generally not primitive: the program calculates and prints the multiplicity. Then the atoms of the new 3D cell are classified according their geometric distance from of the three faces parallel to the two given planes.

The thickness of the nanocrystal, the 0D system, is defined by the number of layers parallel to the faces. No reference is made to the chemical units in the nanocrystal. The neutrality is checked by the program.

1. The crystallographic (Miller) indices of the plane refer to the crystallographic cell .
2. A point group is derived from the 3D symmetry group of the original crystal structure:

the origin may be shifted to maximize the order of the layer group (keyword **ORIGIN**, page 56).

NANOJMOL - Graphical visualisation of nanotubes with Jmol

A file named NANOJMOL.DAT containing the nanotube structure is generated. This file can be directly used by the 3D structure viewer Jmol (www.jmol.org). This keyword must appear in the geometry block *before* all the keywords related to nanotube construction.

NANORE

To be used for tubes built with *NANOTUBE* (page 52).

| rec | variable | meaning |
|-----|---|---|
| • * | <i>nold</i> ₁ , <i>nold</i> ₂ | Nanotube rebuild: indices of the starting nanotube. |
| * | <i>n</i> ₁ , <i>n</i> ₂ | New indices of the rolling vector. |

Consider, for example, the (8,8) and the (10,10) carbon nanotubes (built with *NANOTUBE*, indices refer to the 120° unit cell choice). We have optimised the structure of the former, and we want to build the latter starting from its geometry. With *NANORE* the (8,8) nanotube is unrolled and re-rolled as (10,10). In order to do this, the information on geometry of both the starting slab (graphene) and the (8,8) nanotube is required. The first one is given in input (or read with *EXTERNAL* from file fort.34), the second one is read with an *EXTERNAL* strategy from file fort.35. The input syntax is then:

```
SLAB
77
2.47
1
6 0.333333 0.666667 0.000000
NANORE
8 8
10 10
```

For nanotubes built with *SWCNT* (page 66) see *SWCNTRE* (page 67).

NANOROD (ROD)

| rec | variable | meaning |
|-----|-----------------------------------|---|
| • * | <i>h1</i> , <i>k1</i> , <i>l1</i> | crystallographic (Miller) indices of the first plane parallel to the first nanorod face |
| • * | <i>h2</i> , <i>k2</i> , <i>l2</i> | crystallographic (Miller) indices of the second plane parallel to the second nanorod face |
| • * | ISUP1 | label of the surface layer of the first nanorod face |
| | NL1 | number of atomic layers parallel to the first nanorod face |
| • * | ISUP2 | label of the surface layer of the second nanorod face |
| | NL2 | number of atomic layers parallel to the second nanorod face |
| • * | NCUT | number of further cutting operations |

The **NANOROD** option is used to create a nanorod of given thickness, where two faces are parallel to given planes of the crystal. The other two faces are parallel to the first pair. A new 3D crystal unit cell is defined, with two faces parallel to the given planes. The new 3D cell is in general not primitive: the program calculates and prints the multiplicity. Then the atoms of the new 3D cell are classified according to their geometric distance from the two faces parallel to the two given planes.

The thickness of the nanorod, the 1D system, is defined by the number of layers parallel to the two faces. No reference is made to the chemical units in the nanorod. The neutrality is checked by the program.

1. The crystallographic (Miller) indices of the plane refer to the crystallographic cell .
2. A rod group is derived from the 3D symmetry group of the original crystal structure: the origin may be shifted to maximize the order of the layer group (keyword **ORIGIN**, page 56).

NANOTUBE - Building a nanotube from a slab

Nanotubes are cylindrical structures, periodic along one direction. They are therefore characterised by a single lattice vector. However, in order to study their symmetry and orientation, it is easier to start from a 2D lattice where the additional periodicity becomes the cylinder period. This 2D periodic flat structure will be referred in the following, as the nanotube flat lattice.

In this flat lattice, 3 vectors are important for the structure description: the rolling vector, \vec{R} , the longitudinal vector, \vec{L} and the helical vector, \vec{H} .

- The rolling vector, $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2$ (where \vec{a}_1 and \vec{a}_2 are the slab cell vectors), is sufficient to completely define a nanotube. It is used in the literature to characterise the systems (for example the (4,3) nanotube is a nanotube with a rolling vector $\vec{R} = 4\vec{a}_1 + 3\vec{a}_2$). In the flat nanotube lattice, \vec{R} is a nanotube unit cell vector. Once the nanotube wrapped, the rolling vector becomes a circle normal to the cylinder axis; its norm corresponds to the cylinder perimeter. If \vec{R} passes \mathcal{N} times through the lattice nodes, a \mathcal{N} -order rotational axis will exist along the corresponding nanotube axis.
- The longitudinal vector, $\vec{L} = l_1\vec{a}_1 + l_2\vec{a}_2$, is the shortest lattice vector normal to \vec{R} . In the nanotube, it becomes the 1D lattice parameter and gives the 1D periodicity along the tube axis.
- The helical vector, $\vec{H} = h_1\vec{a}_1 + h_2\vec{a}_2$, is a lattice vector defining with \vec{R} an area which is \mathcal{N} times the area of the unit cell of the flat slab. It satisfies, then, the following relationship

$$\frac{S(\vec{R}, \vec{H})}{S(\vec{a}_1, \vec{a}_2)} = |n_1h_2 - n_2h_1| = \mathcal{N} \quad (2.6)$$

where $S(\vec{v}_i, \vec{v}_j)$ is the surface defined by the \vec{v}_i and \vec{v}_j vectors. The helical vector defines a correspondence between a translation in the flat slab and a roto-translation in the curved surface; \vec{H} has a rotational component along the circumference vector and a translational component along the lattice parameter.

The direct product between the rotational and roto-translational operations generates the full symmetry of the nanotube.

The three vectors listed previously are represented in figure 2.4 for graphene; the example refers to the construction of a (4,2) single-walled carbon nanotube (SWCNT).

Further information about the implemented method, the computational costs and the symmetry features of nanotubes are found in Ref. [40] and [184, 11].

For further details and explanatory animations, please refer to the tutorial page:

<http://www.crystal.unito.it> → tutorials → Nanotube systems

Users of the nanotube construction options are kindly requested to cite the following paper[121]:

Y. Noël, Ph. D'Arco, R. Demichelis, C.M. Zicovich-Wilson and R. Dovesi, *J. Comput. Chem.*, **31**, 855 (2010). *On the Use of Symmetry in the Ab Initio Quantum Mechanical Simulation of Nanotubes and Related Materials.*

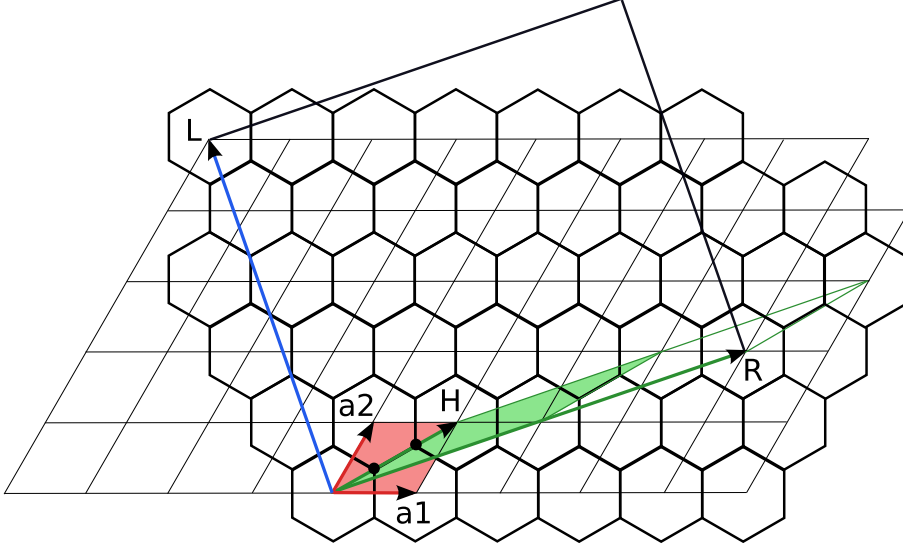


Figure 2.4: Building the (4,2) SWCNT from graphene.

| rec variable | meaning |
|----------------|--|
| • * n_1, n_2 | components of the roll-up-vector of the nanotube in the slab unit cell basis. The roll-up-vector, whose length corresponds to the tube circumference, is expressed as a linear combination of the unit cell vectors of the slab before rolling up, n_1 and n_2 being integer coefficients. |

The convention adopted in CRYSTAL is $n_1 \geq n_2$. In cases when n_2 is required to be larger than n_1 , it is sufficient to exchange the x and y coordinates of the reference 2D slab.

NANOTUBE can be used with the following 2D systems:

- square and hexagonal lattices: any (n_1, n_2) combination
- rectangular lattices: any $n_1, n_2 = 0$
- rhombohedral lattices: $n_2 = \pm n_1$

In the other cases, the existence of a lattice vector perpendicular to \vec{R} (so the 1D periodicity along the tube axis) is not guaranteed.

The orthogonality condition between \vec{R} and \vec{L} provides the following equation:

$$\vec{L} \cdot \vec{R} = (l_1 \vec{a}_1 + l_2 \vec{a}_2) \cdot (n_1 \vec{a}_1 + n_2 \vec{a}_2) = n_1 l_1 |\vec{a}_1|^2 + n_2 l_2 |\vec{a}_2|^2 + (n_1 l_2 + n_2 l_1) |\vec{a}_1| |\vec{a}_2| \cos(\gamma) = 0 \quad (2.7)$$

γ being the angle between \vec{a}_1 and \vec{a}_2 . From Equation 2.7 one obtains:

$$\frac{l_1}{l_2} = -\frac{n_2 |a_2|^2 + n_1 |a_1| |a_2| \cos(\gamma)}{n_1 |a_1|^2 + n_2 |a_1| |a_2| \cos(\gamma)} \quad (2.8)$$

If the right term is divided and multiplied by $|a_2|^2$, one obtains

$$\frac{l_1}{l_2} = -\frac{n_2 + n_1 a_q \cos(\gamma)}{a_q (n_1 a_q + n_2 \cos(\gamma))} \quad (2.9)$$

with $a_q = \frac{|a_1|}{|a_2|}$.

The above equation cannot be satisfied for any $(\vec{a}_1, \vec{a}_2, \cos(\gamma))$ combination. This observation is based on the fact that, as l_1 and l_2 are integers, $\frac{l_1}{l_2}$ is a rational number, whereas, in general, $\cos(\gamma)$ and a_q are real numbers. In the following the five 2D Bravais lattices are considered separately, in order to show which conditions satisfy the periodicity along the tube axis and which do not.

- Hexagonal lattice: $\vec{a}_1 = \vec{a}_2$, $\cos(\gamma) = \pm 1/2$. Equation 2.9 becomes:

$$\frac{l_1}{l_2} = -\frac{n_2 + n_1/2}{n_1 + n_2/2} = -\frac{2n_2 + n_1}{2n_1 + n_2} \quad (2.10)$$

Any roll-up vector is possible.

- Square lattice: $\vec{a}_1 = \vec{a}_2$, $\cos(\gamma) = 0$.

$$\frac{l_1}{l_2} = -\frac{n_2}{n_1} \quad (2.11)$$

Any roll-up vector is possible.

- Rectangular lattice: $\vec{a}_1 \neq \vec{a}_2$, $\cos(\gamma) = 0$.

$$\frac{l_1}{l_2} = -\frac{n_2|a_2|^2}{n_1|a_1|^2} \quad (2.12)$$

In this case the right term corresponds to a rational number either if $|a_1| = n|a_2|$, with n being a rational number, or if $n_2=0$. More generally, for rectangular lattices, the periodicity along the tube axis is always satisfied for $(n, 0)$ and $(0, n)$ roll-up vectors.

- Rhombohedral (centred rectangular) lattice: $\vec{a}_1 = \vec{a}_2$, any $\cos(\gamma)$.

$$\frac{l_1}{l_2} = -\frac{n_2 + n_1\cos(\gamma)}{n_1 + n_2\cos(\gamma)} \quad (2.13)$$

The right term provides a rational number only when $n_1 = n_2$ or $n_1 = -n_2$, so that Equation 2.13 becomes:

$$\frac{l_1}{l_2} = -\frac{n_1[1 + \cos(\gamma)]}{n_1[1 + \cos(\gamma)]} = -1 \quad \frac{l_1}{l_2} = \frac{n_1[1 - \cos(\gamma)]}{n_1[1 - \cos(\gamma)]} = 1 \quad (2.14)$$

- Oblique lattice: $\vec{a}_1 \neq \vec{a}_2$, any $\cos(\gamma)$. Equation 2.9 remains as such, and the right term is always an irrational number.

When the above conditions are not satisfied, however, it is possible to manipulate the geometry of the starting slab and force it to assume a suitable form, by building supercells or with minor modifications to the cell parameters.

Note that, in cases of hexagonal lattices, the standard convention adopted in CRYSTAL considers the reference flat lattice cell vectors forming a 120° angle. In the carbon nanotube literature, however, the rolling indices refer to a 60° angle. For this reason, the same input can be obtained with the following choices, where the (6,3) indices in the 60° unit cell become (9,3) in the 120° option:

Example I: (6,3) SWCNT from graphene, 60 degrees

```
SLAB
1
2.47  2.47  60.000
2
6    0.3333333333  0.3333333333  0.000
6   -0.3333333333 -0.3333333333  0.000
NANOTUBE
6    3
```

Example II: (6,3) SWCNT from graphene, default choice

```
SLAB
77
2.47
1
6    0.333333  0.666667  0.000000
NANOTUBE
9    3
```

In order to avoid ambiguity in the choice of the carbon nanotubes indices, use the *SWCNT* (page 66) keyword.

SWCNT - Building a nanotube from an hexagonal slab (60° unit cell choice)

| rec variable | meaning |
|----------------|---|
| • * n_1, n_2 | Only for hexagonal cells. Same as <i>NANOTUBE</i> keyword but the components of the rolling vector refer to a 60° hexagonal cell. |

vspace0.3cm

Example: (6,3) SWCNT from graphene

SLAB

77

2.47

1

6 0.333333 0.666667 0.000000

SWCNT

6 3

See *NANOTUBE* (page 52) for further details.

Nanotube rebuild: build a nanotube starting from the structure of another one, with same directions but a different radius.

Two restart keywords, *NANORE* and *SWCNTRE*, allow to build a (n_1, n_2) nanotube by starting from the structure of another one (a previously $(nold_1, nold_2)$ optimised one, read from file fort.35). The "old" nanotube is unrolled and re-rolled according to a "new" \vec{R} vector, with minor modifications to the structure. The rolling direction of the two tubes must be the same.

It is particularly helpful for the geometry optimisation of inorganic nanotubes (thick slabs, large systems, the geometry of the tubes is very different from the one of the slab), as the number of optimisation steps is reduced (see Ref. [43] for documentation of computational gain).

NANORE

To be used for tubes built with *NANOTUBE* (page 52).

| rec variable | meaning |
|----------------------|---|
| • * $nold_1, nold_2$ | Nanotube rebuild: indices of the starting nanotube. |
| * n_1, n_2 | New indices of the rolling vector. |

Consider, for example, the (8,8) and the (10,10) carbon nanotubes (built with *NANOTUBE*, indices refer to the 120° unit cell choice). We have optimised the structure of the former, and we want to build the latter starting from its geometry. With *NANORE* the (8,8) nanotube is unrolled and re-rolled as (10,10). In order to do this, the information on geometry of both the starting slab (graphene) and the (8,8) nanotube is required. The first one is given in input (or read with *EXTERNAL* from file fort.34), the second one is read with an *EXTERNAL* strategy from file fort.35. The input syntax is then:

SLAB

77

2.47

1

6 0.333333 0.666667 0.000000

NANORE

8 8

10 10

For nanotubes built with *SWCNT* (page 66) see *SWCNTRE* (page 67).

SWCNTRE

It is the same as *NANORE*, with the same input syntax, but in for hexagonal lattices with 60° unit cell reference (see *SWCNT*, page 66).

| rec | variable | meaning |
|-----|---|---|
| • * | <i>nold</i> ₁ , <i>nold</i> ₂ | Nanotube rebuild: indices of the starting nanotube. |
| * | <i>n</i> ₁ , <i>n</i> ₂ | New indices of the rolling vector. |

NANOJMOL - Graphical visualisation of nanotubes with Jmol

A file named NANOJMOL.DAT containing the nanotube structure is generated. This file can be directly used by the 3D structure viewer Jmol (www.jmol.org). This keyword must appear in the geometry block *before* all the keywords related to nanotube construction.

NEIGHBOR/NEIGHPRT

| rec | variable | meaning |
|-----|----------|--|
| • * | INEIGH | number of neighbours of each non-equivalent atom to be printed |

The option is active when analyzing the crystal structure (bond lengths and bond angles) and when printing the bond populations following Mulliken analysis. Full input deck must be given (block 1-2-3), in order to obtain neighbors analysis of all the non-equivalent atoms

For each non-equivalent atom information on the first INEIGH neighbours is printed: number, type, distance, position (indices of the direct lattice cell).

Warning: the neighbors analysis is performed after the symmetry analysis and the screening of the integrals. If very soft tolerances for the integrals screening are given in input, it may happen that the information is not given for all the neighbors requested, as their are not taken into account when truncation criteria are applied.

NOSHIFT

It may be used before **SUPERCEL** keyword. It avoids shift of the origin in order to minimize the number of symmetry operators with finite translation component. No input data are required.

OPTGEOM - Full geometry optimization

See Chapter 3, page 118.

ORIGIN

The origin is moved to minimize the number of symmetry operators with finite translation components. Suggested before cutting a slab from a 3D structure (option **SLABCUT**, page 61). No input data are required.

PBAND - Phonon Bands -

This keyword, to be inserted in the geometry input block, is specific for phonon dispersion calculations (the use of the **DISPERSI** keyword is then mandatory in the subsequent **FREQCALC** block, similarly to the **SCELPHONO** keyword, see page 63). It can be used for phonon band calculations, and allows for the specification of the path in reciprocal space along which the Hessian matrix is obtained.

| rec | variable | meaning |
|-----|----------|--|
| • * | ISS | shrinking factor in terms of which the coordinates of the extremes of the segment are expressed. If ISS=0, input by label (see below). |
| | NK | total number of \mathbf{k} -points along the line. |
| | FLAG1 | if > 1 , activates interpolation (see keyword INTERPHESS at page 161) |
| | FLAG2 | coordinates given in terms of primitive (FLAG2=0) or conventional (FLAG2=1) lattice |
| | | if ISS > 0 then |
| • * | I1,I2,I3 | integers that define the starting point of the line ($I1/ISS \mathbf{b}_1 + I2/ISS \mathbf{b}_2 + I3/ISS \mathbf{b}_3$), with $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ reciprocal lattice vectors. |
| | J1,J2,J3 | integers that define the final point of the line ($J1/ISS \mathbf{b}_1 + J2/ISS \mathbf{b}_2 + J3/ISS \mathbf{b}_3$) with $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ reciprocal lattice vectors. |
| | | if ISS = 0 then |
| • * | LABELA | label of the the starting point of the line (see tables 9.1 and 9.2 for a legend). |
| | LABELB | label of the the final point of the line (see tables 9.1 and 9.2 for a legend). |

Given two points that define a line in reciprocal space, and the number of sampling points required along this line, a supercell is constructed to allow for the exact calculation of the Hessian matrix at these points. The formal relationship between the direct space supercell and the reciprocal space sampling can be found in the phonon dispersion section (page 161). Multiple runs on supercells constructed in this way allow for the complete calculation and plotting of phonon band structures.

FLAG1 is normally set to 1. If FLAG1 > 1 then NK \times FLAG1 \mathbf{k} -points are obtained without building a bigger supercell. The assumptions are the same as those used for the keyword **INTERPHESS** (see page 161). FLAG2 is 1 if the input coordinates refer to the conventional cell, 0 if they refer to the primitive cell.

The computed frequencies at all the requested points are written in output and stored in units fort.25 and PBANDS.DAT (in $x-y$ format) for plotting, in the same formats used for electronic band structures.

An input example is:

```

MGO BULK
CRYSTAL
0 0 0
225
4.16563249
2
12 0. 0. 0.
8 0.5 0.5 0.5
PBAND
0 10 1 0
G
X
FREQCALC
DISPERSI
END
END

```

which, in this particular case, will result in the supercell:

```

EXPANSION MATRIX OF PRIMITIVE CELL
E1 1.000 0.000 -1.000
E2 0.000 1.000 0.000
E3 0.000 0.000 18.000

```

PLANES

| rec | variable | meaning |
|-----|----------|--|
| • * | f | minimum of the interplane distance d_{hkl} for the plane families to be printed and indexed, expressed as the fraction f |

Crystallographic planes are indexed and printed, grouped in families of symmetry-related planes. All the hkl planes are analyzed that have the interplane distance belonging to the interval $[f d_{hkl}^{max}, d_{hkl}^{max}]$, where d_{hkl}^{max} is the maximum interplane distance for a given family hkl and f a number between 0 and 1. If the crystal structure has a primitive cell different from the crystallographic one, the plane indices are printed relatively to both frames.

POINTCHG

| rec | variable | meaning |
|-----|----------|--|
| • * | NCH | number of point charges to be added |
| | | _____ insert NCH records _____ II |
| • * | X,Y,Z,QC | cartesian coordinates [\AA], charge(au). Coordinates refer to the primitive cell. |

Dummy atoms with formal atomic number 93, mass zero, nuclear charge as given in input (file POINTCHG.INP), are added to the primitive cell. Data are read in free format.

| record | type of data | content |
|----------|--------------|----------------------------|
| 1 | 1 integer | N, number of point charges |
| 2..2+N-1 | 4 real | x y z charge |

Coordinates are in \AA strom, unless otherwise requested (keyword **BOHR**, page 33). Charges are net charges (1 electron = -1). The symmetry of the system must be removed by the keyword **SYMMREMO**.

As point charges are formally considered as "atoms", *they must be the last addition of centres to the system.*

No electron charge should be attributed to those atoms in basis set input (no atomic wave function calculation is possible). The default basis set defined by the program is a single s gaussian, with exponent 100000.

Attention should be paid to the neutrality of the cell. If the absolute value of the sum of the charges is less than 10^{-3} , the value of the charges is "normalized" to obtain 0.

The data given in input are printed. To obtain printing of coordinates and neighbour analysis of the dummy atoms in geometry output, insert the keyword **PRINTCHG**.

Not compatible with: OPTGEOM, FREQCALC, ANHARM, ELASTCON, EOS, FIELD, FIELDCON, NOBIPOLA.

PRIMITIV

Some properties (**XFAC**, **EMDL**, **EMDP**, **PROF**) input the oblique coordinates of the \mathbf{k} points in the reciprocal lattice with reference to the conventional cell, though the computation refers to the primitive one. This option allows entering directly the data with reference to the primitive cell. The transformation matrix from primitive to crystallographic (Appendix A.5, page 301) is set to the identity. No effect on the CPU time: CRYSTAL always refers to the primitive cell. No input data are required.

PRINTCHG

Coordinates of the dummy atoms inserted after the keyword **POINTCHG** are printed in geometry output, basis set output, neighbor analysis. No input data required.

PRINTOUT - Setting of printing environment

Extended printout can be obtained by entering selected keywords in a printing environment beginning with the keyword **PRINTOUT** and ending with the keyword **END**. The possible keywords are found in the fifth column of the table on page 317.

Extended printing request can be entered in any input block. Printing requests are not transferred from wave function to properties calculation.

See Appendix C, page 315.

PRSYMDIR

Printing of the so-called *symmetry allowed directions* adopted in the geometry optimization. The printing is done after the neighbor analysis, before computing the wave function. Full input must be supplied (3 blocks). Test run allowed with the keyword **TESTPDIM**.

No input data required.

PURIFY

This cleans up the atomic positions so that they are fully consistent with the group (to within machine rounding error). Atomic position are automatically redefined after basic geometry input. No input data are required.

RADFULLE

When printing atomic coordinates of the molecule, an additional column is added that contains the radial distances of the atoms from the origin. The **FULLE** (page 45) keyword constructs fullerenes and automatically displays the radius column. The present option is useful when running a fullerene calculation without using the **FULLE** keyword, i.e. by means of the **MOLECULE** (page 15) and **EXTERNAL** (page 16) keywords.

RADNANO

When printing atomic coordinates of a 1-D system, an additional column is added that contains the radial distances of the atoms from the x axis. The **NANOTUBE** (page 52) and **SWCNT** (page 66) keywords construct nanotubes and automatically display the radius column. The present option is useful when running a nanotube calculation without using the **NANOTUBE**/**SWCNT** keywords, i.e. by means of the **MOLECULE** (page 15) and **EXTERNAL** (page 16) keywords.

RAYCOV - covalent radii modification

| rec | variable | meaning |
|-----|----------|---|
| • * | NCOV | number of atoms for which the covalent radius is redefined |
| | | _____ insert NCOV records _____ II |
| • * | NAT | atomic number ($0 \leq \text{NAT} \leq 92$) |
| | RAY | covalent radius of the atom with atomic number NAT ([Å], default, or bohr, if the keyword BOHR precedes in the deck) |

The option **RAYCOV** allows modification of the covalent radius default value for a given atom.

Table of covalent radii (Angstrom)

| | | | | | | | | | | | | | | | | | |
|-------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| H | | | | | | | | | | | | | | | | He | |
| 0.68 | | | | | | | | | | | | | | | | 1.47 | |
| ----- | | | | | | | | | | | | | | | | | |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| 1.65 | 1.18 | | | | | | | | | | | 0.93 | 0.81 | 0.78 | 0.78 | 0.76 | 1.68 |
| ----- | | | | | | | | | | | | | | | | | |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| 2.01 | 1.57 | | | | | | | | | | | 1.50 | 1.23 | 1.15 | 1.09 | 1.05 | 1.97 |
| ----- | | | | | | | | | | | | | | | | | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| 2.31 | 2.07 | 1.68 | 1.47 | 1.41 | 1.47 | 1.47 | 1.47 | 1.41 | 1.41 | 1.41 | 1.41 | 1.36 | 1.31 | 1.21 | 1.21 | 1.21 | 2.10 |
| ----- | | | | | | | | | | | | | | | | | |
| Rb | Sr | Y | Zr | Ni | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| 2.31 | 2.10 | 1.94 | 1.60 | 1.52 | 1.52 | 1.42 | 1.36 | 1.42 | 1.47 | 1.68 | 1.62 | 1.62 | 1.52 | 1.52 | 1.47 | 1.47 | 2.66 |
| ----- | | | | | | | | | | | | | | | | | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| 2.73 | 2.10 | 1.94 | 1.63 | 1.63 | 1.63 | 1.63 | 1.63 | 1.63 | 1.63 | 1.63 | 1.63 | 1.99 | 1.89 | 1.68 | 1.42 | 1.42 | 1.62 |
| ----- | | | | | | | | | | | | | | | | | |

The choice of the covalent radius of hydrogen may be very critical when extracting a molecule from a hydrogen bonded molecular crystal. See test 15.

ROTCRY - Rotation of the crystal with respect to the reference system - developers only

This option allows to rotate the crystal with respect to the original orthonormal Cartesian reference system. The SCF procedure, both for HF and DFT calculations, is performed in the rotated geometry.

The rotation can be performed in three different ways:

1. By defining the Euler rotation angles α, β, γ and the origin of the rotating system. (The rotation is given by: $R_z^\alpha R_x^\beta R_z^\gamma$, where R_t^θ are the rotation matrices about t by angle θ).
2. By explicitly defining the rotation matrix.
3. An automatic procedure that reorient the crystal aligning \vec{c} along z Cartesian axis.

| | | |
|---------------|------------------|--|
| ANGROT | | Rotation defined by Euler angles α, β, γ |
| rec | variable | meaning |
| • * | ALPHA,BETA,GAMMA | α, β, γ rotation Euler angles (degrees) |
| or | | |
| MATROT | | Rotation matrix by input |
| rec | variable | meaning |
| • * | R11 R12 R13 | first row of the matrix. |
| • * | R21 R22 R23 | second row of the matrix. |
| • * | R31 R32 R33 | third row of the matrix. |
| or | | |
| AUTO | | Automatically align c along z |

The rotation involves: direct and reciprocal lattice parameters, coordinates of atoms and symmetry operators. When a DFT calculation is performed also the points of the numerical integration grid are rotated in order to preserve numerical accuracy.

Note that this keyword is different from **ATOMROT** (see page 35) that rotates a group of atoms without affecting the reference system.

SETINF - Setting of INF values

| rec | variable | meaning |
|-----|------------------|--|
| • * | NUM | number of INF vector positions to set |
| • * | J,INF(J),I=1,NUM | position in the vector and corresponding value |

The keyword **SETINF** allows setting of a value in the INF array. It can be entered in any input section.

SETPRINT - Setting of printing options

| rec | variable | meaning |
|-----|---------------------|--|
| • * | NPR | number of LPRINT vector positions to set |
| • * | J,LPRINT(J),I=1,NPR | prtrec ; position in the vector and corresponding value |

The keyword **SETPRINT** allows setting of a value in the LPRINT array, according to the information given in Appendix C, page 317. It can be entered in any input section.

SLABCUT (SLAB)

| rec | variable | meaning |
|-----|-----------|--|
| • * | h, k, l | crystallographic (Miller) indices of the plane parallel to the surface |
| • * | ISUP | label of the surface layer |
| | NL | number of atomic layers in the slab |

The **SLABCUT** option is used to create a slab of given thickness, parallel to the given plane of the 3D lattice.

A new Cartesian frame, with the z axis orthogonal to the (hkl) plane, is defined. A *layer* is defined by a set of atoms with same z coordinate, with reference to the new Cartesian frame. The thickness of the slab, the 2D system, is defined by the number of layers. No reference is made to the chemical units in the slab. The neutrality of the slab is checked by the program.

1. The crystallographic (Miller) indices of the plane refer to the conventional cell (cubic and hexagonal systems).
2. A two-sided layer group is derived from the 3D symmetry group of the original crystal structure: the origin may be shifted to maximize the order of the layer group (keyword **ORIGIN**, page 56).
3. The unit cell is selected with upper and lower surface parallel to the (hkl) plane.
4. The 2D translation vectors \mathbf{a}_1 and \mathbf{a}_2 are chosen according to the following criteria:
 - (a) minimal cell area;
 - (b) shortest translation vectors;
 - (c) minimum $|\cos(\gamma)|$, where γ is the angle between \mathbf{a}_1 and \mathbf{a}_2 .
5. The surface layer ISUP may be found from an analysis of the information printed by the **SLABINFO** (page 62) option. This information can be obtained by a test run, inserting in the geometry input block the keyword **TESTGEOM** (page 68). Only the geometry input block is processed, then the program stops.

Two separate runs are required in order to get the information to prepare the input for a full **SLABCUT** option run:

1. keyword **SLABINFO**: Rotation of the 3D cell, to have the z axis perpendicular to the (hkl) plane, with numbering of the atomic layers in the rotated reference cell, according to the z coordinate of the atoms (insert **STOP** after **SLABINFO** to avoid further processing).
2. keyword **SLAB**: Definition of the 2D system, a slab of given thickness (NL, number of atomic layers) parallel to the (hkl) crystallographic plane, with the ISUP-th atom on the surface layer

The **SLABCUT** option, combined with **ATOMINSE** (page 34), **ATOMDISP** (page 34), etc. can be used to create a slab of given thickness, with an atom (or group of atoms) adsorbed at given position. This is achieved by adding new atoms to the 2D structure, obtained after executing the **SLAB** option.

Test cases 5-6-7 refer to a 2D system; test cases 25-26-27 refer to the same system, but generated from the related 3D one. See also tests 35, 36, 37.

SLABINFO - 3D cell with z axis orthogonal to a given plane

| rec | variable | meaning |
|-----|----------|--|
| • * | h,k,l | Crystallographic (Miller) indices of the basal layer of the new 3D unit cell |

1. A new unit cell is defined, with two lattice vectors perpendicular to the [hkl] direction. The indices refer to the Bravais lattice of the crystal; the hexagonal lattice is used for the rhombohedral systems, the cubic lattice for cubic systems (non primitive).
2. A new Cartesian reference system is defined, with the xy plane parallel to the (hkl) plane.
3. The atoms in the reference cell are re-ordered according to their z coordinate, in order to recognize the layered structure, parallel to the (hkl) plane.
4. The layers of atoms are numbered. This information is necessary for generating the input data for the **SLABCUT** option.
5. After neighboring analysis, the program stops. If the keyword **ROTATE** was entered, execution continues. The shape of the new cell may be very different, computational parameters must be carefully checked.
6. the keyword **ORIGIN** can be used to shift the origin after the rotation of the cell, and minimize the number of symmetry operators with translational component. Useful to maximize the point group of the 2D system that can be generated from 3D using the keyword **SLABCUT** (page 61).

STOP

Execution stops immediately. Subsequent input records are not processed.

STRUCPRT

A formatted deck with cell parameters and atoms coordinates (bohr) in cartesian reference is written in the file STRUC.INCOOR . See appendix D, page 325.

SCELCONF

| rec | variable | meaning |
|-----|----------|---|
| • * | E | expansion matrix E (IDIMxIDIM elements, input by rows: 9 reals (3D); 4 reals (2D); 1 real (1D)) |

This keyword is specific for configuration counting calculations for disordered systems or solid solutions. Always use **SCELCONF** instead of **SUPERCELL/SUPERCON** in calculations with **CONF_COUNT** and **CONF_RAND**.

A supercell is constructed, as in the case of keyword **SUPERCELL** (see page 64), as linear combination of the primitive cell unit vectors.

The number of symmetry operators of the resulting supercell is higher compared to the **SUPERCELL** case. The product group is constructed between the space group of the original system and the group of translation operators associated with the chosen supercell.

SCELPHONO

| rec | variable | meaning |
|-----|----------|---|
| • * | E | expansion matrix E (IDIMxIDIM elements, input by rows: 9 reals (3D); 4 reals (2D); 1 real (1D)) |

This keyword is specific for phonon dispersion calculations.

A supercell is constructed, as in the case of keyword **SUPERCELL** (see page 64), as linear combination of the primitive cell unit vectors.

The atomic ordering of the resulting supercell is different with respect to the **SUPERCELL** case. The first atoms in the list are the ones of the primitive cell, as required for phonon dispersion calculations. Example:

```

TEST11 - MGO BULK
CRYSTAL
0 0 0
  225
4.21
2
12 0.  0.  0.
8 0.5  0.5  0.5
SCELPHONO
2 0 0
0 2 0
0 0 2
TESTGEOM
END
===== output - atoms in the small cell first =====
PRIMITIVE CELL - CENTRING CODE 1/0 VOLUME= 149.236922 - DENSITY 3.559 g/cm^3
      A          B          C          ALPHA          BETA          GAMMA
      5.95383910  5.95383910  5.95383910  60.000000  60.000000  60.000000
*****
ATOMS IN THE ASYMMETRIC UNIT 5 - ATOMS IN THE UNIT CELL: 16
      ATOM          X/A          Y/B          Z/C
*****
  1 T  12 MG    0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
  2 T   8  O    2.500000000000E-01  2.500000000000E-01  2.500000000000E-01
  3 T  12 MG    0.000000000000E+00 -5.000000000000E-01  0.000000000000E+00
  4 F  12 MG    0.000000000000E+00 -5.000000000000E-01 -5.000000000000E-01
  5 F  12 MG   -5.000000000000E-01  0.000000000000E+00  0.000000000000E+00
  6 F  12 MG   -5.000000000000E-01  0.000000000000E+00 -5.000000000000E-01
  7 F  12 MG   -5.000000000000E-01 -5.000000000000E-01  0.000000000000E+00

```

```

 8 T 12 MG -5.000000000000E-01 -5.000000000000E-01 -5.000000000000E-01
 9 F 12 MG  0.000000000000E+00  0.000000000000E+00 -5.000000000000E-01
10 T  8  0   2.500000000000E-01  2.500000000000E-01 -2.500000000000E-01
11 F  8  0   2.500000000000E-01 -2.500000000000E-01  2.500000000000E-01
12 F  8  0   2.500000000000E-01 -2.500000000000E-01 -2.500000000000E-01
13 F  8  0  -2.500000000000E-01  2.500000000000E-01  2.500000000000E-01
14 F  8  0  -2.500000000000E-01  2.500000000000E-01 -2.500000000000E-01
15 F  8  0  -2.500000000000E-01 -2.500000000000E-01  2.500000000000E-01
16 F  8  0  -2.500000000000E-01 -2.500000000000E-01 -2.500000000000E-01

```

TEST11 - MGO BULK

CRYSTAL

0 0 0

225

4.21

2

12 0. 0. 0.

8 0.5 0.5 0.5

SUPERCEL

2 0 0

0 2 0

0 0 2

TESTGEOM

===== output - atoms of same type first =====

PRIMITIVE CELL - CENTRING CODE 1/0 VOLUME= 149.236922 - DENSITY 3.559 g/cm³

| A | B | C | ALPHA | BETA | GAMMA |
|------------|------------|------------|-----------|-----------|-----------|
| 5.95383910 | 5.95383910 | 5.95383910 | 60.000000 | 60.000000 | 60.000000 |

ATOMS IN THE ASYMMETRIC UNIT 5 - ATOMS IN THE UNIT CELL: 16

| ATOM | X/A | Y/B | Z/C |
|------|-----|-----|-----|
|------|-----|-----|-----|

```

 1 T 12 MG  0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
 2 T 12 MG  0.000000000000E+00  0.000000000000E+00 -5.000000000000E-01
 3 F 12 MG  0.000000000000E+00 -5.000000000000E-01  0.000000000000E+00
 4 F 12 MG  0.000000000000E+00 -5.000000000000E-01 -5.000000000000E-01
 5 F 12 MG -5.000000000000E-01  0.000000000000E+00  0.000000000000E+00
 6 F 12 MG -5.000000000000E-01  0.000000000000E+00 -5.000000000000E-01
 7 F 12 MG -5.000000000000E-01 -5.000000000000E-01  0.000000000000E+00
 8 T 12 MG -5.000000000000E-01 -5.000000000000E-01 -5.000000000000E-01
 9 T  8  0  -2.500000000000E-01 -2.500000000000E-01  2.500000000000E-01
10 T  8  0  -2.500000000000E-01 -2.500000000000E-01 -2.500000000000E-01
11 F  8  0  -2.500000000000E-01  2.500000000000E-01  2.500000000000E-01
12 F  8  0  -2.500000000000E-01  2.500000000000E-01 -2.500000000000E-01
13 F  8  0   2.500000000000E-01 -2.500000000000E-01  2.500000000000E-01
14 F  8  0   2.500000000000E-01 -2.500000000000E-01 -2.500000000000E-01
15 F  8  0   2.500000000000E-01  2.500000000000E-01  2.500000000000E-01
16 F  8  0   2.500000000000E-01  2.500000000000E-01 -2.500000000000E-01

```

It can be used to generate a supercell for a phonon dispersion calculation only (keyword **DISPERSI**, page 161).

SUPERCEL

| rec | variable | meaning |
|-----|----------|---|
| • * | E | expansion matrix E (IDIMxIDIM elements, input by rows: 9 reals (3D); 4 reals (2D); 1 real (1D)) |

A supercell is obtained by defining the new unit cell vectors as linear combinations of the

primitive cell unit vectors (See **SUPERCON** for crystallographic cell vectors reference). The point symmetry is defined by the number of symmetry operators in the new cell. It may be reduced, not increased.

The new translation vectors $\mathbf{b}'_1, \mathbf{b}'_2, \mathbf{b}'_3$ are defined in terms of the old vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ and of the matrix E, read in input by rows, as follows:

$$\begin{aligned}\mathbf{b}'_1 &= e_{11} \cdot \mathbf{b}_1 + e_{12} \cdot \mathbf{b}_2 + e_{13} \cdot \mathbf{b}_3 \\ \mathbf{b}'_2 &= e_{21} \cdot \mathbf{b}_1 + e_{22} \cdot \mathbf{b}_2 + e_{23} \cdot \mathbf{b}_3 \\ \mathbf{b}'_3 &= e_{31} \cdot \mathbf{b}_1 + e_{32} \cdot \mathbf{b}_2 + e_{33} \cdot \mathbf{b}_3\end{aligned}$$

The symmetry is automatically reduced to the point symmetry operators without translational components and a further reduction of the symmetry is also possible.

Before building the supercell, the origin is shifted in order to minimize the number of symmetry operators with translational components (see page 18). To avoid this operation, insert **NOSHIFT** before **SUPERCEL**

Atoms that are related by translational symmetry in the unit cell are considered nonequivalent in a supercell.

The supercell option is a useful starting point for the study of defective systems, of chemisorption and anti ferromagnetism, by combining the **SUPERCEL** option with the options described in this chapter: **ATOMREMO** (page 35), **ATOMSUBS** (page 36), **ATOMINSE** (page 34), **ATOMDISP** (page 34), **SLAB** (page 61).

To study anti ferromagnetic (AFM) states, it may be necessary to generate a supercell, and then attribute different spin to atoms related by translational symmetry (**ATOMSPIN**, input block 3, page 80). See tests 17, 30, 31, 34, 37, 43, 47.

Example. Construction of supercells of face-centred cubic 3D system ($a = 5.42 \text{ \AA}$).

The crystallographic cell is non-primitive, the expansion matrix refers to primitive cell vectors. The E matrix has 9 elements:

| PRIMITIVE CELL | | | | | | | | |
|---|--------|--------|--------|----|--------|--------|--------|--|
| DIRECT LATTICE VECTORS COMPONENTS | | | | | | | | |
| | X | Y | Z | | | | | |
| B1 | .000 | 2.710 | 2.710 | | | | | |
| B2 | 2.710 | .000 | 2.710 | | | | | |
| B3 | 2.710 | 2.710 | .000 | | | | | |
| | | | | | | | | |
| 2 UNITS SUPERCELL (a) | | | | | | | | |
| EXPANSION MATRIX | | | | | | | | |
| E1 | .000 | 1.000 | 1.000 | B1 | 5.420 | 2.710 | 2.710 | |
| E2 | 1.000 | .000 | 1.000 | B2 | 2.710 | 5.420 | 2.710 | |
| E3 | 1.000 | 1.000 | .000 | B3 | 2.710 | 2.710 | 5.420 | |
| | | | | | | | | |
| 2 UNITS SUPERCELL (b) | | | | | | | | |
| EXPANSION MATRIX | | | | | | | | |
| E1 | 1.000 | 1.000 | -1.000 | B1 | .000 | .000 | 5.420 | |
| E2 | .000 | .000 | 1.000 | B2 | 2.710 | 2.710 | .000 | |
| E3 | 1.000 | -1.000 | .000 | B3 | -2.710 | 2.710 | .000 | |
| | | | | | | | | |
| 4 UNITS SUPERCELL (c) crystallographic cell | | | | | | | | |
| EXPANSION MATRIX | | | | | | | | |
| E1 | -1.000 | 1.000 | 1.000 | B1 | 5.420 | .000 | .000 | |
| E2 | 1.000 | -1.000 | 1.000 | B2 | .000 | 5.420 | .000 | |
| E3 | 1.000 | 1.000 | -1.000 | B3 | .000 | .000 | 5.420 | |
| | | | | | | | | |
| 8 UNITS SUPERCELL | | | | | | | | |
| EXPANSION MATRIX | | | | | | | | |
| E1 | 2.000 | .000 | .000 | B1 | .000 | 5.420 | 5.420 | |
| E2 | .000 | 2.000 | .000 | B2 | 5.420 | .000 | 5.420 | |
| E3 | .000 | .000 | 2.000 | B3 | 5.420 | 5.420 | .000 | |
| | | | | | | | | |
| 16 UNITS SUPERCELL | | | | | | | | |
| EXPANSION MATRIX | | | | | | | | |
| E1 | 3.000 | -1.000 | -1.000 | B1 | -5.420 | 5.420 | 5.420 | |
| E2 | -1.000 | 3.000 | -1.000 | B2 | 5.420 | -5.420 | 5.420 | |
| E3 | -1.000 | -1.000 | 3.000 | B3 | 5.420 | 5.420 | -5.420 | |
| | | | | | | | | |
| 27 UNITS SUPERCELL | | | | | | | | |
| EXPANSION MATRIX | | | | | | | | |
| E1 | 3.000 | .000 | .000 | B1 | .000 | 8.130 | 8.130 | |

```

E2      .000      3.000      .000      B2      8.130      .000      8.130
E3      .000      .000      3.000      B3      8.130      8.130      .000

```

```

32 UNITS SUPERCELL
EXPANSION MATRIX
E1     -2.000     2.000     2.000     B1     10.840     .000     .000
E2      2.000    -2.000     2.000     B2      .000     10.840     .000
E3      2.000     2.000    -2.000     B3      .000     .000     10.840

```

a), b) Different double cells

c) quadruple cell. It corresponds to the crystallographic, non-primitive cell, whose parameters are given in input (page 18).

Example. Construction of supercells of hexagonal $R\bar{3}$ (corundum lattice) cubic 3D system. The crystallographic cell is non-primitive: CRYSTAL refer to the primitive cell, with volume 1/3 of the conventional one. The E matrix has 9 elements:

```

GEOMETRY INPUT DATA:
LATTICE PARAMETERS (ANGSTROMS AND DEGREES) - CONVENTIONAL CELL
  A      B      C      ALPHA      BETA      GAMMA
4.76020  4.76020  12.99330  90.00000  90.00000  120.00000

TRANSFORMATION WITHIN CRYSTAL CODE FROM CONVENTIONAL TO PRIMITIVE CELL:

LATTICE PARAMETERS (ANGSTROMS AND DEGREES) - PRIMITIVE CELL
  A      B      C      ALPHA      BETA      GAMMA      VOLUME
5.12948  5.12948  5.12948  55.29155  55.29155  55.29155  84.99223

3 UNITS SUPERCELL crystallographic cell
EXPANSION MATRIX
E1      1.000     -1.000     .000     B1      4.122     -2.380     .000
E2      .000     1.000     -1.000    B2      .000     4.760     .000
E3      1.000     1.000     1.000    B3      .000     .000     12.993

LATTICE PARAMETERS (ANGSTROM AND DEGREES)
  A      B      C      ALPHA      BETA      GAMMA      VOLUME
4.76020  4.76020  12.99330  90.000    90.000    120.000    254.97670

```

SUPERCON

The first step in geometry definition in CRYSTAL is the transformation of the cell from crystallographic to primitive, according to the transformation matrices given in appendix A.5, when the crystallographic cell is non-primitive.

From the point of view of CRYSTAL, the crystallographic cell is a supercell, in that case.

Using the keyword **SUPERCON**, the crystallographic cell is built from the primitive one, before applying the expansion matrix.

See **SUPERCEL**, page 64 for expansion matrix input instructions.

Note - The easiest way to work on crystallographic cell is the following input:

```

SUPERCON
1. 0. 0.
0. 1. 0.
0. 0. 1.

```

The expansion matrix is the identity, leaving the crystallographic cell unmodified.

SWCNT - Building a nanotube from an hexagonal slab (60° unit cell choice)

| rec variable | meaning |
|----------------|---|
| • * n_1, n_2 | Only for hexagonal cells. Same as <i>NANOTUBE</i> keyword but the components of the rolling vector refer to a 60° hexagonal cell. |

vspace0.3cm

Example: (6,3) SWCNT from graphene

SLAB

77

2.47

1

6 0.333333 0.666667 0.000000

SWCNT

6 3

See *NANOTUBE* (page 52) for further details.

Nanotube rebuild: build a nanotube starting from the structure of another one, with same directions but a different radius.

Two restart keywords, *NANORE* and *SWCNTRE*, allow to build a (n_1, n_2) nanotube by starting from the structure of another one (a previously $(nold_1, nold_2)$ optimised one, read from file fort.35). The "old" nanotube is unrolled and re-rolled according to a "new" \vec{R} vector, with minor modifications to the structure. The rolling direction of the two tubes must be the same.

It is particularly helpful for the geometry optimisation of inorganic nanotubes (thick slabs, large systems, the geometry of the tubes is very different from the one of the slab), as the number of optimisation steps is reduced (see Ref. [43] for documentation of computational gain).

SWCNTRE

It is the same as *NANORE*, with the same input syntax, but in for hexagonal lattices with 60° unit cell reference (see *SWCNT*, page 66).

| rec | variable | meaning |
|-----|------------------|---|
| • * | $nold_1, nold_2$ | Nanotube rebuild: indices of the starting nanotube. |
| * | n_1, n_2 | New indices of the rolling vector. |

SYMMDIR

The symmetry allowed directions, corresponding to internal degrees of freedom are printed. No input data are required.

SYMMOPS

Point symmetry operator matrices are printed in the Cartesian representation. No input data are required.

SYMMREMO

All the point group symmetry operators are removed. Only the identity operator is left. The wave function can be computed. No input data are required.

Warning: the CPU time may increase by a factor MVF (order of point-group), both in the integral calculation and in the **scf** step. The size of the bielectronic integral file may increase by a factor MVF^2 .

TENSOR

| rec | variable | meaning |
|-----|----------|----------------------------------|
| • * | IORD | order of the tensor (≤ 4) |

This option evaluates and prints the non zero elements of the tensor of physical properties up to order 4.

TESTGEOM

Execution stops after reading the geometry input block and printing the coordinates of the atoms in the conventional cell. Neighbours analysis, as requested by the keyword **NEIGHBOR**, is not executed. The geometry input block must end with the keyword **END** or **ENDG**. No other input blocks (basis set etc) are required.

TRASREMO

Point symmetry operators with fractional translation components are removed. It is suggested to previously add the keyword **ORIGIN** (page 56), in order to minimize the number of symmetry operators with finite translation component. No input data are required.

USESAED

| rec | variable | meaning |
|-----|--------------------------------|------------------------------|
| • * | $\delta(i), i=1, \text{nsaed}$ | δ for each distortion |

Given the symmetry allowed elastic distortion (SAED), (printed by the keyword **MAKE-SAED**, page 47) δ for the allowed distortion are given in input.

WULFF

| rec | variable | meaning |
|-----|-----------|-------------------------------------|
| • * | IPLN | number of crystal planes |
| | | <i>insert IPLN records</i> _____ II |
| • * | h, k, l | Miller indices of the plane |
| • * | ESRF | surface energy in J/m^2 |

The **WULFF** option is used to determine the equilibrium shape of real (finite) crystals by ensueing the minimization of the total surface free energy according to the Gibbs-Wulff theorem [188].

The execution stops after the Wulff construction is completed. It generates a three dimensional model, wulff.pms, that may be displayed with the free application Mesh Viewer (<http://mview.sourceforge.net>).

2.2 Basis set input

| | | | |
|----------------------------------|---|----|---|
| Symmetry control | | | |
| ATOMSYMM | printing of point symmetry at the atomic positions | 36 | – |
| Basis set modification | | | |
| CHEMOD | modification of the electronic configuration | 69 | I |
| GHOSTS | eliminates nuclei and electrons, leaving BS | 71 | I |
| Auxiliary and control keywords | | | |
| CHARGED | allows non-neutral cell | 69 | – |
| NOPRINT | printing of basis set removed | 71 | – |
| PRINTOUT | setting of printing options | 59 | I |
| SETINF | setting of inf array options | 61 | I |
| SETPRINT | setting of printing options | 61 | I |
| STOP | execution stops immediately | 62 | – |
| SYMMOPS | printing of point symmetry operators | 67 | – |
| END/ENDB | terminate processing of basis set definition keywords | | – |
| Output of data on external units | | | |
| GAUSS98 | printing of an input file for the GAUSS94/98 package | 71 | – |

Basis set input optional keywords

ATOMSYMM

See input block 1, page 36

CHARGED - charged reference cell

The unit cell of a periodic system must be neutral. This option forces the overall system to be neutral even when the number of electrons in the reference cell is different from the sum of nuclear charges, by adding a uniform background charge density to neutralize the charge in the reference cell.

Warning - Do not use for total energy comparison.

CHEMOD - modification of electronic configuration

| rec | variable | meaning |
|-----|--------------|--|
| • * | NC | number of configurations to modify |
| • * | LA | <i>label</i> of the atom with new configuration |
| * | CH(L),L=1,NS | shell charges of the LA-th atom. The number NS of shells must coincide with that defined in the basis set input. |

The **CHEMOD** keyword allows modifications of the shell charges given in the basis set input, which are used in the atomic wave function routines. The original geometric symmetry is checked, taking the new electronic configuration of the atoms into account. If the number of symmetry operators should be reduced, information on the new symmetry is printed, and the program stops. No automatic reduction of the symmetry is allowed. Using the information printed, the symmetry must be reduced by the keyword **MODISYMM** (input block 1, page 48).

See test 37. MgO supercell, with a Li defect. The electronic configuration of the oxygen nearest to Li corresponds to O^- , while the electronic configuration of those in bulk MgO is O^{2-} . The basis set of oxygen is unique, while the contribution of the two types of oxygen to the initial density matrix is different.

END

Terminate processing of block 2, basis set, input. Execution continues. Subsequent input records are processed, if required.

GAUSS98 - Printing of input file for GAUSS98 package

The keyword **GAUSS98** writes in file GAUSSIAN.DAT an input deck to run Gaussian (Gaussian 98 or Gaussian03) [76, 75]. The deck can be prepared without the calculation of the wave function by entering the keyword **TESTPDIM** in input block 3 (page 115). For periodic systems, coordinates and basis set for all the atoms in the reference cell only are written (no information on translational symmetry).

If the keyword is entered many times, the data are overwritten. The file GAUSSIAN.DAT contains the data corresponding to the last call.

The utility program *gautocry* reads basis set input in Gaussian format (as prepared by <http://www.emsl.pnl.gov/forms/basisform.html>) and writes it in CRYSTAL format. No input data required.

1. The route card specifies:

| | |
|-------------|---------------------|
| method | HF |
| basis set | GEN 5D 7F |
| type of job | SP |
| geometry | UNITS=AU GEOM=COORD |

2. The title card is the same as in *CRYSTAL* input.
3. The molecule specification defines the molecular charge as the net charge in the reference cell. If the system is not closed shell, the spin multiplicity is indicated with a string "???", and must be defined by the user.
4. Input for effective core pseudopotentials is not written. In the route card PSEUDO = CARDS is specified; the pseudopotential parameters used for the crystal calculation are printed in the *crystal* output.
5. The scale factors of the exponents are all set to 1., as the exponents are already scaled.
6. the input must be edited when different basis sets are used for atoms with the same atomic number (e.g., CO on MgO, when the Oxygen basis set is different in CO and in MgO)

Warning: Only for 0D systems! The programs does not stop when the keyword **GAUSS98** is entered for 1-2-3D systems. Coordinates and basis set of all the atoms in the primitive cell are written, formatted, in file GAUSSIAN.DAT, following Gaussian scheme.

Warning If you run Gaussian 98 using the input generated by CRYSTAL with the keyword GAUSS98, you do not obtain the same energy. There are 3 main differences between a standard CRYSTAL run and a GAUSSIAN run.

1. CRYSTAL adopts by default bipolar expansion to compute coulomb integrals when the two distributions do not overlap. To compute all 2 electron integrals exactly, insert keyword NOBIPOLA in input block 3;
2. CRYSTAL adopts truncation criteria for Coulomb and exchange sums: to remove them, in input block 3 insert:

TOLINTEG
20 20 20 20 20

3. CRYSTAL adopts the NIST conversion factor bohr/Angstrom CODATA98:
1 Å= 0.5291772083 bohr
To modify the value, in input block 1 insert:

BOHRANGS
value_of_new_conversion_factor

GHOSTS

| rec | variable | meaning |
|-----|--------------|---|
| • * | NA | number of atoms to be transformed into ghosts |
| • * | LA(L),L=1,NA | <i>label</i> of the atoms to be transformed. |

Selected atoms may be transformed into *ghosts*, by deleting the nuclear charge and the shell electron charges, but leaving the basis set centred at the atomic position. The conventional atomic number is set to zero., the symbol is “XX”.

If the system is forced to maintain the original symmetry (**KEEPSYMM**), all the atoms symmetry related to the given one are transformed into ghosts.

Useful to create a vacancy (Test 37), leaving the variational freedom to the defective region and to evaluate the basis set superposition error (BSSE), in a periodic system. The periodic structure is maintained, and the energy of the isolated components computed, leaving the basis set of the other one(s) unaltered. For instance, the energy of a mono-layer of CO molecules on top of a MgO surface can be evaluated including the basis functions of the first layer of MgO, or, vice-versa, the energy of the MgO slab including the CO ad-layer basis functions.

See test36 and test37.

Warning Do not use with ECP.

Warning The keyword **ATOMREMO** (input block 1, page 35) creates a vacancy, removing nuclear charge, electron charge, and basis functions. The keyword **GHOSTS** creates a vacancy, but leaves the basis functions at the site, so allowing better description of the electron density in the vacancy.

Warning - Removal of nuclear and electron charge of the atoms selected is done after complete processing of the input. They look still as ”atoms” in the printed output before that operation.

NOPRINT

Printing of basis set is removed. No input data required.

PRINTOUT - Setting of printing environment

See input block 1, page 59.

SETINF - Setting of INF values

See input block 1, page 61.

SETPRINT - Setting of printing options

See input block 1, page 61.

STOP

Execution stops immediately. Subsequent input records are not processed.

TEST[BS]

Basis set input is checked, then execution stops. Subsequent input records (block3) are not processed.

SYMMOPS

See input block 1, page 67

Effective core pseudo-potentials - ECP

| rec | variable | value | meaning |
|--|----------|--------|--|
| • A | PSN | | pseudo-potential keyword: |
| | | HAYWLC | Hay and Wadt large core ECP. |
| | | HAYWSC | Hay and Wadt small core ECP. |
| | | BARTHE | Durand and Barthelat ECP. |
| | | DURAND | Durand and Barthelat ECP. |
| | | INPUT | free ECP - input follows. |
| | | | _____ II |
| <i>if PSN = INPUT insert</i> | | | |
| • * | ZNUC | | effective core charge (ZN in eq. 2.16). |
| | M | | Number of terms in eq. 2.17 |
| | M0 | | Number of terms in eq. 2.18 for $\ell = 0$. |
| | M1 | | Number of terms in eq. 2.18 for $\ell = 1$. |
| | M2 | | Number of terms in eq. 2.18 for $\ell = 2$. |
| | M3 | | Number of terms in eq. 2.18 for $\ell = 3$. |
| | M4 | | Number of terms in eq. 2.18 for $\ell = 4$. - CRYSTAL09 |
| | | | |
| <i>insert M+M0+M1+M2+M3+M4 records</i> | | | |
| • * | ALFKL | | Exponents of the Gaussians: $\alpha_{k\ell}$. |
| | CGKL | | Coefficient of the Gaussians: $C_{k\ell}$. |
| | NKL | | Exponent of the r factors: $n_{k\ell}$. |

Valence-electron only calculations can be performed with the aid of effective core pseudo-potentials (ECP). The ECP input must be inserted into the basis set input of the atoms with conventional atomic number > 200 .

The form of pseudo-potential W_{ps} implemented in *CRYSTAL* is a sum of three terms: a Coulomb term (C), a local term (W0) and a semi-local term (SL):

$$W_{ps} = C + W0 + SL \quad (2.15)$$

where:

$$C = -Z_N/r \quad (2.16)$$

$$W0 = \sum_{k=1}^M r^{n_k} C_k e^{-\alpha_k r^2} \quad (2.17)$$

$$SL = \sum_{\ell=0}^4 \left[\sum_{k=1}^{M_\ell} r^{n_{k\ell}} C_{k\ell} e^{-\alpha_{k\ell} r^2} \right] P_\ell \quad (2.18)$$

Z_N is the effective nuclear charge, equal to total nuclear charge minus the number of electrons represented by the ECP, P_ℓ is the projection operator related to the ℓ angular quantum number, and M , n_k , α_k , M_ℓ , $n_{k\ell}$, $C_{k\ell}$, $\alpha_{k\ell}$ are atomic pseudo-potential parameters.

1. Hay and Wadt (HW) ECP ([96, 94]) are of the general form 2.15. In this case, the NKL value given in the tables of ref. [96, 94] must be decreased by 2 ($2 \rightarrow 0$, $1 \rightarrow -1$, $0 \rightarrow -2$).

2. Durand and Barthelat (DB) ([12] - [56], [13], [14]), and Stuttgart-Dresden [146] ECPs contain only the Coulomb term C and the semi-local SL term.
3. In Durand and Barthelat ECP the exponential coefficient α in SL depends only on ℓ (i.e. it is the same for all the M_k terms).

$$SL = \sum_{\ell=0}^3 e^{-\alpha_{\ell} r^2} \left[\sum_{k=1}^{M_{\ell}} r^{n_{k\ell}} C_{k\ell} \right] P_{\ell} \quad (2.19)$$

The core orbitals replaced by Hay and Wadt *large core* and Durand-Barthelat ECPs are as follows:

| | |
|---------------|--------------------------|
| Li-Ne | = [He] |
| Na-Ar | = [Ne] |
| first series | = [Ar] |
| second series | = [Kr] |
| third series | = [Xe]4f ¹⁴ . |

The core orbitals replaced by Hay and Wadt *small core* ECPs are as follows:

| | |
|-------|---------------------------|
| K-Cu | = [Ne] |
| Rb-Ag | = [Ar] 3d ¹⁰ |
| Cs-Au | = [Kr] 4d ¹⁰ . |

The program evaluates only those integrals for which the overlap between the charge distribution φ_{μ}^0 φ_{ν}^g (page 275) and the most diffuse Gaussian defining the pseudopotential is larger than a given threshold T_{ps} (the default value is 10^{-5}). See also **TOLPSEUD** (Section 1.3).

Pseudopotential libraries

The following periodic tables show the effective core pseudo-potentials included as internal data in the *CRYSTAL* code.

HAY AND WADT LARGE CORE ECP. CRYSTAL92 DATA

```
-----
Na Mg                               Al Si P S Cl Ar
-----
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
-----
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
-----
Cs Ba Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi
-----
```

HAY AND WADT SMALL CORE ECP. CRYSTAL92 DATA

```
-----
K Ca Sc Ti V Cr Mn Fe Co Ni Cu
-----
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag
-----
Cs Ba Hf Ta W Re Os Ir Pt Au
-----
```

DURAND AND BARTHELAT'S LARGE CORE ECP - CRYSTAL92 DATA

```
-----
Li Be                               B C N O F Ne
-----
Na Mg                               Al Si P S Cl Ar
-----
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
-----
Rb Y                               Ag In Sn Sb I
-----
Tl Pb Bi
-----
```

BARTHE, **HAYWSC** and **HAYWLC** pseudopotential coefficients and exponents are inserted as data in the **CRYSTAL** code. The data defining the pseudo-potentials were included in **CRYSTAL92**, and never modified. The keyword **INPUT** allows entering updated pseudo-potentials, when available. An *a posteriori* check has been possible for **HAYWLC** and **HAYWSC** only, as the total energy of the atoms for the suggested configuration and basis set has been published [96, 95]. Agreement with published atomic energies data is satisfactory (checked from Na to Ba) for Hay and Wadt small core and large core pseudo-potentials, when using the suggested basis sets. The largest difference is of the order of 10^{-3} hartree. For Durand and Barthelat the atomic energies are not published, therefore no check has been performed. The printed data should be carefully compared with those in the original papers. The authors of the ECP should be contacted in doubtful cases.

Valence Basis set and pseudopotentials

Hay and Wadt ([96, 95]) have published basis sets suitable for use with their small and large core pseudopotentials. and in those basis set the s and p gaussian functions with the same quantum number have different exponent. It is common in **CRYSTAL** to use sp shells, where basis functions of *s* and *p* symmetry share the same set of Gaussian exponents, with a consequent considerable decrease in CPU time. The computational advantage of pseudopotentials over all-electron sets may thus be considerably reduced.

Basis set equivalent to those suggested by Hay and Wadt can be optimized by using **CRYSTAL** as an atomic package (page 79), or any atomic package with effective core pseudopotentials. See Chapter 9.2 for general comments on atomic basis function optimization. Bouteiller *et al*

[23] have published a series of basis sets optimized for Durand and Barthelat ECPs.

Stuttgart-Dresden ECP (formerly STOLL and PREUSS ECP)

The most recent pseudopotential parameters, optimized basis sets, a list of references and guidelines for the choice of the pseudopotentials can be found in:

<http://www.theochem.uni-stuttgart.de/pseudopotentials/index.en.html>

The clickable periodic table supplies, in CRYSTAL format, ECP to be used in CRYSTAL via the INPUT keyword (basis set input, block2, page 72).

<http://www.theochem.uni-stuttgart.de/pseudopotentials/clickpse.en.html>

RCEP Stevens et al.

Conversion of Stevens et al. pseudopotentials An other important family of pseudopotentials for the first-, second-, third-, fourth and fifth-row atoms of the periodic Table (excluding the lanthanide series) is given by Stevens et al. [167, 168]. Analytic Relativistic Compact Effective Potential (RCEP) are generated in order to reproduce the "exact" pseudo-orbitals and eigenvalues as closely as possible. The analytic RCEP expansions are given by:

$$r^2 V_i(r) = \sum_k A_{lk} r^{n_{l,k}} e^{-B_{lk} r^2}$$

An example of data for Ga atom (Table 1, page 616 of the second paper) is:

| | A_{lk} | n_{lk} | B_{lk} |
|-----------|------------|----------|----------|
| V_d | -3.87363 | 1 | 26.74302 |
| V_{s-d} | 4.12472 | 0 | 3.46530 |
| | 260.73263 | 2 | 9.11130 |
| | -223.96003 | 2 | 7.89329 |
| V_{p-d} | 4.20033 | 0 | 79.99353 |
| | 127.99139 | 2 | 17.39114 |

The corresponding Input file for the CRYSTAL program will be as follows:

```
INPUT
21. 1 3 2 0 0 0
    26.74302 -3.87363 -1
    3.46530 4.12472 -2
    9.11130 260.73263 0
    7.89329 -223.96003 0
    79.99353 4.20033 -2
    17.39114 127.99139 0
```

Note that for the r -exponent (n_{lk}), -2 has been subtracted to the value given in their papers, as in the case of Hay and Wadt pseudopotentials.

2.3 Computational parameters, Hamiltonian, SCF control

| Single particle Hamiltonian | | | |
|--|--|-----|---|
| RHF | Restricted Closed Shell | 109 | – |
| UHF | Unrestricted Open Shell | 116 | – |
| MP2 | Electron correlation energy | 107 | – |
| DFT | DFT Hamiltonian | 116 | – |
| | SPIN spin-polarized solution | 88 | – |
| Choice of the exchange-correlation functionals | | | |
| EXCHANGE | exchange functional | 83 | I |
| <i>LDA functionals</i> | | | |
| | LDA Dirac-Slater [44] (LDA) | | |
| | VBH von Barth-Hedin [178] (LDA) | | |
| <i>GGA functionals</i> | | | |
| | BECKE Becke 1988[17] (GGA) | | |
| | PBE Perdew-Becke-Ernzerhof 1996 [128] (GGA) | | |
| | PBESOL GGA. PBE functional revised for solids [130] | | |
| | mPW91 modified Perdew-Wang 91 (GGA) | | |
| | PWGGA Perdew-Wang 91 (GGA) | | |
| | SOGGA second order GGA. [195] | | |
| | WCGGA GGA - Wu-Cohen [187] | | |
| CORRELAT | correlation functional | 83 | I |
| <i>LDA functionals</i> | | | |
| | PZ Perdew-Zunger [134] (LDA) | | |
| | VBH von Barth-Hedin [178] (LDA) | | |
| | VWN Vosko,-Wilk-Nusair [179] (LDA) | | |
| <i>GGA functionals</i> | | | |
| | LYP Lee-Yang-Parr [109] (GGA) | | |
| | P86 Perdew 86 [126] (GGA) | | |
| | PBE Perdew-Becke-Ernzerhof [128] (GGA) | | |
| | PBESOL GGA. PBE functional revised for solids [130] | | |
| | PWGGA Perdew-Wang 91 (GGA) | | |
| | PWLSLSD Perdew-Wang 92 [132, 133, 131] (GGA) | | |
| | WL GGA - Wilson-Levy [185] | | |
| Standalone keywords: exchange+correlation | | | |
| SVWN | see [44, 179] | 84 | |
| BLYP | see [17, 109] | 84 | |
| PBEXC | see [128] | 84 | |
| PBESOLXC | see [130] | 84 | |
| SOGGAXC | see [195] | 84 | |
| Global Hybrid functionals | | | |
| Standalone keywords | | | |
| B3PW | B3PW parameterization | 84 | – |
| B3LYP | B3LYP parameterization | 84 | – |
| PBE0 | Adamo and Barone [6] | 84 | |
| PBESOL0 | Derived from PBE0 | 84 | |
| B1WC | see [20] | 84 | |
| WC1LYP | see [42] | 84 | |
| B97H | see [5, 68] | 84 | |
| PBE0-13 | see [29] | 84 | |
| User defined global hybrids | | | |
| HYBRID | hybrid mixing | 85 | I |
| NONLOCAL | local term parameterization | 85 | I |

Range-Separated Hybrid functionals

Short-range Corrected RSH functionals

HSE06 Screened-Coulomb PBE XC functional [3, 128] 86 –

HSESOL Screened-Coulomb PBESOL XC functional [108, 130] 86 –

Middle-range Corrected RSH functionals

HISS MC based on PBE XC functional [169, 170] 86 –

Long-range Corrected RSH functionals

RSHXLDA LC LDA XC functional [2, 102] 86 –

wB97 Chai/Head-Gordon LC functional [103, 5] 86 –

wB97X Chai/Head-Gordon SC/LC functional [103, 5] 86 –

LC-wPBE LC hybrid based on PBE XC functional [57] 86 –

LC-wPBESOL LC hybrid based on PBESOL XC functional [57] 86 –

LC-wBLYP LC hybrid based on BLYP XC functional [57] 86 –

meta-GGA functionals

Pure mGGA functionals

M06L pure mGGA M06-type functional [190] 87 –

Global hybrid mGGA functionals

M05 Minnesota 2005 functional [194] 87 –

M052x M05-2X functional [193] 87 –

M06 Minnesota 2006 functional [192] 87 –

M062X M06-2X functional [192] 87 –

M06HF M06-type functional with 100% HF [190] 87 –

Double Hybrid functionals

B2PLYP DH method based on BLYP functional [152] 87 –

B2GPPLYP General purpose variant of B2PLYP [1] 87 –

mPW2PLYP DH method based on mPW91-LYP functional [172] 87 –

DHYBRID HF exchange and MP2-like mixing for double hybrids 88 I

Numerical accuracy control

ANGULAR definition of angular grid 88 I

RADIAL definition of radial grid 88 I

[BECKE] selection of Becke weights (default) 88 –

SAVIN selection of Savin weights 88 –

OLDGRID "old" default grid 90

LGRID "large" predefined grid 91

[XLGRID] "extra large" predefined grid (new default)

XXLGRID "extra extra large" predefined grid 91

RADSAFE safety radius for grid point screening I

TOLLDENS density contribution screening [6] 92 I

TOLLGRID grid points screening [14] 92 I

[BATCHPNT] grid point grouping for integration 92 I

CHUNKS max n. points in a batch for numerical int. 92 I

DISTGRID distribution of DFT grid across nodes 92

LIMBEK size of local arrays for integration weights [400] ?? I

Atomic parameters control

RADIUS customized atomic radius 93 I

FCHARGE customized formal atomic charge 93 I

Auxiliary

END close DFT input block

Numerical accuracy and computational parameters control

| | | | |
|--|--|-----|---|
| BIPOLAR | Bipolar expansion of bielectronic integrals | 81 | I |
| BIPOSIZE | size of coulomb bipolar expansion buffer | 104 | I |
| EXCHSIZE | size of exchange bipolar expansion buffer | 104 | I |
| EXCHPERM | use permutation of centers in exchange integrals | 95 | - |
| ILASIZE | Maximum size of array ILA for 2-electron integral calculation ?? 6000 | | I |
| INTGPACK | Choice of integrals package 0 | 104 | I |
| MADLIND | reciprocal lattice vector indices for Madelung sums 50 | 106 | I |
| NOBIPCOU | Coulomb bielectronic integrals computed exactly | 108 | - |
| NOBIPEXCH | Exchange bielectronic integrals computed exactly | 108 | - |
| NOBIPOLA | All bielectronic integrals computed exactly | 108 | - |
| POLEORDR | Maximum order of multipolar expansion 4 | 108 | I |
| TOLINTEG | Truncation criteria for bielectronic integrals 6 6 6 6 12 | 115 | I |
| TOLPSEUD | Pseudopotential tolerance 6 | 115 | I |
| Type of run | | | |
| ATOMHF | Atomic wave functions | 79 | I |
| SCFDIR | SCF direct (mono+biel int computed) | 109 | - |
| EIGS | S(k) eigenvalues - basis set linear dependence check | 93 | - |
| FIXINDEX | Reference geometry to classify integrals | 98 | - |
| Basis set - AO occupancy | | | |
| FDAOSYM | f and d degeneracies analysis | 96 | I |
| FDAOCCUP | f and d orbital occupation guess | 97 | I |
| GUESDUAL | Density matrix guess - different Basis set | 102 | I |
| Integral file distribution | | | |
| BIESPLIT | writing of bielectronic integrals in n files $n = 1$, max=10 | 81 | I |
| MONSPLIT | writing of mono-electronic integrals in n file $n = 1$, max=10 | 106 | I |
| Numerical accuracy control and convergence tools | | | |
| ANDERSON | Fock matrix mixing | 79 | I |
| BROYDEN | Fock matrix mixing | 82 | I |
| FMIXING | Fock/KS matrix (cycle i and $i-1$) mixing 0 | 99 | I |
| LEVSHIFT | level shifter no | 105 | I |
| MAXCYCLE | maximum number of cycles 50 | 106 | I |
| SMEAR | Finite temperature smearing of the Fermi surface no | 112 | I |
| TOLDEE | convergence on total energy 6 | 115 | I |
| Initial guess | | | |
| EIGSHIFT | alteration of orbital occupation before SCF no | 94 | I |
| EIGSHROT | rotation of the reference frame no | 94 | I |
| GUESSP | density matrix from a previous run | 103 | - |
| GUESSPAT | superposition of atomic densities | 104 | - |
| Spin-polarized system | | | |
| ATOMSPIN | setting of atomic spin to compute atomic densities | 80 | I |
| BETALOCK | beta electrons locking | 80 | I |
| SPINLOCK | spin difference locking | 114 | I |
| SPINEDIT | editing of the spin density matrix used as SCF guess | 113 | I |
| Auxiliary and control keywords | | | |

| | | | |
|------------------|---|----------|---|
| END | terminate processing of block3 input | | – |
| FULLTIME | detailed report on running time | 100 | – |
| KSYMPRT | printing of Bloch functions symmetry analysis | 105 | – |
| LOWMEM | inhibits allocation of large arrays | 108 | – |
| NOLOWMEM | allows allocation of large arrays | 108 | – |
| MAXNEIGHB | maximum number of equidistant neighbours from an atom | 47 | I |
| NEIGHBOR | number of neighbours to analyse in PPAN | 56 | I |
| MEMOPRT | Synthetic report about dynamic memory usage | 106 | – |
| MEMOPRT2 | Detailed report about dynamic memory usage | 106 | – |
| PRINTOUT | setting of printing options | 59 | I |
| QVRSGDIM | maximum size of multipole moment gradient array | 90000000 | I |
| NOSYMADA | No Symmetry Adapted Bloch Functions | 108 | – |
| SYMADAPT | Symmetry Adapted Bloch Functions (default) | 114 | – |
| SETINF | setting of inf array options | 61 | I |
| SETPRINT | setting of printing options | 61 | I |
| STOP | execution stops immediately | 62 | – |
| TESTPDIM | stop after symmetry analysis | 115 | – |
| TEST[RUN] | stop after integrals classification and disk storage estimate | 115 | – |

Restricted to *MPPcrystal*

| | | | |
|-----------------|---|-----|---|
| CMPLXFAC | Overloading in handling matrices at “complex” k points with 82 respect to “real” k points | 2.3 | I |
| REPLDATA | to run <i>MPPcrystal</i> as <i>Pcrystal</i> | 109 | – |
| STDIAG | Enable standard diagonalization method (D&C method disabled) | 114 | – |

Output of data on external units

| | | | |
|---------------|---|-----|---|
| NOFMWF | wave function formatted output not written in file fort.98. | 108 | – |
| SAVEWF | wave function data written every two SCF cycles | 110 | – |

Post SCF calculations

| | | | |
|-----------------|---|-----|-----|
| POSTSCF | post-scf calculations when convergence criteria not satisfied | 109 | – |
| EXCHGENE | exchange energy evaluation (spin polarized only) | 95 | – |
| GRADCAL | analytical gradient of the energy | 100 | – |
| PPAN | population analysis at the end of the SCF | no | 109 |

Computational parameters, Hamiltonian, SCF control optional keywords

ANDERSON

Anderson’s method [7], as proposed by Hamann [92], is applied. No input data are required. See test49_dft, a metallic Lithium 5 layers slab, PWGGA Hamiltonian.

ATOMHF - Atomic wave function calculation

The Hartree-Fock atomic wave functions for the symmetry unique atoms in the cell are computed by the atomic program [150]. Full input (geometry, basis set, general information, SCF) is processed. No input data are required. The density matrix, constructed from a superposition of atomic densities, is computed and written on Fortran unit 9, along with the wave function information. The *crystal* program then stops. It is then possible to compute charge

density (**ECHG**) and classical electrostatic potential (**CLAS**) maps by running the program *properties*. This option is an alternative to the keyword **PATO** in the program *properties* (page 229), when the calculation of the periodic wave function is not required. The atomic wave function, eigenvalues and eigenvectors, can be printed by setting the printing option 71.

1. The atomic basis set may include diffuse functions, as no periodic calculation is carried out.
2. A maximum of two open shells of different symmetry (*s, p, d*) are allowed in the electronic configuration. In the electronic configuration given in input the occupation number of the shells must follow the rules given in Section 1.2.
3. For each electronic configuration, the highest multiplicity state is computed. Multiplicity cannot be chosen by the user.

Warning: DFT wave function for isolated atoms can not be computed.

ATOMSPIN - Setting of atomic spin

| rec | variable | meaning |
|-----|------------------|--|
| • * | NA | number of atoms to attribute a spin |
| • * | LA,LS(LA),L=1,NA | <i>atom labels</i> and spin (1, 0, -1) |

The setting of the atomic spins is used to compute the density matrix as superposition of atomic densities (**GUESSPAT** must be SCF initial guess); it does not work with **GUESSP**). The symmetry of the lattice may be reduced by attributing a different spin to geometrically symmetry related atoms. In such cases a previous symmetry reduction should be performed using the **MODISYMM** keyword. The program checks the symmetry taking the spin of the atoms into account. If the spin pattern does not correspond to the symmetry, the program prints information on the new symmetry, and then stops.

The formal spin values are given as follows:

- 1 atom spin is taken to be alpha;
- 0 atom spin is irrelevant;
- 1 atom spin is taken to be beta.

In a NiO double-cell (four atoms, Ni1 Ni2 O1 O2) we might use:

| | | | | |
|------|-----|-----|--|-----|
| atom | Ni1 | Ni2 | | |
| spin | 1 | 1 | for starting ferromagnetic solutions: | ↑ ↑ |
| spin | 1 | -1 | for starting anti ferromagnetic solutions: | ↑ ↓ |

SPINLOCK forces a given $n_\alpha - n_\beta$ electrons value: to obtain a correct atomic spin density to start SCF process, the atomic spins must be set even for the ferromagnetic solution. See test 30 and 31.

BETALOCK - Spin-polarized solutions

| rec | variable | meaning |
|-----|----------|--|
| • * | INF97 | n_β electrons |
| * | INF98 | number of cycles the n_β electrons is maintained |

The total number of of β electrons at all **k** points can be locked at the input value. The number of α electrons is locked to $(N + \text{INF95})/2$, where N is the total number of electrons in the

unit cell. INF95 must be odd when the number of electrons is odd, even when the number of electrons is even. See **SPINLOCK** for alternative way to define spin setting.

Note: if INF98 is < 0 , then the lock duration is controlled by energy difference between successive cycles (disappears when $< 10^{-INF98}$) instead of by number of cycles. This is useful when the locking must be relaxed before the convergence of the SCF -otherwise there is a risk to arrive to a spurious solution- but at the same time one does not know exactly in which SCF cycle the density matrix can be considered to be close enough to the right electronic structure so as to avoid a divergent behavior after the locking finishes.

Situations like this may occur in geometry optimizations of ferromagnetic systems, for instance: the SCF of the first optimization point converges in CYC 20 with the locking finishing in CYC 12; in the remaining points, as the density matrix of the previous one is used as initial guess, the SCF converges in CYC 10 under locking and, so, the true convergence is not ensured. Using FINALRUN=4 this situation could lead to an extremely large or even non convergent optimization process.

On the other hand, to fix locking since the energy difference between cycles is less than a given threshold is a quite handy criterion that could be in several cases preferable than fixing the duration in terms of number of cycles.

BIESPLIT - Splitting of large bielectronic integral files

| rec | variable | meaning | |
|-----|----------|----------------------------|------------|
| • * | NFILE | number of files to be used | 1 (max 10) |

Very compact crystalline systems, and/or very diffuse basis functions and/or very tight tolerances can produce billions integrals to be stored. The storage of bielectronic integrals can be avoided by running the direct SCF code **scfdir** rather than the standard SCF, at the expenses of a certain amount of CPU time.

When the standard SCF code is used, distributing the integrals on several disk files can improve performance.

BIPOLAR - Bipolar expansion approximation control

| rec | variable | meaning | |
|-----|----------|--------------------------------|----|
| • * | ITCOUL | overlap threshold for Coulomb | 18 |
| * | ITEXCH | overlap threshold for exchange | 14 |

The bipolar approximation is applied in the evaluation of the Coulomb and exchange integrals (page 279). ITCOUL and ITEXCH can be assigned any intermediate value between the default values (18 and 14) (see page 279) and the values switching off the bipolar expansion (20000 and 20000).

Note that default values have become tighter, 18 and 14, from CRYSTAL14, whereas before they were 14 and 10, respectively. Results are now expected to be more accurate but the program might be slower.

BIPOSIZE -Size of buffer for Coulomb integrals bipolar expansion

| rec | variable | meaning | |
|-----|----------|-----------------------------|--|
| • * | ISIZE | size of the buffer in words | |

Size (words) of the buffer for bipolar expansion of Coulomb integrals (default value is 4000000, that is 32 Mb, per core). The size of the buffer is printed in the message:

BIPO BUFFER LENGTH (WORDS) = XXXXXXX

or

COULOMB BIPO BUFFER TOO SMALL - TO AVOID I/O SET BIPOSIZE = XXXXXX

BROYDEN

| rec | variable | meaning |
|-----|----------|---|
| • * | W0 | $W0$ parameter in Anderson's paper [104] |
| * | IMIX | percent of Fock/KS matrices mixing when Broyden method is switched on |
| * | ISTART | SCF iteration after which Broyden method is active (minimum 2) |

A modified Broyden [25] scheme, following the method proposed by Johnson [104], is applied after the ISTART SCF iteration, with IMIX percent of Fock/KS matrices simple mixing. The value of % mixing given in input after the keyword **FMIXING** is overridden by the new one. Level shifter should be avoided when Broyden method is applied.

Suggested values:

FMIXING

80

BROYDEN

0.0001 50 2

See test50_dft, a metallic Lithium 5 layers slab, PWGGA Hamiltonian.

CMPLXFAC - Weight for diagonalization time

This directive is supported by *MPPcrystal* only.

| rec | variable | meaning |
|-----|----------|---|
| • * | WEIGHT | estimated ratio of the computational time required to diagonalize complex and real matrices. Default value: $2.\bar{3}$. |

Fock matrix elements at a general k point in reciprocal space are complex numbers. At special k points (such as Γ , for example) those elements are real. Computational times required to diagonalize real (t_r) and complex (t_c) matrices are different. WEIGHT is an estimate of the ratio: $\text{WEIGHT} = t_c/t_r$.

An appropriate assessment of WEIGHT improves load balancing. The default value is: $2.\bar{3}$.

DFT

The Kohn-Sham [106, 101] DFT code is controlled by keywords, that must follow the general keyword **DFT**, in any order. These keywords can be classified into three groups:

- 1 Choice of the exchange-correlation functional
- 2 *Integration grid and numerical accuracy control (optional)*
- 3 *Atomic parameters (optional)*

The DFT input block ends with the keyword **END** or **ENDDFT**. Default values are supplied for all computational parameters. Choice of exchange and/or correlation potential is mandatory.

1. Choice of the exchange-correlation functional

Many different approximate exchange-correlation functionals are available in CRYSTAL: from semilocal (i.e. LDA, GGA and mGGA) to global and range-separated hybrid functionals, as well as double hybrid methods.

EXCHANGE and **CORRELAT** keywords, each followed by an alpha-numeric record, allow the selection of the exchange and correlation functionals.

If the correlation potential is not set (keyword **CORRELAT**), an exchange-only potential is used in the Hamiltonian. If the exchange potential is not set (keyword **EXCHANGE**), the Hartree-Fock potential is used.

A list of the exchange and correlation functionals that can be select in input is reported below.

| | | |
|------------------------|---|----|
| EXCHANGE | Exchange potential (default: Hartree-Fock exchange). Insert one of the following keywords _____ | II |
| <i>LDA functionals</i> | | |
| LDA | LSD. Dirac-Slater [44] | |
| VBH | LSD. von Barth-Hedin [178] | |
| <i>GGA functionals</i> | | |
| BECKE | GGA. Becke 1988 functional [17] | |
| mPW91 | GGA. modified Perdew-Wang 1991 functional [?] | |
| PBE | GGA. Perdew-Becke-Ernzerhof [128] | |
| PBESOL | GGA. PBE functional revised for solids [130] | |
| PWGGA | GGA. Perdew-Wang [129] | |
| SOGGA | GGA. Second Order corrected GGA functional. It must be used in combination with the PBE correlation functional[195] | |
| WCGGA | GGA - Wu-Cohen 2006 functional [187] | |

| | | |
|------------------------|--|----|
| CORRELAT | Correlation Potential (default: no correlation). Insert one of the following keywords _____ | II |
| <i>LDA functionals</i> | | |
| PWLSD | LSD. Perdew-Wang parameterization of the Ceperley-Alder free electron gas correlation results [131] | |
| PZ | LSD. Perdew-Zunger parameterization of the Ceperley-Alder free electron gas correlation results [134] | |
| VBH | LSD. von Barth-Hedin [178] | |
| VWN | LSD. Vosko-Wilk-Nusair parameterization of the Ceperley-Alder free electron gas correlation results. Also known as VWN5. [179] | |
| <i>GGA functionals</i> | | |
| LYP | GGA. Lee-Yang-Parr [109] | |
| P86 | GGA. Perdew 86 [126] | |
| PBE | GGA. Perdew-Burke-Ernzerhof [128] | |
| PBESOL | GGA. PBE functional revised for solids [130] | |
| PWGGA | GGA. Perdew-Wang [129] | |
| WL | GGA - Wilson-Levy [185] | |

Examples of possible selection of the correlation and exchange functionals are:

| exchange | correlation | |
|----------|-------------|--|
| — | PWGGA | Hartree-Fock exchange, GGA Perdew-Wang correlation. |
| LDA | VWN | probably the most popular LDA formulation, also known as S-VWN |
| VBH | VBH | was the most popular LDA scheme in the early LDA solid state applications (1975-1985). |
| PBE | PBE | the well-known PBE XC functional |
| BECKE | LYP | B-LYP |

Standalone keywords for common exchange-correlation functionals are also available.

| | |
|-----------------|--|
| SVWN | Combination of Slater for exchange and VWN for correlation [44, 179] |
| BLYP | Combination of B88 for exchange and LYP for correlation [17, 109] |
| PBEXC | Full PBE XC GGA functional [128] |
| PBESOLXC | XC GGA revised PBE functional for solids [130] |
| SOGGAXC | Combination of SOGGA for exchange and PBE for correlation [195] |

Global Hybrid functionals

Global hybrid (GH) functionals have the general formula:

$$E_{xc}^{GH} = (1 - A) * E_x^{DFA} + A * E_x^{HF} + E_c^{DFA}$$

They include a constant fraction of HF exchange (A).

Standalone keywords are available to define global hybrid functionals completely.

| | |
|-------------|--|
| B3PW | Becke's 3 parameter functional [18] combined with the non-local correlation PWGGA [127, 132, 133, 131] |
|-------------|--|

| | |
|--------------|---|
| B3LYP | Becke's 3 parameter functional [18] combined with the non-local correlation LYP. B3LYP in CRYSTAL is based on the 'exact' form of the Vosko-Wilk-Nusair correlation potential (corresponds to a fit to the Ceperley-Alder data). In the original paper [179]) it is reported as functional V, which is used to extract the 'local' part of the LYP correlation potential. |
|--------------|---|

| | |
|-------------|---|
| PBE0 | Hybrid version of the PBE XC functional with 25% (1/4) of HF exchange. Adamo and Barone [6] |
|-------------|---|

| | |
|----------------|---|
| PBESOL0 | Same as PBE0 but with the PBESol XC functional instead of PBE |
|----------------|---|

| | |
|-------------|---|
| B1WC | One-parameter hybrid functional which combines WC exchange functional with 16% of HF exchange and the PWGGA correlation functional (see [20]) |
|-------------|---|

| | |
|---------------|---|
| WC1LYP | As for the B1WC functional, but with the LYP correlation functional instead of the PWGGA (see [42]) |
|---------------|---|

| | |
|-------------|--|
| B97H | Hybrid functional based on the B97 XC functional [5, 68] |
|-------------|--|

| | |
|----------------|--|
| PBE0-13 | Revised version of the PBE0 functional with 33.3333% (1/3) of HF exchange [29] |
|----------------|--|

User-defined global hybrid functionals

It is possible to define other global hybrid functionals by specifying an exchange functional (see

the **EXCHANGE** keyword) and a correlation one (see the **CORRELAT** keyword) and then include a given amount of exact Hartree-Fock exchange into the exchange functional through the keyword **HYBRID**.

HYBRID Hybrid method - 1 record follows:
 • * A Fock exchange percentage (default 100.)

Any mixing (0-100) of exact Hartree-Fock and DFT exchange can be used. The keyword **HYBRID** can also be used to modify the fraction of HF exchange in existing GH functionals.

NONLOCAL setting of non-local weighting parameters - 1 record follows:
 • * B exchange weight of the non-local part of exchange
 C weight of the non-local correlation

NONLOCAL allows users to modify the relative weight of the local and non-local part both in the exchange and the correlation potential with respect to standard definition of Becke's 3 parameter functional types:

$$E_{xc} = (1 - A) * (E_x^{LDA} + B * E_x^{BECKE}) + A * E_x^{HF} + (1 - C) * E_c^{LDA} + C * E_c^{GGA}$$

A , B , and C are the input data of **HYBRID** and **NONLOCAL**. Becke's 3 parameter functionals currently implemented in CRYSTAL are B3PW and B3LYP.

For example, the following sequences correspond to the stand-alone keywords for some of the available GH functionals.

B3PW

corresponds to the sequence:
 EXCHANGE
 BECKE
 CORRELAT
 PWGGA
 HYBRID
 20
 NONLOCAL
 0.9 0.81

PBE0

corresponds to the sequence:
 EXCHANGE
 PBE
 CORRELAT
 PBE
 HYBRID
 25

B1WC

corresponds to the sequence:
 EXCHANGE
 WCGGA
 CORRELAT
 PWGGA
 HYBRID
 16

B3LYP

corresponds to the sequence:
 EXCHANGE
 BECKE
 CORRELAT
 LYP
 HYBRID
 20
 NONLOCAL
 0.9 0.81

PBESOL0

corresponds to the sequence:
 EXCHANGE
 PBESOL
 CORRELAT
 PBESOL
 HYBRID
 25

WC1LYP

corresponds to the sequence:
 EXCHANGE
 WCGGA
 CORRELAT
 LYP
 HYBRID
 16

Range-Separated Hybrid functionals

CRYSTAL offers a wide variety of range-separated hybrid (RSH) functionals in which the amount of HF exchange included depends on the distance between electrons. They are obtained from the separation of the Coulomb operator in different ranges (three ranges in the current implementation) by means of the *error function* as:

$$\frac{1}{r_{12}} = \underbrace{\frac{\text{erfc}(\omega_{SR}r_{12})}{r_{12}}}_{SR} + \underbrace{\frac{1 - \text{erfc}(\omega_{SR}r_{12}) - \text{erf}(\omega_{LR}r_{12})}{r_{12}}}_{MR} + \underbrace{\frac{\text{erf}(\omega_{LR}r_{12})}{r_{12}}}_{LR}$$

where ω is the length scale of separation. Then, the general form of a range-separated hybrid is:

$$E_{xc}^{RSH} = E_{xc}^{DFA} + c_{SR}(E_{x,SR}^{HF} - E_{x,SR}^{DFA}) + c_{MR}(E_{x,MR}^{HF} - E_{x,MR}^{DFA}) + c_{LR}(E_{x,LR}^{HF} - E_{x,LR}^{DFA})$$

According to the values of c_{SR} , c_{MR} , c_{LR} , ω_{SR} and ω_{LR} , short-, middle- and long-range corrected RSH functionals can be defined.

The following RSH functionals are available:

Short-range Corrected (SC) functionals

| | |
|---------------|--|
| HSE06 | Screened-Coulomb PBE functional [3, 128] combined with PBE correlation |
| HSEsol | Screened-Coulomb PBEsol functional [108, 130] combined with PBEsol correlation |

Middle-range Corrected (MC) functionals

| | |
|-------------|--|
| HISS | Middle-range corrected functional based on the PBE exchange hole [169, 170]) combined with PBE correlation (labeled B in ref. [169]) |
|-------------|--|

Long-range Corrected (LC) functionals

| | |
|-------------------|--|
| RSHXLDA | Long-range corrected LDA exchange functional [2, 102] combined with VWN for correlation |
| wB97 | Chai-Head-Gordon long-range corrected RSH functional[103, 5] |
| wB97X | Chai-Head-Gordon long-range corrected RSH functional[103, 5] with a small contribution of HF exchange at short-range |
| LC-wPBE | long-range corrected RSH functional[57] based on PBE XC functional |
| LC-wPBEsol | long-range corrected RSH functional[57] based on PBEsol XC functional |
| LC-wBLYP | long-range corrected RSH functional[57] based on BLYP XC functional |

Details of the amount of RS-HF exchange and the length scale separation ω for the RSH functionals available in CRYSTAL are given in the table below:

| Method | Exchange | c_{SR} | c_{MR} | c_{LR} | $\omega_{SR}(a_0^{-1})$ | $\omega_{LR}(a_0^{-1})$ | Correlation | Ref. |
|---------------------|----------|----------|----------|----------|-------------------------|-------------------------|-------------|-----------------|
| HSE06 | PBE | 0.25 | 0.00 | 0.00 | 0.11 | 0.11 | PBE | [3, 128] |
| HSEsol | PBEsol | 0.25 | 0.00 | 0.00 | 0.11 | 0.11 | PBEsol | [108, 130] |
| HISS | PBE | 0.00 | 0.60 | 0.00 | 0.84 | 0.20 | PBE | [169, 170, 128] |
| LC- ω PBE | PBE | 0.00 | 0.00 | 1.00 | 0.40 | 0.40 | PBE | [57, 128] |
| LC- ω PBEsol | PBEsol | 0.00 | 0.00 | 1.00 | 0.60 | 0.60 | PBEsol | [57, 130] |
| LC- ω BLYP | B88 | 0.00 | 0.00 | 1.00 | 0.60 | 0.60 | LYP | [57, 17, 109] |
| RSHXLDA | S | 0.00 | 0.00 | 1.00 | 0.40 | 0.40 | VWN | [2, 102, 179] |
| ω B97 | B97 | 0.00 | 0.00 | 1.00 | 0.40 | 0.40 | B97 | [103, 5] |
| ω B97-X | B97 | 0.157706 | 0.00 | 1.00 | 0.30 | 0.30 | B97 | [103, 5] |

Notes for RSH functionals:

- (i) the bipolar expansion is not active in the calculation of the exchange integrals (on average, the cost can increase by a factor 2 to 3);
- (ii) one- and two-electron repulsion integrals are computed in direct mode;

- (iii) implementation of HSE06, HISS, LC-wPBE and related RSH methods is based on the Henderson-Janesko-Scuseria model of the PBE exchange hole[171].

meta-GGA functionals

Both pure and hybrids meta-GGA (mGGA) functionals are available. In the current version, all implemented mGGA functionals belong to the Minnesota set of functionals as proposed by Truhlar and co-workers[], in particular the M05 and M06 families.

Pure mGGA functionals

M06L pure mGGA version of the M06 hybrid functional[190]

Global hybrid mGGA functionals

M05 Minnesota 2005 global hybrid mGGA XC functional hybridized with 28% of HF exchange[194]

M052X as M05 but with a doubled amount of HF exchange[193]

M06 Minnesota 2006 global hybrid mGGA XC functional hybridized with 27% of HF exchange[192]

M062X as M06 but with twice amount of HF exchange[192]

M06HF global hybrid mGGA with 100% HF exchange[191]

Double Hybrid functionals

Double hybrid (DH) functionals implemented in CRYSTAL have the general formula:

$$E_{xc}^{DH} = (1 - A) * E_x^{DFA} + A * E_x^{HF} + (1 - B) * E_c^{DFA} + B * E_c^{MP2}$$

as proposed by S. Grimme [152].

The following DH functionals are currently available:

| | | A% | B% |
|-----------------|---|----|----|
| B2PLYP | Becke88's exchange functional [?] combined with the LYP correlation functional[152] | 53 | 27 |
| B2GPPLYP | General purpose (GP) version of B2PLYP DH functional [1] | 63 | 36 |
| mPW2PLYP | Modified PW91 exchange functional[] combined with the LYP correlation functional[172] | 55 | 25 |

DH functionals can only be used in combination with a post-SCF MP2-like calculation through the CRYSCOR program.

Notes:

- (i) the total energy printed at the end of the SCF process is meaningless because it does not include the MP2 correlation correction;
- (ii) current implementation is limited to the LYP correlation functional;
- (iii) there are neither numeric nor analytic gradients for DH functionals;
- (iv) the MP2 correlation correction is available for closed shell systems, only;
- (v) DH methods have the same computational cost as MP2, rather than that of DFT;
- (vi) DH methods are available only for sequential runnings.

See the CRYSCOR User's Manual for further details on the post-SCF MP2-like calculation.

The amount of HF exchange and MP2 correlation correction can be modified by means of the **DHYBRYD** keyword.

| | |
|----------------|--|
| DHYBRID | Double Hybrid method - 1 record follows: |
| • * A | Fock exchange percentage (default 100.) |
| B | MP2 correlation correction percentage (default 0.) |

Availability of XC functionals

Not all functionals are available for all types of calculations and computed properties. A summary is given in the following table (Y=Yes, N=Not)

| DFA | Energy Gradients CPKS | | |
|--------------------------|-----------------------|---|---|
| LDA | Y | Y | Y |
| GGA | Y | Y | Y |
| mGGA | Y | Y | N |
| Global hybrids (LDA,GGA) | Y | Y | Y |
| Global hybrids (mGGA) | Y | Y | N |
| Range-separated hybrids | Y | Y | N |
| Double hybrids | Y | N | N |

Note that only a subset of the pure and hybrid LDA/GGA XC functionals can be used in the CPKS scheme, namely: LDA, VWN, BECKE, PBE (XC), PBEsol (XC), SOGGA, LYP, WCGGA, B3LYP, PBE0, PBEsol0, WC1LYP, B1WC.

The calculation of properties that require the solution of the CPKS equations, such as linear and non-linear electric susceptibilities (e.g. dielectric constant), Raman intensities and photoelasticity, is then limited to that subset of XC functionals.

Spin-polarized systems

All functionals are formulated in terms of total density and spin density. Default is total density. To use functionals of spin density insert the keyword **SPIN**.

SPIN unrestricted spin DF calculation (default: restricted)

2. Integration grid and numerical accuracy control

No input data are required: Becke weights are chosen by default, as well as a set of safe values for the computational parameters of integration.

The generation of grid points in CRYSTAL is based on an atomic partition method, originally developed by Becke [15] for molecular systems and then extended to periodic systems [174]. Each atomic grid consists of a radial and an angular distribution of points. Grid points are generated through a radial and an angular formula: Gauss-Legendre radial quadrature and Lebedev two-dimensional angular point distribution are used.

Lebedev angular grids are classified according to progressive accuracy levels, as given in the following table:

| LEV | CR98 | ℓ | N_{ang} | LEV | CR98 | ℓ | N_{ang} |
|-----|------|--------|-----------|-----|------|--------|---|
| 1 | 1 | 9 | 38 | 16 | 53 | 974 | |
| 2 | 2 | 11 | 50 | 17 | 59 | 1202 | |
| 3 | | 13 | 74 * | 18 | 65 | 1454 | Index of Lebedev accuracy levels |
| 4 | | 15 | 86 | 19 | 71 | 1730 | LEV: Lebedev accuracy level |
| 5 | 3 | 17 | 110 | 20 | 77 | 2030 | CR98: corresponding index in CRYSTAL98 |
| 6 | | 19 | 146 | 21 | 83 | 2354 | ℓ : maximum quantum number of spherical harmonics used in Lebedev derivation |
| 7 | | 21 | 170 | 22 | 89 | 2702 | |
| 8 | 4 | 23 | 194 | 23 | 95 | 3074 | |
| 9 | | 25 | 230 * | 24 | 101 | 3470 | N_{ang} : number of angular points generated per radial point |
| 10 | 5 | 27 | 266 * | 25 | 107 | 389 | |
| 11 | 6 | 29 | 302 | 26 | 113 | 4334 | * : sets with negative weights, to be avoided |
| 12 | | 31 | 350 | 27 | 119 | 4802 | |
| 13 | 7 | 35 | 434 | 28 | 125 | 5294 | |
| 14 | | 41 | 590 | 29 | 131 | 5810 | |
| 15 | | 47 | 770 | | | | |

If one Lebedev accuracy level is associated with the whole radial range, the atomic grid is called *unpruned*, or *uniform*. In order to reduce the grid size and maintain its effectiveness, the atomic grids of spherical shape can be partitioned into shells, each associated with a different angular grid. This procedure, called grid *pruning*, is based on the assumption that core electron density is usually almost spherically symmetric, and surface to be sampled is small.

Also, points far from the nuclei need lower point density, as associated with relatively small weights, so that more accurate angular grids are mostly needed within the valence region than out of it.

The choice of a suitable grid is crucial both for numerical accuracy and need of computer resources.

Different formulae have been proposed for the definition of grid point weights. In CRYSTAL Becke and Savin weights are available; Becke weights are default, and provide higher accuracy.

[BECKE] Becke weights [16]. Default choice.

SAVIN Savin weights [160]

A default grid is available in CRYSTAL, however the user can redefine it by the following keywords:

| RADIAL | | Radial integration information |
|---------------|--------------|---|
| rec | variable | meaning |
| • * | NR | number of intervals in the radial integration [default 1] |
| • * | RL(I),I=1,NR | radial integration intervals limits in increasing sequence [default 4.0] (last limit is set to ∞) |
| • * | IL(I),I=1,NR | number of points in the radial quadrature in the I-th interval [default 55]. |

| ANGULAR | | Angular integration information |
|----------------|---------------|--|
| rec | variable | meaning |
| • * | NI | number of intervals in the angular integration [default 1] |
| • * | AL(I),I=1,NI | upper limits of the intervals in increasing sequence. The last limit must be 9999.0 [default 9999.0] |
| • * | LEV(I),I=1,NI | accuracy level in the angular integration over the I-th interval; positive for Lebedev level (see Lev in page 88) [default 13] |

Note: A new default grid has been set. It corresponds to the XLGRID in CRYSTAL09

The *default grid* is a pruned (75,974) grid, having 75 radial points and a maximum number of 974 angular points in regions relevant for chemical bonding. Each atomic grid is split into five shells with different angular grids.

This grid guarantees accurate integration of the XC potential when numerical derivatives of energy or related properties (i.e. spontaneous polarization) and gradients have to be computed (e.g. bulk modulus, elastic constants, piezoelectric tensor, ferroelectric transitions). It also provides accurate results for atoms up to fourth-row and heavier.

Default grid - corresponds to the sequence:

| | |
|---------------------------|--|
| RADIAL | Keyword to specify the radial grid |
| 1 | Number of intervals in the radial part |
| 4.0 | Radial integration limits of the i-th interval |
| 75 | Number of radial points in the i-th interval |
| ANGULAR | Keyword to specify the angular grid |
| 5 | Number of intervals in the angular part |
| 0.1667 0.5 0.9 3.5 9999.0 | Angular integration limits of the i-th interval |
| 4 8 12 16 12 | Angular grid accuracy level of the i-th interval |

Information on the size of the grid, grid thresholds, and radial (angular) grid is reported in the CRYSTAL output with the following format:

```
SIZE OF GRID=          44707

BECKE WEIGHT FUNCTION
RADSAFE =           2.00
TOLERANCES - DENSITY:10**- 6; POTENTIAL:10**- 9; GRID WGT:10**-14

RADIAL INTEGRATION - INTERVALS (POINTS,UPPER LIMIT):          1( 75,  4.0*R)

ANGULAR INTEGRATION - INTERVALS (ACCURACY LEVEL [N. POINTS] UPPER LIMIT):
 1(  4[ 86]  0.2)  2(  8[ 194]  0.5)  3( 12[ 350]  0.9)  4( 16[ 974]  3.5)
 5( 12[ 350]9999.0)
```

Three more pre-defined grids are available which can be selected to improve accuracy (or reduce the cost) by inputting the following global keywords:

OLDGRID Old default grid

This is the old default grid in CRYSTAL09. It is a pruned (55,434) grid, having 55 radial points and a maximum number of 434 angular points in regions relevant for chemical bonding. Each atomic grid is split into ten shells with different angular grids.

This grid is good enough for either single-point energy calculations or medium-accuracy geometry optimizations. Due to the large pruning, the cost of the calculation is modest.

Default grid - corresponds to the sequence:

| | |
|--|--|
| RADIAL | Keyword to specify the radial grid |
| 1 | Number of intervals in the radial part |
| 4.0 | Radial integration limits of the i-th interval |
| 55 | Number of radial points in the i-th interval |
| ANGULAR | Keyword to specify the angular grid |
| 10 | Number of intervals in the angular part |
| 0.4 0.6 0.8 0.9 1.1 2.3 2.4 2.6 2.8 9999.0 | Angular integration limits of the i-th interval |
| 1 2 5 8 11 13 11 8 5 1 | Angular grid accuracy level of the i-th interval |

LGRID Large grid

Global keyword to choose a smaller grid than default, corresponding to the sequence:

```
RADIAL
1
4.0
75
ANGULAR
5
0.1667 0.5 0.9 3.05 9999.0
2 6 8 13 8
```

The *large grid* is a pruned (75,434) grid, having 75 radial points and a maximum number of 434 angular points in the region relevant for chemical bonding. Five shells with different angular points are adopted to span the radial range as proposed by Gill et al. [86].

[XLGRID] Extra large grid (default)

XXLGRID Extra extra large grid

The *extra-extra-large grid* is a pruned (99,1454) grid, consisting of 99 radial points and 1454 angular points in the region of chemical interest. This is very large and accurate grid which can be used for benchmark calculations. It corresponds to:

```
RADIAL
1
4.0
99
ANGULAR
5
0.1667 0.5 0.9 3.5 9999.0
6 10 14 18 14
```

Unpruned grids

To switch from a pruned grid to the corresponding unpruned grid, only one shell must be defined in the radial part and the same angular accuracy is used everywhere. The use of unpruned grids increases the cost of the calculations by about 50-60% with respect to the pruned grid.

For example, to transform the default grid to the corresponding unpruned grid input the following data:

ANGULAR

1

9999.0

13

Numerical accuracy and running time are also controlled by the following keywords:

TOLLGRID

- * IG DFT grid weight tolerance [default 14]

TOLLDENS

- * ID DFT density tolerance [default 6]
-

The DFT density tolerance ID controls the level of accuracy of the integrated charge density N_{el} (number of electron per cell):

$$N_{el} = \int_{cell} \rho(\mathbf{r}) d\mathbf{r} = \sum_{\mu, \nu, \mathbf{g}, \mathbf{l}} P_{\mu, \nu}^{\mathbf{g} + \mathbf{g}'} \sum_i w(\mathbf{r}_i) \varphi_{\mu}^{\mathbf{g}}(\mathbf{r}_i) \varphi_{\nu}^{\mathbf{g}'}(\mathbf{r}_i)$$

all contributions where $|\varphi_{\mu}(\mathbf{r}_i)| < 10^{-ID}$ or $|\varphi_{\nu}(\mathbf{r}_i)| < 10^{-ID}$ are neglected (see Chapter 13.12 for notation). The default value of ID is 6.

Grid points with integration weights less than 10^{-IG} are dropped. The default value of IG is 14.

RADSAFE

- * RAD for developers only [default 2]
-

BATCHPNT

- * BATCH average number of points in a batch for numerical integration [default 100]
-

In CRYSTAL (serial and parallel versions), in the calculation of the exchange-correlation contribution to the Kohn-Sham Hamiltonian matrix elements and energy gradients, a grid of NPOINT points is partitioned into batches of points as suggested by Ahlrichs [175]. The unit cell volume is then divided into a number of equivalent sub-volumes which approximates the following ratio: NPOINT/BATCH. Each grid point is assigned to a sub-volume and the set of points inside a sub-volume forms a batch. Since the distribution of grid points is not uniform in the unit cell (it is an atomic grid) the population of batches may vary from a few points to a few thousands. For this reason BATCH does not correspond to the maximum number of points in a batch. For example, batches of grid points close to the nuclei contain many more points than batches in internuclear regions. This may produce load unbalancing in parallel calculations (see **CHUNKS**).

The number of sub-volumes into which subdivided the unit cell is altered by changing BATCH. Reducing BATCH may result in some degree of inefficiency (minimum value: 1). Changing the value of BATCH can also affect results at some extent if TOLDENS is not sufficiently accurate, as the selection of contributions to the total density at a point can be influenced by the definition of the sub-volumes.

Default value of BATCH is 100, as averagely good balance between accuracy and efficiency.

CHUNKS

- * NCHU maximum number of points allowed in a batch for numerical integration [default 10000000]
-

This option is available for replicated-data calculations (Pcrystal only). Since different batches can contain a different number of points in a rather wide range, task farming can be unbalanced. **CHUNKS** allows user to set the maximum number of points per batch so improving load balancing. Recommended value of NCHU: 200.

CHUNKS is not implemented under **DISTGRID**.

DISTGRID

This option is available for both replicated-data and massive-parallel calculations. It forces the code to distribute the DFT grid information, which becomes huge for large unit cell cases, across all available processors. This permits a reduction in memory usage per processor.

LIMBEK

- * LBEK size of local arrays for integration weights [default 400]
-

3. Atomic parameters

The radius attributed to each atom for the integration is computed from the formal charge as specified in the initial electronic configuration. It is possible to enter for selected atoms a given atomic radius or a different formal charge.

• A RADIUS

- * NUMAT number of atoms selected
_____ insert NUMAT records _____ II
 - * LB *label* of the atom
 RAD(LB) radius (Å) attributed to the atom
-

• A FCHARGE

- * NUMAT number of atoms selected
_____ insert NUMAT records _____ II
 - * LB *label* of the atom
 FCH(LB) formal charge attributed to the atom
-

For a given atom, the new atomic radius or formal charge is not automatically applied to symmetry related ones. The full list of atoms must be specified. The keyword **ATOMSYMM** inserted in the first input block (geometry) prints the set of atoms symmetry related.

EIGS - Check of basis set linear dependence

In order to check the risk of basis set linear dependence, it is possible to calculate the eigenvalues of the overlap matrix. Full input (geometry, basis set, general information, SCF) is processed. No input data are required. The overlap matrix in reciprocal space is computed at all the **k**-points generated in the irreducible part of the Brillouin zone, and diagonalized. The eigenvalues are printed.

The higher the numerical accuracy obtained by severe computational conditions, the closer to 0 can be the eigenvalues without risk of numerical instabilities. Negative values indicate numerical linear dependence. The *crystal* program stops after the check (even if negative eigenvalues are not detected).

The Cholesky reduction scheme [107], adopted in the standard SCF route, requires linearly independent basis functions.

MPP doesn' support EIGS.

EIGSHIFT - Alteration of orbital occupation before SCF

| rec | variable | meaning |
|-----|----------|---|
| • * | NORB | number of elements to be shifted > 0 level shift of diagonal elements only < 0 off-diagonal level shift |
| | | insert NORB records |
| | | if NORB > 0 |
| • * | IAT | label of the atom |
| | ISH | sequence number of the shell in the selected atom Basis Set (as given in Basis Set input) |
| | IORB | sequence number of the AO in the selected shell (see Section 1.2, page 22). |
| | SHIF1 | α (or total, if Restricted) Fock/KS matrix shift |
| | [SHIF2 | β Fock/KS matrix shift - spin polarized only] |
| | | if NORB < 0 |
| • * | IAT | label of the atom |
| | ISH | sequence number of the shell in the selected atom Basis Set |
| | IORB1 | sequence number of the AO in the selected shell |
| | IORB2 | sequence number of the AO in the selected shell |
| | SHIF1 | α (or total, if Restricted) Fock/KS matrix shift |
| | [SHIF2 | β Fock/KS matrix shift - spin polarized only] |

Selected diagonal Fock/KS matrix elements can be shifted upwards when computing the initial guess, to force orbital occupation. This option is particularly useful in situations involving d orbital degeneracies which are not broken by the small distortions due to the crystal field, but which are broken by some higher-order effects (e.g. spin-orbit coupling). The **EIGSHIFT** option may be used to artificially remove the degeneracy in order to drive the system to a stable, non-metallic solution. The eigenvalue shift is removed after the first SCF cycle.

If the shift has to be applied to matrix elements of atoms symmetry related, the input data must be repeated as many times as the atoms symmetry related.

Example: KCoF_3 (test 38). In the cubic environment, two β electrons would occupy the three-fold degenerate t_{2g} bands. A state with lower energy is obtained if the degeneracy is removed by a tetragonal deformation of the cell (keyword **ELASTIC**), and the d_{xy} orbital (see page 22 for d orbital ordering) is shifted upwards by 0.3 hartree.

Warning **EIGSHIFT** acts on the atoms as specified in input. If there are atoms symmetry-related to the chosen one, hamiltonian matrix elements shift is not applied to the others. The programs checks the symmetry compatibility, and, if not satisfied, stops execution. The matrix elements of all the atoms symmetry-related must be shifted, if the symmetry of the systems must be kept

The keyword **ATOMSYMM** (input block 1, page 36) prints information on the atoms symmetry related in the cell.

EIGSHROT

Consider now the case of CoF_2 . The first six neighbors of each Co^{2+} ion form a slightly distorted octahedron (2 axial and 4 equatorial equivalent distances); also in this case, then, we are interested in shifting upwards the d_{xy} orbital, in order to drive the solution towards the following occupation:

α : all five d orbitals
 β : d_{xz} and d_{yz}

The principal axis of the CoF_6 octahedron, however, is not aligned along the z direction, but lies in the xy plane, at 45° from the x axis. The cartesian reference frame must then be reoriented before the shift of the d_{xy} orbital.

To this aim the option **EIGSHROT** must be used. The reoriented frame can be specified in two ways, selected by a keyword:

| rec | variable | meaning |
|---|---------------|---|
| • | MATRIX | keyword - the rotation matrix R is provided |
| • * | R11 R12 R13 | first row of the matrix. |
| • * | R21 R22 R23 | second row of the matrix. |
| • * | R31 R32 R33 | third row of the matrix. |
| or | | |
| • | ATOMS | keyword - the rotation is defined by three atoms of the crystal |
| • * | IA | <i>label</i> of first atom in the reference cell |
| | AL,AM,AN | indices (direct lattice, input as reals) of the cell where the first atom is located |
| • * | IB | <i>label</i> of second atom in the reference cell |
| | BL,BM,BN | indices (direct lattice, input as reals) of the cell where the second atom is located |
| • * | IC | <i>label</i> of third atom in the reference cell |
| | CL,CM,CN | indices (direct lattice, input as reals) of the cell where the third atom is located |
| _____ insert EIGSHIFT input records (Section 2.3, page 94) _____ | | |

When the rotation is defined by three atoms, the new reference frame is defined as follows :
 Z-axis from atom 2 to atom 1
 X-axis in the plane defined by atoms 1-2-3
 Y-axis orthogonal to Z- and X-axis

Notice that the wave function calculation is performed in the original frame: the aim of the rotation is just to permit a shift of a particular orbital. An equivalent rotation of the eigenvectors can be obtained in *properties* by entering the keyword **ROTREF**, so allowing AO projected Density of States according to the standard orientation of the octahedron.

Example:

CoF2 example

END

Terminate processing of block 3,(last input block). Execution continues. Subsequent input records are not processed.

EXCHGENE - Exchange energy calculation

In RHF calculations Coulomb and exchange integrals are summed during their calculation, and there is no way to separate the exchange contribution to the total energy. In UHF/ROHF calculations, this option allows the independent calculation and printing of the exchange contribution to the total energy. See equation 13.19, page 278.

No input data are required. See tests 29, 30, 31, 38.

EXCHPERM - Use permutation of center in exchange integrals

In HF and hybrids calculations exact exchange integrals (see equation 13.19, page 278) are normally calculated in the same routine that calculates Coulomb integrals, exploiting the symmetry of the system in order to reduce the number of computed integrals. In case of systems without symmetry (having only the identity as symmetry operator), this option separates the calculation of exchange from that of Coulomb integrals, and exploits invariance of bielectronic integrals under permutation of centers instead of symmetry.

Given a bielectronic integral $(\mu\rho|\nu\sigma)$, where $\mu \nu \rho \sigma$ label the four centers (see chapter 13), the integrals obtained with the permutations:

$$\mu \leftrightarrow \rho, \nu \leftrightarrow \sigma \text{ and } (\mu\rho) \leftrightarrow (\nu\sigma) \quad (2.20)$$

are related to the original one by hermiticity. Of the $2^3 = 8$ equivalent integrals only 4 are used to obtain the irreducible part of the Fock matrix, since hermiticity of the Fock matrix is already

exploited. With this option the time required for the calculation of the exchange contribution to the Fock matrix is reduced to 40-50% of the normal value. The option is usable only in a SCFDIR run (see page 109) and it is automatically switched off in presence of symmetry. No input data are required.

EXCHSIZE - Size of buffer for exchange integrals bipolar expansion

| rec | variable | meaning |
|-----|----------|-----------------------------|
| • * | ISIZE | size of the buffer in words |

Size (words) of the buffer for bipolar expansion of exchange integrals (default value is 4000000, that is 32 Mb, per core).

The size of the buffer is printed in the message:

EXCH. BIPO BUFFER: WORDS USED = XXXXXXXX

or

EXCH. BIPO BUFFER TOO SMALL - TO AVOID I/O SET EXCHSIZE = XXXXXX

FDAOSYM - f and d degeneracies analysis

| rec | variable | meaning |
|-----|-----------------|---|
| • * | NA | number of atoms for which the AOs mixing check is performed |
| • * | ISCAT(J),J=1,NA | atomic label (output order) of atoms to be checked |

This keyword performs the symmetry analysis that permits to know if AOs belonging to the same shell are mixed or not by the symmetry operators that don't move the atom, to which they belong to. This analysis is implemented for *d* and *f* shell types only. The FDAOSYM keyword must be inserted in the third block of the CRYSTAL input.

In the output, the subgroup of operators that do not move the atom is performed first (ATOM-SYMM keyword). Then the AOs are listed with the indication of mixing with other AOs (if any).

This keyword is useful for partially occupied shells (*d* or *f*). AOs that mix will form a symmetry constrained degeneracy subset. If *n* AOs of the shell mix generating these subsets, and $m < n$ (open shell case) electrons are supposed to populate the shell, then Jan-Teller symmetry breaking should be taken into account. If a guess AOs occupation is defined with FDOCCUP keyword or forced with EIGSHIFT keyword, information obtained by FDAOSYM can indicate which AOs will have the same occupation.

Example. Ce₂O₃ bulk. Structure *4d* shell is completely filled and *4f* shell contains one electron. Suppose Ce atom is labeled 1. Information produced by FDAOSYM indicates which AOs will have the same occupation. If combined with TESTRUN such information is obtained at zero cost and then a new input with FDOCCUP or EIGSHIFT keywords can be run. The input is

```
FDAOSYM
1
1
TESTRUN
```

Output obtained contains also *d* shell information, here just *f* part is reported.

```
ANALYSIS FOR SHELL TYPE F
COMPONENT      MIXES WITH      SYMMETRY OPERATORS
  1
  2              3          2  3 10 12
  3              2          2  3 10 12
  4              5          2  3 10 12
  5              4          2  3 10 12
  6
  7
```


That is: AOs 1, 6 and 7 do not mix with any other AO, 2 and 3 mix as well as 4 and 5. Label and characteristic polynomial for quantum angular symmetry d and f are reported in the FDOCCUP keyword description.

FDOCCUP - f and d orbital occupation guess

| rec | variable | meaning |
|-----|--------------|---|
| • * | INSELOC | number of records describing the occupation of d or f shells <i>insert INSELOC records</i> |
| | IATNUM | atom label, output order |
| | ISHATO | shell label, atomic list |
| | SHTYP | angular quantum label of ISHATO(I) |
| • * | IAOCALPH(J) | α occupation of the 5 d (J=1,5) or 7 f (J=1,7) AOs of the shell |
| • * | IAOC BETA(J) | β occupation of the 5 d (J=1,5) or 7 f (J=1,7) AOs of the shell |

Label and characteristic polynomial for quantum angular symmetry d and f are reported in the following. Spherical harmonics are used, it follows that 5 and 7 functions are reported for d and f symmetry respectively.

| Symmetry d , label 3 | Symmetry f , label 4 |
|------------------------|--------------------------|
| Label Polynomial | label Polynomial |
| 1 $(2z^2 - x^2 - y^2)$ | 1 $(2z^2 - 3x^2 - 3y^2)$ |
| 2 xz | 2 $x(4z^2 - x^2 - y^2)$ |
| 3 yz | 3 $y(4z^2 - x^2 - y^2)$ |
| 4 $(x^2 - y^2)$ | 4 $z(x^2 - y^2)$ |
| 5 xy | 5 (xyz) |
| | 6 $x(x^2 - 3y^2)$ |
| | 7 $y(3x^2 - y^2)$ |

The option FDOCCUP permits to define the occupation of specific f or d orbitals in a given shell in the initial guess calculation. This option can be used only for open shell cases, where electrons belonging to partially filled shells can be assigned to selected AOs.

INSELOC specifies the number of shell occupation descriptions; for each shell, the atom IATNUM (output order) and the shell label ISHATO (basis set order) is specified. As a cross check, also the shell label type SHTYP (3 and 4 for d and f respectively) is required. Finally the α and β occupation for the 5 (d) or 7 (f) AOs in the shell is indicated. The occupation numbers in IAOCALPH(J) and IAOCBETA(J) are normalized *a posteriori* to the number of d or f electrons resulting from the input charges.

Note that the input information must be inserted just one time per atomic number (say 26, Fe) and IATNUM can be any of the output order atom labels for the selected atom. See EXAMPLE 1 for test case.

To attribute different AOs guess occupation to atoms with the same atomic number, it is just needed to insert as many input as the number of different occupation one wants to set with IATNUM indicating atom labels of atoms with same atomic number but not symmetry related. If different AOs occupation for atoms symmetry related is required, the program stops and an indication of symmetry relations between atoms is reported (as the one obtained by the use of ATOMSYMM keyword).

FDOCCUP can be used in conjunction with EIGSHIFT, ATOMSPIN and SPINLOCK. Note that FDOCCUP and ATOMSPIN act at CYCLE 0, EIGSHIFT at CYCLE 1 and SPINLOCK works from CYCLE 1 for a defined number of cycles.

On the contrary FDOCCUP, as ATOMSPIN, is incompatible with SPINEDIT, where the initial guess calculation is bypassed because the initial guess is obtained by a previous calculation.

Example. Ce_2O_3 . The Ce^{3+} ion is required to have one f electron. Suppose Ce is the first atom in the input list and that the seventh shell in the Basis Set list is the f shell with charge one. Suppose to distribute the f electron in two AOs with similar occupation: $f_{(2z^2-3x^2-3y^2)z}$ (first f AO) and $f_{(x^2-3y^2)y}$ (sixth f AO). Use of FDOCCUP in this case is reported in the following:

```
FDOCCUP
1
1 7 4
```

```
1 0 0 0 0 1 0
0 0 0 0 0 0 0
```

Output is printed in the ATOMIC WAVEFUNCTION(S) part and is reported in the following. Note that the nuclear charge is 30 instead of 58 because pseudopotential is used.

```
NUCLEAR CHARGE 30.0 SYMMETRY SPECIES          S   P   D
N. ELECTRONS   27.0 NUMBER OF PRIMITIVE GTOS  11  11  5
                NUMBER OF CONTRACTED GTOS   4   4   1
                NUMBER OF CLOSED SHELLS     2   2   1
                OPEN SHELL OCCUPATION       0   0   0

ZNUC SCFIT  TOTAL HF ENERGY  KINETIC ENERGY  VIRIAL THEOREM ACCURACY
30.0   7   -4.706164398E+02  1.769968771E+02 -3.658896854E+00  3.4E-06

FDOCCUP ACTIVE - ATOM   1 SHELL  6 F SYMMETRY WITH CHARGE  1.0
                DIAGONAL ELEMENTS OF DENSITY MATRIX FOR SHELL  6
                ALPHA+BETA   0.500 0.000 0.000 0.000 0.000 0.500 0.000
                ALPHA-BETA   0.500 0.000 0.000 0.000 0.000 0.500 0.000
```

Note: the printed information refers to $\alpha + \beta$ and $\alpha - \beta$, while in input α and β are inserted separately.

FIXINDEX

No input data required.

When the geometrical and/or the basis set parameters of the system are changed, **maintaining the symmetry and the setting**, the truncation criteria of the Coulomb and exchange series, based on overlap (Chapter 13) can lead to the selection of different numbers of bi-electronic integrals. This may be the origin of numerical noise in the optimization curve. **When small changes are made on the lattice parameter or on the Gaussian orbital exponents, the indices of the integrals to be calculated can be selected for a reference geometry (or basis set), "frozen", and used to compute the corresponding integrals with the modified geometry (or basis set).**

对参考结构选择
积分指数用于后
面的积分

This procedure is recommended only when basis set or geometry modifications are relatively small.

- The corresponding irreducible atoms in the two geometries must be entered in the same order, and their position in the second geometry must be slightly shifted in comparison with the first geometry (reference);
- the reference geometry must correspond to the most compact structure;
- the reference basis set must have the lowest outer exponent.

This guards against the loss of significant contributions after, for example, expansion of the lattice.

If estimate of resource is requested with TESTRUN, the reference geometry is used.

Two sets of input data must be given:

1. complete input (geometry, Section 1.1; basis set, Section 1.2; general information, Section 1.3; SCF, Section 1.3), defining the reference basis set and/or geometry;
2. "restart" option input, selected by one of the following keywords (format A) to be added after the SCF input:

```

_____ restart with new geometrical parameters
GEOM
_____ insert geometry input, page 14 _____
                or
_____ restart with new basis set
BASE
_____ insert basis set input, page 20 _____
                or
_____
```

| | |
|-------------|---|
| GEBA | restart with new basis set and new geometrical parameters |
| | insert geometry input, page 14 |
| | insert basis set input, page 20 |

BASE: the only modification of the basis set allowed is the value of the orbital exponent of the GTFs and the contraction coefficient; the number and type of shells and AOs cannot change.

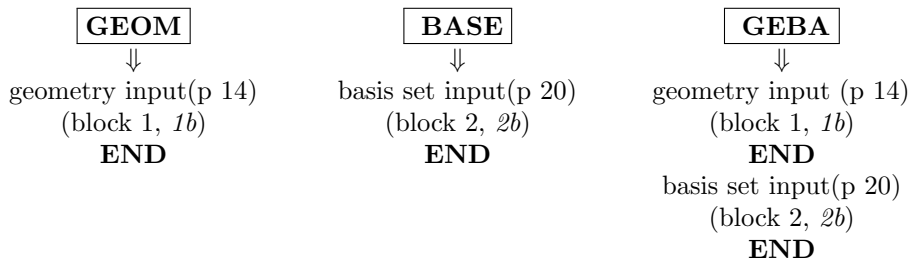
GEOM: geometry variation *must* keep the symmetry and the setting unchanged.

The resulting structure of the input deck is as follows:

```

0  Title
1  standard geometry input (reference geometry). Section 1.1
1b geometry editing keywords (optional; Section 2.1)
END
2  standard basis set input (reference basis set). Section 1.2
2b basis set related keywords (optional; Section 2.2)
END
3  FIXINDEX
3  block3 keywords
END

```



Warning: The reference geometry and/or basis set is overwritten by the new one, after symmetry analysis and classification of the integrals. If the reference geometry is edited through appropriate keywords, *the same editing must* be performed through the second input. Same for basis set input.

If the geometry is defined through the keyword EXTERNAL, the reference geometry data should be in file fort.34, the wave function geometry in file fort.35.

Note In geometry optimization (**OPTGEOM**, page 118) **FIXINDEX** is automatically set, with input geometry as reference geometry. See keyword **FINALRUN**, page 126 to redefine the reference geometry.

See tests 5 and 20.

FMIXING - Fock/KS matrix mixing

| rec | variable | meaning |
|-----|----------|---------------------------------------|
| • * | IPMIX | percent of Fock/KS matrices mixing 30 |

The Fock/KS matrix at cycle i is defined as:

$$F'_i = (1 - p)F_i + pF'_{i-1}$$

where p , input datum IPMIX, is the % of mixing. Too high a value of p (>50%) causes higher number of SCF cycles and can force the stabilization of the total energy value, without a real self consistency.

Note that from CRYSTAL14, a Fock/KS mixing of 30 % is activated by default. Set IPMIX = 0 to switch this option off.

FULLTIME - Detailed timing report

A more detailed report of the timing data is generated:

```
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT SHELXG  TELAPSE   19.68 TCPU   18.42
WWWWWWWWWWWWWWWW SHELXG      MX    1.07 MN    1.07 MD    1.07
QQQQQQQQQQQQQQQQ SHELXG      MX    1.07 MN    0.92 MD    0.98
```

The first line is the standard data. The second line reports the minimum, maximum and mean wall time since the last report. The last line reports the minimum, maximum and mean cpu time since the last report. The minimum, maximum and mean operations are across processors, and so this directive is most useful for parallel job.

GRADCAL

No input data required.

Analytic calculation of the nuclear coordinates gradient of the HF, UHF, DFT energies after SCF (all electrons and ECP).

If numerical gradient is requested for the geometry optimization (**NUMGRALL**, page 127; **NUMGRATO**, page 127; **NUMGRCEL**, page 127;), analytical gradient is not computed.

GRIMME - Grimme dispersion correction for energy and gradient

The keyword **GRIMME**, inserted in third input block, calculates a London-type pairwise empirical correction to the energy as proposed by Grimme [89], to include long-range dispersion contributions to the computed ab initio total energy and gradients.

Therefore geometry optimization and vibrational frequency calculation can be carried out by including the empirical correction.

| rec | variable | meaning |
|-----|------------------------------------|--|
| • A | GRIMME | keyword |
| • * | s_6 | scaling factor |
| * * | d | steepness |
| * * | R_{cut} | cutoff distance to truncate direct lattice summation |
| • * | NATS | number of atomic species |
| II | _____ insert NATS records _____ II | |
| • * | NAT | “conventional” atomic number (page 21). |
| * * | C_6 | dispersion coefficient for atomic number NAT (Jnm^6mol^{-1}) |
| * * | R_{vdw} | van der Waals radius for atomic number NAT (Å) |

The keyword GRIMME is followed by a set of computational parameters [i.e. scaling factor, steepness and cutoff radius for **g** (direct lattice) summation], the number of atomic species and for each atomic species the “conventional atomic number” (page 21) and the value of C_6 and R_{vdw} (in Jnm^6mol^{-1} and Å, respectively).

Note that the atomic number is defined as the “conventional atomic number”. In this way, if one wants to use different atomic parameters for the same atomic species, a different conventional atomic number can be used. For example, 1 and 101 for hydrogen.

The current implementation has been mainly tested and used in combination with the B3LYP method [36, 37, 176], even if it can be applied to whatever level of theory.

The original proposal by Grimme was to augment DFT methods with an empirical London-type correction. To that purpose, Grimme defined a general set of atomic empirical parameters (see Table 1 of ref. [89]) and used an optimized scaling factor to adjust the dispersion correction for each DFT method.

The total energy is given by

$$E_{DFT-D} = E_{KS-DFT} + E_{disp}$$

where E_{disp} , the empirical dispersion correction, is given as

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \sum_{\mathbf{g}} \frac{C_6^{ij}}{R_{ij,\mathbf{g}}^6} f_{dmp}(R_{ij,\mathbf{g}})$$

The summation is over all atom pairs and \mathbf{g} lattice vectors with the exclusion of the $i=j$ contribution (i.e. self interaction) for $\mathbf{g} = 0$, C_6^{ij} is the dispersion coefficient for the atom pair ij , s_6 is a scaling factor that depends only on the adopted DFT method (e.g. s_6 is 1.05 for B3LYP) and $R_{ij,\mathbf{g}}$ is the interatomic distance between atoms i in the reference cell and j in the neighbouring cells at distance $|\mathbf{g}|$. For a set of molecular crystals, a cutoff distance of 25.0 Å was used to truncate the summation over lattice vectors which corresponds to an estimated error of less than 0.02 kJ/mol on computed cohesive energies with respect to larger cutoffs [36, 37].

A damping function is used to avoid near-singularities for small interatomic distances:

$$f_{dmp}(R_{ij,\mathbf{g}}) = \frac{1}{1 + \exp^{-d(R_{ij,\mathbf{g}}/R_{vdw}-1)}}$$

where R_{vdw} is the sum of atomic van der Waals radii (i.e. $R_{vdw} = R_{vdw}^i + R_{vdw}^j$) and d determines the steepness of the damping function ($d = 20$). Van der Waals radii and atomic C_6 coefficients were taken from Table 1 of ref. [89]. From the latter, the C_6^{ij} dispersion coefficients are computed by using a geometric mean:

$$C_6^{ij} = \sqrt{C_6^i C_6^j}$$

The input requires to specify all parameters that enter equations above and it looks like (urea molecular crystal):

```

Urea
CRYSTAL
0 0 0
113
5.565 4.684
5
6 0.0000 0.5000 0.3260
8 0.0000 0.5000 0.5953
7 0.1459 0.6459 0.1766
1 0.2575 0.7575 0.2827
1 0.1441 0.6441-0.0380
Optional keywords
END (ENDG)
Basis set input
END
DFT
. . . . .
END
. . . . .

```

```

GRIMME
1.05 20. 25.
1.05 20. 25.      s6 (scaling factor)  d (steepness)  Rcut (cutoff radius)
4
1  0.14  1.001  Hydrogen Conventional Atomic number , C6 , Rvdw
6  1.75  1.452  Carbon   Conventional Atomic number , C6 , Rvdw
7  1.23  1.397  Nitrogen Conventional Atomic number , C6 , Rvdw
8  0.70  1.342  Oxygen   Conventional Atomic number , C6 , Rvdw
SHRINK
. . . . .
END

```

GUESDUAL - SCF guess (density matrix from a previous run with a different basis set)

| rec | variable | value | meaning |
|---|----------|-------|--|
| • * | NFR | | number of modification ($NFR \geq 1$) in the atomic basis set given in input |
| | IC | 1 | complete SCF calculation |
| | | 0 | stop before the first hamiltonian matrix diagonalization (to be used in CRYSCOR - see http://www.cryscor.unito.it when the dual basis set option is activated) |
| _____ insert NFR records - for each shell _____ | | | |
| • * | NAT | | formal atomic number of the atom whose basis set is modified |
| * | NSH | | sequence number of the reference shell in the atomic basis set, starting from which shell(s) is(are) inserted/deleted |
| * | NU | | number of shells inserted/deleted after the reference shell NSH |

The keyword is to be inserted in the third (Hamiltonian-SCF) input block. It defines how the basis set given in input differs from the one used to compute the density matrix used as SCF guess. The two basis sets must be marginally different. It can be used to add polarization functions, or diffuse functions (see <http://www.cryscor.unito.it>).

The present calculation and the one used to compute the density matrix SCF guess have same symmetry and number of atoms, but different number of shells in the BS of some atoms. Different geometrical parameters and computational conditions are allowed.

The density matrix P^0 (direct lattice) of the previous run, SCF guess, is read from external unit (copy file fort.9 of the previous run in file fort.20). Density matrix is reorganized: elements corresponding to basis functions removed are removed, elements corresponding to basis functions added are set to 0.

Warning. The efficiency of this guess can be dramatically compromised if not congruent BS modifications, i.e. insertion or elimination of significantly populated shells, are made. Check the normalization factor.

Example. LiH bulk. The BS of Li in the reference calculation is referred to as BS1 and reported on the left, the modified one is referred to as BS2 and reported on the right. The GUESDUAL option following BS2 illustrates how BS2 differs with respect to BS1.

| BS1 | | | | BS2 |
|------|---------|--|------|---------|
| 3 | 3 | | 3 | 4 |
| 0 | 0 | | 0 | 0 |
| | 6 | | 6 | 2.0 |
| | 2.0 | | 2.0 | 1.0 |
| 700. | .001421 | | 700. | .001421 |
| 220. | .003973 | | 220. | .003973 |
| 70. | .01639 | | 70. | .01639 |
| 20. | .089954 | | 20. | .089954 |
| 5. | .31565 | | 5. | .31565 |
| 1.5 | .4946 | | 1.5 | .4946 |

```

0 0 1 0.0 1.0 | 0 0 1 0.0 1.0
  0.5 1. | 0.5 1.
0 2 1 0.0 1.0 | 0 2 1 0.0 1.0
  0.6 1. | 0.6 1.
1 4 | 0 3 1 0. 1.
0 0 5 2. 1. | 0.4 1.
 120. .000267 | 1 5
  40. .002249 | 0 0 5 2. 1.
  12. .006389 | 120. .000267
   4. .032906 | 40. .002249
  1.2 .095512 | 12. .006389
0 0 1 0. 1. | 4. .032906
  0.45 1. | 1.2 .095512
0 0 1 0. 1. | 0 0 1 0. 1.
  0.13 1. | 0.45 1.
0 2 1 0. 1. | 0 0 1 0. 1.
  0.3 1. | 0.13 1.
99 0 | 0 2 1 0. 1.
END | 0.6 1.
 | 0 2 1 0. 1.
 | 0.3 1.
 | 99 0
 | END
 | GUESDUAL
 | 2 0
 | 3 3 1
 | 1 3 1
 | END

```

In this case two modifications (NFR=2) has been introduced in BS2 with respect to BS1. Complete SCF calculation (IC=1) is required.

First modification in Li (formal atomic number NAT=3) basis set, after the third shell (NSH=3), one shell was added (NU=1).

Second modification in H (atomic number IA=1) basis set, after the third shell (NSH=3), one shell (NU=1) was inserted.

GUESSP - SCF guess - Density matrix from a previous run

The density matrix from a previous run, P^0 (direct lattice), is read from disk, and used as SCF guess. No input data are required.

The density matrix can be edited to modify the spin state. See **SPINEDIT**, page 113.

The density matrix used as SCF guess was written with wave function information in file fort.9 at the end of a previous SCF run, and read as file fort.20.

The two cases, the present one and that used for the restart, must have same symmetry, and same number of atoms, basis functions and shells. Atoms and shells must be in the same order. The program does not check the 1:1 old–new correspondence.

Different geometrical parameters, computational conditions or exponents of the Gaussian primitives are allowed.

In geometry and/or basis set optimization, this technique will significantly reduce the number of SCF cycles. The following scheme shows how to proceed.

1. First run to generate the density matrix

| Program | inp. | block | section | comments |
|--|------|-------|---------|--|
| <i>crystal</i> | 0 | 1 | | Title |
| | 1 | 1.1 | | geometry input |
| | 2 | 1.2 | | basis set input |
| | 3 | 1.3 | | computational parameters and SCF input |
| save wf in file fort.9 (binary) or file.98 (formatted) | | | | |

2. Second run - the density matrix is read in as a guess to start SCF

| copy file fort.9 to fort.20 (or convert file fort.98 and then copy) | | | | |
|---|------|-------|---------|---|
| Program | inp. | block | section | comments |
| <i>crystal</i> | 0 | 1 | | Title |
| | 1 | 1.1 | | geometry input |
| | 2 | 1.2 | | basis set input |
| | 3 | 1.3 | | computational parameters and SCF input (GUESSP) |

Warning The modification of the geometry may result in a different order in the storage of the matrix elements associated to each overlap distribution in the present and the previous run. To avoid the mismatch it is strongly recommended to classify the integrals of the present case using the geometry of the previous case (**FIXINDEX**, page 98).

Warning When wave function information are stored formatted in file fort.98, the data must be converted to binary by the keyword **RDFMWF**, page 213 of the *properties* program).

Warning SCF guess from a density matrix computed with a different basis set is allowed by the keyword **GUESDUAL**, page 102.

GUESSPAT - Superposition of atomic densities

The standard initial guess to start the SCF cycle is the superposition of atomic (or ionic) densities. No input data are required. The electronic configuration of the atoms is entered as a shell occupation number in the basis set input (page 20). Different electronic configurations may be assigned to atoms with the same atomic number and basis set (but not symmetry related) through the keyword **CHEMOD** (page 20).

ILASIZE - set the new size for array ILA used in the calculation of Coulomb 2-electron integrals

| rec | variable | meaning |
|-----|----------|-------------------|
| • * | ISIZE | size of array ILA |

ILA is an array containing a list of contributions to be computed in the evaluation of the Coulomb series. Use of this option is recommended upon receiving the following error message: "ILA DIMENSION EXCEEDED - INCREASE ILASIZE". Default value of ISIZE is: 6000.

INTGPACK - Choice of bielectronic integrals package

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • * | IPACK | [0] | <i>s</i> , <i>sp</i> shells → POPLE; <i>p</i> , <i>d</i> shells → ATMOL |
| | | 1 | ATMOL for Coulomb integrals; POPLE for exchange integrals |
| | | 2 | POPLE for Coulomb integrals; ATMOL for exchange integrals |
| | | 3 | ATMOL for Coulomb integrals; ATMOL for exchange integrals |

By default the bielectronic integrals are computed using a set of routines derived from Pople's GAUSSIAN 70 package [97], if s and sp shells are involved, and by routines derived from ATMOL [118] for p and d shells. The value of IPACK allows different choices. Integrals involving p or d shells are always computed by ATMOL. The ATMOL package can compute integrals over functions of any quantum number, but the symmetry treatment implemented in the CRYSTAL package allows usage of s , p and d functions only. The use of sp shells (s and p orbitals sharing the same exponent) reduces the time required to compute the integrals considerably.

KSYMMPRT

Symmetry Adapted Bloch Functions [196, 197] (page 114) are used as basis for the Fock/KS matrix diagonalization. The results of the symmetry analysis in reciprocal space are printed. At each \mathbf{k} -point: number of point symmetry operators, number of active IRs, maximum IR dimension and maximum block dimension in the Fock/KS matrix factorization. TESTRUN stops execution after this information is printed.

No input data required.

Extended information can be obtained by setting the value N of LPRINT(47) (keyword **SET-PRINT**, page 61) before **KSYMMPRT**.

| N | information |
|------|---|
| 0 | Basic Symmetry Information - At each \mathbf{k} -point: list of point symmetry operators, IR dimensions and number of Irreducible Sets. |
| > 0 | Symmetry Information - At each \mathbf{k} -point $\leq N$: class structure, character table and IR information concerning the K-Little Group. For the rest of the \mathbf{k} -point the same information as -1 is printed. |
| < -1 | Full Symmetry Information - At each \mathbf{k} -point: the same information as $N > 0$, together with the matrix representatives of the point operators. |

MPP doesn't support KSYMMPRT.

LEVSHIFT - Eigenvalue level shifting

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | ISHIFT | | The level shifter is set to ISHIFT *0.1 hartree. |
| | ILOCK | 0 | no locking |
| | | 1 | causes a lock in a particular state (eg non-conducting) even if the solution during the SCF cycles would normally pass through or even converge to a conducting state. |

1: 即便是SCF收敛到其它态 (如 conducting) 也仍然锁定在指定状态 (如 non-conducting)

The eigenvalue level shifting technique is well known in molecular studies [90, 38], and may also be used for periodic systems. The technique involves the addition of a negative energy shift to the diagonal Fock/KS matrix elements (in the Crystalline Orbital basis) of the *occupied* orbitals and thus reducing their coupling to the "unoccupied" set. This shift may be maintained (ILOCK=1) or removed (ILOCK=0) after diagonalization. The former case causes a lock in a particular state (eg non-conducting) even if the solution during the SCF cycles would normally pass through or even converge to a conducting state.

This option provides an alternative damping mechanism to Fock/KS matrix mixing (**FMIXING**, page 99). The locking is effective only if ISHIFT is large enough. If locking is used, the Fermi energy and the eigenvalues are depressed by the value of the level shifter. Suggested values :

1. Normal cases require no mixing of Fock/KS matrices in successive cycles to converge: ISHIFT=0 (default).
2. When 20% to 30% mixing of Fock/KS matrices is necessary, an ISHIFT value of between 1 and 3 (giving a level shift of 0.1 to 0.3 hartree) may produce an equivalent or even superior convergence rate.

3. If serious convergence difficulties are encountered, ISHIFT=10 will normally be adequate, corresponding to a level shift of 1 hartree. But it may happen that the system moves towards an excited state, and no convergence is obtained.

Warning - Hamiltonian eigenvalues are modified by the level shifter. Take into account when looking at top and bottom bands eigenvalues printed.

See tests 29, 30, 31, 32, 38.

LOWMEM - Reduce memory storage requirements

When this option is active, none of the largest arrays is allocated. This option is very efficient in decreasing random access memory requirements for calculations with large unit cells. Usage of **LOWMEM** may affect running time. It is default in *MPPcrystal* calculations.

MAXCYCLE

| rec | variable | meaning |
|-----|----------|-----------------------------------|
| • * | NMAX | maximum number of SCF cycles [50] |

The possibility to modify the maximum number of SCF cycles allows: increasing the number of cycles in case of very slow convergence (metals, magnetic systems, DFT);

The keyword **POSTSCF** forces saving wave function data in file fort.9, even if SCF ends before reaching convergence for "too many cycles".

MADELIND - parameter for Madelung series

| rec | variable | meaning |
|-----|----------|--------------|
| • * | IIND | mql inf(103) |

Maximum number of indices for reciprocal lattice vectors to be considered in reciprocal lattice Madelung sums. Default value of IIND: 50.

MEMOPRT - Synthetic report about dynamic memory usage

Memory usage is printed at every step of a CRYSTAL calculation, that is, every time running-time information is also printed. Printed information includes: the total memory allocated by core 0 at that stage of the calculation and the maximum amount of memory required within that step, as well as the total amount of memory allocated by all cores.

MEMOPRT2 - Detailed report about dynamic memory usage

Memory status is printed at every allocation or deallocation of an array. Printed information includes: size of the allocated/deallocated array/matrix and the total amount of memory used by core 0 up to that stage of the calculation.

MONSPLIT - Splitting of large monoelectronic integral files

| rec | variable | meaning |
|-----|----------|---|
| • * | NFILE | number of files to be used [1] (max 10) |

Very large basis sets can produce billions monoelectronic integrals to be stored, as the number of monoelectronic integrals scales as the square of basis set size. The multipolar expansion technique based on the atoms reduces the disk space up to a factor 3, compared to the value printed as estimate. The distribution of the integrals over several disk files may be necessary, if available disk space is limited.

MP2 - Electron correlation energy at second order Møller-Plesset

| rec | variable | meaning |
|-----|----------|---|
| • A | MP2 | Begin MP2 input block |
| • A | KNET | reconstruction of the HF Density Matrix |
| • I | 8 | Shrinking factor |
| • A | MEMORY | Memory required |
| • I | 3000 | Value in Mbytes |
| • A | DFITTING | Density Fitting input block |
| • A | PG-VTZ | Density Fitting auxiliary basis set |
| • A | ENDDF | End Density Fitting input block |
| • A | DOMMOL | Definition of the excitation domains |
| • A | ENDMP2 | End MP2 input block |

The public CRYSCOR code, a **post-HF local**-correlation program for periodic crystals,[?, ?] has been fully incorporated into the CRYSTAL14 package. This means that it is now possible to perform, on top of and HF-SCF run, a calculation of the electron correlation energy contribution for systems periodic in 1 to 3 dimensions. A simple input example is here reported: for more details about how to run a CRYSCOR calculation please refer to *Cryscor User's Manual*[?] and to CRYSCOR web page: www.cryscor.unito.it.

The post-HF method currently implemented is a perturbative method, namely Møller-Plesset at the second-order (**MP2**). Well localized Wannier Functions (WF) [?] are adopted instead of delocalized Bloch functions for the description of the occupied manifold; this permits the exploitation of the **short-range** nature ($E \propto r^{-6}$) of electron correlation following the general Pulay scheme[?]. An MP2 correction to the HF Density Matrix is feasible so that many of the PROPERTIES can be currently evaluated taking into account the effects of the dynamic correlation.

The code has been widely used to study, among others, the structure and stability of different polymorph,[?, ?] the energetic balance in van der Waals and hydrogen-bonded crystals,[?] interactions between molecules and surfaces,[?] and the upshot of electron correlation on some fundamental properties such as vibrational spectra,[?] electron density and Compton profiles.[65] **Note that the localization procedure and the MP2 technique implemented in CRYSCOR are not suitable for open-shell systems, for conductors, or for semiconductors with very small gap.**

MYBIPOLA - Bipolar expansion approximation control

| rec | variable | meaning |
|-----|----------|--|
| • * | ILCOUL | maximum multipole order for Coulomb 4 |
| * | ITCOUL | overlap threshold for Coulomb 14 |
| * | IFCOUL | reducing factor for Coulomb 90 |
| • * | ILEXCH | maximum multipole order for exchange 2 |
| * | ITEXCH | overlap threshold for exchange 10 |
| * | IFEXCH | reducing factor for exchange 70 |

The bipolar approximation is applied in the evaluation of the Coulomb and exchange integrals (page 279). Maximum values for ILCOUL and ILEXCH are 8 and 4, respectively. ITCOUL and ITEXCH can be assigned any intermediate value between the default values (14 and 10) (see page 279) and the values switching off the bipolar expansion (20000 and 20000). Increasing IFCOUL and IFEXCH the threshold is lightly modified in order to increase the number of approximated integrals, and vice versa.

Warning - for developers only

NEIGHBOR/NEIGHPRT

See input block 1, page 56

NOBIPOLA - Bipolar expansion approximation suppression

All the bielectronic integrals, coulomb and exchange, are evaluated exactly. The overlap threshold both for coulomb and exchange integrals is set to 2000000.

No input data required. The CPU time in the **integrals** program may increase up to a factor 3.

NOBIPCOU - Bipolar expansion approximation of coulomb integrals suppression

Coulomb bielectronic integrals are evaluated exactly. The overlap threshold for coulomb integrals is set to 2000000.

No input data required.

NOBIPEXC - Bipolar expansion approximation of exchange integrals suppression

Exchange bielectronic integrals are evaluated exactly. The overlap threshold for exchange integrals is set to 2000000. No input data required.

NOFMWF - Wave function formatted output

CRYSTAL writes the formatted wave function in file fort.98 at the end of SCF by default. This keyword deletes this feature.

NOLOWMEM - Disable reduction of memory storage requirements

LOWMEM option is disabled. CRYSTAL calculations are speeded up but the amount of requested memory increases. It is default in Pcrystal calculations.

NOMONDIR - Monoelectronic integrals on disk

No input data required.

In the SCF step bielectronic integrals are computed at each cycle, while monoelectronic integrals are computed once and read from disk at each cycle.

NOSYMADA

The Symmetry Adapted Functions are not used in the Hamiltonian matrix diagonalization. No input data are required. This choice increases the diagonalization CPU time when the system has symmetry operators.

POLEORDR - Maximum order of multipolar expansion

| rec | variable | meaning |
|-----|----------|---------------------------|
| • * | IDIPO | maximum order of pole [4] |

Maximum order of shell multipoles in the long-range zone for the electron-electron Coulomb interaction. Maximum value = 6. See Section 13.3, page 277.

POSTSCF

Calculation to be done after scf (gradient, population analysis) are performed even if convergence is not reached. It may be useful when convergence is very slow, and scf ends for "TOO MANY CYCLES" very close to the convergence criteria required.

No input data are required.

PPAN/MULPOPAN - Mulliken Population Analysis

Mulliken population analysis is performed at the end of SCF process.

No input data are required.

Bond populations are analysed for the first n neighbours (n default value 3; see **NEIGHBOR**, page 56, to modify the value).

Computed data:

1. $a_\mu = \sum_\nu \sum_g P_{\mu\nu}^g S_{\mu\nu}^g$ orbital charges
2. $s_l = \sum_{\mu \in l} a_\mu$ shell charges
3. $q_A = \sum_{l \in A} s_l$ atomic charges
4. $b(A^0, B^g) = \sum_{\mu \in A} \sum_{\nu \in B} P_{\mu\nu}^g S_{\mu\nu}^g$ bond populations between the non-equivalent atoms in the unit cell (A^0) and their first NVI neighbours (B^g in cell g). The printed values must be multiplied by 2 when $B \neq A$ to compare with standard molecular calculations.

Formatted data are written in file PPAN.DAT (opened in fortran unit 24).

See Appendix D, page 325.

PRINTOUT - Setting of printing environment

See input block 1, page 59.

QVRSGDIM - limiting size switch for multipole moments gradients

| rec | variable | meaning |
|-----|----------|---|
| • * | NFILE | limiting size of multipole moment gradients to switch from generation by pairs to generation by shells. Default 90000000. |

NFILE limits the maximum amount of data to be stored to memory. This is a way to reduce memory storage requirements with some possible reduction of performance.

REPLDATA - Replicated-data mode

This option is supported by *MPPcrystal* only. It allows the User to run *MPPcrystal* as *Pcrystal*. All computational parameters and settings are changed accordingly.

RHF [default]

A restricted closed-shell hamiltonian calculation is performed ([151, 142], Chapter 8 of ref. [139]). Default choice.

ROHF

Obsolete. See **UHF**

SCFDIR

No input data required.

In the SCF step mono-electronic and bi-electronic integrals are evaluated at each cycle. No screening of the integrals is performed. **This option is activated by default from CRYSTAL14.** It can be deactivated by inserting the **NODIRECT** keyword.

SAVEWF

The wave function is written in file fort.79 every two cycles. The format is the same as in file fort.9, written at the end of SCF.

To restart SCF cycles using the density matrix written in file fort.79, it has to be copied in file fort.20

No input data required.

SETINF - Setting of INF values

See input block 1, page 61

SETPRINT - Setting of printing options

See input block 1, page 61.

SHRINK - Pack-Monkhorst/Gilat shrinking factors

| rec | variable | value | meaning | |
|---|-------------|-------|--|----|
| <i>if the system is periodic insert</i> | | | | II |
| • * | IS | | Shrinking factor in reciprocal space (Section 13.7, page 281) | |
| | ISP | | Shrinking factor for a denser k point net (Gilat net) in the evaluation of the Fermi energy and density matrix. | |
| <i>if IS = 0 insert</i> | | | | II |
| • * | IS1,IS2,IS3 | | Shrinking factors along B1,B2,B3 (reciprocal lattice vectors); to be used when the unit cell is highly anisotropic | |
| optional keywords terminated by END or STOP | | | | II |

For periodic systems, 1D, 2D, 3D, the mandatory input information is the shrinking factor, IS, to generate a commensurate grid of \mathbf{k} points in reciprocal space, according to Pack-Monkhorst method. The Hamiltonian matrix computed in direct space, $H_{\mathbf{g}}$, is Fourier transformed for each \mathbf{k} value, and diagonalized, to obtain eigenvectors and eigenvalues:

$$H_{\mathbf{k}} = \sum_{\mathbf{g}} H_{\mathbf{g}} e^{i\mathbf{g}\cdot\mathbf{k}}$$

$$H_{\mathbf{k}} A_{\mathbf{k}} = S \mathbf{k} A_{\mathbf{k}} E_{\mathbf{k}}$$

A second shrinking factor, ISP, defines the sampling of \mathbf{k} points, "Gilat net" [85, 84], used for the calculation of the density matrix and the determination of Fermi energy in the case of conductors (bands not fully occupied).

In 3D crystals, the sampling points belong to a lattice (called the Pack-Monkhorst net), with basis vectors:

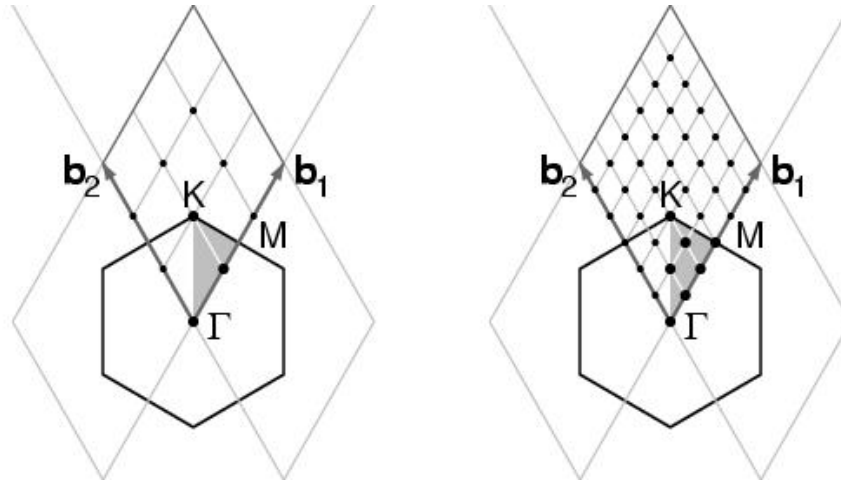
$$b_1/is_1, b_2/is_2, b_3/is_3 \quad is_1=is_2=is_3=IS, \text{ unless otherwise stated}$$

where b_1, b_2, b_3 are the reciprocal lattice vectors, and is_1, is_2, is_3 are integers "shrinking factors".

In 2D crystals, IS3 is set equal to 1; in 1D crystals both IS2 and IS3 are set equal to 1. Only points k_i of the Pack-Monkhorst net belonging to the irreducible part of the Brillouin Zone (IBZ) are considered, with associated a geometrical weight, w_i . The choice of the reciprocal space integration parameters to compute the Fermi energy is a delicate step for metals. See Section 13.7, page 281. Two parameters control the accuracy of reciprocal space integration for Fermi energy calculation and density matrix reconstruction:

- IS shrinking factor of reciprocal lattice vectors. The value of IS determines the number of \mathbf{k} points at which the Fock/KS matrix is diagonalized. Multiples of 2 or 3 should be used, according to the point symmetry of the system (order of principal axes).

In high symmetry systems, it is convenient to assign IS *magic* values such that all low multiplicity (high symmetry) points belong to the Monkhorst lattice. Although this choice does not correspond to maximum efficiency, it gives a safer estimate of the integral. The \mathbf{k} -points net is automatically made anisotropic for 1D and 2D systems.



The figure presents the reciprocal lattice cell of 2D graphite (rhombus), the first Brillouin zone (hexagon), the irreducible part of Brillouin zone (in grey), and the coordinates of the \mathbf{k}_i points according to a Pack-Monkhorst sampling, with shrinking factor 3 and 6.

ISP shrinking factor of reciprocal lattice vectors in the Gilat net (see [142], Chapter II.6). ISP is used in the calculation of the Fermi energy and density matrix. Its value can be equal to IS for insulating systems and equal to $2 \cdot \text{IS}$ for conducting systems.

The value assigned to ISP is irrelevant for non-conductors. However, a non-conductor may give rise to a conducting structure at the initial stages of the SCF cycle, owing, for instance, to a very unbalanced initial guess of the density matrix. The ISP parameter must therefore be defined in all cases.

Note. The value used in the calculation is $\text{ISP} = \text{IS} \cdot \text{NINT}(\text{MAX}(\text{ISP}, \text{IS}) / \text{IS})$, a multiple integer of IS. For instance:

| input data | IS | ISP | ISP for wf calculation |
|------------|----|-----|------------------------|
| | 3 | 4 | 3 |
| | 3 | 6 | 6 |
| | 3 | 8 | 6 |

In the following table the number of sampling points in the IBZ and in BZ is given for a fcc lattice (space group 225, 48 symmetry operators) and hcp lattice (space group 194, 24 symmetry operators). The CRYSTAL code allows 413 \mathbf{k} points in the Pack-Monkhorst net, and 2920 in the Gilat net.

| IS | points in IBZ | points in IBZ | points BZ |
|----|---------------|---------------|-----------|
| | fcc | hcp | |
| 6 | 16 | 28 | 112 |
| 8 | 29 | 50 | 260 |
| 12 | 72 | 133 | 868 |
| 16 | 145 | 270 | 2052 |
| 18 | 195 | 370 | 2920 |
| 24 | 413 | 793 | 6916 |
| 32 | 897 | 1734 | 16388 |
| 36 | 1240 | 2413 | 23332 |
| 48 | 2769 | 5425 | 55300 |

1. When an anisotropic net is user defined (IS=0), the ISP input value is taken as ISP1 (shrinking factor of Gilat net along first reciprocal lattice) and ISP2 and ISP3 are set to:
ISP2=(ISP*IS2)/IS1,
ISP3=(ISP*IS3)/IS1.
2. User defined anisotropic net is not compatible with SABF (Symmetry Adapted Bloch Functions). See **NOSYMADA**, page 108.

Some tools for accelerating convergence are given through the keywords **LEVSHIFT** (page 105 and tests 29, 30, 31, 32, 38), **FMIXING** (page 99), **SMEAR** (page 112), **BROYDEN** (page 82) and **ANDERSON** (page 79).

At each SCF cycle the total atomic charges, following a Mulliken population analysis scheme, and the total energy are printed.

The default value of the parameters to control the exit from the SCF cycle ($\Delta E < 10^{-6}$ hartree, maximum number of SCF cycles: 50) may be modified entering the keywords:

TOLDEE (tolerance on change in total energy) page 115;

TOLDEP (tolerance on SQM in density matrix elements) page ??;

MAXCYCLE (maximum number of cycles) page 106.

SMEAR

| rec | variable | meaning |
|-----|----------|---------------------------------------|
| • * | WIDTH | temperature smearing of Fermi surface |

Modifies the occupancy of the eigenvalues (f_j) used in reconstructing the density matrix from the step function, (equation 13.9, page 276) to the Fermi function;

$$f_j = (1 + e^{\frac{\epsilon_j - \epsilon_F}{k_b T}})^{-1} \quad (2.21)$$

where ϵ_F is the Fermi energy and $k_b T$ is input as WIDTH in hartree.

The smearing of the Fermi surface surface may be useful when studying metallic systems in which the sharp cut-off in occupancy at ϵ_F can cause unphysical oscillations in the charge density. It may also result in faster convergence of the total energy with respect to k-point sampling.

In density functional theory the use of Fermi surface smearing finds a formal justification in the finite temperature DFT approach of Mermin [117]. In this case the “free energy” of the system may be computed as:

$$\begin{aligned} F &= E(T) - TS(T) \\ &= E + k_b T \sum_i^{N_{states}} f_i \ln f_i + (1 - f_i) \ln(1 - f_i) \end{aligned} \quad (2.22)$$

where S is the electronic entropy. Often we wish to compute properties for the athermal limit (T=0). For the free electron gas the dependencies of the energy and entropy on temperature are:

$$\begin{aligned} E(T) &= E(0) + \alpha T^2 \\ S(T) &= 2\alpha T \end{aligned} \tag{2.23}$$

and so the quantity

$$E_0 = \frac{F(T) + E(T)}{2} = E(0) + O(T^3) \tag{2.24}$$

may be used as an estimate of $E(0)$.

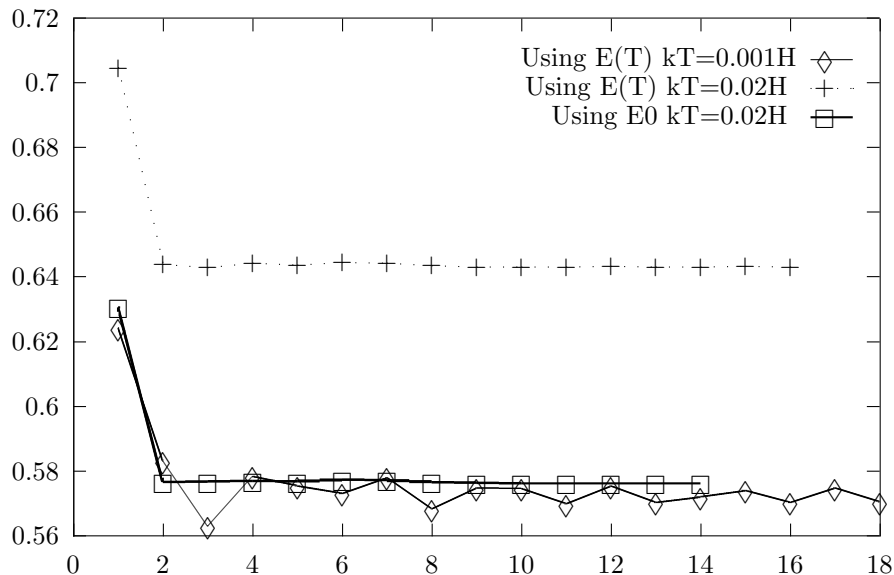


Figure 2.5: The surface energy (J/M^2) of Li(100) for various numbers of layers in a slab model showing the effects of WIDTH (0.02H and 0.001H) and the use of E(T) or E0

Figure 2.5 shows the effect of WIDTH on the convergence of the Li(100) surface energy. Despite the dense k-space sampling ($IS=24$, $ISP=48$) the surface energy is rather unstable at low temperature (0.001H). There is a significant improvement in the stability of the solution for higher values of WIDTH (0.02H) but use of E(T) results in a surface energy of $0.643 \text{ J}/\text{M}^2$ significantly above that obtained by extrapolating E(T) to the $T=0$ limit ($0.573 \text{ J}/\text{M}^2$). The use of E0 at WIDTH=0.02H results in an excellent estimate of the surface energy - $0.576 \text{ J}/\text{M}^2$.

Note that for conducting systems analytic first derivatives are not fully implemented when the keyword **SMEAR** is used. In that case, *numerical* first derivatives should be computed (see page 127). For very small value of smearing (around 0.001 hartree) analytical gradients should be reliable in geometry optimization.

SPINEDIT - Editing of the spin density matrix

| rec | variable | meaning |
|-----|-----------|---|
| • * | N | number of atoms for which spin must be reversed |
| • * | LB, L=1,N | atom labels |

The spin density matrix from a previous run is edited to generate an approximate guess for a new spin configuration. The sign of the elements of the spin density matrix of selected atoms is reversed. The keyword **SPINEDIT** must be combined with **UHF** (input block 3, page 116) or **DFT/SPIN** (input block 3, page 88) and **GUESSP**.

Example: the anti ferromagnetic solution for the spinel MnCr_2O_4 can be obtained by calculating the ferro magnetic solution, and using as guess to start the SCF process the density matrix of the ferromagnetic solution with reversed signs on selected atoms.

SPINLOCK - Spin-polarized solutions

| rec | variable | meaning |
|-----|----------|---|
| • * | NSPIN | $n_\alpha - n_\beta$ electrons |
| * | NCYC | number of cycles the difference is maintained |

The difference between the number of α and β electrons at all \mathbf{k} points can be locked at the input value. The number of α electrons is locked to $(N + \text{NSPIN})/2$, where N is the total number of electrons in the unit cell; the number of β electrons is locked to $(N - \text{NSPIN})/2$. NSPIN must be odd when the number of electrons is odd, even when the number of electrons is even.

Example. Bulk NiO. If a anti ferromagnetic solution is required, a double cell containing 2 NiO units must be considered (test 30). The two Ni atoms, related by translational symmetry, are considered nonequivalent. The number of electron is 72, each Ni ion is expected to have two unpaired electrons.

| INF95 | type of solution | corresponding to the spin setting |
|-------|--------------------|---|
| 0 | anti ferromagnetic | $\uparrow \downarrow \uparrow \downarrow$ |
| 4 | ferromagnetic | $\uparrow \uparrow \uparrow \uparrow$ |

Warning To lock the difference between α and β electrons α and β eigenvalues are forced to be split. Their printed value is meaningless, until locking is active.

See tests 29, 30, 32, 33, 37, 38.

Note: if NCYC is < 0 , then the lock duration is controlled by energy difference between successive cycles (disappears when $< 10^{-\text{NCYC}}$) instead of by number of cycles. This is useful when the locking must be relaxed before the convergence of the SCF -otherwise there is a risk to arrive to a spurious solution- but at the same time one does not know exactly in which SCF cycle the density matrix can be considered to be close enough to the right electronic structure so as to avoid a divergent behavior after the locking finishes.

Situations like this may occur in geometry optimizations of ferromagnetic systems, for instance: the SCF of the first optimization point converges in CYC 20 with the locking finishing in CYC 12; in the remaining points, as the density matrix of the previous one is used as initial guess, the SCF converges in CYC 10 under locking and, so, the true convergence is not ensured. Using FINALRUN=4 this situation could lead to an extremely large or even non convergent optimization process.

On the other hand, to fix locking since the energy difference between cycles is less than a given threshold is a quite handy criterion that could be in several cases preferable than fixing the duration in terms of number of cycles.

STDIAG - Force standard diagonalization method

This option is supported by *MPPcrystal* only. Matrix diagonalization method in reciprocal space is switched from “Divide and Conquer method” (default, more efficient) to standard.

STOP

Execution stops immediately. Subsequent input records are not processed.

SYMADAPT

A computational procedure for generating space-symmetry-adapted Bloch functions, when BF are built from a basis of local functions (AO), is implemented. The method, that applies to any space group and AOs of any quantum number, is based on the diagonalization of Dirac characters [196, 197].

The Symmetry Adapted Functions are used in the Hamiltonian matrix diagonalization. No input data are required. This choice reduces the diagonalization CPU time when the system has symmetry operators. Default choice.

Not supported by MPP execution.

TESTPDIM

The program stops after processing of the full input (all four input blocks) and performing symmetry analysis. The size of the Fock/KS and density matrices in direct space is printed. No input data are required.

It may be useful to obtain information on the neighbourhood of the non equivalent atoms (up to 3, default value; redefined through the keyword **NEIGHBOR**, input block 1, page 56).

TEST[RUN] - Integrals classification and selection

Full input (geometry, basis set, general information, SCF) is processed.

The symmetry analysis is performed, and the mono-electronic and bi-electronic integrals classified and selected, according to the truncation criteria adopted. The size of the Fock/KS and density matrices (direct lattice) and the disk space required to store the bi-electronic are printed. The value printed as "disk space for mono-electronic integrals" is an upper limit. The new technique of *atomic* multipolar expansion reduces the required space to about 1/3 of the printed value.

No input data required.

This type of run is fast, and allows an estimate of the resources to allocate for the traditional SCF wave function calculation.

TOLDEE - SCF convergence threshold on total energy

| rec | variable | meaning |
|-----|----------|--|
| • * | ITOL | 10^{-ITOL} threshold for convergence on total energy |

Different default values are set for different type of calculation:

| | | |
|-----------------------|----------|----|
| SCF single point | | 6 |
| Geometry optimization | OPTGEOM | 7 |
| Frequency calculation | FREQCALC | 10 |
| Elastic constants | ELASTCON | 8 |
| Equation of state | EOS | 8 |

TOLINTEG - Truncation criteria for bi-electronic integrals (Coulomb and HF exchange series)

| rec | variable | meaning |
|-----|----------|--|
| • * | ITOL1 | overlap threshold for Coulomb integrals- page 277 7 |
| | ITOL2 | penetration threshold for Coulomb integrals-page 278 7 |
| | ITOL3 | overlap threshold for HF exchange integrals-page 278 7 |
| | ITOL4 | pseudo-overlap (HF exchange series-page 278) 7 |
| | ITOL5 | pseudo-overlap (HF exchange series-page 278) 14 |

The five ITOL parameters control the accuracy of the calculation of the bi-electronic Coulomb and exchange series. Selection is performed according to overlap-like criteria: when the overlap between two Atomic Orbitals is smaller than 10^{-ITOL} , the corresponding integral is disregarded or evaluated in a less precise way. Criteria for choosing the five tolerances are discussed in Chapter 13.

TOLPSEUD - Truncation criteria for integrals involving ECPs

| rec | variable | meaning |
|-----|----------|---|
| • * | ITPSE | overlap threshold for ECP integrals 6 |

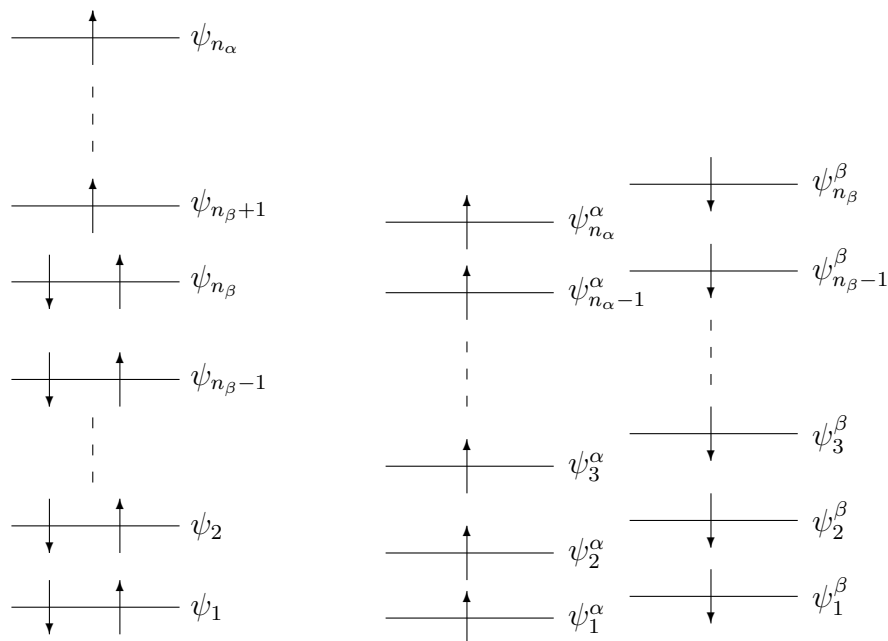


Figure 2.6: Molecular Orbitals diagram for the Restricted Open Shell method (ROHF, left) and for the Unrestricted Open Shell method (UHF, right)

The program evaluates only those integrals for which the overlap between the charge distribution φ_μ^0 φ_ν^g (page 275) and the most diffuse Gaussian defining the pseudopotential is larger than a given threshold $T_{ps}=10^{-ITPSE}$ (default value 10^{-6} ; it was 5 in CRYSTAL98).

UHF - Hamiltonian for Open Shell Systems

For the description of systems containing unpaired electrons (such as molecules with an odd number of electrons, radicals, ferromagnetic and anti ferromagnetic solids) a single determinant is not an appropriate wave-function; in order to get the correct spin eigenfunction of these systems, it is necessary to choose a linear combination of Slater determinants (whereas, in closed shell systems, a single determinant gives always the appropriate spin eigenfunction) ([142, 8], Chapter 6 of ref. [139]).

In the Restricted Open Shell [151] Hamiltonian, the same set of molecular (i.e. crystalline) orbitals describes alpha and beta electrons; levels can be doubly occupied (by one alpha and one beta electron, as in the RHF closed shell approach), singly occupied or left vacant. The wave-function is multi-determinantal; in the special case of *half-closed shell* systems, where we can define a set of orbitals occupied by paired electrons and a second set occupied by electrons with parallel spins, the wave-function is formed by a single determinant.

Another mono-determinantal approach for the study of open-shell systems is the UHF method [144]. In this theory, the constraint of double occupancy is absent and α electrons are allowed to populate orbitals other than those occupied by the β electrons. Energy levels corresponding to a ROHF and UHF description are plotted in fig. 2.6.

The double occupancy constraint allows the ROHF approach to obtain solutions that are eigenfunctions of the spin operator, \widehat{S}^2 , whereas UHF solutions are formed by a mixture of spin states. The greater variational freedom allows the UHF method to produce wave-functions that are energetically more stable than the corresponding ROHF ones; another advantage of the UHF method is that it allows solutions with locally negative spin density (i.e. anti ferromagnetic systems), a feature that ROHF solutions can never exhibit.

ROHF solution is not supported by CRYSTAL any more.

Related keywords

SPINLOCK definition of ($n_\alpha - n_\beta$ electrons)

BETALOCK definition of n_β electrons.

Chapter 3

Geometry optimization

Geometry optimization at constant symmetry is invoked by the keyword **OPTGEOM** in input block 1 (geometry). **OPTGEOM** must be the last keyword in geometry input. **OPTGEOM** input block admits several options (sub keywords), and terminates with keyword **END** (or **END[OPT]**, **END[—]**: the first three characters only are processed).

crystal allows geometry optimization of systems with any periodicity: molecules, polymers, slabs, and crystals. Unconstrained relaxation of the structure and different optimizations with constraints can be carried out. The full symmetry of the system is preserved.

Geometry optimization can be performed in either symmetrized fractional coordinates with [default] and without cell parameters, or redundant internal coordinates (optional choice, page 128).

OPTGEOM sub keywords can be classified as follow:

1. *General sub keywords:*
 - A - Optimization type (page 122)
 - B - Initial Hessian (page 122)
 - C - Hessian updating technique (page 120)
 - D - Convergence criteria (page 119)
 - E - Step control (page 124)
 - F - Coordinate system related options (page 125)
 - G - Optimization procedure control (page 126)
 - H - Numerical (first) derivatives (page 127)
 - I - Printing options (page 128)
2. *Geometry optimization in redundant coordinates* (page 128).
3. *Geometry optimization with constraints* (page 132).
 - A - Constant volume optimization (page 133)
 - B - Fixing lattice deformations (page 133)
 - C - Linear constraints between atomic coordinates (page 134)
 - D - Partial optimization of atomic positions (page 135)
 - E - Fixing internal coordinates (page 135)
4. *Geometry optimization with application of an external stress* (page 137)
5. *Searching a transition state* (page 139)

Default values are supplied for all computational parameters.

By default a full geometry optimization (atomic positions and cell) is performed. This was not the case with previous versions of the program, where atomic positions only were optimized by default.

Users can find supplementary information and input examples in the CRYSTAL Tutorials Project web page at the CRYSTAL web site (<http://www.crystal.unito.it/tutorials>).

Geometry optimization strategy

A Quasi-Newton optimization scheme is implemented. Gradients are evaluated every time the total energy is computed; the second derivative matrix (i.e. Hessian matrix) is built from the gradients. The default choice for the initial Hessian matrix is obtained from a model Hessian, as proposed by Schlegel and updated by using the BFGS algorithm[26, 27, 74, 87, 165].

By default the step considered is the Newton step (direction and length) controlled by the Trust Radius scheme (see **ALLOWTRUSTR** page 124). **NOTRUSTR** to remove trust radius control (CRYSTAL06 default choice).

HF and DFT (pure and hybrid functionals) analytical gradients for atomic positions and cell parameters, are used for insulators and conductors, both for all-electron and ECP calculations. Note that for conducting systems analytic first derivatives are not fully implemented when the keyword **SMEAR** (page 112) is used. In that case, *numerical* first derivatives should be computed (see page 127). For very small value of smearing (around 0.001 hartree) analytical gradients can be used.

For atomic positions (**ATOMONLY** option), geometry optimization is performed in symmetrized fractional coordinates, in order to exploit the point group symmetry of the lattice. The keyword **PRSYMDIR** (input block 1, page 59) may be used to print the so-called *symmetry allowed directions* adopted in the geometry optimization. If there are no symmetry allowed directions, the program prints a warning message and stops.

To optimize the lattice parameters a set of symmetry preserving cell deformations (see Symmetry Allowed Elastic Distortions, **USESSED**, page 68) related to changes of isotropic volume and of axial ratios is defined. By default, the *symmetry allowed deformations* are printed in the output file.

When a full optimization of atom positions and cell parameters is carried out, a conveniently normalized combined set of symmetrized directions and deformations is adopted.

Optional choice (keyword **INTREDUN**, page 128) is the geometry optimization in redundant internal coordinates. In such a case, atomic displacements and cell deformations are implicitly determined by the internal coordinate system.

Default choices

- Type of optimization:

The default geometry optimization type is the relaxation of both the nuclear coordinates and the lattice parameters. Optional choices: see page 122.

- Convergence criteria

A stationary point on the potential energy surface is found when the forces acting on atoms are numerically zero. Geometry optimization is usually completed when the gradients are below a given threshold.

In *crystal*, the optimization convergence is checked on the root-mean-square (RMS) and the absolute value of the largest component of both the gradients and the estimated displacements. When these four conditions are all satisfied at a time, optimization is considered complete.

In some cases (see page. 138), the optimization process stops with a warning message controlled by the threshold in the energy change between consecutive optimization steps.

Default values are set for all computational parameters, and they may be modified through keywords. Default choices:

| | default | keyword |
|--|----------------|--------------|
| RMS on gradient | 0.000300 a.u. | TOLDEG |
| largest component of gradient | 1.5 * 0.000300 | 1.5 * TOLDEG |
| RMS on estimated displacements | 0.0012 a.u. | TOLDEX |
| absolute value of largest displacement | 1.5 * 0.0012 | 1.5 * TOLDEX |
| max number of optimization cycles | 100 | MAXCYCLE |
| energy change between optimization steps threshold | 10^{-7} a.u. | TOLDEE |

Optimization convergence criteria are set to different values according to the context where geometry optimization is performed.

| | RMS on gradient | RMS on displacement |
|---------------------------------|-----------------|---------------------|
| Standard geometry opt | 0.0003 | 0.0012 |
| preopt in frequency calculation | 0.00003 | 0.00012 |
| preopt in EOS | 0.00006 | 0.00012 |
| preopt in elastic constants | 0.00006 | 0.00012 |

- Initial Hessian guess

The initial Hessian is generated by means of a classical model as proposed by Schlegel.

H.B. Schlegel, Theoret. Chim. Acta 66 (1984) 333

J.M. Wittbrodt and H.B. Schlegel, J. Mol. Struct. (Theochem) 398-399 (1997) 55

It adopts a simple valence force field. Empirical rules are used to estimate the diagonal force constants for a set of redundant internal coordinates (stretches, bends and torsions). Parameters are available from H to At.

Warning - To define bonds the sum of covalent radii (see page 59) is used. For ionic systems it may be necessary to modify the default values (see **RAYCOV**, page 59).

- Hessian updating technique

BFGS Broyden-Fletcher-Goldfarb-Shanno scheme [26, 27, 74, 87, 165].

Optional choices:

1. Schlegel's updating scheme [162], (**OLDCG**, page 123), optimization scheme as in CRYSTAL03
2. Powell's updating scheme (**POWELL**, page 123)

- SCF convergence and guess

The default value for SCF convergence criterion on total energy is set to 10^{-7} (TOLDEE in input block 3 to modify it: never reduce accuracy).

After the first step, at each SCF cycle, the density matrix is recovered from the previous geometry optimization step (implicit GUESSP, page 103 option).

This choice may be modified by inserting the keyword **NOGUESS**. A superposition of atomic densities is then adopted on each step as SCF initial guess.

If the SCF solution at a given optimization step does not correspond to real convergence,

but to an energy stabilization due to the techniques applied to help convergence (LEVSHIFT, FMIXING, BROYDEN..), the hamiltonian eigenvalues may be unphysical, and there is no chance to recover the SCF process. In those cases it may be better to use an atomic guess (keyword **NOGUESS**).

- Output files

The following formatted files are written during geometry optimization, and may be saved for further processing.

fort.33 Cartesian coordinates of the atoms in the unit cell and total energy for each geometry optimization step are written to file fort.33 in a simple *xyz* format (see Appendix D, page 324). This file is suitable to be read by molecular graphics programs (e.g. Molden...) to display the animation of a geometry optimization run.

fort.34 If optimization is successful, the last geometry is written in file fort.34 (format described in Appendix D, page 326).

The file can be read to define the basic geometry input. See **EXTERNAL**, page 16

opta(c)xxx At each xxx optimization step, the geometry is written in file optaxxx (optimization of atoms coordinates only), or optcxxx (optimization of cell parameters or full optimization) in the format of "fort.34" file (see Appendix D, page 326). The file must be renamed "fort.34" if used to enter geometry input (keyword **EXTERNAL**).

The "history" of the optimization allows restarting from a given step with different parameters, when the procedure did not converge.

OPTINFO.DAT contains information to restart optimization. (see keyword **RESTART** in **OPTGEOM** input block, page 127).

HESSOPT.DAT The hessian matrix is written, and can be read to define the initial guess for the Hessian (keyword **HESSOPT**) in geometry optimization of a system with same geometry and symmetry (it may have different BS, Hamiltonian, computational parameters).

SCFOUT.LOG SCF and optimization process printout is routed to file SCFOUT.LOG after the first cycle. Keyword **ONELOG**: full printing on standard output.

1 - General sub keywords

A number of optional keywords allow tuning of the optimization procedure.

- A - Type of optimization (page 122)
- B - Initial Hessian (page 122)
- C - Hessian updating technique (page 123)
- D - Convergence criteria (page 119)
- E - Step control (page 124)
- F - Coordinate system related options (page 125)
- G - Optimization procedure control (page 126)
- H - Numerical first derivatives (page 127)
- I - Printing options (page 128)

A - Type of optimization

Optional choices:

ATOMONLY Only atomic coordinates are optimized. This was the default before CRYSTAL14

FULLOPTG full optimization, atom coordinates and cell parameters (default in CRYSTAL14). The cell volume may change (see **CVOLOPT**, page 133, to optimize at constant volume)

CELLONLY only cell parameters are optimized. Default: the cell volume may change (see **CVOLOPT**, page 133, to optimize at constant volume)

ITATOCEL full optimization, iterative procedure optimization: atoms-cell-atoms-cell-
.....

INTREDUN full optimization of atomic positions and cell parameters in redundant internal coordinates (page 128).

B - Initial Hessian

By default an estimated model Hessian is adopted. The Hessian matrix is stored in file HESSOPT.DAT at each optimization step. This may be useful to restart the optimization from a previous run performed at a lower level of theory (e.g. a smaller basis set). An initial Hessian can also be obtained as numerical first-derivative (HESSNUM), but this process can be very expensive.

HESSFREQ initial guess for the hessian - input from file HESSFREQ.DAT obtained from frequencies calculations (developers only)

HESSIDEN initial guess: identity matrix

HESSOPT external guess (read from file HESSOPT.DAT)

HESSMOD1 initial guess: Lindh's model Hessian [112]

A model Hessian based on a simple 15-parameter function of the nuclear positions as proposed by Lindh et al. is used as initial Hessian. Parameters are available for the first three rows of the periodic table.

R. Lindh, A. Bernhardsson, G. Karlstrom and P.-A. Malmqvist, Chem. Phys. Lett. 241 (1996) 423

HESSMOD2 initial guess: Schlegel's model Hessian [163, 186] [default]

The initial Hessian is generated by means of a classical model as proposed by Schlegel.

H.B. Schlegel, Theoret. Chim. Acta 66 (1984) 333

J.M. Wittbrodt and H.B. Schlegel, J. Mol. Struct. (Theochem) 398-399 (1997) 55

It adopts a simple valence force field. Empirical rules are used to estimate the diagonal force constants for a set of redundant internal coordinates (stretches, bends and torsions). Parameters are available from H to At.

Warning - To define bonds the sum of covalent radii (see page 59) is used. For ionic systems it may be necessary to modify the default values (see **IONRAD** in what follows in order to use tabulated ionic radii in place of the covalent ones provided by default or **RAYCOV**, page 59, for customizing the value of covalent radii, page 59).

HESSNUM initial guess: numerical estimate

Tabulated atomic radii

The construction of the set of internal coordinates which is used in the definition of the Schlegel model Hessian relies on tabulated values for the atomic radii, according to which bonds, angles and dihedrals are defined. Two different tables can be chosen in input with the following keywords:

COVRAD The covalent radii table is used in the construction of the internal coordinates. This is the default choice, which is reasonable in most cases but may lead to a ill defined Schlegel model Hessian in some compact ionic structures.

IONRAD The ionic radii table is used in the construction of the internal coordinates. This leads to a better initial Schlegel model Hessian in ionic compounds.

C - Hessian updating technique

Different Hessian updating schemes are available for minimization:

BFGS Hessian update - Broyden-Fletcher-Goldfarb-Shanno scheme [26, 27, 74, 87, 165] - [default]

OLDCG Hessian updating - old Schlegel updating scheme[162] (CRYSTAL03)
BERNY Synonym

POWELL Hessian update - symmetric Powell scheme [145]

D - Optimization convergence criteria

These options are available to modify the default values:

TOLDEE threshold on the energy change between optimization steps
• * IG $|\Delta E| < 10^{-IG}$ (default: 7)

The value of IG must be larger or equal to the threshold adopted for the SCF convergence. The value is checked when input block 3, defining the SCF convergence criteria, is processed.

TOLDEG convergence criterion on the RMS of the gradient
• * TG max RMS of the gradient (default: 0.0003)

TOLDEX convergence criterion on the RMS of the displacement
• * TX max RMS of the displacement (default: 0.0012)

E - Step control

To avoid the predicted step size being too large, two options are available:

Simple scaling

Simple scaling of the displacement vector. Each component is scaled by a factor that makes the largest component of the displacement vector equal to 0.5 a.u.

Trust Radius [default]

A more sophisticated and accurate technique to control the step size is the trust radius region scheme. The trust radius limits the step length of the displacement at each cycle, according to the quadratic form of the surface in the actual region. The default maximum value for minimization is 0.5.

To run CRYSTAL06 as CRYSTAL09 the keyword **ALLOWTRUSTR** must be specified along with **BFGS**.

To run CRYSTAL09 as CRYSTAL06, the keyword **NOTRUSTR** must be specified in geometry optimization input

Related keywords are discussed below:

ALLOWTRUSTR activate the trust radius technique to control the step size [0.5 for geometry optimization; 0.1 for transition state search] [default]

The step at each cycle is computed by means of a Newton-like scheme, in case it exceeds trust radius it is re-scaled using the scheme proposed by Simmons and Nichols [Simmons, J., and Nichols, J.: , Int. J. Quantum Chem. Symp. 24, volume 24, 263, (1990)] (see also page 139).

MAXTRADIUS optional

• * TRMAX maximum value allowed for the trust radius

This is useful in transition state optimizations or in minimizations along flat potential surfaces in order to avoid too large displacements from one point to the next one. Default value: geometry optimization: 4.0 ; transition states search: 0.3.

NOTRUSTR not using trust radius to limit displacement

TRUSTRADIUS

- * **TRADIUS** set the initial value for trust radius

Set the initial value of the trust radius to [TRADIUS]. The trust radius limitates the step length of the displacement at each cycle. The value is updated at each optimization point by analysis of the local quadraticity of the potential energy function.

Default: geometry optimization 0.5; transition state search 0.1.

Warning - When the Trust Radius technique is active, the value of the trust radius could become too small and the geometry optimization process stops with an error message: "TRUST RADIUS TOO SMALL".

In this case, we suggest to restart the optimization from the last geometry, written to file optc(a)xxx, being xxx the optimization cycle number.

F - Coordinate system related options

Geometry optimization can be performed in fractional (default) or redundant internal coordinates (see **INTREDUN**). Default fractional coordinates are defined as symmetry allowed directions (atomic positions) and deformations (cell). The latter are related to changes of isotropic volume and of axial ratios.

Some options related to the choice of the coordinate systems are also available:

CRYDEF crystallographic-like symmetrized cell deformations, corresponding to symmetrized strains of the unit-cell edges (consistent with symmetry). This set of deformations is useful for fixing lattice parameters in constrained optimizations in combination with the keyword **FIXDEF** (page 133) - 3D only.

FRACTION optimization in fractional coordinates

FRACTIOO optimization in normalized fractional coordinates [default when **FULLOPTG** is requested]

FRACTCOOR third type of symmetrized fractional coordinates (non-orthogonal; the origin on polar axes must be explicitly fixed by the **FIXCOOR** option [to be used with constraints])

RENOSAED renormalize symmetry allowed deformations [default when **FULLOPTG** is requested]

G - Optimization procedure control

EXPDE

- * DE expected energy change used to estimate the initial step [default 10^{-3} Ha, if model 1 initial hessian; 10^{-4} Ha, otherwise]
-

FINALRUN

- action after geometry optimization - integrals classification is based on the last geometry. See page 138. **Note that in the previous versions of the program the default choice was 0. Now it is 4.**
- * ICODE Action type code:
 - 0 the program stops
 - 1 single-point energy calculation
 - 2 single-point energy and gradient calculation
 - 3 single-point energy and gradient calculation - if convergence criteria on gradients are not satisfied, optimization restarts
 - 4 step 3 is iterated until full stable optimization (default)
-

FIXDELTE

- * IE 10^{-ie} hartree: threshold on the total energy change for redefining the geometry to which integral classification is referred - see **FIXINDEX**, page 98 - [default -1000, no reclassification]
-

FIXDELTX

- * DX RMS (bohr) of the displacement for redefining the geometry to which integral classification is referred - [default: -1, no reclassification]
-

FIXDEIND

the reference geometry for integrals classification does not change during optimization [default choice]

FITDEGR

- * N degree of polynomial fitting function for linear search:
 - 2 parabolic fit [default]
 - 3 cubic polynomial function
 - 4 constrained quartic fitting
-

HESEVLIM

- * VMIN limits for the allowed region of hessian eigenvalues (hartree)
 - VMAX lower limit [default 0.001]
 - upper limit [default 1000.]
-

ITACCONV

- * DE energy difference threshold for ITATOCEL [default $0.1 * \text{TOLDEE}$ between 2 optimization cycles]
-

MAXITACE

- * MAXI max number of iteration cycles in atom/cell iterative optimization [default 100]
-

MAXCYCLE

- * MAX maximum number of optimization steps [default 100]
-

N.B. When optimization is restarted, the first restarted optimization cycle number is the last of the previous run + 1. Set MAXCYCLE value accordingly.

NOGUESS SCF guess at each geometry point: superposition of atomic densities at each SCF calculation (default choice in geometry optimization: **GUESSP**)

NRSTEPS

- * DE number of stored steps to be used in the OLDCG Hessian updating scheme [default: number of degrees of freedom]
-

RESTART restart geometry optimization from a previous run.
See page 138

SORT sorting of the previous optimization steps information when the OLDCG scheme is active [default:nosort]

H - Numerical first derivatives

The nuclear coordinate gradients of the energy can also be computed numerically. A three-point numerical derivative formula is adopted. A finite positive (and then negative) displacement is applied to the desired coordinate and a full SCF calculation is performed. The gradient is then computed as

$$g_i = \frac{E_{\Delta x_i} - E_{-\Delta x_i}}{2 \Delta x_i}$$

where Δx_i is the finite displacement along the i -coordinate.

Such a computation is very expensive compared to analytical gradients, since the cost is $2 \cdot N \cdot t$, where N is the number of coordinates to be optimized and t the cost of the SCF calculation. Numerical first-derivatives should be avoided whenever possible, but sometimes they are the only way to obtain gradients (i.e. for conducting systems and the **SMEAR** option - page 112) and therefore to optimize the atoms coordinates.

One choice only, **NUMGRCEL**, **NUMGRATO**, **NUMGRALL**, is allowed.

NUMGRALL geometry optimization - numerical atomic and cell gradient

NUMGRATO geometry optimization - numerical atomic gradients

NUMGRCEL geometry optimization - numerical cell gradients

| | |
|-----------------|---|
| STEPSIZE | modify step for numerical gradient [default 0.001 au] (developers only) |
| • * STEP | new stepsize value |

I - Printing options

| | |
|---------------|--|
| ONELOG | This causes all output to be sent to the standard log file, instead of to SCFOUT.LOG |
|---------------|--|

| | |
|--------------|--|
| NOXYZ | printing of cartesian coordinates at the end of optimization removed |
|--------------|--|

| | |
|------------------|---|
| NOSYMMOPS | printing of symmetry operators at the end of optimization removed |
|------------------|---|

| | |
|--------------------|---------------------------|
| PRINTFORCES | printing atomic gradients |
|--------------------|---------------------------|

| | |
|------------------|------------------------------|
| PRINTHESS | printing Hessian information |
|------------------|------------------------------|

| | |
|-----------------|--|
| PRINTOPT | prints information on optimization process |
|-----------------|--|

| | |
|--------------|------------------|
| PRINT | verbose printing |
|--------------|------------------|

2 - Optimization in redundant internal coordinates

| | |
|-----------------|---|
| INTREDUN | geometry optimization in internal redundant coordinates |
|-----------------|---|

An optimization in redundant internal coordinates is performed when the keyword **INTREDUN** is inserted in **OPTGEOM** input block.

Optional keywords related to geometry optimization in redundant internal coordinates must follow.

A symmetrized set of internal coordinates (i.e. bonds, angles and torsions) is automatically defined, which contains much more coordinates than the requisite internal degrees of freedom.

Redundant internal coordinates are generated according to a hierarchical scheme: bond lengths are firstly identified by using covalent radii. Then, angles are determined on the basis of the irreducible set of distances and, finally, dihedral angles are defined. Note that to define bonds the sum of covalent radii (see page 59) is used. For ionic systems the default values can be automatically set by using the **IONRAD** directive (see pag. 123), or explicitly setting them with the **RAYCOV** keyword (page 59). In case of systems constituted by unconnected fragments (*ie* some molecular crystals or adsorption complexes), fragments are automatically

linked to each other by *pseudo* “bond lengths” between the closest pair of atoms belonging to each fragment.

There has been substantial controversy in recent years concerning the optimal coordinate system for optimizations. For molecular systems, it is now well-established that redundant internal coordinates require fewer optimization steps than Cartesian coordinates. However, this is not definitely demonstrated for periodic systems. Nevertheless, the use of internal coordinates can be very useful in several respects: for a chemical intuitive view (e.g. internal coordinates can easily be added), for constrained geometry optimization (see below) and for searching transition states.

By default, optimization of internal redundant coordinates involves both atomic positions and cell parameters. To avoid optimizing cell parameters the keyword **FIXCELL** page 132 must be specified.

Before running a geometry optimization in redundant internal coordinates, the set of coordinates generated automatically by CRYSTAL should be checked for consistency. This can be done by specifying the keyword **TESTREDU**.

Optional keywords related to the geometry optimization in redundant internal coordinates are listed below.

Managing with almost linear angles

Linear or almost linear angles (i.e. close to 180°) can lead to numerical instabilities in the computation of the dihedrals. To avoid this problem a common practice is to split the angle in two ones. Double angles are defined as a couple of angles obtained by projection of the vectors onto two suitable perpendicular planes. This avoids the indetermination around 180° . The threshold value, beyond which the almost linear angle is split, is controlled by the keyword **ANGTODOUBLE**.

ANGTODOUBLE minimum value (degrees) beyond which a double angle is defined

- * AL value of the angle (degrees) - default [165°]

The default value is set to 165° . This means that all angles larger than 165° are automatically split into two.

This option can be required, for instance, when optimizing zeolitic structures where siloxane bridges could change a lot during the geometry minimization. In that case, it is better to reduce the default value to 150° .

A list of angles to be converted into two can also be explicitly given by specifying

DBANGLIST list of angles chosen to be converted in double angles - advanced option

- * MU number of angles to convert in double
- * (IN(I), list of the angles
I=1,MU)

This keyword provides the list of angles chosen to be converted in double angles (i.e. defined by the angles obtained by projection of the vectors onto two suitable perpendicular planes) in order to avoid the indetermination around 180 degrees). The labels used for the angles are those provided by a previous automatic generation of internal coordinates computed in a test run (**TESTREDU** keyword).

Double angles have to be defined at the starting of the optimization. If any single angle approaches 180° the program stops with a message. For this reason, it is strongly recommended foresee **before** the optimization which are the angles that may evolve to close to 180° degree and protect them making them explicitly double. A less recommendable alternative is to set an **ANGTODOUBLE** value very small ($< 90^\circ$) so as to make double any eventual tricky angle. Such a procedure requires less effort to the user but must be used with caution as the number of angles and dihedrals based on them may explode.

Explicitly defining internal coordinates - bonds and angles

When some relevant internal coordinates are missing (e.g. intermolecular bonds) they can be explicitly defined by means of two keywords: **DEFLNGS** and **DEFANGLS**.

| | | |
|----------------|---|----|
| DEFLNGS | definition of bond lengths | |
| • * NL | number of bonds to be added | |
| | insert NL sets of 5 data to define the bond \overline{AB} | II |
| LA | <i>label</i> of the atom A (it must be in the reference cell) | |
| LB | <i>label</i> of the atom B | |
| I1, I2, I3 | indices of the cell where the atom B is located | |

| | | |
|-----------------|---|----|
| DEFANGLS | definition of bond angles | |
| • * NL | number of angles to be defined | |
| | insert NL sets of 9 data to define the angle \widehat{ABC} | II |
| LA | <i>label</i> of the atom A (it must be in the reference cell) | |
| LB | <i>label</i> of the atom B | |
| I1, I2, I3 | indices of the cell where the atom B is located | |
| LC | <i>label</i> of the atom C | |
| I1, I2, I3 | indices of the cell where the atom C is located | |

Choosing method for back-transformation

By default CRYSTAL employs an iterative method (P. Pulay and G. Fogarasi, “Geometry optimization in redundant internal coordinates”, *J. Chem. Phys.* 96, 2856 (1992)) so as to compute the atomic positions and cell parameters corresponding to the set of redundant internal coordinates obtained at each optimization point. For those periodic systems in which the generated internal coordinates have a high degree of redundancy and/or the displacement is relatively large (for instance in the starting points of the optimization when geometry is very far from the target one) such a method may fail for large steps and provide inaccurate displacements making the whole optimization less efficient. As an alternative you might change the strategy for back-transformation using the keyword **BKTRNSF2**

Under such an option, the program performs back-transformations from redundant (internal) to fractional+cell coordinate systems through an alternative procedure based on the conjugate gradient (CG) algorithm. The idea of the method is as follows. Given a reference set of redundant parameters, the best point in terms of atomic positions and lattice parameters is the one that is the closest as possible to the reference one in the redundant parameter space. The distance function is defined as a weighted mean square of the differences between redundant parameters of the trial and reference sets. This function is fastly minimized by the CG strategy.

The main drawback is that the new method is slightly more costly in cpu time and memory

space than the default iterative one.

In all tests done, this new scheme for the back-transformation works better than the iterative procedure originally proposed by Pulay for molecules and extended in Crystal to periodic systems:

1. It is safer in its convergence; specially when the displacement step in terms of redundant coordinates is very large and the structure displays a large number of connectivity loops (this happens in most natural crystals). In such cases the "old" method fails and the program performs a rough conversion that is often very poor in accuracy.
2. As concerns the optimization process, the use of this more accurate alternative allows in most cases to save a few points leading to an overall gain in computational time, even if the conjugate gradient scheme is a bit more costly than the simple iterative procedure.

An additional advantage of the algorithm is that it allows to set weights to the squared deviations of the redundant parameters used in the deviation function so as to force some of them to be better approached than the others in the back-transformation procedure. This permits a more controlled definition of the steps in terms of internal redundant coordinates. The choice is optative in the **MODINTCOOR** option, and during the optimization it can be set by means of the keyword **WGHTDREDU**.

WGHTDREDU Assign weights for back-transformation

- * **NMODI** Number of internal coordinates to be given an specific weight
 DEFWGTH Default weight for internal coordinates not explicitly defined
- * **NRED(I),**
 WEIGHT(I),
 I=1,NMODI Label of coordinate (in the list of internal redundants coordinates produced in output with directive **TESTREDU**) and specific weight.

Specific weights may be used to provide priorities when different internal coordinates are in conflict in the back-transformation, as the corresponding redundant set of values does not correspond to any real atomic arrangement. This typically occurs for instance when the connectivity graph exhibits a high degree of nested loops.

Modifying geometry before the optimization through internal coordinates

Geometry modification in terms of internal coordinates. This option allows to modify the value of any internal coordinate. The keyword is set in the **OPTGEOM** block (together with **INTREDUN** and the syntax is as follows:

MODINTCOOR Modification of internal coordinates
(**ADJUSTGEO**)

- * **NMODI** Number of internal coordinates to be modified
 IWGHT > 0 Weight given to the parameters to be modified using **BKTRNSF2** as back-transformation scheme. The min value (1) means the new parameters will be approached trying to move as less as possible the values of the remaining ones in the redundant set. The max value is 1000 and means the new value of the chosen parameters will be as close as possible to the new provided values while the rest of redundant parameters will accomodate to allow this.
 < 0 Use the old back-transformation; no weight is actually assigned.
- * **NRED(I),**
 VALNEW(I),
 I=1,NMODI Label (in the list of internal redundants coordinates produced in output with directive **TESTREDU**) and new value of the internal coordinates to be modified.

Together with **TESTREDU** it allows to perform geometry modifications in terms of internal coordinates without performing any optimization. In such a case, a file called “optc000” is written in the execution directory that contains the modified geometry in external format. Conveniently renamed, this file can be used with the keyword **EXTERNAL** (page 16) as starting geometry for a new calculation.

Other optional keywords

FIXCELL keep cell parameters fixed in internal coordinates optimization

STEPBMAT step used for numerical bmat calculation (developers only)
• * **I** integer - step = 10^I (default 7: step= 10^7)

TESTREDU request test run for checking automatic definition of internal coordinates
.

TOLREDU tolerance used to eliminate redundancies (developers only)
• * **I** tolerance 10^{-I} (default: 7, 10^{-7})
.

3 - Geometry optimization with constraints

Along with an unconstrained relaxation of the crystalline structure, options are available to perform different optimizations with constraints.

In particular:

A - Constant volume optimization (page 133)

B - Fixing lattice deformations (page 133)

C - Linear constraints between atomic coordinates (page 134)

D - Partial optimization of atomic positions (page 135)

E - Fixing internal coordinates (page 135)

Constraining strategies *A-D* are compatible with any choice of coordinate system adopted for the optimization process to perform the optimization process. On the other hand, option *E* is only operative together with the choice of a redundant internal coordinate system (**INTREDUN** page 128).

The examples in the CRYSTAL Tutorial Project web page illustrate the use of the available keywords for constrained geometry optimizations.

A - Constant volume optimization

CVOLOPT constant volume optimization.

Only active with **CELLONLY** (cell parameters only optimization), **FULLOPTG** (atom coordinates and cell parameters optimization) or **INTREDUN** (redundant coordinates optimization).

The volume is kept fixed at the value corresponding to the input unit cell; all cell angles and ratios between cell edges unconstrained by the point-group symmetry are optimized.

Examples: in the tetragonal symmetry, only the *c/a* ratio, and in the monoclinic symmetry the *a/b* and *b/c* ratios and the beta angle, respectively, are optimized.

This option is useful for computing E vs V curves point-by-point by relaxing the crystalline structure at different values of the cell volume. In this case, the keyword **FIXINDEX** must be used to obtain a smooth curve. The reference geometry must correspond either to the smallest volume to be explored, or to the equilibrium structure obtained from a prior optimization run (**FULLOPTG**).

Warning: if large changes of the individual unit-cell parameters occur in the optimization process, the linear strain approximation may not be strictly obeyed and very small volume variations (of the order of 0.01%) may ensue.

B - Fixing lattice deformations

Linear constraints between unit cell deformations can be set up during optimization by means of the keyword **FIXDEF**:

| | |
|---------------|--|
| FIXDEF | optimization with constrained symmetrized cell deformation - 3D only |
| • * NFIXC | number of constraints relating pairs of cell deformations |
| | _____ insert NFIXC records _____ II |
| • * LA, LB | integer sequence number of the two constrained symmetrized cell deformations. |
| CA, CB | real coefficients multiplying the two cell deformations in the linear combination constraint. If LA=0, the cell deformation denoted by the second integer (LB) is kept fixed during the optimization (the coefficients in this case can take any value). |

FIXDEF can also be combined with the keyword **CRYDEF** (p. 125, that sets crystallographic-like cell deformations (i.e. *a, b, c, α, β, γ*) to fix lattice parameters. Integer sequence number given as input refer to the minimal set of lattice parameters:

| | 1 | 2 | 3 | 4 | 5 | 6 |
|--------------|-------------------|------------|------------|------------|-----------|----------|
| cubic | <i>a</i> | | | | | |
| hexagonal | <i>a</i> , | <i>c</i> | | | | |
| rhombohedral | hexagonal cell | <i>a</i> , | <i>c</i> | | | |
| | rhombohedral cell | <i>a</i> , | α | | | |
| tetragonal | <i>a</i> , | <i>c</i> | | | | |
| orthorhombic | <i>a</i> , | <i>b</i> , | <i>c</i> | | | |
| monoclinic | <i>a</i> , | <i>b</i> , | <i>c</i> , | β | | |
| | <i>a</i> , | <i>b</i> , | <i>c</i> , | γ | | |
| | <i>a</i> , | <i>b</i> , | <i>c</i> , | α | | |
| triclinic | <i>a</i> , | <i>b</i> , | <i>c</i> , | α , | β , | γ |

Note that the labels of the symmetry allowed deformations must correspond to the ones printed in the output file.

As an example, a constrained optimization of the crystalline structure of α -quartz (hexagonal) with the *c* unit cell edge kept fixed follows

```

QUARTZ ALFA  STO-3G
CRYSTAL
0 0 2
154
0 0 16
4.916  5.4054
2
  14 0.4697      0.      0.
   8 0.4135      0.2669   0.1191
OPTGEOM
FULLOPTG
CRYDEF
FIXDEF
1
0 2 0.0 0.0      : the second lattice parameter, c, is kept fixed
ENDOPT
END

```

C - Linear constraints between atomic coordinates

Linear constraints between atomic coordinates can be set up during optimization by using the keyword **FIXCOOR**.

| | |
|----------------|--|
| FIXCOOR | optimization with constrained symmetrized coordinates |
| • * NFIX | number of constraints relating pairs of coordinates |
| | _____ insert NFIX records _____ II |
| • * LA, LB | integer sequence number of the two constrained symmetrized coordinates (sequence numbers are read from the output of PRSYMDIR) |
| CA, CB | real coefficients multiplying the two coordinates in the linear combination constraint. If LA=0, the coordinate denoted by the second integer (LB) is kept fixed during the optimization (the coefficients in this case can take any value). |

Note that the labels of the symmetry allowed directions must correspond to the one printed in the output file (**PRSYMDIR** keyword for coordinates).

In the following example on α -quartz, two constraints are set up on coordinates

```

QUARTZ ALFA      -      Linear constraints between atomic coordinates
CRYSTAL
0 0 2
154
0 0 16
4.916  5.4054
2
  14 0.4697      0.          0.
   8 0.4135      0.2669     0.1191
OPTGEOM
FULLOPTG
FRACTCOOR
FIXCOOR
2
2 3 1.0 1.0
0 4 0.0 0.0
ENDOPT
END

```

1. The x and y fractional coordinates of Oxygen are forced to change by the same amount, so that their difference remains constant.
2. The z coordinate of Oxygen is kept fixed.

In general, any of the structural parameters can be kept fixed in the optimization process by the combined use of **FIXCOOR** and **FIXDEF** keywords.

D - Partial optimization of atomic positions

FRAGMENT Partial geometry optimization (default: global optimization)

- * NL number of atoms "free"
- * LB(L),L=1,NL *label* of the atoms to move

Optimization is limited to an atomic fragment (synonym **ATOMFREE**). Symmetrized cartesian coordinates are generated according to the list of atoms allowed to move. Note that no advantage is taken in the gradient calculation to reduce the number of atoms, i.e. gradients are calculated on the whole system. The symmetrized forces are then computed by using the new set of symmetrized coordinates. See example in section 11.4, page 260.

E - Fixing internal coordinates

Constraints on internal coordinates can be easily imposed during geometry optimization. The following two options allow users to both define and freeze one or more bond lengths or angles:

LNGSFROZEN explicitly freezes bond lengths

- * MU number of bond lengths to freeze
-
- | | | |
|------------|---|----|
| | insert NL sets of 5 data to define the bond \overline{AB} | II |
| LA | <i>label</i> of the atom A (it must be in the reference cell) | |
| LB | <i>label</i> of the atom B | |
| I1, I2, I3 | indices of the cell where the atom B is located | |
-

ANGSFROZEN definition of bond angles to be frozen

- * NL number of angles to be frozen

insert NL sets of 9 data to define the angle \widehat{ABC} II

| | |
|------------|---|
| LA | <i>label</i> of the atom A (it must be in the reference cell) |
| LB | <i>label</i> of the atom B |
| I1, I2, I3 | indices of the cell where the atom B is located |
| LC | <i>label</i> of the atom C |
| I1, I2, I3 | indices of the cell where the atom C is located |

According to the list of redundant internal coordinates automatically generated by the code, bond lengths or angles can also be frozen by means of the **FREEZINT** option:

FREEZINT freeze internal coordinates (active with **INTREDUN** only):

- * NB first NB bond length are frozen
- NA first NA bond angles are frozen
- ND first ND dihedral angles are frozen (not active)

The list of redundant coordinates can be obtained from a prior run, by inserting the keyword **TESTREDU** (the program stops after printing internal coordinates).

Note that for a better control over the selected frozen internal coordinates we suggest using the keywords **LNGSFROZEN** and **ANGSFROZEN**. These options reorder the internal coordinates list so as the frozen parameters to be the first ones in the lengths and angles entries of the output. The frozen coordinates will appear with the label (T) in the FRZ column.

Constrained optimization combining internal coordinates and fractional coordinates can also be performed.

For instance, one can keep fixed a bond angle together with the constraint that the x and y fractional coordinates of a given atom change by the same amount. Such a combination of constraining strategies must be used with caution, as it may lead to undesired behavior in the optimization process.

The constraining of internal coordinates is performed with numerical techniques (particularly in the back-transformation from redundant internal to cell/atomic coordinate systems) and the fixed values may be affected by some small changes (in general of the order of 10^{-4} au). The use of **BKTRNSF2** (page 130) may improve the numerical behaviour.

The following example corresponds to a rigid tetrahedral geometry optimization of α -quartz:

```

QUARTZ ALFA fixing internal coordinates
CRYSTAL
0 0 2
154
0 0 16
4.916 5.4054
2
  14 0.4697      0.      0.
   8 0.4135      0.2669  0.1191
OPTGEOM
INTREDUN
LGNSFROZEN
2
4 1 0 0 0

```



```

5  1 -1 0 0
ANGSFROZEN
4
4  1  0 0 0  7  0 0 0
4  1  0 0 0  5  1 0 0
4  1  0 0 0  8  1 0 0
5  1 -1 0 0  8  0 0 0
ENDOPT
END

```

The two independent Si-O bond lengths and then the four O-Si-O angles of the SiO₄ tetrahedron are frozen in order to relax just the Si-O-Si bridges and the dihedral angles.

FREEZDIH freeze a list of dihedral (active with **INTREDUN** only):

- * NDH number of dihedrals to be frozen
- * IFR(I), list of dihedrals to be frozen
I=1,NDH)

The list of dihedrals, to choose the ones to be frozen, is obtained performing a previous run with the keyword **TESTREDU** into **OPTGEOM** input block (the program stops after the printing of the internal coordinates, see page 132).

After using **FREEZINT** (page 136) it turns out that the order of the dihedral angles in the output changes: the frozen parameters appear at the beginning of the list. All of them are now labeled as frozen ("FRZ=T") in the printed list of redundant coordinates.

4 - Geometry optimization with application of an external stress

Geometry optimization can be done under an hydrostatic pressure (**EXTPRESS**).

EXTPRESS to apply external, hydrostatic pressure

- * pres pressure in hartree/bohr³

Input example:

```

EXTPRESS
0.001 hydrostatic pressure of hartree/bohr^3 s applied

```

The directive should be introduced in any place within the **OPTGEOM** block.

Notes on geometry optimization

On the integrals classification during a geometry optimization

Truncation of infinite Coulomb and exchange series, based on the overlap between two atomic functions (see chapter 13.12), depends on the geometry of a crystal. With default thresholds, different selection of integrals are evaluated with different geometries. This introduces small discontinuities in the PES, producing artificial noise in the optimization process. To avoid noise in interpolation of PES, the **FIXINDEX** option is always active during optimization. The adopted selection pattern refers to the starting geometry.

If equilibrium geometry is significantly different from the starting point, reference truncation pattern may be inappropriate and the use of proper truncation becomes mandatory.

Since both total energy and gradients are affected by the integrals classification, a single-point energy calculation ought to be run always with the final structure, and integrals classified according to the new final geometry, to calculate correct total energy and gradients.

If during the final run the convergence test on the forces is not satisfied, optimization has to be restarted, keeping the integrals classification based on the new geometry. The **FINALRUN** option has been implemented to this aim.

The four different options of **FINALRUN** allow the following actions, after classification of integrals:

1. single-point energy calculation (correct total energy),
2. single-point energy and gradient calculation (correct total energy and gradients),
3. single-point energy and gradient computation, followed by a new optimization process, starting from the final geometry of the previous one, (used to classify the integrals), if the convergence test is not satisfied.
4. step 3 is iterated until full stable optimization

If the starting and final geometry are close, the energy and gradient calculated from the final geometry, with integral classification based on the initial geometry, are not very different from the values obtained with correct classification of integrals. In some cases (e.g. optimization of the geometry of a surface, with reconstruction) the two geometries are very different, and a second optimization cycle is almost mandatory (ICODE=4 in FINALRUN input). This is the default in *crystal*.

Optimization of flat surfaces

Flat regions of surfaces often behave as non quadratic. This may give rise to erratic optimization paths when using the linear minimization to control the step length. In these cases it is recommendable using the trust radius strategy set by the keyword **ALLOWTRUSTR**. Under this scheme the step is controlled so as to never go out from the quadratically behaved regions of the surface (the trust regions). Additionally, one can set the maximum trust radius to a given value **MAXTRADIUS** [def ∞], in order to avoid too large displacements from one point to the next one.

Additional combined test on gradient and energy are adopted for treating special cases:

1. If the gradient criteria are satisfied (but not the displacement criteria) and the energy difference between two steps is below a given threshold (see **TOLDEE**), the optimization stops with a warning message;
2. If both the gradient and displacements criteria are not satisfied, but the energy does not change (**TOLDEE** parameter) for four subsequent steps, the optimization stops with a warning message.

Restart optimization

Restart of geometry optimization is possible for a job which is abruptly terminated (e.g. number of steps exceeded, available cpu time exceeded,...).

The optimization restarts from the last complete step of the previous run.

The geometry at each step is written to file `optc_number_of_step`, and can be read by **EXTERNAL** (see page 16).

If optimization ended successfully, the optimized geometry is written to file `fort.34` (**EXTERNAL** format).

When restarting an optimization, information on previous optimization steps is read from file `OPTINFO.DAT`. Optimization then proceeds, saving information in the same file at each step.

The SCF guess, read from file `fort.20`, is the density matrix written in file `fort.9` at the end of

SCF of the last successful step of the optimization process.

*The same input deck as for the initial geometry optimization must be used when the **RESTART** keyword is added.*

Visualizing the optimization process

CRYSTAL output is read by the software MOLDRAW:

<http://www.moldraw.unito.it> to visualize the optimization process.

File fort.33 contains the geometry at each step, in *xyz* format.

5 - Searching a transition state

TSOPT transition state search requested [default: false]

Transition state optimization is invoked by the keyword **TSOPT** in **OPTGEOM** input block.

The reference to be quoted is:

C. M. Zicovich-Wilson, M. L. San-Romn, A. Ramirez-Sols,
Mechanism of F⁻ Elimination from Zeolitic D4R Units: A Periodic B3LYP Study on the Octadecasil Zeolite
J. Phys. Chem. C 114 (2010) 2989-2995.

An example of transition state search is presented in <http://www.crystal.unito.it/tutorials>

By default the eigenvector that corresponds to the lowest eigenvalue is followed uphill according to the scheme proposed by Simmons and Nichols [Simmons, J., and Nichols, J.: , Int. J. Quantum Chem. Symp. 24, volume 24, 263, (1990)].

To adopt other choices for directions to be followed uphill see keywords: **MODEFOLLOW**, **PATHFOLLOW**, **FITTOPATH** and **CHNGTSFOL**.

Transition state control keywords

MODEFOLLOW

- * **MODEFOL** mode to follow
-

ABS(MODEFOL) is the label of the eigenvector to be followed uphill initially, namely DIR(0).

If MODEFOL < 0, the initial uphill direction, DIR(0), is the opposite to that of the eigenvector of label ABS(MODEFOL)

In a general optimization step, NSTEP, the current uphill direction DIR(NSTEP) is chosen as the hessian eigenvector of maximum overlap with the direction chosen in the previous step, DIR(NSTEP-1). In this scheme the uphill direction is allowed to smoothly change along the optimization. Some problems might appear when there are quasi-degeneracies between the Hessian eigenvalue of the uphill direction and other that corresponds to a direction to be followed downhill. In such a case the optimization might go in troubles. Using **PATHFOLLOW** is a safer way to define the uphill direction and so the reaction path.

PATHFOLLOW only with redundant internal coords

- * **NPATHFOL** max coord to choose the mode to follow
-

Only valid together with INTREDUN.

The uphill direction is the eigenvector that has maximal absolute contribution of the internal valence coordinate labeled ABS(NPATHFOL), which is thus supposed to dominate the reaction path.

If NPATHFOL < 0, the uphill search is such that the value of coordinate ABS(NPATHFOL) decreases along the reaction coordinate, otherwise the opposite direction is chosen.

At variance with the MODEFOLLOW case, where the reference direction changes from step to step, here the same strategy is employed in every step of the optimization. This prevents troubles when near-degeneracies occur (see keyword **MODEFOLLOW**).

FITTOPATH only with redundant internal coords
• * NPATHFOL2 integer
 NPATHWEIGHT integer

Only valid together with INTREDUN and PATHFOLLOW

ABS(NPATHFOL2) is the label of a second internal valence coordinate, namely coordinate (II), that together with the one labeled ABS(NPATHFOL), coordinate (I), mostly contributes to the reaction coordinate.

Once the eigenvector with maximum contribution of coordinate (I), namely XMAXCONTR, is obtained (see **PATHFOLLOW** keyword), the eigenvectors are once more scanned and those having a contribution of this coordinate larger in absolute value than XMAXCONTR*(100-NPATHWEIGHT)/100 selected. If NPATHFOL2 > 0 the previously selected eigenvector with maximum contribution of coordinate (II) with the same sign of XMAXCNTR is chosen as uphill direction. Otherwise, the one with maximum contribution having opposite sign is considered.

CHNGTSFOL only with redundant internal coords

Valid together with **INTREDUN**, **PATHFOLLOW** (**FITTOPATH**).

The optimization follows uphill the path according to the **PATHFOLLOW** (**+FITTOPATH**) scheme while the chosen eigenvector is not the first one in the list ordered by increasing eigenvalues, i.e. it has not the lowest eigenvalue. Once such a situation reverts, the scheme changes to **MODEFOLLOW** in the following steps and the uphill direction is chosen according to the criterion of maximum overlap with the previous uphill direction (see **MODEFOLLOW** keyword).

Scan keywords

SCANATOM
• * NATSCAN (integer): label of the atom to be scanned
 TARGET (real array dim 3): last position of the atom in the scan
 MSCAN number of steps in which the previous displacement is carried out

Only for P1 structures.

Perform a series of optimizations in which one atom is kept fixed at different contiguous positions and the remainder of the structure fully or partially relaxed.

Compatible with the optimization of atomic positions (default) and atoms+cell (**FULLOPTG**).

| |
|--|
| <p><i>Not compatible with INTREDUN. The atom chosen for scan and any other one with the only condition that belongs to that part of the system chosen to remain associated to the center of mass, must be defined as fixed with the FRAGMENT option.</i></p> |
|--|

This directive may be used associated with **FRAGSCAN**. The keyword has the same syntax as **FRAGMENT** and defines a set of atoms that after each step of the scan have the same displacement of the scanned atom, **NATSCAN**, so as to set the geometry of the starting point of the next optimization of the sequence.

| | |
|--------------------|--|
| SCANREDU | To be used with INTREDUN only |
| • * IREDSKA | (integer): type of valence coordinate to be scanned (1, bond length; 2 angle; 3 dihedral) |
| ENDSKA | (real): last value taken by the chosen coordinate along the scan The initial value is the current one with the geometry defined for the structure. |
| MAXSKA | number of points considered in the scan |

Perform a series of optimizations (scan) in which one (or two) redundant valence internal coordinate(s) are kept fixed at different values while the remainder are fully relaxed.

To be used only with **INTREDUN**.

The directive **SCANREDU** must be accompanied with freezing the redundant valence internal coordinate(s) one wants to scan (see keywords **FREEZINT** (page 136), **FREEZDIH** (page 137), **ANGSFROZEN** (page 135), **LNGSFROZEN** (page 135).

According to the order of the coordinates given in the output (see **INTREDUN**, **TESTREDU**) the scan is performed on the last frozen coordinate (indicated in the output by a "T") of type **IREDSKA**. If **SCANREDU** is requested twice with the same **IREDSKA**, the second time it refers to the last but one frozen coordinate of type **IREDSKA**.

SCANREDU may be requested at maximum twice so as to carry out a bidimensional scan.

The use of **BKTRNSF2** (see pag. 130) may improve the accuracy in the displacements between two consecutive optimizations of the scan, particularly when they are rather large.

Chapter 4

Vibration Frequencies

FREQCALC - Calculation of vibration frequencies

The calculation of the vibration harmonic frequencies is invoked by the keyword **FREQCALC** in input block 1 (geometry). **FREQCALC** must be the last keyword in the geometry input block. **FREQCALC** admits several options (subkeywords) listed below and terminates with keyword **END** (or END[FREQ], END[—]: only the first three characters are processed).

References to be quoted when using this module:

F. Pascale, C.M. Zicovich-Wilson, F. Lopez, B. Civalleri, R. Orlando, R. Dovesi
The calculation of the vibration frequencies of crystalline compounds and its implementation in the CRYSTAL code., J. Comput. Chem. 25 (2004) 888-897

C.M. Zicovich-Wilson, F. Pascale, C. Roetti, V.R. Saunders, R. Orlando, R. Dovesi
The calculation of the vibration frequencies of alpha-quartz: the effect of Hamiltonian and basis set., J. Comput. Chem. 25 (2004) 1873-1881

Besides harmonic vibration frequency calculation at the Γ -point [default] it allows:

1. Calculation of infrared (IR) intensities (**INTENS**, page 150).
2. Calculation of Raman intensities (**INTRAMAN**, page 152).
3. Scanning of geometry along selected normal modes (**SCANMODE**, page 154).
4. Calculation of the infrared spectra (**IRSPEC**, page 158).
5. Calculation of the Raman spectra (**RAMSPEC**, page 160).
6. Phonon dispersion at the harmonic level (**DISPERSION**, page 161).
7. Calculation of the atomic Anisotropic Displacement Parameters (ADP) at any temperature (**ADP**, page 164).
8. Thermodynamical properties at different temperatures and pressures (see page 148).

The second derivatives of the energy are computed numerically by using the analytical first derivatives (gradients). Frequencies are obtained by diagonalizing the mass-weighted Hessian in Cartesian coordinates.

Symmetry exploitation

The point group symmetry of the lattice is used to reduce the number of SCF+gradient calculations to be performed. At each point, the residual symmetry is exploited for the SCF calculation.

Second derivatives calculations are done on the irreducible atoms only. The full Hessian matrix is then generated by applying the point group symmetry to the irreducible part. The

mass-weighted Hessian matrix is diagonalized to obtain eigenvalues, which are converted in frequencies (cm^{-1}), and eigenvectors, i.e. the normal modes.

Geometry

The first step to compute frequencies is the calculation of the wave function at the equilibrium geometry. The geometry of the system **must** correspond to a stationary point on the potential energy surface.

Geometry optimization can be either performed on a previous run or controlled by two sub-keywords of **FREQCALC**:

NOOPTGEOM do not perform previous optimization in **FREQCALC** job [default]

PREOPTGEOM perform optimization before starting the vibrational modes calculation.

_____ insert **OPTGEOM** keywords (close with **END**) _____ II

_____ keyword **END** _____ II

An input block is opened that must finish with keyword **END**. The numerical conditions for the optimization are controlled by means of the same keywords as documented in page 118 (keyword **OPTGEOM**).

The conditions adopted by default in geometry optimization before frequency calculation are different than those considered for normal optimizations in order to obtain much more accurate minima numerical second derivatives. This ensures a good accuracy in the computation of the frequencies and modes. The defaults are:

| | |
|--------------------|---------|
| TOLDEG | 0.00003 |
| TOLDEX | 0.00012 |
| FINALRUN | 4 |
| MAXRADIUS | 0.25 |
| TRUSTRADIUS | .TRUE. |

If frequency calculation is restarted (keyword **RESTART**, page 149) the input geometry must be the final optimized geometry found by **PREOPTGEOM**.

Default choices

The SCF wave-function starting guess for the calculations of all the displaced geometries necessary to compute the numerical second derivatives of the total energy is the density matrix obtained at the equilibrium geometry.

The default value for SCF convergence criterion on total energy is set to 10^{-9} (use the **TOLDEE** keyword in input block 3 to modify it).

The default choice for DFT grid, when a DFT Hamiltonian is used, corresponds to **XLGRID** (page 91).

The calculation of longitudinal-optical (LO) frequencies and infrared (IR) intensities is not performed by default. If the **INTENS** (page 150) keyword is used, intensities are evaluated. The **FREQCALC** input block must be closed by the keyword **END** (or **ENDFREQ**). All additional keywords (see below) to be put in between are optional.

Output files

Here is a list of the files that are written during a frequency calculation, to be saved in order to restart a calculation:

SCFOUT.LOG The output from the wave function and gradient calculation is printed in standard output for the reference geometry only. The output for the displaced configurations is then written in file SCFOUT.LOG.

FREQINFO.DAT Formatted. Contains information on the Hessian. Updated at each point, it is necessary to restart a frequency calculation.

HESSFREQ.DAT Formatted. Contains the Hessian in Cartesian coordinates to be read by **HESSFREQ** in geometry optimization input block.

fort.9 Binary. Wave function computed at the equilibrium geometry. Full symmetry exploited by default. When those data are used to restart, file fort.9 is read as file fort.20 (SCF guess).

fort.13 Binary. Reducible density matrix at central point. To exploit maximum symmetry in numerical second derivatives calculations.

fort.28 Binary. Data for restart of IR intensities calculation through Berry phase approach.

fort.80 Binary. Localized Wannier functions, computed only if IR intensities are computed through Wannier functions.

Optional keywords

This is a list of some possible (optional) subkeywords to be inserted after **FREQCALC**. This is just a partial list since the main subkeywords are described into details in the following sections of this chapter:

-
- A **ANALYSIS** Analysis of the vibrational modes
-
- A **CHI2TENS** to be used if **INTRAMAN** is active (pages 150,152). Reads the second-order anisotropic dielectric tensor for the calculation of the LO Raman intensities.
 - * **TENS(1:27)** second-order dielectric tensor matrix TENS (3x9 elements, input by rows: 27 reals (3D)).
The tensor elements can be computed using the **CPHF** keyword (see page 168) at **FOURTH** order (page 5).
-

-
- A **COMBMODE** Evaluation of transverse optical combination modes and overtones at the Γ point. A set of options are available, which are described below. This keyword opens an input block that must be closed by **END**.
 - A .. Optional sub-keywords
 - A **END**
- List of optional sub-keywords
- A **IR** Only infrared (IR) active combination modes and overtones are displayed in the output.
 - A **RAMAN** Only Raman active combination modes and overtones are displayed in the output.
 - A **IRRAMAN** IR and Raman active combination modes and overtones are displayed in the output.[default]
 - A **ALL** All vibrational combination modes and overtones are displayed in the output.
 - A **FREQ** Combination modes and overtones are sorted according to the frequency value. [default]
 - A **IRREP** Combination modes and overtones are sorted according to the IRREP.
 - A **FREQRANGE** Only combination modes and overtones with frequency included within FMIN and FMAX are displayed in the output.
 - * FMIN,FMAX Boundaries of the frequency range. Default: $[0., 1.3 \nu_{max}]$.
-

-
- A **DIELISO** to be used if **INTENS** is active (page 150). Reads the isotropic diagonal dielectric tensor (dielectric constant) for the calculation of the LO/TO splitting. The dielectric constant has to be computed on a previous run with options **CPHF** (page 168) or **SUPERCEL - FIELD** and **DIEL** (see page 42) applied for each axis of the system.
 - * **DIEL** dielectric constant
-

- A **DIELTENS** to be used if **INTENS** is active (page 150). Reads the anisotropic dielectric tensor for the calculation of the LO/TO splitting. If **INTRAMAN** is active, the keyword **CHI2TENS** should also be declared.
 - * **TENS(1:9)** Dielectric tensor matrix TENS (3x3 elements, input by rows: 9 reals (3D).
The dielectric tensor elements can be obtained from the literature or computed using the **CPHF** keyword (see page 168) or the **SUPERCEL - FIELD** keywords (see page 42).
-

- A **ECKART** Eckart conditions imposed to project out of the Hessian matrix purely translational and rotational degrees of freedom (see page 291 for more details). **Note that this option is now active by default. This was not the case in the previous versions**
-

-
- A **FRAGMENT** Frequency calculation on a moiety of the system
 - * NL number of atoms active for frequencies
 - * LB(L),L=1,NL *label* of the active atoms
-

Frequency calculation can be limited to an atomic fragment, instead of the whole system. Symmetry is removed. If a fragment contains symmetry related atoms, they must be explicitly defined. A reduced Hessian is computed, according to the list of atoms belonging to the fragment. A chemically sound moiety of the system must be considered to avoid random results.

-
- A **ISOTOPES** atomic masses modified
 - * NL number of atoms whose atomic mass must be modified
- II _____ *insert NL records* _____ II
- * LB,AMASS *label* and new atomic mass (amu) of the atom.
- II _____ II

When the isotopic mass of one atom symmetry related to others is modified, the symmetry of the electronic wave function is not modified, as the mass of the atoms is not present in the single particle electronic Hamiltonian. For instance, if in a methane molecule (point group T_d) we want to substitute H with D, we can redefine the mass of the 1, 2, 3, 4 hydrogen atoms; if C is the first atom, the corresponding input are:

| 1 H atom | 2 H atoms | 3 H atoms | 4 H atoms |
|------------|------------|------------|------------|
| ISOTOPES | ISOTOPES | ISOTOPES | ISOTOPES |
| 1 | 2 | 3 | 4 |
| 2 2.000 | 2 2.000 | 2 2.000 | 2 2.000 |
| | 3 2.000 | 3 2.000 | 3 2.000 |
| | | 4 2.000 | 4 2.000 |
| | | | 5 2.000 |

If a single D is inserted, the symmetry is reduced, (point group C_{3v}), the three-fold degeneracy becomes two-fold. When all the four hydrogens are substituted, the three-fold degeneracy is restored.

If a frequency calculation was performed with standard atomic masses, new frequencies values with different atomic masses for selected atoms can be computed from the Hessian already computed, at low computational cost, by inserting the keyword **RESTART** in **FREQCALC** input block, and supplying the file **FREQINFO.DAT** written by the previous run.

-
- **A MODES** Printing of eigenvectors [default]
-
- **A MULTITASK** This keyword allows the simultaneous execution of independent SCF+G calculations. It is aimed at the exploitation of the large processor counts available on High Performance Computing facilities. Allocation of too many processors results in performance degradation due to the communication overhead between the processors. When many independent tasks are usually performed sequentially, MULTITASK performs N tasks at the same time, so that an N-fold increase in the number of allocated processors can be requested, without losing performance.
 - * N Number of tasks. For example if N=8 is requested and the job is running on a total of NCPU=128 cores, 8 tasks with 16 cores each will be created. N should be greater than one and smaller than the total number of cores NCPU ($1 < N \leq \text{NCPU}$). N should be a divider of NCPU, so that each task will run on the same amount of processors.
-
- **A NEGLEFRE** Reads the number of lowest vibration frequencies to be neglected in the computation of the thermodynamical properties. By default, the (rotational)+translational degrees of freedom are automatically neglected. This keyword allows to neglect further soft vibrations with low frequencies which may carry numerical issues on the computation of thermodynamical properties.
 - * N Number of frequencies to be neglected
-
- **A NOANALYSIS** No analysis of the vibrational modes [default]
-
- **A NOECKART** Eckart conditions not imposed to the Hessian.
-
- **A NOINTENS** No calculation of the IR intensities [default choice].
-
- **A NOMODES** No printing of eigenvectors
-
- **A NORMBORN** Normalize Born tensor to fulfill sum rule
-
- **A NOUSESMM** Symmetry is removed, the space group is set to P_1
-

| | |
|-----------------------|--|
| • A NUMDERIV | specifies the technique to compute the numerical first-derivatives $h(x)=dg(x)/dx$ of the gradient $g(x)=dE(x)/dx$ |
| • * N | 1 different quotient formula: $h(x)=(g(x+t)-g(x))/t$ $t=0.001 \text{ \AA}$ (one displacement for each atom along each cartesian direction) 2 Central-difference formula: $h(x)=(g(x+t)-g(x-t))/2t$ $t=0.001 \text{ \AA}$ (two displacements for each atom along each cartesian direction) |
| • A PRESSURE | Pressure range for thermodynamic analysis |
| • * NP,P1,P2 | 3 reals, NP is the number of intervals in the pressure range P1 to P2 (MPa) [1,0.101325,0.101325] |
| • A PRINT | Extended printing active (Hessian and Hessian eigenvectors) |
| • A RAMANEXP | Takes into account experimental conditions (temperature, incoming laser) in the calculation of Raman intensities, according to Eq. 4.9 (see page 153). |
| • * T,FREQ | 2 reals, T is the temperature, FREQ is the frequency (in nm) of the incoming laser. |
| • A RESTART | Restart frequency calculation from a previous run. See page 149. |
| • A STEPWISE | Modify the step size of displacement along each cartesian axis |
| • * STEP | step (\AA) for numerical derivatives [0.003] |
| • A TEMPERAT | Temperature range for thermodynamic analysis |
| • * NT,T1,T2 | 3 reals, NT is the number of interval in the range T1 to T2 temperature (K) [1,298.0,298.0] |
| • A TEST[FREQ] | Frequency test run |
| • A USESMM | Maximum space group symmetry used to compute wave function at each point [default] |

Partition of the modes into Building Unit contributions

The external portion of the motion of the b -th Building Unit (BU) in mode i is quantified by means of

$$\epsilon_{bi} = \frac{(\mathbf{P}^{(b)}\mathbf{e}_i)^2}{N_{bi}}, \quad (4.1)$$

where matrix $\mathbf{P}^{(b)} \equiv P_{A\alpha,B\beta}^{(b)}$, with atoms A, B belonging to the b -th BU, is the projector onto the roto-translational degrees of freedom of the unit taken as an isolated fragment and $N_{bi} = \sum_{A \in b} \sum_{\alpha=1}^3 e_{i,A\alpha}^2$ is a normalization factor. Accordingly, the corresponding internal contribution is given by $1 - \epsilon_{bi}$.

The contribution of the b -th BU to mode i is computed as

$$\xi_{bi} = \sum_{\alpha=1}^3 \sum_{A \in b} \frac{e_{i,A\alpha}^2}{m_A}, \quad (4.2)$$

where m_A is the number of BUs to which atom A belongs. If the mode vector is normalized Eq. (4.2) ensures that $\sum_b \xi_{bi}$ gives the portion of the mode covered by the partition (1 if a full partition is considered). By adopting such partitions, the internal and external contributions (per cent) of the b -th BU to mode i are given by $\Gamma_{bi}^{(n)} = (1 - \epsilon_{bi}) \times \xi_{bi} \times 100$ and $\Gamma_{bi}^{(x)} = \epsilon_{bi} \times \xi_{bi} \times 100$, respectively. In some cases one may be interested in considering the overall external contribution under a given BU partition. This is given by

$$\Xi_i = \frac{\sum_b \Gamma_{bi}^{(x)}}{\sum_b \xi_{bi}}, \quad (4.3)$$

where $\sum_i \Xi_i$ is not 100%, but the percentage of the structure covered by the BUs considered in the partition.

Though this analysis may be somehow arbitrary, the resulting indices provide a systematic and clear description of most of the significant features of the vibrational modes of the system under study.

The keyword **BUNITSDECO** performs a building unit decomposition of the vibrational modes. The vibrational modes are decomposed in terms of internal and external motions of some units defined by input. The latter correspond to rotations and translations of the units behaving like rigid, while the former to the relative motions of the constitutive atoms.

| | |
|---|---|
| BUNITSDECO | perform a building unit decomposition of the vibrational modes. |
| • * NBDNGUNIT | number of building units irreducible by symmetry considered (the units symmetry-equivalent are automatically generated) |
| • * MBDNGUNIT(I), I=1,NBDNGUNIT | number of atoms of each unit. The sum defines NATOMS, the total number of atoms considered |
| • * (LBDNGUNIT(JA,IU), JA=1,4,IU=1,NATOMS) | identification of the atoms: for each atom, the sequence number and three cell indexes, in the order given in MBDNGUNIT |

Restart a calculation

A frequency calculation for a job abruptly terminated (e.g. machine crash, exceeded the available cpu time,...). can be restarted exactly from the last point of the previous run.

The same input deck used for the incomplete calculation, with the keyword **RESTART** in the **FREQCALC** input block is submitted. The following files, written by the previous job, must be present:

FREQINFO.DAT formatted - information on the part of the hessian already computed.

fort.20 binary - wave function at the equilibrium geometry, with no symmetry, as guess for SCF process (fort.9 saved at the end of single point calculation).

fort.28 (binary) Data for restart of IR intensities calculation through Berry phase approach.

fort.80 (binary) localized Wannier functions (if IR intensities through Wannier functions are computed).

fort.13 binary - Reducible density matrix at central point. To exploit maximum symmetry in numerical second derivatives calculations.

IR intensities calculation using Berry phase or Wannier functions must be present in the first frequency calculation, it can not be inserted in restart only. It is however possible to do so with CPHF analytical intensities.

The restart option can be used to modify the algorithm used to compute gradients (switch from different quotient formula to Central-difference formula, keyword **NUMDERIV**). In this case the new points only are calculated. The same input deck as for the initial frequency calculation must be used.

Restart can be used to evaluate frequencies for a system with different isotopes of selected atoms (keyword **RESTART** followed by **ISOTOPES** 146).

1 - IR intensities

Calculation of IR intensities is invoked by the keyword **INTENS** in **FREQCALC** input block.

Three different techniques can be adopted:

- IR intensities through Berry phase - keyword **INTPOL** [default]
- IR intensities through Wannier functions - keyword **INTLOC**
- IR intensities through CPHF approach - keyword **INTCPHF**

The first two approaches imply numerical differentiations, while the latter is entirely analytical. Atomic Born tensors are the key quantities for the calculation of the IR intensities, the oscillator strengths, the LO/TO splitting and the static dielectric tensor. Such quantities are written in the external formatted unit BORN.DAT.

In order to compute the LO/TO splitting, the high frequency dielectric tensor must be provided. See keyword **DIELTENS**, page 145.

The integrated IR intensity I_p for the p - th mode is computed according to:

$$I_p = \frac{\pi N_A}{3 c^2} \cdot d_p \cdot |\vec{Z}_p|^2 \quad (4.4)$$

where N_A is the Avogadro's number, c is the speed of light, d_p is the degeneracy of the mode, \vec{Z}_p is the mass-weighted effective mode Born charge vector.

The oscillator strength tensor f_p for the p - th mode is computed according to:

$$f_{p,ij} = \frac{4\pi}{\Omega} \frac{\vec{Z}_{p,i} \vec{Z}_{p,j}}{\nu_p^2} \quad (4.5)$$

here Ω is the unit cell volume, ν_p is the mode TO frequency and \vec{Z}_p is again the mass-weighted effective mode Born charge vector.

- IR intensities through Berry phase [default]

Calculation of IR intensities through Berry Phase approach, keyword **INTPOL**, is the default choice.

This is possible for 3D, 2D, 1D and 0D systems, but only for insulating system.

The Berry phase approach consists in evaluating the atomic Born tensors, that is the derivative of the dipole moment with respect to the atomic displacements, as polarization differences between the central and the distorted geometries: the polarization difference is then equal to the time-integrated transient macroscopic current that flows through the insulating sample during the vibrations.

The scheme operates on the crystalline-orbital eigenfunctions in the reciprocal space. As a

consequence of that, the accuracy of IR intensities might be sensitive to the density of the Monkhorst net.

There are no additional keywords related to this method.

- IR intensities through Wannier functions

Calculation of IR intensities through Wannier functions is invoked by the keyword **INTLOC** following **INTENS** in **FREQCALC** input block.

Many keywords are related to the Wannier functions calculation that should be used by developers and very experienced users only.

If keyword **INTLOC** is activated in **FREQCALC** input block, IR intensities, atomic Born tensors and LO/TO splitting are evaluated through the Wannier functions, obtained by localizing the crystalline orbitals. This is possible for insulators only.

IR intensities calculation through localization is very demanding, in terms of memory allocation. **NOINTENS**, default choice, avoids intensity calculation, when not necessary.

As regards the computation of the IR intensities, they are obtained by means of the Wannier Function (WF) approach, in which those functions span the occupied manifold and are explicitly constructed in real space. They are at time obtained from the eigenvectors of the one-electron Hamiltonian (Bloch Functions) by numerical integration in reciprocal space through the definition of a Pack-Monkhorst net. The system must be an insulator. By default the dipole moment in the non central points are computed with Wannier Functions that are the projection onto the occupied space of the current point of those obtained by localization at the central point. If **RELOCAL** is requested these WFs are relocalized at each point

This procedure leads not to real WFs, but to an approximation contained into a cyclic space. In the mapping (unfolding) that permits to convert cyclic to real WFs, **CRYSTAL** exploits the classification of the lattice vectors made at the very beginning of the SCF calculation that, obviously, does not involve the infinite space, but just a cluster of a finite number of cells, ordered by increasing length (i.e. it covers a close to spherical region of the real space).

In all the tested cases, this classification provides sufficient room to represent the matrices needed in the SCF part within the required accuracy. This is also so in what concerns the (post-SCF) computation of the WFs, apart from very particular cases in which the primitive cell is oblong and the corresponding unfolded cyclic cluster associated to the Monkhorst-Pack net (also very elongated in one direction) does not fit into the real cluster (always close to spherical shape).

A set of keywords can be used to modify the localization process (see *properties* input, keyword **LOCALWF**, page 215) They are entered after the **DIPOMOME** keyword. Modification of default choices is not recommended, it should be restricted to developers only.

The keyword **DIPOMOME** defines an input block (closed by **END**) with keywords allowing modification of the localization process.

To be modified by developers only.

- A **DIPOMOME** Calculation of the dipole moment - see Localisation part (properties, keyword **LOCALWF**, page 215
To be modified by developers only.
 - A **END** end of the **DIPOMOME** block.
-
- all keywords are optional* II
- A **DMACCURA** (Optional) Change the final dipole moment tolerance
 - * **NTOL** Value of the new tolerance as $TOLWDM=0.1^{-NTOL}$
-
- A **RELOCAL** (Optional) Relocalize all points in frequency calculations
 - A **BOYSCTRL** see **LOCALWF**, page 218
 - A **CAPTURE** see **LOCALWF**, page 220
 - A **WANDM** see **LOCALWF**, page 225
 - A **FULLBOYS** see **LOCALWF**, page 225
 - A **MAXCYCLE** see **LOCALWF**, page 218
 - A **CYCTOL** see **LOCALWF**, page 217
 - A **ORTHNDIR** see **LOCALWF**, page 224
 - A **CLUSPLUS** see **LOCALWF**, page 224
 - A **PHASETOL** see **LOCALWF**, page 217
 - A **RESTART** see **LOCALWF**, page 217
 - A **IGSSBND** see **LOCALWF**, page 220
 - A **IGSSVCTS** see **LOCALWF**, page 220
 - A **IGSSCTRL** see **LOCALWF**, page 220
-

- IR intensities through CPHF/CPKS

Calculation of IR intensities through Coupled-Perturbed Hartree-Fock/Kohn-Sham approach, keyword **INTCPHF**, allows for completely analytical calculation of Born charges and, hence, IR intensities.

A few optional keywords are available:

- **IRREA**: reads the tensor of Born charges from file **TENS_IR.DAT**. Note that if a frequency restart is performed, the tensor is automatically retrieved from file **FREQINFO.DAT** unless the keyword **DOINTCPHF** is used (see below).
- **IRSPEC**: The IR spectrum is produced using Lorentzian broadening and stored in file **IRSPEC.DAT**

The **INTCPHF** keyword opens a CPHF input block, that must be closed by **END**. Here all keywords proper to the **CPHF** keyword (page 168) can be adopted.

-
- all keywords are optional* II
-
- A **FMIXING** see **CPHF**, page 168
 - A **RESTART** see **CPHF**, page 168
 - A **TOLALPHA** see **CPHF**, page 168
 - A **MAXCYCLE** see **CPHF**, page 168
-

Alternatively to the **INTCPHF** keyword, users can use **DOINTCPHF**. It has the same meaning and optional keywords, but in a case of a frequency restart it forces the calculation of Born (or Raman, see below) tensor instead of reading it from **FREQINFO.DAT**

2 - Raman intensities

The calculation of analytical Raman intensities [115, 116] can be activated through the **INTRAMAN** keyword. If the Raman tensor is not already available (on unit **TENS_RAMAN.DAT** or inside **FREQINFO.DAT**) it must be computed by inserting the keyword **INTCPHF**. As for IR intensities, **INTCPHF** opens a CPHF block that must be closed

by the **END** keyword. Be careful that the **INTRAMAN** should be always used *together with the INTENS keyword*. A Coupled-Perturbed Hartree–Fock/Kohn–Sham approach calculation up to fourth-order (CPHF2) will be performed, prior to the calculation of frequencies. The Raman tensor, after a successful calculation, is written in a formatted unit named **TENS_RAMAN.DAT**. The same information is stored in the file **FREQINFO.DAT**. The simplest possible input of the frequency block is, then:

```
FREQCALC
INTENS
INTRAMAN
INTCPHF
END
END
```

For an oriented single-crystal the Raman Stokes scattering intensity associated with, for instance, the xy component of the polarizability tensor corresponding to the i -vibrational mode of frequency ω_i may be calculated as:

$$I_{xy}^i \propto \left(\frac{\alpha_{xy}}{\partial \mathcal{Q}_i} \right)^2 \quad (4.6)$$

where \mathcal{Q}_i is the the normal mode coordinate for mode i .

While the intensity of the transverse optical (TO) modes is straightforwardly computed once the appropriate polarizability derivative is obtained, the corresponding calculation for longitudinal optical (LO) modes requires a correction[105, 177] due to $\chi_{bcd}^{(2)}$:

$$\begin{aligned} \left. \frac{\partial \alpha_{b,c}}{\partial \mathcal{R}_a^A} \right|_{\mathcal{R}_0} &= \frac{1}{V} \left. \frac{\partial^3 E^{TOT}}{\partial \mathcal{R}_a^A \partial \mathcal{E}_b \partial \mathcal{E}_c} \right|_{\mathcal{E}=0, \mathcal{R}_0} \\ &\quad - 2 \sum_{b'} Z_{b'aA}^* \sum_{d'} \epsilon_{b',d'}^{-1} \chi_{bcd'}^{(2)} \end{aligned} \quad (4.7)$$

In Eq. (4.7) ϵ^{-1} is the inverse of the high-frequency (*i.e.* pure electronic) dielectric tensor. $\chi^{(2)}$ is defined as in Eq. (69) of Ref. [69]. All these quantities ($Z_{b'aA}^*$, ϵ^{-1} and $\chi_{bcd'}^{(2)}$) are saved in **FREQINFO.DAT** file for restart, since they are obtained as a byproduct of the Raman intensities calculation. Otherwise, the first and second-order dielectric tensors can be provided in input through the keywords **DIELTENS** and **CHI2TENS**, respectively.

Finally, as commonly done in the reporting of experimental data, the intensities are normalized to the highest peak, arbitrarily set to 1000.00.

A few optional keywords are available:

- **RAMANEXP**: In the case the user desires to reproduce experimental conditions, Eq. 4.6 is substituted by

$$I_{xy}^i \propto C \left(\frac{\alpha_{xy}}{\partial \mathcal{Q}_i} \right)^2 \quad (4.8)$$

The prefactor C depends[177] on the laser frequency ω_L and the temperature T :

$$C \sim (\omega_L - \omega_i)^4 \frac{1 + n(\omega_i)}{30\omega_i} \quad (4.9)$$

with the Bose occupancy factor $n(\omega_i)$ given by

$$1 + n(\omega_i) = \left[1 - \exp \left(-\frac{\hbar\omega_i}{K_B T} \right) \right]^{-1} \quad (4.10)$$

The polycrystalline (powder) spectrum can be computed by averaging over the possible orientations of the crystallites as described in Eq. (4) and (5) of Ref. [147], which we used for our implementation.

- **RAMANREA**: reads the Raman tensor from file **TENS_RAMAN.DAT**. Note that if a frequency restart is performed, the tensor is automatically retrieved from file **FREQINFO.DAT** unless the keyword **DOINTCPHF** is used (see below)
- **NORENORM**: Turns off renormalization of the Raman intensity to the highest peak
- **RAMSPEC**: The Raman spectrum is produced using Lorentzian broadening and stored in file **RAMSPEC.DAT**
- **TENSONLY**: After the calculation of the IR and Raman tensors, and their storage in files **TENS_IR.DAT** and **TENS_RAMAN.DAT**, the calculation stops
- **ROTRAMAN**
 θ, φ, ψ
 The Raman tensor is rotated according to the three angles (in degrees) provided in input. For the meaning of such angles and see the effect of the rotations see <http://www.cryst.ehu.es/cryst/transformtensor.html>

Here all keywords proper to the **CPHF** keyword (page 168) can be adopted. Note that in the case of a DFT calculation the CPHF defaults are set to **FMIXING=FMIXING2=60**, **MAXCYCLE=MAXCYCLE2=200**.

_____ all keywords are optional _____ II

| | |
|----------------------|----------------------------|
| • A FMIXING2 | see CPHF , page 168 |
| • A TOLGAMMA | see CPHF , page 168 |
| • A MAXCYCLE2 | see CPHF , page 168 |

Alternatively to the **INTCPHF** keyword, users can use **DOINTCPHF**. It has the same meaning and optional keywords, but in a case of a frequency restart it forces the calculation of Born and Raman tensor instead of reading it from **FREQINFO.DAT**

3 - Scanning of geometry along selected normal modes

Scanning of geometry along selected normal modes is invoked by the keyword **SCANMODE** in **FREQCALC** input block. Preliminary frequency calculation is required to single out the selected mode.

| rec | variable | meaning |
|-----|--------------|---|
| • * | NMO | NMO number of modes to be scanned. > 0 SCF calculation at each point along the path - energy is computed < 0 only the geometry along the path is computed (no SCF calculation) |
| | INI | Initial point for the scan |
| | IFI | Final point for the scan |
| | STEP | Step given as a fraction of the maximum classical displacement, that corresponds to the 1.0 value |
| • * | N(I),I=1,NMO | sequence number of the modes selected. |

Let $|r_0\rangle$ be the equilibrium configuration; then the following configurations are explored: $|r_i\rangle = |r_0\rangle + i\Delta|u\rangle$, where $|u\rangle$ is the eigenvector of the selected mode, i is a positive or negative integer, running from **INI** to **IFI**, and Δ is the step. $IFI - INI + 1$ is the number of points that will be considered in the $INI * STEP - IFI * STEP$ interval. If the **STEP** variable is set to 1.0, the maximum classical displacement is computed. This displacement corresponds to the point where the potential energy in the harmonic approximation is equal to the energy of the fundamental vibrational state as follows:

$$V = E_0^{vib}$$

$$\frac{1}{2}kx^2 = \frac{1}{2}\hbar\omega$$

Where $x = |r_{max}\rangle - |r_0\rangle$ and the force constant k is given by:

$$k = \omega^2 \mu$$

The final expression of the maximum classical displacement is therefore:

$$x = \sqrt{\frac{\hbar}{\omega \mu}}$$

This option can be useful in two different situations.

Let us consider ν_i as the frequency of the Q_i normal mode:

$\nu_i > 0$ we want to explore the energy curve along Q_i normal mode and check the deviation of the energy from the harmonic behaviour. See example 1;

$\nu_i < 0$ the system is in a transition state. We want to explore the Q_i normal mode in order to find a total energy minimum; usually Q_i is not total-symmetric, the symmetry of the structure needs to be reduced. CRYSTAL determines automatically the subgroup of the original group to which the symmetry of the mode belongs. See example 2.

At each point, the geometry is written in file "SCANmode_number.frequencyvalue.DISP_iΔ" (see below), in a format suitable to be read by the keyword **EXTERNAL** (geometry input, page 16).

The geometry of the system then has to be re-optimized in this new subgroup using as a starting geometry one of those external files (better the one corresponding to the minimum). Frequencies can then be evaluated in the new minimum and the new set of frequencies should contain only positive values (apart from the three referring to translations).

Example 1 - Methane molecule

First run: optimization of the geometry (full input at page 266).

Second run: calculation of the vibrational frequencies of CH_4 in the optimized geometry. The optimized geometry corresponds to a minimum, as all frequencies are positive (modes 1-3, translational mode; modes 4-6, rotational modes).

| MODES | EIGV (HARTREE**2) | FREQUENCIES (CM**-1) | IRREP | IR | RAMAN |
|--------|----------------------|-------------------------|-------|----|-------|
| 1- 3 | -0.1863E-11 | -0.2995 | (F2) | A | A |
| 4- 6 | 0.7530E-07 | 60.2270 | (F1) | I | I |
| 7- 9 | 0.4821E-04 | 1523.8308 | (F2) | A | A |
| 10- 11 | 0.6302E-04 | 1742.3056 | (E) | I | A |
| 12- 12 | 0.2099E-03 | 3179.3763 | (A) | I | A |
| 13- 15 | 0.2223E-03 | 3272.4193 | (F2) | A | A |

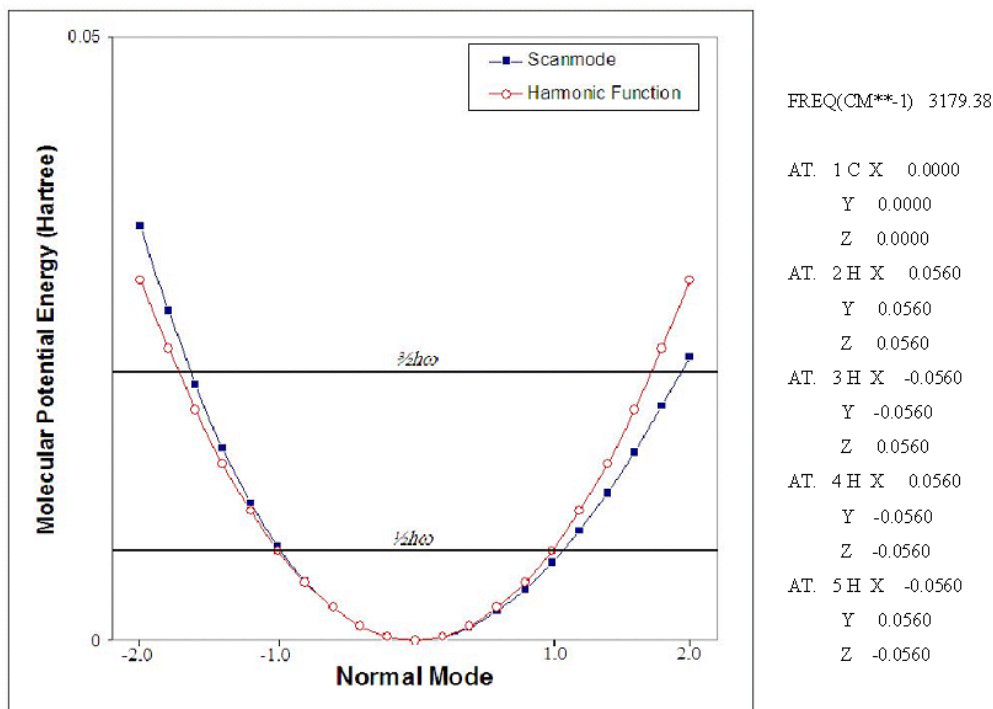
Third run: Scanning of a selected mode.

To explore the 12th normal mode, corresponding to C-H symmetric stretching, the following lines must be inserted before the end of geometry input (RESTART to read from external file vibrational modes, computed in 2nd run):

```
FREQCALC
RESTART
SCANMODE
1 -10 10 0.2
12
END
```

The potential energy function as well as its harmonic approximation is computed and represented in the figure. The anharmonicity of C-H stretching is evident.

Figure 4.1: Scanning of the energy along normal mode 12, $\nu=3179.3763\text{ cm}^{-1}$, corresponding to C–H symmetric stretching



Example 2 - PbCO_3

The space group of this carbonate, as it can be found in the literature [ICSD database], is $Pm\bar{c}n$ (orthorhombic lattice).

First run: full optimization of the geometry in $Pm\bar{c}n$ space group (full input at page 266).

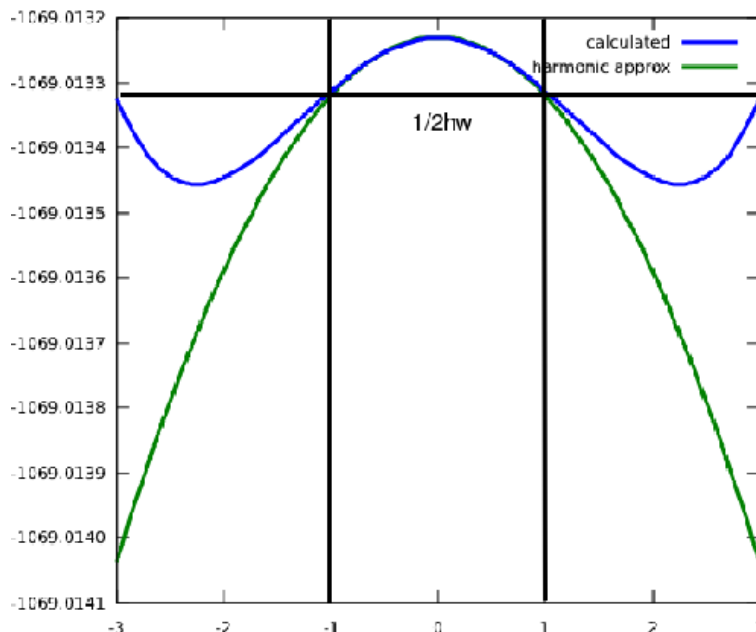
Second run: frequency calculation. The output would look as follows:

| MODES | EIGV (HARTREE**2) | FREQUENCIES (CM**-1) | IRREP | IR | RAMAN |
|--------|----------------------|-------------------------|-------|----|-------|
| 1- 1 | -0.3212E-07 | -39.3362 | (AU) | I | I |
| 2- 2 | -0.1388E-09 | -2.5858 | (B3U) | A | I |
| 3- 3 | -0.6924E-10 | -1.8262 | (B2U) | A | I |
| 4- 4 | -0.2405E-11 | -0.3404 | (B1U) | A | I |
| 5- 5 | 0.4141E-07 | 44.6637 | (AG) | I | A |
| 6- 6 | 0.4569E-07 | 46.9137 | (B3G) | I | A |
| 7- 7 | 0.5304E-07 | 50.5476 | (B1G) | I | A |
| | | | | | |
| 53- 53 | 0.4245E-04 | 1429.9950 | (AU) | I | I |
| 54- 54 | 0.4338E-04 | 1445.5993 | (B1G) | I | A |
| 55- 55 | 0.4340E-04 | 1445.8649 | (AG) | I | A |
| 56- 56 | 0.4401E-04 | 1455.9714 | (B1U) | A | I |
| 57- 57 | 0.4408E-04 | 1457.1539 | (B3G) | I | A |
| 58- 58 | 0.4417E-04 | 1458.5583 | (B3U) | A | I |
| 59- 59 | 0.4475E-04 | 1468.2070 | (B2U) | A | I |
| 60- 60 | 0.5007E-04 | 1553.0286 | (B2G) | I | A |

Four negative frequencies are present. Modes 2, 3 and 4 are translations, as results from their small values ($< 2\text{ cm}^{-1}$) and from a visual analysis (program MOLDRAW [125]); mode 1, frequency -39.3362 cm^{-1} , corresponds to a maximum along the Q_1 normal coordinate.

Third run: scanning of the first normal mode. The input lines for the frequency calculation

Figure 4.2: Scanning of the energy along normal mode 1, corresponding to a frequency of -39.3362 cm^{-1} (L. Valenzano, unpublished results)



block are now the following:

```
FREQCALC
RESTART
SCANMODE
1 -10 10 0.4 scanning of 1 mode, initial point -10, final +10, step 0.4
1
END
```

where we are asking to perform the scan of 1 mode (mode 1), computing energy in 21 points in the interval $-10/+10$ with a step equal to 0.4. Figure 2 shows the energy computed, and the energy in the harmonic approximation.

The optimized geometry of PbCO_3 in $Pm\bar{c}n$ space group corresponds to a transition state.

Fourth run:

We need to fully re-optimize the geometry of the system with symmetry as a subgroup ($P2_12_12$, space group number 19) of the original space group ($Pm\bar{c}n$). The geometry, with correct reduced symmetry, is read (EXTERNAL, page 16) from one of the files written during the scan, copied as file fort.34. For instance SCAN1_-39.3361_DISP_-2.400 (scan of mode 1, frequency -39.3361 cm^{-1} , displacement -2.4 the classical amplitude).

Please refer to the standard script for running CRYSTAL09 to handle input/output file names.

Fifth run:

After full geometry optimization, we are ready to run a new frequency calculation. The new frequency output looks like (just the first four lines are given):

| Modes | EIGV (HARTREE**2) | FREQUENCIES (CM**-1) | FREQUENCIES (THZ) | IRREP | IR | INTENS (KM/MOL) | RAMAN |
|-------|----------------------|-------------------------|----------------------|---------|-------|--------------------|-------|
| 1- | 1 | -0.1504E-09 | -2.6917 | -0.0807 | (B1) | A (0.00) | A |
| 2- | 2 | -0.1414E-09 | -2.6097 | -0.0782 | (B3) | A (0.00) | A |
| 3- | 3 | -0.1690E-11 | -0.2853 | -0.0086 | (B2) | A (0.00) | A |
| 4- | 4 | 0.4363E-07 | 45.8409 | 1.3743 | (A) | I (0.00) | A |

[.]

Only the three expected negative (translational) modes are present, the fourth negative frequency is not present any more. The PbCO_3 structure corresponds now to a minimum in the potential energy surface.

4 - Calculation of the infrared spectra

Keyword **IRSPEC**, inserted in the **FREQCALC** input block, activates the calculation of the infrared spectra. Prior calculation of IR intensities is required (keyword **INTENS**, page 150) and definition of the dielectric tensor matrix (keyword **DIELTENS**, page 145) or of the isotropic dielectric constant (keyword **DIELISO**, page 145).

The keyword **IRSPEC** defines an input block (closed by **END**).

The key quantity is the complex dielectric tensor $\epsilon(\nu)$, which is computed for each inequivalent polarization direction on the basis of a classical Drude-Lorentz model:

$$\epsilon_{ii}(\nu) = \epsilon_{\infty,ii} + \sum_p \frac{f_{p,ii}\nu_p^2}{\nu_p^2 - \nu^2 - i\nu\gamma_p} \quad (4.11)$$

where ii indicates the polarization direction, ϵ_{∞} is the optical dielectric tensor, ν_p , f_p and γ_p are the TO frequency, oscillator strength and damping factor for the p^{th} vibrational mode, respectively. The real and imaginary parts of $\epsilon(\nu)$ are computed; the maxima of the latter function correspond to the TO frequencies. The imaginary part of $1/\epsilon(\nu)$ is computed as well, whose maxima correspond to the LO frequencies.

The real and imaginary parts of the refractive index $n(\nu)$ are obtained for each inequivalent polarization direction by exploiting the relations:

$$\begin{aligned} \{Re[n_{ii}(\nu)]\}^2 - \{Im[n_{ii}(\nu)]\}^2 &= Re[\epsilon_{ii}(\nu)] \\ 2 \cdot Re[n_{ii}(\nu)] \cdot Im[n_{ii}(\nu)] &= Im[\epsilon_{ii}(\nu)] \end{aligned} \quad (4.12)$$

The reflectance curve $R(\nu)$ is computed for each inequivalent polarization direction through:

$$R_{ii}(\nu) = \left| \frac{\sqrt{\epsilon_{ii}(\nu) - \sin^2(\theta)} - \cos(\theta)}{\sqrt{\epsilon_{ii}(\nu) - \sin^2(\theta)} + \cos(\theta)} \right|^2 \quad (4.13)$$

where θ is the angle between the incident beam and the normal to the crystal surface.

The absorbance spectrum $A(\nu)$ is calculated according to four different models:

1. raw superposition of Lorentzian (or Gaussian) peaks; this is the only quantity not requiring the dielectric function, as it only requires the TO frequencies ν_p and the integrated intensities I_p computed as described from page 150 on:

$$A_{raw,Lor}(\nu) = \sum_p \frac{I_p}{\pi} \frac{\gamma_p/2}{(\nu - \nu_p)^2 + \gamma_p^2/4} \quad (4.14)$$

$$A_{raw,Gau}(\nu) = \sum_p 2\sqrt{\frac{\ln 2}{\pi}} \frac{I_p}{\gamma_p} \exp\left[-\frac{4 \ln 2 (\nu - \nu_p)^2}{\gamma_p^2}\right] \quad (4.15)$$

2. classical absorption formula, averaged over the polarization directions 1, 2, and 3 (according to Voigt notation, page 286):

$$A_{clas}(\nu) = \frac{1}{3} \sum_{ii=1}^3 \frac{4\pi}{\lambda\rho} Im[n_{ii}(\nu)] \quad (4.16)$$

where λ is the wavelength of the incident beam and ρ is the crystal density;

3. Rayleigh approximation of spherical particles [22], averaged over the directions 1,2 and 3:

$$A_{sph}(\nu) = \frac{1}{3} \sum_{ii=1}^3 \frac{2\pi}{\lambda\rho} \text{Im} \left[\frac{\epsilon_{ii}(\nu) - 1}{\epsilon_{ii}(\nu) + 2} \right] \quad (4.17)$$

4. Rayleigh approximation of particles as continuous distribution of ellipsoids (CDE) [22], averaged over the directions 1,2 and 3:

$$A_{CDE}(\nu) = \frac{1}{3} \sum_{ii=1}^3 \frac{2\pi}{\lambda\rho} \text{Im} \left[\frac{2\epsilon_{ii}(\nu)}{\epsilon_{ii}(\nu) - 1} \log \epsilon_{ii}(\nu) \right] \quad (4.18)$$

Reflectance spectrum, dielectric function and refractive index are at the moment limited to:

- frequency-independent optical dielectric tensor (CPHF) and frequency-dependent vibrational (IR) contributions
- directions 1, 2 and 3 only (Voigt notation, $\epsilon_{11}, \epsilon_{22}, \epsilon_{33}$)

Generalization is in progress.

IRSPEC data are written in files **IRSPEC.DAT**, **IRREFR.DAT** and **IRDIEL.DAT** and can be directly plotted with *gnuplot* (<http://www.gnuplot.info>, appendix D, page 328).

Once the vibrational frequencies, IR intensities and dielectric tensor are calculated, the infrared spectra can be calculated at almost zero computational time with a **RESTART** in the **FREQCALC** input block (the **FREQINFO.DAT** file is required):

```
FREQCALC
RESTART
INTENS
[options for INTENS]
DIELTENS or DIELISO
...
[optional keywords]
IRSPEC
...
[optional keywords]
...
END           [end IRSPEC]
END           [end FREQCALC]
```

By default, only the absorption and reflectance spectra are generated.

If the dielectric tensor is omitted, only the raw absorption spectrum is computed.

To enable the generation of the dielectric function and refractive index, specific keywords are required:

| rec | variable | meaning |
|-----|----------|---------|
|-----|----------|---------|

- **REFRIND** Activates the generation of the refractive index (same directions than reflectance spectrum).
- **DIELFUN** Activates the generation of the dielectric function (same directions than reflectance spectrum).

There are several keywords which allow to modify the **default** values.

| rec variable | meaning |
|--------------------|--|
| • A LENSTEP | |
| • * X | Step size used for the spectra [1 cm ⁻¹]. |
| • A NUMSTEP | |
| • * N | Number of points used for the spectra [no default]. To be used as an alternative to LENSTEP. |
| • A RANGE | |
| • * X1,X2 | Frequency range used for the spectra Default: [0., 1.3 ν_{max}], where ν_{max} is the frequency of the highest calculated mode. |
| • GAUSS | Gaussian line shape is adopted for the raw absorbance spectrum, instead of the Lorentzian one [which is the default]. |
| • A DAMPFAC | |
| • * GAMMA | Damping factor (related to peak width) used for the spectra [8.0]. |
| • A ANGLE | |
| • * ALPH | Angle of incidence used for the reflectance spectrum (degrees) [10.0]. |

5 - Calculation of the Raman spectra

Keyword **RAMSPEC**, inserted in the **FREQCALC** input block, activates the calculation of the Raman spectra. Prior calculation of Raman intensities is required (keyword **INTENS** with **INTRAMAN** option, page 150).

The keyword **RAMSPEC** defines an input block (closed by **END**).

The Raman spectra $A(\nu)$ are computed for both the cases of polycrystalline powder (total intensity, parallel polarisation, perpendicular polarisation) and single crystal (xx , xy , xz , yy , yz , zz polarisations). They are constructed by using the Transverse Optical (TO) modes and by adopting a pseudo-Voigt functional form:

$$A(\nu) = \eta \cdot L(\nu) + (1 - \eta) \cdot G(\nu) \quad (4.19)$$

with:

$$L(\nu) = \sum_p \frac{I_p}{\pi} \frac{\gamma_p/2}{(\nu - \nu_p)^2 + \gamma_p^2/4} \quad (4.20)$$

$$G(\nu) = \sum_p 2\sqrt{\frac{\ln 2}{\pi}} \frac{I_p}{\gamma_p} \exp \left[-\frac{4 \ln 2 (\nu - \nu_p)^2}{\gamma_p^2} \right] \quad (4.21)$$

where ν_p and I_p are the computed TO frequencies and Raman intensities, respectively, for each mode p ; γ_p is the full width at half maximum; η is the Lorentz factor, with values in the range 0 – 1. Raman intensities in **CRYSTAL** are normalized, so that the largest value is set to 1000 (non-normalized intensities can be obtained by inserting the **NORENORM** sub-keyword). Note that η values of 1 and 0 correspond to pure Lorentzian and pure Gaussian functional forms, respectively.

RAMSPEC data are written in file **RAMSPEC.DAT** and can be directly plotted with *gnuplot* (<http://www.gnuplot.info>, appendix D, page 329).

Once the vibrational frequencies and Raman intensities are calculated, the Raman spectra can be calculated at almost zero computational cost with a **RESTART** in the **FREQCALC** input block (the **FREQINFO.DAT** and **TENS_RAMAN.DAT** files are required):


```

FREQCALC
RESTART
INTENS
[options for INTENS]
INTRAMAN
RAMANREA
...
[optional keywords]
RAMSPEC
...
[optional keywords]
...
END          [end RAMSPEC]
END          [end FREQCALC]

```

There are several keywords which allow to modify the **default** values.

| rec | variable | meaning |
|-----|----------------|---|
| • A | LENSTEP | |
| • * | X | Step size used for the spectra [1 cm ⁻¹]. |
| • A | NUMSTEP | |
| • * | N | Number of points used for the spectra [no default]. To be used as an alternative to LENSTEP. |
| • A | RANGE | |
| • * | X1,X2 | Frequency range used for the spectra [0., 1.3 ν_{max}], where ν_{max} is the frequency of the highest calculated mode. |
| • A | VOIGT | |
| • * | ETA | Lorentz factor, determining mixing between Lorentzian and Gaussian contributions [1.0]. |
| • A | DAMPFAC | |
| • * | FWHM | Full width at half maximum used for the spectra [8.0]. |

6 - Phonon dispersion

The keyword **DISPERSION**, inserted in the **FREQCALC** input block, activates the calculation of vibration frequencies and normal modes on a set of points in reciprocal space, defined in terms of a direct-space supercell to be generated in input with the **SCELPHONO** keyword (page 63).

In the presence of interatomic interactions the static (non-vibrating) crystal assumes an equilibrium configuration $\mathcal{R}_0 \equiv \{ \dots, [(\mathbf{R}_0)_a + \mathbf{g}], \dots \}$ that is unambiguously defined by the equilibrium positions $\{(\mathbf{R}_0)_a\}$ of the N atoms of the cell ($a = 1, \dots, N$); the lattice vector $\mathbf{g} = \sum_{m=1}^3 l_m^g \mathbf{a}_m$ identifies the general crystal cell where \mathbf{a}_m are the direct lattice basis vectors: within Born von Kármán periodic boundary conditions the integers l_m^g run from 0 to $L_m - 1$. The parameters $\{L_m\}$ define the size and shape of a supercell (SC) in direct space (to be generated with the **SCELPHONO** keyword).

When nuclear motion (due to Heisenberg principle, finite temperature or other external perturbations) is considered, the atomic equilibrium positions become the static average positions of the atoms displaced by \mathbf{u}_a^g which define the general configuration $\mathcal{R} \equiv \{ \dots, [(\mathbf{R}_0)_a + \mathbf{g} + \mathbf{u}_a^g], \dots \}$.

Let us introduce the $L = L_1 \times L_2 \times L_3$ Hessian matrices $\{\mathbf{H}^g\}$ whose elements are the second

derivatives of the total energy per cell with respect to the atomic displacements:

$$H_{ai,bj}^{\mathbf{g}} = \left(\frac{\partial^2 E}{\partial u_{ai}^{\mathbf{0}} \partial u_{bj}^{\mathbf{g}}} \right) \quad (4.22)$$

where atom a in the reference cell is displaced along the i -th Cartesian direction and atom b in cell \mathbf{g} is displaced, along with all its periodic images in the crystal, along the j -th Cartesian direction. First derivatives are computed analytically while second derivatives are computed numerically.

The set of L Hessian matrices $\{\mathbf{H}^{\mathbf{g}}\}$ can be Fourier transformed into a set of *dynamical matrices* $\{\mathbf{W}^{\mathbf{k}}\}$ each one associated with a wavevector $\mathbf{k} = \sum_{n=1}^3 (\kappa_n/L_n) \mathbf{b}_n$ where \mathbf{b}_n are the reciprocal lattice vectors and the integers κ_n run from 0 to $L_n - 1$:

$$\mathbf{W}^{\mathbf{k}} = \sum_{\mathbf{g}=1}^L \mathbf{M}^{-\frac{1}{2}} \mathbf{H}^{\mathbf{g}} \mathbf{M}^{-\frac{1}{2}} \exp(i\mathbf{k} \cdot \mathbf{g}), \quad (4.23)$$

where \mathbf{M} is the diagonal matrix of the nuclear masses. The diagonalization of the dynamical matrices

$$(\mathbf{U}^{\mathbf{k}})^\dagger \mathbf{W}^{\mathbf{k}} \mathbf{U}^{\mathbf{k}} = \mathbf{\Lambda}^{\mathbf{k}} \quad \text{with} \quad (\mathbf{U}^{\mathbf{k}})^\dagger \mathbf{U}^{\mathbf{k}} = \mathbf{I}. \quad (4.24)$$

provides with the *vibration frequencies* $\nu_i^{\mathbf{k}} = \sqrt{\lambda_i^{\mathbf{k}}}$ (from the eigenvalues) and the *normal modes* (from the columns of $\mathbf{U}^{\mathbf{k}}$):

$$\mathbf{q}^{\mathbf{k}} = \mathbf{M}^{\frac{1}{2}} (\mathbf{U}^{\mathbf{k}})^\dagger \mathbf{u}^{\mathbf{k}} \quad \text{with} \quad \mathbf{u}^{\mathbf{k}} = \frac{1}{\sqrt{L}} \sum_{\mathbf{g}=1}^L \mathbf{u}^{\mathbf{g}} \exp(i\mathbf{k} \cdot \mathbf{g}).$$

To each \mathbf{k} -point in the first Brillouin zone, $3N$ oscillators (*i.e.* phonons) are associated which are labeled by a *phonon band index* i ($i = 1, \dots, 3N$).

In principle, equation (4.23) can be used to compute, and then diagonalize according to equation (4.24), the dynamical matrices of just the L \mathbf{k} -points defined above. However, if the energy second derivatives $\{\mathbf{H}^{\mathbf{g}}\}$ vanish within the supercell (SC) defined by the keyword **SCELPHONO** then such an expression can be used to construct the dynamical matrices of a denser set of \mathbf{k} -points represented by three parameters $\{L'_m \geq L_m\}$, with $m = 1, \dots, D$ (where D is the dimensionality of the system: 1, 2, 3 for 1D, 2D, 3D periodic systems). The quantum contributions to the second derivatives of the total energy usually vanish within a SC of radius ≈ 10 -15 Å. Such an *interpolation technique*, can be easily activated with the **INTERPHESS** keyword (to be inserted after **DISPERSION**) and can be quite effective in the case of a fully covalent crystal without long-range electrostatic contribution to the total energy.

On the contrary, when such electrostatic contributions become relevant (as in ionic crystals), they have to be explicitly accounted for with appropriate corrections (see the **WANG** keyword below). In this case one should use a SC large enough to contain all relevant quantum contributions and the two keywords **INTERPHESS** and **WANG**.

Phonon bands and phonon density of states can be computed with sub-keywords **BANDS** and **PDOS**, respectively.

A detailed description of these options follows:

-
- A **NOKSYMDISP** The dynamical matrices $\{\mathbf{W}^{\mathbf{k}}\}$ in reciprocal space are not factorized according to the irreducible representations of the Space Group when diagonalized. Phonons are not labeled according to symmetry.
-
- A **PDOS** Phonon density of states is computed. To make the reciprocal space sampling denser and the resulting PDOS curve smoother, the **INTERPHESS** (and **WANG** for polar materials) sub-keywords can be used.
 - * **NUMA** Maximum frequency considered (value in cm^{-1}).
 - NBIN** Number of intervals in which the frequency range $0 < \omega < \text{NUMAX}$ is partitioned for the representation of the PDOS.
 - * **LPRO** 0 No projected atomic DOS.
1 Projected atomic DOS enabled.
-
- A **BANDS** Phonon bands calculation for plotting purposes. Phonon bands are sampled along given directions in reciprocal space. Data is stored in file fort.25 for plotting. Note: **BANDS** implies **NOKSYMDISP**.
 - * **ISS** Shrinking factor in terms of which the coordinates of the extremes of the segments are expressed.
 - NSUB** Total number of k points along each of the lines in the path.
 - * **NLINE** Number of lines in reciprocal space to be explored.
_____ if $\text{ISS} > 0$ then _____
_____ add NLINE records _____
 - * **I1,I2,I3** Integers that define the starting point of the line ($\text{I1}/\text{ISS} \mathbf{b}_1 + \text{I2}/\text{ISS} \mathbf{b}_2 + \text{I3}/\text{ISS} \mathbf{b}_3$), with $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ reciprocal lattice vectors.
 - J1,J2,J3** Integers that define the final point of the line ($\text{J1}/\text{ISS} \mathbf{b}_1 + \text{J2}/\text{ISS} \mathbf{b}_2 + \text{J3}/\text{ISS} \mathbf{b}_3$) with $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ reciprocal lattice vectors.
_____ if $\text{ISS} = 0$ then _____
_____ add NLINE records _____
 - * **LABELA** Label of the starting point of the line (see tables 9.1 and 9.2 below for a legend).
 - LABELB** Label of the final point of the line (see tables 9.1 and 9.2 below for a legend).
-
- A **INTERPHESS** Activates the Hessian Fourier interpolation that permits the calculation of vibration frequencies on a denser set of points in reciprocal space. This option has to be used only if the starting supercell (SC) is sufficiently large (radius $\approx 10\text{-}15 \text{ \AA}$) so that any quantum contribution to the energy second derivatives vanishes within it. This keyword has to be combined with the keyword **LRFC** if long-range electrostatic contributions to the energy exist (ionic crystals).
 - * L'_m $m = 1, \dots, D$ where D is the dimensionality of the system: 1, 2, 3 for 1D, 2D, 3D periodic systems. These three integers are the expansion parameters of the starting SC.
 - * **IPRINT** 0 Output printings disabled for each \mathbf{k} -point.
1 Output printings active for each \mathbf{k} -point.
-

| | |
|---------------|---|
| • A WANG | For 3D systems only. Used in combination with INTERPHESS , BANDS and PDOS when dealing with polar materials, activates the correction to the dynamical matrices to take into account the long range Coulomb interactions. The mixed-space approach as proposed by Wang and coworkers [180] is implemented. Born tensor charges are read from the external file BORN.DAT which is obtained by performing a Γ only vibrational frequencies calculation with IR intensities active (see INTENS subkeyword, page 150). |
| • * TENS(1:9) | Dielectric tensor matrix TENS (3x3 elements, input by rows: 9 reals (3D)). |

7 - Anisotropic Displacement Parameters (ADP)

The keyword **ADP**, inserted in the **FREQCALC** block, allows to compute the anisotropic displacement parameters (ADP) as 3×3 tensors \mathbf{U}_A associated to each atom A of the cell. Such tensors can be used for computing Debye-Waller thermal factors and obtaining dynamic structure factors (see the **XFAC** keyword). Each 3×3 atomic tensor \mathbf{U}_A can be diagonalized as $\mathbf{U}_A \mathbf{E}_A = \mathbf{e}_A \mathbf{E}_A$ where \mathbf{e}_A is the diagonal matrix of the eigenvalues. If the three eigenvalues are positive, then the surfaces of constant probability are *ellipsoids* enclosing some definite probability for atomic displacement. The lengths of the principal axes of the ellipsoids are proportional to the eigenvalues e_1 , e_2 and e_3 of \mathbf{U}_A which are usually expressed in 10^{-4} \AA^2 . The orientation of the ellipsoid with respect to the reference Cartesian frame is given by the eigenvectors \mathbf{E}_A .

Let us consider the set of L (number of cells in the cyclic crystal) $3n \times 3n$ (with n number of atoms per cell) Hessian matrices $\mathbf{H}(\mathbf{g})$ whose elements are the second derivatives of the energy E with respect to the atomic displacements \mathbf{u} :

$$H_{A0i,A'g'i'}(\mathbf{g}) = \frac{\partial^2 E}{\partial u_{A0i} \partial u_{A'g'i'}}$$

where \mathbf{g} labels a crystal cell and i a Cartesian component of \mathbf{u} . The usual way of dealing with lattice dynamics is considering the set of L $3n \times 3n$ dynamical matrices $\mathbf{D}(\mathbf{k})$ defined as the (mass-weighted) Fourier transform of the $\mathbf{H}(\mathbf{g})$:

$$\mathbf{D}(\mathbf{k}) = \sum_{\mathbf{g}}^L \mathbf{M}^{-\frac{1}{2}} \mathbf{H}(\mathbf{g}) \mathbf{M}^{-\frac{1}{2}} e^{i\mathbf{k} \cdot \mathbf{g}}$$

where \mathbf{M} is a $3n \times 3n$ real symmetric (diagonal) matrix with the nuclear masses on the diagonal. To each \mathbf{k} , $3n$ oscillators (phonons) are associated whose label is $s = 1, \dots, 3n$ and whose frequencies and eigenvectors are obtained by diagonalizing $\mathbf{D}(\mathbf{k})$:

$$\mathbf{D}(\mathbf{k}) \mathbf{W}(\mathbf{k}) = \Omega(\mathbf{k}) \mathbf{W}(\mathbf{k}) \quad \text{with} \quad \mathbf{W}^\dagger(\mathbf{k}) \mathbf{W}(\mathbf{k}) = \mathbf{I}$$

To each phonon $k \equiv (\mathbf{k}s)$, an atomic displacement vector \mathbf{u}_k can be associated. Let us introduce the frequency-scaled normal coordinate proper of each phonon k : $\xi_k = \Omega^{\frac{1}{4}}(\mathbf{k}) \mathbf{W}^\dagger(\mathbf{k}) \mathbf{M}^{\frac{1}{2}} \mathbf{u}_k$. The Boltzman probability density function $p(\{\xi_k\}; T)$ for the nuclei, at a given temperature T can be expressed as the product of independent probabilities, associated to the different phonons $p(\{\xi_k\}; T) = \prod_k p(\xi_k; T)$. Let us introduce the so-called *Gaussian approximation* that consists in expressing such probabilities as Gaussian functions with standard deviations $\sigma_{k,T}$ (k_B is Boltzman's constant):

$$p(\xi_k; T) \approx G(\xi_k; \sigma_{k,T}) \quad \text{with} \quad (\sigma_{k,T})^2 = |\xi_k\rangle \langle \xi_k| = \left[\frac{1}{e^{\frac{\omega_k}{k_B T}} - 1} + \frac{1}{2} \right]$$

Within such an approximation, $p(\{\xi_k\}; T) = e^{-\sum_{\mathbf{k}} \langle \mathbf{u}_{\mathbf{k}} | \mathbf{U}(\mathbf{k}; T)^{-1} | \mathbf{u}_{\mathbf{k}} \rangle}$ with

$$\mathbf{U}(\mathbf{k}; T) = \mathbf{M}^{-\frac{1}{2}} \mathbf{W}(\mathbf{k}) \Omega^{-\frac{1}{4}}(\mathbf{k}) \Xi(T) \Omega^{-\frac{1}{4}}(\mathbf{k}) \mathbf{W}^\dagger(\mathbf{k}) \mathbf{M}^{-\frac{1}{2}}$$

where $\Xi(T)$ is a $3n \times 3n$ diagonal matrix with $(\sigma_{k,T})^2$ as diagonal elements, so that we can define the total mean square displacement tensors $\mathbf{U}(\mathbf{g}; T) = 1/L \sum_{\mathbf{k}} \mathbf{U}(\mathbf{k}; T) e^{-i\mathbf{k}\cdot\mathbf{g}}$. The 3×3 diagonal blocks of $\mathbf{U}(\mathbf{g} = \mathbf{0}; T)$ are the ADPs \mathbf{U}_A .

The default temperature at which the ADPs are computed is 298.15 K. Different temperatures can be defined with the keyword **TEMPERAT**. The ADPs are saved (in atomic units) in the external formatted unit ADP.DAT that can be used by the keyword **XFAC** of **PROPERTIES** for computing Debye-Waller thermal factors for dynamic structure factors.

Users of this option are kindly requested to cite the following paper [62]:

A. Erba, M. Ferrabone, R. Orlando and R. Dovesi, *J. Comput. Chem.*, **34**, 346 (2013). *Accurate dynamical structure factors from ab initio lattice dynamics: The case of crystalline silicon.*

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | NTYP | 0 | Recommended algorithm for the computation of the ADPs |
| | NNEGL | | Number of additional modes at the Γ -point to be neglected (others than rotations+translations that are already neglected) in the computation of the ADPs |

ANHARM - Anharmonic calculation of frequencies of X-H (X-D) bond stretching

Anharmonic calculation of frequencies of X-H, or X-D, bond stretching (where H and D stand for hydrogen and deuterium and X for any element) is invoked by the keyword **ANHARM** that has to be inserted outside from the **FREQCALC** block (a **FREQCALC** run is not needed at all for this purpose).

| rec | variable | meaning |
|-----|------------|---|
| • * | LB | <i>label</i> of the atom to be displaced (it must have atomic number 1, Hydrogen or Deuterium. The first neighbour (NA) of the LB atom is identified. LB moves along the (NA-LB) direction. |
| • A | END | End of ANHARM input block |

This keyword allows the calculation of the anharmonic X-Y stretching. The selected X-Y bond is considered as an independent oscillator. This condition is fulfilled when H or D are involved. It can be used for X-H (or X-D) only.

S. Tosoni, F. Pascale, P. Ugliengo, R. Orlando, V.R. Saunders and R. Dovesi, "Vibrational spectrum of brucite, Mg(OH)(2): a periodic ab initio quantum mechanical calculation including OH anharmonicity" *Chem. Phys. Lett.* **396**, 308-315 (2004)].

Frequencies are calculated as follows:

- i) the X-H distance is varied around the equilibrium value, d_0 [default: $d_0 + (-0.2, -0.16, -0.06, 0.00, 0.16, 0.24, 0.3 \text{ \AA})$], all other geometrical features being constant (only H moves);
- ii) the total potential energy is calculated for each value of the X-H distance [default 7 points];
- iii) a polynomial curve of sixth degree is used to best fit the energy points; the root mean square error is well below 10^{-6} hartree;
- iv) the corresponding nuclear Schrödinger equation is solved numerically following the method proposed in reference [111]. See P. Ugliengo, "ANHARM, a program to solve the mono dimensional nuclear Schrödinger equation", Torino, 1989.

The anharmonicity constant and the harmonic XH stretching frequency are computed from the first vibrational transitions ω_{01} and ω_{02} , as:

$$\omega_e x_e = (2\omega_{01} - \omega_{02}) / 2$$

$$\omega_e = \omega_{01} + 2\omega_e x_e$$

Stretching of the X-H bond may reduce the symmetry (default). If keyword **KEEPSYMM** is inserted, all equivalent X-H bonds will be stretched, to maintain the symmetry. For example, in CH₄ (point group T_d), KEEPSYMM forces the four CH bonds to stretch in phase; otherwise only the selected C-H bond is stretched, and the symmetry reduced (point group C_{3v}).

Optional keywords of ANHARM input block

| | | |
|-----------------|---|----|
| ISOTOPES | atomic mass of selected atoms modified | |
| • * NL | number of selected atoms | |
| II | <i>insert NL records</i> | II |
| • * LB,AMASS | <i>label</i> and new atomic mass (amu) of the atom. | |
| II | | II |

| | |
|-----------------|---|
| KEEPSYMM | all atoms symmetry equivalent to the selected one are displaced |
|-----------------|---|

| | |
|----------------|---|
| NOGUESS | scf guess at each geometry point: superposition of atomic densities at each scf calculation |
|----------------|---|

| | |
|-----------------|---|
| POINTS26 | 26 points: d_{X-H} range: $d_0 - 0.2 \div d_0 + 0.3$ with a step of 0.02 Å. |
|-----------------|---|

| | |
|--------------|-------------------|
| PRINT | extended printing |
|--------------|-------------------|

| | |
|-----------------|--------------------------|
| PRINTALL | printing for programmers |
|-----------------|--------------------------|

| | |
|-------------------|---|
| TEST[ANHA] | Preliminary test to check if the neighbour(s) of the selected atom is correctly identified and the X-Y direction properly set. No energy calculations is performed. |
|-------------------|---|

It has been verified that calculations with 7 points provides very similar results to the ones obtained with 26 points. In the following table, results for POINTS=7 and 26 are reported for three systems. All values are in cm^{-1} .

| system | | NPOINTS 26 | NPOINTS 7 |
|----------------------------|-----------|------------|-----------|
| HF (molecule) | W_{01} | 4358.6 | 4359.0 |
| | W_{02} | 8607.3 | 8608.1 |
| | W_e | 4468.6 | 4468.8 |
| | $W_e X_e$ | 55.0 | 54.9 |
| Be(OH) ₂ (bulk) | W_{01} | 3325.3 | 3325.8 |
| | W_{02} | 6406.3 | 6407.4 |
| | W_e | 3569.5 | 3569.9 |
| | $W_e X_e$ | 122.1 | 122.1 |
| Ca(OH) ₂ (bulk) | W_{01} | 3637.2 | 3637.5 |
| | W_{02} | 7111.4 | 7111.9 |
| | W_e | 3800.3 | 3800.7 |
| | $W_e X_e$ | 81.5 | 81.6 |

Chapter 5

Dielectric Properties up to Fourth Order via the Coupled Perturbed HF/KS Method

CPHF - Coupled-Perturbed HF/KS Calculation of Dielectric Properties up to Fourth Order

This keyword computes the polarizability and the first and second order hyper-polarizabilities via the Coupled Perturbed HF/KS method. **CPHF** (or **CPKS**) must be the last keyword in the geometry input block:

```
. . . geometry input . . . .
CPHF
END      ! close CPHF input block
END      ! close geometry input block
```

The density functionals that are currently available for **CPHF** calculations are:

| | |
|-----------------|---|
| CORRELAT | Correlation Potential (default: no correlation). |
| LYP | GGA. Lee-Yang-Parr [109] |
| PBE | GGA. Perdew-Burke-Ernzerhof [128] |
| PBESOL | GGA. PBE functional revised for solids [130] |
| PWLSLSD | LSD. Perdew-Wang parameterization of the Ceperley-Alder free electron gas correlation results [131] |
| PWGGA | GGA. Perdew-Wang [129] |
| VWN | LSD. Vosko-Wilk-Nusair parameterization of the Ceperley-Alder free electron gas correlation results [179] |
| EXCHANGE | Exchange potential (default: Hartree-Fock exchange). |
| BECKE | GGA. Becke [17] |
| LDA | LSD. Dirac-Slater [44] |
| PBE | GGA. Perdew-Becke-Ernzerhof [128] |
| PBESOL | GGA. PBE functional revised for solids [130] |
| PWGGA | GGA. Perdew-Wang [129] |
| SOGGA | second order GGA. [195] |
| WCGGA | GGA - Wu-Cohen [187] |

| | |
|----------------|--|
| HYBRID | Hybrid method - 1 record follows: |
| B3PW | Becke's 3 parameter functional [18] combined with the non-local correlation PWGGA [127, 132, 133, 131] |
| B3LYP | Becke's 3 parameter functional [18] combined with the non-local correlation LYP |
| PBE0 | Adamo and Barone [6] |
| PBESOL0 | Same than PBE0 but with PBEsol instead of PBE |
| B1WC | see [20] |
| WC1LYP | see [42] |
| SOGGAXC | see [195] |

Users of this module are kindly requested to cite the following papers:

M. Ferrero, M. Rérat, R. Orlando and R. Dovesi
Coupled perturbed Hartree-Fock for periodic systems: the role of symmetry and related computational aspects
 J. Chem. Phys. 128, Art.N. 014100 (2008)

M. Ferrero, M. Rérat, R. Orlando and R. Dovesi
The calculation of static polarizabilities in 1-3D periodic compounds. The implementation in the CRYSTAL code
 J. Comput. Chem. 29, 1450–1459 (2008)

M. Ferrero, M. Rérat, B. Kirtman and R. Dovesi
Calculation of first and second static hyper-polarizabilities of 1-3D periodic compounds. Implementation in the CRYSTAL code
 J. Chem. Phys. 129, Art.N. 244110 (2008)

The total energy E of a crystal in a constant static electric field $\boldsymbol{\varepsilon}$ can be expressed as

$$\begin{aligned}
 E(\boldsymbol{\varepsilon}) = E(0) &- \sum_t \mu_t \varepsilon_t - \frac{1}{2!} \sum_{tu} \alpha_{tu} \varepsilon_t \varepsilon_u + \\
 &- \frac{1}{3!} \sum_{tuv} \beta_{tuv} \varepsilon_t \varepsilon_u \varepsilon_v - \frac{1}{4!} \sum_{tuvw} \gamma_{tuvw} \varepsilon_t \varepsilon_u \varepsilon_v \varepsilon_w + \dots
 \end{aligned} \quad (5.1)$$

with $E(0)$ the field-free energy and $\boldsymbol{\mu}, \boldsymbol{\alpha}, \boldsymbol{\beta}, \boldsymbol{\gamma} \dots$ the total energy derivative tensors of order 1, 2, 3, 4... with respect to the electric field (Cartesian components indicated by Roman subscripts t, u, v, w):

$$\mu_t = - \left. \frac{\partial E}{\partial \varepsilon_t} \right|_0 \quad (5.2)$$

$$\alpha_{tu} = - \left. \frac{\partial^2 E}{\partial \varepsilon_t \partial \varepsilon_u} \right|_0 \quad (5.3)$$

$$\beta_{tuv} = - \left. \frac{\partial^3 E}{\partial \varepsilon_t \partial \varepsilon_u \partial \varepsilon_v} \right|_0 \quad (5.4)$$

$$\gamma_{tuvw} = - \left. \frac{\partial^4 E}{\partial \varepsilon_t \partial \varepsilon_u \partial \varepsilon_v \partial \varepsilon_w} \right|_0 \quad (5.5)$$

As for the corresponding physical properties, $\boldsymbol{\mu}$ represents the dipole moment, $\boldsymbol{\alpha}$ the polarizability, $\boldsymbol{\beta}$ the first hyperpolarizability and $\boldsymbol{\gamma}$ the second hyperpolarizability.

By default, the perturbative series 5.1 is truncated at the second order and only the second energy derivatives α_{tu} are calculated (the dipole moment μ_t is ill-defined in the reciprocal space) using the expression

$$\alpha_{tu} = - \frac{4}{n_k} \sum_{\mathbf{k}} \Re \left\{ \sum_{\mu\nu}^{\text{occ}} \sum_a^{\text{virt}} \sum_p C_{a\mu}^{\mathbf{k}*} \Omega_{\mu\nu}^{\mathbf{k},t} C_{\nu p}^{\mathbf{k}} U_{pa}^{\mathbf{k},u} \right\} \quad (5.6)$$

where n_k is the number of \mathbf{k} points in the first Brillouin Zone (BZ) and the indices a ($b, c \dots$) and p ($q, r \dots$) run over the occupied and virtual crystalline orbitals, respectively.

$\mathbf{U}^{\mathbf{k},u}$ is the unknown anti-Hermitian off-diagonal-block matrix that linearly transforms the unperturbed eigenvectors $C^{\mathbf{k}}$ under the effect of the electric field perturbation represented by the matrix $\Omega^{\mathbf{k}}$:

$$\mathbb{C}_{\mu i}^{\mathbf{k},u} \equiv \left. \frac{\partial C_{\mu i}^{\mathbf{k}}}{\partial \varepsilon_u} \right|_0 = \sum_j^{\text{all}} C_{\mu j}^{\mathbf{k}} \mathbf{U}_{j i}^{\mathbf{k},u} \quad (5.7)$$

The off-diagonal blocks $\mathbf{U}_{ap}^{\mathbf{k},u}$ are defined as

$$\mathbf{U}_{ap}^{\mathbf{k},u} = \sum_{\mu\nu} \frac{C_{a\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},u} C_{\nu p}^{\mathbf{k}}}{E_p^{\mathbf{k}} - E_a^{\mathbf{k}}} \quad (5.8)$$

and are functions of both the energy gap $(E_p^{\mathbf{k}} - E_a^{\mathbf{k}})$, and the perturbed Fock matrix,

$$\begin{aligned} \mathbb{F}_{\mu\nu}^{\mathbf{k},u} \equiv \left. \frac{\partial F_{\mu\nu}^{\mathbf{k}}}{\partial \varepsilon_u} \right|_0 &= \Omega_{\mu\nu}^{\mathbf{k},u} + \sum_{\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} \sum_{\lambda\rho} \sum_{\mathbf{k}'} \sum_{\mathbf{g}'}^{BZ} e^{-i\mathbf{k}'\cdot\mathbf{g}'} \sum_a \left(C_{a\lambda}^{\mathbf{k}',u*} C_{\rho a}^{\mathbf{k}'} + C_{a\lambda}^{\mathbf{k}'*} C_{\rho a}^{\mathbf{k}',u} \right) \times \\ &\quad \times \sum_{\mathbf{g}''} \left[\left(\mu^0 \nu^{\mathbf{g}} \left| \lambda^{\mathbf{g}'} \rho^{\mathbf{g}''} \right. \right) - \frac{1}{2} \left(\mu^0 \lambda^{\mathbf{g}'} \left| \nu^{\mathbf{g}} \rho^{\mathbf{g}''} \right. \right) \right] \end{aligned} \quad (5.9)$$

Hence, according to Eq. (5.7), a Self-Consistent Coupled-Perturbed procedure (SC-CP) is to be carried out.

Convergence of the SC-CP cycle might be helped and/or tuned using the following optional keywords within the **CPHF** input block:

| rec | variable | meaning |
|-----|-------------------|--|
| • | A ANDERSON | mixing of Fock/KS matrix derivatives (page 79) |
| • | A BROYDEN | mixing of Fock/KS matrix derivatives (page 82) |
| * | W0 | W0 parameter in Anderson's paper [104] |
| * | IMIX | percent of Fock/KS derivative matrices mixing |
| * | ISTART | SC-CP iteration after which Broyden method is active (minimum 2) |
| • | A FMIXING | mixing of Fock/KS matrix derivatives from iterations n and $n - 1$ |
| * | IPMIX | percentage of cycle $n - 1$ [IPMIX=0, no mixing] |
| • | A MAXCYCLE | modify the maximum number of SC-CP iterations |
| * | NMAX | maximum number of iterations [default: 100] |
| • | A SELEDIR | set the maximum number of iterations along each cartesian direction |
| • | * NX, NY, NZ | maximum number of SC-CP iterations along x, y, z |
| • | A TOLALPHA | threshold on α variation between two SC-CP iterations |
| * | ITOL | $ \Delta\alpha < 10^{-ITOL}$ [default: 3] |

The **CPHF** calculation can also be extended up to the third perturbative order by including the optional keyword:

| rec | variable | meaning |
|-----|----------------|---|
| • | A THIRD | computes energy derivatives up to the third order |

THIRD provides third order energy derivatives (see Eq. 5.4) calculated through the $(2n + 1)$ scheme:

$$\begin{aligned} \beta_{tuv} &= -\frac{2}{n_k} \sum_{\mathbf{k}} \Re \sum_a \sum_p \mathcal{P}_{t,u,v} \times \\ &\quad \times \left\{ \mathbf{U}_{ap}^{\mathbf{k},t*} \left[\sum_{\mu\nu} \left(\sum_q C_{p\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},u} C_{\nu q}^{\mathbf{k}} \mathbf{U}_{qa}^{\mathbf{k},v} - \sum_b \mathbf{U}_{pb}^{\mathbf{k},u} C_{b\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},v} C_{\nu a}^{\mathbf{k}} \right) + i \frac{\partial \mathbf{U}_{pa}^{\mathbf{k},v}}{\partial k_u} \right] \right\} \end{aligned} \quad (5.10)$$

The operator \mathcal{P} permutes the indices of derivation. The derivative $\partial \mathbf{U}_{pa}^{\mathbf{k},v} / \partial k_u$ depends on the derivative of the coefficients $C_{\mu i}^{\mathbf{k}}$ with respect to \mathbf{k} , that is

$$\frac{\partial C_{\mu i}^{\mathbf{k}}}{\partial k_u} = \sum_j^{\text{all}} C_{\mu j}^{\mathbf{k}} \mathbf{Q}_{j i}^{\mathbf{k},u} \quad (5.11)$$

similarly to Eq. (5.7). When $i \neq j$, the expression for matrix $\mathbf{Q}^{\mathbf{k},\mathbf{u}}$ elements is

$$\mathbf{Q}_{ij}^{\mathbf{k},\mathbf{u}} = \frac{\sum_{\mu\nu} \left[C_{i\mu}^{\mathbf{k}*} \frac{\partial F_{\mu\nu}^{\mathbf{k}}}{\partial k_u} C_{\nu j}^{\mathbf{k}} - C_{i\mu}^{\mathbf{k}*} \frac{\partial S_{\mu\nu}^{\mathbf{k}}}{\partial k_u} C_{\nu j}^{\mathbf{k}} E_j^{\mathbf{k}} \right]}{E_j^{\mathbf{k}} - E_i^{\mathbf{k}}} \quad (5.12)$$

A threshold value (10^{-6} , by default) is defined below which eigenvalues are considered degenerate. Users can change this threshold using the keyword **TOLUDIK** as follows:

| rec variable | meaning |
|--------------------|---|
| • A TOLUDIK | minimum allowed difference between non-degenerate unperturbed eigenvalues |
| • * ITOLU | $ E_j^{\mathbf{k}} - E_i^{\mathbf{k}} = 10^{-ITOLU}$ [default: 6] |

Calculation of the second hyperpolarizability tensor γ is performed only if required:

| rec variable | meaning |
|-------------------|--|
| • A FOURTH | computes energy derivatives up to fourth order |

The keyword **FOURTH** activates a second Self-Consistent Coupled-Perturbed procedure (SC-CP2) to provide matrix $\mathbf{U}^{\mathbf{k},\mathbf{u},\mathbf{v}}$ such that

$$\mathbb{C}_{\mu i}^{\mathbf{k},\mathbf{u},\mathbf{v}} \equiv \left. \frac{\partial^2 C_{\mu i}^{\mathbf{k}}}{\partial \varepsilon_u \partial \varepsilon_v} \right|_0 = \sum_j^{all} C_{\mu j}^{\mathbf{k}} \mathbf{U}_{ji}^{\mathbf{k},\mathbf{u},\mathbf{v}} \quad (5.13)$$

By means of $\mathbf{U}^{\mathbf{k},\mathbf{u},\mathbf{v}}$, both derivatives (5.4) and (5.5) are defined:

$$\beta_{tuv} = -\frac{1}{n_k} \sum_{\mathbf{k}} \Re \left\{ \mathcal{P}_{t,u,v} \sum_a \sum_p \left(\sum_{\mu\nu} C_{a\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},t} C_{\nu p}^{\mathbf{k}} \mathbf{U}_{pa}^{\mathbf{k},\mathbf{u},\mathbf{v}} - \sum_{\mu\nu} C_{a\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},uv} C_{\nu p}^{\mathbf{k}} \mathbf{U}_{pa}^{\mathbf{k},t} \right) \right\} \quad (5.14)$$

in the $n+1$ formulation (equivalent to Eq. 5.10), and

$$\begin{aligned} \gamma_{tuvw} = & -\frac{1}{n_k} \sum_{\mathbf{k}} \Re \left\{ \mathcal{P}_{t,u,v,w} \sum_a \sum_p \sum_{\mu\nu} \mathbf{U}_{ap}^{\mathbf{k},t*} \times \right. \\ & \times \left[\sum_q C_{p\mu}^{\mathbf{k}*} \left(\mathbb{F}_{\mu\nu}^{\mathbf{k},u} C_{\nu q}^{\mathbf{k}} \mathbf{U}_{qa}^{\mathbf{k},vw} + \frac{1}{2} \mathbb{F}_{\mu\nu}^{\mathbf{k},vw} C_{\nu q}^{\mathbf{k}} \mathbf{U}_{qa}^{\mathbf{k},u} \right) + \right. \\ & - \sum_b \left(\mathbf{U}_{pb}^{\mathbf{k},vw} C_{b\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},u} + \frac{1}{2} \mathbf{U}_{pb}^{\mathbf{k},u} C_{b\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},vw} \right) C_{\nu a}^{\mathbf{k}} + \\ & \left. \left. - \sum_b \mathbf{U}_{pb}^{\mathbf{k},u} C_{b\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},v} \sum_q C_{\nu q}^{\mathbf{k}} \mathbf{U}_{qa}^{\mathbf{k},w} \right] + i \mathbf{U}_{ap}^{\mathbf{k},tw*} \frac{\partial \mathbf{U}_{pa}^{\mathbf{k},u}}{\partial k_v} \right\} \quad (5.15) \end{aligned}$$

The off-diagonal blocks of matrix $\mathbf{U}^{\mathbf{k},\mathbf{u},\mathbf{v}}$,

$$\begin{aligned} \mathbf{U}_{ap}^{\mathbf{k},\mathbf{u},\mathbf{v}} = & \frac{1}{E_p^{\mathbf{k}} - E_a^{\mathbf{k}}} \left\{ \mathcal{P}_{u,v} \left[\sum_b \sum_{\mu\nu} C_{a\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},u} C_{\nu b}^{\mathbf{k}} \mathbf{U}_{bp}^{\mathbf{k},v} + \right. \right. \\ & \left. \left. - \sum_q \sum_{\mu\nu} \mathbf{U}_{aq}^{\mathbf{k},u} C_{q\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},v} C_{\nu p}^{\mathbf{k}} + i \frac{\partial \mathbf{U}_{ap}^{\mathbf{k},v}}{\partial k_u} \right] + \sum_{\mu\nu} C_{a\mu}^{\mathbf{k}*} \mathbb{F}_{\mu\nu}^{\mathbf{k},uv} C_{\nu p}^{\mathbf{k}} \right\} \quad (5.16) \end{aligned}$$

depend on themselves through the second derivative of the Fock matrix

$$\begin{aligned} \mathbb{F}_{\mu\nu}^{\mathbf{k},\mathbf{u},\mathbf{v}} \equiv & \left. \frac{\partial^2 F_{\mu\nu}^{\mathbf{k}}}{\partial \varepsilon_u \partial \varepsilon_v} \right|_0 = \sum_{\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} \sum_{\lambda\rho} \sum_{\mathbf{k}'} \sum_{\mathbf{g}'} e^{-i\mathbf{k}'\cdot\mathbf{g}'} \sum_a \left(\mathbb{C}_{a\lambda}^{\mathbf{k}',uv*} C_{\rho a}^{\mathbf{k}'} + \right. \\ & \left. + \mathcal{P}_{u,v} \mathbb{C}_{a\mu}^{\mathbf{k}',u*} C_{\nu a}^{\mathbf{k}',v} + C_{a\lambda}^{\mathbf{k}'} \mathbb{C}_{\rho a}^{\mathbf{k}',uv} \right) \left[\left(\mu^0 \nu^{\mathbf{g}} \left| \lambda^{\mathbf{g}'} \rho^{\mathbf{g}''} \right. \right) - \frac{1}{2} \left(\mu^0 \lambda^{\mathbf{g}'} \left| \nu^{\mathbf{g}} \rho^{\mathbf{g}''} \right. \right) \right] \quad (5.17) \end{aligned}$$

and therefore, must be determined iteratively. Convergence of the SC-CP2 cycle is controlled with the following optional keywords:

| rec | variable | meaning |
|-----|------------------------------|---|
| • A | ANDERSON2 | mixing of Fock/KS matrix 2nd derivatives (page 79) |
| • A | BROYDEN2 | mixing of Fock/KS matrix 2nd derivatives (page 82) |
| * | W02 | W0 parameter in Anderson's paper [104] |
| * | IMIX2 | percentage of Fock/KS second derivative matrices mixing |
| * | ISTART2 | SC-CP2 iteration after which Broyden method is activated (minimum 2) |
| • A | FMIXING2 | mixing of Fock/KS matrix second derivatives from SC-CP2 iterations n and $n - 1$ |
| * | IPMIX2 | percentage of cycle $n - 1$ [IPMIX2=0, no mixing] |
| • A | MAXCYCLE2 | modify the maximum number of SC-CP2 iterations |
| * | NMAX2 | maximum number of iterations [default: 100] |
| • A | SELEDIR2 | set the maximum number of SC-CP2 iterations along each couple of cartesian indices |
| • * | NXX, NXY, NXZ, NYY, NYZ, NZZ | maximum number of SC-CP2 iterations along mixed directions xx, xy, xz, yy, yz, zz |
| • A | TOLGAMMA | threshold on $U^{k,tu}$ variation between two SC-CP2 iterations |
| * | ITOL2 | $ \Delta U^{k,tu} = 10^{-ITOL2}$ [default: 3] |

RESTART

A CPHF/KS run can be restarted from a previous run (even an incomplete run). Every CPHF/KS run writes the necessary information for a restart to file fort.31. This file must be provided as file fort.32 before running the new calculation with the **RESTART** keyword. **GUESSP** (SCF guess from density matrix of a previous run, input block 3, page 103) is not applied by default, but its use is recommended.

For details about the CPHF/KS method and its implementation see Refs. [70, 71, 72, 148].

Chapter 6

Tools for Studying Solid Solutions

The theoretical modeling of disordered systems and solid solutions relies on obtaining average properties over a number of *configurations*, namely distributions of different species (atoms or vacancies) at a given set of atomic positions. Symmetry plays a key role in this context as shown in the following reference papers:

S. Mustapha, Ph. D'Arco, M. De La Pierre, Y. Noel, M. Ferrabone and R. Dovesi
On the use of symmetry in configurational analysis for the simulation of disordered solids
J. Phys.: Condens. Matter 25, 105401 (2013)

Ph. D'Arco, S. Mustapha, M. Ferrabone, Y. Noel, M. De La Pierre and R. Dovesi
Symmetry and random sampling of symmetry independent configurations for the simulation of disordered solids
J. Phys.: Condens. Matter 25, 355401 (2013)

See also <http://www.crystal.unito.it> \Rightarrow **tutorials** \Rightarrow **Disordered systems and solid solutions**

Consider, for example, a structure (any dimension) of symmetry group G , characterized by one irreducible crystallographic position d of multiplicity $|D|$. Such a $|D|d$ position (in Wyckoff's notation) is occupied by the atomic species \mathcal{A} . Suppose that a different atomic species \mathcal{X} can replace \mathcal{A} in any proportion on d . Then, $|D| + 1$ compositions are possible:

$$\mathcal{A}_{|D|-\alpha}\mathcal{X}_\alpha \quad , \quad \alpha = 0 \dots |D| \quad (6.1)$$

For each composition, there exist

$$|S_\alpha| = \binom{|D|}{\alpha} = \frac{|D|!}{\alpha!(|D|-\alpha)!} \quad (6.2)$$

different possibilities to place atoms \mathcal{A} and \mathcal{X} , that are different *configurations*. Overall, we expect a total number of $|S| = 2^{|D|}$ configurations for $|D| + 1$ compositions. Figure 6.1 shows the set of configurations for two atomic species (\mathcal{A} and \mathcal{X}) distributed over four positions.

As the group of symmetry G acts on the whole set of configurations (S), the latter is partitioned in $|\Delta(S)|$ classes of equivalence, each one being a symmetry-independent class (SIC). Two configurations belong to the same SIC if there exists at least one element of G that transforms one configuration into the other. Figure 6.2 shows the partitioning of the configurations under the action of C_{4v} group.

All the configurations of a given class are degenerate and share the same properties (composition, symmetry group...). Therefore, in order to fully characterize the system, it is sufficient to determine:

- the number of SIC,

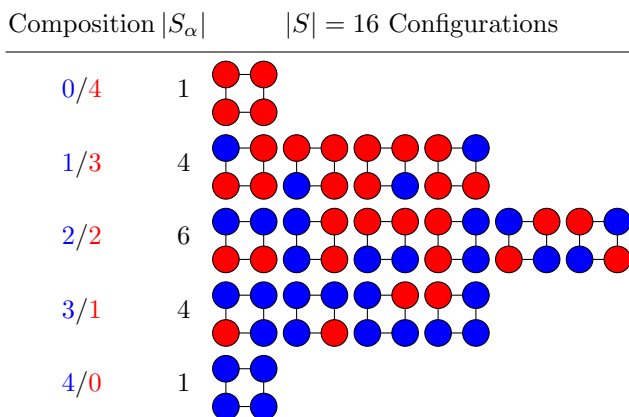


Figure 6.1: Possible configurations for 2 atomic species sitting on 4 positions. The two species are represented by red and blue circles. Configurations are ordered per composition. The number of configurations ($|S_\alpha|$) per composition is indicated.

- the number of configurations per SIC;
- one representative configuration for each SIC.

Such analysis is performed by the CRYSTAL alternative options **CONF CNT** (174) and **CONF RAND** (176). In order to study supercell configurations, the keyword **SCELCONF** (63) is to be coupled with the above mentioned options.

6.1 Counting and Enumerating Configurations

The keyword **CONF CNT** must be inserted in the geometry input block. It allows to calculate the number of classes as a function of the composition and provides a representative for each class.

In the present implementation:

- the number of different atomic species is restricted to two (\mathcal{A} and \mathcal{X});
- substitutions might take place on one or more crystallographic irreducible sites; for each irreducible site, all the symmetry equivalent positions are involved.

The minimal **CONF CNT** input is as follows:

| rec | variable | meaning |
|-----|-------------------|---------------------------------------|
| • | A CONF CNT | |
| • | * NIS | number of irreducible sites |
| • | * IAT(I),I=1,NIS | atomic label of each irreducible site |
| • | A END | end of the CONF CNT sub-block |

This yields the number of SIC over the full range of (NIS+1) compositions corresponding to NIS irreducible crystallographic positions. For each SIC, a representative configuration is given, along with its multiplicity and the number of symmetry operators of its group (being a subgroup of the group of the original cell). The representative configurations are printed in lexicographic order. By default, the *replacing* species is labeled as 'XX'.

The following optional keywords may be adopted for tuning **CONF CNT** calculations:

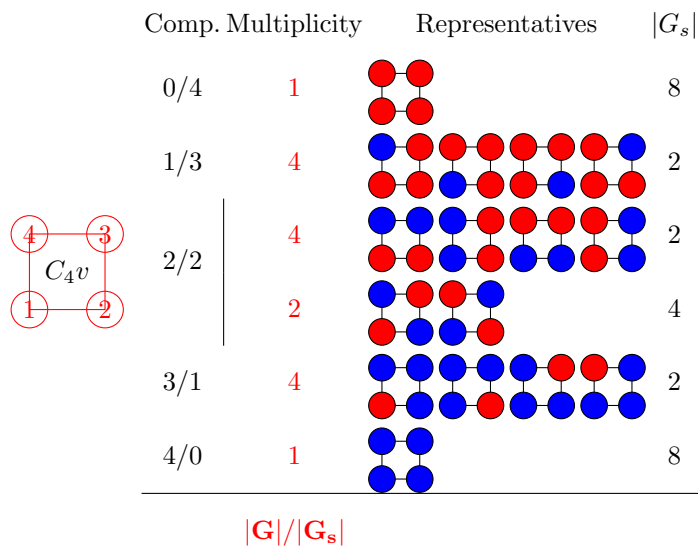


Figure 6.2: The six symmetry independent classes of configurations resulting of the action of the C_{4v} group on the set of 2-color configurations on 4 positions. The number of configurations per class or multiplicity is indicated. The number of symmetry operators in the group of each configuration is given ($|G_s|$). The multiplicity of each class equals $|G|/|G_s|$.

| rec variable | meaning |
|---------------------|--|
| • <i>A</i> ATOMB | identifies the species \mathcal{X} |
| • * NATB | atomic number of \mathcal{X} (default 'XX') |
| • <i>A</i> ONLYCOMP | selects certain compositions |
| • * NC | number of compositions to be considered |
| • * TC(I),I=1,NC | number of atoms \mathcal{X} in composition I |
| • <i>A</i> CONFPRT | prints information about the configurations |
| • * IP1 | integer $0 \div 2$ 0 - number of SIC only 1 - listing in compact form 2 - extended output [default] |

Further options exist for counting and enumerating two-body interactions. Two-body interactions are presented as:

$$\text{label At.1} - \text{label At.2 [I J L]}$$

At.1 is supposed to be in the reference cell $[0\ 0\ 0]$ but At.2 can be in another cell whose position is given by $[I\ J\ L]$. Interactions are presented adding the so-called empty and one-body terms, that are related to the cluster expansion formalism. These two terms are configuration independent; they depend only on chemistry.

| rec variable | meaning |
|-----------------------|--|
| • <i>A</i> INTPRT | prints information about the interactions |
| • * IP2 | integer $0 \div 2$ 0 - no information printed [default] 1 - condensed output (symmetry-independent interactions) 2 - extended output (full set of interactions) |
| • <i>A</i> INTMAXDIST | defines the distance cut-off for 2-body interactions |
| • * RLIM | distance in Å [default 6Å] |

6.2 Uniform Random Sampling of Symmetry Independent Configurations

When the number of classes is too large, a symmetry adapted Monte Carlo uniform at random sampling of the symmetry independent classes may be performed. In this case, the keyword **CONFRAND** must be inserted in the geometry input block and terminated by **END**. **CONFRAND** switches on a symmetry-adapted sampling of the SIC at a given composition IX (equivalent to α in equations (6.1) and (6.2)):

| rec | variable | meaning |
|-----|-----------------|---|
| • A | CONFRAND | |
| • * | NIS | number of irreducible sites |
| • * | IAT(I),I=1,NIS | atomic label of each irreducible site |
| • * | IX | number of positions occupied by the 2nd species |
| • A | END | end of the CONFRAND sub-block |

A file named CONFIGURATIONS.DAT is generated (see **RUNCONFS** at page 177) containing the following information:

- structure and symmetry of the *aristotype* supercell (written the same way as in a regular unit fort.34);
- number of equivalent crystallographic sites involved for substitutions ($|D|$) and number of substitutions (IX);
- labels of the atoms involved for substitutions;
- number of SIC found;
- list of the configurations. Each configuration is identified by its multiplicity and its rank.

For example:

```
. . . fort.34 . . . .
      8          4          ! 8 sites, 4 substitutions
1  2   3   4   5   6   7   8 ! labels of the involved sites
      4          ! 4 SIC found:
      1          8          1          ! label, multip, rank
      2          8          2          ! " " "
      3          48         6          ! " " "
      4          6          60         ! " " "
```

For each configuration found by sampling the SIC space, the corresponding *canonical* configuration (that is the equivalent configuration of minimum rank) is detected as well. One may consider only canonical configurations (and thus save the canonical rank in file CONFIGURATIONS.DAT) by entering the keyword **CANONIC** within the **CONFRAND** block.

By default, the SIC space is sampled entirely and uniformly at random. The user may limit either the number of tries or the number of SIC to be searched by exploiting the **UNIFORM** option (see below). Further optional keywords, namely **SYMONLY** and **SYASYM**, manage a tuned probability distribution according to whether the SIC are symmetric (that is having symmetry operators other than the identity) or not. **SYMONLY**, in particular, sets to 0 the probability of asymmetric SIC. Then, by using a large number of tries NTC, all the symmetric SIC might be found at no significant computational cost. Few runs are enough to establish the exact number of symmetric SIC, the less the larger the total number of SIC.

| rec variable | meaning |
|---------------|--|
| • A UNIFORM | uniform at random selection |
| • * NTC | integer number NTC > 0 number of tries to be performed NTC < 0 number of SIC to be searched; (maximum number of tries set to 10×NTC) |
| rec variable | meaning |
| • A SYMONLY | search for symmetric SIC only |
| • * NTC | NTC > 0 number of tries to be performed NTC < 0 number of SIC to be found |
| rec variable | meaning |
| • A SYASYM | search for symmetric SIC first; then for any SIC |
| • * NTCS,NTCA | > 0, NTCS tries on symmetric SIC and NTCA tries on any other SIC < 0, search NTCS symmetric SIC and NTCA other the SIC |

6.3 Calculations on Predefined Configurations

The keyword **RUNCONF**S must be inserted in the geometry input block. It opens the following minimal input sub-block:

| rec variable | meaning |
|--------------|---|
| • A RUNCONFS | |
| • A ATOMSUBS | identify the species involved for substitutions |
| • * IZA IZB | atomic numbers |
| • A END | |

By default, once specified the two elements involved for substitutions, **RUNCONF**S builds a set of configurations from the list of ranks written in file CONFIGURATIONS.DAT (176) and performs single point calculations. Geometry optimizations are also allowed, and may be activated with the keyword **OPTGEOM** (for the relative options see page 118).

The basis set complete with the functions for atom IZB must be given in input after the SCF block: the keyword **BASE** opens a new input block where a standard basis set must be inserted (Section 2.2).

Independent calculations on different configurations might be carried on simultaneously exploiting the option

| rec variable | meaning |
|----------------------|---------------------------------------|
| • A MULTITASK | perform multiple tasks simultaneously |
| • * N | number of tasks |

Further optional keywords are:

| rec variable | meaning |
|---------------------|---|
| • A SYMORDER | sort SIC from file CONFIGURATIONS.DAT in order of increasing multiplicity |
| • A INICO | select the first configuration to be considered |
| • * IB | 1st configuration label |
| • A IFICO | select the last configuration to be considered |
| • * IE | last configuration label |

The order of execution follows that of the list of configurations written in file CONFIGURATIONS.DAT unless the option **SYMORDER** is introduced which rearranges the SIC in order of increasing multiplicity (that is with a decreasing number of symmetry operators).

The options **INICO** and **IFICO** allow to perform "multi-step" calculations by consecutively selecting different subsets of configurations from file CONFIGURATIONS.DAT or from the list rearranged by **SYMORDER**. This possibility might be useful not only to manage wall-time queues, but also to restart **RUNCONF**S from the configuration closest to the point where it eventually failed.

Chapter 7

Equations of State

The program can perform an automated scan over the volume in order to compute energy E vs. volume V curves that are then fitted to various Equations of State (EOS) as Murnaghan's, third-order isothermal Birch-Murnaghan's, "universal" logarithmic Poirier-Tarantola's and exponential Vinet's, in order to compute equilibrium properties such as bulk modulus B_0 and its first derivative with respect to the pressure B'_0 and volume/pressure dependence of the energy, enthalpy and bulk modulus. For each volume, a full V -constrained geometry optimization is performed. This option is activated by inserting the keyword **EOS** at the end of the Geometry input block, which opens a sub-block that must be closed with a keyword **END**:

```
. . . geometry input . . . .  
EOS  
[Optional keywords]  
END   close EOS input block  
END   close Geometry input block
```

A volume range and a number of volumes N_V can be defined in input (default values are used otherwise) with the **RANGE** sub-keyword. The initial geometry is assumed to be fully optimized; if not, the **PREOPTGEOM** sub-keyword must be used to perform a preliminary optimization of both lattice parameters and atomic positions. For each considered volume V_i , a V_i -constrained optimization is performed (in fractional coordinates only) and the corresponding minimum energy E_i determined. The set of N_V data points $\{V_i, E_i\}$ is fitted to the various EOSs implemented. The fitted energy, enthalpy and bulk modulus are printed at the end of the calculation, for each EOS, as a function of volume and pressure at various points. These volume/pressure ranges can be defined with sub-keywords **VRANGE** and **PRANGE**, respectively. Typically, this kind of final information analysis can be performed with a complete restart of the calculation, using the **RESTART2** sub-keyword. A partial restart from a previous incomplete run can be activated with the sub-keyword **RESTART**. These two restart options require the external restart file EOSINFO.DAT.

7.1 A few theoretical remarks

The equilibrium bulk modulus B_0 of a crystal can be defined as follows:

$$B_0 = -V \left(\frac{\partial P}{\partial V} \right)_T . \quad (7.1)$$

A dimensionless parameter B'_0 can then be defined as its first derivative with respect to the pressure, at constant temperature T :

$$B'_0 = \left(\frac{\partial B_0}{\partial P} \right)_T . \quad (7.2)$$

Let us recall that the pressure P may be written as a function of the volume V as:

$$P(V) = - \left(\frac{\partial E}{\partial V} \right)_S . \quad (7.3)$$

According to equation (7.3) we can redefine the bulk modulus in equation (7.1) as the second energy derivative with respect to the volume:

$$B(V) = V \left(\frac{\partial^2 E}{\partial V^2} \right)_{T,S} . \quad (7.4)$$

We can now define the enthalpy H (coinciding with Gibbs' free energy G at $T = 0$ K) as a function of the volume V simply as:

$$H(V) = E(V) + P(V) \times V . \quad (7.5)$$

Several $E(V)$ equations of state have been proposed. We have implemented four among them.

1. In 1944, Murnaghan proposed his famous equation of state:

$$E(V) = E_0 + \frac{B_0 V}{B'_0} \left[\left(\frac{V_0}{V} \right)^{B'_0} \frac{1}{B'_0 - 1} + 1 \right] - \frac{B_0 V_0}{B'_0 - 1} , \quad (7.6)$$

where V_0 and E_0 are the equilibrium volume and energy, at zero pressure. Application of equation (7.3) to equation (7.6), gives $P(V)$ Murnaghan's EOS:

$$P(V) = \frac{B_0}{B'_0} \left[\left(\frac{V_0}{V} \right)^{B'_0} - 1 \right] . \quad (7.7)$$

2. The third-order Birch-Murnaghan isothermal equation of state, published in 1947, reads like:

$$E(V) = E_0 + \frac{9V_0 B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\} . \quad (7.8)$$

Again, according to equation (7.3), we can get $P(V)$ third-order Birch-Murnaghan's EOS:

$$P(V) = \frac{3B_0}{2} \left[\left(\frac{V_0}{V} \right)^{\frac{7}{3}} - \left(\frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\} . \quad (7.9)$$

3. The third-order "universal" Poirier-Tarantola logarithmic equation of state, proposed in 1998, is:

$$E(V) = E_0 + \frac{B_0 V_0}{2} \left[\ln \left(\frac{V_0}{V} \right) \right]^2 + \frac{B_0 V_0}{6} \left[\ln \left(\frac{V_0}{V} \right) \right]^3 (B'_0 - 2) , \quad (7.10)$$

while $P(V)$ Poirier-Tarantola's EOS is:

$$P(V) = B_0 \frac{V_0}{V} \left[\ln \left(\frac{V_0}{V} \right) + \frac{(B'_0 - 2)}{2} \left[\ln \left(\frac{V_0}{V} \right) \right]^2 \right] . \quad (7.11)$$

4. The exponential Vinet's equation of state, published in 1987, reads:

$$\begin{aligned} E(V) &= E_0 + \frac{2B_0 V_0}{(B'_0 - 1)^2} \left\{ 2 - \left[5 + 3 \left(\frac{V}{V_0} \right)^{\frac{1}{3}} (B'_0 - 1) - 3B'_0 \right] \times \right. \\ &\times \left. \exp \left[-\frac{3}{2} (B'_0 - 1) \left[\left(\frac{V}{V_0} \right)^{\frac{1}{3}} - 1 \right] \right] \right\} \end{aligned} \quad (7.12)$$

According to equation (7.3), we get $P(V)$ Vinet's EOS:

$$P(V) = 3B_0 \left(\frac{V}{V_0} \right)^{-\frac{2}{3}} \left[1 - \left(\frac{V}{V_0} \right)^{\frac{1}{3}} \right] \exp \left[-\frac{3}{2} (B'_0 - 1) \left[\left(\frac{V}{V_0} \right)^{\frac{1}{3}} - 1 \right] \right] . \quad (7.13)$$

7.2 Keywords, options and defaults

A default value is chosen for all computational parameters. The SCF energy convergence threshold is set to 10^{-8} . Optional keywords are (in any order):

| rec | variable | meaning |
|-----|----------------|--|
| • | A RANGE | keyword to specify the range of volumes and number of points in the $E(V)$ curve where optimizations have to be performed. |
| * | VOL1 | minimum (compression) variation of the initial volume [<i>default</i> = 0.92] |
| * | VOL2 | maximum (expansion) variation of the initial volume [<i>default</i> = 1.08] |
| * | NPOINTS | number N_V of points in the selected range [<i>default</i> = 10] |

The interval is specified as the minimum (compression) and maximum (expansion) variation of the volume of the initial geometry. The set of volumes is then defined according to the number of points in the selected range. For instance, to set the default values:

```
EOS
RANGE
0.92 1.08 10
END
```

that corresponds to 10 points between $0.92 \times V_{eq}$ and $1.08 \times V_{eq}$, where V_{eq} is the volume of the equilibrium geometry given as input (assumed to be the fully optimized structure) or as obtained after a preliminary geometry optimization. Note that the equilibrium values V_0 and E_0 are always included in the final data for fitting (*i.e.* 11 points are used for fitting in the example above).

| rec | variable | meaning |
|-----|-----------------|--|
| • | A VRANGE | Defines the volume range and the number of points where fitted values of pressure, energy, enthalpy and bulk modulus are printed at the end of the calculation. This keyword is for output purposes only. |
| * | VMIN | minimum volume |
| * | VMAX | maximum volume |
| * | NVOL | number of points in the selected range |
| • | A PRANGE | Defines the pressure range and the number of points where fitted values of volume, energy, enthalpy and bulk modulus are printed at the end of the calculation. This keyword is for output purposes only. |
| * | PMIN | minimum pressure |
| * | PMAX | maximum pressure |
| * | NPRE | number of points in the selected range |
| • | A PRINT | This option turns on a higher level of diagnostic printing and will generally not be necessary for the typical user. Fitting of the $E(V)$ points is also performed for increasing set of points from 4 to the maximum number of points. (<i>default</i> is minimal printing) |

| rec variable | meaning |
|-----------------------|--|
| • A RESTART | Allows for partial restart from a previous incomplete run, using file EOSINFO.DAT. |
| • A RESTART2 | Allows for complete restart from a previous complete run, using file EOSINFO.DAT. This option can be used when one wants to explore different ranges of volume/pressure at the end of the calculation, using keywords VRANGE and PRANGE (see example below). |
| • A PREOPTGEOM | A preliminary geometry optimization of cell and atomic positions is performed before starting the $E(V)$ curve calculation. |

Geometry optimization is performed at convergence criteria tighter than the ones given in **OPTGEOM**. Some values can be modified by inserting the following keywords:

| | |
|-----------------------|---|
| • A TOLDEG | EOS default [0.0003] - see OPTGEOM , page 124 |
| • A TOLDEX | EOS default [0.00062] - see OPTGEOM , page 124 |
| • A TOLDEE | EOS default [8] - see OPTGEOM , page 124 |
| • A MAXCYCLE | see OPTGEOM , page 126 |
| • A NOTRISTR | see OPTGEOM , page 124 |
| • A TRUSRADIUS | see OPTGEOM , page 125 |
| • A MAXRADIUS | see OPTGEOM , page 124 |

7.3 Output Information

Let us consider the case of α -quartz, with the following input:

```
EOS
RANGE
0.90 1.05 10
PRANGE
-5 10 20
END
```

At the end of the calculation, the 11 volume/energy data points obtained after the geometry optimizations are sorted and printed as follows:

```

SORTING VOLUMES/ENERGIES

VOLUME (A^3)    ENERGY (a.u.)

105.093052     -1.319745599801E+03
106.955671     -1.319747774744E+03
108.858269     -1.319749524843E+03
110.762118     -1.319750838191E+03
112.687177     -1.319751759039E+03
114.634069     -1.319752307968E+03
116.602831     -1.319752502563E+03
116.803375     -1.319752503067E+03
118.593687     -1.319752358314E+03
120.606573     -1.319751889709E+03
122.641225     -1.319751107890E+03
```

The following table is then reported with the fitted values of the minimum volume, energy, bulk modulus B_0 and its first derivative B'_0 :

+++++++ FITTING USING ALL POINTS +++++++

| EQUATION OF STATE | VOL(A ³) | E(AU) | BM(GPA) | BM PRIME |
|------------------------|----------------------|----------------|---------|----------|
| MURNAGHAN 1944 | 116.7247 | -1319.75250331 | 43.81 | 3.78 |
| BIRCH-MURNAGHAN 1947 | 116.7202 | -1319.75250331 | 43.83 | 3.88 |
| POIRIER-TARANTOLA 1998 | 116.7172 | -1319.75250341 | 43.85 | 3.95 |
| VINET 1987 | 116.7186 | -1319.75250334 | 43.84 | 3.92 |

Additionally, for each EOS, the following fitted data are reported (for instance Vinet's ones) in the pressure range (from -5 GPa to 10 GPa in this case) defined by input with the **PRANGE** sub-keyword (the **VRANGE** sub-keyword could be used instead for defining an explored volume range):

+++++++
THERMODYNAMIC FUNCTIONS OBTAINED WITH EOS: VINET 1987
+++++++

V = VOLUME, P = PRESSURE, E = ENERGY, G = GIBBS FREE ENERGY, B = BULK MODULUS

| V (A ³) | P (GPa) | E (a.u.) | G (a.u.) | B (GPa) |
|---------------------|---------|----------------|----------------|---------|
| 136.37 | -5.00 | -1319.73967343 | -1319.89603452 | 21.96 |
| 131.93 | -4.21 | -1319.74437012 | -1319.87175596 | 25.86 |
| 128.22 | -3.42 | -1319.74762603 | -1319.84821045 | 29.53 |
| 125.02 | -2.63 | -1319.74985141 | -1319.82528837 | 33.03 |
| 122.21 | -1.84 | -1319.75129893 | -1319.80290843 | 36.40 |
| 119.70 | -1.05 | -1319.75213646 | -1319.78100994 | 39.65 |
| 117.43 | -0.26 | -1319.75248193 | -1319.75954364 | 42.81 |
| 115.35 | 0.53 | -1319.75242166 | -1319.73847018 | 45.89 |
| 113.45 | 1.32 | -1319.75202088 | -1319.71775646 | 48.90 |
| 111.68 | 2.11 | -1319.75133026 | -1319.69737458 | 51.86 |
| 110.04 | 2.90 | -1319.75038992 | -1319.67730070 | 54.75 |
| 108.51 | 3.69 | -1319.74923235 | -1319.65751494 | 57.61 |
| 107.06 | 4.47 | -1319.74788404 | -1319.63799827 | 60.41 |
| 105.71 | 5.26 | -1319.74636708 | -1319.61873479 | 63.18 |
| 104.42 | 6.05 | -1319.74470011 | -1319.59971153 | 65.91 |
| 103.20 | 6.84 | -1319.74289869 | -1319.58091375 | 68.61 |
| 102.04 | 7.63 | -1319.74097644 | -1319.56233179 | 71.28 |
| 100.94 | 8.42 | -1319.73894489 | -1319.54395405 | 73.91 |
| 99.89 | 9.21 | -1319.73681430 | -1319.52577266 | 76.53 |
| 98.88 | 10.00 | -1319.73459329 | -1319.50777698 | 79.11 |

Chapter 8

Calculation of Elastic, Piezoelectric and Photoelastic Constants

The program can compute elastic, piezoelectric and photoelastic (elasto-optic) tensors with a fully-automated procedure by means of keywords **ELASTCON**, **PIEZOCON** and **PHOTOELA**, to be inserted at the end of the Geometry input block. Elastic and piezoelectric constants can be computed at once with the **ELAPIEZO** keyword. Each of these keywords opens a block which must be terminated with an **END** keyword. When elastic constants are computed, the bulk modulus is also printed.

8.1 A few theoretical remarks

The elements of the elastic tensor, for 3D systems, are usually defined as:

$$C_{vu} = \frac{1}{V} \left. \frac{\partial^2 E}{\partial \eta_v \partial \eta_u} \right|_0, \quad (8.1)$$

where η is the rank-2 symmetric tensor of pure strain and Voigt's notation is used according to which $v, u = 1, \dots, 6$ ($1 = xx$, $2 = yy$, $3 = zz$, $4 = yz$, $5 = xz$, $6 = xy$). Since volume V is not uniquely defined for 1D and 2D systems, it is here omitted (length or surface could be used instead) and all the elements involving non-periodic directions (y, z for 1D and z for 2D systems) are null by definition. As a consequence, for 1D and 2D systems, elastic constants are expressed in energy units (hartree). Second derivatives in equation (8.1) are computed as first numerical derivatives of analytical energy gradients in the present implementation.

In the linear regime, *direct* \mathbf{e} and *converse* \mathbf{d} piezoelectric tensors describe the polarization \mathbf{P} induced by strain η and the strain induced by an external electric field \mathbf{E} at constant electric field and stress, respectively:

$$\text{direct effect} \quad \mathbf{P} = \mathbf{e} \eta \quad \text{at constant field} \quad (8.2)$$

$$\text{converse effect} \quad \eta = \mathbf{d}^T \mathbf{E} \quad \text{at constant stress} \quad (8.3)$$

Our approach consists in directly computing the intensity of polarization induced by strain (again, since the volume is not defined for 1D and 2D systems, in those cases the polarization reduces to a dipole moment.). The Cartesian components of the polarization can then be expressed as follows in terms of the strain tensor components:

$$P_i = \sum_v e_{iv} \eta_v \quad \text{so that} \quad e_{iv} = \left(\frac{\partial P_i}{\partial \eta_v} \right)_E. \quad (8.4)$$

In the above expression, $i = 1, \dots, 3$; η is the pure strain tensor, the derivative is taken at constant electric field and Voigt's notation is used. In **CRYSTAL** the polarization can be

computed either via localized Wannier functions or via the Berry phase (BP) approach. The latter scheme is used in the present automated implementation according to which direct piezoelectric constants can be written as follows in terms of numerical first derivatives of the BP φ_l with respect to the strain:

$$e_{iv} = \frac{|e|}{2\pi V} \sum_l a_{li} \frac{\partial \varphi_l}{\partial \eta_v}, \quad (8.5)$$

where a_{li} is the i -th Cartesian component of the l -th direct lattice basis vector \mathbf{a}_l . Again, for 1D and 2D systems, the volume is omitted, the polarization reduces to a dipole moment and the piezoelectric constants are reported in units of $|e| \times bohr$.

A simple direct connection exists between *direct* \mathbf{e} and *converse* \mathbf{d} piezoelectric tensors:

$$\mathbf{e} = \mathbf{d}\mathbb{C} \quad \text{and} \quad \mathbf{d} = \mathbf{e}\mathbb{S}, \quad (8.6)$$

where \mathbb{C} is the fourth rank elastic tensor of energy second derivatives with respect to pairs of deformations and $\mathbb{S} = \mathbb{C}^{-1}$ is the fourth rank compliance tensor.

Photoelastic constants are the elements of the fourth rank photoelastic (Pockels) tensor and are defined as:

$$p_{ijkl} = \frac{\partial \Delta \epsilon_{ij}^{-1}}{\partial \eta_{kl}}, \quad (8.7)$$

where $\Delta \epsilon^{-1}$ is the difference of the inverse dielectric tensor between strained and unstrained configurations.

The derivatives in the right-hand-sides of equations (8.1), (8.5) and (8.7) are computed numerically by applying finite strains to the crystal lattice. For each strain, N_s configurations are defined according to a strain step δ . By default, $N_s = 3$, corresponding to one “expanded”, one unstrained and one “contracted” configuration, and $\delta = 0.01$ for elastic and $\delta = 0.015$ for piezoelectric and photoelastic constants. Parameter N_s can be modified with the sub-keyword **NUMDERIV** while δ can be modified with sub-keyword **STEPSIZE**.

We recall that elastic, piezoelectric and photoelastic constants can be decomposed into purely electronic “clamped-ion” and nuclear “internal-strain” contributions; the latter, computed by default, measures the effect of relaxation of the relative positions of atoms induced by the strain and can be computed by optimizing the atomic positions within the crystal cell. If one wants to compute “clamped-ion” constants can use the sub-keyword **CLAMPION**.

The input geometry is assumed to be optimized; nevertheless, the user can ask this module to perform a pre-optimization of the structure by means of the **PREOPTGEOM** sub-keyword; convergence tolerances on gradient and displacement can be modified by means of the **TOLDEG** and **TOLDEX** sub-keywords.

For elastic, piezoelectric and photoelastic constants a flexible restart option has been prepared which can be activated with the **RESTART** sub-keyword and which uses an external formatted file called ELASINFO.DAT. Detailed printings (recommended) can be activated with the **PRINT** sub-keyword.

8.2 The algorithm

We present here the fully automated procedure for the calculation of the elastic, piezoelectric and photoelastic constants as implemented in CRYSTAL:

1. The starting geometrical structure of the crystal is accurately optimized as concerns both lattice parameters and atomic positions;
2. A single-point self-consistent-field (SCF) calculation is performed on the optimized reference structure. Energy gradients, Berry phase or dielectric tensor (via a CPHF/KS scheme) are also computed;
3. A symmetry analysis is performed in order to find the minimal set of strains, out of a maximum of six, which have to be explicitly applied in order to get all the independent constants. The symmetry features of third and fourth rank tensors is printed in the following way:


```

| 1 A    1 F    1 C    .    1 B    .    |
|         1 A    1 C    .   -1 B    .    |
|                1 E    .    .    .    |
|                    1 D    .   -1 B    |
|                        1 D    .    |
|                                &    |

```

4. For each irreducible strain, the deformation is applied to the structure and the residual symmetry determined. N_s strained configurations are defined according to a strain step δ ;
5. For each strained configuration, the atomic positions are relaxed with an optimization (default option) or not depending on whether one wants to go beyond the “clamped-ion” approximation or not. An SCF calculation is then performed with gradient, Berry phase or dielectric tensor calculation;
6. After the loop over the N_s strained configurations, the energy gradients, Berry phases or dielectric tensors are fitted with singular-value-decomposition routines and their first derivatives determined numerically; Elastic, piezoelectric or photoelastic constants are finally computed and printed.

8.3 Second-order Elastic Constants

A fully-automated procedure for calculating the second-order elastic constants for an arbitrary crystal is activated by specifying the keyword **ELASTCON** in input block 1 (geometry). **ELASTCON** must be the last keyword in geometry input:

```

. . . geometry input . . . .
ELASTCON
END      close ELASTCON input block
END      close geometry input block

```

Note that the user must be confident that the input structure is already well optimized. At the beginning of the run, the forces at the central point are calculated and if they exceed 10^{-4} , then a warning is printed suggesting re-optimization.

Users of this option are kindly requested to cite the following papers[135, 63]:

W.F. Perger, J. Criswell, B. Civalleri and R. Dovesi, *Comp. Phys. Comm.*, **180**, 1753-1759 (2009). *Ab-initio calculation of elastic constants of crystalline systems with the CRYSTAL code*

A. Erba, A. Mahmoud, R. Orlando and R. Dovesi, *Phys. Chem. Minerals*, Doi: 10.1007/s00269-013-0630-4 (2013). *Elastic properties of six silicate garnet end-members from accurate ab initio simulations.*

Users of this option for 1D and 2D systems are kindly requested to cite the following paper[61]:

A. Erba, M. Ferrabone, J. Baima, R. Orlando, M. Rérat and R. Dovesi, *J. Chem. Phys.*, **138**, 054906 (2013). *The vibration properties of the (n,0) Boron Nitride nanotubes from ab initio quantum chemical simulations.*

Keywords, options, and defaults

A default value is chosen for all computational parameters. SCF energy convergence threshold is set to 10^{-8} . To modify it, see keyword **TOLDEE** in input block 3, page 115.

Default choices can be modified by optional keywords (in any order):

| rec variable | meaning |
|--------------------------------------|---|
| • A NUMBERIV * INUM | This sets the number of points for the numerical second derivative number of points including the central (zero displacement) one [<i>default</i> = 3] |
| • A STEPSIZE * STEP | This gives the size of the displacement to be used for the calculation of the numerical second derivative. size of the strain step along a given deformation [<i>default</i> = 0.01] |
| • A DEFORM * DEF(I), I=1,6 | Specific deformations are asked for Six integers have to be provided, each one associated to a given deformation (<i>xx</i> , <i>yy</i> , <i>zz</i> , <i>yz</i> , <i>xz</i> , <i>xy</i>) that tell the program which deformations have to be considered as active. Put 1 for active and 0 for inactive. By default, the program performs a symmetry analysis and finds which deformations are necessary. |

| rec variable | meaning |
|-------------------------------|---|
| • A CLAMPION | This option activates the computation of “clamped-ion” constants. |
| • A PRINT | This option turns on a higher level of diagnostic printing [<i>default</i> minimal printing]. |
| • A RESTART | Allows restart using file <i>ELASINFO.DAT</i> from a previous incomplete run. |
| • A RESTART2 | Allows a full restart using file <i>ELASINFO.DAT</i> from a previous complete run. |
| • A PREOPTGEOM | A preliminary geometry optimization of cell and atomic positions is performed before starting elastic constant calculation. |
| • A SEISMDIR * NDIR | Defines additional directions along which seismic wave velocities are computed. Number of additional directions |
| | Insert NDIR records II |
| * DX,DY,DZ | Cartesian components of each additional direction II |

Geometry optimization is performed at convergence criteria tighter than the ones given in **OPTGEOM**. Some values can be modified by inserting the following keywords:

| | |
|------------------------|--|
| • A TOLDEG | ELASTCON default [0.0003] - see OPTGEOM , page 124 |
| • A TOLDEX | ELASTCON default [0.00062] - see OPTGEOM , page 124 |
| • A TOLDEE | ELASTCON default [8] - see OPTGEOM , page 124 |
| • A MAXCYCLE | see OPTGEOM , page 126 |
| • A NOTRISTR | see OPTGEOM , page 124 |
| • A TRUSTRADIUS | see OPTGEOM , page 125 |
| • A MAXTRADIUS | see OPTGEOM , page 124 |

Input Example:

```

. . . geometry input . . . .
ELASTCON
NUMBERIV  modify default choice of n. points [3]
5
STEPSIZE  modify step size for numerical gradient [0.01]
0.02
PRINT     extended printing
END       end of ELASTCON input
END       geometry input

```

The information on the computed elastic constants is printed at the end of the output with the following format:

SYMMETRIZED ELASTIC CONSTANTS FOR HEXAGONAL CASE, IN GPa

| | | | | | | | |
|--|--------|--------|---------|--------|---------|---------|--|
| | 89.130 | 13.792 | 20.473 | 0.000 | 12.584 | 0.000 | |
| | | 89.130 | 20.473 | 0.000 | -12.584 | 0.000 | |
| | | | 113.498 | 0.000 | 0.000 | 0.000 | |
| | | | | 58.682 | 0.000 | -12.584 | |
| | | | | | 58.682 | 0.000 | |
| | | | | | | 37.669 | |

Compliance tensor is also printed as:

ELASTIC MODULI (COMPLIANCE TENSOR), IN TPa⁻¹

| | | | | | | | |
|--|-----------|-----------|-----------|-----------|-----------|-----------|--|
| | 12.382521 | -1.915287 | -1.888081 | 0.000000 | -3.066002 | 0.000000 | |
| | | 12.382521 | -1.888081 | 0.000000 | 3.066002 | 0.000000 | |
| | | | 9.491835 | 0.000000 | 0.000000 | 0.000000 | |
| | | | | 18.355822 | 0.000000 | 6.132004 | |
| | | | | | 18.355822 | 0.000000 | |
| | | | | | | 28.595616 | |

According to the elastic continuum theory, the three acoustic wave velocities of a crystal, along any general direction represented by unit wave-vector $\hat{\mathbf{q}}$, are related to the elastic constants by Christoffel's equation which can be given an eigenvalues/eigenvectors form, as follows:

$$\mathbf{A}^{\hat{\mathbf{q}}}\mathbf{U} = \mathbf{V}^2\mathbf{U} \quad \text{with} \quad A_{kl}^{\hat{\mathbf{q}}} = \frac{1}{\rho}\hat{q}_i C_{iklj}\hat{q}_j, \quad (8.8)$$

where ρ is the crystal density, $i, j, k, l = x, y, z$ represent Cartesian directions, \hat{q}_i is the i -th element of the unit vector $\hat{\mathbf{q}}$, \mathbf{V} is a 3×3 diagonal matrix whose three elements give the acoustic velocities and $\mathbf{U} = (\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{u}}_3)$ is the eigenvectors 3×3 matrix where each column represents the polarization $\hat{\mathbf{u}}$ of the corresponding eigenvalue. The three acoustic wave velocities, also referred to as seismic velocities, can be labeled as longitudinal v_p , slow transverse v_{s1} and fast transverse v_{s2} , depending on the polarization direction $\hat{\mathbf{u}}$ with respect to wave-vector $\hat{\mathbf{q}}$. The seismic wave velocities are computed by default along some Cartesian directions and printed as follows (note that slow and fast transverse wave velocities are sorted according to their values; crossing are possible which should be carefully checked):

SEISMIC VELOCITIES BY CHRISTOFFEL EQUATION (km/s)

| WAVE VECTOR | Vp | Vs1 | Vs2 |
|----------------------|-------|-------|-------|
| [0.000 0.000 1.000] | 9.237 | 5.068 | 5.068 |
| [0.000 1.000 0.000] | 9.237 | 5.068 | 5.068 |
| [1.000 0.000 0.000] | 9.237 | 5.068 | 5.068 |
| [1.000 1.000 0.000] | 9.166 | 5.195 | 5.068 |
| [1.000 0.000 1.000] | 9.166 | 5.195 | 5.068 |
| [0.000 1.000 1.000] | 9.166 | 5.195 | 5.068 |
| [1.000 1.000 1.000] | 9.142 | 5.153 | 5.153 |

User-defined Cartesian directions can be added by means of the **SEISMDIR** sub-keyword, along which the seismic wave velocities are computed and printed (typically, this can be done *a posteriori* with a complete restart using the **RESTART2** sub-keyword).

Internal Diagnostics

In order to monitor the quality of the calculation as it proceeds, the total energy after optimization is stored. The recommended use of the **ELASTCON** option assumes that the user supplies an input file from a previously optimized geometry (and not experimental lattice constants and atomic positions, for example). Therefore, in principle, as the various deformations are made, the optimized total energy for each of the deformed geometries should be higher than the energy at the undeformed, equilibrium, geometry. The code monitors each optimized total energy for each deformed geometry and if any deformation lowers the total energy from the equilibrium value, a warning is printed for the user to verify that the input file was really from a previously optimized geometry.

8.4 First-order Piezoelectric Constants

A fully-automated procedure for calculating the first-order piezoelectric constants for an arbitrary crystal is activated by specifying the keyword **PIEZOCON** in input block 1 (geometry). **PIEZOCON** must be the last keyword in geometry input:

```
. . . geometry input . . . .
PIEZOCON
END          close PIEZOCON input block
END          close geometry input block
```

Note that the user must be confident that the input structure is already well optimized. At the beginning of the run, the forces at the central point are calculated and if they exceed 10^{-4} , then a warning is printed suggesting re-optimization.

Users of this option are kindly requested to cite the following papers[122, 60]:

Y. Noel and C. M. Zicovich-Wilson and B. Civalleri and Ph. D'Arco and R. Dovesi, *Phys. Rev. B*, **65**, 014111 (2001). *Polarization properties of ZnO and BeO: An ab initio study through the Berry phase and Wannier functions approaches.*

A. Erba, Kh. E. El-Kelany, M. Ferrero, I. Baraille and M. Rérat, *Phys. Rev. B*, **88**, 035102 (2013). *Piezoelectricity of SrTiO₃: An ab initio description.*

Users of this option for 1D and 2D systems are kindly requested to cite the following paper[61]:

A. Erba, M. Ferrabone, J. Baima, R. Orlando, M. Rérat and R. Dovesi, *J. Chem. Phys.*, **138**, 054906 (2013). *The vibration properties of the (n,0) Boron Nitride nanotubes from ab initio quantum chemical simulations.*

Keywords, options, and defaults

A default value is chosen for all computational parameters. SCF energy convergence threshold is set to 10^{-8} . To modify it, see keyword **TOLDEE** in input block 3, page 115.

Default choices can be modified by optional keywords (in any order):

| rec variable | meaning |
|--------------------------------------|---|
| • A NUMBERIV * INUM | This sets the number of points for the numerical second derivative number of points including the central (zero displacement) one [<i>default = 3</i>] |
| • A STEPSIZE * STEP | This gives the size of the displacement to be used for the calculation of the numerical second derivative. size of the strain step along a given deformation [<i>default = 0.015</i>] |
| • A DEFORM * DEF(I), I=1,6 | Specific deformations are asked for Six integers have to be provided, each one associated to a given deformation (<i>xx, yy, zz, yz, xz, xy</i>) that tell the program which deformations have to be considered as active. Put 1 for active and 0 for inactive. By default, the program performs a symmetry analysis and finds which deformations are necessary. |

| rec variable | meaning |
|-----------------------|---|
| • A CLAMPION | This option activates the computation of “clamped-ion” constants. |
| • A PRINT | This option turns on a higher level of diagnostic printing [<i>default minimal printing</i>] |
| • A RESTART | Allows restart using file <i>ELASINFO.DAT</i> from a previous incomplete run. |
| • A RESTART2 | Allows a full restart using file <i>ELASINFO.DAT</i> from a previous complete run. |
| • A PREOPTGEOM | A preliminary geometry optimization of cell and atomic positions is performed before starting elastic constant calculation. |

Geometry optimization is performed at convergence criteria tighter than the ones given in **OPTGEOM**. Some values can be modified by inserting the following keywords:

| | |
|------------------------|--|
| • A TOLDEG | PIEZOCON default [0.0003] - see OPTGEOM , page 124 |
| • A TOLDEX | PIEZOCON default [0.00062] - see OPTGEOM , page 124 |
| • A TOLDEE | PIEZOCON default [8] - see OPTGEOM , page 124 |
| • A MAXCYCLE | see OPTGEOM , page 126 |
| • A NOTRISTR | see OPTGEOM , page 124 |
| • A TRUSTRADIUS | see OPTGEOM , page 125 |
| • A MAXTRADIUS | see OPTGEOM , page 124 |

Input Example:

```
. . . geometry input . . . .
PIEZOCON
NUMBERIV  modify default choice of n. points [3]
5
STEPSIZE  modify step size for numerical gradient [0.015]
0.02
CLAMPION  activates "clamped-ion" approximation
PRINT     extended printing
END       end of PIEZOCON input
END       geometry input
```

The computed piezoelectric tensor is printed as follows at the end of the output:

PIEZOELECTRIC CONSTANTS FOR HEXAGONAL CASE, IN C/m²

| | | | | | | | |
|--|--------|--------|-------|--------|--------|-------|--|
| | 0.000 | 0.000 | 0.000 | 0.000 | -0.090 | 0.000 | |
| | 0.000 | 0.000 | 0.000 | -0.090 | 0.000 | 0.000 | |
| | -0.187 | -0.187 | 0.282 | 0.000 | 0.000 | 0.000 | |

8.5 Elastic and Piezoelectric Constants

A fully-automated procedure for calculating the second-order elastic constants and the first-order piezoelectric (direct and converse) constants for an arbitrary crystal is activated by specifying the keyword **ELAPIEZO** in input block 1 (geometry).

ELAPIEZO must be the last keyword in geometry input:

```
. . . geometry input . . . .
ELAPIEZO
END          close ELAPIEZO input block
END          close geometry input block
```

Note that the user must be confident that the input structure is already well optimized. At the beginning of the run, the forces at the central point are calculated and if they exceed 10^{-4} , then a warning is printed suggesting re-optimization.

Users of this option are kindly requested to cite the following papers[122, 60]:

Y. Noel and C. M. Zicovich-Wilson and B. Civalleri and Ph. D'Arco and R. Dovesi, *Phys. Rev. B*, **65**, 014111 (2001). *Polarization properties of ZnO and BeO: An ab initio study through the Berry phase and Wannier functions approaches.*

A. Erba, Kh. E. El-Kelany, M. Ferrero, I. Baraille and M. Rérat, *Phys. Rev. B*, **88**, 035102 (2013). *Piezoelectricity of SrTiO₃: An ab initio description.*

Users of this option for 1D and 2D systems are kindly requested to cite the following paper[61]:

A. Erba, M. Ferrabone, J. Baima, R. Orlando, M. Rérat and R. Dovesi, *J. Chem. Phys.*, **138**, 054906 (2013). *The vibration properties of the (n,0) Boron Nitride nanotubes from ab initio quantum chemical simulations.*

Keywords, options, and defaults

A default value is chosen for all computational parameters. SCF energy convergence threshold is set to 10^{-8} . To modify it, see keyword **TOLDEE** in input block 3, page 115.

Default choices can be modified by optional keywords (in any order):

| rec variable | meaning |
|--|---|
| <ul style="list-style-type: none"> • A NUMDERIV * INUM | This sets the number of points for the numerical second derivative number of points including the central (zero displacement) one [<i>default</i> = 3] |
| <ul style="list-style-type: none"> • A STEPSIZE * STEP | This gives the size of the displacement to be used for the calculation of the numerical second derivative. size of the strain step along a given deformation [<i>default</i> = 0.015] |
| <ul style="list-style-type: none"> • A DEFORM * DEF(I), I=1,6 | Specific deformations are asked for Six integers have to be provided, each one associated to a given deformation (<i>xx, yy, zz, yz, xz, xy</i>) that tell the program which deformations have to be considered as active. Put 1 for active and 0 for inactive. By default, the program performs a symmetry analysis and finds which deformations are necessary. |

| rec variable | meaning |
|-----------------------|---|
| • A CLAMPION | This option activates the computation of “clamped-ion” constants. |
| • A PRINT | This option turns on a higher level of diagnostic printing [<i>default</i> minimal printing] |
| • A RESTART | Allows restart using file <i>ELASINFO.DAT</i> from a previous incomplete run. |
| • A RESTART2 | Allows a full restart using file <i>ELASINFO.DAT</i> from a previous complete run. |
| • A PREOPTGEOM | A preliminary geometry optimization of cell and atomic positions is performed before starting elastic constant calculation. |

Geometry optimization is performed at convergence criteria tighter than the ones given in **OPTGEOM**. Some values can be modified by inserting the following keywords:

| | |
|------------------------|--|
| • A TOLDEG | ELAPIEZO default [0.0003] - see OPTGEOM , page 124 |
| • A TOLDEX | ELAPIEZO default [0.00062] - see OPTGEOM , page 124 |
| • A TOLDEE | ELAPIEZO default [8] - see OPTGEOM , page 124 |
| • A MAXCYCLE | see OPTGEOM , page 126 |
| • A NOTRISTR | see OPTGEOM , page 124 |
| • A TRUSTRADIUS | see OPTGEOM , page 125 |
| • A MAXTRADIUS | see OPTGEOM , page 124 |

Input Example:

```

. . . geometry input . . . .
ELAPIEZO
NUMBERIV  modify default choice of n. points [3]
5
STEPWISE  modify step size for numerical gradient [0.015]
0.02
CLAMPION  activates "clamped-ion" approximation
PRINT     extended printing
END       end of ELAPIEZO input
END       geometry input

```

Elastic and piezoelectric tensors are printed at the end of the output (see keywords **ELASTCON** and **PIEZOCN** above). Moreover, piezoelectric strain tensor (converse piezoelectric tensor) is printed:

```

PIEZOELECTRIC STRAIN (CONVERSE) CONSTANTS (pC/N = pm/V)
|   0.000   0.000   0.000   0.000  -14.351   0.000 |
|   0.000   0.000   0.000  -14.351   0.000   0.000 |
|  -0.256  -0.256   2.859   0.000   0.000   0.000 |

```

8.6 Photoelastic Constants

A fully-automated procedure for calculating the photoelastic constants for an arbitrary crystal is activated by specifying the keyword **PHOTOELA** in input block 1 (geometry). Dielectric tensor is computed via a CPHF/KS procedure. The electronic contribution is evaluated in the limit of infinite frequency $\omega \rightarrow \infty$. Dielectric tensor at finite frequency can be computed with sub-keyword **DYNAMIC**.

PHOTOELA must be the last keyword in geometry input:

```

. . . geometry input . . . .
PHOTOELA

```

```

END          close PHOTOELA input block
END          close geometry input block

```

Note that the user must be confident that the input structure is already well optimized. At the beginning of the run, the forces at the central point are calculated and if they exceed 10^{-4} , then a warning is printed suggesting re-optimization.

Users of this option are kindly requested to cite the following paper[59]:

A. Erba and R. Dovesi, *Phys. Rev. B*, **88**, 045121 (2013). *Photoelasticity of crystals from theoretical simulations*.

Keywords, options, and defaults

A default value is chosen for all computational parameters. SCF energy convergence threshold is set to 10^{-8} . To modify it, see keyword **TOLDEE** in input block 3, page 115.

Default choices can be modified by optional keywords (in any order). There are some specific sub-keywords controlling CPHF/KS parameters:

| rec variable | meaning |
|---------------------|--|
| • A TOLALPHA | threshold on energy first derivative change between CPHF/KS cycles |
| * ITOL | $ \Delta E < 10^{-ITOL}$ [default: 4] |
| • A FMIXING | permits to mix the Fock/KS matrix derivatives between CPHF/KS cycles n and $n - 1$ |
| * IPMIX | percentage of cycle $n - 1$ [IPMIX=0, no mixing; default IPMIX=60] |
| • A DYNAMIC | Activates the computation of frequency-dependent polarizabilities and dielectric constants. |
| ILAMBD | wave-length of radiation (expressed in nm). |
| • A ANDERSON | Convergence accelerator. Mixing of Fock/KS matrix derivatives (page 79) |
| • A BROYDEN | Convergence accelerator. Mixing of Fock/KS matrix derivatives (page 82) |
| * W0 | W0 parameter in Anderson's paper [104] |
| * IMIX | Percentage of Fock/KS derivative matrices mixing |
| * ISTART | Iteration after which Broyden method is activated (minimum 2) |
| • A NUMDERIV | This sets the number of points for the numerical second derivative |
| * INUM | number of points including the central (zero displacement) one [default = 3] |
| • A STEPsize | This gives the size of the displacement to be used for the calculation of the numerical second derivative. |
| * STEP | size of the strain step along a given deformation [default = 0.015] |
| • A DEFORM | Specific deformations are asked for |
| * DEF(I), I=1,6 | Six integers have to be provided, each one associated to a given deformation (xx , yy , zz , yz , xz , xy) that tell the program which deformations have to be considered as active. Put 1 for active and 0 for inactive. By default, the program performs a symmetry analysis and finds which deformations are necessary. |

| rec variable | meaning |
|-----------------------|---|
| • A CLAMPION | This option activates the computation of “clamped-ion” constants. |
| • A PRINT | This option turns on a higher level of diagnostic printing [<i>default</i> minimal printing] |
| • A PREOPTGEOM | A preliminary geometry optimization of cell and atomic positions is performed before starting elastic constant calculation. |
| • A RESTART | Allows restart using file <i>ELASINFO.DAT</i> from a previous incomplete run. |
| • A RESTART2 | Allows a full restart using file <i>ELASINFO.DAT</i> from a previous complete run. |

Geometry optimization is performed at convergence criteria tighter than the ones given in **OPTGEOM**. Some values can be modified by inserting the following keywords:

- | | |
|-----------------------|--|
| • A TOLDEG | PHOTOELA default [0.0003] - see OPTGEOM , page 124 |
| • A TOLDEX | PHOTOELA default [0.00062] - see OPTGEOM , page 124 |
| • A TOLDEE | PHOTOELA default [8] - see OPTGEOM , page 124 |
| • A MAXCYCLE | see OPTGEOM , page 126 |
| • A NOTRISTR | see OPTGEOM , page 124 |
| • A TRUSRADIUS | see OPTGEOM , page 125 |
| • A MAXRADIUS | see OPTGEOM , page 124 |

Input Example:

```

. . . geometry input . . . .
PHOTOELA
NUMBERIV  modify default choice of n. points [3]
5
STEPWISE  modify step size for numerical gradient [0.015]
0.02
CLAMPION  activates "clamped-ion" approximation
PRINT     extended printing
END       end of PHOTOELA input
END       geometry input

```

The elasto-optic (Pockels) tensor is printed at the end of the output:

```

          ELASTO-OPTIC (PHOTOELASTIC) POCKELS TENSOR
|   0.160   0.297   0.299   0.000  -0.059   0.000 |
|   0.297   0.160   0.299   0.000   0.059   0.000 |
|   0.299   0.299   0.108   0.000   0.000   0.000 |
|   0.000   0.000   0.000  -0.089   0.000   0.059 |
|  -0.059   0.059   0.000   0.000  -0.089   0.000 |
|   0.000   0.000   0.000   0.059   0.000  -0.069 |

```

Chapter 9

Properties

One-electron properties and wave function analysis can be computed from the SCF wave function by running **properties**. At the end of the SCF process, data on the crystalline system and its wave function are stored as unformatted sequential data in file fort.9, and as formatted data in file fort.98 . The wave function data can be transferred formatted from one platform to another (see keyword **RDFMWF**, page 213).

The data in file fort.9 (or fort.98) are read when running **properties**, and cannot be modified. The data include:

1. Crystal structure, geometry and symmetry operators.
2. Basis set.
3. Reciprocal lattice k-points sampling information.
4. Irreducible Fock/KS matrix in direct space (Unrestricted: F_α , F_β).
5. Irreducible density matrix in direct space (Unrestricted: $P_{\alpha+\beta}$ $P_{\alpha-\beta}$).

The **properties** input deck is terminated by the keyword **END**. See Appendix C, page 317, for information on printing.

9.1 Preliminary calculations

In order to compute the one-electron properties it is necessary to access wave function data as binary data set: if binary data are not available in file fort.9, the keyword **RDFMWF**, entered as 1st record, will read formatted data from file fort.98 and write them unformatted in file fort.9.

Full information on the system is generated: :

- | | | |
|-----|-------------------------------|--|
| a. | symmetry analysis information | stored in COMMON areas and modules |
| b. | reducible Fock/KS matrix | stored on Fortran unit 11 |
| c. | reducible density matrix | |
| c.1 | all electron | stored on Fortran unit 13 (1st record) |
| c.2 | core electron | stored on Fortran unit 13 (2nd record) |
| c.3 | valence electron | stored on Fortran unit 13 (3rd record) |
| d. | reducible overlap matrix | stored on Fortran unit 3 |
| e. | Fock/KS eigenvectors | stored on Fortran unit 10 |
1. a, b, c1, d, are automatically computed and stored any time you run the **properties** program.
 2. in unrestricted calculations, the total electron density matrix ($\alpha + \beta$) and the spin density matrix ($\alpha - \beta$) are written as a unique record in fortran unit 13.

3. The core and valence electron density matrices (c.2, c.3) are computed *only* by the **NEWK** option when IFE=1. They are stored as sequential data set on Fortran unit 13, after the all electron density matrix. Calculation of Compton profiles and related quantities requires such information.
4. Properties can be calculated using a new density matrix, projected into a selected range of bands (keyword **PBAN**, **PGEOMW**), range of energy (keyword **PDIDE**), or constructed as a superposition of the atomic density matrices relative to the atoms (or ions) of the lattice (keyword **PATO**). In the latter case a new basis set can be used.

When a specific density matrix is calculated [band projected (**PBAN**), energy projected (**PDIDE**), atomic superposition (**PATO**)], all subsequent properties are calculated using that matrix.

The option **PSCF** restores the SCF density matrix.

The keyword **PMP2** (see page 230) reads the MP2 correction to the valence density matrix. Properties can then be computed from a MP2 corrected density matrix.

9.2 Properties keywords

RDFMWF wave function data conversion formatted-binary (fort.98 → fort.9)

| Preliminary calculations | | | |
|--|--|-----|---|
| NEWK | Eigenvectors calculation | 228 | I |
| COMMENS | Density Matrix commensurate to the Monchorst net | 204 | I |
| NOSYMADA | No symmetry Adapted Bloch Functions | 108 | – |
| PATO | Density matrix as superposition of atomic (ionic) densities | 229 | I |
| PBAN | Band(s) projected density matrix (preliminary NEWK) | 229 | I |
| PGEOMW | Density matrix from geometrical weights (preliminary NEWK) | 230 | I |
| PDIDE | Energy range projected density matrix (preliminary NEWK) | 230 | I |
| PSCF | Restore SCF density matrix | 236 | – |
| Properties computed from the density matrix | | | |
| ADFT | Atomic density functional correlation energy | 197 | I |
| BAND | Band structure | 199 | I |
| BIDIERD | Reciprocal form factors | 202 | I |
| CLAS | Electrostatic potential maps (point multipoles approximation) | 204 | I |
| ECHG | Charge density and charge density gradient - 2D grid | 209 | I |
| ECH3 | Charge density - 3D grid | 208 | I |
| EDFT | Density functional correlation energy (HF wave function only) | 209 | I |
| EMDLDM | Electron momentum distribution (along a line) | 211 | I |
| EMDPDM | Electron momentum distribution (in a plane) | 211 | I |
| KINETEMD | Kinetic tensor from electron momentum density | 215 | I |
| PMP2 | MP2 correction to the Valence Density Matrix | 230 | |
| POLI | Atom and shell multipoles evaluation | 231 | I |
| POTM | Electrostatic potential - 2D grid | 234 | I |
| POT3 | Electrostatic potential - 3D grid | 232 | I |
| POTC | Electrostatic properties | 233 | I |
| PPAN | Mulliken population analysis | 109 | |
| XFAC | X-ray structure factors | 237 | I |
| Properties computed from the density matrix (spin-polarized systems) | | | |
| ANISOTRO | Hyperfine electron-nuclear spin tensor | 198 | I |
| ISOTROPIC | Hyperfine electron-nuclear spin interaction - Fermi contact | 214 | I |
| POLSPIN | Atomic spin density multipoles | 231 | I |

| Properties computed from eigenvectors (after keyword NEWK) | | | |
|--|--|-----|---|
| ANBD | Printing of principal AO component of selected CO | 197 | I |
| BWIDTH | Printing of bandwidth | 203 | I |
| DOSS | Density of states | 207 | I |
| EMDL | Electron momentum distribution - line | 210 | I |
| EMDP | Electron momentum distribution - plane maps | 213 | I |
| PROF | Compton profiles and related quantities | 235 | I |
| New properties | | | |
| SPOLBP | Spontaneous polarization (Berry phase approach) | 240 | - |
| SPOLWF | Spontaneous polarization (localized CO approach) | 241 | - |
| LOCALWF | Localization of Wannier functions | 215 | I |
| DIEL | Optical dielectric constant | 205 | I |
| ISO+POTC | Mössbauer isomer shift and quadrupolar effects | 241 | I |
| TOPO | Topological analysis of the electron density | 244 | I |
| Auxiliary and control keywords | | | |
| ANGSTROM | Set input unit of measure to Ångstrom | 33 | - |
| BASISSET | Printing of basis set, Fock/KS, overlap and density matrices | 202 | - |
| BOHR | Set input unit of measure to bohr | 36 | - |
| CHARGED | Non-neutral cell allowed (PATO) | 69 | - |
| END | Terminate processing of properties input keywords | | - |
| FRACTION | Set input unit of measure to fractional | 45 | - |
| MAPNET | Generation of coordinates of grid points on a plane | 226 | I |
| MAXNEIGHB | maximum number of equidistant neighbours from an atom | 47 | I |
| NEIGHBOR | Number of neighbours to analyse in PPAN | 56 | I |
| PRINTOUT | Setting of printing options | 59 | I |
| RAYCOV | Modification of atomic covalent radii | 59 | I |
| SETINF | Setting of inf array options | 61 | I |
| SETPRINT | Setting of printing options | 61 | I |
| STOP | Execution stops immediately | 62 | - |
| SYMMOPS | Printing of point symmetry operators | 67 | - |
| Info - Output of data on external units | | | |
| ATOMIRR | Coordinates of the irreducible atoms in the cell | 198 | - |
| ATOMSYMM | Printing of point symmetry at the atomic positions | 36 | - |
| COORDPRT | Coordinates of all the atoms in the cell | 40 | - |
| CRYAPI_OUT | geometry, BS, direct lattice information | 205 | - |
| EXTPRT | Explicit structural/symmetry information | 41 | - |
| FMWF | Wave function formatted output in file fort.98. Section 9.2 | 213 | - |
| INFOGUI | Generation of file with wf information for visualization | 214 | - |
| CRYAPI_OUT | Reciprocal lattice information + eigenvalues | 205 | - |

ANBD - Principal AO components of selected eigenvectors

| rec | variable | value | meaning |
|-------------------------------------|--------------|-------|--|
| • * | NK | n | Number of k points considered. |
| | | 0 | All the k points are considered. |
| | NB | n | Number of bands to analyse |
| | | 0 | All the valence bands + 4 virtual are analysed. |
| | TOL | | Threshold to discriminate the important eigenvector coefficients. The square modulus of each coefficient is compared with TOL. |
| <i>if NK > 0 insert</i> _____ II | | | |
| • * | IK(J),J=1,NK | | Sequence number of the k points chosen (printed at the top of NEWK output) |
| <i>if NB > 0 insert</i> _____ II | | | |
| • * | IB(J),J=1,NB | | Sequence number of the bands chosen |

The largest components of the selected eigenvectors are printed, along with the corresponding AO type and centre.

ADFT/ACOR - *A posteriori* Density Functional atomic correlation energy

The correlation energy of all the atoms not related by symmetry is computed. The charge density is always computed using an Hartree-Fock Hamiltonian (even when the wave function is obtained with a Kohn-Sham Hamiltonian).

The input block ends with the keyword **END**. Default values are supplied for all the computational parameters.

A new atomic basis set can be entered. It must be defined for *all* the atoms labelled with a different conventional atomic number (not the ones with modified basis set only).

| BECKE | Becke weights [default] [16] | |
|-----------------|--|--|
| | or | |
| SAVIN | Savin weights [160] | |
| RADIAL | Radial integration information | |
| rec | variable | meaning |
| • * | NR | number of intervals in the radial integration [1] |
| • * | RL(I),I=1,NR | radial integration intervals limits in increasing sequence [4.] |
| • * | IL(I),I=1,NR | number of points in the radial quadrature in the I-th interval [55]. |
| ANGULAR | Angular integration information | |
| rec | variable | meaning |
| • * | NI | number of intervals in the angular integration [default 10] |
| • * | AL(I),I=1,NI | angular intervals limits in increasing sequence. Last limit is set to 9999. [default values 0.4 0.6 0.8 0.9 1.1 2.3 2.4 2.6 2.8] |
| • * | IA(I),I=1,NI | accuracy level in the angular Lebedev integration over the I-th interval [default values 1 2 3 4 6 7 6 4 3 1]. |
| PRINT | printing of intermediate information - no input | |
| PRINTOUT | printing environment (see page 59) | |
| TOLLDENS | | |
| • * | ID | DFT density tolerance [default 9] |
| TOLLGRID | | |
| • * | IG | DFT grid weight tolerance [default 18] |
| NEWBASIS | a new atomic basis set is input | |
| | _____ insert complete basis set input, Section 1.2 _____ | |

ANGSTROM - unit of measure

Unit of measure of coordinates (**ECHG**, **POTM**, **CLAS**) See input block 1, page 33.

ANISOTRO - anisotropic tensor

| rec | variable | meaning |
|------|---------------|---|
| • A | keyword | enter one of the following keywords: |
| • A3 | ALL | The anisotropic tensor is evaluated for all the atoms in the cell _____ or _____ |
| • A6 | UNIQUE | (alias NOTEQUIV) The anisotropic tensor is evaluated for all the non-equivalent atoms in the cell _____ or _____ |
| • A6 | SELECT | The anisotropic tensor is evaluated for selected atoms |
| • * | N | number of atoms where to evaluate the tensor |
| • * | IA(I),I=1,N | label of the atoms |
| • A | PRINT | extended printing |

The anisotropic hyperfine interaction tensor is evaluated. This quantity is given in bohr⁻³ and is transformed into the hyperfine coupling tensor through the relationship [183]

$$\mathbf{T}[\text{mT}] = \frac{1000}{(0.529177 \cdot 10^{-10})^3} \frac{1}{4\pi} \mu_0 \beta_{\text{N}} g_{\text{N}} \mathbf{T} = 3.4066697 g_{\text{N}} \mathbf{T}$$

(see **ISOTROPIC** for the units and conversion factors). The elements of the \mathbf{T} tensor at nucleus A are defined as follows:

$$T_{ij}^{\text{A}} = \sum_{\mu\nu} \sum_{\text{g}} P_{\mu\nu\text{g}}^{\text{spin}} \int \varphi_{\mu}(\mathbf{r}) \left(\frac{r_{\text{A}}^2 \delta_{ij} - 3r_{\text{A}i} r_{\text{A}j}}{r_{\text{A}}^5} \right) \varphi_{\nu}^{\text{g}}(\mathbf{r}) d\mathbf{r}$$

where $r_{\text{A}} = |\mathbf{r} - \text{A}|$ and $r_{\text{A}i} = (\mathbf{r} - \text{A})_i$ (ith component of the vector).

For extended printing (tensor in original cartesian axes and in principal axis system) insert, before the keyword ANISOTRO:

SETPRINT

1

18 1

See tests 29, 31, 32, 33.

ATOMIRR - coordinates of irreducible atoms

Cartesian and fractional coordinates of the irreducible atoms are printed. No input data required.

ATOMSYMM

See input block 1, page 36

BAND - Band structure

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • A | TITLE | | any string (max 72 characters). |
| • * | NLINE | > 0 | number of lines in reciprocal space to be explored (max 20)). |
| | ISS | | shrinking factor in terms of which the coordinates of the extremes of the segments are expressed. |
| | NSUB | | total number of k points along the path. |
| | INZB | | first band |
| | IFNB | | last band |
| | IPLO | 0 | eigenvalues are not stored on disk. |
| | | = 1 | formatted output for plotting; see Appendix D, page 322 |
| | LPR66 | ≠ 0 | printing of eigenvalues |
| | | | _____ if ISS > 0 then _____ |
| | | | _____ add NLINE records _____ |
| • * | I1,I2,I3 | | integers that define the starting point of the line (I1/ISS \mathbf{b}_1 +I2/ISS \mathbf{b}_2 +I3/ISS \mathbf{b}_3), with $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ reciprocal lattice vectors. |
| | J1,J2,J3 | | integers that define the final point of the line (J1/ISS \mathbf{b}_1 +J2/ISS \mathbf{b}_2 +J3/ISS \mathbf{b}_3) with $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ reciprocal lattice vectors. |
| | | | _____ if ISS = 0 then _____ |
| | | | _____ add NLINE records _____ |
| • * | LABELA | | label of the the starting point of the line (see tables 9.1 and 9.2 below for a legend). |
| | LABELB | | label of the the final point of the line (see tables 9.1 and 9.2 below for a legend). |

The band structure along a given path n the Brillouin zone is computed. The data are printed in standard output and (if IPLO = 1) written in file fort.25 (formatted data processed by Cr-gra2006) and in file BAND.DAT (processed by DLV; see <http://www.cse.clrc.ac.uk/cmg/DLV>). See Appendix D, page 322).

When all the starting and terminal points are chosen to coincide with special (high symmetry) ones, it is possible to write the conventional label of each point instead of its coordinates (this option is activated by putting ISS=0). These labels have to be expressed as letters in the latin alphabet: the Γ point is identified by letter G. Apart from Γ , the labels of the special points are different for each Bravais lattice: the convention adopted for the special points and their position in the Brillouin zone can be found in tables 9.1 and 9.2 below. For instance, in the MgO case (fcc lattice), two equivalent inputs would read:

```
BAND
MGO
2 0 30 1 18 1 0
G X
X W
```

and:

```
BAND
MGO
2 12 30 1 18 1 0
0 0 0 6 0 6
6 0 6 6 3 9
```

1. **Warning** : does not run for molecules!! (0D)
2. For a correct interpretation of HF band-structure and DOS's, it must be stressed that the HF eigenvalues are not a good approximation to the optical excitation spectrum of the crystal. However, as discussed in section III.2 of reference [142] and in Chapter 2 of

- reference [139], the band structures, in conjunction with total and projected DOS's, can be extremely useful in characterizing the system from a chemical point of view.
- Note on band extremes coordinates: in two-(one-) dimensional cases I3, J3 (I2,I3,J2,J3) are formally input as zero (0). See test 3 and 6.
 - The only purpose of ISS is to express the extremes of the segments in integer units (see tests 8-9). It does not determine the density of k points along the lines, which depends only on NSUB. The number of k points for each line is computed by the program. The step is constant along each line. The step is taken as close as possible to a constant along different lines.
 - If symmetry adapted Bloch functions are used (default option), **BAND** generates symmetry information in k points different from the ones defined by the Monkhorst net. Eigenvectors computed by NEWK in k points corresponding to the Monkhorst net are not readable any more. To compute density of states and bands, the sequence must be: BAND - NEWK - DOSS.
 - The ISS=0 option does not recognize the labels of every special points; the ones recognized are only those reported in tables 9.1 and 9.2.

See tests 3, 4, 6, 7, 8, 9, 11, 12 and 30.

Table 9.1: Labels and fractional coordinates (referred to reciprocal space lattice parameters of the primitive cell) of the special points recognized in input for each Bravais lattice. FC = face centered, BC = body centered, AC = base centered.

| Lattice | Point | Coordinates |
|--------------------|----------|--|
| Cubic | <i>M</i> | $\frac{1}{2} \frac{1}{2} 0$ |
| | <i>R</i> | $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ |
| | <i>X</i> | $0 \frac{1}{2} 0$ |
| FC Cubic | <i>X</i> | $\frac{1}{2} 0 \frac{1}{2}$ |
| | <i>L</i> | $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ |
| | <i>W</i> | $\frac{1}{2} \frac{1}{4} \frac{3}{4}$ |
| BC Cubic | <i>H</i> | $\frac{1}{2} \frac{-1}{2} \frac{1}{2}$ |
| | <i>P</i> | $\frac{1}{4} \frac{1}{4} \frac{1}{2}$ |
| | <i>N</i> | $0 0 \frac{1}{2}$ |
| Hexagonal/Trigonal | <i>M</i> | $\frac{1}{2} 0 0$ |
| | <i>K</i> | $\frac{1}{3} \frac{1}{3} 0$ |
| | <i>A</i> | $0 0 \frac{1}{2}$ |
| | <i>L</i> | $\frac{1}{2} 0 \frac{1}{2}$ |
| Rhombohedral | <i>H</i> | $\frac{1}{3} \frac{1}{3} \frac{1}{2}$ |
| | <i>T</i> | $\frac{1}{2} \frac{1}{2} \frac{-1}{2}$ |
| | <i>F</i> | $0 \frac{1}{2} \frac{1}{2}$ |
| | <i>L</i> | $0 0 \frac{1}{2}$ |
| Monoclinic | <i>A</i> | $\frac{1}{2} \frac{-1}{2} 0$ |
| | <i>B</i> | $\frac{1}{2} 0 0$ |
| | <i>C</i> | $0 \frac{1}{2} \frac{1}{2}$ |
| | <i>D</i> | $\frac{1}{2} 0 \frac{1}{2}$ |
| | <i>E</i> | $\frac{1}{2} \frac{-1}{2} \frac{1}{2}$ |
| | <i>Y</i> | $0 \frac{1}{2} 0$ |
| AC Monoclinic | <i>Z</i> | $0 0 \frac{1}{2}$ |
| | <i>A</i> | $\frac{1}{2} 0 0$ |
| | <i>Y</i> | $0 \frac{1}{2} \frac{1}{2}$ |
| | <i>M</i> | $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ |

Table 9.2: Labels and fractional coordinates (referred to reciprocal space lattice parameters of the primitive cell) of the special points recognized in input for each Bravais lattice. FC = face centered, BC = body centered, AC = base centered.

| Lattice | Point | Coordinates |
|----------------|----------|--|
| Orthorombic | <i>S</i> | $\frac{1}{2} \frac{1}{2} 0$ |
| | <i>T</i> | $0 \frac{1}{2} \frac{1}{2}$ |
| | <i>U</i> | $\frac{1}{2} 0 \frac{1}{2}$ |
| | <i>R</i> | $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ |
| | <i>X</i> | $\frac{1}{2} 0 0$ |
| | <i>Y</i> | $0 \frac{1}{2} 0$ |
| | <i>Z</i> | $0 0 \frac{1}{2}$ |
| FC Orthorombic | <i>Z</i> | $\frac{1}{2} \frac{1}{2} 0$ |
| | <i>Y</i> | $\frac{1}{2} 0 \frac{1}{2}$ |
| | <i>T</i> | $1 \frac{1}{2} \frac{1}{2}$ |
| AC Orthorombic | <i>S</i> | $0 \frac{1}{2} 0$ |
| | <i>T</i> | $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ |
| | <i>R</i> | $0 \frac{1}{2} \frac{1}{2}$ |
| | <i>Y</i> | $\frac{1}{2} \frac{1}{2} 0$ |
| | <i>Z</i> | $0 0 \frac{1}{2}$ |
| BC Orthorombic | <i>S</i> | $\frac{1}{2} 0 0$ |
| | <i>T</i> | $0 0 \frac{1}{2}$ |
| | <i>R</i> | $0 \frac{1}{2} 0$ |
| | <i>X</i> | $\frac{1}{2} \frac{-1}{2} \frac{1}{2}$ |
| | <i>W</i> | $\frac{1}{4} \frac{1}{4} \frac{1}{4}$ |
| Tetragonal | <i>M</i> | $\frac{1}{2} \frac{1}{2} 0$ |
| | <i>R</i> | $0 \frac{1}{2} \frac{1}{2}$ |
| | <i>A</i> | $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ |
| | <i>X</i> | $0 \frac{1}{2} 0$ |
| | <i>Z</i> | $0 0 \frac{1}{2}$ |
| BC Tetragonal | <i>M</i> | $\frac{1}{2} \frac{1}{2} \frac{-1}{2}$ |
| | <i>P</i> | $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ |
| | <i>X</i> | $0 0 \frac{1}{2}$ |

BASISSET - Printing of basis set and data from SCF

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | NPR | | number of printing options. |
| | | | <i>if NPR ≠ 0 insert prtrec (see page 61)</i> |

II

This option allows printing of the basis set and the computational parameters, and, on request (keyword **PRINTOUT** before **BASISSET**), of the Fock/KS matrix (**FGRED**), the overlap matrix (**OVERLAP**), and the reducible density matrix (**PGRED**), in direct lattice representation.

Warning: the contraction coefficients of the primitive gaussians are different from the ones given in input. See “Normalization coefficients”, Appendix E.

Printing options:

59 (Density matrix); 60 (Overlap matrix); 64 (Fock/KS matrix).

BIDIARD - Reciprocal form factors

This option evaluates the reciprocal form factors (RFF) (also called auto-correlation function) for any direction directly from the direct space density matrix.

Compton Profiles (CPs) can be computed by Fourier transforming the RFF with the **PROF** sub-keyword below. The starting auto-correlation function must be of good quality in order to get good CPs. Both RFFs and CPs can be convoluted (see **CONV** sub-keyword) in order to be compared with the experiments (affected by the finite resolution of the spectrometer); this procedure is performed by multiplying the RFF by the gaussian function $g(r)_{\sigma_r}$:

$$g(r)_{\sigma_r} = e^{-\frac{r^2}{2\sigma_r^2}} \quad \text{where} \quad \sigma_r = \frac{1}{\sigma_p} = \frac{2\sqrt{2\log 2}}{FWHM_p}$$

where $FWHM_p$, the convolution parameter, has to be defined in input by the user (in atomic units); the r and p subscripts identify quantities in coordinates and momentum space, respectively. The anisotropies of the RFFs and the CPs can be evaluated via the **DIFF** sub-keyword. This block must be ended by **ENDB**. It works also for open-shell systems.

By using the alternative **PROF** keyword (see page 235), followed by the **BR** sub-keyword, it is possible to obtain the RFF by Fourier transforming the Compton profiles. As the latter implies numerical integration, the **BIDIARD** keyword is expected to provide more accurate results.

Both auto-correlation functions and Compton profiles are saved in two-column format in the external unit CP.DAT

Users of this option for the calculation of CPs are kindly requested to cite the following paper[65]:

A. Erba, C. Pisani, S. Casassa, L. Maschio, M. Schütz and D. Usvyat, *Phys. Rev. B.*, **81**,165108 (2010). *A MP2 versus DFT theoretical investigation of the Compton profiles of crystalline urea.*

| rec | variable | value | meaning |
|------|---------------|-------|--|
| • * | NDIR | | number of directions along which the RFF are evaluated |
| | NPU | | number of sampling points along each direction |
| | STEP | | step along each direction |
| | IMODO | 0: | the direction is defined by the Cartesian coordinates (bohr) of a point |
| | | ≠ 0: | the direction is defined by the atom label and indices of the cell where the atom is located |
| | ICASO | 1: | the total density matrix is used |
| | | 2: | the core density matrix is used |
| | | 3: | the valence density matrix is used |
| • A4 | CONV | | Convolution of the $B(r)$ previously computed |
| • * | $FWHM_p$ | | convolution parameter (a.u.) |
| • A4 | PROF | | Compton Profiles computed as Fourier Transforms of the $B(r)$ |
| • * | NPOIP | | number of points along each direction |
| | STEP | | step along each direction (a.u.) |
| • A4 | DIFF | | $B(r)$ and CPs anisotropies are computed |
| • A3 | DIR | | The directions are specified _____ if $IMODO=0$, insert <i>NDIR</i> records _____ |
| • * | X Y Z | | the explored direction is defined by the straight line going from the origin to (X,Y,Z) _____ if $IMODO \neq 0$, insert <i>NDIR</i> records _____ |
| • * | I XG YG ZG | | label of the atom and indices of the cell where the atom is located. The explored direction is defined by the straight line going from the origin to the atom position |
| • A4 | END | | End block autocorrelation functions |

Notes:

The explored interval is $(NPU-1) \times STEP$ long; X,Y,Z or I,XG,YG,ZG data are just used for defining the direction, **NOT** the length of the explored interval.

BOHR - unit of measure

Unit of measure of coordinates (**ECHG**, **POTM**, **CLAS**) See input block 1, page 36.

BWIDTH - Printing of band width

| rec | variable | meaning |
|-----|----------|--------------------------------------|
| • * | INZB | first band considered |
| | 0 | analysis from first valence band |
| | IFNB | last band considered |
| | 0 | analysis up to first 4 virtual bands |

The Fock/KS eigenvalues are ordered in bands following their values. Band crossing is not recognized.

CHARGED - charged reference cell

See input block 2, page 69.

To be used before **PATO**, when new basis set and/or electron configuration of the atoms result in a charged cell.

CLAS - Point charge electrostatic potential maps

| rec | variable | value | meaning |
|-----|--------------|-------|---|
| • * | IDER | 0 | potential evaluation |
| | | 1 | calculation of potential and its first derivatives |
| | IFOR | 0 | point multipoles have to be evaluated by POLI option |
| | | 1 | point formal charges given as input |
| | | | _____ if <i>IFOR</i> \neq 0 insert _____ II |
| • * | Q(I),I=1,NAF | | formal net charge for all the NAF atoms in the unit cell (equivalent and non equivalent, following the sequence printed at the top of the <i>properties</i> printout) |
| | | | _____ insert MAPNET input records (page 226) _____ |

1. When $IDER=0$, the electrostatic potential is calculated at the nodes of a 2-dimensional net in a parallelogram-shaped domain defined by the segments AB and BC (see keyword **MAPNET**, page 226). The potential values are written formatted in file fort.25. (see Appendix D, page 321).
2. When $IDER \neq 0$, the electrostatic potential gradient is computed at the nodes of the same grid. The x, y and z components are printed on the standard output.
3. The potential is generated by an array of point multipoles up to a maximum order IDIPO defined in the **POLI** option input, or by atomic point charges given in input ($IFOR=1$; $IDIPO = 0$ is set in that case).
4. The multipoles *must* be previously computed by running the option **POLI** when $IFOR$ is equal to zero.

COORPRT

See input block 1, page 40.

COMMENS - Density Matrix commensurate to Monkhorst grid

| rec | variable | value | meaning |
|-----|----------|-------|------------------------|
| • * | ICASO | 0 | total density matrix |
| | | 1 | core density matrix |
| | | 2 | valence density matrix |

The **COMMENS** keyword has to be inserted as first record in the **PROPERTIES** input before the **NEWK** keyword. It activates the construction of the Density Matrix (DM) $\mathbf{P} \equiv P_{\mu\nu}^{\mathbf{g}}$ (where μ and ν label two atomic orbitals $\chi_{\mu}(\mathbf{r})$ and $\chi_{\nu}(\mathbf{r})$ and \mathbf{g} represents a lattice vector) with the index \mathbf{g} running over a number of cells L commensurate to the number L of \mathbf{k} -points of the Monkhorst-Pack grid where the one-electron Hamiltonian is diagonalized and the crystalline orbitals computed.

If this option is not activated, the truncation over \mathbf{g} in the definition of the DM is imposed by the first tolerance **TOL1** of the integrals: those elements $P_{\mu\nu}^{\mathbf{g}}$ are disregarded that correspond to product distributions $\Pi(\mathbf{r}) = \chi_{\mu\mathbf{0}}(\mathbf{r})\chi_{\nu\mathbf{g}}(\mathbf{r})$ for which the pseudo-overlap between the two AOs is less than 10^{-TOL1} .

The DM obtained in this way can be used for computing electron momentum densities, auto-correlation functions and Compton profiles (see keywords **BIDIARD**, **EMDLDM**, **EMD-PDM**). See the discussion in section 13.8 (page 281) for further details.

DENSMAT - First order density matrix $\rho(r, r')$ - developers only

First order density matrix $\rho(r, r')$ along a given path is computed. The variable r' explores the same interval as r .

For UHF cases two matrices are generated, one corresponding to the total and the other to the spin density matrix.

| rec | variable | value | meaning |
|--|----------|------------|---|
| • * | NKN | | number of knots in the path (=number of segments+1) |
| | NPU | | number of sampling points along the full path |
| | IPLOT | 0: | data are not saved for plot |
| | | = 1: | data are saved in file fort.25 |
| | IMODO | 0: | knot coordinates (x, y, z) in a. u. |
| | | $\neq 0$: | knots are defined through atom labels |
| | LPR | $\neq 0$: | print the $\rho(r, r')$ matrix in integer form (values are multiplied by 10000) |
| _____ <i>if IMODO=0, insert NKN records</i> _____ | | | |
| • * | X Y Z | | Cartesian coordinates (bohr) of the i-th knot |
| _____ <i>if IMODO\neq0, insert:</i> _____ | | | |
| • * | DX DY | | displacement (bohr) applied to all atoms defining the path |
| | DZ | | |
| _____ <i>insert NKN records</i> _____ | | | |
| • * | I XG YG | | label of the atom and indices of the cell where the atom is located |
| | ZG | | |

- A $NPU \times NPU$ square matrix is generated.
- The step between contiguous sampling points belonging to different segments is the same.
- Meaning of the displacement: suppose you want the density matrix corresponding to the π structure of benzene. Define, for example, the path H-C-C-C-H through the atom labels and then displace it along z (if the molecule is in the $x-y$ plane) by an appropriate amount.

CRYAPI_OUT - Geometry, BS, and full wave function information

Geometry, local function Basis Set, overlap, hamiltonian, density matrices n direct lattice are written formatted in file GRED.DAT

Wannier functions (if file fort.80 is present; see keyword **LOCALWF**, page 215) are appended to file GRED.DAT

k points coordinates (Monkhorst sampling net) and eigenvectors (if computed by **NEWK** page 228) in the full Brillouin zone are written formatted in file KRED.DAT.

The scripts *runcry06/runprop06* save files GRED.DAT and KRED.DAT (if present) as infilename.GRED and infilename.KRED

The utility program *cryapi_inp* reads and prints the data. The organization of data can be understood from the output of *cryapi_inp* and from its source.

See Appendix D, page 330.

DIEL/DIELECT - Optical dielectric constant

Computes the dielectric constant of the system along the periodic direction where an external electric field has been applied during the SCF calculation (using keyword **FIELD**, page 42).

The dielectric constant is calculated by using the concept of macroscopic average of the total charge density (see for example Fu *et al.* [78]) and Poisson's equation. The charge density is first averaged with respect to the (infinite) plane orthogonal to the field

$$\bar{\rho}(z) = \frac{1}{A} \int_A \rho(z) dA \quad (9.1)$$

where $A = |\vec{a} \times \vec{b}|$, and \vec{a} and \vec{b} are the lattice parameters of the supercell orthogonal to the field direction. When a Fourier representation of the charge density is used, the previous equation becomes:

$$\bar{\rho}(z) = \frac{1}{V} \sum_{\ell=-\infty}^{+\infty} F_{00\ell} e^{-i \frac{2\pi\ell z}{C}} \quad (9.2)$$

$F_{00\ell}$ are structure factors (note that the two first indices are always zero) calculated analytically from the SCF crystalline orbitals depending now on the applied field. The quantity $\bar{\rho}$ is then averaged with respect to the z coordinate

$$\bar{\rho}(z) = \frac{1}{\Delta z} \int_{z-\Delta z/2}^{z+\Delta z/2} \bar{\rho}(z') dz' \quad (9.3)$$

that is

$$\bar{\rho}(z) = \frac{1}{V} \sum_{\ell=-\infty}^{+\infty} F_{00\ell} \operatorname{sinc} \left(\ell\pi \frac{\Delta z}{C} \right) e^{-i \frac{2\pi\ell z}{C}} \quad (9.4)$$

where the *sinc* function is the *cardinal sinus* ($\operatorname{sinc}(u) = \frac{\sin(u)}{u}$) and Δz has been chosen equal to c ; we can now apply Poisson's equation to $\bar{\rho}(z)$:

$$\frac{\partial^2 \bar{V}(z)}{\partial z^2} = -4\pi \bar{\rho}(z) \quad (9.5)$$

or

$$\frac{\partial \bar{E}(z)}{\partial z} = 4\pi \bar{\rho}(z) \quad (9.6)$$

because

$$\frac{\partial \bar{V}(z)}{\partial z} = -\bar{E}(z) \quad (9.7)$$

$\bar{V}(z)$, $\bar{E}(z)$ and $\bar{\rho}(z)$ are the mean values of the macroscopic electric potential, electric field and electron density at z position along the electric field direction.

Structure factors can be separated in a real and an imaginary part:

$$F_{00\ell} = F_{00\ell}^{\Re} + i F_{00\ell}^{\Im} \quad (9.8)$$

Exploiting the following properties of the structure factors:

$$\begin{aligned} F_{000} &= N_e \quad (\text{number of electrons in the supercell}) \\ F_{00\ell}^{\Re} &= F_{00-\ell}^{\Re} \\ F_{00\ell}^{\Im} &= -F_{00-\ell}^{\Im} \end{aligned} \quad (9.9)$$

the real and imaginary parts of $\bar{\rho}$ take the following form:

$$\Re [\bar{\rho}(z)] = \frac{N_e}{V} + \frac{2}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \cos \left(\frac{2\pi\ell z}{C} \right) + F_{00\ell}^{\Im} \sin \left(\frac{2\pi\ell z}{C} \right) \right] \operatorname{sinc} \left(\ell\pi \frac{\Delta z}{C} \right) \quad (9.10)$$

$$\Im [\bar{\rho}(z)] = 0 \quad (9.11)$$

As expected, the imaginary part is null. The N_e/V term can be disregarded, as it is exactly canceled by the nuclear charges in the supercell.

According to equation 9.7, the local macroscopic field corresponds to minus the slope of $\bar{V}(z)$, it has opposite sign with respect to the imposed outer field, according to the Lenz law, and is obtained from $\bar{\rho}(z)$ (eq. 9.6):

$$\bar{E}(z) = \frac{8\pi}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \frac{\sin \left(\frac{2\pi\ell z}{C} \right)}{\left(\frac{2\pi\ell}{C} \right)} - F_{00\ell}^{\Im} \frac{\cos \left(\frac{2\pi\ell z}{C} \right)}{\left(\frac{2\pi\ell}{C} \right)} \right] \operatorname{sinc} \left(\ell\pi \frac{\Delta z}{C} \right) \quad (9.12)$$

The corresponding macroscopic electric potential can be written as follows:

$$\bar{V}(z) = \frac{-8\pi}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \frac{\cos \left(\frac{2\pi\ell z}{C} \right)}{\left(\frac{2\pi\ell}{C} \right)^2} + F_{00\ell}^{\Im} \frac{\sin \left(\frac{2\pi\ell z}{C} \right)}{\left(\frac{2\pi\ell}{C} \right)^2} \right] \operatorname{sinc} \left(\ell\pi \frac{\Delta z}{C} \right) \quad (9.13)$$

Since $-\overline{E}$ and E_0 have opposite sign, the ratio $E_0/(E_0 + \overline{E})$ is larger than one, and characterizes the relative dielectric constant of the material along the direction of the applied field:

$$\epsilon = \frac{E_0}{E_0 + \overline{E}} \quad (9.14)$$

The number of structure factors computed for a Fourier representation of the perturbed charge density by default is equal to 300, the structure factors from F_{001} to $F_{00\ 300}$.

The data computed are written in file DIEL.DAT in append mode. See Appendix D, page 322. Available keywords are:

| rec | variable | meaning | |
|-----|----------|--------------------------------|----|
| • | A END | end of DIEL input block | |
| | | <i>optional keywords</i> | II |
| • | A PRINT | extended output | |

DOSS - Density of states

| rec | variable | value | meaning | |
|-----|--------------|-------|--|----|
| • * | NPRO | 0 | only total DOS is calculated | |
| | | > 0 | total DOS and NPRO projected densities are calculated. The maximum number of projections is 15. | |
| | NPT | | number of uniformly spaced energy values (\leq LIM019) where DOSs are calculated, from bottom of band INZB to top of band IFNB. | |
| | INZB | | first band considered in DOS calculation | |
| | IFNB | | last band considered in DOS calculation | |
| | IPLO | 0 | DOSs are not stored on disk | |
| | | 1 | formatted output to file fort.25 for plotting (Appendix D, page 322). | |
| | | 2 | formatted output to file DOSS.DAT for plotting (Appendix D, page 323). | |
| | NPOL | | number of Legendre polynomials used to expand DOSS (≤ 25) | |
| | NPR | | number of printing options to switch on | |
| | | | <i>if INZB and IFNB < 0 insert</i> | II |
| • * | BMI,BMA | | Minimum and maximum energy (hartree) values to span for DOSS. They must be in a band gap | |
| | | | <i>if NPRO \neq 0, insert NPRO records</i> | II |
| • * | N | > 0 | DOS projected onto a set of N AOs | |
| | | < 0 | DOS projected onto the set of all AOs of the N atoms. | |
| | NDM(J),J=1,N | | vector NDM identifies the AOs (N>0) or the atoms (N<0) by their sequence number (basis set order) | |
| | | | <i>if NPR \neq 0, insert prtrec (see page 61)</i> | II |

Following a Mulliken analysis, the orbital (ρ_μ), atom (ρ_A) and total (ρ_{tot}) density of states can be defined for a closed shell system as follows:

$$\rho_\mu(\epsilon) = 2/V_B \sum_j \sum_\nu \sum_{\underline{g}} \int_{BZ} d\underline{k} S_{\mu\nu}(\underline{k}) a_{\mu j}(\underline{k}) a_{\nu j}^*(\underline{k}) e^{i\underline{k}\cdot\underline{g}} \delta[\epsilon - \epsilon_j(\underline{k})] \quad (9.15)$$

$$\rho_A(\epsilon) = \sum_{\mu \in A} \rho_\mu(\epsilon) \quad (9.16)$$

$$\rho_{tot}(\epsilon) = \sum_A \rho_A(\epsilon) \quad (9.17)$$

where the last sum extends to all the atoms in the unit cell. Bond population density of states are not computed.

1. **Warning:** do not run for molecules!

- The **NEWK** option must be executed (to compute Hartree-Fock/KS eigenvectors and eigenvalues) before running **DOSS**. The values of the input parameters IS and ISP of **NEWK** have a consequent effect on the accuracy of the DOSS calculation. Suggested values for IS: from 4 to 12 for 3-D systems, from 6 to 18 for 2-D and 1-D systems (Section 13.7, page 281). ISP must be equal or greater than 2*IS; low values of the ratio ISP/IS can lead to numerical instabilities when high values of NPOL are used. If **BAND** is called between **NEWK** and **DOSS**, and symmetry adapted Bloch functions are used (default option), the information generated by NEWK is destroyed. To compute density of states and bands, the sequence must be: BAND - NEWK - DOSS.
- DOSS are calculated according to the Fourier-Legendre technique described in Chapter II.6 of reference 1, and in C. Pisani et al, ([140, 141]). Three computational parameters must be defined: NPOL, IS, ISP. IS and ISP are entered in the **NEWK** option input.
- NPOL is the number of Legendre polynomials used for the expansion of the DOS. The value of NPOL is related to the values of IS and ISP, first and second input data of **NEWK** option.
Suggested values for NPOL: 10 to 18.
- Warning NEWK** with IFE=1 must be run when spin-polarized solutions (**SPIN-LOCK**, page 114) or level shifter (**LEVSHIFT**, page 105) were requested in SCF, to obtain the correct Fermi energy and eigenvalues spectra.
- Unit of measure: energy: hartree; DOSS: state/hartree/cell.

Computed data are written in file fort.25 (in Crgra2006 format), and in file DOSS.DAT
Printing options: 105 (density of states and integrated density of states); 107 (symmetrized plane waves).

See tests 3, 4, 5, 6, 7, 8, 9, 11 and 30.

ECH3 - Electronic charge (spin) density on a 3D grid

| rec | variable | meaning |
|--|----------------------|--|
| • * | NP | Number of points along the first direction |
| <i>if non-3D system</i> | | |
| keyword to choose the type of grid on the non-periodic direction(s): | | |
| SCALE | | RANGE |
| length scales for non-periodic dimensions | | boundary for non-periodic dimensions (au) |
| <i>if 2D system</i> | | |
| • * | ZSCALE | • * ZMIN • * ZMAX |
| <i>if 1D system</i> | | |
| • * | YSCALE,ZSCALE | • * YMIN,ZMIN • * YMAX,ZMAX |
| <i>if 0D system</i> | | |
| • * | XSCALE,YSCALE,ZSCALE | • * XMIN,YMIN,ZMIN • * XMAX,YMAX,ZMAX |

The electronic charge [and spin density] (electron/bohr³) is computed at a regular 3-dimensional grid of points. The grid is defined by the lattice vectors of the primitive unit cell and user defined extents in non-periodic directions. NP is the number of points along the first lattice vector (or XMAX-XMIN for a molecule). Equally spacing is used along the other vectors. Non-periodic extents may be specified as an explicit range (RANGE) or by scaling the extent defined by the atomic coordinates (SCALE).

Formatted data are written to file fort.31 (function value at the grid points) in the format required by the visualization program DLV.

See Appendix D, page 327, for description of the format.

Function data computed at 3D grid points are written according to GAUSSIAN CUBE format in files:

DENS_CUBE.DAT charge density
SPIN_CUBE.DAT spin density

PS. The sum of the density values divided by the number of points and multiplied by the cell volume (in bohr, as printed in the output) gives a very rough estimate of the number of electrons in the cell.

ECHG - Electronic charge density maps and charge density gradient

| rec | variable | value | meaning |
|-----|----------|-------|-------------------------------|
| • * | IDER | n | order of the derivative - < 2 |

_____ insert MAPNET input records (Section 9.2, page 226) _____

1. IDER=0

The electron charge density (and in sequence the spin density, for unrestricted wave functions) is calculated at the nodes of a 2-dimensional net in a parallelogram-shaped domain defined by the segments AB and BC (see keyword **MAPNET**, page 226). The electron density values (electron bohr⁻³) are written formatted in file fort.25 (see Appendix D, page 321).

2. IDER=1

electron charge density, x, y, z component of first derivative, and modulus of the derivative, are written. The string in the header is always "MAPN".

3. When the three points define a segment (A≡B or B≡C), function data are written in file RHOLINE.DAT. (see Appendix D, page 321)

4. When IDER ≠ 0, the charge density gradient is computed at the nodes of the same grid. The x, y and z components are printed on the standard output and written formatted in file fort.25 (see Appendix D, page 321).

5. The electron charge density is computed from the density matrix stored in file fort.31. The density matrix computed at the last cycle of **SCF** is the default.

6. Band projected (keyword **PBAN**), energy projected (keyword **PDIDE**) or atomic superposition (keyword **PATO**) density matrices can be used to compute the charge density. The sequence of keywords must be: (**NEWK-PBAN-ECHG**), (**NEWK-PDIDE-ECHG**) or (**PATO-ECHG**).

EDFT/ENECOR - *A posteriori* Density Functional correlation energy

Estimates *a posteriori* the correlation energy via a HF density. It is controlled by keywords. The input block ends with the keyword **END**. All the keywords are optional, as default values for all the integration parameters are supplied by the program, to obtain reasonably accurate integration of the charge density. Please check the integration error printed on the output.

| | |
|------------------|--|
| BECKE | Becke weights [default] [16] |
| | or |
| SAVIN | Savin weights [160] |
| RADIAL | Radial integration information |
| rec variable | meaning |
| • * NR | number of intervals in the radial integration [1] |
| • * RL(I),I=1,NR | radial integration intervals limits in increasing sequence [4.] |
| • * IL(I),I=1,NR | number of points in the radial quadrature in the I-th interval [55]. |
| ANGULAR | Angular integration information |
| rec variable | meaning |
| • * NI | number of intervals in the angular integration [default 10] |
| • * AL(I),I=1,NI | angular intervals limits in increasing sequence. Last limit is set to 9999. [default values 0.4 0.6 0.8 0.9 1.1 2.3 2.4 2.6 2.8] |
| • * IA(I),I=1,NI | accuracy level in the angular Lebedev integration over the I-th interval [default values 1 2 3 4 6 7 6 4 3 1]. |
| PRINT | printing of intermediate information - no input |
| PRINTOUT | printing environment (see page 59) |
| TOLLDENS | |
| • * ID | DFT density tolerance [default 9] |
| TOLLGRID | |
| • * IG | DFT grid weight tolerance [default 18] |

EMDL - Electron Momentum Density - line maps

| rec | variable | value | meaning |
|-----|--------------------------|----------|--|
| • * | N | | number of directions (≤ 10) |
| | PMAX | | maximum momentum value (a.u.) for which the EMD is to be calculated |
| | STEP | | interpolation step for the EMD |
| | IPLO | 0 | no data stored on disk |
| | | 1 | formatted output to file fort.25 for plotting (Appendix D, page 323). |
| | | 2 | formatted output to file LINEA.DAT for plotting (Appendix D, page 323). |
| | LPR113 | $\neq 0$ | printing of EMD before interpolation |
| • * | (K(I,J), I=1,3),J=1,N | | directions in oblique coordinates |
| • * | NPO | | number of orbital projections (≤ 10) |
| | NPB | | number of band projections (≤ 10) |
| | | | <i>if NPO $\neq 0$ insert NPO sets of records</i> _____ II |
| • * | NO | | number of A.O.'s in the I-th projection |
| • * | IQ(I),I=1,NO | | sequence number of the A.O.'s in the I-th projection - basis set sequence. |
| | | | <i>if NPB $\neq 0$ insert NPB sets of records</i> _____ II |
| • * | NB | | number of bands in the I-th projection |
| • * | IB(I),I=1,NB | | sequence number of the bands in the I-th projection |

Warning The calculation of the Fermi energy is necessary for metallic systems (**NEWK** keyword with $IFE = 1$). The Electron Momentum Density is calculated along given directions (equation 13.22, page 282). It can be computed also for open-shell systems. The electron momentum distribution, EMD, is a non-periodic function; it falls rapidly to zero outside the first Brillouin zone. $\rho(\underline{0})$ gives the number of electrons at rest. The oblique coordinates directions given in input refer to the conventional cell, *not* to the primitive cell, for 3D systems.

Example: in a FCC system the input directions refer to the orthogonal unit cell frame (sides of the cube) not to the primitive non-orthogonal unit cell frame.

EMDLDM - Electron Momentum Density from Density Matrix - line path

Users of this option are kindly requested to cite the following papers[64, 143]:

A. Erba and C. Pisani, *J. Comput. Chem.*, **33**, 822 (2012). *Evaluation of the electron momentum density of crystalline systems from ab initio linear combination of atomic orbitals calculations.*

C. Pisani, A. Erba, S. Casassa, M. Itou and Y. Sakurai, *Phys. Rev. B*, **84**, 245102 (2011). *The anisotropy of the electron momentum distribution in α -quartz investigated by Compton scattering and ab initio simulations.*

| rec | variable | value | meaning |
|------------------------------|----------|-------|---|
| • * | N | | number of directions (≤ 10) |
| | PMAX | | maximum momentum value (a.u.) for which the EMD is computed |
| | STEP | | discretization step for the EMD |
| | IPLO | 0 | no data stored on disk |
| | | 1 | formatted output to file fort.25 for plotting (Appendix D, page 323). |
| | | 2 | formatted output to file EMDLDM.DAT for plotting (Appendix D, page 323). |
| _____ insert N records _____ | | | |
| • * | H K L | | three integers defining the direction with respect to the conventional cell |
| _____ end _____ | | | |
| • * | ICASO | 1 | the total density matrix is used |
| | | 2 | the core density matrix is used |
| | | 3 | the valence density matrix is used |
| • * | NSA1 | 0 | no spherically averaged EMD |
| | | 1 | the spherically averaged EMD is computed |
| | NSA2 | 0 | no EMD-anisotropy |
| | | 1 | EMD-anisotropies are computed |

The Electron Momentum Density (EMD) is calculated along given crystallographic directions (defined in oblique coordinates with respect to the conventional cell) directly from the Density Matrix. The EMD is a non-periodic function; it falls rapidly to zero outside the first Brillouin zone. $\pi(\mathbf{0})$ gives the number of electrons at rest. For Open-Shell systems the $\alpha + \beta$ and the $\alpha - \beta$ EMD are computed.

The **NEWK** keyword must be called with the option activating the Fermi level calculation before **EMDLDM** if the core or valence Density Matrix is desired (ICASO=2,3).

The spherically averaged EMD $\pi_{SA}(|\mathbf{p}|)$ is computed according to the procedure described in section 13.8 (page 281). The EMD-anisotropy is $\Delta\pi(\mathbf{p}) = \pi(\mathbf{p}) - \pi_{SA}(|\mathbf{p}|)$.

EMDPDM- Electron Momentum Density from Density Matrix - maps

Users of this option are kindly requested to cite the following papers[64, 143]:

A. Erba and C. Pisani, *J. Comput. Chem.*, **33**, 822 (2012). *Evaluation of the electron momentum density of crystalline systems from ab initio linear combination of atomic orbitals calculations.*

C. Pisani, A. Erba, S. Casassa, M. Itou and Y. Sakurai, *Phys. Rev. B*, **84**, 245102 (2011). *The anisotropy of the electron momentum distribution in α -quartz investigated by Compton scattering and ab initio simulations.*

| rec | variable | value | meaning |
|-----|----------|----------|---|
| • * | N | | number of planes (≤ 10) |
| | PMAX | | maximum momentum value (a.u.) for which the EMD is computed in the two main directions defining the plane |
| | STEP | | discretization step for the EMD |
| | IPLO | 0 | no data stored on disk (data only in output) |
| | | 1 | formatted output to file fort.25 for plotting (Appendix D, page 321) |
| | | 2 | formatted output to files 3DEMDTOTAL.DAT and 3DEMDANISO.DAT for 3D plotting of total EMD and EMD-anisotropy (for squared map-windows only); see below |
| | IDIR | 0 | planes defined via the MAPNET dummy keyword |
| | | 1 | planes defined via two crystallographic directions |
| • * | ICASO | 1 | the total density matrix is used |
| | | 2 | the core density matrix is used |
| | | 3 | the valence density matrix is used |
| • * | NSA1 | 0 | no spherically averaged EMD |
| | | 1 | the spherically averaged EMD is computed |
| | NSA2 | 0 | no EMD-anisotropy |
| | | 1 | EMD-anisotropies are computed |
| | NSA3 | 0 | no restart of spherically averaged EMD |
| | | $\neq 0$ | a previously computed spherically averaged EMD is read from input <i>if NSA3 $\neq 0$ insert NSA3 records</i> |
| • * | P | | value of $ \mathbf{p} $ |
| | SAEMD | | value of the spherically averaged EMD $\pi(\mathbf{p})$ <i>end</i> |
| | | | <i>insert N records</i> |
| | | | <i>if IDIR = 0</i> |
| | | | insert MAPNET input records (Section 9.2, page 226) |
| | | | <i>else if IDIR = 1</i> |
| • * | H K L | | three integers defining the first direction with respect to the conventional cell |
| | H' K' L' | | three integers defining the second direction with respect to the conventional cell <i>end if</i> |
| | | | <i>end</i> |

The Electron Momentum Density (EMD) is calculated in given crystallographic planes (defined in oblique coordinates with respect to the conventional cell) directly from the Density Matrix. The EMD is a non-periodic function; it falls rapidly to zero outside the first Brillouin zone. $\pi(\mathbf{0})$ gives the number of electrons at rest. EMD-maps can be computed for closed-shell systems only.

The **NEWK** keyword must be called with the option activating the Fermi level calculation before **EMDPDM** if the core or valence Density Matrix is desired (ICASO=2,3).

The spherically averaged EMD $\pi_{SA}(|\mathbf{p}|)$ is computed according to the procedure described in section 13.8 (page 281). The EMD-anisotropy is $\Delta\pi(\mathbf{p}) = \pi(\mathbf{p}) - \pi_{SA}(|\mathbf{p}|)$. If one activates the computation of the spherically averaged EMD (NSA1=1), the STEP should be small in order to reduce the numeric noise in its fitting procedure.

Formatted external units 25 (fort.25) are generated that can be read by the Crgra2006 graphics software for creating 2D maps. See Appendix D at page 321. The formatted external files 3DEMDTOTAL.DAT and 3DEMDANISO.DAT consist of a series of records PX, PY, EMD(PX,PY) and can easily be used for representing 3D surfaces of the EMD on a plane.

EMDP - Electron Momentum Density - plane maps

| rec | variable | value | meaning |
|--|---------------------------------|-------|--|
| • * | NP | | number of planes (< 5) |
| | IS | | shrinking factor. |
| | IPLO | 0 | no data stored on disk. |
| | | 1 | formatted output on Fortran unit 25 for plotting |
| | LPR115 | | printing of the EMD function in output |
| _____ insert NP set of records _____ | | | |
| • * | (L1(J),J=1,3), (L2(J),J=1,3) | | fractional coordinates of the reciprocal lattice vectors that identify the plane |
| • * | PMX1 | | maximum p value along the first direction |
| | PMX2 | | maximum p value along the second direction |
| • * | NPO | | number of orbital projections (≤ 10) |
| | NPB | | number of band projections (≤ 10) |
| _____ if NPO $\neq 0$ insert NPO set of records _____ II | | | |
| • * | NO | | number of A.O.'s in the I-th projection |
| • * | IQ(I),I=1,NO | | sequence number of the A.O.'s in the I-th projection - basis set order |
| _____ if NPB $\neq 0$ insert NPB set of records _____ II | | | |
| • * | NB | | number of bands in the I-th projection |
| • * | IB(I),I=1,NB | | sequence number of the bands in the I-th projection |

Warning The Fermi energy must be computed for metallic systems (**NEWK** keyword with $IFE = 1$). Calculation of electron momentum density on definite planes (equation 13.22, page 282). It works also for open-shell systems. If $LPR115 \neq 0$ the EMD function is printed in output (recommended). The fractional coordinates of the reciprocal lattice vectors given in input refer to the conventional cell, *not* to the primitive cell, for 3D systems. Example: in a FCC system the input directions refer to the orthogonal unit cell frame (sides of the cube) not to the primitive non-orthogonal unit cell frame.

END

Terminate processing of *properties* input. Normal end of the program *properties*. Subsequent input records are not processed.

EXTPRT

See input block 1, page 41

FMWF - Wave function formatted output

The keyword **FMWF**, entered in *properties* input, writes formatted wave function data (same data are written in file fort.9, unformatted, at the end of SCF) in file fort.98 (LRECL=80). The formatted data can then be transferred to another platform. No input data required.

The resources requested to compute the wave function for a large system (CPU time, disk storage) may require a mainframe or a powerful workstation, while running *properties* is not so demanding, at least in terms of disk space. It may be convenient computing the wave function on a given platform, and the properties on a different one.

The keyword **RDFMWF**, entered in the first record of the *properties* input deck reads formatted data from file fort.98, and writes unformatted data in file fort.9. The key dimensions of the program computing the wave function and the one computing the properties are checked. If the dimensions of the arrays are not compatible, the program stops, after printing the PARAMETER statement used to define the dimension of the arrays in the program which computed the wave function. The sequence of the operations, when transferring data from one platform to another is the following:

| platform | program | input | action |
|----------|-------------------|---------------|--|
| 1 | properties | FMWF | wave function formatted to file fort.98 |
| | | | ftp file fort.98 from platform 1 to platform 2 |
| 2 | properties | RDFMWF | wf read from file fort.98 (formatted) and written in file fort.9 (unformatted) |

FRACTION - unit of measure

Unit of measure of coordinates in the periodic direction (**ECHG**, **POTM**, **CLAS**) See input block 1, page 45.

GRID3D - Selected property computed on a 3D grid

| rec | variable | meaning |
|-----|-----------|--|
| • * | NP | Number of points along the first direction |
| • A | CHARGE | electronic charge selected - see ECH3 input |
| or | | |
| • * | POTENTIAL | electronic charge selected - see POT3 input |

The property to be computed at the grid points is chosen by a keyword. Input as required by the selected property follows.

Computed data are written, formatted, to file fort.31. See Appendix D, page 327, for description of the format.

INFOGUI/INFO - output for visualization

No input data required.

Information on the system and the computational parameters are written formatted in fortran unit 32, in a format suitable for visualization programs.

See Appendix D, page 327, for description of the format.

ISOTROPIC - Fermi contact - Hyperfine electron-nuclear spin interaction isotropic component

| rec | variable | meaning |
|-----|---------------|---|
| • A | keyword | enter one of the following keywords: |
| | ALL | Fermi contact is evaluated for all the atoms in the cell |
| or | | |
| | UNIQUE | Fermi contact is evaluated for all the non-equivalent atoms in the cell |
| or | | |
| | SELECT | Fermi contact is evaluated for selected atoms |
| • * | N | number of atoms where to evaluate Fermi contact |
| • * | IA(I),I=1,N | label of the atoms |

As an additional information, the total electron density at the nuclei is computed for all systems.

In the case of open shell systems, the spin density at the nuclei ($\langle \rho^{\text{spin}}(\mathbf{r}_N) \rangle$) is evaluated. This quantity is given in bohr⁻³ and is transformed into the hyperfine coupling constant $a_N[\text{mT}]$ through the relationship [183]

$$a_N[\text{mT}] = \frac{1000}{(0.529177 \cdot 10^{-10})^3} \frac{2}{3} \mu_0 \beta_N g_N \langle \rho^{\text{spin}}(\mathbf{r}_N) \rangle = 28.539649 g_N \langle \rho^{\text{spin}}(\mathbf{r}_N) \rangle$$

where

$$\mu_0 = 4\pi \cdot 10^{-7} = 12.566370614 \cdot 10^{-7} [\text{T}^2 \text{J}^{-1} \text{m}^3] \quad (\text{permeability of vacuum})$$

$$\beta_N = 5.0507866 \cdot 10^{-17} [\text{JT}^{-1}] \quad (\text{nuclear magneton})$$

the nuclear g_N factors for most of the nuclei of interest are available in the code and are taken from [183]. Conversion factors:

$$a_N[\text{MHz}] = \frac{a_N[\text{mT}]g_e\beta_e}{10^9 h[\text{Js}]} = 28.026 \cdot a_N[\text{mT}]$$

$$a_N[\text{cm}^{-1}] = \frac{a_N[\text{MHz}]10^8}{c[\text{ms}^{-1}]} = 0.33356410 \cdot 10^{-4} \cdot a_N[\text{MHz}]$$

$$a_N[\text{J}] = g_e \beta_e 10^{-3} a_N[\text{mT}] = 1.856954 \cdot 10^{-26} a_N[\text{mT}]$$

where:

$$\beta_e = 9.2740154 \cdot 10^{-24} [\text{JT}^{-1}] \quad (\text{bohr magneton})$$

$$g_e = 2.002319304386 \quad (\text{free-electron } g \text{ factor})$$

$$c = 2.99792458 \cdot 10^8 [\text{ms}^{-1}] \quad (\text{speed of light in vacuum})$$

$$h = 6.6260755 \cdot 10^{-34} [\text{Js}] \quad (\text{Planck constant})$$

For extended printing (tensor in original cartesian axes and in principal axis system) insert, before the keyword ISOTROPIC:

SETPRINT

1

18 1

See tests 29, 31, 32, 33.

KINETEMD - Kinetic Tensor computed from the Electron Momentum Distribution

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • * | PMAX | | maximum momentum value (a.u.) for which the EMD is computed |
| | PINT | | Maximum momentum value (a.u.) defining an inner sphere where the EMD is computed exactly (PINT < PMAX) |
| | STEP | | discretization step for the computation of the EMD in the inner region of \mathbf{p} -space ($p < \text{PINT}$) |
| | STEPDIST | | discretization step for the computation of the EMD in the outer region of \mathbf{p} -space (PINT < $p < \text{PMAX}$) |
| • * | ICASO | 1 | the total density matrix is used |
| | | 2 | the core density matrix is used |
| | | 3 | the valence density matrix is used |

The **KINETEMD** keyword activates the computation of the kinetic tensor \mathbf{T} , whose trace is the total kinetic energy of the system, as the set of second moments of the electron momentum distribution. See the discussion in section 13.8 (page 281).

KNETOUT - Reciprocal lattice information - Fock/KS eigenvalues

Obsolete. See **CRYAPI.OUTPUT**, page 205.

LOCALWF - Localization of Wannier Functions (WnF)

Wannier functions are computed from Bloch functions, and then localized, following the method described in [199] and [198]. The method applies to non-conductor systems only.

The localization of Wannier Functions (WnF) is controlled by parameters. Default values are supplied for all parameters.

Optional keywords allow modification of the default choices, recommended to developers only. The **LOCALWF** block is closed by the **END** keyword.

For UHF calculations two set of blocks must be inserted for the α and β electrons, each one ending with the keyword **END**.

1. The **NEWK** option must be executed before running **LOCALWF**, to compute the Bloch functions.
2. The number of **k** points required for a good localization depends on the characteristics of the bands chosen. For core electrons or valence bands in non-conducting materials, an **IS** slightly larger than that used in the SCF part is enough to provide well localized WnFs. For valence bands in semiconductors or conduction bands the **k**-point net is required to be denser, but there are no recipes to determine *a priori* the optimum **IS** value. The **IS** value chosen determines a Born-von Karman supercell (or cyclic cluster) from which the program *a priori* estimates the memory space that should be enough to contain all WnF coefficients lower than the threshold 10^{-ITDP} (see the meaning of *ITDP* in what follows) in real space. The size of this crystal domain in terms of unit cells is provided in output before the localization procedure. If the crystal domain is too small usually the localization fails and **IS** must be increased. On the other hand, if it is too large (very large **IS**) the memory space reserved for the WnF coefficients becomes overestimated and the calculation may stop because of a lack of memory for array allocation.
3. The efficiency of the localization can be controlled using the **CYCTOL** parameters. In most cases, increasing **ITDP** and/or **ICONV** leads to larger and more accurate localization of the WnFs.
4. The **RESTART** option admits **MAXCYCLE** = 0, then the program just reconstructs all the information about the WnFs given in file fort.81 but does not continue the localization. This two options together with a **IS**=1 in **NEWK** is useful to perform the analysis of the WnFs after localization by means of the **PRINTPLO** option.

Definition of the set of bands considered in the localization process

VALENCE

Valence bands are chosen for localization.

OCCUPIED

All the occupied bands are chosen for localization [default].

INIFIBND

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | IBAN | | initial band considered for localization |
| | LBAN | | last band considered for localization |

BANDLIST

| rec | variable | meaning |
|-----|--------------|----------------------------|
| • * | NB | number of bands considered |
| • * | LB(I),I=1,NB | labels of the bands. |

Tolerances for short and large cycles

A short cycle is a sequence of wannierization and Boys localization steps. The accuracies in both, the calculation of the Dipole Moments (DM) and the definition of the phases assigned to each periodically irreducible atom, are controlled so that they increase as the localization process evolves. This results in a significant saving of computational cost. Therefore, each time a given criterion is fulfilled, the accuracy in the DM evaluation increases and a new large cycle starts.

CYCTOL

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | ITDP0 | > 0 | Initial tolerance used to calculate the DM matrix elements: 10^{-ITDP0} [2] |
| | ITDP | > 0 | Final tolerance used to calculate the DM matrix elements: 10^{-ITDP} [5] |
| | ICONV | > 0 | Convergence criterion to finish a large cycle: $ABS(ADI(N) - ADI(N-1)) < 10^{-ICONV}$, where ADI is the atomic delocalization index and N is the short cycle number [5] |

PHASETOL

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • * | ITPH0 | > 0 | 10^{-ITPH0} is the initial tolerance on the atomic charge population to attribute the phase to atoms in the wannierization step [2] |
| | ITPH | > 0 | 10^{-ITPH} is the final tolerance used to attribute this phase [3] |
| | ICTOL | > 0 | DM tolerance of the cycle where ITPH0 changes to ITPH. [ITDP0+1] |

Restart Keywords

With this option the WnFs of a previous run are read from file fort.81 (copy of file fort.80, written by the previous run) and projected onto the current occupied subspace. Along with the projection the WnFs are re-orthonormalized within the Born-von Karman cyclic cluster. Tolerances and active bands must be the same as in the previous run. Three variants are possible, corresponding to three different keywords.

RESTART: can be used to start a new localization or to improve a previous one. After the projection, cycles of wannierization and localization are performed until convergence is attained.

RESTORTH: similar to the RESTART keyword but here the WnF are orthonormalized in direct space (where the tails feature different topological properties than in the Born-von Karman cyclic cluster) immediately after their reading. Next the localization properties in direct space of the resulting WnFs *may optionally* be improved using the appropriate keywords (**WANDM** and **FULLBOYS**).

FIXWF: this keyword can be used only if file fort.80 of the previous run has been generated with the keyword **SYMMWF**. After projection, no further Boys localization step is performed. Both the original symmetry and the WnF labeling are kept with a negligible loss in the localization indices.

The last option is recommended when a sequence of CRYSCOR calculations are to be performed corresponding each time to small geometrical changes. Accordingly, to ensure a smooth evolution of the energy and wave function, all indices concerning the symmetry and the labeling of the WnFs are kept to be the same along the sequence. This is required in particular in geometry optimizations and scanning along geometrical parameters (for instance: in the calculation of molecular physisorption energy curves – see the *CRYSCOR Users's Manual* and the *CRYSCOR Tutorials* for a detailed description of the procedure). As for the **FIXINDEX** option (page 98), the reference calculation should be the one with the most compact structure.

General Keywords

MAXCYCLE

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • * | NCYC | > 0 | maximal number of short cycles for the iterative process 30 |

BOYSCTRL

Parameters that control the Boys localization step. Convergence of the process is achieved when the orbital-stability conditions: $B_{st} = 0$; $A_{st} > 0$, (see Pipek and Mezey 1989 [138]) are fulfilled for all pairs st of WnFs. Additionally, in order to avoid nearly free rotations (for instance in core or lone-pair WnFs) those pairs st with A_{st} close to 0 are not mixed (frozen).

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | IBTOL | | $10^{-\text{IBTOL}}$ is the threshold used for the stability condition on B_{st} . 4 |
| | IBFRZ | | If for a pair of WnFs st , $ A_{st} \leq 10^{-\text{IBFRZ}}$, then the corresponding WnFs are not mixed. 4 |
| | MXBCYC | | Maximum number of cycles allowed in the Boys localization process 500 |

EMDWF

The **EMDWF** keyword activates the computation of the contribution to the total Electron Momentum Density (EMD) $\pi(\mathbf{p})$ of a selected Wannier Function, according to the partitioning scheme illustrated in section 13.8 (page 281). Partitioning the EMD in terms of contributions coming from chemically meaningful objects like WFs (that can easily be assigned to bonds, lone pairs, etc.) is an appealing way of extracting information from a function which is still far from being completely understood.

The contribution to the EMD is computed on a given plane. The user can provide, via input, a previously computed spherically averaged EMD (see keywords **EMDLDM** and **EMDPDM**) in order to compute the contribution of a selected WF to the global anisotropy of the EMD. See the discussion of section 13.8 (page 281).

The formatted external file WFEMD.DAT consists of a series of records PX, PY, EMD(PX,PY), [SAEMD(PX,PY)] and can easily be used for representing 3D surfaces or 2D maps of the EMD on the plane.

Users of this option are kindly requested to cite the following papers[64, 143]:

A. Erba and C. Pisani, *J. Comput. Chem.*, **33**, 822 (2012). *Evaluation of the electron momentum density of crystalline systems from ab initio linear combination of atomic orbitals calculations.*

C. Pisani, A. Erba, S. Casassa, M. Itou and Y. Sakurai, *Phys. Rev. B*, **84**, 245102 (2011). *The anisotropy of the electron momentum distribution in α -quartz investigated by Compton scattering and ab initio simulations.*

| rec | variable | value | meaning |
|-----|----------|----------|--|
| • * | WF | | label of the selected WF |
| | NTOL1 | [1] | initial tolerance used to calculate the Dipole Moment matrix elements: $10^{-\text{NTOL1}}$ |
| | IDIR | 0 | planes defined via the MAPNET dummy keyword |
| | | 1 | planes defined via two crystallographic directions |
| | PMAX | | maximum momentum value (a.u.) for which the EMD is computed in the two main directions defining the plane |
| | STEP | | discretization step for the EMD |
| | IPLO | 0 | no data stored on disk (data only in output) |
| | | 1 | formatted output to file WFEMD.DAT for 2-3D plotting of total EMD and EMD-anisotropy (for squared map-windows only) |
| • * | NSA1 | 0 | the spherically averaged EMD is not read |
| | | $\neq 0$ | the spherically averaged EMD is read from input |
| | NELVAL | | number of valence electron for which the spherically averaged EMD has been computed. If NSA1=0 then NELVAL becomes a dummy entry <i>if NSA1 \neq 0 insert NSA1 records</i> |
| • * | P | | value of $ \mathbf{p} $ |
| | SAEMD | | value of the spherically averaged EMD $\pi(\mathbf{p})$ <i>end</i> |
| | | | <i>if IDIR = 0</i> |
| | | | insert MAPNET input records (Section 9.2, page 226) |
| | | | <i>else if IDIR = 1</i> |
| • * | H K L | | three integers defining the first direction with respect to the conventional cell |
| | H' K' L' | | three integers defining the second direction with respect to the conventional cell <i>end if</i> |

EMDWFKIN

The **EMDWFKIN** keyword activates the computation of the kinetic tensor \mathbf{T}^i related to a selected Wannier function W_i . The contribution of W_i to the electron momentum density $\pi_i(\mathbf{p})$ is computed and then its second moment is obtained via numerical integration (see the discussion in section 13.8 at page 281).

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • * | WF | | label of the selected WF |
| | NTOL1 | [1] | initial tolerance used to calculate the Dipole Moment matrix elements: $10^{-\text{NTOL1}}$ |
| • * | PMAX | | maximum momentum value (a.u.) for which the EMD is computed |
| | PINT | | Maximum momentum value (a.u.) defining an inner sphere where the EMD is computed exactly (PINT < PMAX) |
| | STEP | | discretization step for the computation of the EMD in the inner region of \mathbf{p} -space ($p < \text{PINT}$) |
| | STEPDIST | | discretization step for the computation of the EMD in the outer region of \mathbf{p} -space (PINT < p < PMAX) |

Initial guess options

The iterative localization process of the WnFs needs to start from a reasonable initial guess. By default the starting functions are obtained automatically from the Hamiltonian eigenvectors at the Γ point. When required (pure covalent bonds that link atoms in different unit cells), a pre-localization is performed using a scheme similar to that suggested by Magnasco and Perico (1967) [114].

IGSSCTRL

Parameters used to control the pre-localization of the Γ point eigenvectors.

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | CAPTURE | | The capture distance between atoms I and J is given by $\text{CAPTURE} * (\text{RAYCOV}(\text{I}) + \text{RAYCOV}(\text{J}))$ (RAYCOV, covalent radius (default value table page 59). An inter-atomic distance lower than the capture indicates that I and J can be covalently bonded. Default value $\boxed{2.0}$. |
| | MPMAXIT | | Maximum number of iterations in the pre-localization process $\boxed{200}$ |
| | ICNVMP | | $10^{-\text{ICNVMP}}$ is the convergence threshold for the Magnasco-Perico pre-localization $\boxed{8}$ |
| | IOVPOP | | Just those pairs of atoms whose overlap population are greater than $10^{-\text{IOVPOP}}$ are considered covalently bonded $\boxed{4}$ |

The initial guess can be given as input in two mutually exclusive ways, controlled by the keywords **IGSSVCTS** and **IGSSBNDS**:

IGSSVCTS

The eigenvectors and the phases are given explicitly after the LOCALWF block (and before the plot parameters if required), in the following format.

| rec | variable | value | meaning |
|-----|----------------------|-------|---|
| • * | NGUES | | Number of bands whose phase is pre-assigned such that the involved atoms are to be located in a given cell. <i>insert $2 \times \text{NGUES}$ records</i> |
| • * | IB | | |
| • * | IGAT(I,IB),I=1,NAF | | Index of the direct lattice vector corresponding to the cell where atom I is expected to have the largest charge population in Wannier IB (NAF is the number of atoms per cell) <i>insert:</i> |
| | GUESSV(I),I=NDF*NOCC | | where NDF is the basis set dimension and NOCC the number of bands considered. GUESSV is a matrix containing the initial guess vectors for the iterative Wannier-Boys procedure (GUESSV is written in free format as a one-dimensional array). |

IGSSBNDS

Use this option to explicitly indicate the WnFs that are to be assigned to covalent bonds.

| rec | variable | value | meaning |
|-----|-------------|-------|---|
| • * | NBOND | | Number of covalent bonds given as input. <i>insert NBOND records</i> |
| • * | NAT1 | | Label of the first atom of the bond, it is assumed to be located in the reference cell. |
| | NAT2 | | Label of the second atom of the covalent bond |
| | IC1,IC2,IC3 | | Indices of the cell where atom NAT2 is located |
| | NBNDORD | | Bond Order |

CAPTURE

The value of the CAPTURE parameter (see **IGSSCTRL**) can be redefined.

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • * | CAPTURE | | The capture distance between atoms I and J is given by $CAPTURE * (RAYCOV(I) + RAYCOV(J))$ (RAYCOV, covalent radius (default value table page 59). An inter-atomic distance lower than the capture indicates that I and J can be covalently bonded. Default value $\llbracket 2.0 \rrbracket$. |

Symmetry adaptation of Wannier Functions

SYMMWF

The WnFs *a-posteriori* symmetrization procedure [31], activated by the **SYMMWF** keyword, is mandatory in the case of a subsequent CRYSCOR calculations. A brief outline of the procedure can help to orient in the particular nomenclature adopted to define the symmetrized WnFs and their symmetry relations.

1. after the localization step, the WnFs are centered at different Wickoff sites of the reference cell which are invariant with respect to point-symmetry subgroup H of the space group G of the crystal;
2. for each site, a coset decomposition of G by H is performed, thus leading to the definition of $N_F = \frac{|G|}{|H|}$ symmetry operators (coset representatives) which rotate the reference site into equivalent ones;
3. among each set of equivalent sites, a reference site is chosen;
4. the WnFs of the reference site are symmetrized according to the corresponding subgroup H : each of these symmetrized WnFs is basis of an irreducible representations (IRREP) of the subgroup H and hereafter each component of the irreducible basis set will be referred to as *petal*;
5. the collection of *petals* belonging to the same IRREP of H , the whole irreducible basis set, constitutes a so-called *flower*. It is worth noting that bi/three-dimensional IRREPs gives rise to *flower* made up of two/three *petals*, respectively;
6. the rotation of the reference *flower* performed by means of the corresponding N_F-1 coset representatives (identity excluded) yields the creation of others N_F-1 symmetry related *flowers*; the set of such equivalent *flowers* constitutes a *bunch*;
7. in general, more than one *bunch* could be associated to the same reference site;
8. as a result of this procedure, each WnF is fully classified by four indices $|\mathbf{b}, \mathbf{f}, \mathbf{p}, \mathbf{g}\rangle$ (\mathbf{b} = bunch, \mathbf{f} =flower, \mathbf{p} = petal, \mathbf{g} = crystal cell) such that a general symmetry operator of the system $\hat{R} \in G$, applied to a WnF gives: $\hat{R} |\mathbf{b}, \mathbf{f}, \mathbf{p}, \mathbf{g}\rangle = \sum_{p'} [A(R)]_{pp'} |\mathbf{b}, \mathbf{f}^R, \mathbf{p}', \mathbf{g}^R\rangle$.

In addition to the general keywords of the localization step, a set of optional keywords, recommended to developers only, can be used to modify some default settings.

The **SYMMWF** input block must be closed by the keyword **END**.

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • A | TOLBOND | | redefinition of the tolerance to classify WFs as <i>bond</i> or <i>atomic</i> - default value $\llbracket 0.2 \rrbracket$ |
| • F | TOLB | | if $\ p_1^i - p_2^i\ < tol_b$ then the WnF ω_i is a <i>bond</i> one (p_x^i is the atomic population of the two atoms which most contribute to the WnF i) |
| • F | TOLSYM | | a WnF ω_i is classified as already symmetric if $\langle \omega_j R \omega_i \rangle > TOLSYM$ - default value $\llbracket 0.99 \rrbracket$ |
| • A | NOSYMAP | | an alternative algorithm for the unpacking of WnFs (from the reciprocal to the direct lattice) is followed |
| • A | PRINT | | default value $\llbracket 0 \rrbracket$ |

WnFs's Quality. Get WnFs of good quality, in terms of norm and symmetry, is a necessary prerequisites for obtaining reliable energy at the MP2 level. The output file contains some useful information that can be used to check the quality of the solution: as a general and safety rule, the final value for "ERR PER WF" should be less than $1 \cdot 10^{-5}$ and the precision on the scalar products between WnFs (printed by setting the PRINT option equals 2) should not be less than $1 \cdot 10^{-5}$.

The solution can be eventually improved by tuning some computational parameters; in particular the user can:

- set tighter tolerances for the evaluation of two-electron integrals in the HF reference solution (**TOLINTEG**): despite the increase of computational time, it turns out that the localization procedure is particularly sensitive to the the first threshold;
- increase the number of **k** points (**NEWK**) according to the suggestions reported in the LOCALWF introduction paragraph;
- use more severe values for the short and large cycles tolerances (**CYCTOL**).

Finally, in some case, the activation of the **FULLBOYS** option can be decisive.

Printing Options and Plot of the WnFs

WnFs can be printed in terms of their coefficients or can be plotted as 2D or 3D maps.

PRINTPLO

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | IPRT | 0 | Does not print Wannier coefficients [default] |
| | | > 0 | Prints Wannier coefficients at each cycle up to the IPRT-th star of direct lattice vectors <input type="text" value="0"/> |
| | IPRP | 0 | Prints population analysis only at the end of the localization. |
| | | ≠ 0 | Prints analysis at each W-B cycle <input type="text" value="0"/> |
| | ITPOP | | Only atomic population larger than 10^{-ITPOP} are printed <input type="text" value="2"/> |
| | IPLLOT | 0 | WnFs are not computed for plot |
| | | ≠ 0 | WnFs are computed in a grid of points, IPLLOT being the number of stars of direct lattice vectors taken into account for WnF coefficients. Data are written in file fort.25 <input type="text" value="0"/> |

If IPLLOT ≠ 0 insert after the LOCALWF keyword block (defining the localization procedure computational parameters, and terminated by END) the following data:

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • * | NWF | | number of WnF to plot |
| | | | <i>insert NWF blocks of data</i> |
| • * | NUMBWF | | sequence number (output order) of the WnF to plot |
| | | | <i>MAPNET input data (Section 9.2, page 226)</i> |

Each block defines the index number of WnF to be computed in a grid of points, followed by data defining the frame inside which the value of localized WnF has to be computed in a grid of points (see **MAPNET**, 226. The package Crgra2006 (<http://www.crystal.unito.it/Crgra2006.html>) allows plotting the function as contour lines. The WnFs and the WnFs densities (in this order) within the selected regions are given in file fort.25.

If IPLO < 0 the WnFs are computed in a 3D grid, which is generated considering the coordinates of WnFs centroids. Insert the following data:

| rec | variable | value | meaning |
|-----|-------------|-------|---|
| • * | ICUBE | 0 | data are saved in fort.31 |
| | | > 0 | data are saved in fort.31 and in the CUBE format in the external units <i>inputfilename</i> _WAN_CUBE.DAT |
| | RADIUS | R | defines the spatial region of the 3D grid. The value is in Angstrom |
| | NPOINTS | NP | number of points along the x direction |
| | NWFS | 0 | all the WnFs are plotted |
| | | > 0 | number of WnFs to plot |
| | | | <i>if NWFS > 0 insert</i> |
| • * | WnFs=1,NWFS | | sequence number (output order) of the WnFs to be plotted |

Let us consider the following input for generating the values of WnFs on a 3D grid of points:

```

NEWK
4 4
0 0
LOCALWF
VALENCE
SYMMWF
END
PRINTPLO
0 0 0 -8
1 2 60 2
1 2
END
END
END

```

The previous input allows for the computation of all the valence (see keyword **VALENCE**) WnFs of the system and for the 3D plotting of the first and second valence WnFs. The data are saved in CUBE format in external units *inputfilename*_WAN_CUBE.DAT. It is possible to visualize the structure of the considered system and the WnFs contained in the CUBE files by using the Jmol program, for instance. In that case, it would be necessary to insert these commands in the Jmol console:

```

load "file: path-to-the-cube-file"
isosurface sign red blue cutoff 0.7 "file: path-to-the-cube-file"

```

The default cutoff value is 0.2 but it is possible to modify it as shown above, in order to get a better graphical representation. Some examples of graphical representations are given in Figures (9.1 and 9.2).

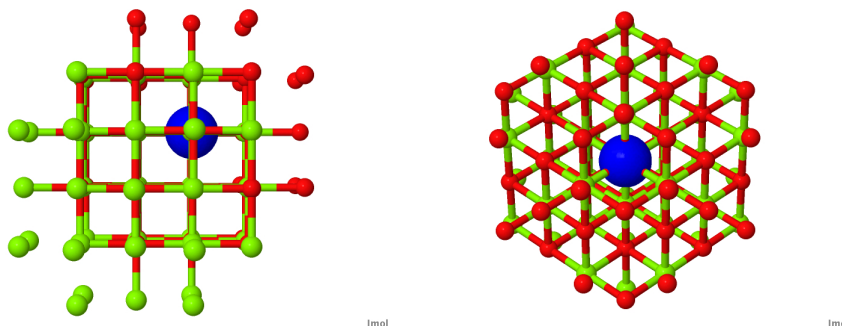


Figure 9.1: First valence WnF of MgO; two different views.

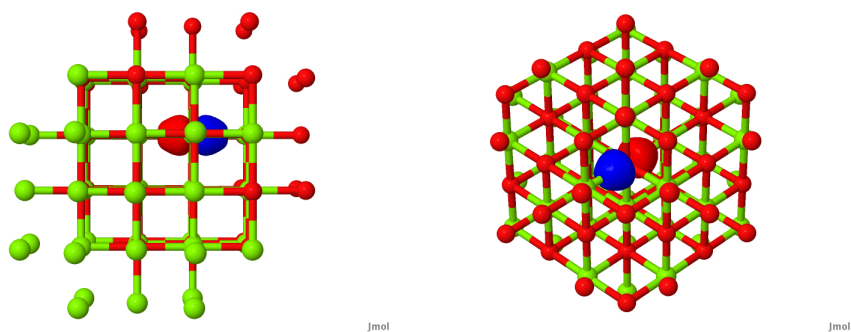


Figure 9.2: Second valence WnF of MgO; two different views.

New keywords - developers only

CLUSPLUS

Upon transformation from Bloch Functions to Wannier Function, the latter are defined within a region with cyclic boundary condition imposed. We call it the "cyclic cluster". The volume of this region depends on the shrinking factor used in the previous NEWK. For instance, if IS=4, then the cyclic cluster in a 3D system will be 4^3 times larger than the primitive cell. For the localization part to work the WnFs are required to be described in the real space, hence the cyclic conditions and the WnFs are mapped onto a cluster in direct space. The size of this cluster where the localization is performed is defined as follows:

1. We define a small cluster, as a spherical region that contains the minimum number of G-vectors that fully map the cyclic cluster. Let's call R0 its radius.
2. As the centroid of some WnFs may be at the border of the reference cell we should consider some additional space in the direct cluster so as to allow the tails to be fully included in the region. This additional distance R1 is calculated as the maximum G-vector modulus of the set of cells at the neighbours of the reference one.
3. The radius of the resulting direct cluster will read: $R = R0 + IPLUSCLUS * R1$, where IPLUSCLUS is given in input. By default IPLUSCLUS is 5.

| rec | variable | value | meaning |
|-----|-----------|-------|---|
| • * | iplusclus | | factor to define the radius of direct cluster |

ORTHNDIR

After the WANNIER-BOYS localization the WnFs are not fully orthonormal in direct space (they are just orthonormal within the cyclic cluster). To perform a true localization in direct space (see **FULLBOYS**) a previous re-orthonormalization in direct space is required. This is carried out by constructing the first order approximation of the Lowdin transformation and applying it to the WnFs. This process is performed iteratively up to fulfill a given criterion. ORTHNDIR sets the parameters that control this process.

| rec | variable | value | meaning |
|-----|----------|----------|--|
| • * | ISTORTH | > 0 | number of stars of G-vectors that contains the transformation matrix. |
| | | = 0 | the number of stars is computed so as to contain the reference cell and all its neighbors [default]. |
| | ITOLORTH | > 0 | the overlap matrix elements are computed just between WnF components gt $10^{*-ITOLORTH}$ in absolute value [default 5]. |
| | NREORTHN | ≥ 0 | maximum number of iterations [default 10 in <i>properties</i> , 0 in <i>crystal</i> . |
| | | < 0 | the iterative procedure is performed up to the mean normalization error of the WnFs is $< 10^{*NREORTHN}$ in absolute value (Default -7) |

WANDM

WANDM controls the computation of the DM matrix elements between WnFs assigned to the reference and the neighboring cells (translational images of the former).

| rec | variable | value | meaning |
|-----|----------|-------|--|
| • * | INEIGH | | controls the extent of the DM matrix by limiting the neighboring cell around the origin considered in the computation of the matrix elements: |
| | | > 0 | number of stars of neighboring cells considered for the matrix elements of DM |
| | | < 0 | the DM matrix is computed up to star of neighbor ISTAR with the condition that $\text{ABS}(\text{ALOCLEN}(\text{ISTAR}) - \text{ALOCLEN}(\text{ISTAR}-1)) \leq 10^{**(-\text{ABS}(\text{INEIGH}))}$, where $\text{ALOCLEN}(\text{ISTAR})$ means "localization length computed up to star ISTAR" |
| • * | TOLDM | | tolerance in the WnF coefficients used to calculate the DM matrix elements (see CYCTOL) |

FULLBOYS

| rec | variable | value | meaning |
|-----|----------|-------|---|
| • * | ITOLWPG | > 0 | TOLWPG $10^{**(-\text{ITOLWPG})}$ tolerance on the DM matrix elements |

Request of Foster-Boys localization in direct space. The set of WnFs considered in the calculation of the DM matrix (see WANDM) are orthogonally transformed so as to obtain maximally localized WnFs under the Boys criterion. The resulting functions keep both, orthonormality and translational equivalence.

TOLWPG $10^{**(-\text{TOLWPG})}$ tolerance on the DM matrix elements to keep and use it in compact form. A small TOLWPG means that only a few DM matrix elements are considered in the localization process, then the calculation is quite fast and not very demanding in memory. A very large value would bring about very accurate LWFs with high computational cost. Recommended values: 4-6.

Bibliography

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S. F. Boys Rev. Mod. Phys 32 (1960) 296.
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V. Magnasco and A. Perico, J. Chem. Phys. 47 (1967) 971.

MAPNET - coordinates of grid points on a plane

This is a dummy keyword, to explain the way is generated the grid of points in which is evaluated a given function F: charge density and spin density (**ECHG**), electrostatic potential (**CLAS**, **POTM**). The graphic representation of the resulting 2D function is made by external software.

| rec | variable | meaning |
|-----|-----------------|---|
| • * | NPY | number of points on the B-A segment. |
| • | A keyword | enter a keyword to choose the type of coordinate: |
| • | COORDINA | |
| • * | XA,YA,ZA | cartesian coordinates of point A |
| • * | XB,YB,ZB | cartesian coordinates of point B |
| • * | XC,YC,ZC | cartesian coordinates of point C |
| | | or |
| • | ATOMS | |
| • * | IA | <i>label</i> of the atom at point A |
| | AL,AM,AN | indices (direct lattice, input as reals) of the cell where the atom is located |
| • * | IB | <i>label</i> of the atom at point B |
| | BL,BM,BN | indices (direct lattice, input as reals) of the cell where the atom is located |
| • * | IC | <i>label</i> of the atom at point C |
| | CL,CM,CN | indices (direct lattice, input as reals) of the cell where the atom is located |
| | | <i>optional keyword</i> _____ II |
| • | RECTANGU | definition of a new A'B'C'D' rectangular window, with B'C' on BC, A'D' on AD and diagonals A'C'=B'D'=max(AC,BD) (see Fig 9.3) |
| | | <i>optional keyword</i> _____ II |
| • | MARGINS | definition of a new A'',B'',C'',D'' window including ABCD (or A'B'C'D') |
| | | (see Fig 9.4) |
| • * | ABM | margins along AB |
| | CDM | margins along CD |
| | ADM | margins along AD |
| | BCM | margins along BC |
| | | <i>optional keyword</i> _____ II |
| • | PRINT | printing of the values of the function in the net |
| • | ANGSTROM | cartesian coordinates in Ångstrom (default) |
| • | BOHR | cartesian coordinates in bohr |
| • | FRACTION | cartesian coordinates in fractional units |
| • | END | end of MAPNET input block |

- Function F is mapped in a ABCD parallelogram-shaped domain defined by the sides AB and BC of any \widehat{ABC} angle. F is calculated at the $n_{AB} * n_{BC}$ nodes of a commensurate net (n_{AB} and n_{BC} integers).
- If $C \equiv B$, F is calculated along the line AB. Data are written in file RHOLINE.DAT D.
- n_{BC} is set by the program such that all points in the net are as equally spaced as possible ($\delta_{AB} \approx \delta_{BC}$).
- formatted output is written in file fort.25 (processed by Crgra2006; see Appendix D, page 321).
- The position of the three points A, B and C can be specified in two alternative ways:
 - COORDINA** the cartesian coordinates of the three points are given in bohr / Ångstrom / fractional units (default Ångstrom; see Section 2.1, page 33)
 - ATOMS** A,B,C correspond to the position of 3 nuclei, identified by their sequence number in the reference cell, and the crystallographic indices of the cell in which they are located (input as real numbers).

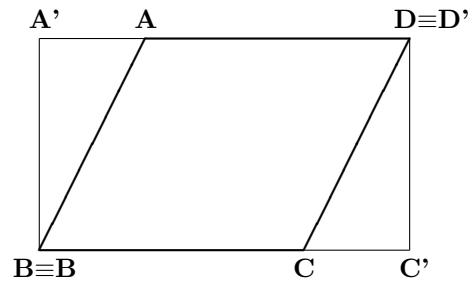


Figure 9.3: Definition of the window where the function F is mapped Effect of optional keyword RECTANGU.

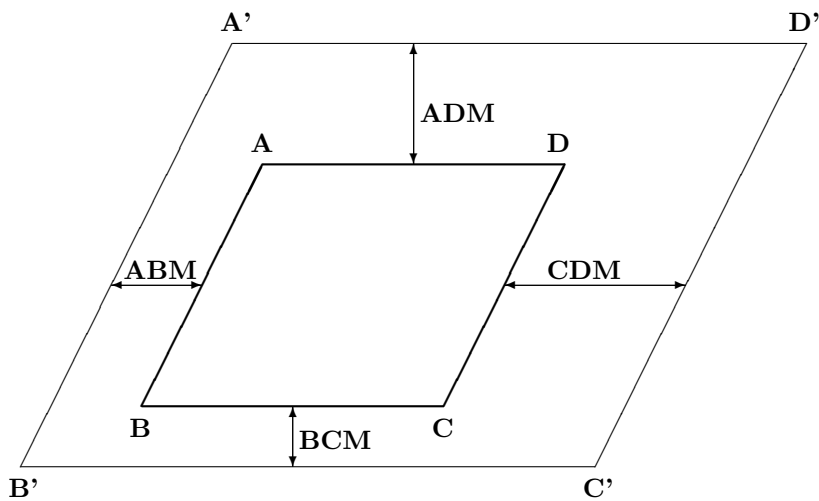


Figure 9.4: Definition of frame around the original window where the function F is mapped. Effect of optional keyword MARGINS.

6. The symmetry is used to restrict the calculation of the function to the irreducible part of the parallelogram chosen. To maximize the use of symmetry, the points of the net should include the low multiplicity positions in the selected plane. For example, $B=(0,0,0)$, $A=(a,0,0)$, $C=(0,b,0)$ (a,b lattice vectors). Choose $NPY=4n+1$ for (100) faces of cubic crystals, or $NPY = 6n+1$ for (0001) faces of hexagonal crystals.

NEIGHBOR/NEIGHPRT

See input block 1, page 56

NEWK - Hamiltonian eigenvectors

| rec | variable | value | meaning | |
|-----|----------|-------|--|----|
| | | | <i>if system is periodic, insert</i> | II |
| • * | IS | | Shrinking factor for reciprocal space net (Monkhorst net). The number NKF of \mathbf{k} points, where the Fock/KS matrix is diagonalized, is roughly proportional to IS^{IDIM}/MVF where IDIM denotes the periodic dimensionality of the system, and MVF denotes the number of point symmetry operators (see page 25). | |
| | ISP | | Shrinking factor of the secondary reciprocal space net (Gilat net) for the evaluation of the Fermi energy and density matrix. | |
| | | | <i>if system is periodic and IS=0, insert</i> | II |
| • * | | | Shrinking factors of reciprocal lattice vectors | |
| | IS1 | | Shrinking factor along B1 | |
| | IS2 | | Shrinking factor along B2 | |
| | IS3 | | Shrinking factor along B3. | |
| • * | IFE | 0 | no Fermi energy calculation is performed; | |
| | | 1 | Fermi energy is computed, by performing integration on the new \mathbf{k} points net. Total, valence and core density matrices are written on Fortran unit 13 | |
| | NPR | | number of printing options to switch on | |
| | | | <i>if NPR \neq 0 insert prtrec (see page 61)</i> | II |

The Fock/KS eigenvectors are computed at a number of \mathbf{k} points in reciprocal space, defined by the shrinking factor IS, and written unformatted in file fort.10 (in the basis of symmetry adapted Bloch functions) and in file fort.8 (in the basis of AO). Eigenvalues and related information (coordinates of \mathbf{k} points in reciprocal lattice, weights etc) are written in file KIBZ.DAT by inserting the keyword **CRYAPI_OUT** (page 205).

1. The Fock/KS matrix in direct space is always the SCF step final one. If the SCF convergence was poor, and convergence tools were used, eigenvalues and eigenvectors may be different from the ones that could be obtained after one more cycle without any convergence trick.
2. The shrinking factors IS and ISP (Section 13.7, page 281) can be redefined with respect to the ones used in the SCF process. If this value is smaller than the one used in the **scf** step, numerical inaccuracy may occur in the Fourier transform of the Fock/KS matrix, $F_g \rightarrow F_k$ (Chapter 13, equation 13.5).
3. A Fermi energy calculation must be performed (IFE=1) to run the Compton profiles option **PROF**, the electron momentum density options **EMDL** and **EMDP**, **PBAN** and **PDIDE** in order to compute the weight associated to each eigenvalue.
4. **Warning** NEWK with IFE=1 must be run to obtain the correct Fermi energy and eigenvalues spectra when a shift of eigenvalues was requested in SCF (**LEVSHIFT**, page 105; **SPINLOCK**, page 114; **BETALOCK**, 80).
A new density matrix is computed. If the convergence of scf was poor, and convergence tools were used (FMIXING, LEVSHIFT, ..), the density matrix obtained from the eigenvectors computed by NEWK may be different from the matrix that could be calculated with one more scf cycle. Properties depending on the density matrix may be different if computed before or after NEWK.
5. if **BAND** is called after **NEWK**, and symmetry adapted Bloch functions are used (default option), the information generated by NEWK is destroyed. For instance, to compute density of states and bands, the sequence must be: BAND - NEWK - DOSS. The sequence NEWK BAND DOSS will give the error message:

NEWK_MUST_BE_CALLED_BEFORE_DOSS

Printing options: 59 (Density matrix - direct lattice); 66 (Hamiltonian eigenvalues); 67 (Hamiltonian eigenvectors).

NOSYMADA

See input block 3, page 108

PARAMPRT - - printing of parametrized dimensions

See input block 1, page ??.

PATO - Density matrix as superposition of atomic densities

| rec | variable | value | meaning |
|--|----------|----------|--|
| • * | IBN | 0 | density matrix computed with the same basis set as in the crystal calculation. |
| | | $\neq 0$ | new basis set and/or new electron configuration is given |
| | NPR | $\neq 0$ | printing of the density matrix for the first NPR direct lattice vectors |
| <i>if IBN $\neq 0$ insert basis set input (page 20)</i> | | | |

1. The **PATO** option is used for calculating crystal properties, such as charge density (**ECHG**), structure factors (**XFAC**) with a periodic density matrix obtained as a superposition of atomic solutions (periodic array of non interacting atoms). The reducible density matrix is written to file fort.13.
2. The atomic wave function is computed by the atomic program [150], using HF hamiltonian, s , p , d orbitals basis set, properly handling the open shell electronic configuration.
3. If the basis set used for the crystalline calculation (given as input of the **integral** part) is not suitable for describing a free- atom or free-ion situation, a new basis set can be supplied (see Section 1.2). When this option is used (IBN.NE.0) the basis set of *all* the atoms with different conventional atomic number has to be provided.
4. The electronic configuration of selected atoms may be modified (**CHEMOD** in basis set input). This allows calculation of the density matrix as superposition of atomic densities or ionic densities, for the same crystal structure.
5. The wave function data stored in file fort.9 at the end of the SCF cycles are not modified. Only the data stored on the temporary data set (reducible density matrix in fortran unit 13 and overlap matrix in fortran unit 3) are modified. The keyword **PSCF** restores the scf density matrix and all the original information (including geometry and basis set).
6. See also **ATOMHF**, input block 3, page 79, and **CHARGED**, input block 2, page 69.

PBAN/PDIBAN - Band(s) projected density matrix

| rec | variable | meaning |
|-----|-------------|--|
| • * | NB | number of bands to consider. |
| | NPR | printing of the density matrix for the first NPR direct lattice cells. |
| • * | N(I),I=1,NB | sequence number of the bands summed up for the projected density matrix. |

A density matrix projected onto a given range of bands is computed and stored in fortran unit 13. The properties will subsequently be computed using such a matrix.

For spin polarized systems, two records are written:

first record, total density matrix ($N=n_\alpha + n_\beta$ electrons);

second record, spin density matrix ($Ns=n_\alpha - n_\beta$ electrons).

To be combined *only* with **ECHG** and **PPAN**. Fock/Kohn-Sham eigenvectors and band weights must be precomputed by running **NEWK** and setting IFE=1.

PGEOMW - Density matrix from geometrical weights

A density matrix projected onto the range of bands defined in input (see **PBAN** input instructions) is computed, using the geometrical weights of the **k** points in the reciprocal lattice. The properties will subsequently be computed using such a matrix. All the bands are attributed an occupation number 1., independently of the position of the Fermi energy. The density matrix does not have any physical meaning, but the trick allows analysis of the virtual eigenvectors. For spin polarized systems, two records are written:

first record, total density matrix ($N=n_\alpha + n_\beta$ electrons);
second record, spin density matrix ($Ns=n_\alpha - n_\beta$ electrons).

To be combined *only* with **ECHG** and **PPAN**.

Fock/Kohn-Sham eigenvectors and band weights must be computed by running **NEWK** and setting IFE=1. Symmetry adaptation of Bloch functions is not allowed, the keyword NOSY-MADA must be inserted before NEWK.

PDIDE - Density matrix energy projected

| rec | variable | meaning |
|-----|----------|--|
| • * | EMI,EMAX | lower and upper energy bound (hartree) |

A density matrix projected onto a given energy range is computed and stored in file fort.13. The properties will subsequently be computed using such a matrix. To be combined *only* with **DOSS**, **ECHG** and **PPAN**. Fock/Kohn-Sham eigenvectors and band weights must be computed by running **NEWK** and setting IFE=1.

The charge density maps obtained from the density matrix projected onto a given energy range give the STM topography [110] within the Tersoff-Haman approximation [173].

PMP2 - Reads the MP2 correction to the Valence Density Matrix

1. The MP2 correction to the Valence Density Matrix, as computed by the CRYSCOR program, is read from the external unformatted file fort.63, which has to be provided by the user.
2. The **PMP2** keyword must be preceded by **NEWK** (with IFE=1) since the Fermi energy has to be computed in order to split the total SCF DM into core and valence density matrices. The MP2 correction to the DM is summed to the valence SCF DM.
3. By default the PROPERTIES program adopts the SCF density matrix (DM) but if one adds the **PMP2** keyword in the input file then any property whose corresponding keyword is inserted after **PMP2** is computed using the HF+MP2 density matrix.
4. For instance, in order to evaluate the MP2 correction to the X-rays Structure Factors F_{hkl} , the following sequence of keywords has to be used: **NEWK-XFAC-PMP2-XFAC-END**; in the output file will be printed the HF F_{hkl} followed by the HF+MP2 F_{hkl} .

We report in the following the list of the properties for which the MP2 correction can be evaluated, along with some advices one has to take in mind:

- *Directional Compton Profiles* (**PROF**) The ICORE variable must be 1 or 3 and the IVIA variable must be 1
- *Auto-correlation Function and Compton Profiles* (**BIDIARD**) The ICASO variable must be 1 or 3
- *Electron Momentum Density* (**EMDLDM** and **EMDPDM**) The ICASO variable must be 1 or 3
- *Electron Charge Density* (**ECHG**)
- *Mulliken's Populations* (**PPAN**)
- *Structure Factors* (**XFAC**)

POLI - Spherical harmonics multipole moments

| rec | variable | value | meaning |
|-----|----------|----------|---|
| • * | IDIPO | | multipole order (maximum order $\ell=6$) |
| * | ITENS | 1 | the quadrupole cartesian tensor is diagonalized |
| | | 0 | no action |
| | LPR68 | | maximum pole order for printing: |
| | | < 0 | atom multipoles up to pole IDIPO |
| | | ≥ 0 | atom and shell multipoles up to pole IDIPO |

The multipoles of the shells and atoms in the primitive cell are computed according to a Mulliken partition of the charge density, up to quantum number IDIPO ($0 \leq \text{IDIPO} \leq 6$). The first nine terms, corresponding to $\ell=0,1,2$ (for the definition of higher terms, see Appendix A1, page 170 in reference [142]) are defined as follow:

| | | |
|--------|----|-------------------------|
| ℓ | m | |
| 0 | 0 | s |
| 1 | 0 | z |
| 1 | 1 | x |
| 1 | -1 | y |
| 2 | 0 | $z^2 - x^2/2 - y^2/2$ |
| 2 | 1 | $3xz$ |
| 2 | -1 | $3yz$ |
| 2 | 2 | $3(x^2 - y^2)$ |
| 2 | -2 | $6xy$ |
| 3 | 0 | $(2z^2 - 3x^2 - 3y^2)z$ |
| 3 | 1 | $(4z^2 - x^2 - y^2)x$ |
| 3 | -1 | $(4z^2 - x^2 - y^2)y$ |
| 3 | 2 | $(x^2 - y^2)z$ |
| 3 | -2 | xyz |
| 3 | 3 | $(x^2 - 3y^2)x$ |
| 3 | -3 | $(3x^2 - y^2)y$ |

If ITENS=1, the cartesian quadrupole tensor is computed, and its eigenvalues and eigenvectors are printed after diagonalization. The components of the cartesian tensor are: $x^2, y^2, z^2, xy, xz, yz$

Warning: the shell multipoles are *not* printed by default. On request (keyword **POLIPRT**), they are printed in atomic units (electron charge = +1).

POLSPIN - Spin multipole moments

| rec | variable | value | meaning |
|-----|----------|----------|---|
| • * | IDIPO | | multipole order (maximum order $\ell=6$) |
| * | ITENS | 1 | the quadrupole cartesian tensor is diagonalized |
| | | 0 | no action |
| | LPR68 | | maximum pole order for printing: |
| | | < 0 | atom multipoles up to pole IDIPO |
| | | ≥ 0 | atom and shell multipoles up to pole IDIPO |

The electron spin density is partitioned in atomic contributions according to the Mulliken scheme, and the spherical harmonic atomic multipoles up to the IDIPO angular quantum number are evaluated (see the **POLI** keyword for definition of the multipoles and references). The Cartesian tensor $T_{ij} = \int x_i x_j \rho^{spin}(\mathbf{r}) d\mathbf{r}$ is computed and diagonalized, and its eigenvalues and eigenvectors are printed. This option may be useful in the analysis of the size, shape and orientation of localized electron holes.

POT3 - Electrostatic potential on a 3D grid

| rec | variable | meaning |
|-----|----------|---|
| • * | NP | Number of points along the first direction |
| • * | ITOL | penetration tolerance (suggested value: 5) (see POTM , page 234) |

if non-3D system

keyword to choose the type of grid on the non-periodic direction(s):

| SCALE | RANGE |
|---|---|
| length scales for non-periodic dimensions | boundary for non-periodic dimensions (au) |
| <i>if 2D system</i> | |
| • * ZSCALE | • * ZMIN • * ZMAX |
| <i>if 1D system</i> | |
| • * YSCALE,ZSCALE | • * YMIN,ZMIN • * YMAX,ZMAX |
| <i>if 0D system</i> | |
| • * XSCALE,YSCALE,ZSCALE | • * XMIN,YMIN,ZMIN • * XMAX,YMAX,ZMAX |

The electrostatic potential is computed at a regular 3-dimensional grid of points. The grid is defined by the lattice vectors of the primitive unit cell and user defined extents in non-periodic directions. NP is the number of points along the first lattice vector (or XMAX-XMIN for a molecule). Equally spacing is used along the other vectors. Non-periodic extents may be specified as an explicit range (RANGE) or by scaling the extent defined by the atomic coordinates (SCALE).

Formatted data are written in fortran unit 31 (function value at the grid points), in the format required by the visualization program DLV.

See Appendix D, page 327, for description of the format.

Function data computed at 3D grid points are written according to GAUSSIAN CUBE format in file POT_CUBE.DAT

POTC - Electrostatic potential and its derivatives

| rec | variable | meaning |
|--|----------|--|
| • * | ICA | 0 calculation of potential (V), its first derivative (E) and second derivatives (E') in one or more points 1 not implemented 2 calculation of $V(z)$, $E(z)$, $E'(z)$ and $\rho(z)$ averaged in the plane at z position (2D only) 3 calculation of $V(z)$, $E(z)$, $E'(z)$ and $\rho(z)$ averaged in the volume between $z-ZD$ and $z+ZD$ (2D only) |
| | NPU | n number of points at which these properties are computed 0 these properties are computed at the atomic positions defined by IPA value |
| | IPA | 0 calculations are performed at each atomic positions in the cell 1 calculations are performed just for non equivalent atomic positions in the cell |
| _____ if ICA = 0 then _____ | | |
| _____ if NPU > 0 insert NPU records _____ II | | |
| • * | X,Y,Z | point coordinates (cartesian, bohr) _____ if NPU < 0 data are read from file POTC.INP _____ II _____ if ICA = 2 insert _____ II |
| • * | ZM,ZP | properties are averaged over NPU planes orthogonal to the z axis from $z = ZP$ to $z = ZM$ by step of $(ZP-ZM)/(NPU-1)$ (bohr) _____ if ICA = 3 insert _____ II |
| • * | ZM,ZP | properties are averaged over NPU volumes centered on planes orthogonal to the z axis, same as ICA = 2 |
| | ZD | half thickness of the volume (bohr) |

The exact electrostatic potential V , its derivatives E (electric field) and E' (electric field gradient) are evaluated for molecules (0D), slabs (2D) and crystals (3D). Plane and volume averaged properties can be computed for slabs (2D) only. The plane is orthogonal to the z axis.

For ICA = 3, the volume average is performed around a middle plane at z position, from $z-ZD$ to $z+ZD$, giving a thickness of $2*ZD$.

According to Poisson's law, the charge density $\rho(z)$ is defined as

$$\rho(z) = -\frac{1}{4\pi} \frac{d^2V(z)}{dz^2} = \frac{-E'(z)}{4\pi}$$

If an electric field of intensity E_0 is present (keyword **FIELD**, see page 2.1, only for slabs), the total potential $V_{field}(z)$ is calculated:

$$V_{field}(z) = V(z) - E_0z$$

where $V(z)$ is the potential of the slab itself and $-E_0z$ is the perturbation applied.

- ICA = 0 ; NPU > 0; 2D or 3D system

It is possible to enter the cartesian coordinates (bohr) of the points where the exact value of the properties must be computed. It is useful when applying fitting procedure to obtain formal point charges.

- ICA = 0 ; NPU < 0; 2D or 3D system

coordinates in bohr are read (free format) from file POTC.INP

| record | type of data | content |
|----------|--------------|---------------------|
| 1 | 1 integer | N, number of points |
| 2..2+N-1 | 4 real | x y z |

- ICA ≠ 0; NPU ≠ 0; 2D or 3D system

The data computed are written in file POTC.DAT. See Appendix D, page 324.

POTM - Electrostatic potential maps and electric field

| rec | variable | value | meaning |
|---|----------|-------|---|
| • * | IDER | 0 | the electrostatic potential is evaluated |
| | | 1 | the potential and its first derivatives are evaluated |
| | ITOL | | penetration tolerance (suggested value: 5) |
| insert MAPNET input records (page 226) | | | |

1. When IDER=0, the electrostatic potential is calculated at the nodes of a 2-dimensional net in a parallelogram-shaped domain defined by the segments AB and BC (see keyword **MAPNET**, page 226). The electrostatic potential values are written formatted in file fort.25 (see Appendix D, page 321).
2. When IDER \neq 0, the electrostatic potential gradient is computed at the nodes of the same grid. The x, y and z components are printed in the standard output, and written formatted in file fort.25 (see Appendix D, page 321).
3. The electrostatic potential at \mathbf{r} is evaluated [159] by partitioning the periodic charge density $\rho(r)$ in shell contributions ρ_λ^h :

$$\rho(\underline{r}) = \sum_h \sum_\lambda \rho_\lambda(\underline{r} - \underline{h})$$

(\underline{h} translation vector).

4. The long range contributions are evaluated through a multipolar expansion of $\rho_\lambda(\underline{r} - \underline{h})$ [158]. The short range contributions are calculated exactly.
5. The separation between long and short range is controlled by ITOL: $\rho_\lambda(\mathbf{r} - \mathbf{h})$ is attributed to the short range (exact) region if

$$e^{-\alpha_\lambda(\mathbf{r} - \mathbf{s}_\lambda - \mathbf{h})^2} > 10^{-ITOL}$$

where: α_λ = exponent of the adjoined gaussian of shell λ ; \mathbf{s}_λ = internal coordinates of shell λ in cell at \mathbf{h} .

The difference between the exact and the approximated potential is smaller than 1% when ITOL=5 (input datum to **POTM**), and IDIPO=4 (input datum to **POLI**), and smaller than 0.01% when ITOL=15 and IDIPO=6 [159, 158].

6. The multipoles of shell charges are computed if **POLI** option was not run before **POTM**.

PPAN/MULPOPAN - Mulliken Population Analysis

See input block 3, page 109.

PRINTOUT - Setting of printing environment

See input block 1, page 59.

PROF - Compton Profiles

| rec | variable | value | meaning |
|------|-----------------------------|-------|--|
| • * | ICORE | 1 | core plus valence calculation. |
| | | 2 | core only calculation. |
| | | 3 | valence only calculation. |
| | IVIA | 0 | valence contribution is computed by numerical integration. |
| | | 1 | valence contribution is computed analytically. |
| | NPR | | number of printing options to switch on. |
| | IPLO | 0 | CP related data are not stored on disk |
| | | 1 | formatted CP data stored in file fort.25 (Appendix D, page 323) |
| | | 2 | formatted CP data stored in Fortran unit 24 (Appendix D, page 323) |
| | | | <i>if NPR ≠ 0 insert prtrec (see page 61)</i> _____II |
| • A2 | CP | | calculation of Compton profiles (J(q)) along selected directions (eq. 13.26). |
| • * | ND | | number of directions (≤ 6). |
| | REST | | maximum value of q for J(q) calculation (bohr ⁻¹). |
| | RINT | | internal sphere radius (bohr ⁻¹). |
| | IRAP | | shrinking factor ratio. |
| • * | (KD(J,N), J=1,3), N=1,ND | | directions in oblique coordinates; see note 9 |
| • * | STPJ | | interpolation step (in interpolated Compton profiles calculation). |
| • A4 | DIFF | | CP difference between all computed directional CPs. |
| • A2 | BR | | auto-correlation function B(r) calculation. |
| • * | RMAX | | maximum r value (bohr) at which B(r) is computed |
| | STBR | | step in computation of B(r). |
| • A4 | CONV | | convolution of the data previously computed (CP, DIFF, BR) |
| • * | FWHM | | convolution parameter (a.u.) full width half maximum; $\sigma = \sqrt{(FWHM)^2 / (8 \cdot 2 \log 2)}$. |
| • A4 | ENDP | | End of input records for CP data |

The keyword **PROF** starts the calculation of Compton profiles (J(q)) along selected directions (eq. 13.26). The specific keywords **DIFF BR CONV** allow the calculation of the related quantities. The card with the keyword **ENDP** ends the Compton profiles input section.

1. The input of the options must be given in the order in which they appear in the above description. To enter this property, the **CP** option must always be selected after **PROF**, while the others are optional.
2. Core and valence contributions are computed by using different algorithms. Core contribution to CP's is always computed analytically via the Pg matrix (direct lattice summation); the valence contribution is computed numerically (IVIA=0) by integrating the EMD. Valence contribution can be evaluated analytically, setting IVIA=1.
3. The numerical integration is extended to a sphere (radius RINT) where EMD is sampled at the points of a commensurate net characterized by a shrinking factor IS (in the IBZ) and at all the points (with modulus less than RINT) obtained from these by applying reciprocal lattice translations.

It is possible to define a second sphere (with radius REST); in the volume between the two spheres a second net is employed with shrinking factor IS1 greater than IS. IRAP=IS1/IS is given in INPUT card 2; a reasonable value is IRAP=2. The outer contribution is supposed to be the same for different CP's, and is obtained by integrating the average EMD.

4. If ICORE \neq 2 (valence electron CP's are required) the **NEWK** option, with IFE=1,

must be run before the **PROF** option, in order to generate the eigenvectors required for the EMD calculation, as well as the weights associated with each k point.

5. If $ICORE \neq 2$ and $IVIA = 0$ the CPs are evaluated at points resulting from the IS partition of the reciprocal lattice translators. The interpolation is performed at STPJ intervals (STPJ is given in input).

If $ICORE = 2$ or $IVIA = 1$ the CPs are, in any case, evaluated at points resulting from STPJ intervals.

IVIA=0 (numerical integration) produces much more accurate results;

IVIA=1 (analytical integration) is to be used only for molecular calculations or for non conducting polymers.

6. Total CP's are always obtained by summing core and valence contributions.
7. Reasonable values of the integration parameters depend on the system under investigation. The normalization integral of the CP's is a good check of the accuracy of the calculation. For instance, in the case of the valence electron of beryllium (test 9), good values of RINT and IS are 10. a.u. and 4 respectively. In the case of silicon (test 10), good values of the same variables are 8. a.u. and 8 respectively. Much greater RINT values are required in order to include all the core electrons (70. a.u. in the case of silicon, and 25. a.u. in the case of beryllium).
8. BR (auto-correlation function or reciprocal space form factor) should be calculated only for valence electrons. All electron BR are reliable when the normalization integral, after the analytical integration for core electrons contribution, is equal to the number of core electrons.
9. The oblique coordinates directions given in input refer to the conventional cell, *not* to the primitive cell for 3D systems.

Example: in a FCC system the input directions refer to the orthogonal unit cell frame (sides of the cube) not to the primitive non-orthogonal unit cell frame.

Printing options: 116 (Compton profiles before interpolation); 117 (average EMD before interpolation); 118 (printing of core, valence etc. contribution). The LPRINT(118) option should be used only if $ICORE=1$, that is, if core plus valence calculation are chosen.

PSCF - Restore SCF density matrix

The wave function data computed at the last SCF cycle are restored in common areas and fortran units 3 (overlap matrix), 11 (Fock/KS matrix), 13 (density matrix). The basis set defined in input block 2 is restored. Any modification in the default settings introduced in *properties* is overwritten. No input data required.

RAYCOV - covalent radii modification

See input block 1, page 59

ROTREF - Rotation of eigenvectors and density matrix

This option permits the rotation of the cartesian reference frame before the calculation of the properties.

It is useful, for example, in the population analysis or in the AO projected density of states of systems containing transition metal atoms with partial d occupation.

Consider for example a d^7 occupation as in CoF_2 , where the main axis of the (slightly distorted) CoF_6 octahedron in the rutile structure makes a 45° angle with the x axis, and lies in the xy plane, so that the three empty β states are a combination of the 5 d orbitals. Re-orienting the octahedron permits to assign integer β occupations to d_{xz} and d_{yz} .

Input for the rotation as for **EIGSHROT** (page 94)

SETINF - Setting of INF values

See input block 1, page 61

SETPRINT - Setting of printing options

See input block 1, page 61.

STOP

Execution stops immediately. Subsequent input records are not processed.

SYMADAPT

See input block 3, page 114

XFAC - X-ray structure factors

The Fourier transform of the *static* ground state charge density $\rho(\mathbf{r})$ of a crystalline system provides the set of *static* structure factors $\{F_{hkl}\}$ of the crystal, which can be determined experimentally, after taking into account a number of corrective terms, in particular those related to thermal and zero point motion of nuclei (*vide infra*):

$$F_{hkl} = \int d\mathbf{r} \rho(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \quad \text{with} \quad \mathbf{k} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3 ,$$

where \mathbf{b}_1 , \mathbf{b}_2 and \mathbf{b}_3 are the fundamental reciprocal lattice vectors and h, k, l are Miller's indices. The electron charge density is a function that exhibits translational invariance so that we can consider its expression just in the reference cell $\rho_{cell}(\mathbf{r})$. Let us introduce an, to some extent arbitrary, approximation: the partition of $\rho_{cell}(\mathbf{r})$ into *atomic* contributions, based on some criteria:

$$\rho_{cell}(\mathbf{r}) = \sum_{A \in cell} \rho_A(\mathbf{r} - \mathbf{r}_A)$$

where \mathbf{r}_A is the equilibrium position of atom A in the cell. Within such an approximation the expression of the *static* structure factors simply becomes:

$$F_{hkl} = \sum_{A \in cell} f_A(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}_A} \quad \text{with} \quad f_A(\mathbf{k}) = \int d\mathbf{r} \rho_A(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}}$$

A simple way for introducing the effect of thermal nuclear motion in the above expression is represented by the so-called *atomic* Debye-Waller factors $DW_A(\mathbf{k})$:

$$\tilde{F}_{hkl} = \sum_{A \in cell} f_A(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}_A} \times e^{-DW_A(\mathbf{k})}$$

where the symbol \tilde{F}_{hkl} represents *dynamic* structure factors and where, if one assumes a harmonic anisotropic potential acting over the atoms and a Gaussian probability of finding an atom displaced by its equilibrium position, the Debye-Waller factors can be expressed as

$$DW_A(\mathbf{k}) = \frac{1}{2} \langle \mathbf{k} | \mathbf{U}_A | \mathbf{k} \rangle$$

where \mathbf{U}_A is the mean square displacement tensor (that depends upon temperature):

$$\mathbf{U}_A = \begin{bmatrix} \langle x_1^2 \rangle & \langle x_1 x_2 \rangle & \langle x_1 x_3 \rangle \\ \langle x_2 x_1 \rangle & \langle x_2^2 \rangle & \langle x_2 x_3 \rangle \\ \langle x_3 x_1 \rangle & \langle x_3 x_2 \rangle & \langle x_3^2 \rangle \end{bmatrix}$$

with x_i components of the displacement of atom A with respect to its equilibrium position. The above tensor and its eigenvalues are sometimes referred to as *anisotropic displacement parameters* (ADP).

Users of this option for the calculation of dynamical structure factors are kindly requested to cite the following paper [62]:

A. Erba, M. Ferrabone, R. Orlando and R. Dovesi, *J. Comput. Chem.*, **34**, 346 (2013). *Accurate dynamical structure factors from ab initio lattice dynamics: The case of crystalline silicon.*

| rec | variable | value | meaning |
|---|----------|-------|---|
| • * | ISS | > 0 | number of reflections whose theoretical structure factors are calculated. |
| | | < 0 | a set of non-equivalent reflections with indices $h,k,l < ISS $ is generated |
| | PC | 0 | Miller's indices h,k,l refer to the <i>primitive</i> cell |
| | | 1 | Miller's indices h,k,l refer to the <i>conventional</i> cell (if any) |
| <i>if ISS > 0 insert ISS records</i> | | | |
| • * | H,K,L | | Miller's indices h,k,l of the reflections |
| • | A2DW | | Debye-Waller atomic factors $DW_A(\mathbf{k})$ are computed to obtain dynamic structure factors. Anisotropic displacement parameters (ADP) for a given temperature are read from the external unit ADP.DAT where they are inserted as tensors |
| • * | UNITS | 0 | The ADP in the unit are given in atomic units (bohr ²) |
| | | 1 | The ADP in the unit are given in 10^{-4} \AA^2 |
| | | 2 | The ADP in the unit are given in \AA^2 |
| | DWPRT | 0 | Debye-Waller atomic factors are not printed |
| | | 1 | Debye-Waller atomic factors are printed |
| • | A2END | | End of the block of instructions of XFAC |

Note: if dynamic structure factors are computed for a given temperature T , the corresponding ADPs have to be provided via the external formatted unit ADP.DAT. Such unit has to be put in the scratch directory where the PROPERTIES program is executed. If the standard script `runprop09` is used, then such unit can be renamed *inputfilename.adp* and put in the same directory where the input file *inputfilename.d3* is.

The structure of the ADP.DAT unit is as follows (this example refers to the crystal of silicon):

```

298.1500
1
0.017717  0.000000  0.000000
0.000000  0.017717  0.000000
0.000000  0.000000  0.017717
2
0.017717  0.000000  0.000000
0.000000  0.017717  0.000000
0.000000  0.000000  0.017717

```

where the first entry is the temperature (in Kelvin) at which the ADPs have been measured/computed. After that, a list of the ADP tensors is given for all the atoms in the cell. In the example above there are just two atoms per cell and their ADP tensors are equal and diagonal.

9.3 Spontaneous polarization

The ferroelectric phases of a ferroelectric material exhibit two possible enantiomorphic non centrosymmetric structures, which can be labelled by the geometric parameters $\lambda=+1$ and $\lambda=-1$. An external electric field can force the system to change from one structure to the other, passing through a small energy maximum. The centrosymmetric unstable structure which sits in the middle of the $\lambda=+1$ and $\lambda=-1$ structures can be labelled by the geometric parameters $\lambda=0$.

The spontaneous polarization in ferroelectric materials is then evaluated through either a Berry phase approach [149, 39] or a localized Wannier functions approach, as the polarization difference between one of the two enantiomorphic structures ($\lambda=+1$ or $\lambda=-1$) and the intermediate geometric structure ($\lambda=0$).

Three subsequent runs are required.

1. First run: preliminary calculation related to $\lambda=0$ structure
2. Second run: preliminary calculation related to $\lambda=+1$ (or $\lambda=-1$) structure
3. Third run: merging of previous data

Some comments:

1. The unit-cell has to contain an even number of electrons.
2. Cell parameters have to be the same for whatever value of the geometric parameter λ . The difference between the $\lambda=+1$, $\lambda=0$, and $\lambda=-1$ structures is only in the atomic positions.
3. Numerical accuracy and computational parameters in input block 3 (such as **TOLINTEG**, **POLEORDR**, etc.) should be the same for the first and the second run.
4. See page 228 for the **NEWK** input, which has to be the same for the first and the second run. The shrinking factor **IS** should be at least equal to 4. Fermi energy calculation is not necessary, then set **IFE=0**.
5. Data evaluated with the keywords **POLARI** or **LOCALI** in the first two runs do not have any physical meaning if considered independently. Only the output produced choosing the keywords **SPOLBP** or **SPOLWF** in the third run is significant.
6. When the $\lambda=-1$ geometric structure is chosen in the second run, the spontaneous polarization vector obtained at the end will have the same modulus and direction but opposite versus with respect to the vector obtained by choosing the $\lambda=+1$ structure.
7. The spontaneous polarization is obtained through either the Berry phase approach or the localized Wannier functions approach. Since a phase is defined only in the interval $-\pi$ to $+\pi$, each component of the spontaneous polarization vector is defined to within an integer number (positive or negative) of the correspondent component of the "quantum of polarization" vector, which is automatically shown in the output of the third run. Usually there is not need to take into account the quantum of polarization vector, unless the ferroelectric material shows a large value of the spontaneous polarization. In case of doubt whether the quantum of polarization vector has to be considered or not, it is possible to evaluate the spontaneous polarization by setting in the second run a geometric structure corresponding to an intermediate geometric parameter, e.g. $\lambda=0.25$, and then to extrapolate linearly the result to the $\lambda=1$ structure.

Deck 1**Potassium niobate - KNbO₃**

| | |
|----------------|--|
| CRYSTAL | 3D system |
| 0 0 0 | IFLAG IFHR IFSO |
| 123 | space group, $P4/mmm$ |
| 3.997 4.063 | lattice parameters |
| 4 | 4 non equivalent atoms (5 atoms in the primitive cell) |
| 19 0.5 0.5 0.5 | Z=19, Potassium; x, y, z (multiplicity 1) |
| 8 0.0 0.0 0.5 | Z=8, Oxygen I; x, y, z (multiplicity 1) |
| 8 0.5 0.0 0.0 | Z=8, Oxygen II; x, y, z (multiplicity 2) |
| 41 0.0 0.0 0.0 | Z=41, Niobium; x, y, z (multiplicity 1) |
| END | end of geometry input records |

Deck 2**Potassium niobate - KNbO₃**

| | |
|------------------|--|
| CRYSTAL | 3D system |
| 0 0 0 | IFLAG IFHR IFSO |
| 123 | space group, $P4/mmm$ |
| 3.997 4.063 | lattice parameters |
| 4 | 4 non equivalent atoms (5 atoms in the primitive cell) |
| 19 0.5 0.5 0.5 | Z=19, Potassium; x, y, z (multiplicity 1) |
| 8 0.0 0.0 0.5 | Z=8, Oxygen I; x, y, z (multiplicity 1) |
| 8 0.5 0.0 0.0 | Z=8, Oxygen II; x, y, z (multiplicity 2) |
| 41 0.0 0.0 0.0 | Z=41, Niobium; x, y, z (multiplicity 1) |
| FRACTION | fractional coordinates |
| ATOMDISP | displacement of atoms |
| 4 | four atoms to be displaced |
| 1 0.0 0.0 -0.023 | displacement of atom no. 1 (Potassium) |
| 2 0.0 0.0 -0.042 | displacement of atom no. 2 (Oxygen II) |
| 3 0.0 0.0 -0.042 | displacement of atom no. 3 (Oxygen II) |
| 4 0.0 0.0 -0.040 | displacement of atom no. 4 (Oxygen I) |
| END | end of geometry input records |

SPOLBP - Spontaneous polarization (Berry phase approach)

To calculate the spontaneous polarization, a preliminary with the keyword POLARI run is needed for each of the two systems $\lambda = 1$ and $\lambda = 0$. Then a third run with the keyword **SPOLBP** gives the difference of polarization between both systems.

1. First run: preliminary calculation related to system $\lambda = 0$

| Program | Keyword | comments |
|----------------------------------|---------|--------------------------------------|
| crystal | | see deck 1 for input blocks 1 and 1b |
| properties | NEWK | additional keywords allowed |
| | POLARI | see above |
| save Fortran unit 27 as sys0.f27 | | |

2. Second run: preliminary calculation related to system $\lambda = 1$

| Program | Keyword | comments |
|----------------------------------|---------|--------------------------------------|
| crystal | | see deck 2 for input blocks 1 and 1b |
| properties | NEWK | same input as in first run |
| | POLARI | |
| save Fortran unit 27 as sys1.f27 | | |

3. Third run: merging of previous data.

| | | |
|----------------------------------|---------------|----------|
| copy sys0.f27 to Fortran unit 28 | | |
| copy sys1.f27 to Fortran unit 29 | | |
| Program | Keyword | comments |
| properties | SPOLBP | |

SPOLWF - The spontaneous polarization (localized CO approach)

To calculate the spontaneous polarization, two preliminary runs with the keyword **LOCALI** is needed for each of the two systems $\lambda = 1$ and $\lambda = 0$. Then a third run with the keyword **SPOLWF** computes the difference of polarization between both systems.

1. First run: preliminary calculation related to system $\lambda = 0$

| | | |
|----------------------------------|---------|--------------------------------------|
| Program | Keyword | comments |
| crystal | | see deck 1 for input blocks 1 and 1b |
| properties | NEWK | additional keywords allowed |
| | LOCALI | see above |
| save Fortran unit 37 as sys0.f37 | | |

2. Second run: preliminary calculation related to system $\lambda = 1$

| | | |
|----------------------------------|---------|--------------------------------------|
| Program | Keyword | comments |
| crystal | | see deck 2 for input blocks 1 and 1b |
| properties | NEWK | same input as in first run |
| | LOCALI | |
| save Fortran unit 37 as sys1.f37 | | |

3. Third run: merging of previous data.

| | | |
|----------------------------------|---------------|----------|
| copy sys0.f37 to Fortran unit 38 | | |
| copy sys1.f37 to Fortran unit 39 | | |
| Program | Keyword | comments |
| properties | SPOLWF | |

9.4 Mössbauer Spectroscopy

A nuclear spin transition can be promoted when a γ photon, originated from a nuclear spin relaxation, interacts with a chemical equivalent nucleus. The resonant condition are satisfied if the crystal lattice can conveniently absorb the recoil energy. This transition, that in the case of ^{57}Fe occurs between $I_{1/2} \rightarrow I_{3/2}$ and involves an energy of 14.4 keV, can be accompanied by at least two effects resulting in a sensitive shift of the energy levels:

- the isotropic effect and
- the anisotropic or quadrupolar interaction.

The code is capable of calculating the electron density and the eigenvalues of the 3x3 matrix of the electric field gradient, at the nuclei. These particular quantities can be related to experimental observable, as shown in the following subsections, and can provide a deeper insight into the chemical-physical environment surrounding the resonant nucleus. For a better

comprehension of the Mossbauer effect and its exploitation in the characterization of solid state materials, please refer to literature[120, 166, 66, 73].

Isotropic effect (IS)

The energy associated to a nuclear spin transition, ΔE_γ , is directly proportional to the total electron density $\rho(\mathbf{r})$ and this means than nuclei subjected to a different field due to their chemical surrounding, absorb at a slightly different frequency. Experimentally what is observed is the shift δ , expressed in terms of the Doppler velocity (mm/s) needed to achieve the resonance absorption between the source S (i.e. the nucleus which emits the γ -ray) and the absorber A (i.e. the nucleus which undergoes the spin transition):

$$\delta = \frac{c}{E_\gamma} (\Delta E_\gamma^A - \Delta E_\gamma^S) \quad (9.18)$$

where c is the light velocity and E_γ the energy of the γ ray. Exploiting the proportionality between ΔE_γ and $\rho(\mathbf{r})$, it is possible to state that:

$$\delta = A[\rho_e^A(0) - \rho_e^S(0)] \quad (9.19)$$

where the constant A groups a certain number of terms (relativist effects among the others) for a given isotope. Since all components in equation 9.19 are constant for a given isotope but the electron density of the absorber, it is sufficient to consider the simplified equation:

$$\delta = a[\rho_e^A(0) - b] \quad (9.20)$$

with a and b to be determined in a calibration procedure in which the calculated electron density at a given nucleus is plotted versus the experimentally determined isotopic shift (IS) δ , for a series of compounds containing that nucleus. Once the a and b parameters, for a series of omogeneous compounds (i.e. organic, organo-metallic, inorganic,..) of a given nucleus, have been calculated can be used to infer the chemical shift of such nucleus in systems for which the experimental data are unknown or ambiguous[189, 181].

Anisotropic effect

If the nucleus possess a quadrupolar tensor, Q , the first excited nuclear spin state splits into two double degenerated and equally probable spin states, characterized by the energies $E_{3/2} \pm E_{\text{QI}}$, where the quadrupolar interaction (QI) is of the form:

$$E_{\text{QI}} = -e^2 \frac{1}{6} \sum_{i,j=1,3} V_{ij} Q_{ij} = V \cdot Q \quad (9.21)$$

the Q tensor, representing the deviation of the nuclear charge from the ideal spherical shape, is almost a constant for a given nucleus and can be obtained experimentally. The 3x3 V matrix contains the electric field gradients at the nucleus and can be diagonalize to obtain the eigenvalues $V_{\text{AA}}, V_{\text{BB}}$ and V_{CC} and the asymmetric parameter:

$$\eta = \frac{V_{\text{BB}} - V_{\text{AA}}}{V_{\text{CC}}} \quad (9.22)$$

being always $|V_{\text{CC}}| \geq |V_{\text{BB}}| \geq |V_{\text{AA}}|$. Experimentally a doublet is observed, corresponding to the transitions from the ground state ($I = 1/2$) towards the two excited states and the difference between the two peaks can be directly related to η and V_{CC} :

$$\begin{aligned} \Delta E_{\text{QI}} &= E_{[3/2, \text{QI}]} - E_{[3/2, -\text{QI}]} = E_{3/2} + E_{\text{QI}} - E_{3/2} + E_{\text{QI}} = \\ &= 2E_{\text{QI}} = \frac{1}{2} e Q V_{\text{CC}} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \end{aligned} \quad (9.23)$$

where Q is generally expressed in *barn* ($1 \text{ barn} = 10^{-28} \text{ m}^2$). Equation 9.23 can be used in two ways: (i) if the quadrupolar moment, Q , is known the value of ΔE_{QI} can be estimated; (ii) if ΔE_{QI} is given then Q can be derived.

9.4.1 Input and Output

By mean of the following input (see page 214 for the *ISOTROPIC* keyword and page 233 for the *POTC* one):

```
ISOTROPIC
UNIQUE
POTC
0 0 0
END
```

the following information for metal Iron, at the B3LYP level, can be obtained:

```
..
*****
TOTAL DENSITY AT THE NUCLEAR POSITIONS
*****
POINT  ATOM       X(AU)       Y(AU)       Z(AU)      BOHR**(-3)
   1     1 FE    0.0000    0.0000    0.0000    11613.823418809
*****
...
..
*****

TOTAL ELECTROSTATIC POTENTIAL

*****
.....

TRACELESS ELECTRIC FIELD GRADIENT TENSOR

POINT  1 POSITION    2.7483  -4.7602   0.5717

TENSOR IN PRINCIPAL AXIS SYSTEM
AA -1.316699E-14 BB -3.355213E-12 CC  3.368380E-12

....
CONVERSION FACTORS (CODATA RECOMMENDED VALUES 1998)
...
THE PRODUCT OF THE EFG COMPONENT [AU] AND THE NUCLEAR
QUADRUPOLE MOMENT COMPONENT [BARN] MUST BE MULTIPLIED BY 6.073349
TO OBTAIN THE QUADRUPOLE COUPLING CONSTANT [mm/s]

TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT POTC          TELAPSE          95.57 TCPU          95.37
```

The tensor "in principal axis system" represent the electric field gradients (EFG). To get the multiplicative factor, let's rewrite equation 9.23 in terms of units (written in bold for sake of clarity):

$$\begin{aligned} \Delta E_{QI}[\mathbf{mm/s}] &= \frac{1}{2} e Q V_{CC} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \\ &= \frac{1}{2} 1.6021761 \cdot 10^{-19} [\mathbf{JV}^{-1}] Q \cdot 10^{-28} [\mathbf{m}^2] \cdot \\ &\quad \cdot 9.71736153 \cdot 10^{21} V_{CC} \left(1 + \frac{\eta^2}{3}\right)^{1/2} [\mathbf{Vm}^{-2}] \\ &= \frac{1}{2} 15.5689 \cdot 10^{-26} Q V_{CC} \left(1 + \frac{\eta^2}{3}\right)^{1/2} \mathbf{J} \end{aligned}$$

using the following conversion factors:

$$\begin{aligned} 1\mathbf{J} &= 6.2415097510^{18}\mathbf{eV} \\ 1\mathbf{eV} &= 0.12510^8\mathbf{mm/s} \end{aligned}$$

we end with:

$$\Delta E_{QI} = 6.073349 Q V_{CC} \left(1 + \frac{\eta^2}{3}\right)^{1/2} [\mathbf{mm/s}] \quad (9.24)$$

where Q has to be expressed in *barn* and V_{CC} and η in atomic unit.

9.5 Topological analysis

The *TOPOND*[79] public code, written by C. Gatti and interfaced to previous public versions of *CRYSTAL*[30], has presently been embedded in the code itself. By mean of the keyword *TOPO*, after the evaluation of the wave function, it is now possible to perform a topological analysis of the electron density, according to the Quantum Theory of Atoms in Molecules (QTAIM) developed by Bader and coworkers[10]. QTAIM allows to perform a detailed study of the electron density through different steps, ruled by various keywords the use of which is fully explained and documented in the *TOPOND* Reference Manual[82]. A brief summary is here presented.

The first step in the study of the electron density is the search of its critical points (CP) i.e. the points where its gradient, $\nabla\rho(r)$, vanishes. CPs can be classified in terms of their type and a two-way correspondence with chemically recognizable structures, namely atoms, bonds, ring and cages, can be performed providing lighting information on the bond nature[80]. A second step concerns the topological analysis of the Laplacian of the electron density, $\nabla^2\rho(r)$. This analysis can reveal the atomic shell structure and the degree of sharing of paired electrons among neighboring atoms. A comparison with the corresponding properties in the case of isolated molecules, or atoms, enable to evaluate the effects of the crystal packing on the bonding structure. A third step deals with the determination of the atomic basins and their local and integrated properties. Electronic population, Lagrangian and Hamiltonian kinetic energy, virial density, Becke electron localization function[19] can be defined and calculated in terms of atomic contributions[81]. Finally, for sake of completeness, a certain number of quantities can be plotted and visualize in 2 and 3 dimensions: in figure 9.5 the electron density, its Laplacian and the gradient trajectories of the Urea crystal are reported.

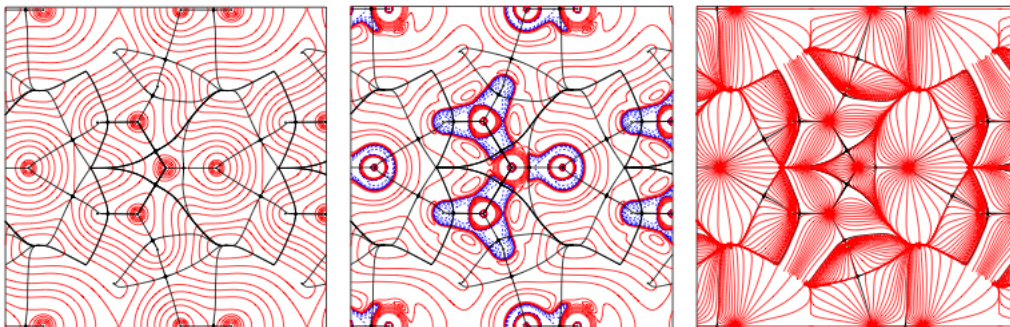


Figure 9.5: From left to right: electron density, ρ , its Laplacian, $\nabla^2\rho$ and the $\nabla\rho$ trajectories for Urea bulk. Bond paths are indicated in heavy black lines and the bond critical points are denoted by filled circles. Dotted blue lines indicate negative contour levels.

Chapter 10

Running CRYSTAL in parallel

The CRYSTAL package contains the following parallel binaries:

- *Pcrystal*
- *Pproperties*
- *MPPcrystal*

Pcrystal (parallel crystal) and *Pproperties* (parallel properties) are replicated-data versions of *crystal* and *properties*, whereas *MPPcrystal* (massively parallel crystal) distributes data and tasks to cores more efficiently than *Pcrystal* and is particularly suitable to large unit cell cases with large memory requirements. *Pcrystal* and *MPPcrystal* differ essentially for the way they handle data in reciprocal space and for the algorithms used to diagonalize the Fock matrix and process the eigenvectors. On the other hand, data in real space, such as the calculation of one and two-electron integrals are processed by *Pcrystal* and *MPPcrystal* through the same algorithms and parallelization strategy.

Parallelism in CRYSTAL is based on the MPI libraries. *Pcrystal* and *Pproperties* link no other libraries. *MPPcrystal* relies on the use of Massive Parallel Libraries (Scalapack).

10.1 Running *Pcrystal* and *Pproperties*

Pcrystal is fairly efficient for small up to medium sized systems, particularly with high symmetry. Matrices in reciprocal space are distributed to cores over the irreducible representations of the group of the system. In fact, if represented in the basis of the symmetry adapted atomic orbitals (**SYMADAPT**, default; see page 114), such matrices are decomposed into a block-diagonal form, each block (or sub-matrix) corresponding to a row of an irreducible representation. In the case of no symmetry adaptation (**NOSYMADA**, page 108) or P1 symmetry, matrices are distributed over the k points of the Pack-Mokhorst net (or the k points along a selected path in *Pproperties*, for example, to plot energy bands). Thus, the number of cores to be employed to run *Pcrystal* efficiently should not exceed the total number of the irreducible representations for all k points in the Pack-Mokhorst net (or the number of k points when P1 or **NOSYMADA**), unless the diagonalization step is negligible in terms of computational time with respect to the other steps of a calculation. Double-counting must be considered for open-shell systems.

Both *Pcrystal* and *Pproperties* expect to read input data from a file called INPUT in a directory of those discs where the programs store temporary data (fortran units). Output data are addressed to the standard error.

Use of option **CHUNKS** (page 92) is recommended to improve load balancing in DFT calculations. Option **LOWMEM** can be used to reduce memory requirements.

Parallelism in *Pcrystal* and *Pproperties* is enabled by calls to routines of the MPI library. Communication speed is generally not an issue in this case as inter-process communication is limited to a relatively small amount of data at few steps throughout a calculation.

10.2 Running *MPPcrystal*

MPPcrystal is designed to compute the total energy and wavefunction of large unit cell systems with large memory requirements, as matrices in the reciprocal space are fully distributed over the processors. [124] In particular, MPP running is recommended when n_{irr}/n_{procs} (or n_k/n_{procs}), *i.e.* the ratio of the number of irreducible representations at all k points (or the number of k points sampled in the reciprocal space) to the number of processors used is small.

Advantages of *MPPcrystal*:

- Matrix diagonalization is well balanced because many processors are involved in the diagonalization of one matrix;
- Memory requirement per processor decreases with n_{procs} because data are distributed to processors
- I/O is limited to reading the user's input deck and writing the output files with the results of a job.

Such features make it particularly suitable to run on High Performance computers, but it can also run on smaller clusters. Since communications are more intensive than with *Pcrystal*, performance is improved by fast connections.

In choosing n_{procs} , the user should consider that *MPPcrystal* is efficient when $n_{AO}/n_{procs} \geq 50$ (n_{AO} is the number of Atomic Orbitals per cell, or basis functions). If n_{procs} is too large compared to the size of the system, some parts of the calculation (matrix diagonalization) become inefficient because of increasing communications among processors.

In evaluating the best choice for n_{procs} a user must take into account that *MPPcrystal* uses a double-level parallelization in order to reduce communications and improve performance:

1. over the k points in the Pack-Monkhorst net
2. over blocks of a matrix for a k point

Level 1 of parallelization is enabled when $n_{procs} \geq n_{tasks}$, with $n_{tasks} = n_r + n_c * \text{WEIGHT}$. n_r and n_c denote the number of k points in the Pack-Monkhorst net where the Fock matrix elements are real or complex numbers, respectively, and WEIGHT (see **CMPLXFAC** on page 82) accounts for the overloading due to the diagonalization of a complex matrix relative to a real matrix (n_{tasks} is doubled in open-shell cases). If $n_{procs} < n_{tasks}$, every matrix for each k point is diagonalized by all processors. If otherwise, the n_{procs} cores are subdivided into $n_r + n_c$ subsets of cores. Each subset is assigned the the task of diagonalizing a matrix for one of the k points. The composition of each subset depends on the value of WEIGHT and is such as to achieve the best load-balancing.

MPPcrystal sets the following standards and defaults:

- “Divide and Conquer” method for matrix diagonalization (disabled by **STDIAG**);
- Reduced memory storage is enabled as with **LOWMEM** (page 108); disabled by **NOLOWMEM**
- two- and one-electron integrals are computed in real time within a SCF cycle as enabled by **SCFDIR** (page 109);
- multipole moments for the evaluation of those two-electron integrals which are approximated through bipolar expansions and exceed the storage memory limit set by **BIPO-SIZE** and **EXCHSIZE** are computed in real time (they are stored to disc by *Pcrystal*);
- Data relative to the grid of points used to integrate the exchange-correlation functionals are distributed over n_{procs} cores as enabled by **DISTGRID** (page 92); disabled by **REPLGRID**;

- Symmetry adaptation of the crystalline orbitals is inhibited as with **NOSYMADA** (page 108);
- Eigenvectors are stored to memory and distributed over all cores; thus, they cannot be printed nor stored to disc at the end of a calculation.

The following options are not available:

| | keyword | block |
|--|-------------------------------------|-------|
| CPHF | CPHF | 1 |
| Infrared intensities in phonon spectra | FREQCALC/INTENS | 1 |
| Raman intensities in phonon spectra | FREQCALC/INTRAMAN | 1 |
| Piezoelectric constants | PIEZOCON and ELAPIEZO | 1 |
| Photoelastic constants | PHOTOELA | 1 |
| Bloch Functions Symmetry Adapted | SYMADAPT | 3 |
| Printing of eigenvalues of overlap matrix in k space | EIGS | 3 |

SCF convergence may proceed along slightly different paths with *Pcrystal* and *MPPcrystal*, particularly in those cases where convergence is difficult to be achieved, so that SCF convergence acceleration methods may exhibit different behaviours. A particular setting of convergence tool parameters, for example a given mixing rate of matrices along several SCF steps, may result to be effective with *Pcrystal* and ineffective with *MPPcrystal*. However, a proper choice of the parameters will always result into achievement of the SCF cycle convergence in both cases.

Like *Pcrystal*, *MPPcrystal* expects to read input data from a file called INPUT in a directory of those discs where the programs store temporary data (fortran units). Output data are addressed to the standard error.

MPPcrystal runs as *Pcrystal* if keyword **REPLDATA** (page 109) is added to the input deck.

Chapter 11

Input examples

11.1 Standard geometry input

3D - Crystalline compounds - 1st input record keyword: CRYSTAL

Atom coordinates: fractional units of the crystallographic lattice vectors.

Sodium Chloride - NaCl (Rock Salt Structure)

| | |
|-------------|-----------------------------------|
| CRYSTAL | |
| 0 0 0 | IFLAG IFHR IFSO |
| 225 | space group, $Fm\bar{3}m$, cubic |
| 5.64 | a (Å) |
| 2 | 2 non equivalent atoms |
| 11 .5 .5 .5 | Z=11, Sodium, 1/2, 1/2, 1/2 |
| 17 .0 .0 .0 | Z=17, Chlorine |

Diamond - C (2nd Setting - 48 symmops - 36 with translational component)

| | |
|------------------|---|
| CRYSTAL | |
| 0 0 0 | IFLAG IFHR IFSO |
| 227 | space group, $Fd\bar{3}m$, cubic |
| 3.57 | a (Å) |
| 1 | 1 non equivalent atom |
| 6 .125 .125 .125 | Z=6, Carbon, 1/8, 1/8, 1/8 (multiplicity 2) |

Diamond - C (1st Setting - 48 symmops - 24 with translational component)

| | |
|------------|---------------------------------------|
| CRYSTAL | |
| 0 0 1 | IFLAG IFHR IFSO |
| 227 | space group 227, $Fd\bar{3}m$, cubic |
| 3.57 | a (Å) |
| 1 | 1 non equivalent atom |
| 6 .0 .0 .0 | Z=6, Carbon (multiplicity 2) |

Zinc Blend - ZnS

| | |
|----------------|---------------------------------------|
| CRYSTAL | |
| 0 0 0 | IFLAG IFHR IFSO |
| 216 | space group 216, $F\bar{4}3m$, cubic |
| 5.42 | a (Å) |
| 2 | 2 non equivalent atoms |
| 30 .25 .25 .25 | Z=30, Zinc, (1/4, 1/4, 1/4) |
| 16 .0 .0 .0 | Z=16, Sulphur |

Wurtzite - ZnS

| | |
|-------------------------------|---|
| CRYSTAL | |
| 0 0 0 | IFLAG IFHR IFSO |
| 186 | space group 186, $P\bar{6}_3mc$, hexagonal |
| 3.81 6.23 | a, c (Å) |
| 2 | 2 non equivalent atoms |
| 30 .666666667 .333333333 .0 | Zinc, (2/3, 1/3, 0.) |
| 16 .666666667 .333333333 .375 | Sulphur, (2/3, 1/3, 3/8) |

Cuprite - Cu₂O

CRYSTAL

0 0 0
208
4.27
2
8 .0 .0 .0
29 .25 .25 .25IFLAG IFHR IFSO
space group 208, $P4_232$, cubic
 a (Å)
2 non equivalent atoms
Z=8, Oxygen
Z=29, Copper (1/4, 1/4, 1/4)

Aragonite - CaCO₃

CRYSTAL

1 0 0
P M C N
4.9616 7.9705 5.7394
4
20 .25 .4151 .2103
6 .25 .7627 .085
8 .25 .9231 .0952
8 .4729 .6801 .087IFLAG (1, SPGR symbol) IFHR IFSO
space group $Pm\bar{c}n$, orthorhombic
 a, b, c (Å)
4 non equivalent atoms
Z=20, Calcium
Z=6, Carbon
Z=8, Oxygen
Z=8, Oxygen

Fluorite - CaF₂

CRYSTAL

0 0 0
225
5.46
2
9 .25 .25 .25
20 .0 .0 .0IFLAG IFHR IFSO
space group 225, $Fm\bar{3}m$, cubic
 a (Å)
2 non equivalent atoms
Fluorine
Calcium

Cesium chloride - CsCl

CRYSTAL

0 0 0
221
4.12
2
55 .5 .5 .5
17 .0 .0 .0IFLAG IFHR IFSO
space group 221, $Pm\bar{3}m$, cubic
 a (Å)
2 non equivalent atoms
Cesium
Chlorine

Rutile - TiO₂

CRYSTAL

0 0 0
136
4.59 2.96
2
22 .0 .0 .0
8 .305 .305 .0IFLAG IFHR IFSO
space group 136, $P4_2/mmm$, tetragonal
 a, c (Å)
2 non equivalent atoms
Titanium
Oxygen

Graphite - C (Hexagonal)

CRYSTAL

0 0 0
194
2.46 6.70
2
6 .0 .0 .25
6 .3333333333 .6666666667 .25IFLAG IFHR IFSO
space group 194, $P\bar{6}_3/mmc$, hexagonal
 a, c (Å)
2 non equivalent atoms
Carbon, 0, 0, 1/4
Carbon, 1/3, 2/3, 1/4

Pyrite - FeS₂

CRYSTAL

0 0 0
205
5.40
2
26 .0 .0 .0
16 .386 .386 .386IFLAG IFHR IFSO
space group 205, $Pa\bar{3}$, cubic
 a (Å)
2 non equivalent atoms
Iron
Sulphur

Calcite - CaCO₃

CRYSTAL

| | |
|-----------------|---|
| 0 1 0 | IFLAG IFHR (=1, rhombohedral representation) IFSO |
| 167 | space group 167, $R\bar{3}c$, hexagonal |
| 6.36 46.833 | a (Å), α° |
| 3 | 3 non equivalent atoms |
| 20 .0 .0 .0 | Calcium |
| 6 .25 .25 .25 | Carbon |
| 8 .007 .493 .25 | Oxygen |

Corundum - Al₂O₃ (hexagonal representation)

CRYSTAL

| | |
|-------------------|--|
| 0 0 0 | IFLAG IFHR IFSO |
| 167 | space group 167, $R\bar{3}c$, hexagonal |
| 4.7602 12.9933 | a, c (Å) |
| 2 | 2 non equivalent atoms |
| 13 0. 0. 0.35216 | Aluminium |
| 8 0.30621 0. 0.25 | Oxygen |

Corundum - Al₂O₃ (rhombohedral representation)

CRYSTAL

| | |
|----------------------------|--|
| 0 1 0 | IFLAG IFHR (=1, rhombohedral cell) IFSO |
| 167 | space group 167, $R\bar{3}c$, hexagonal |
| 5.12948 55.29155 | a (Å), α° |
| 2 | 2 non equivalent atoms |
| 13 0.35216 0.35216 0.35216 | Aluminium |
| 8 0.94376 0.25 0.55621 | Oxygen |

Zirconia - ZrO₂ - monoclinic structure

CRYSTAL

| | |
|----------------------------|--|
| 0 0 1 | IFLAG IFHR IFSO (=1, standard shift of origin) |
| 14 | space group 14, $P2_1/c$, monoclinic |
| 5.03177 5.03177 5.258 90.0 | a, b, c (Å), β° |
| 3 | 3 non equivalent atoms |
| 240 0.2500 0.0000 0.25000 | Zirconium, Pseudopotential ($Z' > 200$) |
| 208 0.0000 0.2500 0.07600 | Oxygen, Pseudopotential |
| 208 -0.500 -0.250 0.07600 | Oxygen, Pseudopotential |

Zirconia - ZrO₂ - tetragonal structure

CRYSTAL

| | |
|--------------------|--|
| 0 0 1 | IFLAG IFHR IFSO (=1, standard shift of origin) |
| 137 | space group 137, $P4_2/nmc$, tetragonal |
| 3.558 5.258 | a, c (Å) |
| 3 | 3 non equivalent atoms |
| 240 0.0 0.0 0.0 | Zirconium, Pseudopotential ($Z' > 200$) |
| 208 0.0 -0.5 0.174 | Oxygen, Pseudopotential |
| 208 0.5 0.0 0.326 | Oxygen, Pseudopotential |

Zirconia - ZrO₂ - cubic structure

CRYSTAL

| | |
|-----------------------|--|
| 0 0 1 | IFLAG IFHR IFSO (=1, standard shift of origin) |
| 225 | space group 225, $Fm\bar{3}m$, cubic |
| 5.10 | a (Å) |
| 3 | 3 non equivalent atoms |
| 240 0.00 0.00 0.00 | Z=40 Zirconium, Pseudopotential ($Z' > 200$) |
| 208 0.25 0.25 0.25 | Oxygen, Pseudopotential |
| 208 -0.25 -0.25 -0.25 | Oxygen, Pseudopotential |

SiO₂, Chabazite

CRYSTAL

0 1 0

166

9.42 94.47

5

14 .1045 .334 .8755

8 .262 -.262 .0

8 .1580 -.1580 .5000

8 .2520 .2520 .8970

8 .0250 .0250 .3210

IFLAG IFHR (=1,rhombohedral representation) IFSO
space group 166 $R\bar{3}m$, hexagonal a (Å), β°

5 non equivalent atoms (36 atoms in the primitive cell)

Silicon (multiplicity 12)

Oxygen (multiplicity 6)

Oxygen (multiplicity 6)

Oxygen (multiplicity 6)

Oxygen (multiplicity 6)

SiO₂, Siliceous Faujasite

CRYSTAL

0 0 0

227

21.53

5

14 .1265 -.0536 .0370

8 .1059 -.1059 .0

8 -.0023 -.0023 .1410

8 .1746 .1746 -.0378

8 .1785 .1785 .3222

IFLAG IFHR IFSO

space group 227, $Fd\bar{3}m$, cubic a (Å)

5 non equivalent atoms (144 atoms in the primitive cell)

Silicon (multiplicity 48)

Oxygen (multiplicity 24)

Oxygen (multiplicity 24)

Oxygen (multiplicity 24)

Oxygen (multiplicity 24)

SiO₂, Siliceous Edingtonite

CRYSTAL

0 0 0

115

6.955 6.474

5

14 .0 .0 .5000

14 .0 .2697 .1200

8 .0 .189 .3543

8 .50000 .0 .8779

8 .189 .189 .0

IFLAG IFHR IFSO

space group 115, $P\bar{4}m2$, tetragonal a, c (Å)

5 non equivalent atoms (15 atoms in the primitive cell)

Silicon (multiplicity 1)

Silicon (multiplicity 4)

Oxygen (multiplicity 4)

Oxygen (multiplicity 2)

Oxygen (multiplicity 4)

SiO₂, Siliceous Sodalite

CRYSTAL

0 0 0

218

8.950675

3

14 .25000 .50000 .0

14 .25000 .0 .50000

8 .14687 .14687 .50000

IFLAG IFHR IFSO

space group 218, $P\bar{4}3n$, cubic a (Å)

3 non equivalent atoms (36 atoms in the primitive cell)

Silicon (multiplicity 6)

Silicon (multiplicity 6)

Oxygen (multiplicity 24)

2D - Slabs (surfaces) - 1st input record keyword: SLAB

A 2D structure can either be created by entering directly the 2D cell parameters and irreducible atoms coordinates to obtain a slab of given thickness (keyword **SLAB** in the first record of the geometry input), or it can be derived from the 3D structure through the keyword **SLABCUT** (page 61), entered in the geometry editing section of 3D structure input. In that case the layer group is automatically identified by the program. The input tests 4-24, 5-25, 6-26 and 7-27 show the two different ways to obtain the same 2D structure.

Atom coordinates: z in Ångstrom, x , y in fractional units of the crystallographic cell translation vectors.

Test05 - graphite 2D (see test 25)

| | |
|-----------------------------------|---------------------------|
| SLAB | |
| 77 | layer group (hexagonal) |
| 2.47 | lattice vector length (Å) |
| 1 | 1 non equivalent atom |
| 6 -0.33333333333 0.33333333333 0. | Z=6; Carbon; x,y,z |

Beryllium - 3 layers slab

| | |
|-------------------------------------|-------------------------------|
| SLAB | |
| 78 | layer group (hexagonal) |
| 2.29 | lattice vector length (Å) |
| 2 | 2 non equivalent atoms |
| 4 0.33333333333 0.66666666667 0. | Z=4, Beryllium; $1/3, 2/3, z$ |
| 4 0.66666666667 0.33333333333 1.795 | Z=4, Beryllium; $2/3, 1/3, z$ |

Test06 - beryllium - 4 layers slab (see test 26)

| | |
|--|---------------------------|
| SLAB | |
| 72 | layer group (hexagonal) |
| 2.29 | lattice vector length (Å) |
| 2 | 2 non equivalent atoms |
| 4 0.33333333333 0.66666666667 0.897499 | Z=4, Beryllium; x,y,z |
| 4 0.66666666667 0.33333333333 2.692499 | Z=4, Beryllium; x,y,z |

Test04 - Corundum 001 (0001) 2 layers slab (see test 24)

| | |
|------------------------------------|---------------------------|
| SLAB | |
| 66 | layer group (hexagonal) |
| 4.7602 | lattice vector length (Å) |
| 3 | 3 non equivalent atoms |
| 13 0. 0. 1.9209 | Z=13, Aluminum; x,y,z |
| 8 0.333333333 0.027093 1.0828 | Z=8, Oxygen; x,y,z |
| 13 -0.333333333 0.333333333 0.2446 | Z=13, Aluminum; x,y,z |

Test07 - Corundum 110 (1010) slab (see test 27)

| | |
|----------------------------|------------------------------|
| SLAB | |
| 7 | layer group (Oblique) |
| 5.129482 6.997933 95.8395 | a,b (Å) α (degrees) |
| 6 | 6 non equivalent atoms |
| 8 -0.25 0.5 2.1124 | Z=8, Oxygen; x,y,z |
| 8 0.403120 0.153120 1.9189 | Z=8, Oxygen; x,y,z |
| 8 0.096880 0.346880 0.4612 | Z=8, Oxygen; x,y,z |
| 8 -0.25 0.00 0.2677 | Z=8, Oxygen; x,y,z |
| 13 0.454320 0.397840 1.19 | Z=13, Aluminum; x,y,z |
| 13 0.045680 0.102160 1.19 | Z=13, Aluminum; x,y,z |

MgO (110) 2 layers slab

| | |
|----------------------|----------------------------|
| SLAB | |
| 40 | layer group |
| 4.21 2.97692 | lattice vectors length (Å) |
| 2 | 2 non equivalent atoms |
| 12 0.25 0.25 0.74423 | Z=12, Magnesium; x,y,z |
| 8 0.75 0.25 0.74423 | Z=8, Oxygen; x,y,z |

MgO (110) 3 layers slab

SLAB

37

4.21 2.97692

4

12 0. 0. 1.48846

8 0.5 0. 1.48846

12 0.5 0.5 0.

8 0. 0.5 0.

lattice vectors length (Å)

4 non equivalent atoms

Z=12, Magnesium; x, y, z Z=8, Oxygen; x, y, z Z=12, Magnesium; x, y, z Z=8, Oxygen; x, y, z

CO on MgO (001) two layers slab - one-side adsorption

SLAB

55

2.97692

6

108 0. 0. 4.5625

6 0. 0. 3.4125

12 0. 0. 1.0525

8 0.5 0.5 1.0525

12 0. 0. -1.0525

8 0.5 0.5 -1.0525

lattice vector length $[4.21/\sqrt{2}]$ (Å)

6 non equivalent atoms

Z=8, Oxygen; x, y, z Z=6, Carbon; x, y, z Z=12, Magnesium; x, y, z Z=8, Oxygen; x, y, z Z=12, Magnesium; x, y, z Z=8, Oxygen; x, y, z

Two different conventional atomic numbers (8 and 108) are attributed to the Oxygen in CO and to the Oxygen in MgO. Two different basis sets will be associated to the two type of atoms (see Basis Set input, page 20, and test 36).

CO on MgO (001) two layers slab - two-side adsorption

SLAB

64

2.97692

4

108 0.25 0.25 4.5625

6 0.25 0.25 3.4125

12 0.25 0.25 1.0525

8 0.75 0.75 1.0525

lattice vector length (Å)

4 non equivalent atoms

Z=8, Oxygen; x, y, z Z=6, Carbon; x, y, z Z=12, Magnesium; x, y, z Z=8, Oxygen; x, y, z

Two different conventional atomic numbers (8 and 108) are attributed to the Oxygen in CO and to the Oxygen in MgO.

Diamond slab parallel to (100) face - nine layers slab

SLAB

59

2.52437

5

6 0. 0. 0.

6 0.5 0. 0.8925

6 0.5 0.5 1.785

6 0. 0.5 2.6775

6 0. 0. 3.57

lattice vector length (Å)

5 non equivalent atoms

Z=6, Carbon; x, y, z Z=6, Carbon; x, y, z Z=6, Carbon; x, y, z Z=6, Carbon; x, y, z Z=6, Carbon; x, y, z

Diamond slab parallel to (100) face - ten layers slab

SLAB

39

2.52437 2.52437

5

6 0.25 0. 0.44625

6 0.25 0.5 1.33875

6 0.75 0.5 2.23125

6 0.75 0 3.12375

6 0.25 0. 4.01625

layer group

lattice vectors length (Å)

5 non equivalent atoms

Z=6, Carbon; x, y, z Z=6, Carbon; x, y, z Z=6, Carbon; x, y, z Z=6, Carbon; x, y, z Z=6, Carbon; x, y, z

1D - Polymers - 1st input record keyword: POLYMER

Atom coordinates: y, z in Ångstrom, x in fractional units of the crystallographic cell translation vector.

Test03 - (SN)_x polymer

| | |
|---------------------------------|---------------------------|
| POLYMER | |
| 4 | rod group |
| 4.431 | lattice vector length (Å) |
| 2 | 2 non equivalent atoms |
| 16 0.0 -0.844969 0.0 | Z=16, Sulphur; x, y, z |
| 7 0.141600540 0.667077 -0.00093 | Z=7, Nitrogen; x, y, z |

Water polymer

| | |
|-------------------------------|---------------------------|
| POLYMER | |
| 1 | |
| 4.965635 | lattice vector length (Å) |
| 6 | 6 non equivalent atoms |
| 8 0. 0. 0. | Z=8, Oxygen; x, y, z |
| 1 0.032558 0.836088 -0.400375 | Z=1, Hydrogen; x, y, z |
| 1 0.168195 -0.461051 0. | Z=1, Hydrogen; x, y, z |
| 8 0.5 -1.370589 0. | Z=8, Oxygen; x, y, z |
| 1 0.532558 -2.206677 0.400375 | Z=1, Hydrogen; x, y, z |
| 1 0.668195 -0.909537 0. | Z=1, Hydrogen; x, y, z |

Formamide chain - test40 DFT

| | |
|-----------------------------|---------------------------|
| POLYMER | |
| 4 | rod group |
| 8.774 | lattice vector length (Å) |
| 6 | 6 non equivalent atoms |
| 8 -7.548E-2 5.302E-3 0.7665 | Z=8, Oxygen; x, y, z |
| 7 0.1590 -0.8838 0.3073 | Z=7, Nitrogen; x, y, z |
| 6 5.627E-2 7.051E-2 0.2558 | Z=6, Oxygen; x, y, z |
| 1 0.2677 -0.6952 -9.1548E-2 | Z=1, Hydrogen; x, y, z |
| 1 0.1310 -1.8019 0.7544 | Z=1, Hydrogen; x, y, z |
| 1 9.244E-2 0.9973 -0.2795 | Z=1, Hydrogen; x, y, z |

0D - Molecules - 1st input record keyword: MOLECULE

Atom coordinates: x, y, z in Ångstrom.

Test00 - CO molecule

| | |
|---------------|------------------------|
| MOLECULE | |
| 1 | point group |
| 2 | 2 non equivalent atoms |
| 6 0. 0. 0. | Z=6, Carbon; x, y, z |
| 8 0.8 0.5 0.4 | Z=8, Oxygen; x, y, z |

Test01 - CH₄ Methane molecule

| | |
|---------------------|--------------------------|
| MOLECULE | |
| 44 | point group |
| 2 | 2 non equivalent atoms |
| 6 0. 0. 0. | Z=6, Carbon; x, y, z |
| 1 0.629 0.629 0.629 | Z=1, Hydrogen; x, y, z |

Test02 - CO(NH₂)₂ Urea molecule

| | |
|------------------------------|--------------------------|
| MOLECULE | |
| 15 | point group |
| 5 | 5 non equivalent atoms |
| 6 0. 0. 0. | Z=6, Carbon; x, y, z |
| 8 0. 0. 1.261401 | Z=8, Oxygen; x, y, z |
| 7 0. 1.14824666034 -0.69979 | Z=7, Nitrogen; x, y, z |
| 1 0. 2.0265496501 -0.202817 | Z=1, Hydrogen; x, y, z |
| 1 0. 1.13408048308 -1.704975 | Z=1, Hydrogen; x, y, z |

11.2 Basis set input

Optimized basis sets for periodic systems used in published papers are available on WWW:

<http://www.crystal.unito.it>

All electron Basis sets for Silicon atom

STO-3G

| | |
|-------------|--|
| 14 3 | Z=14, Silicon; 3 shells |
| 1 0 3 2. 0. | Pople BS; s shell; 3G; CHE=2; standard scale factor |
| 1 1 3 8. 0. | Pople BS; sp shell; 3G; CHE=8; standard scale factor |
| 1 1 3 4. 0. | Pople BS; sp shell; 3G; CHE=4; standard scale factor |

6-21G

| | |
|-------------|---|
| 14 4 | Z=14, Silicon; 4 shells |
| 2 0 6 2. 1. | Pople 6-21 BS; s shell; 6G; CHE=2; scale factor 1 (core AO). |
| 2 1 6 8. 1. | Pople 6-21 BS; sp shell; 6G; CHE=8; scale factor 1 (core AOs). |
| 2 1 2 4. 1. | Pople 6-21 BS; sp shell; 2G; CHE=4; scale factor 1 (inner valence). |
| 2 1 1 0. 1. | Pople 6-21 BS; sp shell; 1G; CHE=0; scale factor 1 (outer valence). |

NB. The 4th shell has electron charge 0. The basis functions of that shell are included in the basis set to compute the atomic wave functions, as they correspond to symmetries (angular quantum numbers) occupied in the ground state of the atom. The atomic basis set is: 4s, 3p.

6-21G modified

| | |
|-------------|---|
| 14 4 | Z=14, Silicon; 4 shells |
| 2 0 6 2. 1. | Pople 6-21 BS; s shell; 6G; CHE=2; scale factor 1. |
| 2 1 6 8. 1. | Pople 6-21 BS; sp shell; 6G; CHE=8; scale factor 1. |
| 2 1 2 4. 1. | Pople 6-21 BS; sp shell; 2G; CHE=4; scale factor 1. |
| 0 1 1 0. 1. | free BS; sp shell; 1G; CHE=0; scale factor 1. |
| 0.16 1. 1. | gaussian exponent; s coefficient; p coefficient |

3-21G

| | |
|-------------|---|
| 14 4 | Z=14, Silicon; 4 shells |
| 2 0 3 2. 1. | Pople 3-21 BS; s shell; 3G; CHE=2; scale factor 1. |
| 2 1 3 8. 1. | Pople 3-21 BS; sp shell; 3G; CHE=8; scale factor 1. |
| 2 1 2 4. 1. | Pople 3-21 BS; sp shell; 2G; CHE=4; scale factor 1. |
| 2 1 1 0. 1. | Pople 3-21 BS; sp shell; 1G; CHE=0; scale factor 1. |

3-21G*

| | |
|-------------|---|
| 14 5 | Z=14, Silicon; 5 shells |
| 2 0 3 2. 1. | Pople 3-21 BS; s shell; 3G; CHE=2; scale factor 1. |
| 2 1 3 8. 1. | Pople 3-21 BS; sp shell; 3G; CHE=8; scale factor 1. |
| 2 1 2 4. 1. | Pople 3-21 BS; sp shell; 2G; CHE=4; scale factor 1. |
| 2 1 1 0. 1. | Pople 3-21 BS; sp shell; 1G; CHE=0; scale factor 1. |
| 2 3 1 0. 1. | Pople 3-21 BS; d shell; 1G; CHE=0; scale factor 1. |

NB. The basis functions of the 5th shell, d symmetry, unoccupied in the ground state of Silicon atom, is not included in the atomic wave function calculation.

3-21G modified+polarization

| | |
|-------------|---|
| 14 5 | Z=14, Silicon; 5 shells |
| 2 0 3 2. 1. | Pople 3-21 BS; s shell; 3G; CHE=2; scale factor 1. |
| 2 1 3 8. 1. | Pople 3-21 BS; sp shell; 3G; CHE=8; scale factor 1. |
| 2 1 2 4. 1. | Pople 3-21 BS; sp shell; 2G; CHE=4; scale factor 1. |
| 0 1 1 0. 1. | free BS; sp shell; 1G; CHE=0; scale factor 1. |
| 0.16 1. 1. | gaussian exponent; s contraction coefficient; p contr. coeff. |
| 0 3 1 0. 1. | free BS; d shell; 1G; CHE=0; scale factor 1. |
| 0.5 1. | gaussian exponent; d contraction coefficient. |

free basis set

| | | | |
|-------------|--|--|---|
| 14 4 | Z=14, Silicon; 4 shells | | |
| 0 0 6 2. 1. | free BS; s shell; 6 GTF; CHE=2; scale factor 1. | | |
| 16115.9 | 0.00195948 | 1st gaussian exponent; s contraction coefficient | |
| 2425.58 | 0.0149288 | 2nd gaussian exponent; s contraction coefficient | |
| 553.867 | 0.0728478 | 3rd gaussian exponent; s contraction coefficient | |
| 156.340 | 0.24613 | 4th gaussian exponent; s contraction coefficient | |
| 50.0683 | 0.485914 | 5th gaussian exponent; s contraction coefficient | |
| 17.0178 | 0.325002 | 6th gaussian exponent; s contraction coefficient | |
| 0 1 6 8. 1. | free BS; sp shell; 6 GTF; CHE=8; scale factor 1. | | |
| 292.718 | -0.00278094 | 0.00443826 | 1st gaussian exp.; s contr. coeff.; p contr. coeff. |
| 69.8731 | -0.0357146 | 0.0326679 | 2nd gaussian exp.; s contr. coeff.; p contr. coeff. |
| 22.3363 | -0.114985 | 0.134721 | 3rd gaussian exp.; s contr. coeff.; p contr. coeff. |
| 8.15039 | 0.0935634 | 0.328678 | 4th gaussian exp.; s contr. coeff.; p contr. coeff. |
| 3.13458 | 0.603017 | 0.449640 | 5th gaussian exp.; s contr. coeff.; p contr. coeff. |
| 1.22543 | 0.418959 | 0.261372 | 6th gaussian exp.; s contr. coeff.; p contr. coeff. |
| 0 1 2 4. 1. | free BS; sp shell; 2 GTF; CHE=4; scale factor 1 | | |
| 1.07913 | -0.376108 | 0.0671030 | 1st gaussian exp.; s contr. coeff.; p contr. coeff. |
| 0.302422 | 1.25165 | 0.956883 | 2nd gaussian exp.; s contr. coeff.; p contr. coeff. |
| 0 1 1 0. 1. | free BS; sp shell; 1 GTF; CHE=0; scale factor 1. | | |
| 0.123 | 1. | 1. | gaussian exp.; s contr. coeff.; p contr. coeff. |

Examples of ECP and valence only basis set input

Nickel atom. Electronic configuration: [Ar] 4s(2) 3d(8)

Durand & Barthelat large core

| | | | |
|-------------|---------|----|---|
| 228 4 | | | Z=28,Nickel; 4 shells valence basis set |
| BARTHE | | | keyword; Durand-Barthelat ECP |
| 0 1 2 2. 1. | | | free BS;sp shell;2 GTF;CHE=2;scale factor 1 |
| 1.55 | .24985 | 1. | 1st GTF exponent;s coefficient;p coefficient |
| 1.24 | -.41636 | 1. | 2nd GTF exponent;s coefficient;p coefficient |
| 0 1 1 0. 1. | | | free BS; sp shell; 1 GTF; CHE=0; scale factor 1 |
| 0.0818 | 1.0 | 1. | GTF exponent;s coefficient;p coefficient |
| 0 3 4 8. 1. | | | free BS; d shell; 4 GTF; CHE=8; scale factor 1 |
| 4.3842E+01 | .03337 | | 1st GTF exponent; d coefficient |
| 1.2069E+01 | .17443 | | 2nd GTF exponent; d coefficient |
| 3.9173E+00 | .42273 | | 3rd GTF exponent; d coefficient |
| 1.1997E+00 | .48809 | | 4th GTF exponent; d coefficient |
| 0 3 1 0. 1. | | | free BS; d shell; 1 GTF; CHE=0; scale factor 1 |
| 0.333 | 1. | | GTF exponent; d coefficient |

Hay & Wadt Large Core - [Ar] 4s(2) 3d(8)

| | | | |
|-------------|-------------|-------------|---|
| 228 4 | | | Z=28,Nickel; 4 shells valence basis set |
| HAYWLC | | | keyword; Hay-Wadt large core ECP |
| 0 1 2 2. 1. | | | free BS; sp shell; 2 GTF; CHE=2; scale factor 1 |
| 1.257 | 1.1300E-01 | 2.6760E-02 | exponent,s coefficient,p coefficient |
| 1.052 | -1.7420E-01 | -1.9610E-02 | |
| 0 1 1 0. 1. | | | second shell,sp type,1 GTF |
| 0.0790 | 1.0 | 1. | |
| 0 3 4 8. 1. | | | third shell,d type,4 primitive GTF |
| 4.3580E+01 | .03204 | | |
| 1.1997E+01 | .17577 | | |
| 3.8938E+00 | .41461 | | |
| 1.271 | .46122 | | |
| 0 3 1 0. 1. | | | fourth shell,d type,1 GTF |
| 0.385 | 1. | | |

Hay & Wadt Small Core - [Ne] 3s(2) 3p(6) 4s(2) 3d(8)

| | | | |
|-------------|-------------|-------------|---------------------------------------|
| 228 6 | | | nickel basis set - 6 shells |
| HAYWSC | | | keyword; Hay-Wadt small core ECP |
| 0 1 3 8. 1. | | | first shell,sp type,3 primitive GTF - |
| 2.5240E+01 | -3.7000E-03 | -4.0440E-02 | exponent,s coefficient,p coefficient |
| 7.2019E+00 | -5.3681E-01 | -7.6560E-02 | |
| 3.7803E+00 | 4.2965E-01 | 4.8348E-01 | |
| 0 1 2 2. 1. | | | second shell,sp type,2 primitive GTF |
| 1.40 | .84111 | .55922 | |
| 0.504 | .13936 | .12528 | |
| 0 1 1 0. 1. | | | third shell,sp type,1 GTF |
| 0.0803 | 1.0 | 1. | |
| 0 3 3 8. 1. | | | fourth shell,d type,4 primitive GTF |
| 4.1703E+01 | 3.5300E-02 | | |
| 1.1481E+01 | 1.8419E-01 | | |
| 3.7262E+00 | 4.1696E-01 | | |
| 0 3 1 0. 1. | | | fifth shell,d type,1 GTF |
| 1.212 | 1. | | |
| 0 3 1 0. 1. | | | sixth shell,d type,1 GTF |
| 0.365 | 1.0 | | |

Free input

| | | | |
|-------------|-------------|----|--|
| 228 5 | | | Z=28, nickel basis set - 5 shells (valence only) |
| INPUT | | | keyword: free ECP (Large Core)- input follows |
| 10. | 5 4 5 2 0 0 | | nuclear charge; number of terms in eq. 2.17 and 2.18 |
| 344.84100 | -18.00000 | -1 | eq. 2.17, 5 records: |
| 64.82281 | -117.95937 | 0 | α , C, n |
| 14.28477 | -29.43970 | 0 | |
| 3.82101 | -10.38626 | 0 | |
| 1.16976 | -0.89249 | 0 | |
| 18.64238 | 3.00000 | -2 | eq. 2.18, 4 records $\ell = 0$ |
| 4.89161 | 19.24490 | -1 | |
| 1.16606 | 23.93060 | 0 | |
| 0.95239 | -9.35414 | 0 | |
| 30.60070 | 5.00000 | -2 | eq. 2.18, 5 records $\ell = 1$ |
| 14.30081 | 19.81155 | -1 | |
| 15.03304 | 54.33856 | 0 | |
| 4.64601 | 54.08782 | 0 | |
| 0.98106 | 7.31027 | 0 | |
| 4.56008 | 0.26292 | 0 | eq. 2.18, 2 records $\ell = 2$ |
| 0.67647 | -0.43862 | 0 | _____basis set input follows - valence only _____ |
| 0 1 1 2. 1. | | | 1st shell: sp type; 1 GTF; CHE=2; scale fact.=1 |
| 1.257 | 1. | 1. | exponent, s coefficient, p coefficient |
| 0 1 1 0. 1. | | | 2nd shell: sp type; 1 GTF; CHE=0; scale fact.=1 |
| 1.052 | 1. | 1. | |
| 0 1 1 0. 1. | | | 3rd shell: sp type; 1 GTF; CHE=0; scale fact.=1 |
| 0.0790 | 1.0 | 1. | |
| 0 3 4 8. 1. | | | 4th shell; d type; 4 GTF; CHE=8; scale fact.=1 |
| 4.3580E+01 | .03204 | | |
| 1.1997E+01 | .17577 | | |
| 3.8938E+00 | .41461 | | |
| 1.271 | .46122 | | |
| 0 3 1 0. 1. | | | 5th shell; d type; 1 GTF; CHE=0; scale fact.=1 |
| 0.385 | 1. | | |

11.3 SCF options

Example of how to edit the density matrix obtained for a given magnetic solution to define a scf guess with a different magnetic solution.

Deck 1 - ferromagnetic solution

Spinel MnCr2O4

```
CRYSTAL
0 0 0
227 space group number
8.5985 lattice parameter
3 3 non equivalent atoms (14 atoms in the primitive cell)
24 0.500 0.500 0.500 Chromium - x, y, z - multiplicity 4
25 0.125 0.125 0.125 Manganese - x, y, z - multiplicity 2
8 0.2656 0.2656 0.2656 Oxygen - x, y, z - multiplicity 8
END end of geometry input records - block 1
basis set input terminated by END
UHF Unrestricted Hartree Fock
TOLINTEG the default value of the truncation tolerances is modified
7 7 7 7 14 new values for ITOL1-ITOL2-ITOL3-ITOL4-ITOL5
END end of input block 3
4 0 4 reciprocal lattice sampling (page 25)
SPINLOCK  $n_\alpha - n_\beta$  is locked to be 22 for 50 cycles.
22 50 All the d electrons are forced to be parallel
LEVSHIFT a level shifter of 0.3 hartree, maintained after diagonalization,
3 1 causes a lock in a non-conducting solution
MAXCYCLE the maximum number of SCF cycles is set to 50
50
PPAN Mulliken population analysis at the end of SCF cycles
END
```

Deck 2 (SCF input only)

```

4 0 4
GUESSP          initial guess: density matrix from a previous run
SPINEDIT        elements of the density matrix are modified
2              the diagonal elements corresponding to 2 atoms
5 6            label of the 2 atoms (6 is equivalent to 5)
LEVSHIFT        a level shifter of 0.3 hartree, maintained after diagonalization,
3 1            causes a lock in a non-conducting solution
PPAN           Mulliken population analysis at the end of SCF cycles
END

```

```

=====
First run - geometry output
=====

```

COORDINATES OF THE EQUIVALENT ATOMS (FRACTIONAL UNITS)

| N. ATOM | EQUIVALENT | AT. NUMBER | | X | Y | Z |
|---------|------------|------------|-------|------------|------------|------------|
| 1 | 1 | 1 | 24 CR | -5.000E-01 | -5.000E-01 | -5.000E-01 |
| 2 | 1 | 2 | 24 CR | -5.000E-01 | -5.000E-01 | 0.000E+00 |
| 3 | 1 | 3 | 24 CR | 0.000E+00 | -5.000E-01 | -5.000E-01 |
| 4 | 1 | 4 | 24 CR | -5.000E-01 | 0.000E+00 | -5.000E-01 |
| 5 | 2 | 1 | 25 MN | 1.250E-01 | 1.250E-01 | 1.250E-01 |
| 6 | 2 | 2 | 25 MN | -1.250E-01 | -1.250E-01 | -1.250E-01 |
| 7 | 3 | 1 | 8 O | 2.656E-01 | 2.656E-01 | 2.656E-01 |
| 8 | 3 | 2 | 8 O | 2.656E-01 | 2.656E-01 | -2.968E-01 |
| 9 | 3 | 3 | 8 O | -2.968E-01 | 2.656E-01 | 2.656E-01 |
| 10 | 3 | 4 | 8 O | 2.656E-01 | -2.968E-01 | 2.656E-01 |
| 11 | 3 | 5 | 8 O | -2.656E-01 | -2.656E-01 | -2.656E-01 |
| 12 | 3 | 6 | 8 O | -2.656E-01 | -2.656E-01 | 2.968E-01 |
| 13 | 3 | 7 | 8 O | -2.656E-01 | 2.968E-01 | -2.656E-01 |
| 14 | 3 | 8 | 8 O | 2.968E-01 | -2.656E-01 | -2.656E-01 |

```

=====
Ferromagnetic solution: all unpaired electrons with the same spin
=====

```

SPIN POLARIZATION - ALPHA-BETA = 22 FOR 50 CYCLES

```

=====
Convergence on total energy reached in 33 cycles (level shifter active)
=====

```

CYCLE 33 ETOT(AU) -7.072805900367E+03 DETOT -8.168E-07 DE(K) 9.487E+00

```

=====
Population analysis - ferromagnetic solution
=====

```

MULLIKEN POPULATION ANALYSIS

ALPHA+BETA ELECTRONS - NO. OF ELECTRONS 210.000000

| ATOM | Z | CHARGE | SHELL POPULATION | | | | | | |
|------|----|--------|------------------|-------|-------|-------|-------|-------|------|
| | | | s | sp | sp | sp | sp | d | d |
| 1 CR | 24 | 21.884 | 2.000 | 8.047 | 2.251 | 4.487 | 1.331 | 3.078 | .690 |
| 5 MN | 25 | 23.147 | 2.000 | 8.081 | 2.170 | 4.299 | 1.489 | 4.478 | .629 |
| 7 O | 8 | 9.521 | 1.996 | 2.644 | 2.467 | 2.414 | | | |

MULLIKEN POPULATION ANALYSIS

ALPHA-BETA ELECTRONS - NO. OF ELECTRONS 22.000000

| ATOM | Z | CHARGE | SHELL POPULATION | | | | | | |
|------|----|--------|------------------|-------|-------|------|-------|-------|------|
| | | | s | sp | sp | sp | sp | d | d |
| 1 CR | 24 | 3.057 | .000 | -.002 | .011 | .027 | -.011 | 2.790 | .242 |
| 5 MN | 25 | 4.925 | .000 | -.003 | .019 | .055 | -.052 | 4.408 | .498 |
| 7 O | 8 | -.010 | .000 | .003 | -.014 | .002 | | | |

```

=====
Second run - Anti ferromagnetic solution:

```

Integrals calculation not affected by the spin state

Cr (atoms 1-2-3-4) unpaired electrons spin alpha;

Mn (atoms 5 and 6) unpaired electrons spin beta

```

=====
RESTART FROM A PREVIOUS RUN DENSITY MATRIX

```

SPIN INVERSION IN SPIN DENSITY MATRIX FOR ATOMS: 5 6

```

=====
Convergence on total energy reached in 15 cycles

```

```
=====
CYCLE 15 ETOT(AU) -7.0728080821E+03 DETOT -4.930E-07 DE(K) 6.694E-06
=====
```

```
=====uuuu=====
Population analysis - anti ferromagnetic solution
=====
```

```
MULLIKEN POPULATION ANALYSIS
ALPHA+BETA ELECTRONS - NO. OF ELECTRONS 210.000000
```

| ATOM | Z | CHARGE | SHELL POPULATION | | | | | | | |
|------|----|--------|------------------|-------|-------|-------|-------|-------|-------|------|
| | | | s | sp | sp | sp | sp | d | d | |
| 1 | CR | 24 | 21.884 | 2.000 | 8.047 | 2.251 | 4.487 | 1.331 | 3.078 | .690 |
| 5 | MN | 25 | 23.149 | 2.000 | 8.081 | 2.170 | 4.299 | 1.489 | 4.479 | .631 |
| 7 | O | 8 | 9.521 | 1.997 | 2.644 | 2.467 | 2.414 | | | |

```
MULLIKEN POPULATION ANALYSIS
ALPHA-BETA ELECTRONS - NO. OF ELECTRONS 2.000000
```

| ATOM | Z | CHARGE | SHELL POPULATION | | | | | | | |
|------|----|--------|------------------|------|-------|-------|-------|-------|--------|-------|
| | | | s | sp | sp | sp | sp | d | d | |
| 1 | CR | 24 | 3.049 | .000 | -.002 | .011 | .027 | -.012 | 2.785 | .240 |
| 5 | MN | 25 | -4.917 | .000 | .003 | -.018 | -.055 | .054 | -4.406 | -.495 |
| 7 | O | 8 | -.045 | .000 | -.024 | -.013 | -.008 | | | |

11.4 Geometry optimization

Crystal geometry input section (block1) for the geometry optimization of the urea molecule:

▷ Example

| | |
|-------------------------|--|
| Urea Molecule | Title |
| MOLECULE | Dimension of the system |
| 15 | Point group (C_{2v}) |
| 5 | Number of non equivalent atoms |
| 6 0. 0. 0. | Atomic number and cartesian coordinates |
| 8 0. 0. 1.261401 | |
| 7 0. 1.148247 -0.699790 | |
| 1 0. 2.026550 -0.202817 | |
| 1 0. 1.134080 -1.704975 | |
| OPTGEOM | Keyword to perform a geometry optimization |
| ENDOPT | End of geometry optimization input block |
| END | end og geometry input |
| Basis set input | As in test 12 |
| END | End of basis set input section |
| END | block3 input - Molecule - no information on sampling in \mathbf{K} space |

Crystal output contains additional information on the optimization run after the initial part of the geometry output:

BERNY OPTIMIZATION CONTROL

```

. . . . .
MAXIMUM GRADIENT COMPONENT 0.00045 MAXIMUM DISPLACEMENT COMPONENT 0.00030
R.M.S. OF GRADIENT COMPONENT 0.00180 R.M.S. OF DISPLACEMENT COMPONENTS 0.00120
THRESHOLD ON ENERGY CHANGE 0.100E-06 EXTRAPOLATING POLYNOMIAL ORDER 2
MAXIMUM ALLOWED NUMBER OF STEPS 100 SORTING OF ENERGY POINTS: NO
ANALYTICAL GRADIENTS
. . . . .
```

```
SYMMETRY ALLOWED INTERNAL DEGREE(S) OF FREEDOM: 7
. . . . .
```

At the first step of the optimization, the **Crystal** standard output contains both energy (complete SCF cycle) and gradient parts. At the end of the first step, a convergence check is performed on the initial forces and the optimization stops if the criteria are already satisfied. For the subsequent steps, only few lines on the optimization process are reported in standard output, namely: current geometry, total energy and gradients, and convergence tests (SCF output is routed to file SCFOUT.LOG).

At each optimization step, xxx, the geometry is written in file optcxxx (in a format suitable to be read with EXTERNAL keyword). Optimization step can be restarted from any step geometry, by renaming optcxxx as fort.34.

The standard output for the urea molecule geometry optimization looks as follows:

```

OPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPT
*****
GEOMETRY OPTIMIZATION - POINT      2
*****
ATOMS IN THE ASYMMETRIC UNIT      5 - ATOMS IN THE UNIT CELL:      8
ATOM      X(ANGSTROM)      Y(ANGSTROM)      Z(ANGSTROM)
*****
 1 T      6 C      0.000000000000E+00  0.000000000000E+00  2.645266012706E-02
 2 T      8 O      0.000000000000E+00  0.000000000000E+00  1.241474126876E+00
 3 T      7 N      0.000000000000E+00  1.150483100972E+00 -7.044307566681E-01
 4 F      7 N      0.000000000000E+00 -1.150483100972E+00 -7.044307566681E-01
 5 T      1 H      0.000000000000E+00  2.022583078191E+00 -2.043778206895E-01
 6 F      1 H      0.000000000000E+00 -2.022583078191E+00 -2.043778206895E-01
 7 T      1 H      0.000000000000E+00  1.135517317174E+00 -1.702036316144E+00
 8 F      1 H      0.000000000000E+00 -1.135517317174E+00 -1.702036316144E+00

T = ATOM BELONGING TO THE ASYMMETRIC UNIT

INTRACELL NUCLEAR REPULSION (A.U.)  1.2463005288098E+02

TOTAL ENERGY(HF)(AU)( 11) -2.2379435865343E+02 DE-4.8E-08 DP 7.2E-06

SYMMETRY ALLOWED FORCES (ANALYTICAL) (DIRECTION, FORCE)

 1  4.0854048E-02  2 -2.8460660E-02  3  1.4184257E-03  4 -3.0361419E-03
 5 -1.7599295E-02  6 -1.3809310E-02  7  6.7962224E-03

GRADIENT NORM      0.055108  GRADIENT THRESHOLD      0.500000

MAX GRADIENT      0.040854  THRESHOLD      0.000450  CONVERGED NO
RMS GRADIENT      0.020829  THRESHOLD      0.000300  CONVERGED NO
MAX DISPLAC.      0.024990  THRESHOLD      0.001800  CONVERGED NO
RMS DISPLAC.      0.015649  THRESHOLD      0.001200  CONVERGED NO

```

When all four convergence tests are satisfied, optimization is completed. The final energy and the optimized structure are printed after the final convergence tests.

```

*****
* OPT END - CONVERGED * E(AU): -2.237958289701E+02 POINTS  14 *
*****
. . . . .

FINAL OPTIMIZED GEOMETRY - DIMENSIONALITY OF THE SYSTEM      0
(NON PERIODIC DIRECTION: LATTICE PARAMETER FORMALLY SET TO 500)
*****
ATOMS IN THE ASYMMETRIC UNIT      5 - ATOMS IN THE UNIT CELL:      8
ATOM      X(ANGSTROM)      Y(ANGSTROM)      Z(ANGSTROM)
*****
 1 T      6 C      0.000000000000E+00  0.000000000000E+00  3.468988750953E-02
 2 T      8 O      0.000000000000E+00  0.000000000000E+00  1.230143233209E+00
 3 T      7 N      0.000000000000E+00  1.143750090534E+00 -7.056136525307E-01
 4 F      7 N      0.000000000000E+00 -1.143750090534E+00 -7.056136525307E-01
 5 T      1 H      0.000000000000E+00  2.001317638364E+00 -2.076003454226E-01
 6 F      1 H      0.000000000000E+00 -2.001317638364E+00 -2.076003454226E-01
 7 T      1 H      0.000000000000E+00  1.157946292824E+00 -1.696084062406E+00

```

```

      8 F   1 H   0.000000000000E+00 -1.157946292824E+00 -1.696084062406E+00
T = ATOM BELONGING TO THE ASYMMETRIC UNIT
INTRACELL NUCLEAR REPULSION (A.U.) 1.2541002823701E+02
**** 4 SYMMOPS - TRANSLATORS IN FRACTIONAL UNITS
V INV          ROTATION MATRICES          TRANSLATOR
1 1 1.00 0.00 0.00 0.00 1.00 0.00 0.00 0.00 1.00 0.00 0.00 0.00
2 2 -1.00 0.00 0.00 0.00 -1.00 0.00 0.00 0.00 1.00 0.00 0.00 0.00
3 3 -1.00 0.00 0.00 0.00 1.00 0.00 0.00 0.00 1.00 0.00 0.00 0.00
4 4 1.00 0.00 0.00 0.00 -1.00 0.00 0.00 0.00 1.00 0.00 0.00 0.00

```

The final geometry is both printed in the **Crystal** output and written in file fort.34. The following input defines the geometry, reading data from file fort.34 (keyword **EXTERNAL**, input block1, page 16).

▷ Example

```

      Urea Molecule  Title
      EXTERNAL      Geometry read from file fort.34
      optional keywords
      END              End of the geometry input section

```

Optimization can restart, by adding the keyword **RESTART** in the same input deck used for the first optimization run. Information to restart are read from file OPTINFO.DAT, updated after each optimization cycle.

▷ Example

| Initial input | Restart input |
|-------------------------|-------------------------|
| Urea Molecule | Urea Molecule |
| MOLECULE | MOLECULE |
| 15 | 15 |
| 5 | 5 |
| 6 0. 0. 0. | 6 0. 0. 0. |
| 8 0. 0. 1.261401 | 8 0. 0. 1.261401 |
| 7 0. 1.148247 -0.699790 | 7 0. 1.148247 -0.699790 |
| 1 0. 2.026550 -0.202817 | 1 0. 2.026550 -0.202817 |
| 1 0. 1.134080 -1.704975 | 1 0. 1.134080 -1.704975 |
| OPTGEOM | OPTGEOM |
| ENDOPT | RESTART |
| END | ENDOPT |
| | END |

Partial optimization

In order to optimize the coordinates of the hydrogens in urea molecule, the following input must be entered:

▷ Example

| | |
|-------------------------|--|
| Urea Molecule | Title |
| MOLECULE | Dimension of the system |
| 15 | Point group (C_{2v}) |
| 5 | Number of non equivalent atoms |
| 6 0. 0. 0. | Atomic number and cartesian coordinates |
| 8 0. 0. 1.261401 | |
| 7 0. 1.148247 -0.699790 | |
| 1 0. 2.026550 -0.202817 | |
| 1 0. 1.134080 -1.704975 | |
| KEEPSYMM | maintain symmetry in subsequent operations |
| OPTGEOM | Keyword to perform a geometry optimization |
| FRAGMENT | Keyword for a partial optimization |
| 2 | Number of atoms to be optimized |
| 5 7 | Label of the atoms to be optimized |
| ENDOPT | End of the geometry optimization input block |
| END | End of the geometry input section |

The atoms allowed to move are the two hydrogens irreducible, 5 and 7. The symmetry is maintained, atoms 6 and 7 are allowed to move.

```
*****
* PARTIAL OPTIMIZATION - ATOMS FREE TO MOVE    2  INPUT LIST :
5( 1)  7( 1)
SYMMETRY IS KEPT
ATOM  5 AND  6 ARE LINKED BY SYMMOP  2
ATOM  7 AND  8 ARE LINKED BY SYMMOP  2
*****
```

If the symmetry is not maintained (default, no KEEPSYMM before OPTGEOM) the symmetry operators linking atoms 5 and 6, and atoms 7 and 8, are removed.

```
*****
* PARTIAL OPTIMIZATION - ATOMS FREE TO MOVE    2  INPUT LIST :
5( 1)  7( 1)
SYMMETRY MAY BE BROKEN
THE NUMBER OF SYMMETRY OPERATORS HAS BEEN REDUCED FROM  4 TO  2
*****
.....
SYMMETRY ALLOWED INTERNAL DEGREE(S) OF FREEDOM:  4
.....
```

Final run

During optimization process, the classification of the integrals is done with reference to the input geometry, and used for all subsequent wave function calculations.

In some cases, when the optimized geometry is far from the original one, the series truncation defined with reference to the starting geometry may be inhomogeneous if applied to the final geometry (see keyword **FIXINDEX** for explanation). In those cases, the total energy computed for one geometry, with integrals selected according to a different geometry, may be not correct.

A single point calculation, with the final optimized geometry, allows to check if that is the case.

A safe procedure to check if that geometry corresponds to a real energy minimum, is to perform a second optimization process, with same truncation criteria, starting from the geometry obtained in the first optimization (read from file fort.34, keyword **EXTERNAL**, page 16).

The keyword **FINALRUN** starts the process automatically. (it does not work with Pcrystal)

A typical example is the geometry optimization of a surface, described with a slab model. The optimization process may lead to a structure significantly different from the one cut from the bulk, when there is surface relaxation. As an example, the geometry optimization of the surface (001) of the α -Al₂O₃ is reported.

▷ Example - Optimization of surface

```

α -Al2O3 - (001) surface title
CRYSTAL dimension of the system
0 0 0
167 space group
4.7602 12.9933 lattice parameters
2 number of irreducible atoms
13 0. 0. 0.35216 fractional coordinates of first atom
8 0.30624 0. 0.25 fractional coordinates of second atom
SLABCUT 3D→2D
0 0 1 (h, k, l) Miller indices of the surface
1 6 number of layers, starting from the first classified
OPTGEOM Keyword to perform a geometry optimization
FINALRUN keyword to check gradients vs true series truncation
3 new optimization if convergence criteria are not satisfied
ENDOPT end of the geometry optimization input block
END end of the geometry input section

```

Neighbors analysis on the initial geometry obtained with SLABCUT

```

N = NUMBER OF NEIGHBORS AT DISTANCE R 11 cycles
ATOM N R/ANG R/AU NEIGHBORS (ATOM LABELS AND CELL INDICES)
1 AL 3 1.8551 3.5057 2 0 0 0 0 3 0 0 0 0 4 0 0 1 0
1 AL 3 3.2192 6.0834 5 AL 0 0 0 5 AL 1 1 0 5 AL 0 1 0
1 AL 3 3.2219 6.0885 2 0 -1 0 0 3 0 1 1 0 4 0 0 0 0
1 AL 3 3.4295 6.4808 7 0 0 1 0 8 0 0 1 0 9 0 0 0 0
1 AL 3 3.4990 6.6121 6 AL 0 0 0 6 AL -1 0 0 6 AL 0 1 0
1 AL 1 3.8419 7.2601 10 AL 0 0 0

```

Total energy E = -1399.7999027 hartree

Series truncation is defined with reference to that geometry. Optimization begins. After 11 cycles convergence on gradients and displacements is satisfied.

Neighbors analysis on the optimized geometry:

```

N = NUMBER OF NEIGHBORS AT DISTANCE Ra 6 cycles
ATOM N R/ANG R/AU NEIGHBORS (ATOM LABELS AND CELL INDICES)
1 AL 3 1.6886 3.1911 2 0 0 0 0 3 0 0 0 0 4 0 0 1 0
1 AL 1 2.6116 4.9351 10 AL 0 0 0
1 AL 3 2.8198 5.3286 7 0 0 1 0 8 0 0 1 0 9 0 0 0 0
1 AL 3 3.0425 5.7494 5 AL 0 0 0 5 AL 1 1 0 5 AL 0 1 0

```



```

1 AL 3 3.0430 5.7504 6 AL 0 0 0 6 AL -1 0 0 6 AL 0 1 0
1 AL 3 3.1214 5.8987 2 0 -1 0 0 3 0 1 1 0 4 0 0 0 0

```

Total energy E = -1400.1148194 hartree

A large geometrical relaxation occurred during the optimization: the aluminium atoms move toward the core of the slab. In this case both the total energy and gradients should be recalculate using truncation series which refer to the final relaxed geometry.

This crucial step is automatically performed if the keyword FINALRUN is present in the input file. If this is the case, CRYSTAL03 checks for the numerical consistency and it will find that the gradients do not match the requested convergence criteria. At the end of the new optimization the total energy is:

Total energy E = -1400.1193593 hartree

In this case, FINALRUN was followed by the keyword ICODE=3. This means that the geometry optimization restarts from the very last step of the previous geometry optimization with truncation series criteria defined relative to that geometry. After 6 new optimization cycles, convergence criteria are satisfied.

Neighbors analysis on the final run optimized geometry

```

N = NUMBER OF NEIGHBORS AT DISTANCE R
  ATOM N    R/ANG    R/AU  NEIGHBORS (ATOM LABELS AND CELL INDICES)
1 AL 3    1.6863    3.1867  2 0  0 0 0  3 0  0 0 0  4 0  0 1 0
1 AL 1    2.5917    4.8976 10 AL 0 0 0
1 AL 3    2.8095    5.3092  7 0  0 1 0  8 0  0 1 0  9 0  0 0 0
1 AL 3    3.0382    5.7414  5 AL 0 0 0  5 AL  1 1 0  5 AL  0 1 0
1 AL 3    3.0387    5.7424  6 AL 0 0 0  6 AL -1 0 0  6 AL  0 1 0
1 AL 3    3.1215    5.8987  2 0 -1 0 0  3 0  1 1 0  4 0  0 0 0

```

Total energy E = -1400.1194545 hartree

The final geometry is printed, and written in file fort.34.

A final check on total energy can be done with the following input:

```

alpha-Al2O3 (corundum) 001 2 LAYERS (3D-->2D)
EXTERNAL
OPTGEOM
ENDOPT
END

```

The keyword EXTERNAL routes the basic geometry input stream to file fort.34, written at the end of the optimization run.

No optimization starts, convergence criteria are already satisfied.

Total energy E = -1400.1194544 hartree

/sectionScanning of vibrational modes - SCANMODE

Methane molecule

```
MOLECULE
44
2
6      0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
1      6.252140000000E-01  6.252140000000E-01  6.252140000000E-01
FREQCALC
SCANMODE
-1 -1 0 0.1
12
ENDfreq
END
6 3
0 0 3 2. 1.
172.256000      0.617669000E-01
25.9109000      0.358794000
5.53335000      0.700713000
0 1 2 4. 1.
3.66498000      -0.395897000      0.236460000
0.770545000      1.21584000      0.860619000
0 1 1 0. 1.
0.195857000      1.00000000      1.00000000
1 2
0 0 2 1. 1.
5.44717800      0.156285000
0.824547000      0.904691000
0 0 1 0. 1.
0.183192000      1.00000000
99 0
END
TOLINTEG
20 20 20 20 20
END
TOLDEE
11
END
```

PbCO₃

```
PBCO3 - frequency calculation
CRYSTAL
1 0 0
P m c n
5.20471446      8.45344758      6.16074145
4
282      2.500000000000E-01  4.175726169487E-01  -2.463557995068E-01
6      2.500000000000E-01  -2.363341497085E-01  -8.558132726424E-02
8      2.500000000000E-01  -8.360585350428E-02  -9.431628799197E-02
8      4.648370653436E-01  -3.129222129903E-01  -8.842925698155E-02
FREQCALC
RESTART
SCANMODE
1 -40 40 0.1
1
END
```

```

END
282 4
HAYWLC
0 1 2 4. 1.
  1.335104 -0.1448789 -0.1070612
  0.7516086 1.0 1.0
0 1 1 0. 1.
  0.5536686 1.0 1.0
0 1 1 0. 1.
  0.1420315 1.0 1.0
0 3 1 0. 1.
  0.1933887 1.0
6 4
0 0 6 2.0 1.0
  3048.0 0.001826
  456.4 0.01406
  103.7 0.06876
  29.23 0.2304
  9.349 0.4685
  3.189 0.3628
0 1 2 4.0 1.0
  3.665 -0.3959 0.2365
  0.7705 1.216 0.8606
0 1 1 0.0 1.0
  0.26 1.0 1.0
0 3 1 0.0 1.0
  0.8 1.0
8 4
0 0 6 2.0 1.0
  .5484671660D+04 .1831074430D-02
  .8252349460D+03 .1395017220D-01
  .1880469580D+03 .6844507810D-01
  .5296450000D+02 .2327143360D+00
  .1689757040D+02 .4701928980D+00
  .5799635340D+01 .3585208530D+00
0 1 3 6.0 1.0
  .1553961625D+02 -.1107775490D+00 .7087426820D-01
  .3599933586D+01 -.1480262620D+00 .3397528390D+00
  .1013761750D+01 .1130767010D+01 .7271585770D+00
0 1 1 0.0 1.0
  .2700058226D+00 .1000000000D+01 .1000000000D+01
0 3 1 0.0 1.0
  .8000000000D+00 .1000000000D+01
99 0
ENDBS
SCFDIR
DFT
B3LYP
RADIAL
1
4.0
99
ANGULAR
5
0.1667 0.5 0.9 3.5 9999.0
6 10 14 18 14
END

```

SHRINK
6 6
LEVSHIFT
5 0
TOLDEE
10
MAXCYCLE
200
ENDSCF

Chapter 12

Basis set

The most common source of problems with CRYSTAL is probably connected with the basis set. It should never be forgotten that ultimately the basis functions are Bloch functions, modulated over the infinite lattice: any attempt to use large uncontracted molecular or atomic basis sets, with very diffuse functions can result in the wasting of computational resources. The densely packed nature of many crystalline structures gives rise to a large overlap between the basis functions, and a quasi-linear dependence can occur, due to numerical limitations.

The choice of the basis set (BS) is one of the critical points, due to the large variety of chemical bonding that can be found in a periodic system. For example, carbon can be involved in covalent bonds (polyacetylene, diamond) as well as in strongly ionic situations (Be_2C , where the Mulliken charge of carbon is close to -4).

Many basis sets for lighter elements and the first row transition metal ions have been developed for use in periodic systems. A selection of these which have been used in published work are available on WWW:

<http://www.crystal.unito.it>

We summarize here some general considerations which can be useful in the construction of a BS for periodic systems.

It is always useful to refer to some standard basis set; Pople's STO-nG, 3-21G and 6-21G have proved to be good starting points. A molecular minimal basis set can in some cases be used as it is; larger basis sets must be re-optimized specifically for the chemical periodic structure under study.

Let us explore the adequacy of the molecular BS for crystalline compounds and add some considerations which can be useful when a molecular BS must be modified or when an *ex novo* crystalline BS is defined.

12.1 Molecular BSs performance in periodic systems

Two sets of all electron basis sets are included in CRYSTAL (see Chapter 1.2):

1. Minimal STO-nG basis set of Pople and co-workers
obtained by fitting Slater type orbitals with n contracted GTFs (n from 2 to 6, atomic number from 1 to 54) [100, 99, 137, 136].

The above BSs are still widely used in spite of the poor quality of the resulting wave function, because they are well documented and as a rule provide quite reasonable optimized geometries (due to fortuitous cancellation of errors) at low cost.

2. "Split valence" 3-21 and 6-21 BSs.
The core shells are described as a linear combination of 3 (up to atomic number 54) or 6 (up to atomic number 18) gaussians; the two valence shells contain two and one gaussians, respectively [21, 88]. Exponents (s and p functions of the same shell share the same exponent) and contraction coefficients have been optimized variationally for the isolated atoms.

A single set of polarization functions (p,d) can be added without causing numerical problems. Standard molecular polarization functions are usually also adequate for periodic compounds.

When free basis sets are chosen, two points should be taken into account:

1. From the point of view of CPU time, basis sets with *sp* shells (*s* and *p* functions sharing the same set of exponents) can give a saving factor as large as 4, in comparison with basis sets where *s* and *p* have different exponents.
2. As a rule, extended atomic BSs, or 'triple zeta' type BSs should be avoided. Many of the high quality molecular BSs (Roos, Dunning, Huzinaga) cannot be used in CRYSTAL without modification, because the outer functions are too diffuse. One should not forget that the real basis functions are Bloch functions.

Let us consider in more detail the possibility of using molecular BS for periodic systems. We can refer to five different situations:

| | | |
|---------|------------|--------------------|
| Core | functions | |
| Valence | functions: | molecular crystals |
| | | covalent crystals |
| | | ionic crystals |
| | | metals. |

12.2 Core functions

In this case standard (contracted) molecular BSs can be adopted without modification, because even when very strong crystal field effects are present, the deformation of inner states is small, and can be correctly described through the linear variational parameters in SCF calculation. An adequate description of the core states is important in order to avoid large basis set superposition errors.

12.3 Valence functions

Molecular crystals

Molecular BSs, minimal and split-valence, are perfectly adequate. Tests have been performed on bulk urea [46] and oxalic acid, where the molecules are at relatively small distances, with STO-3G, 6-21, 6-21* and 6-21** BSs presenting no problem.

Covalent crystals.

Standard minimal and split valence BSs are usually adequate. In the split valence case the best exponent of the most diffuse shell is always slightly higher than the one proposed for molecules; in general it is advisable to re-optimize the exponent of this shell. This produces a slightly improved basis, while reducing the cost of the calculation. Let us consider for example the 6-21 basis set for carbon (in diamond) and silicon (bulk).

At an atomic level, the best exponent of the outer shell is 0.196 and 0.093 for C and Si, respectively. Optimization of the valence shell has been repeated in the two crystalline compounds. The innermost valence shell is essentially unaltered with respect to the atomic solution; for the outer single-gaussian shell the best exponent is around 0.22 and 0.11 bohr⁻² for carbon and silicon, as shown in Table 12.1. The last entry of Table 12.1 refers to "catastrophic" behaviour: the low value of the exponent generates unphysical states.

A set of 5 polarization single-gaussian d functions can be added to the 6-21G basis (6-21G* BS); the best exponents for the solid are very close to those resulting from the optimization in molecular contexts: 0.8 for diamond [93] and 0.45 for silicon.

Basis sets for III-V and IV-IV semiconductors (all electron and valence electron (to be associated with effective core pseudopotentials) are given in references [123, 35].

Table 12.1: Total energy per cell and number of computed bielectronic integrals in 10^6 units (N), as a function of the exponent α (bohr $^{-2}$) of the most diffuse shell for carbon and silicon.

| Diamond | | | Silicon | | |
|---------|-----|-------------|---------|-----|-------------|
| a | N | Et | a | N | Et |
| 0.296 | 58 | -75.6633 | 0.168 | 46 | -577.8099 |
| 0.276 | 74 | -75.6728 | 0.153 | 53 | -577.8181 |
| 0.256 | 83 | -75.6779 | 0.138 | 72 | -577.8231 |
| 0.236 | 109 | -75.6800 | 0.123 | 104 | -577.8268 |
| 0.216 | 148 | -75.6802 | 0.108 | 151 | -577.8276 |
| 0.196 | 241 | -75.6783 | 0.093 | 250 | -577.8266 |
| 0.176 | 349 | catastrophe | 0.078 | 462 | catastrophe |

Ionic crystals.

Cations

The classification of covalent or ionic crystals is highly conventional, many systems being midway. Let us first consider totally ionic compounds, such as LiH, MgO, or similar. For these systems the cation valence shell is completely empty. Therefore, for cations it is convenient to use a basis set containing the core functions plus an additional sp shell with a relatively high exponent. For example, we used for Mg in MgO and for Li in LiH (Li₂O and Li₃N) a 'valence' sp shell with exponent 0.4-0.3 and 0.5-0.6, respectively [51, 34].

The crystalline total energies obtained by using only core functions for Li or Mg and by adding a valence shell to the cation differ by 0.1 eV/atom, or less. This figure is essentially the same for a relatively large range of exponents of the valence shell (say 0.5-0.2 for Mg) [34].

It can be difficult (or impossible) to optimize the exponents of nearly empty shells: the energy decreases almost linearly with the exponent. Very low exponent values can give rise to numerical instabilities, or require the calculation of an enormous number of integrals (selected on the basis of overlap criteria). In the latter cases, when the energy gain is small ($\Delta E \leq 1$ mhartree for $\Delta\alpha = 0.2$ bohr $^{-2}$), it is convenient to use a relatively large exponent.

Anions

Reference to isolated ion solutions is only possible for halides, because in such cases the ions are stable even at the HF level. For other anions, which are stabilized by the crystalline field (H^- , O^{2-} , N^{3-} and also C^{4-}), the basis set must be re-designed with reference to the crystalline environment. For example, let us consider the optimization of the O^{2-} BS in Li_2O [51]. Preliminary tests indicated the fully ionic nature of the compound; the point was then to allow the valence distribution to relax in the presence of the two extra electrons. We started from a standard STO-6G BS. Two more gaussians were introduced in the 1s contraction, in order to improve the virial coefficient and total energy, as a check of wave function quality. The 6 valence gaussians were contracted according to a 411 scheme; the exponents of the two outer independent gaussians and the coefficients of the four contracted ones were optimized. Whereas the two most diffuse gaussians are more diffuse than in the neutral isolated atom ($\alpha=0.45$ and 0.15 to be compared with $\alpha=0.54$ and 0.24 respectively), the rest of the O^{2-} valence shell is unchanged with respect to the atomic situation. The introduction of d functions in the oxygen basis-set causes only a minor improvement in energy ($1 \cdot 10^{-4}$ hartree/cell, with a population of 0.02 electrons/atom in the cell). Ionic BSs for H and N can be found in reference 1.

For anions, re-optimization of the most diffuse valence shell is mandatory; when starting from a standard basis set, the most diffuse (or the two most diffuse) gaussians must be allowed to relax.

From covalent to ionics

Intermediate situations must be considered individually, and a certain number of tests must be performed in order to verify the adequacy of the selected BSs.

Let us consider for example α -quartz (SiO_2) and corundum (Al_2O_3). The exponent of the outer shell for the 2 cations in the 6-21G BS is 0.093 (Si) and 0.064 (Al), respectively; in both cases this function is too diffuse (in particular in the Al case it causes numerical catastrophes). For quartz, re-optimization in the bulk gives $\alpha=0.15$ bohr⁻² for Si (the dependence of total energy per Si atom on α is much smaller than the one resulting from Table 12.1; note too that the cost at $\alpha=0.15$ is only 50% of the one at $\alpha=0.09$). On the contrary, the best molecular and crystalline exponent ($\alpha=0.37$) for oxygen coincide. Corundum is more ionic than quartz, and about 2 valence electrons are transferred to oxygen. In this case it is better to eliminate the most diffuse valence shell of Al, and to use as independent functions the two gaussians of the inner valence shells ($\alpha=0.94$ and 0.20 bohr⁻², respectively [153]).

Metals

Very diffuse gaussians are required to reproduce the nearly uniform density characterizing simple metallic systems, such as lithium and beryllium. This is the worse situation, where a full optimization of the atomic basis set is probably impossible. Functions which are too diffuse can create numerical problems, as will be discussed below.

The optimization procedure can start from 6-21 BS; the most diffuse valence shell (exponent 0.028 for Li and 0.077 for Be) can be dropped and the innermost valence shell (exponents 0.54 and 0.10 for Li, and 1.29 and 0.268 for Be) can be split.

Table 12.2: Example of BS for metallic lithium and beryllium derived from the standard 6-21G BS

| Lithium | | | Beryllium | | |
|---------|---------|------------|-----------|---------|------------|
| shell | Exp. | Coeff. | shell | Exp. | Coeff. |
| s | 642.418 | 0.00215096 | s | 1264.50 | 0.00194336 |
| | 96.5164 | 0.0162677 | | 189.930 | 0.0148251 |
| | 22.0174 | 0.0776383 | | 43.1275 | 0.0720662 |
| | 6.1764 | 0.246495 | | 12.0889 | 0.237022 |
| | 1.93511 | 0.467506 | | 3.80790 | 0.468789 |
| sp | 0.640 | 1. 1. | | 1.282 | 1. 1. |
| sp | 0.10 | 1. 1. | | 0.27 | 1. 1. |

At this point the outer gaussian of the 6G core contraction, with very similar exponents (0.64 and 1.28) to those of the innermost valence shell (0.54 and 1.29), can be used as an independent (sp) function, and the innermost valence shell can be eliminated.

The resulting (reasonable) BS, derived from the split valence standard one, is reported in Table 12.2. Finally, the most diffuse gaussian can be optimized; in the two cases the minimum has not been found owing to numerical instabilities.

See [47] for a more extensive discussion of the metallic lithium case.

12.4 Hints on crystalline basis set optimization

In the definition of a valence shell BS, each exponent can be varied in a relatively narrow range: in the direction of higher exponents, large overlaps with the innermost functions may occur (the rule of thumb is: exponents must be in a ratio not too far from 3; ratios smaller than

2 can give linear dependence problems); proceeding towards lower exponents, one must avoid large overlaps with a high number of neighbours (remember: the basis functions are Bloch functions).

Diffuse gaussian orbitals play a critical role in HF-LCAO calculations of crystals, especially the three-dimensional ones; they are *expensive, not always useful, in some cases dangerous*.

- Cost.

The number of integrals to be calculated increases dramatically with decreasing exponents; this effect is almost absent in molecular calculations. Table 12.1 shows that the cost of the calculation (number of bielectronic integrals) for silicon (diamond) can increase by a factor 10 (6) simply by changing the exponent of the most diffuse single-gaussian from 0.168 to 0.078 (0.296 to 0.176). The cost is largely dominated by this shell, despite the fact that large contractions are used for the 1s, 2sp and the innermost valence shell.

A high number of contracted primitives tremendously increases the integrals computation time.

- Usefulness.

In atoms and molecules a large part of the additional variational freedom provided by diffuse functions is used to describe the tails of the wave function, which are poorly represented by the e^{-ar^2} decay of the gaussian function. On the contrary, in crystalline compounds (in particular 3D non-metallic systems), low exponent functions do not contribute appreciably to the wave function, due to the large overlap between neighbours in all directions. A small split valence BS such as the 6-21G one, is nearer to the variational limit in crystals than in molecules.

- Numerical accuracy and catastrophic behaviour.

In some conditions, during the SCF (periodic) calculation, the system 'falls' into non-physical states, characterized by very low single particle and total energies (see for example the last entry in Table 12.1 and the above discussion on metals).

This behaviour, generically interpreted in our early papers as due to 'linear dependence', is actually due to poor accuracy in the treatment of the Coulomb and exchange series. The exchange series is much more delicate, for two reasons: first, long range contributions are not taken into account (whereas the long range Coulomb contributions are included, although in an approximate way); second, the "pseudoverlap" criteria associated with the two computational parameters ITOL4 and ITOL5 mimic only in an approximate way the real behaviour of the density matrix.

The risks of "numerical catastrophes" increase rapidly with a decreasing exponent; higher precision is required in order to obtain physical solutions.

For non-metallic systems, and split-valence type BSs, the default computational conditions given in section 1.3 are adequate for the optimization of the exponents of the valence shell and for systematic studies of the energy versus volume curves.

For metallic systems, the optimization of the energy versus exponent curve could require extremely severe conditions for the exchange series and, as a consequence, for the reciprocal space net. Reasonable values of the valence shell exponent (say 0.23 for beryllium and 0.10 for lithium, see Table 12.2), though not corresponding to a variational minimum, are reasonably adequate for the study of the structural and electronic properties of metallic systems (see reference 1).

12.5 Check on basis-set quasi-linear-dependence

In order to check the risk of linear dependence of Bloch functions, it is possible to calculate the eigenvalues of the overlap matrix in reciprocal space by running **integrals** and entering the keyword **EIGS** (input block 3, page 93). Full input (general information, geometry, basis set, SCF) is to be entered.

The overlap matrix in direct space is Fourier transformed at all the k points generated in the irreducible part of the Brillouin zone, and diagonalized. The eigenvalues are printed.

The higher the numerical accuracy obtained by severe computational conditions, the closer to 0 can be the eigenvalues without risk of numerical instabilities. Negative values indicate numerical linear dependence. The program stops after the check (even if negative eigenvalues are not detected).

The Cholesky reduction scheme [107] requires basis functions linearly independent. A symptom of numerical dependence may produce an error message in RHOLSK or CHOLSK while running **scf**.

Chapter 13

Theoretical framework

13.1 Basic equations

CRYSTAL is an *ab initio* Hartree-Fock LCAO program for the treatment of periodic systems. LCAO, in the present case, means that each Crystalline Orbital, $\psi_i(\mathbf{r}; \mathbf{k})$, is a linear combination of Bloch functions (BF), $\phi_\mu(\mathbf{r}; \mathbf{k})$, defined in terms of local functions, $\varphi_\mu(\mathbf{r})$ (here referred to as Atomic Orbitals, AOs).

$$\psi_i(\mathbf{r}; \mathbf{k}) = \sum_{\mu} a_{\mu,i}(\mathbf{k}) \phi_{\mu}(\mathbf{r}; \mathbf{k}) \quad (13.1)$$

$$\phi_{\mu}(\mathbf{r}; \mathbf{k}) = \sum_{\mathbf{g}} \varphi_{\mu}(\mathbf{r} - \mathbf{A}_{\mu} - \mathbf{g}) e^{i\mathbf{k}\cdot\mathbf{g}} \quad (13.2)$$

\mathbf{A}_{μ} denotes the coordinate of the nucleus in the zero reference cell on which φ_{μ} is centred, and the $\sum_{\mathbf{g}}$ is extended to the set of all lattice vectors \mathbf{g} .

The local functions are expressed as linear combinations of a certain number, n_G , of individually normalized (basis set) Gaussian type functions (GTF) characterized by the same centre, with fixed coefficients, d_j and exponents, α_j , defined in the input:

$$\varphi_{\mu}(\mathbf{r} - \mathbf{A}_{\mu} - \mathbf{g}) = \sum_j^{n_G} d_j G(\alpha_j; \mathbf{r} - \mathbf{A}_{\mu} - \mathbf{g}) \quad (13.3)$$

The AOs belonging to a given atom are grouped into *shells*, λ . The shell can contain all AOs with the same quantum numbers, n and ℓ , (for instance 3s, 2p, 3d shells), or all the AOs with the same principal quantum number, n , if the number of GTFs and the corresponding exponents are the same for all of them (mainly sp shells; this is known as the *sp shells constraint*). These groupings permit a reduction in the number of auxiliary functions that need to be calculated in the evaluation of electron integrals and therefore increase the speed of calculation.

A single, normalized, s-type GTF, G_{λ} , is associated with each shell (the *adjoined Gaussian* of shell λ). The α exponent is the smallest of the α_j exponents of the Gaussians in the contraction. The adjoined Gaussian is used to estimate the AO overlap and select the level of approximation to be adopted for the evaluation of the integrals.

The expansion coefficients of the Bloch functions, $a_{\mu,i}(\mathbf{k})$, are calculated by solving the matrix equation for each reciprocal lattice vector, \mathbf{k} :

$$\mathbf{F}(\mathbf{k})\mathbf{A}(\mathbf{k}) = \mathbf{S}(\mathbf{k})\mathbf{A}(\mathbf{k})\mathbf{E}(\mathbf{k}) \quad (13.4)$$

in which $\mathbf{S}(\mathbf{k})$ is the overlap matrix over the Bloch functions, $\mathbf{E}(\mathbf{k})$ is the diagonal energy matrix and $\mathbf{F}(\mathbf{k})$ is the Fock matrix in reciprocal space:

$$\mathbf{F}(\mathbf{k}) = \sum_{\mathbf{g}} \mathbf{F}^{\mathbf{g}} e^{i\mathbf{k}\cdot\mathbf{g}} \quad (13.5)$$

The matrix elements of $\mathbf{F}^{\mathbf{g}}$, the Fock matrix in direct space, can be written as a sum of one-electron and two-electron contributions in the basis set of the AO:

$$F_{12}^{\mathbf{g}} = H_{12}^{\mathbf{g}} + B_{12}^{\mathbf{g}} \quad (13.6)$$

The one electron contribution is the sum of the kinetic and nuclear attraction terms:

$$H_{12}^{\mathbf{g}} = T_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = \langle \varphi_1^0 | \hat{T} | \varphi_2^{\mathbf{g}} \rangle + \langle \varphi_1^0 | \hat{Z} | \varphi_2^{\mathbf{g}} \rangle \quad (13.7)$$

In core pseudopotential calculations, \hat{Z} includes the sum of the atomic pseudopotentials. The two electron term is the sum of the Coulomb and exchange contributions:

$$B_{12}^{\mathbf{g}} = C_{12}^{\mathbf{g}} + X_{12}^{\mathbf{g}} =$$

$$\sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^0 \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}}) - \frac{1}{2}(\varphi_1^0 \varphi_3^{\mathbf{h}} | \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (13.8)$$

The Coulomb interactions, that is, those of electron-nucleus, electron-electron and nucleus-nucleus, are individually divergent, due to the infinite size of the system. The grouping of corresponding terms is necessary in order to eliminate this divergence.

The $P^{\mathbf{n}}$ density matrix elements in the AOs basis set are computed by integration over the volume of the Brillouin zone (BZ),

$$P_{3,4}^{\mathbf{n}} = 2 \int_{BZ} d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{n}} \sum_j a_{3j}^*(\mathbf{k}) a_{4j}(\mathbf{k}) \theta(\epsilon_F - \epsilon_j(\mathbf{k})) \quad (13.9)$$

where a_{in} denotes the i -th component of the n -th eigenvector, θ is the step function, ϵ_F , the Fermi energy and ϵ_n , the n -th eigenvalue. The total electronic energy per unit cell is given by:

$$E^{elec} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} (H_{12}^{\mathbf{g}} + F_{12}^{\mathbf{g}}) \quad (13.10)$$

A discussion of the different contributions to the total energy is presented in [155, 159] and in Chapter 11 of reference [139].

$$E^{coul} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^0 \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (13.11)$$

$$E^{exch} = -\frac{1}{4} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^0 \varphi_3^{\mathbf{h}} | \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (13.12)$$

13.2 Remarks on the evaluation of the integrals

The approach adopted for the treatment of the Coulomb and exchange series is based on a few simple ideas and on a few general tools, which can be summarized as follows:

1. Where possible, terms of the Coulomb series are aggregated so as to reduce the number of integrals to be evaluated;
2. Exchange integrals which will combine with small density matrix elements are disregarded;
3. Integrals between non-overlapping distributions are approximated;
4. Approximations for large integrals must be very accurate; for small integrals large percentage errors can be accepted;
5. Selection must be very efficient, because a large number of possible terms must be checked (adjoined Gaussians are very useful from this point of view).

13.3 Treatment of the Coulomb series

For the evaluation of the Coulomb contributions to the total energy and Fock matrix, correct coupling of electron-nucleus and electron-electron interactions is essential. The computational technique for doing so was presented by Dovesi et al [50] and by Saunders et al. [159]. It may be summarized as follows.

Consider the Coulomb bielectronic contribution to the Fock matrix ($C_{12}^{\mathbf{g}}$) and to the total energy :

$$E_{ee}^{coul} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^{\mathbf{0}} \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (13.13)$$

Seven indices are involved in equation 13.13; four of them (1, 2, 3 and 4) refer to the AOs of the unit cell; in principle, the other three (\mathbf{g} , \mathbf{n} and \mathbf{h}) span the infinite set of translation vectors: for example, $\varphi_2^{\mathbf{g}}(\mathbf{r})$ is AO number 2 in cell \mathbf{g} . P is the density matrix; the usual notation is used for the bielectronic integrals. Due to the localized nature of the basis set, the total charges, q_1 and q_2 , associated with the two pseudo-overlap distributions: $\{G_{10}G_{2\mathbf{g}}\}$ and $\{G_{3\mathbf{h}}G_{4\mathbf{h}+\mathbf{n}}\}$, decay exponentially to zero with increasing $|\mathbf{g}|$ and $|\mathbf{n}|$ (for example, G_1 is the adjoined gaussian of the shell to which φ_1 belongs).

A *Coulomb overlap* parameter, S_c , can be defined in such a way that when either q_1 or q_2 are smaller than S_c , the bielectronic integral is disregarded, and the sum over \mathbf{g} or \mathbf{n} truncated. The ITOL1 input parameter is defined as **ITOL1** = $-\log_{10} S_c$. The same parameter value is used for selecting overlap, kinetic, and multipole integrals.

The problem of the \mathbf{h} summation in equation 13.13 is more delicate, \mathbf{h} being related to the distance between the two interacting distributions. The multipolar expansion scheme illustrated below is particularly effective when large unit cell or low dimensionality systems are considered. The electron-electron and electron-nuclei series ($C_{12}^{\mathbf{g}}$ and $Z_{12}^{\mathbf{g}}$) can be rearranged as follows:

1. Mulliken shell *net* charge distributions are defined as :

$$\rho_{\lambda}(\mathbf{r} - \mathbf{h}) \equiv \{\lambda\}' \equiv \{\lambda\} - Z_{\lambda} = \sum_{3 \in \lambda} \sum_{4\mathbf{n}} P_{34}^{\mathbf{n}} \varphi_3(\mathbf{r} - \mathbf{h}) \varphi_4(\mathbf{r} - \mathbf{h} - \mathbf{n}) - Z_{\lambda} \quad (13.14)$$

where Z_{λ} is the fraction of nuclear charge formally attributed to shell λ , and $\{\lambda\}$ is the electron charge distribution of shell λ .

2. Z and C contributions are reordered:

$$C_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = \sum_{\lambda} \sum_{\mathbf{h}} \int d\mathbf{r} d\mathbf{r}' \varphi_1^{\mathbf{0}}(\mathbf{r}) \varphi_2^{\mathbf{g}}(\mathbf{r}) |\mathbf{r} - \mathbf{r}' - \mathbf{h}|^{-1} \rho_{\lambda}(\mathbf{r}' - \mathbf{h}) \quad (13.15)$$

3. For a given shell λ , there is a finite set B_{λ} of \mathbf{h} vectors for which the two interacting distributions overlap; in this B_{λ} zone (*bielectronic zone*), all the bielectronic integrals are evaluated explicitly. In the outer, infinite region which we define as M_{λ} , complementary to B_{λ} (the *mono-electronic zone*), ρ_{λ} can be expanded in multipoles and the series can be evaluated to infinity analytically, using Ewald's method combined with recursion formulae [159].

The resulting expression for the Coulomb contribution to the Fock matrix is:

$$\begin{aligned} C_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = & \sum_{\lambda} \{ \sum_{\mathbf{h}}^{B_{\lambda}} [\sum_{3 \in \lambda} \sum_4 \sum_{\mathbf{n}} P_{34}^{\mathbf{n}} (\varphi_1^{\mathbf{0}} \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}}) + \\ & - \sum_{\ell, m} \gamma_{\ell}^m(\mathbf{A}_{\lambda}; \{\lambda\}) \Phi_{\ell}^m(12\mathbf{g}; \mathbf{A}_{\lambda} + \mathbf{h})] + \\ & + \sum_{\mathbf{h}} \sum_{\ell, m} \gamma_{\ell}^m(\mathbf{A}_{\lambda}; \{\lambda\}') \Phi_{\ell}^m(12\mathbf{g}; \mathbf{A}_{\lambda} + \mathbf{h}) \} \end{aligned} \quad (13.16)$$

where:

$$\gamma_{\ell}^m(\mathbf{A}_{\lambda}; \{\lambda\}) = \int d\mathbf{r} \rho_{\lambda}(\mathbf{r} - \mathbf{A}_{\lambda}) N_{\ell}^m X_{\ell}^m(\mathbf{r} - \mathbf{A}_{\lambda}) \quad (13.17)$$

$$\Phi_{\ell}^m(12\mathbf{g}; \mathbf{A}_{\lambda} + \mathbf{h}) = \int d\mathbf{r} \varphi_1^{\mathbf{0}}(\mathbf{r}) \varphi_2^{\mathbf{g}}(\mathbf{r}) X_{\ell}^m(\mathbf{r} - \mathbf{A}_{\lambda} - \mathbf{h}) |\mathbf{r} - \mathbf{A}_{\lambda} - \mathbf{h}|^{-2\ell-1} \quad (13.18)$$

The Ewald term in eq. 13.16 includes zones $B_\lambda + M_\lambda$. The contribution from B_λ is subtracted. The X_ℓ^m functions entering in the definition of the multipoles and field terms are real, solid harmonics, and N_ℓ^m , the corresponding normalization coefficients.

The advantage of using equation 13.16 is that many four-centre (long-range) integrals can be replaced by fewer three-centre integrals.

The attribution of the interaction between $\rho_1 = \{10, 2\mathbf{g}\}$ and ρ_λ to the *exact*, short-range or to the *approximate*, long-range zone is performed by comparing the penetration between ρ_1 and ρ_λ with the ITOL2 input parameter (if **ITOL2** > $-\log S_{1\lambda}$, then ρ_λ is attributed to the *exact* B_λ zone).

The multipolar expansion in the approximate zone is truncated at $L = \ell^{max}$. The default value of L is 4; the maximum possible value is 6, the minimum suggested value, 2 (defined via the input keyword **POLEORDR**, input block 3, page 108).

13.4 The exchange series

The exchange series does not require particular manipulations of the kind discussed in the previous section for the Coulomb series, but needs a careful selection of the terms contributing appreciably to the Fock operator and to the total energy [33]. The exchange contribution to the total energy can be written as follows:

$$E^{ex} = \frac{1}{2} \sum_{12} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \left[-\frac{1}{2} \sum_{34} \sum_{\mathbf{n}} P_{34}^{\mathbf{n}} \sum_{\mathbf{h}} (\varphi_1^{\mathbf{0}} \varphi_3^{\mathbf{h}} | \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h}+\mathbf{n}}) \right] \quad (13.19)$$

where the term in square brackets is the exchange contribution to the $12\mathbf{g}$ element of the direct space Fock matrix. E^{ex} has no counterpart of opposite sign as the Coulomb term has; hence, it must converge by itself.

The \mathbf{h} summation can be truncated after a few terms, since the $\{\varphi_1^{\mathbf{0}} \varphi_3^{\mathbf{h}}\}$ overlap distribution decays exponentially as \mathbf{h} increases. Similar considerations apply to the second charge distribution. In CRYSTAL, the \mathbf{h} summation is, therefore, truncated when the charge associated with either $\{G_1\mathbf{0} G_3\mathbf{h}\}$ or $\{G_2\mathbf{g} G_4\mathbf{h} + \mathbf{n}\}$ is smaller than $10^{-\mathbf{ITOL3}}$.

The situation is more complicated when \mathbf{g} and \mathbf{n} summations are analysed. Let us consider the leading terms at large distance, corresponding to $\varphi_1 = \varphi_3, \varphi_2 = \varphi_4, \mathbf{h} = \mathbf{0}$ and $\mathbf{n} = \mathbf{g}$:

$$e_{12}^{\mathbf{g}} = -1/4(P_{12}^{\mathbf{g}})^2(10\ 10|2\mathbf{g}\ 2\mathbf{g}) = -(p^{\mathbf{g}})^2/(4|\mathbf{g}|) \quad (13.20)$$

(Here $p^{\mathbf{g}}$ indicates the dominant P matrix element at long range). Since the number of terms per unit distance of this kind increases as $|\mathbf{g}|^{d-1}$, where d is the dimensionality of the system, it is clear that the convergence of the series depends critically on the long range behaviour of the bond order matrix.

Cancellation effects, associated in particular with the oscillatory behaviour of the density matrix in metallic systems, are not predominant at long range. Even if the actual behaviour of the P matrix elements cannot be predicted because it depends in a complicated way on the physical nature of the compound [141], on orthogonality constraints and on basis set quality, the different range of valence and core elements can be exploited by adopting a *pseudoverlap* criterion. This consists in truncating \mathbf{g} summations when the $\int d\mathbf{r} \varphi_1^{\mathbf{0}} \varphi_2^{\mathbf{g}}$ overlap is smaller than a given threshold, defined as $P_{ex}^{\mathbf{g}}$ (where **ITOL4** = $-\log_{10}(P_{ex}^{\mathbf{g}})$) and also truncating the \mathbf{n} summation when $\int d\mathbf{r} \varphi_3^{\mathbf{0}} \varphi_4^{\mathbf{n}}$ overlap is smaller than the threshold, $P_{ex}^{\mathbf{n}}$ (**ITOL5** = $-\log_{10}(P_{ex}^{\mathbf{n}})$).

Despite its partially arbitrary nature, this criterion presents some advantages with respect to other more elaborate schemes: it is similar to the other truncation schemes (ITOL1, ITOL2, ITOL3), and so the same classification tables can be used; it is, in addition, reasonably efficient in terms of space occupation and computer time.

This truncation scheme is symmetric with respect to the \mathbf{g} and \mathbf{n} summations. However, if account is not taken of the different role of the two summations in the SC (Self Consistent) stage, distortions may be generated in the exchange field as felt by charge distributions $\varphi_1 \varphi_2^T$, where T labels the largest (in modulus) \mathbf{g} vector taken into account according to ITOL4. This distortion may be variationally *exploited*, and unphysically large density matrix elements build

up progressively along the SC stage, eventually leading to catastrophic behaviour (see Chapter II.5 of reference [142] for a discussion of this point). In order to overcome this problem, the threshold, P_{ex}^n (**ITOL5**) for \mathbf{n} summation must be more severe than that for \mathbf{g} summation (**ITOL4**). In this way, all the integrals whose second pseudo charge $\int d\mathbf{r}\varphi_3^0\varphi_4^n$ is larger than P_{ex}^n are taken into account. A difference in the two thresholds ranging from three to eight orders of magnitude is sufficient to stabilize the SC behaviour in most cases.

13.5 Bipolar expansion approximation of Coulomb and exchange integrals

We may now return to the partition of the \mathbf{h} summation in the Coulomb series shown in equation 13.13. Consider one contribution to the charge distribution of electron 1, centred in the reference cell: $\rho^0 = \varphi_1^0\varphi_2^g$; now consider the charge distribution $\rho_\lambda(\mathbf{h})$ of shell λ centred in cell \mathbf{h} (equation 13.14). For small $|\mathbf{h}|$ values, ρ_λ and ρ^0 overlap, so that all the related bielectronic integrals must be evaluated exactly, one by one; for larger values of $|\mathbf{h}|$, ρ_λ is external to ρ^0 , so that all the related bielectronic integrals are grouped and evaluated in an approximate way through the multipolar expansion of ρ_λ .

However, in many instances, although ρ_λ is not external to ρ^0 , the two-centre $\varphi_3^h\varphi_4^{h+n}$ contributions to ρ_λ are external to $\rho^0 = \varphi_1^0\varphi_2^g$; in this case, instead of exactly evaluating the bielectronic integral, a two-centre truncated bipolar expansion can be used (see Chapter II.4.c in reference [142] and references therein).

In order to decide to which zone a shell may be ascribed, we proceed as follows: when, for a given pair of shells $\lambda_1^0\lambda_2^g$, shell λ_3^h is attributed to the B (*bielectronic*) zone, the penetration between the products of adjoined Gaussians $G_1^0G_2^g$ and $G_3^hG_4^{h+n}$ is estimated: the default value of the penetration parameter is 14, and the block of bielectronic integrals is attributed accordingly to the b_e (*exact*) or to the b_b (*bipolar*) zone. The set of \mathbf{h} vectors defining the B zone of $\rho^0 = \{\lambda_2^g\}$ and $\rho_\lambda \equiv \{\lambda_3^h\}$ is then split into two subsets, which are specific for each partner λ_4^l of λ_3 .

A similar scheme is adopted for the selected exchange integrals (see previous section) whose pseudo charges do not overlap appreciably. The default value of the penetration parameter is 10.

The total energy change due to the bipolar expansion approximation should not be greater than 10^{-4} hartree/atom; exact evaluation of all the bielectronic integrals (obtained by setting the penetration parameter value > 20000) increases the computational cost by a factor of between 1.3 and 3. Multipolar expansion is very efficient, because the following two conditions are fulfilled:

1. A general algorithm is available for reaching high ℓ values easily and economically [50, 159]. The maximum allowed value is $\ell=6$.
2. The multipolar series converges rapidly, either because the interacting distributions are nearly spherical (shell expansion), or because their functional expression is such that their multipoles are zero above a certain (low) ℓ value.

13.6 Exploitation of symmetry

Translational symmetry allows the factorization of the eigenvalue problem in periodic calculations, because the Bloch functions are a basis for irreducible representations of the translational group.

In periodic calculations, point symmetry is exploited to reduce the number of points for which the matrix equations are to be solved. Point symmetry is also explicitly used in the reconstruction of the Hamiltonian, which is totally symmetric with respect to the point group operators of the system.

In the HF-CO-LCAO scheme, the very extensive use of point symmetry allows us to evaluate bielectronic and mono-electronic integrals with saving factors as large as h in the number of bielectronic integrals to be computed or h^2 in the number of those to be stored for the SCF part

of the calculation, where h is the order of the point group. The main steps of the procedure [45] can be summarized as follows:

- The set of Coulomb and exchange integrals whose 3,4 indices identify translationally equivalent pairs of AOs, so that the associated element of the density matrix P_{34} is the same, are summed together to give D_{1234} elements:

$$D_{1,2T;3,4Q} = \sum_{\mathbf{n}} [(\varphi_1^{\mathbf{0}}\varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}}\varphi_4^{\mathbf{h}+\mathbf{n}}) - 1/2(\varphi_1^{\mathbf{0}}\varphi_3^{\mathbf{h}} | \varphi_2^{\mathbf{g}}\varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (13.21)$$

- The products of AOs $\varphi_1\varphi_2$ (and $\varphi_3\varphi_4$) are classified in symmetry-related sets; using the fact that the Fock matrix is totally symmetric, only those quantities are evaluated whose indices 1, 2 refer to the first member of a symmetry set. The corresponding saving factor is as large as h .
- Using the symmetry properties of the density matrix, D quantities referring to 3, 4, couples belonging to the same symmetry set (and with the same 1, 2g index) can be combined after multiplication by appropriate symmetry matrices, so that a single quantity for each 3, 4 symmetry set is to be stored, with a saving factor in storage of the order of h .
- The symmetry $P_{34}^{\mathbf{n}} = P_{43}^{-\mathbf{n}}$ is exploited.
- The symmetry $F_{12}^{\mathbf{g}} = F_{21}^{-\mathbf{g}}$ is exploited.

Symmetry-adapted Crystalline Orbitals

A computational procedure for generating space-symmetry-adapted Bloch functions, when BF are built from a basis of local functions (AO), is implemented in the CRYSTAL98 code. The method, that applies to any space group and AOs of any quantum number, is based on the diagonalization of Dirac characters. For its implementation, it does not require character tables or related data as an input, since the information is automatically generated starting from the space group symbol and the AO basis set. Formal aspects of the method, not available in textbooks, are discussed in:

C. M. Zicovich-Wilson and R. Dovesi

On the use of Symmetry Adapted Crystalline Orbitals in SCF-LCAO periodic calculations. I. The construction of the Symmetrized Orbitals

Int. J. Quantum Chem. **67**, 299–310 (1998)

C. M. Zicovich-Wilson and R. Dovesi

On the use of Symmetry Adapted Crystalline Orbitals in SCF-LCAO periodic calculations. II. Implementation of the Self-Consistent-Field scheme and examples

Int. J. Quantum Chem. **67**, 311–320 (1998).

The following table presents the performance obtained with the new method. In all cases convergence is reached in ten cycles.

| System | Chabazite | | | Pyrope | Faujasite |
|--|-------------|------|------|--------|-----------|
| Space Group | $R\bar{3}m$ | | | $Ia3d$ | $Fd3m$ |
| N. of atoms | 36 | | | 80 | 144 |
| N. of AOs | 432 | | | 1200 | 1728 |
| N. symmetry operators | 12 | 6 | 3 | 48 | 48 |
| CPU time (sec) on IBM RISC-6000/365 | | | | | |
| integrals | 447 | 900 | 1945 | 4286 | 815 |
| Atomic BF(ABF) scf (total) | 1380 | 2162 | 4613 | 24143 | 50975 |
| Atomic BF scf (diagonalization) | 898 | 898 | 898 | 19833 | 44970 |
| Symmetry Adapted BF (SABF) scf (total) | 526 | 1391 | 4335 | 3394 | 2729 |
| Symmetry Adapted BF scf (diagonalization) | 42 | 97 | 570 | 312 | 523 |
| ABF/SABF scf time | 2.62 | 1.55 | 1.06 | 7.11 | 18.7 |

13.7 Reciprocal space integration

The integration in reciprocal space is an important aspect of *ab initio* calculations for periodic structures. The problem arises at each stage of the self-consistent procedure, when determining the Fermi energy, ϵ_F , when reconstructing the one-electron density matrix, and, after self-consistency is reached, when calculating the density of states (DOS) and a number of observable quantities. The P matrix in direct space is computed following equation 13.9. The technique adopted to compute ϵ_F and the P matrix in the SCF step is described in reference [67]. The Fourier-Legendre technique presented in Chapter II.6 of reference [142] is adopted in the calculation of total and projected DOS. The Fermi energy and the integral in equation 13.9 are evaluated starting from the knowledge of the eigenvalues, $\epsilon_n(\mathbf{k})$ and the eigenvectors, $a_{\mu n}(\mathbf{k})$, at a certain set of sampling points, $\{\kappa\}$. In 3D crystals, the sampling points belong to a lattice (called the *Monkhorst net*, [119]) with basis vectors \mathbf{b}_1/s_1 , \mathbf{b}_2/s_2 , \mathbf{b}_3/s_3 , where \mathbf{b}_1 , \mathbf{b}_2 and \mathbf{b}_3 are the ordinary reciprocal lattice vectors; s_1 , s_2 and s_3 (input as IS1, IS2 and IS3) are integer *shrinking factors*. Unless otherwise specified, IS1=IS2=IS3=IS. In 2D crystals, IS3 is set equal to 1; in 1D crystals both IS2 and IS3 are set equal to 1. Only points of the Monkhorst net belonging to the irreducible part of the Brillouin Zone (BZ) are considered, with associated geometrical weights, w_i .

In the selection of the κ points for non-centrosymmetric crystal, time-reversal symmetry is exploited ($\epsilon_n(\kappa) = \epsilon_n(-\kappa)$).

The number of inequivalent sampling points, κ_i , is asymptotically given by the product of the shrinking factors divided by the order of the point group. In high symmetry systems and with small s_i values, it may be considerably larger because many points lie on symmetry planes or axes.

Two completely different situations (which are automatically identified by the code) must now be considered, depending on whether the system is an insulator (or zero gap semiconductor), or a conductor. In the former case, all bands are either fully occupied or vacant. The identification of ϵ_F is elementary, and the Fourier transform expressed by equation 13.9 is reduced to a weighted sum of the integrand function over the set $\{\kappa_i\}$ with weights w_i , the sum over n being limited to occupied bands.

The case of conductors is more complicated; an additional parameter, ISP, enter into play. ISP (or ISP1, ISP2, ISP3) are *Gilat shrinking factors* which define a net *Gilat net* [85, 84] completely analogous to the Monkhorst net. The value of ISP is larger than IS (by up to a factor of 2), giving a denser net.

In high symmetry systems, it is convenient to assign IS *magic* values such that all low multiplicity (high symmetry) points belong to the Monkhorst lattice. Although this choice does not correspond to maximum efficiency, it gives a safer estimate of the integral.

The value assigned to ISP is irrelevant for non-conductors. However, a non-conductor may give rise to a conducting structure at the initial stages of the SCF cycle, owing, for instance, to a very unbalanced initial guess of the density matrix. The ISP parameter must therefore be defined in all cases.

13.8 Electron momentum density and related quantities

Three functions may be computed which have the same information content but different use in the discussion of theoretical and experimental results; the momentum density itself, $\pi(\mathbf{p})$ or EMD; the Compton profile function, $J(\mathbf{p})$ or CP; the autocorrelation function, or reciprocal space form factor, or internally-folded density, $B(\mathbf{r})$ or BR.

With reference to a Crystalline-Orbital (CO)-LCAO wave function, the EMD can be expressed as the sum of the squared moduli of the occupied COs in a momentum representation, or equivalently, as the diagonal element of the six-dimensional Fourier transform of the one-electron density matrix from configuration to momentum space:

$$\pi(\mathbf{p}) = \sum_n^{occ} \sum_{\mu\nu} e^{i\mathbf{p}\cdot(\mathbf{s}_\mu - \mathbf{s}_\nu)} C_{\mu n}(\mathbf{p}_0) C_{\nu n}^*(\mathbf{p}_0) \chi_\mu(\mathbf{p}) \chi_\nu^*(\mathbf{p}) \theta(\epsilon_F - \epsilon_n(\mathbf{p}_0)) \quad (13.22)$$

$$\pi(\mathbf{p}) = \sum_{\mu\nu} P_{\mu\nu}^{\mathbf{g}} e^{i\mathbf{p}\cdot(\mathbf{S}_\mu - \mathbf{g} - \mathbf{s}_\nu)} \chi_\mu(\mathbf{p}) \chi_\nu^*(\mathbf{p}) \quad (13.23)$$

In the above equations \mathbf{p}_0 is the value of momentum in the Brillouin zone (BZ), which is related to \mathbf{p} by a reciprocal lattice vector \mathbf{K} , \mathbf{s}_μ is the fractional coordinate of the χ_μ centre, and $\chi_\mu(\mathbf{p})$ is the Fourier transform of $\chi_\mu(\mathbf{r})$, calculated analytically:

$$\chi_\mu(\mathbf{p}) = \int d\mathbf{r} \chi_\mu(\mathbf{r}) e^{-i\mathbf{p}\cdot\mathbf{r}} \quad (13.24)$$

The two expressions (13.22) and (13.23) are implemented in CRYSTAL and can be used via the **EMDL (EMDP)** and **EMDLDM (EMDPDM)** keywords, respectively for EMD along a line (in a plane). Let us note, however, that the default choice for keywords **EMDL** and **EMDP** is that of computing the core band contribution via equation (13.23) and the valence band contribution via equation (13.22).

At variance with the electron charge density $\rho(\mathbf{r})$, it is generally difficult to fully exploit the information content of the EMD $\pi(\mathbf{p})$ due to its ‘‘collapsed’’ character about the origin $\mathbf{p} = \mathbf{0}$ in momentum space. A relatively simple way of extracting information from the total EMD of a system, is analyzing its anisotropy $\Delta\pi(\mathbf{p})$ with respect to its Spherical Average (SA) function $\pi_{SA}(p)$ which is, of course, a ‘‘radial’’ function of a single variable:

$$\Delta\pi(\mathbf{p}) = \pi(\mathbf{p}) - \pi_{SA}(p) \quad \text{where} \quad p = |\mathbf{p}| \quad (13.25)$$

The average value $\pi_{SA}(p)$ of the function $\pi(\mathbf{p})$ over the surface of a sphere with radius p , can be computed as the average of the function values at the 60 points \mathbf{p}_n (with $n = 1, \dots, 60$) lying on that surface which form an orbit under the icosahedral group. It is possible to exploit the smoothed character of the spherically averaged EMD $\pi_{SA}(p)$ by explicitly evaluating it on a coarse set of values of p and then by interpolating them (we use a cubic spline). Spherically averaged EMD and EMD-anisotropies can be evaluated via the **EMDLDM** and **EMDPDM** keywords.

A *directional* Compton profile $J_{hkl}(p)$ is related to a particular crystallographic directions $[hkl]$, identified by the unit vector \mathbf{e}_{hkl} where hkl are the *Miller indices*. The directional CP $J_{hkl}(p)$ contains information about the distribution of the electron’s momenta along the $[hkl]$ direction of the crystal and can be defined as the 2D integration of $\pi(\mathbf{p})$ over a plane perpendicular to \mathbf{e}_{hkl} through $p\mathbf{e}_{hkl}$:

$$J_{hkl}(p) = \int \pi(\mathbf{p}) \delta(\mathbf{p} \cdot \mathbf{e}_{hkl} - p) d\mathbf{p} \quad (13.26)$$

The weighted average of the directional CPs over all directions is the average CP. Both directional and average CPs can be computed following the expression (13.26) via the **PROF** keyword.

The one-dimensional Fourier transform of a directional CP, gives the so-called directional auto-correlation function $B_{hkl}(r)$:

$$B_{hkl}(r) = \int J_{hkl}(p) e^{-ipr} dp \quad (13.27)$$

$$J_{hkl}(p) = \frac{1}{2\pi} \int B_{hkl}(r) e^{ipr} dr \quad (13.28)$$

Directional CPs can be computed from the corresponding directional auto-correlation function via the keyword **BIDIERD**.

Within the sudden-impulse approximation, $J_{hkl}(p)$ is directly comparable to the outcome of Compton scattering experiments, after correcting the latter for limited resolution and multiple scattering effects. In particular, the effect of limited resolution can be expressed as a convolution of the ‘‘infinite resolution’’ data with a normalized Gaussian function $g(p; \sigma_{cp})$

characterized by a given standard deviation σ_{cp} (or, equivalently, by the fwhm parameter $w_{cp} = \sigma_{cp} \cdot 2\sqrt{2\log 2}$) which quantifies the experimental resolution:

$$\begin{aligned} J_{hkl}^\sigma(p) &= \int_{-\infty}^{+\infty} J_{hkl}(p') g(p-p'; \sigma_{cp}) dp' = \\ &= \frac{1}{2\pi} \int_{-\infty}^{+\infty} B_{hkl}^\sigma(r) e^{-i p r} dr \end{aligned} \quad (13.29)$$

In the last integrand a “finite resolution AF” appears, which is simply the *product* of the AF from equation (13.27) by a Gaussian function $g(r, \sigma_{br})$, with $\sigma_{br} = 1/\sigma_{cp}$, and can be extracted from the experimental CP simply by Fourier back-transformation.

The expectation value of the kinetic energy operator \hat{T} (*i.e.* the kinetic energy of the system E_{kin}) can be expressed in terms of the second moment of the electron momentum distribution $\pi(\mathbf{p})$ as follows:

$$E_{kin} = \langle \hat{T} \rangle = \frac{1}{2} \int \pi(\mathbf{p}) \mathbf{p}^2 d\mathbf{p} \stackrel{virial}{=} -E_0 \quad (13.30)$$

where the last passage recalls that, if the *virial theorem* is satisfied, the kinetic energy equals (apart from the sign that is opposite) the total energy of the system. Let us introduce the kinetic tensor \mathbf{T} whose elements T_{uv} can be defined as:

$$T_{uv} = \frac{1}{2} \int \pi(\mathbf{p}) p_u p_v d\mathbf{p} \quad \text{with } u, v = x, y, z \quad (13.31)$$

The kinetic energy of the system is then the trace of the kinetic tensor:

$$E_{kin} = \langle \hat{T} \rangle = Tr(\mathbf{T}) \quad (13.32)$$

The kinetic tensor can be computed via the **KINETEMD** keyword of **PROPERTIES**.

A possible strategy for partitioning the electron momentum density (EMD) of a periodic system into chemically meaningful contributions is that of exploiting the spatially localized character of Wannier functions (WF).

Let us introduce the so-called Wannier functions that are real-valued, well localized functions of \mathbf{r} , which span altogether the same space as the occupied COs and are translationally equivalent and mutually orthonormal:

$$W_{i,\mathbf{0}}(\mathbf{r}) = W_{i,\mathbf{g}}(\mathbf{r} + \mathbf{g}) \quad ; \quad (13.33)$$

$$\int W_{i,\mathbf{g}}(\mathbf{r}) W_{i',\mathbf{g}'}(\mathbf{r}) d\mathbf{r} = \delta_{ii'} \delta_{\mathbf{g}\mathbf{g}'} \quad (13.34)$$

Such functions are in turn expressed as LCAO:

$$W_{i,\mathbf{g}}(\mathbf{r}) = \sum_{\mu} \sum_{\mathbf{g}'} w_{i,\mathbf{g};\mu\mathbf{g}'} \chi_{\mu}(\mathbf{r} - \mathbf{s}_{\mu} - \mathbf{g}') \quad (13.35)$$

The WFs can be obtained from the set of occupied COs via a unitary transformation that imposes spatial localization. Let us express the EMD in terms of WFs:

$$\pi(\mathbf{p}) = \frac{2}{L} \sum_{i=1}^{N_0/2} \sum_{\mathbf{g}}^L W_{i,\mathbf{g}}(\mathbf{p}) W_{i,\mathbf{g}}(\mathbf{p})^* \quad (13.36)$$

$$= 2 \sum_{i=1}^{N_0/2} W_{i,\mathbf{0}}(\mathbf{p}) W_{i,\mathbf{0}}(\mathbf{p})^* \quad (13.37)$$

$$= \sum_{i=1}^{N_0/2} \pi_i(\mathbf{p}) \quad \text{with} \quad \pi_i(\mathbf{p}) = 2 W_{i,\mathbf{0}}(\mathbf{p}) W_{i,\mathbf{0}}(\mathbf{p})^* \quad (13.38)$$

where N_0 is the number of electrons per cell, L the number of cells in the cyclic cluster; in the second passage we have exploited the translational equivalence of the WFs and in the last

passage we make explicit the partition of the total EMD in contributions $\pi_i(\mathbf{p})$ coming from the different WFs.

Let us define a *momentum* WF $W_{i,\mathbf{g}}(\mathbf{p})$ as:

$$W_{i,\mathbf{g}}(\mathbf{p}) = \int d\mathbf{r} W_{i,\mathbf{0}}(\mathbf{r} - \mathbf{g}) e^{-i\mathbf{p}\cdot\mathbf{r}} \quad (13.39)$$

$$= e^{-i\mathbf{p}\cdot\mathbf{g}} \int d\mathbf{r} W_{i,\mathbf{0}}(\mathbf{r}) e^{-i\mathbf{p}\cdot\mathbf{r}} \quad (13.40)$$

$$= e^{-i\mathbf{p}\cdot\mathbf{g}} \sum_{\mu} \sum_{\mathbf{g}'} w_{i,\mathbf{0};\mu\mathbf{g}'} e^{-i\mathbf{p}\cdot(\mathbf{s}_{\mu} + \mathbf{g}')} \chi_{\mu}(\mathbf{p}) \quad (13.41)$$

Substitution of equation (13.41) into equation (13.37) gives, for the total EMD:

$$\pi(\mathbf{p}) = 2 \sum_{i=1}^{N_0/2} \sum_{\mu} \sum_{\nu} \sum_{\mathbf{g}} \sum_{\mathbf{g}'} w_{i,\mathbf{0};\mu\mathbf{g}} w_{i,\mathbf{0};\nu\mathbf{g}'} e^{-i\mathbf{p}\cdot(\mathbf{s}_{\mu} - \mathbf{s}_{\nu} + \mathbf{g} - \mathbf{g}')} \chi_{\mu}(\mathbf{p}) \chi_{\nu}^*(\mathbf{p}) \quad (13.42)$$

Also the total anisotropy $\Delta\pi(\mathbf{p})$ can be partitioned into contributions coming from the different WFs:

$$\Delta\pi(\mathbf{p}) = \sum_i^{N_0/2} \Delta\pi_i(\mathbf{p}) \quad \text{with} \quad \Delta\pi_i(\mathbf{p}) = \pi_i(\mathbf{p}) - \frac{\pi_{SA}(p)}{N_0/2} \quad (13.43)$$

If one considers as negligible the contribution of core electrons to the total anisotropy of the EMD, can rewrite the previous partitioning as follows:

$$\Delta\pi(\mathbf{p}) = \sum_i^{N_v/2} \Delta\pi_i(\mathbf{p}) \quad \text{with} \quad \Delta\pi_i(\mathbf{p}) = \pi_i(\mathbf{p}) - \frac{\pi_{SA}(p)}{N_v/2} \quad (13.44)$$

where N_v is the number of valence electrons. Both EMD and EMD-anisotropies from selected WFs can be computed via the **EMDWF** sub-keyword of **LOCALWF** that activates the localization of crystalline orbitals into WFs.

Given the contribution $\pi_i(\mathbf{p})$ of WF i to the EMD of the system, a kinetic tensor \mathbf{T}^i can be introduced whose elements T_{uv}^i can be defined as:

$$T_{uv}^i = \frac{1}{2} \int \pi_i(\mathbf{p}) p_u p_v d\mathbf{p} \quad \text{with} \quad u, v = x, y, z \quad (13.45)$$

The computation of such a tensor can be activated via the **EMDWFKIN** sub-keyword of **LOCALWF**.

13.9 Elastic Moduli of Periodic Systems

The elastic constants are *second* derivatives of the energy density with respect to strain components:

$$C_{ij} = 1/V \cdot \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \quad (13.46)$$

where V is the volume of the cell. The energy derivatives must be evaluated numerically. Particular care is required in the selection of the computational parameters and of the points where the energy is evaluated, in order to avoid large numerical errors in the fitting procedure (**FIXINDEX**, page 98; **OPTGEOM**, page 118).

See <http://www.crystal.unito.it> \Rightarrow **tutorials** \Rightarrow **Elastic and piezoelectric tensors**

When the unit cell is deformed, the point group is reduced to a subgroup of the original point group (see examples below). The new point group is automatically selected by the code. Off-diagonal (partial derivatives) elastic constants can be computed as linear combinations of single-variable energy curves. For example, for a cubic system, C_{12} can be obtained from $B = (C_{11} + 2C_{12})/3$ and $(C_{11} - C_{12})$ (see examples below). Following the deformation of the

unit cell, internal relaxation of the atoms may be necessary (depending on the space group symmetry) See test 20, referring to Li_2O .

The analysis of the point group at the atomic positions (printed by the **ATOMSYMM** option, page 36) is useful in finding the atomic coordinates to be relaxed. Examples of deformation strategies are discussed in references [51, 32].

In a crystalline system a point \mathbf{r} is usually defined in terms of its fractional components:

$$\mathbf{r} = \mathbf{h} \mathbf{L}_p$$

where :

$$\mathbf{L}_p = \begin{bmatrix} \mathbf{l}_1 \\ \mathbf{l}_2 \\ \mathbf{l}_3 \end{bmatrix} = \begin{bmatrix} l_{1x} & l_{1y} & l_{1z} \\ l_{2x} & l_{2y} & l_{2z} \\ l_{3x} & l_{3y} & l_{3z} \end{bmatrix} \quad (13.47)$$

$$V = \det(\mathbf{L}_p)$$

$\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$ are the fundamental vectors of the primitive cell, \mathbf{h} is the fractional vector and V the cell volume.

\mathbf{L}_p can be computed from the six cell parameters $a, b, c, \alpha, \beta, \gamma$. For instance, the matrix \mathbf{L}_p for a face centred cubic lattice with lattice parameter a has the form:

$$\mathbf{L}_p = \begin{bmatrix} 0 & a/2 & a/2 \\ a/2 & 0 & a/2 \\ a/2 & a/2 & 0 \end{bmatrix}$$

Under an elastic strain, any particle at \mathbf{r} migrates microscopically to \mathbf{r}' according to the relation:

$$\mathbf{r}' = \mathbf{r} (\mathbf{I} + \epsilon)$$

where ϵ is the symmetric Lagrangian elastic tensor.

In the deformed crystalline system:

$$\begin{aligned} \mathbf{r}' &= \mathbf{h} \mathbf{L}'_p \\ \mathbf{L}'_p &= (\mathbf{I} + \epsilon) \mathbf{L}_p \end{aligned} \quad (13.48)$$

or:

$$\mathbf{L}'_p = \mathbf{L}_p + \mathbf{Z} \quad (13.49)$$

where

$$\begin{aligned} \mathbf{Z} &= \epsilon \mathbf{L}_p \\ V' &= \det(\mathbf{L}'_p) \end{aligned}$$

The deformation may be constrained to be volume-conserving, in which case the lattice vectors of the distorted cell must be scaled as follows:

$$\mathbf{L}_p'' = \mathbf{L}'_p (V/V')^{1/3} \quad (13.50)$$

If a non-symmetric Lagrangian elastic tensor, η , is used, instead of ϵ , the deformation is the sum of a strain (ϵ) and a rotation (ω) of the crystal:

$$\begin{aligned} \epsilon &= (\eta + \eta^+)/2 \\ \omega &= (\eta - \eta^+)/2 \end{aligned}$$

The total energy of the crystal is invariant to a pure rotation, which allows non-symmetric η matrices to be employed. However, a non-symmetric deformation will lower the symmetry of the system, and therefore increase the complexity of the calculation, since the cost required is roughly inversely proportional to the order of the point group.

The elastic constants of a crystal are defined as the second derivatives of the energy with respect to the elements of the infinitesimal Lagrangian strain tensor ϵ .

Let us define, according to the Voigt convention:

$$\begin{aligned}\epsilon_1 &= \epsilon_{11} & \epsilon_4 &= \epsilon_{32} + \epsilon_{23} \\ \epsilon_2 &= \epsilon_{22} & \epsilon_5 &= \epsilon_{13} + \epsilon_{31} \\ \epsilon_3 &= \epsilon_{33} & \epsilon_6 &= \epsilon_{12} + \epsilon_{21}\end{aligned}$$

A Taylor expansion of the energy of the unit cell to second order in the strain components yields:

$$E(\epsilon) = E(\mathbf{0}) + \sum_i^6 \frac{\partial E}{\partial \epsilon_i} \epsilon_i + 1/2 \sum_{i,j}^6 \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \epsilon_i \epsilon_j \quad (13.51)$$

If $E(\mathbf{0})$ refers to the equilibrium configuration the first derivative is zero, since there is no force on any atom in equilibrium. The elastic constants of the system can be obtained by evaluating the energy as a function of deformations of the unit cell parameters. The indices of the non-zero element(s) (in the Voigt convention) of the ϵ matrix give the corresponding elastic constants.

Examples of ϵ matrices for cubic systems

Consider a face-centred cubic system, for example Li_2O , with the $\text{Fm}\bar{3}\text{m}$ space group. For cubic systems there are only three independent elastic constants (C_{11} , C_{12} and C_{44}), as the symmetry analysis shows that:

$$\begin{aligned}C_{11} &= C_{22} = C_{33}; \\ C_{44} &= C_{55} = C_{66}; \\ C_{12} &= C_{13} = C_{23}; \\ C_{ij} &= 0 \quad \text{for } i = 1, 6, \quad j = 4, 6 \quad \text{and } i \neq j.\end{aligned}$$

Calculation of C_{11}

The ϵ matrix for the calculation of C_{11} is

$$\epsilon = \begin{bmatrix} \delta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The energy expression is:

$$E(\delta) = E(0) + 1/2 \frac{\partial^2 E}{\partial \epsilon_1^2} \delta^2 + \dots = a + b\delta^2 + c\delta^3 \dots$$

where a, b, c are the coefficients of a polynomial fit of E versus δ , usually truncated to fourth order (see examples below). Then

$$C_{11} = 1/V \frac{\partial^2 E}{\partial \epsilon_1^2} = \frac{2b}{V}$$

The above distortion reduces the number of point symmetry operators to 12 (tetragonal distortion).

Calculation of $C_{11} - C_{12}$

The ϵ matrix for the calculation of the $C_{11} - C_{12}$ combination has the form:

$$\epsilon = \begin{bmatrix} \delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

The energy expression is:

$$\begin{aligned} E(\epsilon_1, \epsilon_2) &= E(0, 0) + 1/2 \frac{\partial^2 E}{\partial \epsilon_1^2} \delta^2 + 1/2 \frac{\partial^2 E}{\partial \epsilon_2^2} \delta^2 - \frac{\partial^2 E}{\partial \epsilon_1 \partial \epsilon_2} \delta^2 + \dots = \\ &= E(0, 0) + V(C_{11} - C_{12})\delta^2 + \dots = a + b\delta^2 + \dots \end{aligned}$$

Then $C_{11} - C_{12} = b/V$

With the previous form of the ϵ matrix the number of point symmetry operators is reduced to 8, whereas the following ϵ matrix reduces the number of point symmetry operators to 16:

$$\epsilon = \begin{bmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & -2\delta \end{bmatrix}$$

$$E(\epsilon_1, \epsilon_2, \epsilon_3) = E(0, 0, 0) + 3V(C_{11} - C_{12})\delta^2 + \dots = a + b\delta^2 + \dots$$

and $(C_{11} - C_{12}) = b/3V$

Calculation of C_{44}

Monoclinic deformation, 4 point symmetry operators.

The ϵ matrix has the form:

$$\epsilon = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & x \\ 0 & x & 0 \end{bmatrix}$$

The energy expression is ($\delta = 2x$) (see Voigt convention and equation 13.51)

$$E(\epsilon_4) = E(0) + 1/2 \frac{\partial^2 E}{\partial \epsilon_4^2} \delta^2 + \dots = E(0) + 2 \frac{\partial^2 E}{\partial \epsilon_4^2} x^2 + \dots = a + bx^2 + \dots$$

so that $C_{44} = b/2V$.

Calculation of C_{44}

Rhombohedral deformation, 12 point symmetry operators.

The ϵ matrix has the form:

$$\epsilon = \begin{bmatrix} 0 & x & x \\ x & 0 & x \\ x & x & 0 \end{bmatrix}$$

The energy expression is ($\delta = 2x, C_{45} = C_{46} = C_{56} = 0$)

$$E(\epsilon_4, \epsilon_5, \epsilon_6) = E(0) + 3/2 \frac{\partial^2 E}{\partial \epsilon_4^2} \delta^2 + \dots = E(0) + 6 \frac{\partial^2 E}{\partial \epsilon_4^2} x^2 + \dots = a + bx^2 + \dots$$

so that $C_{44} = b/6V$.

Bulk modulus

The bulk modulus can be evaluated simply by varying the lattice constant, (1 in cubic systems) without the use of the ϵ matrix, and fitting the curve $E(V)$.

If the ϵ matrix is used, the relation between B and C_{ij} (cubic systems) must be taken into account:

$$B = (C_{11} + 2C_{12})/3$$

The ϵ matrix has the form:

$$\epsilon = \begin{bmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \delta \end{bmatrix}$$

and the energy:

$$E(\epsilon) = E(\mathbf{0}) + 3/2 \frac{\partial^2 E}{\partial \epsilon_1^2} \delta^2 + 3 \frac{\partial^2 E}{\partial \epsilon_1 \partial \epsilon_2} \delta^2 = \quad (13.52)$$

$$= E(\mathbf{0}) + \frac{3V}{2} [C_{11} + 2C_{12}] \delta^2 \quad (13.53)$$

so that $B = \frac{2}{9V} b$

N.B. Conversion factors:

$$1 \text{ hartree } \text{\AA}^{-3} = 4359.74812 \text{ GPa}$$

$$1 \text{ GPa} = 1 \text{ GN m}^{-2} = 1 \text{ GJ m}^{-3} = 10^{10} \text{ dyne cm}^{-2} = 10^{-2} \text{ Mbar.}$$

13.10 Spontaneous polarization through the Berry phase approach

The electronic phase of a system λ in the direction 1, $\varphi_{el}^{(\lambda,1)}$, can be written as:

$$\varphi_{el}^{(\lambda,1)} = \frac{1}{s2s3} \sum_{j2,j3} \sum_{j1} \Delta\varphi_{j1,j2,j3}^{(\lambda,1)}(\mathbf{k}) \quad (13.54)$$

The electronic contribution to the polarization of a system λ can be written as :

$$\mathbf{P}_{el}^{(\lambda)} = \frac{1}{\Omega(\lambda)} \left(B^{(\lambda)} \right)^{-1} \varphi_{el}^{(\lambda)} \quad (13.55)$$

Where $(B^{(\lambda)})^{-1}$ is the reciprocal lattice vectors components inverse matrix and $\varphi_{el}^{(\lambda)}$ the electronic phase difference vector of a system λ (which components are $\varphi_{el}^{(\lambda,i)}$). The nuclear contribution to the polarization of a system λ , $\mathbf{P}_{nuc}^{(\lambda)}$ can also be written as:

$$\mathbf{P}_{nuc}^{(\lambda)} = \frac{1}{\Omega(\lambda)} \sum_A \mathbf{R}_A^{(\lambda)} \cdot Z_A \quad (13.56)$$

where $\mathbf{R}_A^{(\lambda)}$ and Z_A are the position vector and the nuclear charge of the atom A respectively of the system λ . The total polarization is the sum of these two contributions and can be written as

$$\mathbf{P}_{tot}^{(\lambda)} = \mathbf{P}_{nuc}^{(\lambda)} + \mathbf{P}_{el}^{(\lambda)} \quad (13.57)$$

The spontaneous polarization is the difference between the systems $\lambda = 1$ and $\lambda = 0$

$$\mathbf{P} = \mathbf{P}_{tot}^{(\lambda)} - \mathbf{P}_{tot}^{(\lambda=0)} \quad (13.58)$$

Spontaneous polarization through the localized crystalline orbitals approach

The electronic contribution to the polarization of a system λ , $\mathbf{P}_{el}^{(\lambda)}$, can be written as

$$\mathbf{P}_{el}^{(\lambda)} = \frac{e}{\Omega(\lambda)} \sum_{\mu} \langle \mathbf{r}_{\mu} \rangle \quad (13.59)$$

Where $\langle \mathbf{r}_{\mu} \rangle$ is the centroid of the Wannier function μ .

The nuclear contribution to the polarization of a system λ , $\mathbf{P}_{nuc}^{(\lambda)}$ can also be written as

$$\mathbf{P}_{nuc}^{(\lambda)} = \frac{1}{\Omega(\lambda)} \sum_A \mathbf{R}_A \cdot Z_A \quad (13.60)$$

where \mathbf{R}_A and Z_A are the position vector and the nuclear charge of the atom A respectively. The total polarization is the sum of these two contributions and can be written as

$$\mathbf{P}_{tot}^{(\lambda)} = \mathbf{P}_{nuc}^{(\lambda)} + \mathbf{P}_{el}^{(\lambda)} \quad (13.61)$$

The spontaneous polarization is the difference between the both systems $\lambda = 1$ and $\lambda = 0$:

$$\mathbf{P} = \mathbf{P}_{tot}^{(1)} - \mathbf{P}_{tot}^{(2)} \quad (13.62)$$

To calculate the spontaneous polarization, a preliminary run is needed for each of the two systems $\lambda = 1$ and $\lambda = 0$. Then a third run with the keyword SPOLWF gives the difference of polarization between systems $\lambda = 1$ and $\lambda = 0$.

13.11 Piezoelectricity through the Berry phase approach

The electronic phase vector of a system λ , is given by (2.1). The nuclear phase vector of a system λ , $\varphi_{nuc}^{(\lambda)}$, can be written as

$$\varphi_{nuc}^{(\lambda)} = \Omega^{(\lambda)} B^{(\lambda)} \mathbf{P}_{nuc}^{(\lambda)} \quad (13.63)$$

Where $B^{(\lambda)}$ reciprocal lattice vectors components matrix. The last equation can be simplified thanks to (13.56):

$$\varphi_{nuc}^{(\lambda)} = B^{(\lambda)} \sum_A \mathbf{R}_A^{(\lambda)} \cdot Z_A \quad (13.64)$$

So the phase vector of a system λ , $\varphi^{(\lambda)}$ is:

$$\varphi^{(\lambda)} = \varphi_{nuc}^{(\lambda)} + \varphi_{el}^{(\lambda)} \quad (13.65)$$

The proper piezoelectric constants can be obtained by:

$$\tilde{e}_{ijk} = -\frac{1}{2\pi} \frac{1}{\Omega} \sum_{\alpha} \frac{d\varphi_{\alpha}}{d\epsilon_{jk}} a_{\alpha,i} \quad (13.66)$$

Where φ_{α} is projection of the phase φ along the α direction and $a_{\alpha,i}$ is the component of a lattice vector a_{α} along the cartesian axis i . To obtain the improper piezoelectric constants, the following correction must done:

$$e_{ijk} = \tilde{e}_{ijk} + \delta_{ij} P_k - \delta_{jk} P_i \quad (13.67)$$

In the piezoelectric constants calculations the $\frac{d\varphi_{\alpha}}{d\epsilon_{jk}}$ term is evaluated numerically. The calculated term is:

$$\frac{d\varphi_{\alpha}}{d\epsilon_{jk}} \simeq \frac{\Delta\varphi_{\alpha}}{\Delta\epsilon_{jk}} = \frac{\varphi_{\alpha}^{(1)} - \varphi_{\alpha}^{(0)}}{\epsilon_{jk}^{(1)} - \epsilon_{jk}^{(0)}} \quad (13.68)$$

Piezoelectricity through the localized crystalline orbitals approach

The electronic phase vector of a system λ , is given by:

$$\varphi_{el}^{(\lambda)} = \Omega^{(\lambda)} B^{(\lambda)} \mathbf{P}_{el}^{(\lambda)} \quad (13.69)$$

Where $B^{(\lambda)}$ reciprocal lattice vectors components matrix. The nuclear phase vector of a system λ , $\varphi_{nuc}^{(\lambda)}$, can be written as

$$\varphi_{nuc}^{(\lambda)} = \Omega^{(\lambda)} B^{(\lambda)} \mathbf{P}_{nuc}^{(\lambda)} \quad (13.70)$$

The last equation can be simplified thanks to 13.56:

$$\varphi_{nuc}^{(\lambda)} = B^{(\lambda)} \sum_A \mathbf{R}_A^{(\lambda)} \cdot Z_A \quad (13.71)$$

So the phase vector of a system λ , $\varphi^{(\lambda)}$ is:

$$\varphi^{(\lambda)} = \varphi_{nuc}^{(\lambda)} + \varphi_{el}^{(\lambda)} \quad (13.72)$$

The proper piezoelectric constants can be obtained by:

$$\tilde{e}_{ijk} = -\frac{1}{2\pi} \frac{1}{\Omega} \sum_{\alpha} \frac{d\varphi_{\alpha}}{d\epsilon_{jk}} a_{\alpha,i} \quad (13.73)$$

Where φ_{α} is projection of the phase φ along the α direction and $a_{\alpha,i}$ is the component of a lattice vector a_{α} along the cartesian axis i . To obtain the improper piezoelectric constants, the following correction must done:

$$e_{ijk} = \tilde{e}_{ijk} + \delta_{ij} P_k - \delta_{jk} P_i \quad (13.74)$$

In the piezoelectric constants calculations the $\frac{d\varphi_\alpha}{d\epsilon_{jk}}$ term is evaluated numerically. The calculated term is:

$$\frac{d\varphi_\alpha}{d\epsilon_{jk}} \simeq \frac{\Delta\varphi_\alpha}{\Delta\epsilon_{jk}} = \frac{\varphi_\alpha^{(1)} - \varphi_\alpha^{(0)}}{\epsilon_{jk}^{(1)} - \epsilon_{jk}^{(0)}} \quad (13.75)$$

13.12 Eckart conditions

Since the calculation of the Hessian matrix is a numerical procedure, eigenvalues and eigenvectors are affected by a certain degree of numerical noise which should be reduced as much as possible, especially if anharmonic calculations are going to be performed on top of the harmonic solution. From an operational point of view it is important to optimize the structure carefully and to use accurate computational parameters. Some tools are also available to enhance the numerical quality of the Hessian matrix. Sometimes translational and rotational eigensolutions can mix with low frequency modes. In such cases it is important to project the translations and rotations out of the Hessian. This is equivalent to imposing the Eckart conditions to the nuclear motion problem. We have to generate a projection matrix \mathbf{P} so that rotation and translation of the molecule are separated out. Given that the molecule has N_a atoms we are left with $3N_a - N_e$ internal degrees of freedom. N_e is the number of conditions we have to impose which is 3 for 3D systems and 6 for molecules. We define a \mathbf{D} matrix of dimensions $3N_a \times N_e$ which is the column representation of translations and rotations in the cartesian frame. The first three vectors of \mathbf{D} (corresponding to the translations) are just the square root of the isotopic mass of the atom times the corresponding Cartesian unitary vector. For example in the case of water, assuming $m_H = 1$ and $m_O = 16$ we have

$$\begin{aligned} \mathbf{D}_1 &= (1, 0, 0, 4, 0, 0, 1, 0, 0)^t \\ \mathbf{D}_2 &= (0, 1, 0, 0, 4, 0, 0, 1, 0)^t \\ \mathbf{D}_3 &= (0, 0, 1, 0, 0, 4, 0, 0, 1)^t \end{aligned} \quad (13.76)$$

where t stands for transpose. In order to build a representation for the rotational degrees of freedom we have first to translate the system so that the origin corresponds to the center of mass (COM)

$$\mathbf{r}_{COM} = \frac{\sum_{\alpha=1}^{\alpha=N_a} m_\alpha \mathbf{r}_\alpha}{\sum_{\alpha=1}^{\alpha=N_a} m_\alpha} \quad (13.77)$$

Then we build the inertia axes tensor:

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} = \begin{pmatrix} \sum_\alpha m_\alpha (y_\alpha^2 + z_\alpha^2) & -\sum_\alpha m_\alpha x_\alpha y_\alpha & -\sum_\alpha m_\alpha x_\alpha z_\alpha \\ -\sum_\alpha m_\alpha y_\alpha x_\alpha & \sum_\alpha m_\alpha (x_\alpha^2 + z_\alpha^2) & -\sum_\alpha m_\alpha y_\alpha z_\alpha \\ -\sum_\alpha m_\alpha z_\alpha x_\alpha & -\sum_\alpha m_\alpha z_\alpha y_\alpha & \sum_\alpha m_\alpha (x_\alpha^2 + y_\alpha^2) \end{pmatrix} \quad (13.78)$$

Matrix \mathbf{I} is diagonalized to obtain the eigenvectors matrix \mathbf{X} . The vectors \mathbf{D}_4 , \mathbf{D}_5 and \mathbf{D}_6 for the rotations are obtained as

$$\begin{aligned} D_{4\alpha i} &= \frac{1}{\sqrt{m_\alpha}} ((\mathbf{S}_\alpha)_2 X_{i,3} - (\mathbf{S}_\alpha)_3 X_{i,2}) \\ D_{5\alpha i} &= \frac{1}{\sqrt{m_\alpha}} ((\mathbf{S}_\alpha)_3 X_{i,1} - (\mathbf{S}_\alpha)_1 X_{i,3}) \\ D_{6\alpha i} &= \frac{1}{\sqrt{m_\alpha}} ((\mathbf{S}_\alpha)_1 X_{i,2} - (\mathbf{S}_\alpha)_2 X_{i,1}) \end{aligned} \quad (13.79)$$

where \mathbf{S}_α is obtained as the scalar product of \mathbf{X} with the coordinates of atom α :

$$\mathbf{S}_\alpha = \mathbf{X} \mathbf{r}_\alpha \quad (13.80)$$

Once the columns of \mathbf{D} are computed they are ortho-normalized via a GramSchmidt procedure. We build the projector matrix \mathbf{P} as

$$\mathbf{P} = \mathbf{D} \mathbf{D}^T \quad (13.81)$$

so that we project out the N_e degrees of freedom from the Hessian matrix:

$$\mathbf{H}' = \mathbf{P}^T \mathbf{H} \mathbf{P} \quad (13.82)$$

By diagonalizing the \mathbf{H}' matrix, the translational and rotational eigenvalues are exactly zero.

Appendix A

Symmetry groups

A.1 Labels and symbols of the space groups

The labels are according to the International Tables for Crystallography [91]. The symbols are derived by the standard SHORT symbols, as shown in the following examples:

| Symbol | | Input to CRYSTAL |
|-----------------|---------------|---|
| $P \bar{6} 2 m$ | \rightarrow | $P_{\square} \bar{6}_{\square} 2_{\square} M$; |
| $P 6_3 m$ | \rightarrow | $P_{\square} 63_{\square} M$. |

For the groups 221-230 the symbols are according to the 1952 edition of the International Tables, *not* to the 1982 edition. The difference involves the 3 axis: 3 (1952 edition); $\bar{3}$ (1982 edition) (Example group 221: 1952 ed. $\rightarrow P m \bar{3} m$; 1982 ed. $\rightarrow P m \bar{3} m$)

| IGR | symbol | IGR | symbol | IGR | symbol |
|-----------------------|---|-----|-------------|---------------------|-------------------------------------|
| Triclinic lattices | | 37 | <i>Ccc2</i> | Tetragonal lattices | |
| 1 | <i>P1</i> | 38 | <i>Amm2</i> | 75 | <i>P4</i> |
| 2 | <i>P1</i> | 39 | <i>Abm2</i> | 76 | <i>P4₁</i> |
| Monoclinic lattices | | 40 | <i>Ama2</i> | 77 | <i>P4₂</i> |
| 3 | <i>P2</i> | 41 | <i>Aba2</i> | 78 | <i>P4₃</i> |
| 4 | <i>P2₁</i> | 42 | <i>Fmm2</i> | 79 | <i>I4</i> |
| 5 | <i>C2</i> | 43 | <i>Fdd2</i> | 80 | <i>I4₁</i> |
| 6 | <i>Pm</i> | 44 | <i>Imm2</i> | 81 | <i>P4</i> |
| 7 | <i>Pc</i> | 45 | <i>Iba2</i> | 82 | <i>I4</i> |
| 8 | <i>Cm</i> | 46 | <i>Ima2</i> | 83 | <i>P4/m</i> |
| 9 | <i>Cc</i> | 47 | <i>Pmmm</i> | 84 | <i>P4₂/m</i> |
| 10 | <i>P2/m</i> | 48 | <i>Pnnn</i> | 85 | <i>P4/n</i> |
| 11 | <i>P2₁/m</i> | 49 | <i>Pccm</i> | 86 | <i>P4₂/n</i> |
| 12 | <i>C2/m</i> | 50 | <i>Pban</i> | 87 | <i>I4/m</i> |
| 13 | <i>P2/c</i> | 51 | <i>Pmma</i> | 88 | <i>I4₁/a</i> |
| 14 | <i>P2₁/c</i> | 52 | <i>Pnna</i> | 89 | <i>P422</i> |
| 15 | <i>C2/c</i> | 53 | <i>Pmna</i> | 90 | <i>P42₁2</i> |
| Orthorhombic lattices | | 54 | <i>Pcca</i> | 91 | <i>P4₁22</i> |
| 16 | <i>P222</i> | 55 | <i>Pbam</i> | 92 | <i>P4₁2₁2</i> |
| 17 | <i>P222₁</i> | 56 | <i>Pccn</i> | 93 | <i>P4₂22</i> |
| 18 | <i>P2₁2₁2</i> | 57 | <i>Pbcm</i> | 94 | <i>P4₂2₁2</i> |
| 19 | <i>P2₁2₁2₁</i> | 58 | <i>Pnnm</i> | 95 | <i>P4₃22</i> |
| 20 | <i>C222₁</i> | 59 | <i>Pmnn</i> | 96 | <i>P4₃2₁2</i> |
| 21 | <i>C222</i> | 60 | <i>Pbcn</i> | 97 | <i>I422</i> |
| 22 | <i>F222</i> | 61 | <i>Pbca</i> | 98 | <i>I4₁22</i> |
| 23 | <i>I222</i> | 62 | <i>Pnma</i> | 99 | <i>P4mm</i> |
| 24 | <i>I2₁2₁2₁</i> | 63 | <i>Cmcm</i> | 100 | <i>P4bm</i> |
| 25 | <i>Pmm2</i> | 64 | <i>Cmca</i> | 101 | <i>P4₂cm</i> |
| 26 | <i>Pmc2₁</i> | 65 | <i>Cmmm</i> | 102 | <i>P4₂nm</i> |
| 27 | <i>Pcc2</i> | 66 | <i>Cccm</i> | 103 | <i>P4cc</i> |
| 28 | <i>Pma2</i> | 67 | <i>Cmma</i> | 104 | <i>P4nc</i> |
| 29 | <i>Pca2₁</i> | 68 | <i>Ccca</i> | 105 | <i>P4₂mc</i> |
| 30 | <i>Pnc2</i> | 69 | <i>Fmmm</i> | 106 | <i>P4₂bc</i> |
| 31 | <i>Pmn2₁</i> | 70 | <i>Fddd</i> | 107 | <i>I4mm</i> |
| 32 | <i>Pba2</i> | 71 | <i>Immm</i> | 108 | <i>I4cm</i> |
| 33 | <i>Pna2₁</i> | 72 | <i>Ibam</i> | 109 | <i>I4₁md</i> |
| 34 | <i>Pnn2</i> | 73 | <i>Ibca</i> | 110 | <i>I4₁cd</i> |
| 35 | <i>Cmm2</i> | 74 | <i>Imma</i> | 111 | <i>P42m</i> |
| 36 | <i>Cmc2₁</i> | | | 112 | <i>P42c</i> |

| IGR | symbol | IGR | symbol | IGR | symbol |
|-----|-------------------|-----|--------------------|-----|--------------|
| 113 | $P4_21m$ | 155 | $R32$ | 195 | $P23$ |
| 114 | $P4_21c$ | 156 | $P3m1$ | 196 | $F23$ |
| 115 | $P4m2$ | 157 | $P31m$ | 197 | $I23$ |
| 116 | $P4c2$ | 158 | $P3c1$ | 198 | $P2_13$ |
| 117 | $P4b2$ | 159 | $P31c$ | 199 | $I2_13$ |
| 118 | $P4n2$ | 160 | $R3m$ | 200 | $Pm\bar{3}$ |
| 119 | $I4m2$ | 161 | $R3c$ | 201 | $Pn\bar{3}$ |
| 120 | $I4c2$ | 162 | $P\bar{3}1m$ | 202 | $Fm\bar{3}$ |
| 121 | $I4_2m$ | 163 | $P31c$ | 203 | $Fd\bar{3}$ |
| 122 | $I4_2d$ | 164 | $P\bar{3}m1$ | 204 | $Im\bar{3}$ |
| 123 | $P4/mmm$ | 165 | $P\bar{3}c1$ | 205 | $Pa\bar{3}$ |
| 124 | $P4/mcc$ | 166 | $R\bar{3}m$ | 206 | $Ia\bar{3}$ |
| 125 | $P4/nbm$ | 167 | $R\bar{3}c$ | 207 | $P432$ |
| 126 | $P4/nnc$ | | Hexagonal lattices | 208 | $P4_232$ |
| 127 | $P4/mbm$ | 168 | $P6$ | 209 | $F432$ |
| 128 | $P4/mnc$ | 169 | $P6_1$ | 210 | $F4_132$ |
| 129 | $P4/nmm$ | 170 | $P6_5$ | 211 | $I432$ |
| 130 | $P4/ncc$ | 171 | $P6_2$ | 212 | $P4_332$ |
| 131 | $P4_2/mmc$ | 172 | $P6_4$ | 213 | $P4_132$ |
| 132 | $P4_2/mcm$ | 173 | $P6_3$ | 214 | $I4_132$ |
| 133 | $P4_2/nbc$ | 174 | $P\bar{6}$ | 215 | $P\bar{4}3m$ |
| 134 | $P4_2/nm$ | 175 | $P6/m$ | 216 | $F\bar{4}3m$ |
| 135 | $P4_2/mbc$ | 176 | $P6_3/m$ | 217 | $I\bar{4}3m$ |
| 136 | $P4_2/mnm$ | 177 | $P622$ | 218 | $P\bar{4}3n$ |
| 137 | $P4_2/nmc$ | 178 | $P6_122$ | 219 | $F\bar{4}3c$ |
| 138 | $P4_2/ncm$ | 179 | $P6_522$ | 220 | $I\bar{4}3d$ |
| 139 | $I4/mmm$ | 180 | $P6_222$ | 221 | $Pm\bar{3}m$ |
| 140 | $I4/mcm$ | 181 | $P6_422$ | 222 | $Pn\bar{3}n$ |
| 141 | $I4_1/amd$ | 182 | $P6_322$ | 223 | $Pm\bar{3}n$ |
| 142 | $I4_1/acd$ | 183 | $P6mm$ | 224 | $Pn\bar{3}m$ |
| | Trigonal lattices | 184 | $P6cc$ | 225 | $Fm\bar{3}m$ |
| 143 | $P3$ | 185 | $P6_3cm$ | 226 | $Fm\bar{3}c$ |
| 144 | $P3_1$ | 186 | $P6_3mc$ | 227 | $Fd\bar{3}m$ |
| 145 | $P3_2$ | 187 | $P\bar{6}m2$ | 228 | $Fd\bar{3}c$ |
| 146 | $R3$ | 188 | $P\bar{6}c2$ | 229 | $Im\bar{3}m$ |
| 147 | $P\bar{3}$ | 189 | $P\bar{6}2m$ | 230 | $Ia\bar{3}d$ |
| 148 | $R\bar{3}$ | 190 | $P\bar{6}2c$ | | |
| 149 | $P312$ | 191 | $P6/mmm$ | | |
| 150 | $P321$ | 192 | $P6/mcc$ | | |
| 151 | $P3_112$ | 193 | $P6_3/mcm$ | | |
| 152 | $P3_121$ | 194 | $P6_3/mmc$ | | |
| 153 | $P3_212$ | | | | |
| 154 | $P3_221$ | | | | |

A.2 Labels of the layer groups (slabs)

The available layer groups belong to a subset of the 230 space groups. Therefore they can be identified by the corresponding space group.

The first column gives the label to be used in the input card (IGR variable).

The second column gives the Hermann-Mauguin symbol of the corresponding space group (generally the short one; the full symbol is adopted when the same short symbol could refer to different settings). The third column gives the Schoenflies symbol. The fourth column the number of the corresponding space group, according to the International Tables for Crystallography. The number of the space group is written in parentheses when the orientation of the symmetry operators does not correspond to the first setting in the I. T.

| IGR | Hermann Mauguin | Schoenflies | N | IGR | Hermann Mauguin | Schoenflies | N |
|-------------------------------|--------------------|-------------|------|------------------------|--------------------|-------------|------|
| Oblique lattices (P) | | | | 41 | $Pbam$ | D_{2h}^9 | 55 |
| 1 | $P1$ | C_1^1 | 1 | 42 | $Pmaa$ | D_{2h}^3 | (49) |
| 2 | $P\bar{1}$ | C_i^1 | 2 | 43 | $Pman$ | D_{2h}^7 | (53) |
| 3 | $P112$ | C_2^1 | (3) | 44 | $Pbma$ | D_{2h}^1 | (57) |
| 4 | $P11m$ | C_s^1 | (6) | 45 | $Pbaa$ | D_{2h}^8 | (54) |
| 5 | $P11a$ | C_s^2 | (7) | 46 | $Pban$ | D_{2h}^4 | 50 |
| 6 | $P112/m$ | C_{2h}^1 | (10) | 47 | $Cmmm$ | D_{2h}^9 | 65 |
| 7 | $P112/a$ | C_{2h}^4 | (13) | 48 | $Cmma$ | D_{2h}^2 | 67 |
| Rectangular lattices (P or C) | | | | Square lattices (P) | | | |
| 8 | $P211$ | C_2^1 | (3) | 49 | $P4$ | C_4^1 | 75 |
| 9 | $P2_111$ | C_2^2 | (4) | 50 | $P\bar{4}$ | S_4^1 | 81 |
| 10 | $C211$ | C_2^3 | (5) | 51 | $P4/m$ | C_{4h}^1 | 83 |
| 11 | $Pm11$ | C_s^1 | (6) | 52 | $P4/n$ | C_{4h}^3 | 85 |
| 12 | $Pb11$ | C_s^2 | (7) | 53 | $P422$ | D_4^1 | 89 |
| 13 | $Cm11$ | C_s^3 | (8) | 54 | $P42_12$ | D_4^2 | 90 |
| 14 | $P2/m11$ | C_{2h}^1 | (10) | 55 | $P4mm$ | C_{4v}^1 | 99 |
| 15 | $P2_1/m11$ | C_{2h}^2 | (11) | 56 | $P4bm$ | C_{4v}^2 | 100 |
| 16 | $C2/m11$ | C_{2h}^3 | (12) | 57 | $P\bar{4}2m$ | D_{2d}^1 | 111 |
| 17 | $P2/b11$ | C_{2h}^4 | (13) | 58 | $P42_1m$ | D_{2d}^3 | 113 |
| 18 | $P2/b11$ | C_{2h}^5 | (14) | 59 | $P\bar{4}m2$ | D_{2d}^5 | 115 |
| 19 | $P222$ | D_2^1 | 16 | 60 | $P\bar{4}b2$ | D_{2d}^7 | 117 |
| 20 | $P22_12$ | D_2^2 | (17) | 61 | $P4/mmm$ | D_{4h}^1 | 123 |
| 21 | $P2_12_12$ | D_2^3 | 18 | 62 | $P4/nbm$ | D_{4h}^3 | 125 |
| 22 | $C222$ | D_2^6 | 21 | 63 | $P4/mbm$ | D_{4h}^5 | 127 |
| 23 | $Pmm2$ | C_{2v}^1 | 25 | 64 | $P4/nmm$ | D_{4h}^7 | 129 |
| 24 | $Pma2$ | C_{2v}^4 | 28 | Hexagonal lattices (P) | | | |
| 25 | $Pba2$ | C_{2v}^8 | 32 | 65 | $P3$ | C_3^1 | 143 |
| 26 | $Cmm2$ | C_{2v}^1 | 35 | 66 | $P\bar{3}$ | C_{3i}^1 | 147 |
| 27 | $P2mm$ | C_{2v}^1 | (25) | 67 | $P312$ | D_3^1 | 149 |
| 28 | $P2_1am$ | C_{2v}^2 | (26) | 68 | $P321$ | D_3^2 | 150 |
| 29 | $P2_1ma$ | C_{2v}^2 | (26) | 69 | $P3m1$ | C_{3v}^1 | 156 |
| 30 | $P2mb$ | C_{2v}^4 | (28) | 70 | $P31m$ | C_{3v}^2 | 157 |
| 31 | $P2_1mn$ | C_{2v}^7 | (31) | 71 | $P\bar{3}1m$ | D_{3d}^1 | 162 |
| 32 | $P2aa$ | C_{2v}^3 | (27) | 72 | $P\bar{3}m1$ | D_{3d}^3 | 164 |
| 33 | $P2_1ab$ | C_{2v}^5 | (29) | 73 | $P6$ | C_6^1 | 168 |
| 34 | $P2an$ | C_{2v}^6 | (30) | 74 | $P\bar{6}$ | C_{3h}^1 | 174 |
| 35 | $C2mm$ | C_{2v}^1 | (38) | 75 | $P6/m$ | C_{6h}^1 | 175 |
| 36 | $C2mb$ | C_{2v}^5 | (39) | 76 | $P622$ | D_6^1 | 177 |
| 37 | $Pmmm$ | D_{2h}^1 | 47 | 77 | $P6mm$ | C_{6v}^1 | 183 |
| 38 | $Pmam$ | D_{2h}^5 | (51) | 78 | $P\bar{6}m2$ | D_{3h}^1 | 187 |
| 39 | $Pmma$ | D_{2h}^5 | 51 | 79 | $P\bar{6}2m$ | D_{3h}^3 | 189 |
| 40 | $Pmmn$ | D_{2h}^3 | 59 | 80 | $P6/mmm$ | D_{6h}^1 | 191 |

A.3 Labels of the rod groups (polymers)

The available rod groups belong to a subset of the 230 space groups; the symmetry operators are generated for the space groups (principal axis z) and then rotated by 90° through y , to have the polymer axis along x (CRYSTAL convention).

In the table, the first column gives the label to be used in the input card for identifying the rod group (IGR variable).

The second column gives the "polymer" symbol, according to the the following convention: x is the first symmetry direction, y the second.

The third column gives the Schoenflies symbol.

The fourth column gives the Hermann-Mauguin symbol (generally the short one; the full symbol is adopted when the same short symbol could refer to different settings) of the corresponding space group (principal axis z).

The fifth column gives the number of the corresponding space group, according to the International Tables for Crystallography; this number is written in parentheses when the orientation of the symmetry operators does not correspond to the first setting in the I. T.

| IGR | "Polymer" symbol (x direction) | Schoenflies | Hermann Mauguin (z direction) | Number of space group |
|-----|---|-------------|--|--------------------------|
| 1 | $P1$ | C_1^1 | $P1$ | 1 |
| 2 | $P\bar{1}$ | C_i^1 | $P\bar{1}$ | 2 |
| 3 | $P211$ | C_2^1 | $P112$ | (3) |
| 4 | $P2_111$ | C_2^2 | $P112_1$ | (4) |
| 5 | $P121$ | C_2^1 | $P121$ | (3) |
| 6 | $P112$ | C_2^1 | $P211$ | (3) |
| 7 | $Pm11$ | C_s^1 | $P11m$ | (6) |
| 8 | $P1m1$ | C_s^1 | $P1m1$ | (6) |
| 9 | $P1a1$ | C_s^2 | $P1c1$ | (7) |
| 10 | $P11m$ | C_s^1 | $Pm11$ | (6) |
| 11 | $P11a$ | C_s^2 | $Pc11$ | (7) |
| 12 | $P2/m11$ | C_{2h}^1 | $P112/m$ | (10) |
| 13 | $P2_1/m11$ | C_{2h}^2 | $P112_1/m$ | (11) |
| 14 | $P12/m1$ | C_{2h}^1 | $P12/m1$ | (10) |
| 15 | $P12/a1$ | C_{2h}^4 | $P12/c1$ | (13) |
| 16 | $P112/m$ | C_{2h}^1 | $P2/m11$ | (10) |
| 17 | $P112/a$ | C_{2h}^4 | $P2/c11$ | (13) |
| 18 | $P222$ | D_2^1 | $P222$ | 16 |
| 19 | $P2_122$ | D_2^2 | $P222_1$ | 17 |
| 20 | $P2mm$ | C_{2v}^1 | $Pmm2$ | 25 |
| 21 | $P2_1am$ | C_{2v}^2 | $Pmc2_1$ | 26 |
| 22 | $P2_1ma$ | C_{2v}^2 | $Pcm2_1$ | (26) |
| 23 | $P2aa$ | C_{2v}^3 | $Pcc2$ | 27 |
| 24 | $Pm2m$ | C_{2v}^1 | $Pm2m$ | (25) |
| 25 | $Pm2a$ | C_{2v}^4 | $Pc2m$ | (28) |
| 26 | $Pmm2$ | C_{2v}^1 | $P2mm$ | (25) |
| 27 | $Pma2$ | C_{2v}^4 | $P2cm$ | (28) |
| 28 | $Pmmm$ | D_{2h}^1 | $Pmmm$ | 47 |
| 29 | $P2/m2/a2/a$ | D_{2h}^3 | $Pccm$ | 49 |
| 30 | $P2_1/m2/m2/a$ | D_{2h}^5 | $Pcmm$ | (51) |
| 31 | $P2_1/m2/a2/m$ | D_{2h}^5 | $Pmcm$ | (51) |

| IGR | "Polymer" symbol (x direction) | Schoenflies | Hermann Mauguin (z direction) | Number of space group |
|-----|--------------------------------------|---------------|-------------------------------------|--------------------------|
| 32 | $P4$ | C_4^1 | $P4$ | 75 |
| 33 | $P4_1$ | C_4^2 | $P4_1$ | 76 |
| 34 | $P4_2$ | C_4^3 | $P4_2$ | 77 |
| 35 | $P4_3$ | C_4^4 | $P4_3$ | 78 |
| 36 | $P\bar{4}$ | S_4^1 | $P\bar{4}$ | 81 |
| 37 | $P4/m$ | C_{4h}^1 | $P4/m$ | 83 |
| 38 | $P4_2/m$ | C_{4h}^2 | $P4_2/m$ | 84 |
| 39 | $P422$ | D_4^1 | $P422$ | 89 |
| 40 | $P4_122$ | D_4^3 | $P4_122$ | 91 |
| 41 | $P4_222$ | D_4^5 | $P4_222$ | 93 |
| 42 | $P4_322$ | D_4^7 | $P4_322$ | 95 |
| 43 | $P4mm$ | C_{4v}^1 | $P4mm$ | 99 |
| 44 | $P4_2am$ | C_{4v}^3 | $P4_2cm$ | 101 |
| 45 | $P4aa$ | C_{4v}^5 | $P4cc$ | 103 |
| 46 | $P4_2ma$ | C_{4v}^7 | $P4_2mc$ | 105 |
| 47 | $P\bar{4}2m$ | D_{2d}^1 | $P\bar{4}2m$ | 111 |
| 48 | $P\bar{4}2a$ | D_{2d}^2 | $P\bar{4}2c$ | 112 |
| 49 | $P\bar{4}m2$ | D_{2d}^5 | $P\bar{4}m2$ | 115 |
| 50 | $P\bar{4}a2$ | D_{2d}^6 | $P\bar{4}c2$ | 116 |
| 51 | $P4/mmm$ | D_{4h}^1 | $P4/mmm$ | 123 |
| 52 | $P4/m2/a2/a$ | D_{4h}^4 | $P4/mcc$ | 124 |
| 53 | $P4_2/m2/m2/a$ | D_{4h}^9 | $P4_2/mmc$ | 131 |
| 54 | $P4_2/m2/a2/m$ | D_{4h}^{10} | $P4_2/mcm$ | 132 |
| 55 | $P3$ | C_3^1 | $P3$ | 143 |
| 56 | $P3_1$ | C_3^2 | $P3_1$ | 144 |
| 57 | $P3_2$ | C_3^3 | $P3_2$ | 145 |
| 58 | $P\bar{3}$ | C_{3i}^1 | $P\bar{3}$ | 147 |
| 59 | $P312$ | D_3^1 | $P312$ | 149 |
| 60 | $P3_112$ | D_3^3 | $P3_112$ | 151 |
| 61 | $P3_212$ | D_3^5 | $P3_212$ | 153 |
| 62 | $P321$ | D_3^2 | $P321$ | 150 |
| 63 | $P3_121$ | D_3^4 | $P3_121$ | 152 |
| 64 | $P3_221$ | D_3^6 | $P3_221$ | 154 |
| 65 | $P3m1$ | C_{3v}^1 | $P3m1$ | 156 |
| 66 | $P3a1$ | C_{3v}^3 | $P3c1$ | 158 |
| 67 | $P31m$ | C_{3v}^2 | $P31m$ | 157 |
| 68 | $P31a$ | C_{3v}^4 | $P31c$ | 159 |
| 69 | $P\bar{3}1m$ | D_{3d}^1 | $P\bar{3}1m$ | 162 |
| 70 | $P\bar{3}1a$ | D_{3d}^2 | $P\bar{3}1c$ | 163 |
| 71 | $P\bar{3}m1$ | D_{3d}^3 | $P\bar{3}m1$ | 164 |
| 72 | $P\bar{3}a1$ | D_{3d}^4 | $P\bar{3}c1$ | 165 |

| IGR | "Polymer" symbol (x direction) | Schoenflies | Hermann Mauguin (z direction) | Number of space group |
|-----|--------------------------------------|-------------|-------------------------------------|--------------------------|
| 73 | $P6$ | C_6^1 | $P6$ | 168 |
| 74 | $P6_1$ | C_6^2 | $P6_1$ | 169 |
| 75 | $P6_5$ | C_6^3 | $P6_5$ | 170 |
| 76 | $P6_2$ | C_6^4 | $P6_2$ | 171 |
| 77 | $P6_4$ | C_6^5 | $P6_4$ | 172 |
| 78 | $P6_3$ | C_6^6 | $P6_6$ | 173 |
| 79 | $P\bar{6}$ | C_{3h}^1 | $P\bar{6}$ | 174 |
| 80 | $P6/m$ | C_{6h}^1 | $P6/m$ | 175 |
| 81 | $P6_3/m$ | C_{6h}^3 | $P6_3/m$ | 176 |
| 82 | $P622$ | D_6^1 | $P622$ | 177 |
| 83 | $P6_122$ | D_6^2 | $P6_122$ | 178 |
| 84 | $P6_522$ | D_6^3 | $P6_522$ | 179 |
| 85 | $P6_222$ | D_6^4 | $P6_222$ | 180 |
| 86 | $P6_422$ | D_6^5 | $P6_422$ | 181 |
| 87 | $P6_322$ | D_6^6 | $P6_322$ | 182 |
| 88 | $P6mm$ | C_{6v}^1 | $P6mm$ | 183 |
| 89 | $P6aa$ | C_{6v}^2 | $P6cc$ | 184 |
| 90 | $P6_3am$ | C_{6v}^3 | $P6_3cm$ | 185 |
| 91 | $P6_3ma$ | C_{6v}^4 | $P6_3mc$ | 186 |
| 92 | $P\bar{6}m2$ | D_{3h}^1 | $P\bar{6}m2$ | 187 |
| 93 | $P\bar{6}a2$ | D_{3h}^2 | $P\bar{6}c2$ | 188 |
| 94 | $P\bar{6}2m$ | D_{3h}^3 | $P\bar{6}2m$ | 189 |
| 95 | $P\bar{6}2a$ | D_{3h}^4 | $P\bar{6}2c$ | 190 |
| 96 | $P6/mmm$ | D_{6h}^1 | $P6/mmm$ | 191 |
| 97 | $P6/m2/a2/a$ | D_{6h}^2 | $P6/mcc$ | 192 |
| 98 | $P6_3/m2/a2/m$ | D_{6h}^3 | $P6_3/mcm$ | 193 |
| 99 | $P6_3/m2/m2/a$ | D_{6h}^4 | $P6_3/mmc$ | 194 |

A.4 Labels of the point groups (molecules)

The centre of symmetry is supposed to be at the origin; for the rotation groups the principal axis is z.

The first column gives the label to be used in the input card for identifying the point group (IGR variable). The second column gives the short Hermann-Mauguin symbol. The third column gives the Schoenflies symbol; for the C_2 , C_{2h} and C_s groups the C_2 direction or the direction orthogonal to the plane is indicated. The fourth column gives the number of pure rotations for molecules (σ).

| IGR | Hermann Mauguin | Schoenflies | | σ |
|-----|--------------------|--------------|--|----------|
| 1 | 1 | C_1 | | 1 |
| 2 | $\bar{1}$ | C_i | | 1 |
| 3 | 2 (x) | C_2 (x) | | 2 |
| 4 | 2 (y) | C_2 (y) | | 2 |
| 5 | 2 (z) | C_2 (z) | | 2 |
| 6 | m (x) | C_s (x) | | 1 |
| 7 | m (y) | C_s (y) | | 1 |
| 8 | m (z) | C_s (z) | | 1 |
| 9 | 2/m (x) | C_{2h} (x) | | 2 |
| 10 | 2/m (y) | C_{2h} (y) | | 2 |
| 11 | 2/m (z) | C_{2h} (z) | | 2 |
| 12 | 222 | D_2 | | 4 |
| 13 | 2mm | C_{2v} (x) | | 2 |
| 14 | m2m | C_{2v} (y) | | 2 |
| 15 | mm2 | C_{2v} (z) | | 2 |
| 16 | mmm | D_{2h} | | 4 |
| 17 | 4 | C_4 | | 4 |
| 18 | $\bar{4}$ | S_4 | | 2 |
| 19 | 4/m | C_{4h} | | 4 |
| 20 | 422 | D_4 | | 8 |
| 21 | 4mm | C_{4v} | | 4 |
| 22 | $\bar{4}2m$ | D_{2d} | (σ_v planes along x+y and x-y) | 4 |
| 23 | $\bar{4}m2$ | D_{2d} | (σ_v planes along x and y) | 4 |
| 24 | 4/mmm | D_{4h} | | 8 |
| 25 | 3 | C_3 | | 3 |
| 26 | $\bar{3}$ | C_{3i} | | 3 |
| 27 | 321 | D_3 | (one C_2 axis along y) | 6 |
| 28 | 312 | D_3 | (one C_2 axis along x) | 6 |
| 29 | 3m1 | C_{3v} | (one σ_v plane along x) | 3 |
| 30 | 31m | C_{3v} | (one σ_v plane along y) | 3 |
| 31 | $\bar{3}m1$ | D_{3d} | (one σ_d plane along x) | 6 |
| 32 | $\bar{3}1m$ | D_{3d} | (one σ_d plane along y) | 6 |
| 33 | 6 | C_6 | | 6 |
| 34 | $\bar{6}$ | C_{3h} | | 3 |
| 35 | 6/m | C_{6h} | | 6 |
| 36 | 622 | D_6 | | 12 |
| 37 | 6mm | C_{6v} | | 6 |
| 38 | $\bar{6}m2$ | D_{3h} | (one C_2 axis along x) | 6 |
| 39 | $\bar{6}2m$ | D_{3h} | (one C_2 axis along y) | 6 |
| 40 | 6/mmm | D_{6h} | | 12 |
| 41 | 23 | T | | 12 |
| 42 | $m\bar{3}$ | T_h | | 12 |
| 43 | 432 | O | | 24 |
| 44 | $\bar{4}3m$ | T_d | | 12 |
| 45 | $m\bar{3}m$ | O_h | | 24 |
| 46 | 235 | I | | 60 |
| 47 | $m\bar{3}\bar{5}$ | I_h | | 60 |

A.5 From conventional to primitive cells: transforming matrices

The matrices describing the transformations from conventional (given as input) to primitive (internally used by CRYSTAL) cells of Bravais lattices are coded in CRYSTAL. A point called \mathbf{x} in the *direct lattice* has \mathbf{x}_P coordinates in a primitive cell and \mathbf{x}_C coordinates in a conventional cell. The relation between \mathbf{x}_P and \mathbf{x}_C is the following:

$$W\mathbf{x}_P = \mathbf{x}_C \quad (\text{A.1})$$

Likewise, for a point in the *reciprocal space* the following equation holds:

$$\tilde{W}^{-1}\mathbf{x}_P^* = \mathbf{x}_C^* \quad (\text{A.2})$$

The W transforming matrices adopted in CRYSTAL, and reported below, satisfy the following relation between the two metric tensors \mathbf{G}_P and \mathbf{G}_C :

$$\mathbf{G}_P = W\mathbf{G}_C\tilde{W} \quad (\text{A.3})$$

The values of the elements of the metric tensors \mathbf{G}_P and \mathbf{G}_C agree with those displayed in Table 5.1 of the International Tables of Crystallography (1992 edition).

$$\begin{array}{cccc}
 \begin{array}{c} P \rightarrow A \\ \left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{\bar{1}}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{array} \right) \end{array} &
 \begin{array}{c} P \rightarrow B \\ \left(\begin{array}{ccc} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{\bar{1}}{2} & 0 & \frac{1}{2} \end{array} \right) \end{array} &
 \begin{array}{c} A \rightarrow P \\ \left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & -1 & 1 \end{array} \right) \end{array} &
 \begin{array}{c} B \rightarrow P \\ \left(\begin{array}{ccc} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{array} \right) \end{array} \\
 \\
 \begin{array}{c} P \rightarrow C \\ \left(\begin{array}{ccc} \frac{1}{2} & \frac{\bar{1}}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{array} \right) \end{array} &
 \begin{array}{c} P \rightarrow F \\ \left(\begin{array}{ccc} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{array} \right) \end{array} &
 \begin{array}{c} C \rightarrow P \\ \left(\begin{array}{ccc} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right) \end{array} &
 \begin{array}{c} F \rightarrow P \\ \left(\begin{array}{ccc} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{array} \right) \end{array} \\
 \\
 \begin{array}{c} P \rightarrow I \\ \left(\begin{array}{ccc} \frac{\bar{1}}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{\bar{1}}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{\bar{1}}{2} \end{array} \right) \end{array} &
 \begin{array}{c} R \rightarrow H \\ \left(\begin{array}{ccc} \frac{2}{3} & \frac{\bar{1}}{3} & \frac{\bar{1}}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{\bar{2}}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{array} \right) \end{array} &
 \begin{array}{c} I \rightarrow P \\ \left(\begin{array}{ccc} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{array} \right) \end{array} &
 \begin{array}{c} H \rightarrow R \\ \left(\begin{array}{ccc} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{array} \right) \end{array}
 \end{array}$$

Table A.1: W matrices for the transformation from conventional to primitive and from primitive to conventional cells. P stands for primitive, A, B and C for A-, B- and C-face centred, I for body centred, F for all-face centred, R for primitive rhombohedral ('rhombohedral axes') and H for rhombohedrally centred ('hexagonal axes') cell (Table 5.1, ref. [91]).

Appendix B

Summary of input keywords

All the keywords are entered with an A format; the keywords must be typed left-justified, with no leading blanks. The input is not case sensitive.

Geometry (Input block 1)

| Symmetry information | | | |
|---|--|----|---|
| ATOMSYMM | printing of point symmetry at the atomic positions | 36 | – |
| MAKESAED | printing of symmetry allowed elastic distortions (SAED) | 47 | – |
| PRSYMDIR | printing of displacement directions allowed by symmetry. | 59 | – |
| SYMMDIR | printing of symmetry allowed geom opt directions | 67 | – |
| SYMMOPS | printing of point symmetry operators | 67 | – |
| TENSOR | print tensor of physical properties up to order 4 | 67 | I |
| Symmetry information and control | | | |
| BREAKELAS | symmetry breaking according to a general distortion | 37 | I |
| BREAKSYMM | allow symmetry reduction following geometry modifications | 37 | – |
| KEEPSYMM | maintain symmetry following geometry modifications | 47 | – |
| MODISYMM | removal of selected symmetry operators | 48 | I |
| PURIFY | cleans atomic positions so that they are fully consistent with the group | 59 | – |
| SYMMREMO | removal of all symmetry operators | 67 | – |
| TRASREMO | removal of symmetry operators with translational components | 68 | – |
| Modifications without reduction of symmetry | | | |
| ATOMORDE | reordering of atoms in molecular crystals | 34 | – |
| NOSHIFT | no shift of the origin to minimize the number of symmops with translational components before generating supercell | 56 | – |
| ORIGIN | shift of the origin to minimize the number of symmetry operators with translational components | 56 | – |
| PRIMITIV | crystallographic cell forced to be the primitive cell | 58 | – |
| ROTCRY | rotation of the crystal with respect to the reference system cell | 60 | I |
| Atoms and cell manipulation - possible symmetry reduction (BREAKSYMM) | | | |

| | | | |
|------------------|---|----|---|
| ATOMDISP | displacement of atoms | 34 | I |
| ATOMINSE | addition of atoms | 34 | I |
| ATOMREMO | removal of atoms | 35 | I |
| ATOMROT | rotation of groups of atoms | 35 | I |
| ATOMSUBS | substitution of atoms | 36 | I |
| ELASTIC | distortion of the lattice | 40 | I |
| POINTCHG | point charges input | 58 | I |
| SCELCONF | generation of supercell for configuration counting | 63 | I |
| SCELPHONO | generation of supercell for phonon dispersion | 63 | I |
| SUPERCEL | generation of supercell - input refers to primitive cell | 64 | I |
| SUPERCON | generation of supercell - input refers to conventional cell | 64 | I |
| USESSED | given symmetry allowed elastic distortions, reads δ | 68 | I |

| |
|--------------------------------|
| From crystals to slabs (3D→2D) |
|--------------------------------|

| | | | |
|-----------------|--|----|---|
| SLABINFO | definition of a new cell, with $xy \parallel$ to a given plane | 62 | I |
| SLABCUT | generation of a slab parallel to a given plane (3D→2D) | 61 | I |

| |
|---------------------------------|
| From slabs to nanotubes (2D→1D) |
|---------------------------------|

| | | | |
|-----------------|--|----|---|
| NANOTUBE | building a nanotube from a slab | 52 | I |
| SWCNT | building a nanotube from an hexagonal slab | 66 | I |

| |
|--------------------------------------|
| From periodic structures to clusters |
|--------------------------------------|

| | | | |
|------------------|--|----|---|
| CLUSTER | cutting of a cluster from a periodic structure (3D→0D) | 38 | I |
| CLUSTSIZE | maximum number of atoms in a cluster | 47 | I |
| FULLE | building a fullerene from an hexagonal slab (2D→0D) | 45 | I |
| HYDROSUB | border atoms substituted with hydrogens (0D→0D) | 47 | I |

| |
|--------------------|
| Molecular crystals |
|--------------------|

| | | | |
|-----------------|---|----|---|
| MOLECULE | extraction of a set of molecules from a molecular crystal (3D→0D) | 49 | I |
| MOLEXP | variation of lattice parameters at constant symmetry and molecular geometry (3D→3D) | 49 | I |
| MOLSPLIT | periodic structure of non interacting molecules (3D→3D) | 49 | - |
| RAYCOV | modification of atomic covalent radii | 59 | I |

| |
|-----------------|
| BSSE correction |
|-----------------|

| | | | |
|-----------------|---|----|---|
| MOLEBSSE | counterpoise method for molecules (molecular crystals only) (3D→0D) | 48 | I |
| ATOMBSSE | counterpoise method for atoms (3D→0D) | 34 | I |

| |
|---------------------------------------|
| Systematic analysis of crystal planes |
|---------------------------------------|

| | | | |
|---------------|------------------------------------|----|---|
| PLANES | Prints the possible crystal planes | 58 | I |
|---------------|------------------------------------|----|---|

| |
|--------------------------|
| Gibbs-Wulff construction |
|--------------------------|

| | | | |
|--------------|-------------------------------------|----|---|
| WULFF | Building the Gibbs-Wulff polihedron | 68 | I |
|--------------|-------------------------------------|----|---|

| |
|-----------------------------------|
| From crystals to nanorods (3D→1D) |
|-----------------------------------|

| | | | |
|-----------------|-----------------------------------|----|---|
| NANORODS | Building a nanorod from a crystal | 51 | I |
|-----------------|-----------------------------------|----|---|

| |
|---------------------------------------|
| From crystals to nanocrystals (3D→0D) |
|---------------------------------------|

| | | | |
|--------------------|---------------------------------------|----|---|
| NANOCRYSTAL | building a nanocrystal from a crystal | 50 | I |
|--------------------|---------------------------------------|----|---|

| |
|--------------------------------|
| Auxiliary and control keywords |
|--------------------------------|

| | | | |
|------------------|--|----|---|
| ANGSTROM | sets input units to Ångstrom | 33 | - |
| BOHR | sets input units to bohr | 36 | - |
| BOHRANGS | input bohr to Å conversion factor (0.5291772083 default value) | 36 | I |
| BOHRCR98 | bohr to Å conversion factor is set to 0.529177 (CRY98 value) | - | - |
| END/ENDG | terminate processing of geometry input | | - |
| FRACTION | sets input units to fractional | 45 | - |
| LATVEC | maximum number of classified lattice vectors | ?? | I |
| MAXNEIGHB | maximum number of equidistant neighbours from an atom | 47 | I |
| NEIGHBOR | number of neighbours in geometry analysis | 56 | I |
| PRINTCHG | printing of point charges coordinates in geometry output | 58 | |
| PRINTOUT | setting of printing options by keywords | 59 | - |
| SETINF | setting of inf array options | 61 | I |
| SETPRINT | setting of printing options | 61 | I |
| STOP | execution stops immediately | 62 | - |
| TESTGEOM | stop after checking the geometry input | 68 | - |

| |
|----------------------------------|
| Output of data on external units |
|----------------------------------|

| | | | |
|-----------------|--|----|---|
| COORPRT | coordinates of all the atoms in the cell | 40 | - |
| EXTPRT | write file in CRYSTAL geometry input format | 41 | - |
| FINDSYM | write file in FINDSYM input format | 44 | - |
| STRUCPRT | cell parameters and coordinates of all the atoms in the cell | 62 | - |

| |
|--|
| External electric field - modified Hamiltonian |
|--|

| | | | |
|-----------------|---|----|---|
| FIELD | electric field applied along a periodic direction | 42 | I |
| FIELDCON | electric field applied along a non periodic direction | 44 | I |

| |
|--|
| Geometry optimization - see index for keywords full list |
|--|

| | | | |
|--|--|-----|---|
| OPTGEOM | Geometry optimization input block - closed by END | 118 | I |
| Type of optimization (default: atom coordinates) | | | |
| FULLOPTG | full geometry optimization | | – |
| CELLONLY | cell parameters optimization | | – |
| INTREDUN | optimization in redundant internal coordinates | 128 | – |
| ITATOCEL | iterative optimization (atom/cell) | | – |
| CVOLOPT | full geometry optimization at constant volume | 133 | – |
| Initial Hessian | | | |
| HESSIDEN | initial guess for the Hessian - identity matrix | | – |
| HESSMOD1 | initial guess for the Hessian - model 1 (default) | | – |
| HESSMOD2 | initial guess for the Hessian - model 2 | | – |
| HESSNUM | initial guess for the Hessian - numerical estimate | | – |
| Convergence criteria modification | | | |
| TOLDEG | RMS of the gradient [0.0003] | | I |
| TOLDEX | RMS of the displacement [0.0012] | | I |
| TOLDEE | energy difference between two steps [10^{-7}] | | I |
| MAXCYCLE | max number of optimization steps | | I |
| Optimization control | | | |
| FRAGMENT | partial geometry optimization | 135 | I |
| RESTART | data from previous run | | – |
| FINALRUN | Wf single point with optimized geometry | | I |
| Gradient calculation control | | | |
| NUMGRATO | numerical atoms first derivatives | 127 | – |
| NUMGRCEL | numerical cell first derivatives | 127 | – |
| NUMGRALL | numerical atoms and cell first derivatives | 127 | – |
| External stress | | | |
| EXTSTRESS | apply external stress | 137 | I |
| EXTPRESS | apply external hydrostatic pressure | 137 | I |
| Printing options | | | |
| PRINTFORCES | atomic gradients | | – |
| PRINTHESS | Hessian | | – |
| PRINTOPT | optimization procedure | | – |
| PRINT | verbose printing | | – |

| |
|--|
| Vibrational Frequencies - see index for keywords full list |
|--|

| | | | |
|--|---|-----|---|
| FREQCALC | Harmonic Γ -frequencies calculation input - closed by END | 142 | I |
| <div style="border: 1px solid black; padding: 2px; display: inline-block;">Normal modes analysis</div> | | | |
| ANALYSIS | | 144 | – |
| COMBMODE | TO combination modes and overtones | 145 | I |
| MODES | printing eigenvectors [default] | 147 | – |
| SCANMODE | scan geometry along selected modes | 154 | I |
| <div style="border: 1px solid black; padding: 2px; display: inline-block;">LO/TO splitting</div> | | | |
| DIELISO | isotropic dielectric tensor | 145 | I |
| DIELTENS | anisotropic dielectric tensor | 145 | I |
| <div style="border: 1px solid black; padding: 2px; display: inline-block;">Vibrational spectrum simulation</div> | | | |
| INTENS | intensities calculation active | 150 | – |
| INTCPHF | IR (and Raman) intensities via CPHF | 152 | I |
| INTLOC | IR intensities through Wannier functions | 151 | – |
| INTPOL | IR intensities through Berry phase [default] | 152 | – |
| INTRAMAN | Raman intensities calculation | 152 | I |
| IRSPEC | IR spectrum production | 158 | I |
| RAMSPEC | Raman spectrum production | 160 | I |
| <div style="border: 1px solid black; padding: 2px; display: inline-block;">Calculation control</div> | | | |
| ECKART | Hessian freed by translations and rotations [default] | 145 | I |
| FRAGMENT | partial frequency calculation | 146 | I |
| ISOTOPES | isotopic substitution | 146 | I |
| NORMBORN | normalized Born tensor | 147 | – |
| NUMDERIV | technique to compute numerical 2nd derivatives | 148 | I |
| PRINT | verbose printing | | – |
| RESTART | data from previous run | | – |
| STEPSIZE | set size of cartesian displacements [0.003 Å] | 148 | I |
| TEST[FREQ] | frequency test run | | – |

| | | | |
|---------------------------------|---|-----|---|
| USESMM | full-symmetry exploitation at each point [default] | | – |
| <i>A posteriori</i> corrections | | | |
| SCANPES | anharmonic correction | ?? | I |
| ANSCAN | scan a mode and apply anharmonic corrections | ?? | I |
| Phonon dispersion | | | |
| DISPERSION | frequencies calculated at $\vec{k} \neq \Gamma$ points | 161 | – |
| Thermodynamics | | | |
| ADP | anisotropic displacement parameters | 148 | I |
| PRESSURE | set pressure range | 148 | I |
| TEMPERAT | set temperature range | | I |
| ANHARM | Anharmonic frequencies calculation input block - closed by END | 165 | I |
| ISOTOPES | isotopic substitution | 166 | I |
| KEEPSYMM | displace all symmetry equivalent atoms | ?? | – |
| NOGUESS | | 166 | – |
| POINTS26 | X-H distance varied 26 times around the equilibrium | 166 | – |
| PRINT | verbose printing | | – |
| TEST[ANHA] | test run | | – |

| |
|--|
| Configurations counting and characterization |
|--|

| | | | |
|------------------|--|-----|---|
| CONF CNT | configurations counting and cluster expansion | 174 | I |
| CONF RAND | symmetry-adapted uniform at random Monte Carlo | 176 | I |
| RUNCONF S | single-point calculations and geometry optimizations | 177 | I |

| | |
|--|-----|
| CPHF - Coupled Perturbed Hartree-Fock | 168 |
|--|-----|

| | |
|--|-----|
| ELASTCON - Second order elastic constants | 183 |
|--|-----|

| | |
|--------------------------------|-----|
| EOS - Equation of state | 168 |
|--------------------------------|-----|

Basis set input (Input block 2)

| |
|------------------|
| Symmetry control |
|------------------|

| | | | |
|-----------------|--|----|---|
| ATOMSYMM | printing of point symmetry at the atomic positions | 36 | – |
|-----------------|--|----|---|

| |
|------------------------|
| Basis set modification |
|------------------------|

| | | | |
|---------------|--|----|---|
| CHEMOD | modification of the electronic configuration | 69 | I |
| GHOSTS | eliminates nuclei and electrons, leaving BS | 71 | I |

| |
|--------------------------------|
| Auxiliary and control keywords |
|--------------------------------|

| | | | |
|-----------------|---|----|---|
| CHARGED | allows non-neutral cell | 69 | - |
| NOPRINT | printing of basis set removed | 71 | - |
| PRINTOUT | setting of printing options | 59 | I |
| SETINF | setting of inf array options | 61 | I |
| SETPRINT | setting of printing options | 61 | I |
| STOP | execution stops immediately | 62 | - |
| SYMMOPS | printing of point symmetry operators | 67 | - |
| END/ENDB | terminate processing of basis set definition keywords | | - |

| |
|----------------------------------|
| Output of data on external units |
|----------------------------------|

| | | | |
|----------------|--|----|---|
| GAUSS98 | printing of an input file for the GAUSS94/98 package | 71 | - |
|----------------|--|----|---|

General information, hamiltonian, SCF (Input block 3)

All DFT related keyword are collected under the heading "DFT", closed b **END[DFT]**

| |
|-----------------------------|
| Single particle Hamiltonian |
|-----------------------------|

| | | | |
|------------|-----------------------------|-----|---|
| RHF | Restricted Closed Shell | 109 | - |
| UHF | Unrestricted Open Shell | 116 | - |
| MP2 | Electron correlation energy | 107 | - |

| | | | |
|------------|--|-----|---|
| DFT | DFT Hamiltonian | 116 | – |
| | SPIN spin-polarized solution | 88 | – |
| | Choice of the exchange-correlation functionals | | |
| | EXCHANGE exchange functional | 83 | I |
| | <i>LDA functionals</i> | | |
| | LDA Dirac-Slater [44] (LDA) | | |
| | VBH von Barth-Hedin [178] (LDA) | | |
| | <i>GGA functionals</i> | | |
| | BECKE Becke 1988[17] (GGA) | | |
| | PBE Perdew-Becke-Ernzerhof 1996 [128] (GGA) | | |
| | PBESOL GGA. PBE functional revised for solids [130] | | |
| | mPW91 modified Perdew-Wang 91 (GGA) | | |
| | PWGGA Perdew-Wang 91 (GGA) | | |
| | SOGGA second order GGA. [195] | | |
| | WCGGA GGA - Wu-Cohen [187] | | |
| | CORRELAT correlation functional | 83 | I |
| | <i>LDA functionals</i> | | |
| | PZ Perdew-Zunger [134] (LDA) | | |
| | VBH von Barth-Hedin [178] (LDA) | | |
| | VWN Vosko,-Wilk-Nusair [179] (LDA) | | |
| | <i>GGA functionals</i> | | |
| | LYP Lee-Yang-Parr [109] (GGA) | | |
| | P86 Perdew 86 [126] (GGA) | | |
| | PBE Perdew-Becke-Ernzerhof [128] (GGA) | | |
| | PBESOL GGA. PBE functional revised for solids [130] | | |
| | PWGGA Perdew-Wang 91 (GGA) | | |
| | PWLSLSD Perdew-Wang 92 [132, 133, 131] (GGA) | | |
| | WL GGA - Wilson-Levy [185] | | |
| | Standalone keywords: exchange+correlation | | |
| | SVWN see [44, 179] | 84 | |
| | BLYP see [17, 109] | 84 | |
| | PBEXC see [128] | 84 | |
| | PBESOLXC see [130] | 84 | |
| | SOGGAXC see [195] | 84 | |
| | Global Hybrid functionals | | |
| | Standalone keywords | | |
| | B3PW B3PW parameterization | 84 | – |
| | B3LYP B3LYP parameterization | 84 | – |
| | PBE0 Adamo and Barone [6] | 84 | |
| | PBESOL0 Derived from PBE0 | 84 | |
| | B1WC see [20] | 84 | |
| | WC1LYP see [42] | 84 | |
| | B97H see [5, 68] | 84 | |
| | PBE0-13 see [29] | 84 | |
| | User defined global hybrids | | |
| | HYBRID hybrid mixing | 85 | I |
| | NONLOCAL local term parameterization | 85 | I |

Range-Separated Hybrid functionals

Short-range Corrected RSH functionals

HSE06 Screened-Coulomb PBE XC functional [3, 128] 86 –

HSESOL Screened-Coulomb PBESOL XC functional [108, 130] 86 –

Middle-range Corrected RSH functionals

HISS MC based on PBE XC functional [169, 170] 86 –

Long-range Corrected RSH functionals

RSHXLDA LC LDA XC functional [2, 102] 86 –

wB97 Chai/Head-Gordon LC functional [103, 5] 86 –

wB97X Chai/Head-Gordon SC/LC functional [103, 5] 86 –

LC-wPBE LC hybrid based on PBE XC functional [57] 86 –

LC-wPBESOL LC hybrid based on PBESOL XC functional [57] 86 –

LC-wBLYP LC hybrid based on BLYP XC functional [57] 86 –

meta-GGA functionals

Pure mGGA functionals

M06L pure mGGA M06-type functional [190] 87 –

Global hybrid mGGA functionals

M05 Minnesota 2005 functional [194] 87 –

M052x M05-2X functional [193] 87 –

M06 Minnesota 2006 functional [192] 87 –

M062X M06-2X functional [192] 87 –

M06HF M06-type functional with 100% HF [190] 87 –

Double Hybrid functionals

B2PLYP DH method based on BLYP functional [152] 87 –

B2GPPLYP General purpose variant of B2PLYP [1] 87 –

mPW2PLYP DH method based on mPW91-LYP functional [172] 87 –

DHYBRID HF exchange and MP2-like mixing for double hybrids 88 I

Numerical accuracy control

ANGULAR definition of angular grid 88 I

RADIAL definition of radial grid 88 I

[BECKE] selection of Becke weights (default) 88 –

SAVIN selection of Savin weights 88 –

OLDGRID "old" default grid 90

LGRID "large" predefined grid 91

[XLGRID] "extra large" predefined grid (new default)

XXLGRID "extra extra large" predefined grid 91

RADSAFE safety radius for grid point screening I

TOLLDENS density contribution screening [6] 92 I

TOLLGRID grid points screening [14] 92 I

[BATCHPNT] grid point grouping for integration 92 I

CHUNKS max n. points in a batch for numerical int. 92 I

DISTGRID distribution of DFT grid across nodes 92

LIMBEK size of local arrays for integration weights [400] ?? I

Atomic parameters control

RADIUS customized atomic radius 93 I

FCHARGE customized formal atomic charge 93 I

Auxiliary

END close DFT input block

Numerical accuracy and computational parameters control

| | | | |
|--|--|-----|---|
| BIPOLAR | Bipolar expansion of bielectronic integrals | 81 | I |
| BIPOSIZE | size of coulomb bipolar expansion buffer | 104 | I |
| EXCHSIZE | size of exchange bipolar expansion buffer | 104 | I |
| EXCHPERM | use permutation of centers in exchange integrals | 95 | - |
| ILASIZE | Maximum size of array ILA for 2-electron integral calculation ?? 6000 | | I |
| INTGPACK | Choice of integrals package 0 | 104 | I |
| MADLIND | reciprocal lattice vector indices for Madelung sums 50 | 106 | I |
| NOBIPCOU | Coulomb bielectronic integrals computed exactly | 108 | - |
| NOBIPEXCH | Exchange bielectronic integrals computed exactly | 108 | - |
| NOBIPOLA | All bielectronic integrals computed exactly | 108 | - |
| POLEORDR | Maximum order of multipolar expansion 4 | 108 | I |
| TOLINTEG | Truncation criteria for bielectronic integrals 6 6 6 6 12 | 115 | I |
| TOLPSEUD | Pseudopotential tolerance 6 | 115 | I |
| Type of run | | | |
| ATOMHF | Atomic wave functions | 79 | I |
| SCFDIR | SCF direct (mono+biel int computed) | 109 | - |
| EIGS | S(k) eigenvalues - basis set linear dependence check | 93 | - |
| FIXINDEX | Reference geometry to classify integrals | 98 | - |
| Basis set - AO occupancy | | | |
| FDAOSYM | f and d degeneracies analysis | 96 | I |
| FDAOCCUP | f and d orbital occupation guess | 97 | I |
| GUESDUAL | Density matrix guess - different Basis set | 102 | I |
| Integral file distribution | | | |
| BIESPLIT | writing of bielectronic integrals in n files $n = 1$, max=10 | 81 | I |
| MONSPLIT | writing of mono-electronic integrals in n file $n = 1$, max=10 | 106 | I |
| Numerical accuracy control and convergence tools | | | |
| ANDERSON | Fock matrix mixing | 79 | I |
| BROYDEN | Fock matrix mixing | 82 | I |
| FMIXING | Fock/KS matrix (cycle i and $i-1$) mixing 0 | 99 | I |
| LEVSHIFT | level shifter no | 105 | I |
| MAXCYCLE | maximum number of cycles 50 | 106 | I |
| SMEAR | Finite temperature smearing of the Fermi surface no | 112 | I |
| TOLDEE | convergence on total energy 6 | 115 | I |
| Initial guess | | | |
| EIGSHIFT | alteration of orbital occupation before SCF no | 94 | I |
| EIGSHROT | rotation of the reference frame no | 94 | I |
| GUESSP | density matrix from a previous run | 103 | - |
| GUESSPAT | superposition of atomic densities | 104 | - |
| Spin-polarized system | | | |
| ATOMSPIN | setting of atomic spin to compute atomic densities | 80 | I |
| BETALOCK | beta electrons locking | 80 | I |
| SPINLOCK | spin difference locking | 114 | I |
| SPINEDIT | editing of the spin density matrix used as SCF guess | 113 | I |
| Auxiliary and control keywords | | | |

| | | | |
|------------------|---|-----|---|
| END | terminate processing of block3 input | | – |
| FULLTIME | detailed report on running time | 100 | – |
| KSYMPRT | printing of Bloch functions symmetry analysis | 105 | – |
| LOWMEM | inhibits allocation of large arrays | 108 | – |
| NOLOWMEM | allows allocation of large arrays | 108 | – |
| MAXNEIGHB | maximum number of equidistant neighbours from an atom | 47 | I |
| NEIGHBOR | number of neighbours to analyse in PPAN | 56 | I |
| MEMOPRT | Synthetic report about dynamic memory usage | 106 | – |
| MEMOPRT2 | Detailed report about dynamic memory usage | 106 | – |
| PRINTOUT | setting of printing options | 59 | I |
| QVRSODIM | maximum size of multipole moment gradient array <input type="text" value="90000000"/> | 109 | I |
| NOSYMADA | No Symmetry Adapted Bloch Functions | 108 | – |
| SYMADAPT | Symmetry Adapted Bloch Functions (default) | 114 | – |
| SETINF | setting of inf array options | 61 | I |
| SETPRINT | setting of printing options | 61 | I |
| STOP | execution stops immediately | 62 | – |
| TESTPDIM | stop after symmetry analysis | 115 | – |
| TEST[RUN] | stop after integrals classification and disk storage estimate | 115 | – |

Restricted to *MPPcrystal*

| | | | |
|-----------------|--|-----|---|
| CMPLXFAC | Overloading in handling matrices at “complex” k points with 82 respect to “real” k points <input type="text" value="2.3"/> | | I |
| REPLDATA | to run <i>MPPcrystal</i> as <i>Pcrystal</i> | 109 | – |
| STDIAG | Enable standard diagonalization method (D&C method disabled) | 114 | – |

Output of data on external units

| | | | |
|---------------|---|-----|---|
| NOFMWF | wave function formatted output not written in file fort.98. | 108 | – |
| SAVEWF | wave function data written every two SCF cycles | 110 | – |

Post SCF calculations

| | | | |
|-----------------|---|-----|---|
| POSTSCF | post-scf calculations when convergence criteria not satisfied | 109 | – |
| EXCHGENE | exchange energy evaluation (spin polarized only) | 95 | – |
| GRADCAL | analytical gradient of the energy | 100 | – |
| PPAN | population analysis at the end of the SCF <input type="text" value="no"/> | 109 | – |

Properties

RDFMWF wave function data conversion formatted-binary (fort.98 → fort.9)

Preliminary calculations

| | | | |
|-----------------|--|-----|---|
| NEWK | Eigenvectors calculation | 228 | I |
| COMMENS | Density Matrix commensurate to the Monchorst net | 204 | I |
| NOSYMADA | No symmetry Adapted Bloch Functions | 108 | – |
| PATO | Density matrix as superposition of atomic (ionic) densities | 229 | I |
| PBAN | Band(s) projected density matrix (preliminary NEWK) | 229 | I |
| PGEOMW | Density matrix from geometrical weights (preliminary NEWK) | 230 | I |
| PDIDE | Energy range projected density matrix (preliminary NEWK) | 230 | I |
| PSCF | Restore SCF density matrix | 236 | – |

Properties computed from the density matrix

| | | | |
|-----------------|---|-----|---|
| ADFT | Atomic density functional correlation energy | 197 | I |
| BAND | Band structure | 199 | I |
| BIDIERD | Reciprocal form factors | 202 | I |
| CLAS | Electrostatic potential maps (point multipoles approximation) | 204 | I |
| ECHG | Charge density and charge density gradient - 2D grid | 209 | I |
| ECH3 | Charge density - 3D grid | 208 | I |
| EDFT | Density functional correlation energy (HF wave function only) | 209 | I |
| EMDLDM | Electron momentum distribution (along a line) | 211 | I |
| EMDPDM | Electron momentum distribution (in a plane) | 211 | I |
| KINETEMD | Kinetic tensor from electron momentum density | 215 | I |
| PMP2 | MP2 correction to the Valence Density Matrix | 230 | |
| POLI | Atom and shell multipoles evaluation | 231 | I |
| POTM | Electrostatic potential - 2D grid | 234 | I |
| POT3 | Electrostatic potential - 3D grid | 232 | I |
| POTC | Electrostatic properties | 233 | I |
| PPAN | Mulliken population analysis | 109 | |
| XFAC | X-ray structure factors | 237 | I |

Properties computed from the density matrix (spin-polarized systems)

| | | | |
|------------------|---|-----|---|
| ANISOTRO | Hyperfine electron-nuclear spin tensor | 198 | I |
| ISOTROPIC | Hyperfine electron-nuclear spin interaction - Fermi contact | 214 | I |
| POLSPIN | Atomic spin density multipoles | 231 | I |

Properties computed from eigenvectors (after keyword **NEWK**)

| | | | |
|---------------|---|-----|---|
| ANBD | Printing of principal AO component of selected CO | 197 | I |
| BWIDTH | Printing of bandwidth | 203 | I |
| DOSS | Density of states | 207 | I |
| EMDL | Electron momentum distribution - line | 210 | I |
| EMDP | Electron momentum distribution - plane maps | 213 | I |
| PROF | Compton profiles and related quantities | 235 | I |

New properties

| | | | |
|-----------------|--|-----|---|
| SPOLBP | Spontaneous polarization (Berry phase approach) | 240 | – |
| SPOLWF | Spontaneous polarization (localized CO approach) | 241 | – |
| LOCALWF | Localization of Wannier functions | 215 | I |
| DIEL | Optical dielectric constant | 205 | I |
| ISO+POTC | Mössbauer isomer shift and quadrupolar effects | 241 | I |
| TOPO | Topological analysis of the electron density | 244 | I |

Auxiliary and control keywords

| | | | |
|------------------|--|-----|---|
| ANGSTROM | Set input unit of measure to Ångstrom | 33 | – |
| BASISSET | Printing of basis set, Fock/KS, overlap and density matrices | 202 | – |
| BOHR | Set input unit of measure to bohr | 36 | – |
| CHARGED | Non-neutral cell allowed (PATO) | 69 | – |
| END | Terminate processing of properties input keywords | | – |
| FRACTION | Set input unit of measure to fractional | 45 | – |
| MAPNET | Generation of coordinates of grid points on a plane | 226 | I |
| MAXNEIGHB | maximum number of equidistant neighbours from an atom | 47 | I |
| NEIGHBOR | Number of neighbours to analyse in PPAN | 56 | I |
| PRINTOUT | Setting of printing options | 59 | I |
| RAYCOV | Modification of atomic covalent radii | 59 | I |
| SETINF | Setting of inf array options | 61 | I |
| SETPRINT | Setting of printing options | 61 | I |
| STOP | Execution stops immediately | 62 | – |
| SYMMOPS | Printing of point symmetry operators | 67 | – |

| Info - Output of data on external units | | | |
|---|---|-----|---|
| ATOMIRR | Coordinates of the irreducible atoms in the cell | 198 | - |
| ATOMSYMM | Printing of point symmetry at the atomic positions | 36 | - |
| COORPRT | Coordinates of all the atoms in the cell | 40 | - |
| CRYAPI_OUT | geometry, BS, direct lattice information | 205 | - |
| EXTPRT | Explicit structural/symmetry information | 41 | - |
| FMWF | Wave function formatted output in file fort.98. Section 9.2 | 213 | - |
| INFOGUI | Generation of file with wf information for visualization | 214 | - |
| CRYAPI_OUT | Reciprocal lattice information + eigenvalues | 205 | - |

Appendix C

Printing options

Extended printing can be obtained by entering the keywords **PRINTOUT** (page 59) or **SET-PRINT** (page 61).

In the **scf** (or **scfdir**) program the printing of quantities computed is done at each cycle if the corresponding LPRINT value is positive, only at the last cycle if the LPRINT value is negative. The LPRINT options to obtain intermediate information can be grouped as follows. The following table gives the correspondence between position number, quantity printed, and keyword.

| <code>crystal</code> | Keyword | inp |
|--|--------------------|-----|
| • direct lattice - geometry information: 1 | <i>GLATTICE</i> | – |
| • symmetry operators : 4, 2 | <i>SYMMOPS</i> | – |
| • atomic functions basis set : 72 | <i>BASISSET</i> | – |
| • DF auxiliary basis set for the fitting: 79 | <i>DFTBASIS</i> | – |
| • scale factors and atomic configuration: 75 | <i>SCALEFAC</i> | – |
| • k-points geometrical weight: 53 | <i>KWEIGHTS</i> | – |
| • shell symmetry analysis : 5, 6, 7, 8, 9 | | |
| • Madelung parameters: 28 | | |
| • multipole integrals: 20 | | |
| • Fock/KS matrix building - direct lattice: 63, 64, 74 | <i>FGRED FGIRR</i> | N |
| • Total energy contributions: 69 | <i>ENECYCLE</i> | – |

| <code>crystal</code> - <code>properties</code> | Keyword | inp |
|--|--------------------|-----|
| • shell and atom multipoles: 68 | <i>MULTIPOLE</i> | N |
| • reciprocal space integration to compute Fermi energy: 51, 52, 53, 54, 55, 78 | | |
| • density matrix - direct lattice: irreducible (58); reducible (59) (reducible P matrix in <i>crystal</i> if PPAN requested only) | <i>PGRED PGIRR</i> | N |
| • Fock/KS eigenvalues : 66 | <i>EIGENVAL</i> | N |
| <i>EIGENALL</i> – | | |
| • Fock/KS eigenvectors : 67 | <i>EIGENVEC</i> | N |
| • symmetry adapted functions : 47 | <i>KSYMMPRT</i> | – |

- Population analysis: 70, 73, 77 *MULLIKEN* N
- Atomic wave-function: 71

properties

- overlap matrix S(g) - direct lattice: 60 (keyword **PSIINF**) *OVERLAP* N
- Densities of states: 105, 107 *DOSS* -
- Projected DOSS for embedding: 36, 37, 38
- DF correlation correction to total energy: 106
- Compton profile and related quantities: 116, 117, 118
- Fermi contact tensor : 18 *FTENSOR* -
- rotated eigenvectors (keyword ROTREF): 67 *EIGENVEC* -
- Charge density and electrostatic potential maps: 119 *MAPVALUES* -

Example

To print the eigenvalues at each scf cycle enter:

```
PRINTOUT
EIGENALL
END
```

To print the eigenvalues at the first 5 *k* points at the end of scf only, enter in any input block:

```
SETPRINT
1
66 -5
```

Eigenvectors printed by default are from the first valence eigenvector up to the first 6 virtual ones. Core and virtual eigenvectors are printed by "adding" 500 to the selected value of LPRINT(67). To obtain print all the eigenvectors at the end of scf insert in any input block:

```
SETPRINT
1
66 -505
```

Printing options LPRINT array values

| | subroutine | value | printed information | keyword | input |
|----|------------|-------|---|------------|-------|
| 1 | GCALCO | N | up N=6 stars of direct lattice vectors | GLATTICE | |
| 2 | CRYSTA | ≠ 0 | crystal symmetry operators | SYMMOPS | |
| 3 | EQUPOS | ≠ 0 | equivalent positions in the reference cell | EQUIVAT | |
| 4 | CRYSTA | ≠ 0 | crystal symmops after geometry editing | | |
| 5 | GILDA1 | N>0 | g vector irr- first n set type of couples | | |
| | | N<0 | g vector irr- n-th set type of couples | | |
| 6 | GROTA1 | ≠ 0 | information on shells symmetry related | | |
| 7 | GV | N>0 | stars of g associated to the first n couples | | |
| | | N<0 | stars of g associated to the n-th couple | | |
| 8 | GORDSH | ≠ 0 | information on couples of shells symmetry related | | |
| 9 | GSYM11 | ≠ 0 | intermediates for symmetrized quantities | | |
| 10 | GMFCAL | ≠ 0 | nstatg, idime, idimf, idimcou | | |
| 11 | MAIN2U | ≠ 0 | exchange energy | EXCHGENE | |
| | MAIND | | | EXCHGENE | |
| 12 | IRRPR | ≠ 0 | symmops (reciprocal lattice) | SYMMOPSR | |
| 13 | MATVIC | N | n stars of neighbours in cluster definition | | |
| 14 | GSLAB | ≠ 0 | coordinates of the atoms in the slab | | |
| 15 | symdir | ≠ 0 | print symmetry allowed directions | PRSYMDIR | |
| 18 | Tensor | ≠ 0 | extended printing for hyperfine coupling cost | FTENSOR | |
| 19 | | | | | |
| 20 | MONIRR | N | multipole integrals up to pole l=n | | |
| 21 | | | | | |
| 24 | POINTCH | | printing of point charges coordinates | | |
| 28 | MADDEL2 | ≠ 0 | Madelung parameters | | |
| 29 | | | | | |
| 30 | CRYSTA | ≠ 0 | write file FINDSYM.DAT | | |
| 31 | | ≠ 0 | values of the dimension parameters | PARAMETERS | |
| 32 | | N > 0 | printing of ccartesian coordinates of the atoms | | |
| 33 | COOPRT | N > 0 | cartesian coordinates of atoms in file fort.33 | ATCOORDS | |
| 34 | FINE2 | N > 0 | | KNETOUT | |
| | READ2 | | output of reciprocal space information | KNETOUT | |
| 35 | | N > 0 | printing of symmops in short fomr | | |
| 36 | XCBD | ≠ | properties - exchange correlation printing | | |
| 37 | | | | | |
| 38 | | | | | |
| 39 | | | | | |
| 40 | | | | | |
| 41 | SHELL* | ≠0 | printing of bipolar expansion parameters | | |
| 47 | KSYMBA | n | Symmetry Adapted Bloch Functions printing level | | |
| 48 | KSYMBA | ≠0 | Symmetry Adapted Bloch Functions printing active | KSYMMPRT | |
| 51 | AB | ≠ 0 | B functions orthonormality check | | |
| 52 | DIF | > 0 | Fermi energy - Warning !!!! Huge printout !!! | | |
| 53 | SCFPRT | ≠ 0 | k points geometrical weights | KWEIGHTS | |
| 54 | CALPES | > 0 | k points weights- Fermi energy | | |
| 55 | OMEGA | > 0 | f0 coefficients for each band | | |
| 56 | | | | | |
| 57 | PDIG | N | p(g) matrices-first n g vectors | PGIRR | N |
| 58 | PROT1 | ≠ 0 | mvlu, ksh, idp4 | | |
| 59 | RROTA | N > 0 | P(g) matrices - first N vectors at the end of SCF | PGRED | N |
| | NEWK | N | P(g) matrices - first N vectors | PGRED | N |
| | PSIINF | > 0 | P(g) matrices - first N vectors | PGRED | N |
| | | N < 0 | P(g) matrix for g=N | PGRED | N |
| 60 | PSIINF | > 0 | overlap matrix S(g) - first N vectors | OVERLAP | N |
| | | N < 0 | overlap matrix S(g) for g = N | | N |
| 61 | | | | | |
| 63 | TOTENY | ≠ 0 | bielectronic contribution to irred. F(g) matrix | | |
| 64 | FROTA | N | F(g) matrix - first N g vectors | FGRED | N |
| | PSIINF | N> 0 | | FGRED | N |
| | | N < 0 | f(g) matrix - for g = N (N-th g vector only) | FGRED | N |

| | subroutine | value | printed information | keyword | input |
|------|------------|-------|---|----------------------|-------|
| 65 | | | | | |
| 66 | AOFK | N | e(k)- fock eigenvalues- first N k vectors | EIGENVAL | N |
| | ADIK | N | | | |
| | BANDE | N | | | |
| | DIAG | N | | EIGENALL | |
| | FDIK | N | | | |
| | FINE2 | N | | | |
| | NEWK | N | | | |
| 67 | AOFK | N | a(k) - fock eigenvectors - first N k vectors | EIGENVEC | N |
| | ADIK | N | | | |
| | DIAG | N | | | |
| | FINE2 | N | | | |
| | NEWK | N | | | |
| 68 | POLGEN | N <0 | shell and atom multipoles up to pole l=N | MULTIPOL | N |
| | POLGEN | N >0 | atom multipoles up to pole l=N | MULTIPOL | N |
| | QGAMMA | N | shell multipoles up to pole l=N | MULTIPOL | N |
| 69 | TOTENY | ≠ 0 | contributions to total energy at each cycle | ENECYCLE | |
| | FINE2 | ≠ 0 | Mulliken population analysis | | |
| 70 | | | at the end of scf cycles | | |
| | NEIGHB | | calls PPBOND, to perform Mulliken analysis | | |
| | POPAN | | | | |
| | PDIBAN | | | | |
| 71 | PATIRR | ≠ 0 | atomic wave function | ATOMICWF | |
| | PATIR1 | ≠ 0 | " " | ATOMICWF | |
| 72 | INPBAS | ≠ 0 | basis set | BASISSET | |
| | INPUT2 | ≠ 0 | basis set | BASISSET | |
| | READFG | SET | | | |
| | | = 1 | | | |
| 73 | POPAN | ≠ 0 | Mulliken matrix up to N direct lattice vector | MULLIKEN | N |
| | PPBOND | | | | |
| | PDIBAN | N | | | |
| 74 | TOTENY | N | f(g) irreducible up to g=N | FGIRR | N |
| | DFTTT2 | N | | FGIRR | N |
| 75 | INPBAS | ≠ 0 | printing of scale factor and atomic configuration | SCALEFAC CONFIGAT | |
| 76 | | | | | |
| 77 | PPBOND | 0 | printing of neighbouring relationship | | |
| | | ≠ 0 | no printing of neighbours relationship | | |
| 78 | FERMI | ≠ 0 | informations on Fermi energy calculation | | |
| | EMIMAN | ≠ 0 | | | |
| 79 | | | | | |
| ! 79 | DFGPRT | ≠ 0 | dft auxiliary basis set - default no printing | DFTBASIS | |
| ! 80 | ROTOP | > 0 | printing of atoms coord. in rotated ref. frame | ROTREF | |
| 92 | INPBAS | | G94 deck on ft92 | GAUSS94 | |
| 93 | MOLDRW | | input deck to MOLDRAW | | |
| 105 | DENSIM | < 0 | DOSS along energy points | DOSS | |
| 106 | DFFIT3 | > 0 | DFT intermediate printout | | |
| | | | (keyword PRINT in dft input) | | |
| 107 | STARIN | ≠ 0 | DOSS information | | |
| 112 | PROFCA | ≠ 0 | projected DOSS coefficients | | |
| 116 | PROFI | ≠ 0 | Compton profile information | | |
| 117 | PROFI | ≠ 0 | | | |
| 118 | PROFI | N | | | |
| 119 | INTEG | ≠ 0 | charge density at grid points | MAPVALUES | |
| | JJTEG | ≠ 0 | charge density at grid points | MAPVALUES | |
| | MAPNET | ≠ 0 | electrostatic potential at grid points | MAPVALUES | |
| | NAPNET | ≠ 0 | charge density gradient components | MAPVALUES | |
| 120 | LIBPHD | ≠ 0 | extended printing in beryn optimizer | | |
| 121 | | | reserved for geometry optimizer | | |
| 122 | | | reserved for geometry optimizer | | |
| 123 | | | reserved for geometry optimizer | | |
| 124 | | | reserved for geometry optimizer | | |
| 125 | | | reserved for geometry optimizer | | |

Appendix D

External format

Formatted data are written in files according to the following table:

| program | keyword | ftn | filename | | pg |
|-------------------|----------|-----|----------------|---|-----|
| | OPTGEOM | 34 | optaxxx | Geometry input - opt atoms coord. only - 41 See EXTPRT | |
| | OPTGEOM | 34 | optcxxx | Geometry input - opt cell [atoms] - See 41 EXTPRT | |
| <i>crystal</i> | | 66 | HESSOPT.DAT | Hessian matrix | |
| | | 68 | OPTINFO.DAT | Information to restart optimization | |
| | GAUSS98 | 92 | GAUSSIAN.DAT | Input for GAUSS98 | 71 |
| | FINDSYM | 26 | FINDSYM.DAT | data in crystallographic format - read by 40 program findsym(IUCR) | |
| | STRUCPRT | 33 | STRUC.INCOOR | Cell parameters, coordinates of atoms | 62 |
| <i>crystal</i> | COORPRT | 33 | fort.33 | Coordinates of the atoms in the cell | 40 |
| | EXTPRT | 34 | fort.34 | Geometry input | 41 |
| <i>properties</i> | PPAN | 24 | PPAN.DAT | Mulliken population analysis | 109 |
| <i>properties</i> | BAND | 25 | fort.25 | Bands (Crgra2006) | 199 |
| | | 24 | BAND.DAT | Bands data | 199 |
| | CLAS | 25 | fort.25 | Classical potential | 204 |
| | DIEL | 24 | DIEL.DAT | Dielectric constant | 205 |
| | DOSS | 25 | fort.25 | Density of states (IPLOT=1) | 207 |
| | | 24 | DOSS.DAT | Density of states (IPLOT=2) | 207 |
| | ECHG | 25 | fort.25 | Electronic charge density - 2D grid | 209 |
| | | 25 | RHOLINE.DAT | Electronic charge density - 1 grid | 209 |
| | ECH3 | 31 | — | Electronic charge density - 3D grid | 208 |
| | | | DENS.CUBE.DAT | Electronic charge density - 3D grid CUBE format | 208 |
| | | | SPIN.CUBE.DAT | Spin density - 3D grid CUBE format | 208 |
| | POT3 | | POT.CUBE.DAT | Electrostatic potential - 3D grid CUBE for- mat | 232 |
| | EMDLDM | 25 | fort.25 | EMD along a line | 211 |
| | | 24 | EMDLDM.DAT | EMD along a line | 211 |
| | EMDPDM | 25 | fort.25 | EMD map on a plane | 211 |
| | | 94 | 3DEMDTOTAL.DAT | EMD map on a plane (3D format) | 211 |
| | | 65 | 3DEMDANISO.DAT | EMD-anisotropy map on a plane (3D for- mat) | 211 |
| | EMDL | 25 | fort.25 | EMD line (IPLOT=1) | 210 |
| | | 24 | EMDL.DAT | EMD line(IPLOT=2) | 210 |
| | EMDP | 25 | | EMD - 2D grid | 323 |
| | INFOGUI | 32 | | Data for the graphical user interface | 214 |
| | IRSPEC | | — | Infrared spectra | 158 |
| | | | IRSPEC.DAT | IR Absorbance and Reflectance | 158 |
| | | | IRREFR.DAT | IR Refractive index | 158 |
| | | | IRDIEL.DAT | IR Dielectric function | 158 |
| | RAMSPEC | | — | Raman spectra | 160 |
| | | | RAMSPEC.DAT | Raman spectra for polycrystalline powder and single crystal | 160 |
| | POTC | 24 | POTC.DAT | Electrostatic potential V, Electric field, Electric field gradient | 233 |
| | POTM | 25 | fort.25 | Electrostatic potential - 2D grid | 234 |
| | PROF | 25 | fort.25 | Compton profile and related quantities (IPLOT=1) | 235 |
| | | 24 | PROF.DAT | Compton profile and related quantities (IPLOT=2) | 235 |

Please refer to the standard script for running CRYSTAL09 as to handle input/output file names. See:

<http://www.crystal.unito.it/tutorials> =_i How to run

Data in file fort.25 are read by the programs **maps06**, **doss06**, **band06** of the package Crgra2006. In the same run bands, density of states, value of a function in a 2D grid of points can be computed. The appropriate command (**maps06**, **doss06**, **band06**) selects and plots

the selected data .

The package can be downloaded from:

<http://www.crystal.unito.it/Crgra2006/Crgra2006.html>

CLAS - ECHG - POTM - EMDPDM - Isovalue maps

The value of the function chosen (classic electrostatic potential (CLAS), charge(+spin) density (ECHG), electrostatic potential (POTM), electron momentum density (EMDPDM)) is computed in a given net of points. The data are written in file fort.25.

If the system is spin polarized, total density data are followed by spin density data.

Structure of the file fort.25

```
1ST RECORD : -%- , IHFERM, TYPE, NROW, NCOL, DX, DY, COSXY format: A3, I1, A4, 2I5, 3E12.5
2ND RECORD : XA, YA, ZA, XB, YB, ZB format: 1P, 6E12.5
3RD RECORD : XC, YC, ZC, NAF, LDIM format: 1P, 3E12.5, 4X, 2I4
4TH RECORD
AND FOLLOWING : ((RDAT(I, J), I=1, NROW), J=1, NCOL) format: 1P, 6E12.5
```

Meaning of the variables:

```
1 '-%-' 3 character string marks the beginning of a block of data;
1 IHFERM: 0 : closed shell, insulating system
          1 : open shell, insulating system
          2 : closed shell, conducting system - Fermi level can be drawn
          3 : open shell, conducting system - Fermi level can be drawn

1 TYPE 4 characters string corresponding to the type of data "MAPN"
1 NROW number of rows of the data matrix RDAT
1 NCOL number of columns of the data matrix RDAT
1 DX increment of x (\AA ngstrom) in the plane of the window
1 DY increment of y (\AA ngstrom) in the plane of the window
1 COSXY cosine of the angle between x and y axis;
2 XA, YA, ZA coordinates of the points A, B (see keyword MAPNET) (\AA ngstrom)
2 XB, YB, ZB defining the window where the functions is computed (\AA ngstrom)
3 XC, YC, ZC coordinates of point C (\AA ngstrom)
3 NAF number of atoms in the cell
3 LDIM dimensionality (0 molecule; 1 polymer, 2 slab, 3 bulk)
4-> ncol*nrow values of the function (a.u.) at the nodes of the grid
```

naf records follow, with atomic number, symbol, coordinates (Ångstrom) of the atoms in the cell:

```
NAT, SYMBAT, XA, YA, ZA format: I4, 1X, A, 1P, 3E20.12
```

```
NAT atomic number
SYMBAT Mendeleev symbol
XA, YA, ZA cartesian coordinates of the atoms in the cell (\AA ngstrom)
```

Cartesian components of cell parameters follow (Ångstrom)

```
AX, AY, AZ cartesian component of vector a format: 3E20.12
BX, BY, BZ cartesian component of vector b format: 3E20.12
CX, CY, CZ cartesian component of vector c format: 3E20.12
```

The program **maps06** looks for the atoms lying in the windows used to compute the function, and it can draw the symbol of the atoms, the van der Waals sphere, or the bonds between atoms closer than the sum of their vdW radii.

ECHG Charge (spin) density - 1D profile

When points B and C coincides in **ECHG** 9.2 input, coordinates relative to the origin of the segment and charge density value [coordinate along the line, charge density: charge density derivative x,y,z components] are written with format (2E20.12:3E20.12) in file RHOLINE.DAT. A second set of data, spin density, is written for spin polarized systems, after a blank line.

BAND - Band structure

Hamiltonian eigenvalues are computed at k points corresponding to a given path in the Brillouin zone. Data are written in file BAND.DAT and processed by DLV; see <http://www.cse.clrc.ac.uk/cmgi/DLV> and in file fort.25 (processed by Crgra2006/band06)

Structure of the file fort.25

One block is written for each segment of the path in k reciprocal space: the segment is defined by two k points, whose crystallographic coordinates $(I1,I2,I3)$ and $(J1,J2,J3)$ are given as integers in ISS units (see keyword BAND).

If the system is spin polarized, α electrons bands are followed by β electrons bands.
For each segment:

```
1ST RECORD : -%- ,IHFERM,TYPE,NBAND,NKP,DUM,,DK,EF   format: A3,I1,A4,2I5,3E12.5
2ND RECORD : EMIN,EMAX                               format: 1P,6E12.5
3RD RECORD : I1,I2,I3,J1,J2,J3                       format: 6I3
4TH RECORD
AND FOLLOWING : ((RDAT(I,J),I=1,NROW),J=1,NCOL)      format: 1P,6E12.5
```

Meaning of the variables:

```
1 '-%-'      3 character string marks the beginning of a block of data;
1 IHFERM:    0 : closed shell, insulating system
              1 : open shell,   insulating system
              2 : closed shell, conducting system
              3 : open shell,   conducting system

1 TYPE      4 characters string corresponding to the type of data "BAND"
1 NBAND     number of bands
  NKP      number of k points along the segment
  DUM      not used
  DK       distance in k space between two adjacent sampling points
           along the segment
  EF       Fermi energy (hartree)
2 EMIN     minimum energy of the bands in the explored path (hartree)
  EMAX     maximum energy (hartree)
3 I1,I2,I3,J1,J2,J3 : coordinates of the segment extremes in iunit of ISS
4 EPS(I,J) eigenvalues (hartree): eps(i,j) corresponds to the i-th
..         band, and the j-th k point of the segment.
```

DIEL

The data computed are written in file DIEL.DAT according to the following format:

```
#
@ XAXIS LABEL "DISTANCE(BOHR)"
@ YAXIS LABEL "MACRORHO MACROE MACROV RHOPLANE"
5 columns - format(08E15.7)
last record is blank
```

DOSS Density of states

Total and projected density of states are written in file DOSS.DAT (processed by DLV; see <http://www.cse.clrc.ac.uk/cmgi/DLV>) and in file fort.25 (processed by Crgra2006).

One block is written for each projected density of states, including the total one: so NPRO (number of projections) +1 blocks are written per each run.

If the system is spin polarized, α electrons bands are followed by β electrons bands.

Structure of the file written in file fort.25

1ST RECORD : -%-, IHFERM, TYPE, NROW, NCOL, DX, DY, COSXY
format : A3, I1, A4, 2I5, 1P, (3E12.5)
2ND RECORD : X0, Y0 format : 1P, 6E12.5
3RD RECORD : I1, I2, I3, I4, I5, I6 format : 6I3
4TH RECORD
AND FOLLOWING : ((RDAT(I, J), I=1, NROW), J=1, NCOL) format : 1P, 6E12.5

Meaning of the variables:

| | |
|--------------------|--|
| 1 NROW | 1 (DOSS are written one projection at a time) |
| NCOL | number of energy points in which the DOS is calculated |
| DX | energy increment (hartree) |
| DY | not used |
| COSXY | Fermi energy (hartree) |
| 2 X0 | energy corresponding to the first point |
| Y0 | not used |
| 3 I1 | number of the projection; |
| I2 | number of atomic orbitals of the projection; |
| I3, I4, I5, I6 | not used |
| 4 RO(J), J=1, NCOL | DOS: density of states ro(eps(j)) (atomic units). |

Structure of the file written in file DOSS.DAT

Data written in file DOSS.DAT:

1ST RECORD : NPUNTI, NPRO1, IUHF
format : '# NEPTS', 1X, I5, 1X, 'NPROJ', 1X, I5, 1X, 'NSPIN', 1X, I5
2ND RECORD : '#'
3RD RECORD : '@ YAXIS LABEL "DENSITY OF STATES (STATES/HARTREE/CELL)"'
4TH RECORD : (ENE(I), DOSS(IPR, I), IPR=1, NPRO1)
AND FOLLOWING :
format : 1P, 15E12.4

PROF

The computed quantities are written following the same sequence of the printout. Each record contains:

4F coordinate, all electron, core, valence contribution

EMDL

The computed quantities are written following the same sequence of the printout. NPUNTI records are written. Each records contains (FORMAT: 10E12.4)

p (emdl(p, ipro), ipro=1, nprojections))

EMDP

1ST RECORD : -%-, IHFERM, TYPE, NMAX1, NMAX2, PMAX1, PMAX2, COS12
format : A3, I1, A4, 2I5, 1P, (3E12.5)
2ND RECORD : XDUM, YDUM format : 1P, 6E12.5
3RD RECORD : I11, I12, I13, I21, I22, I23 format : 6I3
4TH RECORD
AND FOLLOWING : ((RDAT(I, J), I=1, NMAX1), J=1, NMAX2) format : 1P, 6E12.5

Meaning of the variables:

| | |
|-----------|--|
| 1 '-%-' | 3 character string marks the beginning of a block of data; |
| 1 IHFERM: | 0 : closed shell, insulating system |
| | 1 : open shell, insulating system |
| | 2 : closed shell, conducting system |
| | 3 : open shell, conducting system |

```

1 TYPE          4 characters string corresponding to the type of data "EMDP"
1 NMAX1         number of points in the first direction
  NMAX2         number of points in the second direction
  PMAX1         maximum p value along the first direction
  PMAX2         maximum p value along the first direction
  COSXY        angle between the two vectors defining the plane
2 X0           not used
  Y0           not used
3 I11,I12,I13  fractional coordinates of the first reciprocal lattice
                vector defining the plane
  I21,I22,I23  fractional coordinates of the second reciprocal lattice
                vector defining the plane
4 RO(J),J=1,NMAX1*NMAX2  electron momentum density at the grid points
                        (atomic units).

```

POTC

When $ICA \neq 0$; $NPU \neq 0$ (2D or 3D systems) the data computed are written in file POTC.DAT according to the following format:

```

#
@ XAXIS LABEL "Z (AU)"
@ YAXIS LABEL "ELECTROSTATIC PROPERTIES (AU)"
@ TITLE "String in the first record in crystal input"
@ SUBTITLE "ELECTRIC FIELD INTENSITY: 0.100 AU" ! if external field applied
@ LEGEND ON
@ LEGEND LENGTH 3
@ LEGEND X1 0.87
@ LEGEND Y1 0.8
@ LEGEND STRING 0 "V"
@ LEGEND STRING 1 "E"
@ LEGEND STRING 2 "DE/DZ"
@ LEGEND STRING 3 "RHO"
@ LEGEND STRING 4 "V+VEXT" ! if external field applied
@ LEGEND STRING 5 "VEXT" ! if external field applied
NPU records of 5 (7 when external field applied) columns - format 08E15.7

```

COORPRT

The keyword **COORPRT**, entered in geometry input or in *properties* writes in file fort.33 (append mode) the following data:

```

record  data  content
#       type
1       I      number of atoms (NAF)
2       A      Title - If written after an SCF calculation, on the same line; totalenergy,
                convergence on energy, number of cycles
3       A,3F   Mendeleev symbol of the atom; x, y, z cartesian coordinates (Å)
.....
NAF+2  A,3F   Mendeleev symbol of the atom; x, y, z cartesian coordinates (Å)

```

The coordinates of the atoms are written at each geometry optimization cycle (keyword **OPT-GEOM**

The file "fort.33" is read by the program **MOLDEN** [161] which can be downloaded from:
www.cmbi.kun.nl/schaft/molden/molden.html

STRUCPRT

The file STRUC.INCOOR is written according to the format given in the example (output for bulk MgO, 2 atoms per cell).

```
$cell vectors          cartesian components of cell parameters (bohr)
  0.00000000000000    3.97787351190423    3.97787351190423
  3.97787351190423    0.00000000000000    3.97787351190423
  3.97787351190423    3.97787351190423    0.00000000000000
$coordinates          cartesian coordinates of atoms (bohr)
MG  0.00000000000000    0.00000000000000    0.00000000000000    12
O   0.00000000000000    0.00000000000000   -3.97787351190423    8
$END
```

PPAN

```
# Mulliken Populations:
# NSPIN,NATOM          n. determinants, number of atoms
  ---- for each atom
# IAT,NSHELL          atomic number, number o shells
# Xiat,Yiat,Ziat (AU) cartesian coordinates (bohr)
# QTOT, QSHELL,I=1,NSHELL atom total electronic charge, (shell charges)
# NORB, QORB, I=1,NORB number of orbitals, (orbital electronic charges)
```

Example:

```
graphite STO-3G basis set, RHF (1 eterminant)
2 atoms, 2 shells per atom, 5 AO per atom
```

```
      1      2      |      1 determinant, 2 atoms
      6      2      |      1st atom: atomic number 6, 2 shells
-1.320 -2.287  0.000 |      cartesian coordinates 1st atom
      6.000  1.993  4.007 |      6, electronic charge of 1st atom
      |      1.993 electronic charge of 1st shell (1s)
      |      4.007 electronic charge of 2nd shell (2sp)
      5      |      5 atomic orbitals
1.993  1.096  0.956  0.956  1.000 | 1.993 electronic charge of 1st AO (1s)
      | 1.096 electronic charge of 2nd AO (2s)
      | 0.956 electronic charge of 3rd AO (px)
      | 0.956 electronic charge of 4th AO (py)
      | 1.000 electronic charge of 5th AO (pz)
      6      2      |      2nd atom: atomic number 6, 2 shells
-2.640  0.000  0.000 |      cartesian coordinates 2nd atom
      6.000  1.993  4.007 |      6, electronic charge of 1st atom
      | 1.993 electronic charge of 1st shell (1s)
      | 4.007 electronic charge of 2nd shell (2sp)
      5      |      5 atomic orbitals
1.993  1.096  0.956  0.956  1.000 | 1.993 electronic charge of 1st AO (1s)
      | 1.096 electronic charge of 2nd AO (2s)
      | 0.956 electronic charge of 3rd AO (px)
      | 0.956 electronic charge of 4th AO (py)
      | 1.000 electronic charge of 5th AO (pz)
      6      2      |      second atom: atomic number 6, 2 shells
-2.640  0.000  0.000 |      cartesian coordinates 2nd atom
```

EXTPRT / EXTERNAL - file fort.34

Geometry information can be read from an external file, fort.34, by entering the keyword **EXTERNAL**. The system can be a molecule, a polymer, a slab or a crystal. The file is written by entering the keyword **EXTPRT** in the input block 1. The file is written at the end of successful geometry optimization. The "history" of the optimization process is written in files optaxxx (xxx number of optimization cycle) or optcxxx. // [0.2cm] The structure of the file is as follow:

```

rec #   data type } contents
2       3I         } dimensionality, centring and crystal type
3       3F         }
4       3F         } cartesian components of the direct lattice vectors
5       3F         }
6       1I         } number of symmetry operators

                For each symmetry operator 4 records:
7       3F         }
8       3F         } symmetry operators matrices in cartesian coordinates
9       3F         }
10      3F         } cartesian components of the translation

n       1I         } number of atoms in the primitive cell
                For each atom, 1 record:
n+1     I,3F       } conventional atomic number, cartesian coordinates of the atoms

```

The keyword **EXTERNAL** and **END** must be inserted at the top and bottom of the deck to use it as **CRYSTAL** geometry input.

Example - Test05 - Graphite 2D - standard geometry input

```

SLAB           dimensionality
77            layer group number
2.42          lattice parameter
1            number of irreducible atoms in the cell
6 -0.333333333333 0.333333333333 0. coordinates of the atoms
EXTPRT
TESTGEOM
END

```

Data written in file fort.34 (Ångstrom):

```

2 1 5 ! dimensionality, centring and crystal type
0.2095781E+01 -0.1210000E+01 0.0000000E+00 ! cartesian components of direct lattice vectors
0.0000000E+00 0.2420000E+01 0.0000000E+00 !
0.0000000E+00 0.0000000E+00 0.5000000E+03 ! 2D system - formal value 500. \AA
12 ! number of symmetry operators
0.1000000E+01 0.0000000E+00 0.0000000E+00 ! 1st symmetry operator - 3x3 transformation matrix
0.0000000E+00 0.1000000E+01 0.0000000E+00 !
0.0000000E+00 0.0000000E+00 0.1000000E+01 !
0.0000000E+00 0.0000000E+00 0.0000000E+00 ! 1st symmetry operator - 3x1 translation component
-0.1000000E+01 0.0000000E+00 0.0000000E+00 ! 2nd symmetry operator
0.0000000E+00 -0.1000000E+01 0.0000000E+00 !
0.0000000E+00 0.0000000E+00 0.1000000E+01 !
0.0000000E+00 0.0000000E+00 0.0000000E+00 !
-0.5000000E+00 -0.8660254E+00 0.0000000E+00 ! 3rd symmetry operator
0.8660254E+00 -0.5000000E+00 0.0000000E+00 !
0.0000000E+00 0.0000000E+00 0.1000000E+01 !
0.0000000E+00 0.0000000E+00 0.0000000E+00 !
-0.5000000E+00 0.8660254E+00 0.0000000E+00 ! 4th symmetry operator
-0.8660254E+00 -0.5000000E+00 0.0000000E+00 !
0.0000000E+00 0.0000000E+00 0.1000000E+01 !
0.0000000E+00 0.0000000E+00 0.0000000E+00 !
0.5000000E+00 -0.8660254E+00 0.0000000E+00 ! 5th symmetry operator
0.8660254E+00 0.5000000E+00 0.0000000E+00 !
0.0000000E+00 0.0000000E+00 0.1000000E+01 !
0.0000000E+00 0.0000000E+00 0.0000000E+00 !
0.5000000E+00 0.8660254E+00 0.0000000E+00 ! 5th symmetry operator
-0.8660254E+00 0.5000000E+00 0.0000000E+00 !
0.0000000E+00 0.0000000E+00 0.1000000E+01 !
0.0000000E+00 0.0000000E+00 0.0000000E+00 !
-0.5000000E+00 0.8660254E+00 0.0000000E+00 ! 7th symmetry operator
0.8660254E+00 0.5000000E+00 0.0000000E+00 !
0.0000000E+00 0.0000000E+00 0.1000000E+01 !

```

```

0.000000E+00 0.000000E+00 0.000000E+00 !
0.100000E+01 0.000000E+00 0.000000E+00 ! 8th symmetry operator
0.000000E+00 -0.100000E+01 0.000000E+00 !
0.000000E+00 0.000000E+00 0.100000E+01 !
0.000000E+00 0.000000E+00 0.000000E+00 !
-0.500000E+00 -0.8660254E+00 0.000000E+00 ! 9th symmetry operator
-0.8660254E+00 0.500000E+00 0.000000E+00 !
0.000000E+00 0.000000E+00 0.100000E+01 !
0.000000E+00 0.000000E+00 0.000000E+00 !
0.500000E+00 0.8660254E+00 0.000000E+00 ! 10th symmetry operator
0.8660254E+00 -0.500000E+00 0.000000E+00 !
0.000000E+00 0.000000E+00 0.100000E+01 !
0.000000E+00 0.000000E+00 0.000000E+00 !
-0.100000E+01 0.000000E+00 0.000000E+00 ! 11th symmetry operator
0.000000E+00 0.100000E+01 0.000000E+00 !
0.000000E+00 0.000000E+00 0.100000E+01 !
0.000000E+00 0.000000E+00 0.000000E+00 !
0.500000E+00 -0.8660254E+00 0.000000E+00 ! 12th symmetry operator
-0.8660254E+00 -0.500000E+00 0.000000E+00 !
0.000000E+00 0.000000E+00 0.100000E+01 !
0.000000E+00 0.000000E+00 0.000000E+00 !
1 ! number of irreducible atoms in the primitive cell
6 -0.6985938 -1.2100000 0.0000000 ! conventional atomic number, cartesian coordinate

```

ECH3/POT3/GRID3D

Functions values computed at 3D grid of points by the keywords **ECH3** (page 208), **POT3** (page232), **GRID3D** (page214) are written according to two formats: . All data in atomic units.

1. Fortran unit 31 is written According to the following format. All data in atomic units.

```

rec #   data type } contents
1       A         } title:  charge density /spin density
2       3I        } npa,npb,npb, number of points along the 3 directions
3       3E        } x,y,z cartesian coordinates of the point (1,1,1)
4       3E        } dxa, dya, dza cartesian components of the step along a
5       3E        } dxb, dyb, dzb cartesian components of the step along b
6       3E        } dxc, dyc, dzc cartesian components of the step along c
7 ...   5E        } npa*npb*nbpc floating point data, 5/record

```

2. Function data computed at 3D grid points are written according to GAUSSIAN CUBE format in files:

```

DENS_CUBEDAT  charge density
SPIN_CUBEDAT  spin density
POT_CUBEDAT   electrostatic potential

```

INFOGUI

Fortran unit 32 is written through the keyword **INFOGUI** (page 214). The format is almost self-explaining. The following data are written for MgO bulk (test11).

```

2 atom(s) per cell
6 shells
18 atomic orbitals
20 electrons per cell
12 core electrons per cell
No eigenvalue level shifting
No Alpha-Beta Spin locking
No N. Beta Spin locking
Type of Calculation: RESTRICTED CLOSED SHELL
Total Energy = -0.27466415E+03H

```

```

Fermi Energy = -0.31018989E+00H
1 -0.31018989E+00
6  18  20  12 | # shells, # A0, # electrons, # core electrons
2          | # atoms
1  12  1  0.000000 0.000000 0.000000 | sequence number, atomic number,?,cartesian coor(bohr)
3 # shells attributed to the first atom
0 shell type (s) of the 1st shell
1 shell type (sp) of the 2nd shell
1 shell type (sp) of the 3rd shell
2   8   2  3.977874 3.977874 3.977874 | sequence number, atomic number,?,cartesian coor(bohr)
3 # shells attributed to the second atom
0 shell type (s) of the 1st shell
1 shell type (sp) of the 2nd shell
1 shell type (sp) of the 3rd shell

```

IRSPEC

IRSPEC in **FREQCALC** input block writes the files IRSPEC.DAT, IRREFR.DAT and IRDIEL.DAT.

IRSPEC.DAT contains: 1 column with frequency ν in cm^{-1} , 1 column with wavelength λ in nm, 4 columns for the 4 different models of absorbance A , 1 column for reflectance R along each inequivalent polarization direction.

IRREFR.DAT contains: 1 column with frequency ν in cm^{-1} , 1 column with wavelength λ in nm, 2 columns for $\text{Re}(n)$ and $\text{Im}(n)$ along each direction (n being the refractive index).

IRDIEL.DAT contains: 1 column with frequency ν in cm^{-1} , 1 column with wavelength λ in nm, 3 columns for $\text{Re}(\epsilon)$, $\text{Im}(\epsilon)$ and $\text{Im}(1/\epsilon)$ along each direction (ϵ being the dielectric function).

Suppose we have the following input block, for a compound with three inequivalent polarization directions:

```

. . . .
FREQCALC
INTENS
[options for INTENS]
DIELTENS or DIELISO
. . . .
[optional FREQCALC keywords]
. . . .
IRSPEC
END
ENDFREQ

```

The first two columns in the generated IRSPEC.DAT contain frequencies and wavelengths, columns from 3 to 6 the raw absorbance, the classical absorbance, the two Rayleigh scattering absorbances, and column 7-9 the reflectance curves for the three directions.

Suppose we want to plot the raw absorbance with respect to frequency. Once *gnuplot* is opened on the terminal (type *gnuplot*), it is sufficient to type

```
plot 'IRSPEC.DAT' using 1:3
```

where 1:3 stands for "first column assigned to x axis and third column to y axis". The plot of the raw absorbance appears on the screen and can be saved with the command

```
save 'name_plot'
```


If we want to save the plot as a Post-Script

```
set size 1.0, 0.6
set terminal postscript portrait enhanced mono dashed lw 1 "Helvetica" 14
set output "my-plot.ps"
replot
```

In a similar way, we can type

```
plot 'IRSPEC.DAT' using 1:7
```

in order to obtain the reflectance along the first polarization direction, and

```
plot 'IRSPEC.DAT' using 1:8
```

for the reflectance along the second direction.

Further details about these commands and manipulation of files at <http://www.duke.edu/hp-gavin/gnuplot.html> and <http://www.gnuplot.info/documentation.html>.

RAMSPEC

RAMSPEC in **FREQCALC** input block writes the file RAMSPEC.DAT.

RAMSPEC.DAT contains: 1 column with frequency ν in cm^{-1} , 3 columns for intensities of polycrystalline powders (total intensity, parallel polarization, perpendicular polarization), 6 columns for spectra of single crystals (1 for each inequivalent polarization direction: xx , xy , xz , yy , yz , zz).

Suppose we want to plot the total Raman intensity of a polycrystalline powder with respect to frequency. Once *gnuplot* is opened on the terminal (type `gnuplot`), it is sufficient to type

```
plot 'RAMSPEC.DAT' using 1:2
```

where 1:2 stands for "first column assigned to x axis and second column to y axis". The plot of the total polycrystalline Raman intensity appears on the screen and can be saved with the command

```
save 'name_plot'
```

If we want to save the plot as a Post-Script

```
set size 1.0, 0.6
set terminal postscript portrait enhanced mono dashed lw 1 "Helvetica" 14
set output "my-plot.ps"
replot
```

In a similar way, we can type

```
plot 'RAMSPEC.DAT' using 1:5
```

in order to obtain the Raman spectrum of a single crystal along the first polarization direction, i.e. xx .

Further details about these commands and manipulation of files at <http://www.duke.edu/hp-gavin/gnuplot.html> and <http://www.gnuplot.info/documentation.html>.

Interface to external programs

The keyword **CRYAPI_OUT**, present into *properties* input stream writes formatted wave function information, both in direct and reciprocal space, in file GRED.DAT and KRED.DAT. The scripts *runcry06* and *runprop06* save them in the current directory as `inpfilename.GRED` and `inpfilename.KRED`.

The program *cryapi_inp*, written in fortran 90, is distributed as source code (<http://www.crystal.unito.it> => documentation => utilities). It reads and prints the data, showing the meaning of the variables and the organization of data.

cryapi_inp should be compiled by any fortran 90 compiler: comments and request for more information are welcome (mail to *crystal@unito.it*).

GRED.DAT

The file GRED.DAT contains:

- Geometry, symmetry operators;
- Local functions basis set (including ECP)
- Overlap matrix in direct lattice
- Hamiltonian matrix in direct lattice
- Density matrix in direct lattice
- Wannier functions (if file `fort.80`, written by **LOCALWF** when localization is successful, is present)

Overlap, hamiltonian, density matrices are written as arrays of non-zero elements. GRED.DAT contains the information to build full matrices.

All data are printed executing *cryapi_inp*

KRED.DAT

The file KRED.DAT is written if eigenvectors have been computed (keyword **NEWK 9.2**) by *properties*.

CRYSTAL works in the irreducible Brillouin (IBZ) zone only: eigenvectors in the full Brillouin zone (BZ) are computed by rotation, and by time reversal symmetry, when necessary. The file KRED.DAT contains:

- Coordinates of k points in irreducible Brillouin zone, according to Pack-Monkhorst net
- Symmetry operators in reciprocal lattice
- Geometrical weight of k points
- Hamiltonian eigenvalues
- Weight of k points for each band (computed by Fermi energy calculation)
- Eigenvectors in full Brillouin zone

Structure of matrices in direct lattice

Overlap, hamiltonian, and density matrices in direct lattice are arrays of non-zero elements: *cryapi_inp* prints the matrices as triangular (hamiltonian) or square matrices of size (local BS x local BS), for a limited number of direct lattice vectors, to show the structure of the arrays.

From IBZ to BZ

CRYSTAL works on irreducible Brillouin zone (IBZ), full information is generated by applying rotation operators.

Time reversal symmetry is exploited in reciprocal lattice: the inversion symmetry is always present, even if the inversion operator is not present in direct lattice.

Given a shrinking factor according to Pack-Monkhorst sampling, to total number of k points is for instance:

| System | n. symmops | shrink factors | IBZ | NOSYMM | BZ |
|---------------|------------|----------------|-----|--------|----|
| graphite (2D) | 12 | 3 | 3 | 5 | 9 |
| SiC (3D) | 24 | 4 | 8 | 36 | 64 |
| MgO (3D) | 48 | 4 | 8 | 36 | 64 |

| | |
|--------|---|
| IBZ | number of points in IBZ |
| NOSYMM | number of points removing direct lattice symmetry |
| BZ | number of points in Brillouin zone |

Appendix E

Normalization coefficients

A. Bert - Thesis 2002

The aim of this appendix is to show how normalization coefficients of the basis functions are defined in CRYSTAL and to describe how they are stored in the program.

Basic Definitions

Let us consider a function, $f(\mathbf{r})$; we have in general:

$$\int d\mathbf{r} |f(\mathbf{r})|^2 \neq 1; \quad (\text{E.1})$$

however, we can always define a related $f'(\mathbf{r})$, multiplying $f(\mathbf{r})$ by a constant N :

$$f'(\mathbf{r}) = Nf(\mathbf{r}), \quad (\text{E.2})$$

such that:

$$\int d\mathbf{r} |f'(\mathbf{r})|^2 = 1. \quad (\text{E.3})$$

$f'(\mathbf{r})$ is said to be a *normalized* function and N is its *Normalization Coefficient* (NC). Substituting eq. E.2 in E.3, we have:

$$N = \left(\int d\mathbf{r} |f(\mathbf{r})|^2 \right)^{-1/2}. \quad (\text{E.4})$$

Gaussians: Product Theorem and Normalization

Let us define Gaussian functions as:

$$G(\alpha_i; \mathbf{r} - \mathbf{A}) = \exp(-\alpha_i(\mathbf{r} - \mathbf{A})^2), \quad (\text{E.5})$$

where \mathbf{A} is the *centroid* of the function.

The Gaussian product theorem states that the product of two Gaussians, is still a Gaussian function:¹

$$G(\alpha; \mathbf{r} - \mathbf{A})G(\beta; \mathbf{r} - \mathbf{B}) = \exp\left(-\frac{\alpha\beta}{\xi}|\mathbf{R}|^2\right) G(\xi; \mathbf{r} - \mathbf{P}); \quad (\text{E.8})$$

¹Let us prove the Gaussian product theorem:

$$\begin{aligned} G(\alpha; \mathbf{r} - \mathbf{A})G(\beta; \mathbf{r} - \mathbf{B}) &= \exp(-\alpha(\mathbf{r} - \mathbf{A})^2) \exp(-\beta(\mathbf{r} - \mathbf{B})^2) \\ &= \exp(-\alpha(\mathbf{r}^2 + \mathbf{A}^2 + 2\mathbf{r}\mathbf{A}) - \beta(\mathbf{r}^2 + \mathbf{B}^2 + 2\mathbf{r}\mathbf{B})) \\ &= \exp\left[-\xi\left((\mathbf{r} - \mathbf{P})^2 + \mathbf{P}^2 - \frac{\alpha\mathbf{A}^2 + \beta\mathbf{B}^2}{\xi}\right)\right]. \end{aligned} \quad (\text{E.6})$$

with:

$$\xi = \alpha + \beta, \quad (\text{E.9})$$

$$\mathbf{P} = \frac{\alpha \mathbf{A} + \beta \mathbf{B}}{\xi}, \quad (\text{E.10})$$

$$\mathbf{R} = \mathbf{A} - \mathbf{B}. \quad (\text{E.11})$$

From eq. E.4, the NC of Gaussian functions, g_i , can be written as:

$$\begin{aligned} g_i &= \left(\int d\mathbf{r} (G(\alpha_i; \mathbf{r}))^2 \right)^{-1/2} \\ &= \left(\int d\mathbf{r} G(2\alpha_i; \mathbf{r}) \right)^{-1/2} \\ &= \left(\frac{\pi}{2\alpha_i} \right)^{-3/4}, \end{aligned} \quad (\text{E.12})$$

where the Gaussian product theorem and the Gaussian integral [182] have been used. $G'(\alpha_i; \mathbf{r})$, defined as:

$$G'(\alpha_i; \mathbf{r}) = g_i G(\alpha_i; \mathbf{r}), \quad (\text{E.13})$$

is a normalized function.

Harmonic Gaussians

The Definition

The *Solid Harmonic Functions*, Y_ℓ^m , [154] are defined as:

$$Y_\ell^m(\mathbf{r}) = r^\ell P_\ell^{|m|}(\cos\vartheta) e^{im\phi}, \quad (\text{E.14})$$

where P_ℓ^m is the *Legendre Polynomial Function* characterized by the integers ℓ and m , such that: $\ell \geq 0$ and $-\ell \leq m \leq \ell$. [4]

Starting from Y_ℓ^m , the *Real Solid Harmonic*, X_ℓ^m , can be defined:

$$X_\ell^{|m|}(\mathbf{r}) = \Re(Y_\ell^{|m|}) = \frac{Y_\ell^{|m|}(\mathbf{r}) + Y_\ell^{-|m|}(\mathbf{r})}{2}, \quad (\text{E.15})$$

$$X_\ell^{-|m|}(\mathbf{r}) = \Im(Y_\ell^{|m|}) = \frac{Y_\ell^{|m|}(\mathbf{r}) - Y_\ell^{-|m|}(\mathbf{r})}{2i}. \quad (\text{E.16})$$

We report some examples of X functions.

$\ell = 0$:

$$X_0^0(\mathbf{r}) = 1; \quad (\text{E.17})$$

$\ell = 1$:

$$X_1^0(\mathbf{r}) = z, \quad X_1^1(\mathbf{r}) = x, \quad X_1^{-1}(\mathbf{r}) = y; \quad (\text{E.18})$$

$\ell = 2$:

$$X_2^0(\mathbf{r}) = z^2 - 0.5(x^2 - y^2), \quad X_2^1(\mathbf{r}) = 3zx, \quad X_2^{-1}(\mathbf{r}) = 3zy, \quad (\text{E.19})$$

$$X_2^2(\mathbf{r}) = 3(x^2 + y^2), \quad X_2^{-2}(\mathbf{r}) = 3xy. \quad (\text{E.20})$$

Using eqs. E.9, E.10 and E.11, eq. E.6 can be rewritten as:

$$G(\alpha; \mathbf{r} - \mathbf{A})G(\beta; \mathbf{r} - \mathbf{B}) = \exp\left(-\frac{\alpha\beta}{\xi}|\mathbf{R}|^2\right) G(\xi; \mathbf{r} - \mathbf{P}). \quad (\text{E.7})$$

We have now the tools required to define the *Solid Harmonic Gaussian*, [154] ξ :

$$\xi^{n\ell m}(\alpha_i; \mathbf{r}) = |\mathbf{r}|^{2n} Y_\ell^m(\mathbf{r}) G_i(\alpha_i; \mathbf{r}), \quad (\text{E.21})$$

where n is a non-negative integer number ($n \geq 0$). We are interested here only in $n = 0$ harmonic Gaussians (that is, $\xi^{0\ell m}$), so we shall simply write (omitting the $n = 0$ index):

$$\xi^{\ell m}(\alpha_i; \mathbf{r}) = Y_\ell^m(\mathbf{r}) G(\alpha_i; \mathbf{r}). \quad (\text{E.22})$$

Substituting Y with X (eqs. E.15 and E.16) in eq. E.22, *Real Harmonic Gaussians*, γ , can be defined:

$$\gamma^{\ell m}(\alpha_i; \mathbf{r}) = X_\ell^m(\mathbf{r}) G(\alpha_i; \mathbf{r}). \quad (\text{E.23})$$

γ are used as basis functions in the CRYSTAL program and are related to the ξ ones by followings relations:

$$\gamma^{\ell|m|} = \frac{\xi^{\ell|m|} + \xi^{\ell-|m|}}{2}, \quad (\text{E.24})$$

$$\gamma^{\ell-|m|} = \frac{\xi^{\ell|m|} - \xi^{\ell-|m|}}{2i}, \quad (\text{E.25})$$

where eqs. E.15 and E.16 have been used.

Note that, when ℓ is equal to 0, ξ and γ functions degenerate to simple Gaussians:

$$\xi^{00} = \gamma^{00} = G, \quad (\text{E.26})$$

where eq. E.17 has been used and ξ degenerates to γ when $m = 0$:

$$\xi^{\ell 0} = \gamma^{\ell 0}, \quad (\text{E.27})$$

where eqs. E.24 and E.25 have been used.

The Normalization Coefficient

Let us consider now ξ and γ 's normalization coefficients (b and c , respectively), from eq. E.4, follows:

$$b_i^{\ell m} = (\Xi)^{-1/2} \quad (\text{E.28})$$

$$c_i^{\ell m} = (\Upsilon)^{-1/2}, \quad (\text{E.29})$$

where

$$\Xi = \int d\mathbf{r} |\xi^{\ell m}(\alpha_i; \mathbf{r})|^2 \quad (\text{E.30})$$

$$\Upsilon = \int d\mathbf{r} (\gamma^{\ell m}(\alpha_i; \mathbf{r}))^2. \quad (\text{E.31})$$

Using eqs. E.5, E.8, E.14, E.22 and a spherical polar coordinate system,² the Ξ integral can be factorized as:

$$\begin{aligned} \Xi &= \int d\mathbf{r} [Y_\ell^m(\mathbf{r}) G(\alpha_i; \mathbf{r})]^* Y_\ell^m(\mathbf{r}) G(\alpha_i; \mathbf{r}) \\ &= \int d\mathbf{r} Y_\ell^{-m}(\mathbf{r}) Y_\ell^m(\mathbf{r}) G(2\alpha_i; \mathbf{r}) \\ &= \Xi_r \Xi_\vartheta \Xi_\phi, \end{aligned} \quad (\text{E.32})$$

² $d\mathbf{r} = r^2 \sin\vartheta dr d\vartheta d\phi$

with:

$$\begin{aligned}
\Xi_r &= \int_0^\infty dr \exp(-2\alpha_i r^2) r^{2\ell+2} \\
&= \frac{\Gamma(\ell + 3/2)}{2(2\alpha_i)^{\ell+3/2}} \\
&= \frac{\pi^{1/2}(2\ell + 1)!!}{2^{\ell+2}(2\alpha_i)^{\ell+3/2}}, \tag{E.33}
\end{aligned}$$

where we have used the Γ function's properties; [4]

$$\begin{aligned}
\Xi_\vartheta &= \int_0^\pi d\vartheta \left(P_\ell^{|m|}(\cos \vartheta) \right)^2 \sin \vartheta \\
&= \frac{2(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!}, \tag{E.34}
\end{aligned}$$

where the Legendre polynomials' properties have been used, [4] and

$$\Xi_\phi = \int_0^{2\pi} d\phi = 2\pi. \tag{E.35}$$

Substituting eqs. E.32, E.33, E.34 and E.35 in the b definition (eq. E.28) we obtain:

$$\begin{aligned}
b_i^{\ell m} &= \frac{\pi^{1/2}(2\ell + 1)!!}{2^{\ell+2}(2\alpha_i)^{\ell+3/2}} \frac{2(\ell + |m|)!}{(2\ell + 1)(\ell - |m|)!} 2\pi \\
&= \left(\frac{\pi^{3/2} (2\ell - 1)!! (\ell + |m|)!}{2^{2\ell+3/2} \alpha_i^{\ell+3/2} (\ell - |m|)!} \right)^{-1/2}. \tag{E.36}
\end{aligned}$$

Note that b is independent from the sign of m (as Ξ is), that is:

$$b_i^{\ell|m|} = b_i^{\ell-|m|}. \tag{E.37}$$

In order to deduce the explicit expression for c , we are interested now in solving the integral of eq. E.31:

$$\Upsilon = \int d\mathbf{r} (X_\ell^m(\mathbf{r}))^2 G(2\alpha_i; \mathbf{r}), \tag{E.38}$$

where eqs. E.8 and E.23 have been used. Substituting eq. E.24 (γ functions with $m \geq 0$) in previous equation, we have:

$$\begin{aligned}
\Upsilon^{m \geq 0} &= \frac{1}{4} \left(\int d\mathbf{r} \left| \xi^{\ell|m|}(\alpha_i; \mathbf{r}) \right|^2 + \int d\mathbf{r} \left| \xi^{\ell-|m|}(\alpha_i; \mathbf{r}) \right|^2 + \right. \\
&\quad \left. + 2 \int d\mathbf{r} \xi^{\ell|m|}(\alpha_i; \mathbf{r}) \xi^{\ell-|m|}(\alpha_i; \mathbf{r}) \right). \tag{E.39}
\end{aligned}$$

The first two integrals in eq. E.39 can be recognized as Ξ (eq. E.32, reminding that Ξ is independent from the m sign); the last one, if $m \neq 0$, is null for the orthogonality properties of the Harmonic functions, [4] therefore:

$$\Upsilon^{m > 0} = \frac{\Xi}{2}. \tag{E.40}$$

The same result is found for negative m , substituting eq. E.25 (instead of eq. E.24, as done) in eq. E.31:

$$\Upsilon^{m < 0} = \frac{\Xi}{2}, \tag{E.41}$$

so Υ (as Ξ is) is independent from the m sign. If $m = 0$, the last integral in eq. E.39 is equal to Ξ , as the first two ones:

$$\Upsilon^{m=0} = \Xi; \quad (\text{E.42})$$

the previous equation can be deduced also from eq. E.27.

Summarizing, from eqs. E.40, E.41 and E.42, we get:

$$\Upsilon = \frac{\Xi}{2 - \delta_{m0}} \quad (\text{E.43})$$

and, finally, substituting eqs. E.32 and E.43 in eq. E.29, we obtain:

$$c_i^{\ell m} = \left(\frac{\pi^{3/2} (2\ell - 1)!! (\ell + |m|)!}{2^{2\ell+3/2} (2 - \delta_{m0}) \alpha_i^{\ell+3/2} (\ell - |m|)!} \right)^{-1/2}. \quad (\text{E.44})$$

The c expression (eq. E.44) can be reorganized in a two factors formula:

$$c_i^{\ell m} = a_i^\ell f^{\ell m}, \quad (\text{E.45})$$

with:

$$a_i^\ell = \left(\frac{\pi^{3/2}}{(2\alpha_i)^{\ell+3/2}} \right)^{-1/2}, \quad (\text{E.46})$$

the α -dependent term, and

$$f^{\ell m} = \left(\frac{(2\ell - 1)!! (\ell + |m|)!}{2^\ell (2 - \delta_{m,0}) (\ell - |m|)!} \right)^{-1/2}, \quad (\text{E.47})$$

the m dependent term.

Note that,

- If $\ell = 0$, γ degenerates in a simple Gaussian (eq. E.26),

$$f^{00} = 1 \quad \text{and} \quad c_i^{00} = a_i^0 = g_i, \quad (\text{E.48})$$

where g_i is the G 's NC (eq. E.12).

- If $\ell = 1$, $f^{1m} = 1/2$ for the three m -values:

$$f^{1m} = 1/2 \quad \text{and} \quad c_i^{1m} = \frac{a_i^1}{2} = \frac{\alpha_i^{5/4} 2^{7/4}}{\pi^{3/4}}, \quad \forall m = -1, 0, 1. \quad (\text{E.49})$$

- If $\ell = 2$, we have:

$$c_i^{20} = \frac{\alpha_i^{7/4} 2^{11/4}}{\pi^{3/4} \sqrt{3}}; \quad c_i^{21} = c_i^{2-1} = \frac{\alpha_i^{7/4} 2^{11/4}}{\pi^{3/4} 3}; \quad c_i^{22} = c_i^{2-2} = \frac{\alpha_i^{7/4} 2^{7/4}}{\pi^{3/4} 3}. \quad (\text{E.50})$$

Let us verify, for two examples, that

$$\gamma' = c \gamma \quad (\text{E.51})$$

is a normalized function, proving that the following integral, I , is equal to 1,

$$I_i^{\ell m} = \int d\mathbf{r} (c_i^{\ell m} \gamma^{\ell m}(\alpha_i; \mathbf{r}))^2. \quad (\text{E.52})$$

The s Case ($\ell = 0, m = 0$)

$$\begin{aligned}
I_i^{00} &= (c_i^{00})^2 \int d\mathbf{r} (\gamma^{00}(\alpha_i; \mathbf{r}))^2 \\
&= (g_i)^2 \int d\mathbf{r} (G(\alpha_i; \mathbf{r}))^2 \\
&= \left(\int (G(\alpha_i; \mathbf{r}))^2 d\mathbf{r} \right)^{-1} \int (G(\alpha_i; \mathbf{r}))^2 d\mathbf{r} = 1,
\end{aligned} \tag{E.53}$$

where eqs. E.48, E.27 and E.12 have been used.

A d Case ($\ell = 2, m = 1$)

$$I_i^{21} = \int d\mathbf{r} (c_i^{21} \gamma^{21}(\alpha_i; \mathbf{r}))^2 = (c_i^{21})^2 J, \tag{E.54}$$

with:

$$J = \int d\mathbf{r} (3zxG(2\alpha_i; \mathbf{r}))^2, \tag{E.55}$$

where eqs. E.23 and E.19 have been used.

Gaussians are separable functions, that is:

$$G(\alpha_i; \mathbf{r}) = G_x(\alpha_i; x) G_y(\alpha_i; y) G_z(\alpha_i; z), \tag{E.56}$$

with:

$$G_x(\alpha_i; x) = \exp(-\alpha_i x^2) \tag{E.57}$$

and similarly for y and z . Substituting eq. E.56 in eq. E.55, we have:

$$J = 9J_x J_y J_z, \tag{E.58}$$

with:

$$J_x = \int x^2 G_x(2\alpha_i; x) dx = \frac{\sqrt{\pi}}{2} (2\alpha_i)^{-3/2}, \tag{E.59}$$

$$J_y = \int G_y(2\alpha_i; y) dy = \left(\frac{\pi}{2\alpha_i} \right)^{1/2}, \tag{E.60}$$

$$J_z = \int z^2 G_z(2\alpha_i; z) dz = \frac{\sqrt{\pi}}{2} (2\alpha_i)^{-3/2}, \tag{E.61}$$

where ref. [182] has been used in solving the integrals. Substituting now eqs. E.49 and E.58 in eq. E.54, we obtain:

$$I_i^{21} = \frac{\alpha_i^{7/2} 2^{11/2}}{\pi^{3/2} 9} 9 \left(\frac{\sqrt{\pi}}{2} (2\alpha_i)^{-3/2} \right)^2 \left(\frac{\pi}{2\alpha_i} \right)^{1/2} = 1. \tag{E.62}$$

Atomic Orbitals Normalization

The variational basis functions of the CRYSTAL program (AOs), φ_μ , are normalized *contractions* (fixed linear combinations) of normalized real solid harmonic Gaussian type functions (*primitive functions*), γ' (eq. E.51). The AOs are organized in *shells*, φ_μ belonging to the same shell, λ , have same radial part, that is, same contraction coefficients, d_i^λ , same Gaussian exponents, α_i^λ and different angular part, X_ℓ^m :

$$\varphi_\lambda^{\ell m} = N_\lambda \sum_i d_i^\lambda c_i^{\ell m} \gamma^{\ell m}(\alpha_i^\lambda; \mathbf{r}) = N_\lambda \sum_i d_i^\lambda c_i^{\ell m} X_\ell^m(\mathbf{r}) G(\alpha_i^\lambda; \mathbf{r}). \tag{E.63}$$

The index i runs over the primitive functions of the contraction, d_i^λ is the contraction coefficient of the i -th primitive in shell λ and, as we have seen, it is the same for all the AOs of λ , that is, it does not depend on ℓ or m . γ and c are the primitive function and its NC (eq. E.29), respectively. N_λ is the NC of AOs belonging to λ and is defined as:

$$N_\lambda = \left(\int d\mathbf{r} \left(\sum_i d_i^\lambda c_i^{\ell m} \gamma^{\ell m}(\alpha_i^\lambda; \mathbf{r}) \right)^2 \right)^{-1/2}, \quad (\text{E.64})$$

in the following will be shown that N depends only on the shell, λ .

We report, as an example, the three AOs of a p -type shell ($\ell = 1$), supposing that λ is classified as the fourth shell of the unitary cell and each AO is a contraction of two primitives.

$$p_z = \varphi_4^{10} = N^4 (d_1^4 c_1^{10} \gamma^{10}(\alpha_1^4; \mathbf{r}) + d_2^4 c_2^{10} \gamma^{10}(\alpha_2^4; \mathbf{r})), \quad (\text{E.65})$$

$$p_x = \varphi_4^{11} = N^4 (d_1^4 c_1^{11} \gamma^{11}(\alpha_1^4; \mathbf{r}) + d_2^4 c_2^{11} \gamma^{11}(\alpha_2^4; \mathbf{r})), \quad (\text{E.66})$$

$$p_y = \varphi_4^{1-1} = N^4 (d_1^4 c_1^{1-1} \gamma^{1-1}(\alpha_1^4; \mathbf{r}) + d_2^4 c_2^{1-1} \gamma^{1-1}(\alpha_2^4; \mathbf{r})). \quad (\text{E.67})$$

Let us put our attention on N_λ . Eq. E.64 can be rewritten as:

$$N^\lambda = \left(\sum_{i,j} d_i^\lambda d_j^\lambda c_i^{\ell m} c_j^{\ell m} \Upsilon' \right)^{-1/2}, \quad (\text{E.68})$$

with:

$$\Upsilon' = \int d\mathbf{r} \gamma^{\ell m}(\alpha_i; \mathbf{r}) \gamma^{\ell m}(\alpha_j; \mathbf{r}), \quad (\text{E.69})$$

where the shell index on α has been omitted for simplicity. Substituting eq. E.23 in eq. E.69, we have:

$$\Upsilon' = \int X_\ell^m(\mathbf{r}) G(\alpha_i; \mathbf{r}) X_\ell^m(\mathbf{r}) G(\alpha_j; \mathbf{r}) d\mathbf{r} = \int (X_\ell^m(\mathbf{r}))^2 G[(\alpha_i + \alpha_j); \mathbf{r}] d\mathbf{r}, \quad (\text{E.70})$$

where the Gaussian product theorem (eq. E.8) has been used.

From eq. E.31, it can be seen that Υ' differs from Υ only in the Gaussian exponent ($\alpha_i + \alpha_j$ instead of $2\alpha_i$), using then eqs. E.43, E.32, E.34 and E.35, Υ' is rewritten as:

$$\Upsilon' = \frac{\Upsilon'_r \Xi_\theta \Xi_\varphi}{2 - \delta_{m0}}, \quad (\text{E.71})$$

with:

$$\begin{aligned} \Upsilon'_r &= \int_0^\infty dr \exp[-(\alpha_i + \alpha_j)r^2] r^{2\ell+2} \\ &= \frac{\Gamma(\ell + 3/2)}{2(\alpha_i + \alpha_j)^{\ell+3/2}} \\ &= \frac{\pi^{1/2} (2\ell + 1)!!}{2^{\ell+2} (\alpha_i + \alpha_j)^{\ell+3/2}}. \end{aligned} \quad (\text{E.72})$$

Substituting eqs. E.44, E.71 and E.72 in eq. E.68, we obtain:

$$N_\lambda = \left(\sum_{i,j} d_i^\lambda d_j^\lambda \left(\frac{2\sqrt{\alpha_i^\lambda \alpha_j^\lambda}}{\alpha_i^\lambda + \alpha_j^\lambda} \right)^{\ell+3/2} \right)^{-1/2}, \quad (\text{E.73})$$

where it is clear that N depends only on λ .

The Code

In order to explain easily the organization of NCs in CRYSTAL, eq. E.63 is reorganized as follows:

$$\varphi_{\lambda}^{\ell m} = \sum_i n_{\lambda,i}^{\ell m} \gamma^{\ell m}(\alpha_i^{\lambda}; \mathbf{r}), \quad (\text{E.74})$$

with:

$$n_{\lambda,i}^{\ell m} = N_{\lambda} d_i^{\lambda} c_i^{\ell m}. \quad (\text{E.75})$$

Note that, while the AO is normalized, the function $\gamma'' = n\gamma$ is not; in fact n is not a normalization factor, and it will be referred as the *pre-Gaussian factor*.

At the moment the CRYSTAL code is able to treat four type of shells: s , sp , p and d .³ An s shell has only an AO, that is a contraction of simple Gaussians ($\ell = 0$); in a p one there are three AOs (different for the m value, p_x , p_y and p_z) with $\ell = 1$ primitives; d shells are obviously formed by five $\ell = 2$ AOs. The three basis functions of a sp shell are contractions of one s primitive function and several ps '.

In the calculation of the integrals required in the SCF process, n must be very often multiplied by the constant factor $\pi^{5/8} 2^{1/4}$; [142] therefore, in the code, pre-Gaussian factors are not stored, but the following quantities, that we shall call *code pre-Gaussian constants*:

$$S_i^{\lambda} = \pi^{5/8} 2^{1/4} n_{\lambda,i}^{00} \quad (\text{E.76})$$

$$P_i^{\lambda} = \pi^{5/8} 2^{1/4} n_{\lambda,i}^{1m} \quad \forall m = 0, 1, -1 \quad (\text{E.77})$$

$$D_i^{\lambda} = \pi^{5/8} 2^{1/4} \sqrt{\frac{(2 + |m|)!}{(2 - \delta_{m0})(2 - |m|)!}} n_{\lambda,i}^{2m} \quad \forall m = 0, 1, -1, 2, -2. \quad (\text{E.78})$$

Note that the square root in eq. E.78 (the inverse of the m -dependent part of c , eq. E.44) makes D independent from the m value, whereas $n_{\lambda,i}^{2m}$ depends from it. In such a way, S , P and D are m -independent

In the `inpbas` routine, contraction coefficients (as defined in input), d_i^{λ} , related to s , p and d AOs, are loaded in the two dimension packed arrays `c1`, `c2` and `c3`, respectively (they are stored in the module `basato_module`). Their length corresponds to the total number of primitives in the unit cell and is the same for the three arrays. The first elements are the contraction coefficients for the first shell (d_i^1), then the d_i^2 (second shell) follows, and so on; the contraction index, i , is the internal one. For an s shell, for example, the elements of `c2` and `c3` are null, of course.

In the `gaunov` routine, `c1`, `c2` and `c3` are redefined and loaded with the code pre-Gaussian constants S , P and D , respectively; naturally they maintain the described organization and module `basato_module` is overwritten.

In `gaunov` two further arrays, `c2w` and `c3w` (that follow the convention used in the ATMOL program) are also defined and loaded in `basato_module`. They have the same organization as `c1`, `c2` and `c3` and contain P_i^{λ} and D_i^{λ} coefficients, respectively:

$$P_i^{\lambda} = \frac{\pi^{5/8} 2^{1/4}}{2\alpha_i} n_{\lambda,i}^{1m} \quad \forall m = 0, 1, -1 \quad (\text{E.79})$$

$$D_i^{\lambda} = \frac{\pi^{5/8} 2^{1/4}}{(2\alpha_i)^2} \sqrt{\frac{(2 + |m|)!}{(2 - \delta_{m0})(2 - |m|)!}} n_{\lambda,i}^{2m} \quad \forall m = 0, 1, -1, 2, -2. \quad (\text{E.80})$$

³The implementation of higher polynomial functions is now in progress.

We give an example of evaluation of an overlap integral $S_{\mu\nu}$ over an s and a $m = 0$ d AO ($\varphi_\mu \equiv \varphi_{00}^\lambda$, $\varphi_\nu \equiv \varphi_{20}^\sigma$) sitting in the reference cell:

$$S_{\mu\nu} = \int d\mathbf{r} \varphi_{00}^\lambda(\mathbf{r}) \varphi_{20}^\sigma(\mathbf{r}). \quad (\text{E.81})$$

Substituting eq. E.74 in the previous equation, we have:

$$S_{\mu\nu} = \sum_{ij} n_{\lambda,i}^{00} n_{\sigma,j}^{20} \int d\mathbf{r} \gamma^{00}(\alpha_i^\lambda; \mathbf{r}) \gamma^{20}(\alpha_j^\sigma; \mathbf{r}). \quad (\text{E.82})$$

Since in the code, S and D are available (but not the n coefficients), we express n as a function of code pre-Gaussian constants, using eqs. E.76 and E.78, and we rewrite the overlap integral as:

$$S_{\mu\nu} = \left(\pi^{5/8} 2^{1/4}\right)^{-2} \sqrt{\frac{(2 - \delta_{m0})(2 - |m|)!}{(2 + |m|)!}} \sum_{ij} S_i^\lambda D_i^\sigma \int d\mathbf{r} \gamma^{00}(\alpha_i^\lambda; \mathbf{r}) \gamma^{20}(\alpha_j^\sigma; \mathbf{r}). \quad (\text{E.83})$$

Note that the m -dependent term contained in n , for d shells, must be multiplied *a posteriori*, because is not included in D. This operation is performed in the `dfac3` routine, that provides McMurchie-Davidson coefficients multiplied by code pre-Gaussian constants and, when λ is a d shell, by the m -dependent part of $n_{\lambda,i}^{2m}$.

Appendix F

CRYSTAL09 versus CRYSTAL06

Geometry

- Roto-translational symmetry
In the case of polymers it can treat helical structures (translation followed by a rotation around the periodic axis). See keyword **HELIX** (page 16) and examples therein. CRYSTAL06 allowed commensurate rotations only, by adopting a suitably large unit cell.
- Nanotubes
A special input option allows generation of 1D structures (nanotubes) from 2D one. See keyword **NANOTUBE** (page 52).

Geometry optimization

- Default choice modified: TRUSRADIUS scheme active.
Use keyword **NOTRISTR** in **OPTGEOM** input block (page 124) to run geometry optimization with CRYSTAL06 default.

Frequencies calculation

- default value for SCF convergence on total energy is 10^{-9}
- default choice for numerical integration grid (DFT Hamiltonian): **XLGRID**. To run DFT Hamiltonian cases with CRYSTAL06 numerical integration accuracy insert **LGRID** in DFT input block (page 91)
- default choice to compute IR intensities: Berry phase approach. To compute IR intensities with CRYSTAL09 as with CRYSTAL06 insert keyword **INTLOC** in **FREQCALC** input block.

Basis set

- *f* orbitals
 - *f* orbitals (local functions basis set) with non-zero occupancy allowed. This new feature allows study of systems with Lanthanides.
 - d* and *f* orbitals occupation guess
 - **FD OCCUP** (input block3, page 97) defines the occupation of specific *f* or *d* orbitals

in a given shell in the SCF initial guess, according to the local atomic symmetry in the crystal lattice.

- - Effective core pseudo potentials Projector operators up to angular quantum number $\ell = 4$ are allowed. ***Input deck has been changed***

Test cases

crystal09 versus crystal06 total energies (hartree)

| | CRYSTAL06 | CRYSTAL09 | diff |
|--------|------------------|------------------|-----------|
| TEST 0 | -110.7649354541 | -110.7649354541 | 0.00E+00 |
| TEST 1 | -39.7267242374 | -39.7267242374 | 0.00E+00 |
| TEST 2 | -223.7874756819 | -223.7874756819 | 0.00E+00 |
| TEST 3 | -893.8746580004 | -893.8746580004 | 0.00E+00 |
| TEST 4 | -1400.1776585535 | -1400.1776585535 | 0.00E+00 |
| TEST 5 | -74.8333583570 | -74.8333583570 | 1.01E-12 |
| TEST 6 | -58.4208255980 | -58.4208255980 | 1.00E-12 |
| TEST 7 | -2800.7355953744 | -2800.7355953744 | 0.00E+00 |
| TEST 8 | -571.3207540595 | -571.3207540595 | 3.00E-11 |
| TEST 9 | -29.2566111179 | -29.2566111179 | 0.00E+00 |
| TEST10 | -577.8265583253 | -577.8265583271 | -1.86E-09 |
| TEST11 | -274.6641530559 | -274.6641530559 | -3.00E-11 |
| TEST12 | -447.6810664796 | -447.6810664796 | -6.00E-11 |
| TEST13 | -23.9856901143 | -23.9856901143 | 0.00E+00 |
| TEST14 | -159.6970601598 | -159.6970601598 | 0.00E+00 |
| TEST15 | -5229.8366027793 | -5229.8366027783 | 1.00E-09 |
| TEST16 | -2995.2869386583 | -2995.2869386582 | 1.00E-10 |
| TEST17 | -2674.3752958019 | -2674.3752958111 | -9.20E-09 |
| TEST18 | -679.2766564082 | -679.2766564082 | 0.00E+00 |
| TEST19 | -223.8070777853 | -223.8070777853 | 0.00E+00 |
| TEST20 | -89.9552981103 | -89.9552981101 | 1.79E-10 |
| TEST21 | -447.5749511978 | -447.5749511978 | 0.00E+00 |
| TEST22 | -460.7186326563 | -460.7186326563 | -3.00E-11 |
| TEST23 | -8.0613160317 | -8.0613160317 | 0.00E+00 |
| TEST24 | -1400.1776188146 | -1400.1776188146 | 0.00E+00 |
| TEST25 | -74.8442039913 | -74.8442039913 | -9.95E-13 |
| TEST26 | -58.4208255860 | -58.4208255860 | 0.00E+00 |
| TEST27 | -2800.7355409839 | -2800.7355409839 | 0.00E+00 |
| TEST28 | -8.0115274157 | -8.0115274157 | -9.95E-14 |
| TEST29 | -2047.6430862971 | -2047.6430862970 | 9.98E-11 |
| TEST30 | -109.0441458665 | -109.0441458665 | 0.00E+00 |
| TEST31 | -4095.2867581787 | -4095.2867581681 | 1.06E-08 |
| TEST32 | -92.1408103960 | -92.1408103960 | 0.00E+00 |
| TEST33 | -92.1416129818 | -92.1416129818 | 0.00E+00 |
| TEST34 | -1117.5230436113 | -1117.5230436113 | 0.00E+00 |
| TEST35 | -936.5017511475 | -936.5017511475 | 3.00E-11 |
| TEST36 | -112.5648952230 | -112.5648952230 | 1.00E-11 |
| TEST37 | -3028.3682392877 | -3028.3682392877 | 0.00E+00 |
| TEST38 | -2279.1395902376 | -2279.1395902366 | 1.00E-09 |

Appendix G

CRYSTAL14 versus CRYSTAL09

Old Settings

- Some default computational parameters have changed with respect to the CRYSTAL09 version of the program (see below). The keyword **OLDREF09**, to be inserted in the geometry input block, switches back them all;

Geometry optimization

- Full geometry optimizations (atomic coordinates and lattice parameters) are now performed as a default option when the **OPTGEOM** keyword is used. The sub-keyword **ATOMONLY** switches back to an atomic positions only optimization;
- The **FINALRUN** = 4 option is now set by default (before it was 0). See page 126 for details;

Density Functional Theory

- The size of the default numerical integration grid has changed. Now it corresponds to the **XLGRID** option. The option **OLDGRID** has been added to set back the old grid size;
- By default, an unlocked energy shifting of 0.6 hartree is applied to separate apart occupied from virtual orbitals, which corresponds to option **LEV-SHIFT** with parameters 6 0.

Frequencies calculation

- Eckart conditions for cleaning the Hessian matrix as regards translational and rotational vibration modes are now activated by default. See page 145 for details;

SCF Parameters

- A Fock (Kohn-Sham) matrix mixing of 30 % between subsequent SCF cycles is now active by default (see keyword **FMIXING**);
- A full direct approach for the computation of the integrals (keyword **SCFDIR**) is now used as a default. Use keyword **NODIRECT** for switching this option off;
- The thresholds governing the bipolar approximation have changed from 14 10 to 18 14. See keyword **BIPOLA** for details;

Test cases

CRYSTAL14 versus CRYSTAL09 total energies (hartree)

| | CRYSTAL09 v.2.0.1 Etot | CRYSTAL14 Old settings Etot | CRYSTAL14 New defaults Etot | CRY14-CRY09 Old settings DEtot |
|------------|------------------------------|-----------------------------------|-----------------------------------|--------------------------------------|
| test00 | -110.76493545 | -110.76493545 | -110.76493545 | 0.00000000 |
| test01 | -39.72672424 | -39.72672424 | -39.72672424 | 0.00000000 |
| test02 | -223.78747568 | -223.78747568 | -223.78754817 | 0.00000000 |
| test03 | -893.87465800 | -893.87465800 | -893.87461008 | 0.00000000 |
| test04 | -1400.17765855 | -1400.17765855 | -1400.17840956 | 0.00000000 |
| test05 | -74.83335836 | -74.83335836 | -74.83336244 | 0.00000000 |
| test06 | -58.42082558 | -58.42082558 | -58.42098571 | 0.00000000 |
| test07 | -2800.73559537 | -2800.73559537 | -2800.73725678 | 0.00000000 |
| test08 | -571.32075406 | -571.32075406 | -571.32081226 | 0.00000000 |
| test09 | -29.25661159 | -29.25661159 | -29.25662600 | 0.00000000 |
| test10 | -577.82655833 | -577.82655832 | -577.82670817 | 0.00000000 |
| test11 | -274.66415306 | -274.66415306 | -274.66419189 | 0.00000000 |
| test12 | -447.68106648 | -447.68106648 | -447.68124595 | 0.00000000 |
| test13 | -23.98569011 | -23.98569011 | -23.98569013 | 0.00000000 |
| test14 | -159.69706016 | -159.69706016 | -159.69729413 | 0.00000000 |
| test15 | -5229.83660278 | -5229.83660278 | -5229.83555014 | 0.00000000 |
| test16 | -2995.28693866 | -2995.28693866 | -2995.28683802 | 0.00000000 |
| test17 | -2674.37529581 | -2674.37529581 | -2674.37559033 | 0.00000000 |
| test18 | -679.27665641 | -679.27665641 | -679.27667659 | 0.00000000 |
| test19 | -223.80707779 | -223.80707779 | -223.80715189 | 0.00000000 |
| test20 | -89.95529811 | -89.95529811 | -89.95529811 | 0.00000000 |
| test21 | -447.57495120 | -447.57495120 | -447.57509617 | 0.00000000 |
| test22 | -460.71863266 | -460.71863266 | -460.71872430 | 0.00000000 |
| test23 | -8.06131603 | -8.06131603 | -8.06132051 | 0.00000000 |
| test24 | -1400.17761881 | -1400.17761881 | -1400.17836984 | 0.00000000 |
| test25 | -74.84420399 | -74.84420399 | -74.84419555 | 0.00000000 |
| test26 | -58.42082557 | -58.42082557 | -58.42098569 | 0.00000000 |
| test27 | -2800.73554098 | -2800.73554098 | -2800.73720223 | 0.00000000 |
| test28 | -8.01152742 | -8.01152742 | -8.01152780 | 0.00000000 |
| test29 | -2047.64308630 | -2047.64308630 | -2047.64342093 | 0.00000000 |
| test30 | -109.04414587 | -109.04414587 | -109.04434229 | 0.00000000 |
| test31 | -4095.28675817 | -4095.28675818 | -4095.28742264 | -0.00000001 |
| test32 | -92.14081040 | -92.14081040 | -92.14081024 | 0.00000000 |
| test33 | -92.14161298 | -92.14161298 | -92.14161286 | 0.00000000 |
| test34 | -1117.52304361 | -1117.52304361 | -1117.52300498 | 0.00000000 |
| test35 | -936.50175115 | -936.50175115 | -936.50185912 | 0.00000000 |
| test36 | -112.56489522 | -112.56489522 | -112.56490316 | 0.00000000 |
| test37 | -3028.36823929 | -3028.36823929 | -3028.36857687 | 0.00000000 |
| test38 | -2279.13959024 | -2279.13959024 | -2279.14018803 | 0.00000000 |
| test43 | -1613.25523877 | -1613.25523877 | -1613.25545994 | 0.00000000 |
| test47 | -4394.62644451 | -4394.62644451 | -4394.62706583 | 0.00000000 |
| test01_dft | -40.32096680 | -40.32096680 | -40.32090900 | 0.00000000 |

| | | | | |
|------------|----------------|----------------|----------------|------------|
| test02_dft | -224.92502981 | -224.92502981 | -224.92495090 | 0.00000000 |
| test03_dft | -895.51814784 | -895.51814784 | -895.51821309 | 0.00000000 |
| test04_dft | -1403.86073017 | -1403.86073017 | -1403.86074899 | 0.00000000 |
| test05_dft | -75.25763976 | -75.25763976 | -75.25766593 | 0.00000000 |
| test08_dft | -573.30069771 | -573.30069771 | -573.30058383 | 0.00000000 |
| test11_dft | -275.43123078 | -275.43123078 | -275.43126854 | 0.00000000 |
| test39_dft | -485.38270022 | -485.38270022 | -485.38264752 | 0.00000000 |
| test40_dft | -337.10879536 | -337.10879536 | -337.10946296 | 0.00000000 |
| test41_dft | -1313.33749919 | -1313.33749919 | -1313.33738975 | 0.00000000 |
| test42_dft | -7.53085315 | -7.53085315 | -7.53085381 | 0.00000000 |
| test44_dft | -1421.65733745 | -1421.65733745 | -1421.65785507 | 0.00000000 |
| test45_dft | -5280.86118400 | -5280.86118400 | -5280.86080258 | 0.00000000 |
| test46_dft | -5280.43937642 | -5280.43937642 | -5280.43953416 | 0.00000000 |
| test47_dft | -4406.89968860 | -4406.89968860 | -4406.90099322 | 0.00000000 |
| test48_dft | -37.61966054 | -37.61966054 | -37.61967775 | 0.00000000 |
| test49_dft | -37.61966059 | -37.61966059 | -37.61967828 | 0.00000000 |
| test50_dft | -37.61966059 | -37.61966059 | -37.61967828 | 0.00000000 |
| test51_dft | -1020.29088144 | -1020.29088144 | -1020.29350751 | 0.00000000 |

Appendix H

Acronyms

AFM – Anti ferromagnetic
AO – Atomic Orbital
APW – Augmented Plane Wave
a.u. – atomic units
BF – Bloch Function
BS – Basis set
BSSE – Basis Set Superposition Error
BZ – Brillouin Zone (first)
B3PW – Becke Perdew Wang
B3LYP – Becke - Lee - Yang - Parr
CO – Crystalline Orbital
CPU – Central Processing Unit
DF(T) – Density Functional (Theory)
DM – Dipole Moment (see Wannier Functions)
DOS – Density of States
ECP – Effective Core Potentials
EFG – Electric Field Gradient
EMD – Electron Momentum Density
FM – Ferromagnetic
GC – Gradient-Corrected
GGA – Generalised Gradient Approximation
GS(ES) – Ground State (Electronic Structure)
GT(O) – Gaussian Type (Orbital)
GT(F) – Gaussian Type (Function)
GUI – Graphical User Interface
KS – Kohn and Sham
HF – Hartree-Fock
IBZ – Irreducible Brillouin zone
IR – Irreducible Representation
LAPW – Linearized Augmented Plane Wave
LCAO – Linear Combination of Atomic Orbitals
LDA – Local Density Approximation
LP – Local Potential
LSDA – Local Spin Density Approximation
LYP – GGA Lee-Yang-Parr
MO – Molecular Orbital

MPP – Massive Parallel Processor
MSI – Molecular Simulation Inc.
NLP – Non-local potential (correlation)
PBE – GGA Perdew-Burke-Ernzerhof
PDOS – Projected Density of States
PP – Pseudopotential
PVM – Parallel Virtual Machine
PW – Plane Wave
PWGGA – GGA. Perdew-Wang
PWLSD – LSD Perdew-Wang
PZ – Perdew-Zunger
P86 – GGA Perdew 86
P91 – Perdew 91
QM – Quantum Mechanics
RCEP – Relativistic Compact Effective Potential
RHF – Restricted Hartree-Fock
ROHF – Restricted Open-shell Hartree-Fock
SAED – Symmetry Allowed Elastic Distortions
SABF – Symmetry Adapted Bloch Functions SC – Supercell
SCF – Self-Consistent-Field
 STO – Slater Type Orbital
UHF – Unrestricted Hartree-Fock
VBH – von Barth-Hedin
VWN – Vosko-Wilk-Nusair
WnF – Wannier Functions 0D – no translational symmetry
1D – translational symmetry in 1 direction (x , CRYSTAL convention)
2D – translational symmetry in 2 directions (x,y , CRYSTAL convention)
3D – translational symmetry in 3 directions (x,y,z CRYSTAL convention)

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