

CRYSTAL09

1.0.0 draft

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 11.

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 21). 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

A special input option allows generation of 1D structures (nanotubes) from 2D ones.

Previous releases of the software in 1988 (CRYSTAL88, [1]), 1992 (CRYSTAL92, [2]), 1996 (CRYSTAL95, [3]), 1998 (CRYSTAL98, [4]), 2003 (CRYSTAL03, [5]) and 2006 (CRYSTAL06) [6] 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/theory.html>

The required citation for this work is:

R. Dovesi, R. Orlando, B. Civalleri, C. Roetti, V.R. Saunders, C.M. Zicovich-Wilson
CRYSTAL: a computational tool for the ab initio study of the electronic properties of crystals
Z. Kristallogr. **220**, 571–573 (2005)

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CRYSTAL09 User's Manual, University of Torino, Torino, 2009

CRYSTAL09 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>

CRYSTAL09 Program Features

New features with respect to CRYSTAL06 are in *italics*.

Hamiltonian

- **Hartree-Fock Theory**

- Restricted
- Unrestricted

- **Density Functional Theory**

- Local functionals [L] and gradient-corrected functionals [G]
 - * Exchange functionals
 - Slater (LDA) [L]
 - von Barth-Hedin (VBH) [L]
 - Becke '88 (BECKE) [G]
 - Perdew-Wang '91 (PWGGA) [G]
 - Perdew-Burke-Ernzerhof (PBE) [G]
 - *Revised PBE functional for solids (PBEsol) [G]*
 - *Second-order expansion GGA for solids (SOGGA) [G]*
 - *Wu-Cohen '06 (WCGGA) [G]*
 - * Correlation functionals
 - VWN (#5 parameterization) (VWN) [L]
 - Perdew-Wang '91 (PWLSD) [L]
 - Perdew-Zunger '81 (PZ) [L]
 - von Barth-Hedin (VBH) [L]
 - Lee-Yang-Parr (LYP) [G]
 - Perdew '86 (P86) [G]
 - Perdew-Wang '91 (PWGGA) [G]
 - Perdew-Burke-Ernzerhof (PBE) [G]
 - *Revised PBE functional for solids (PBEsol) [G]*
 - *Wilson-Levy '90 (WL) [G]*
- Hybrid HF-DFT functionals
 - * B3PW, B3LYP (using the VWN5 functional), PBE0
 - * User-defined hybrid functionals
- Numerical-grid based numerical quadrature scheme
- *London-type empirical correction for dispersion interactions (Grimme 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

Type of calculation

- **Single-point energy calculation**
- **Automated geometry optimization**
 - Uses a quasi-Newton algorithm
 - Optimizes in symmetry-adapted cartesian coordinates
 - Optimizes in redundant coordinates
 - Full geometry optimization (cell parameters and atom coordinates)
 - Freezes atoms during optimization
 - *Constant volume or pressure constrained geometry optimization (3D only)*
 - *Transition state search*
- **Harmonic vibrational frequencies**
 - Harmonic vibrational frequencies at Gamma point
 - *Phonon dispersion using a direct approach (efficient supercell scheme)*
 - IR intensities through either localized Wannier functions or *Berry phase*
 - *Calculation of the reflectance spectrum*
 - 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 (3D only)*
- *Automated E vs V calculation for equation of state (3D only)*
- *Automatic treatment of solid solutions*

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
 - 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)*
- 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*
- 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**

- **Structure factors**

- **Electron Momentum Density and Compton profiles** (*Enhanced version*)

- **Electrostatic potential and its derivatives**

- Quantum and classical electrostatic potential and its derivatives
- Electrostatic potential maps

- **Fermi contact**

- **Localized Wannier Functions (Boys method)**

- **Dielectric properties**

- Spontaneous polarization
 - * Berry Phase
 - * Localized Wannier Functions
- Dielectric constant
 - * *New Coupled Perturbed HF(KS) scheme*
 - * Finite-field approximation

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)*

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	
-	 , []	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:

(*dslist*, $i=m1,m2$)

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

Example (page 32): 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 20. 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. [7], the GAUSS70 gaussian integral package and STO-nG basis set due to Hehre et al. [8], the code of Burzlaff and Hountas for space group analysis [9] and Saunders' ATMOL gaussian integral package [10].

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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Michele Catti significantly contributed to the implementation of the geometry optimizer with discussion, suggestions, contributions to the coding.

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Contribution to validate the new features by applying them to research problem is recognized to all researchers working in the Theoretical Chemistry Group from 2006 to 2009: Marta Corno, Raffaella Demichelis, Alessandro Erba, Matteo Ferrabone, Anna Ferrari, Migen Halo, Valentina Lacivita, Lorenzo Maschio, Alessio Meyer, Alexander Terentyev, Javier F. Torres, Loredana Valenzano.

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

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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 14
SLAB	2D system	page 14
POLYMER	1D system	page 14
HELIX	1D system - roto translational symmetry	page 15
MOLECULE	0D system	page 14
EXTERNAL	geometry from external file	page 15
DLVINPUT	geometry from DLV [11] Graphical User Interface.	page 15

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 15) or **DLVINPUT**, the unit cell, atomic positions and symmetry operators may be provided directly from an external file (see Appendix D, page 263). 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 9.1, page 193.

Geometry input for crystalline compounds. Keyword: CRYSTAL

rec	variable	value	meaning
• *	IFLAG		convention for space group identification (Appendix A.1, page 235):
		0	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
		1	rhombohedral cell. Lattice parameters a, α
	IFSO		setting for the origin of the crystal reference frame:
		0	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)
• *			space group identification code (following IFLAG value):
	IGR		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).
• *	a,[b],[c], [α],[β] [γ]		minimal set of crystallographic cell parameters: translation vector[s] length [\AA strom], crystallographic angle[s] (degrees)
• *	NATR		number of atoms in the asymmetric unit.
			<i>insert NATR records</i> 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 vectors
			<i>optional keywords terminated by END/ENDGEOM or STOP</i> 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 242) 1D - polymers (Appendix A.3, page 239) 2D - slabs (Appendix A.2, page 238) <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 $n = 1, \dots, (N1 - 1)$.

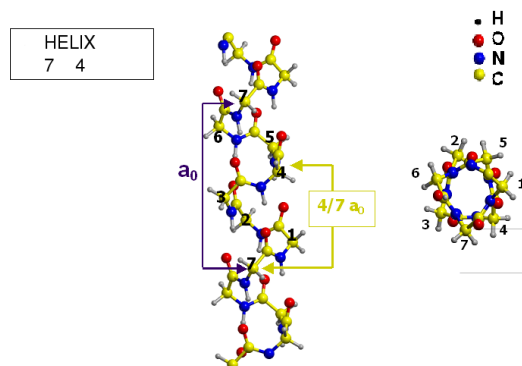
As an example let's consider the α -helix conformer of polyglycine whose structure is sketched in Figure 1.1.

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



263. 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/cmgl/DLV/>).

The geometry defined by **EXTERNAL** can be modified by inserting any geometry editing keyword (page 26) 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 44) or **BOHR** (page 34).
2. The geometry of a system is defined by the crystal structure ([12], Chapter 1 of ref. [13]). Reference is made to the International Tables for Crystallography [14] 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 243, and are taken from Table 5.1 of the International Tables for Crystallography [14].

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 57, 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 52) 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 235.

Examples:

Group number	input symbol
137 (tetragonal)	P ₄ 2/N ₄ M ₄ C
10 (monoclinic)	P ₄ 1 ₂ /M ₄ 1 (unique axis <i>b</i> , standard setting)
	P ₄ 1 ₄ 1 ₂ /M (unique axis <i>c</i>)
	P ₄ 2/M ₄ 1 ₄ 1 (unique axis <i>a</i>)
25 (orthorhombic)	P ₄ M ₄ M ₄ 2 (standard setting)

P₁2₁M₁M₁
P₁M₁2₁M₁

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 19). 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 65).
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 [15], 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 64).
16. The keyword **SLABCUT** (Geometry editing input, page 55) 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 46) and **CLUSTER** (for any n-D structure; page 36) allow the creation of a non-periodic system (molecule(s) or cluster) from a periodic one.

1.2 Basis set

rec	variable	value	meaning		
● *	NAT	n	conventional atomic 3 number		
		<200	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 65)		
		=99	end of basis set input section		
	NSHL	n	number of shells		
		0	end of basis set input (when NAT=99)		
		<i>if NAT > 200 insert ECP input (page 65)</i>		II	
	NSHL sets of records - for each shell				
	● *	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)		
		4	7 f AOs (F shell)		
NG			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		
		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 8.2. When an effective core pseudo-potential is used, the basis set **must** be optimized with reference to that potential (Section 2.2, page 65).

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 32), the corresponding basis set input can remain in the input stream. The keyword **GHOSTS** (page 64) 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 11, page 220).

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 65, 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 [16] (internally stored as in Gaussian 94 [17]).
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. AO	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 8: Mulliken population analysis (**PPAN**, page 96), electrostatic multipoles (**POLI**, page 181), projected density of states (**DOSS**, page 161) and to provide an input for some options (**EIGSHIFT**, input block 3, page 82).

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 $\neq 0$ 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 91). 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 84 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 [18]. This is obtained by entering the keyword **CHARGED** (page 62) 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 62).
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 [19] (keyword **ATOMHF**, input block 3, page 72).

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

http://www.crystal.unito.it

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)	102
tolerances for coulomb and exchange sums :	6 6 6 6 12	TOLINTEG	102
Pole order for multipolar expansion:	4	POLEORDR	95
Max number of SCF cycles:	50	MAXCYCLE	93
Convergence on total energy:	10^{-6}	TOLDEE	101

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 [20]. 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:

$$H_k = \sum_g H_g e^{i\mathbf{g}\mathbf{k}}$$

$$H_k A_k = S k A_k E_k$$

A second shrinking factor, ISP, defines the sampling of \mathbf{k} points, "Gilat net" [21, 22], 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 97).

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

$$b1/is1, b2/is2, b3/is3 \quad is1=is2=is3=IS, \text{ unless otherwise stated}$$

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.

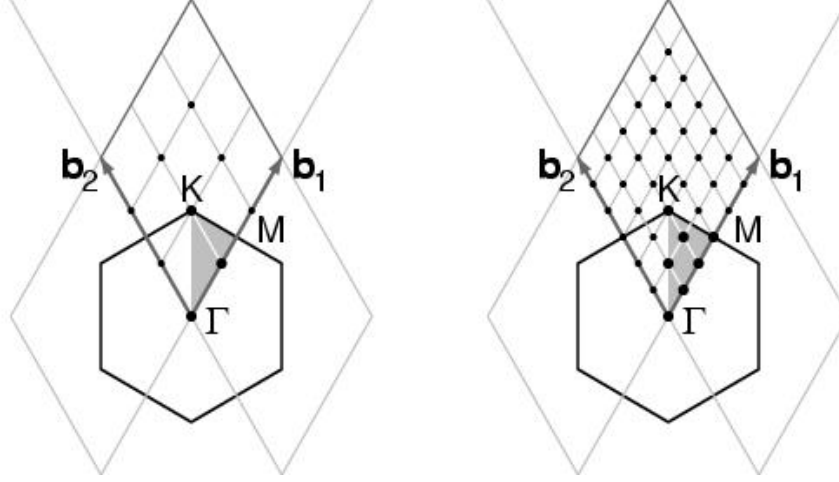
Only points k_i of the Pack-Monkhorst net belonging to the irreducible part of the Brillouin Zone (IBZ) are considered, with associated a geometrical weight, w_i . The choice of the reciprocal space integration parameters to compute the Fermi energy is a delicate step for metals. See Section 11.7, page 226.

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 [23], 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.

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 fcc	points in IBZ hcp	points BZ
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 95.

Some tools for accelerating convergence are given through the keywords **LEVSHIFT** (page 92 and tests 29, 30, 31, 32, 38), **FMIXING** (page 87), **SMEAR** (page 99), **BROYDEN**

(page 73) and **ANDERSON** (page 71).

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 101

TOLDEP (tolerance on SQM in density matrix elements) page 102

MAXCYCLE (maximum number of cycles) page 93

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 100) and **BETALOCK** (page 73).

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	34	–
MAKESAED	printing of symmetry allowed elastic distortions (SAED)	45	–
PRSYMDIR	printing of displacement directions allowed by symmetry.	53	–
SYMMDIR	printing of symmetry allowed geom opt directions	60	–
SYMMOPS	printing of point symmetry operators	60	–
TENSOR	print tensor of physical properties up to order 4	60	I

Symmetry information and control			
BREAKELAS	symmetry breaking according to a general distortion	35	I
BREAKSYM	allow symmetry reduction following geometry modifications	34	–
KEEPSYMM	maintain symmetry following geometry modifications	44	–
MODISYMM	removal of selected symmetry operators	45	I
PURIFY	cleans atomic positions so that they are fully consistent with the group	53	–
SYMMREMO	removal of all symmetry operators	60	–
TRASREMO	removal of symmetry operators with translational components	60	–
Modifications without reduction of symmetry			
ATOMORDE	reordering of atoms in molecular crystals	32	–
NOSHIFT	no shift of the origin to minimize the number of symmops with translational components before generating supercell	52	–
ORIGIN	shift of the origin to minimize the number of symmetry operators with translational components	52	–
PRIMITIV	crystallographic cell forced to be the primitive cell	52	–
ROTCRY	rotation of the crystal with respect to the reference system cell	54	I
Atoms and cell manipulation (possible symmetry reduction (BREAKSYM))			
ATOMDISP	displacement of atoms	32	I
ATOMINSE	addition of atoms	32	I
ATOMREMO	removal of atoms	32	I
ATOMROT	rotation of groups of atoms	33	I
ATOMSUBS	substitution of atoms	34	I
ELASTIC	distortion of the lattice	38	I
POINTCHG	point charges input	52	I
SCELPHONO	generation of supercell for phonon dispersion	58	I
SUPERCEL	generation of supercell - input refers to primitive cell	56	I
SUPERCON	generation of supercell - input refers to conventional cell	56	I
USESSED	given symmetry allowed elastic distortions, reads δ	61	I
From crystals to slabs (3D→2D)			
SLABINFO	definition of a new cell, with $xy \parallel$ to a given plane	56	I
SLABCUT	generation of a slab parallel to a given plane (3D→2D)	55	I
From slabs to nanotubes (2D→1D)			
NANOTUBE	building a nanotube from a slab	47	I
SWCNT	building a nanotube from an hexagonal slab	50	I
From periodic structure to clusters			
CLUSTER	cutting of a cluster from a periodic structure (3D→0D)	36	I
HYDROSUB	border atoms substituted with hydrogens (0D→0D)	44	I
Molecular crystals			
MOLECULE	extraction of a set of molecules from a molecular crystal (3D→0D)	46	I
MOLEXP	variation of lattice parameters at constant symmetry and molecular geometry (3D→3D)	46	I
MOLSPLIT	periodic structure of non interacting molecules (3D→3D)	47	–
RAYCOV	modification of atomic covalent radii	53	I
BSSE correction			

MOLEBSSE	counterpoise method for molecules (molecular crystals only) (3D→0D)	45	I
ATOMBSSE	counterpoise method for atoms (3D→0D)	31	I
Auxiliary and control keywords			
ANGSTROM	sets input units to Ångstrom	31	–
BOHR	sets input units to bohr	34	–
BOHRANGS	input bohr to Å conversion factor (0.5291772083 default value)	34	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	44	–
NEIGHBOR	number of neighbours in geometry analysis	51	I
PARAMPRT	printing of parameters (dimensions of static allocation arrays)	52	–
PRINTCHG	printing of point charges coordinates in geometry output	52	
PRINTOUT	setting of printing options by keywords	53	–
SETINF	setting of inf array options	54	I
SETPRINT	setting of printing options	54	I
STOP	execution stops immediately	56	–
TESTGEOM	stop after checking the geometry input	60	–
Output of data on external units			
COORPRT	coordinates of all the atoms in the cell	37	–
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	56	–
External electric field - modified Hamiltonian			
FIELD	electric field applied along a periodic direction	41	I
FIELDCON	electric field applied along a non periodic direction	43	I
Geometry optimization - see index for keywords full list			

OPTGEOM	Geometry optimization input block - closed by END	105	I
Type of optimization (default: atom coordinates)			
FULLOPTG	full geometry optimization		—
CELLONLY	cell parameters optimization		—
INTREDUN	optimization in redundant internal coordinates	115	—
ITATOCEL	iterative optimization (atom/cell)		—
CVOLOPT	full geometry optimization at constant volume	117	—
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	119	I
RESTART	data from previous run		—
FINALRUN	Wf single point with optimized geometry		I
Gradient calculation control			
NUMGRATO	numerical atoms first derivatives	114	—
NUMGRCEL	numerical cell first derivatives	114	—
NUMGRALL	numerical atoms and cell first derivatives	114	—
External stress			
EXTSTRESS	apply external stress	121	I
EXTPRESS	aooly external hydrostatic pressure	121	I
Printing options			
PRINTFORCES	atomic gradients		—
PRINTHESS	Hessian		—
PRINTOPT	optimization procedure		—
PRINT	verbose printing		—
Frequencies at Γ - Harmonic calculation			

FREQCALC	Frequencies at Γ (harmonic calculation) input block - closed by END	127	I
ANALYSIS			—
[NOANALYSIS]			—
DIELISO			I
DIELTS			I
END[FREQ]			—
FRAGMENT			I
INTENS			—
INTLOC	- IR intensities through Wannier functions	133	—
[INTPOL]	- IR intensities through Berry phase [default]	133	—
ISOTOPES		129	I
[MODES]			—
[NOINTENS]			—
NOMODES			—
NORMBORN			—
NOUSESMM			—
NUMBERIV			I
PRESSURE			I
PRINT			—
RESTART			—
SCANMODE			I
STEPSIZE			I
TEMPERAT			I
TESTFREQ			—
[USESMM]			—
ANHARM	Frequency at Γ (anharmonic calculation) input block - closed by END	141	I
END[ANHA]			—
ISOTOPES	modification of atomic mass	142	I
KEEPSMM		44	—
NOGUESS		142	—
POINTS26		142	—
PRINT			—
TEST[ANHA]			—

CONFCONT - Configuration counting and cluster expansion	146
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CPHF - Coupled Perturbed Hartree-Fock	144
--	-----

ELASTCON - Second order elastic constants	149
--	-----

EOS - Equation of state	144
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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 141.

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.

Warning. The system is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.3, page 23).

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 34). To displace all the atoms symmetry related, **KEEPSYMM** must be inserted before **ATOMDISP**.

Increments are in Ångstrom, unless otherwise requested (keyword **BOHR**, **FRACTION**, page 31). 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 31). Remember that the original symmetry of the system is maintained, applying the symmetry operators to the added atoms if the keyword **KEEPSYMM** (page 34) was previously entered. The default is **BREAKSYM** (page 34). Attention should be paid to the neutrality of the cell (see **CHARGED**, page 62). 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 46) and **MOLSPLIT** (page 47). No input data are required.

For molecular crystals only.

ATOMREMO

rec	variable	meaning
• *	NL	number of atoms to remove
• *	LB(L),L=1,NL	<i>label</i> 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 62).

NB. The keyword **GHOSTS** (basis set input, page 64) 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 <i>label</i> 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 53).	
			<i>if NA > 0, insert NA data</i>	II
• *	LB(I),I=1,NA		<i>label</i> 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		<i>label</i> 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 <i>label</i> IPAR	
			<i>if IRO>0 insert</i>	II
• *	N1,N2		<i>label</i> 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 $A \rightarrow B$.
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 62.

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 38).

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 72) 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 32, 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 121) 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).

CONFCONT - Mapping of CRYSTAL calculations to model Hamiltonians

See Chapter 6, page 146.

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

See Chapter 5, page 144.

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	$\neq 0$	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 $\neq 0$ 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 $\neq 0$ 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.

Warning. The system is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.3, page 23). See test 16.

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 261. No input data are required. The file "fort.33" has the right format for the program **MOLDEN** [24] which can be downloaded from:

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

ELASTCON - Calculation of elastic constants

See Chapter 7, page 149.

ELASTIC

An elastic deformation of the lattice may be defined in terms of the Z or ϵ strain tensors defined in section 11.9, page 228.

rec	variable	value	meaning
• *	IDEF	± 1	deformation through equation 11.36, Z matrix.
		± 2	deformation through equation 11.35: ϵ matrix.
		> 0	volume conserving deformation (equation 11.37).
		< 0	not volume conserving (equation 11.36 or 11.35).
• *	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 31). The suggested value for IDEF is -2 (deformation through equation 11.35, *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 231) elastic constants of Li_2O [25].

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 11.35
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 34).

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

See test38 (KCoF₃).

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.

EOS - Equation of state

E vs V curves can be computed automatically by specifying the keyword **EOS** in input block 1 (geometry). **EOS** must be the last keyword in geometry input.

```
. . . geometry input . . . .
EOS
END[EOS]    close EOS input block
END         close geometry input block
```

EOS input block admits several options (subkeywords), and terminates with keyword **END** (or END[EOS], END[—]: the first three characters only are processed).

A *constant volume* geometry optimization is performed for each point and results are then fitted to most common equation of states (e.g. Birch-Murnaghan 3rd-order). The constant volume geometry optimization can be only performed in fractional coordinates.

Note that the initial geometry must be fully relaxed.

Work is in progress to extend this scheme to E vs P calculations

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 101.

Optional keywords are (in any order):

rec variable	meaning
• A RANGE	keyword to specify the range of volumes in the E(V) curve
* VMIN	minimum (compression) variation of the initial volume [<i>default</i> = 0.92]
* VMAX	maximum (expansion) variation of the initial volume [<i>default</i> = 1.08]
* NPOINTS	number 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[EOS]
...
```

corresponds to 10 points between $0.92 \cdot V_{ini}$ and $1.08 \cdot V_{ini}$, where V_{ini} is the volume of the initial geometry given as input (assumed to be the fully optimized structure) or as obtained after a preliminary geometry optimization.

Note that the initial E-V value is always included in the final data for fitting (i.e. 11 points in the example above).

rec variable	meaning
• A PRINT	This option turns on a higher level of diagnostic printing and will generally not be necessary for the typical user. LPRINT(250) is set equal to 1 with this option. Fitting of the E(V) points is also performed for increasing set of points from 3 to the maximum number of points. (<i>default</i> is minimal printing and no additional lines should exist)
• A RESTART	Allows for a RESTART using file <i>EOSINFO.DAT</i> from a previous run.
• 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 [0.00006] - see OPTGEOM , page 110
• A TOLDEX	EOS default [0.00012] - see OPTGEOM , page 110
• A TOLDEE	EOS default [8] - see OPTGEOM , page 110
• A MAXCYCLE	see OPTGEOM , page 113
• A NOTRISTR	see OPTGEOM , page 111
• A TRUSTRADIUS	see OPTGEOM , page 111
• A MAXTRADIUS	see OPTGEOM , page 111

Important remarks

- The structure given as input should be fully optimized. Note that the same tighter convergence criteria as in the calculation of the E vs V curve must be used as well as

the FINALRUN=4 option.

- Integrals classification is done on the input geometry. Therefore, initial geometry must be the equilibrium structure to avoid slightly shifted curves with respect to the true minimum.

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 deck 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 "optcxxx", being xxx the number of the cycle, and it is automatically written at each cycle.

See Appendix D, page 257. 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.

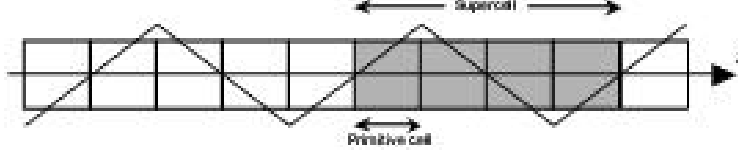
The applied electric field has a square-wave form, that corresponds to a triangular ("sawtooth") electric potential.

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 56).

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 54). After these transformations the field is along the z direction, and the perturbation $\hat{H}_1(\vec{E})$ takes the form:

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

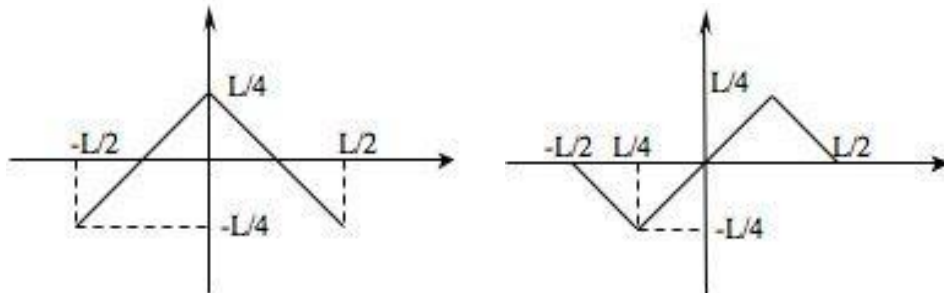
where the f^+ (f^-) function is expanded as a Fourier series and is chosen according to the symmetry of the supercell in the direction of the applied field as follows:

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

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

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 159). In this way the perturbed wave function is used for the calculation of ϵ , following a macroscopic average scheme, as described in references [26], [27].
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.

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



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.
6. 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 92).
7. 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 97).

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.

1. For molecules (N=1) three components of the field must be supplied, as the field can be directed along any direction.
2. 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.
3. 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 127.

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 32, 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.

MAKESAED

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

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 [28] 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 46). The molecule is reconstructed on the basis of the covalent radii reported in Table on page 53. 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

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

For molecular crystals only.

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 23). 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 53).

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 32). 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 19) 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 64)

For molecular crystals only.

Warning. The system is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.3, page 23).

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 16) 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 53)

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 23).

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.

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 2.3 for graphene; the example refers to the construction of a (4,2) single-walled carbon nanotube (SWCNT).

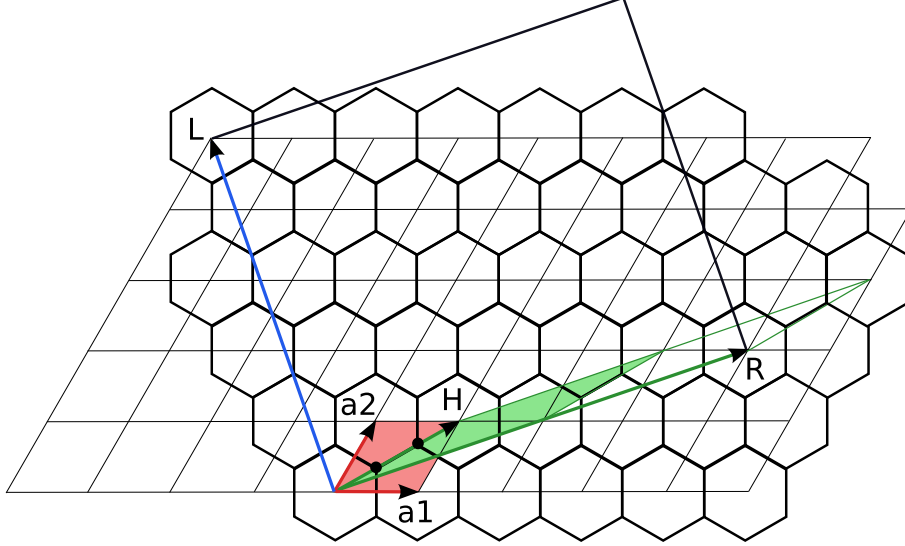


Figure 2.3: Building the (4,2) SWCNT from graphene.

Further information about the implemented method, the computational costs and the symmetry features of nanotubes are found in Ref. [29] and [30, 31].

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 50) 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 47) 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 unit 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. [32] for documentation of computational gain).

NANORE

To be used for tubes built with *NANOTUBE* (page 47).

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 unit fort.34), the second one is read with an *EXTERNAL* strategy from unit 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 50) see *SWCNTRE* (page 51).

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 50).

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/NEIGHPR

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 105.

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 55). No input data are required.

PARAMPRT - printing of parametrized dimensions

The parameters controlling the dimensions of the static allocation arrays of the program are printed. No input data are required.

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 31). 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 **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 243) 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 255.

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 253.

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.

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 0.68												He 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	0.97

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 33) 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 255. 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 52).
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 56) option. This information can be obtained by a test run, inserting in the geometry input block the keyword **TESTGEOM** (page 60). 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 32), **ATOMDISP** (page 32), 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 55).

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 262.

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 17). 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 32), **ATOMSUBS** (page 34), **ATOMINSE** (page 32), **ATOMDISP** (page 32), **SLAB** (page 55).

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 72). 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				DIRECT LATTICE VECTORS			
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				DIRECT LATTICE VECTORS			
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				DIRECT LATTICE VECTORS			
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				DIRECT LATTICE VECTORS			
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				DIRECT LATTICE VECTORS			
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				DIRECT LATTICE VECTORS			
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				DIRECT LATTICE VECTORS			
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 17).

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

```

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 56), 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	O	2.500000000000E-01	2.500000000000E-01	-2.500000000000E-01
11	F	8	O	2.500000000000E-01	-2.500000000000E-01	2.500000000000E-01
12	F	8	O	2.500000000000E-01	-2.500000000000E-01	-2.500000000000E-01
13	F	8	O	-2.500000000000E-01	2.500000000000E-01	2.500000000000E-01
14	F	8	O	-2.500000000000E-01	2.500000000000E-01	-2.500000000000E-01
15	F	8	O	-2.500000000000E-01	-2.500000000000E-01	2.500000000000E-01
16	F	8	O	-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	O	-2.500000000000E-01	-2.500000000000E-01	2.500000000000E-01
10	T	8	O	-2.500000000000E-01	-2.500000000000E-01	-2.500000000000E-01
11	F	8	O	-2.500000000000E-01	2.500000000000E-01	2.500000000000E-01
12	F	8	O	-2.500000000000E-01	2.500000000000E-01	-2.500000000000E-01
13	F	8	O	2.500000000000E-01	-2.500000000000E-01	2.500000000000E-01
14	F	8	O	2.500000000000E-01	-2.500000000000E-01	-2.500000000000E-01
15	F	8	O	2.500000000000E-01	2.500000000000E-01	2.500000000000E-01
16	F	8	O	2.500000000000E-01	2.500000000000E-01	-2.500000000000E-01

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 56 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.

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 52), 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 45) δ for the allowed distortion are given in input.

2.2 Basis set input

Symmetry control			
ATOMSYMM	printing of point symmetry at the atomic positions	34	–
Basis set modification			
CHEMOD	modification of the electronic configuration	62	I
GHOSTS	eliminates nuclei and electrons, leaving BS	64	I
Auxiliary and control keywords			
CHARGED	allows non-neutral cell	62	–
NOPRINT	printing of basis set removed	64	–
PARAMPRT	printing of parameters controlling code dimensions	52	–
PRINTOUT	setting of printing options	53	I
SETINF	setting of inf array options	54	I
SETPRINT	setting of printing options	54	I
STOP	execution stops immediately	56	–
SYMMOPS	printing of point symmetry operators	60	–
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	64	–

Basis set input optional keywords

ATOMSYMM

See input block 1, page 34

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 45).

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) [33, 34]. The deck can be prepared without the calculation of the wave function by entering the keyword **TESTPDIM** in input block 3 (page 101). 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 32) 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.

PARAMPRT - Printing of parametrized dimensions

See input block 1, page 52.

PRINTOUT - Setting of printing environment

See input block 1, page 53.

SETINF - Setting of INF values

See input block 1, page 54.

SETPRINT - Setting of printing options

See input block 1, page 54.

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 60

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.
		<i>if PSN = INPUT insert</i>	
			II
• *	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>	
			II
• *	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 ([35, 36]) are of the general form 2.15. In this case, the NKL value given in the tables of ref. [35, 36] must be decreased by 2 ($2 \rightarrow 0$, $1 \rightarrow -1$, $0 \rightarrow -2$).
2. Durand and Barthelat (DB) ([37] - [38], [39], [40]), and Stuttgart-Dresden [41] 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 $\varphi_{\mu}^0 \varphi_{\nu}^g$ (page 220) 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 [35, 42]. 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 ([35, 42]) 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 72), or any atomic package with effective core pseudopotentials. See Chapter 8.2 for general comments on atomic basis function optimization. Bouteiller *et al*

[43] 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 65).

<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. [44, 45]. 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:

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

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
    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	96	–
UHF	Unrestricted Open Shell	102	–
DFT	DFT Hamiltonian	102	–
SPIN	spin-polarized solution	75	–
Choice of the exchange-correlation functionals			
CORRELAT	correlation functional	74	I
LYP	Lee-Yang-Parr [46] (GGA)		
P86	Perdew 86 [47] (LDA)		
PBE	Perdew-Becke-Ernzerhof [48] (GGA)		
PBESOL	GGA. PBE functional revised for solids [49]		
PWGGA	Perdew-Wang 91 (GGA)		
PWLSD	Perdew-Wang 92 [50, 51, 52] (GGA)		
PZ	Perdew-Zunger [53] (LDA)		
VBH	von Barth-Hedin [54] (LDA)		
WL	GGA - Wilson-Levy [55]		
VWN	Vosko,-Wilk-Nusair [56] (LDA)		
EXCHANGE	exchange functional	75	I
BECKE	Becke [57] (GGA)		
LDA	Dirac-Slater [58] (LDA)		
PBE	Perdew-Becke-Ernzerhof [48] (GGA)		
PBESOL	GGA. PBE functional revised for solids [49]		
PWGGA	Perdew-Wang 91 (GGA)		
SOGGA	second order GGA. [59]		
VBH	von Barth-Hedin [54] (LDA)		
WCGGA	GGA - Wu-Cohen [60]		
Global keywords: exchange+correlation			
B3PW	B3PW parameterization	76	–
B3LYP	B3LYP parameterization	76	–
PBE0	Adamo and Barone [61]	76	
SOGGAXC	see [59]	76	
Custom made dft exchange-local exchange			
HYBRID	hybrid mixing	76	I
NONLOCAL	local term parameterization	76	I

<i>Numerical accuracy control</i>			
ANGULAR	definition of angular grid		I
BATCHPNT	grid point grouping for integration		I
[BECKE]	selection of Becke weights (default)		–
[CHUNKS]	max n. points in a batch for numerical int.		I
LGRID	"large" predefined grid		I
RADSAFE	safety radius for grid point screening		I
RADIAL	definition of radial grid		I
SAVIN	selection of Savin weights		–
TOLLDENS	density contribution screening <input type="text" value="6"/>		I
TOLLGRID	grid points screening <input type="text" value="14"/>		I
XLGRID	"extra large" predefined grid		I
XXLGRID	"extra extra large" predefined grid		I
<i>Atomic parameters control</i>			
RADIUS	customized atomic radius	81	I
FCHARGE	customized formal atomic charge	81	I
<i>Auxiliary</i>			
PRINT	extended printing		
END	close DFT input block		
Numerical accuracy and computational parameters control			
BIPOLAR	Bipolar expansion of bielectronic integrals	73	I
BIPOSIZE	size of coulomb bipolar expansion buffer	73	I
EXCHSIZE	size of exchange bipolar expansion buffer	73	I
INTGPACK	Choice of integrals package <input type="text" value="0"/>	92	I
NOBIPCOU	Coulomb bielectronic integrals computed exactly	95	–
NOBIPEXCH	Exchange bielectronic integrals computed exactly	95	–
NOBIPOLA	All bielectronic integrals computed exactly	95	–
POLEORDR	Maximum order of multipolar expansion <input type="text" value="4"/>	95	I
TOLINTEG	Truncation criteria for bielectronic integrals <input type="text" value="6 6 6 6 12"/>	102	I
TOLPSEUD	Pseudopotential tolerance <input type="text" value="6"/>	102	I
Type of execution			
MPP	MPP execution	93	
Type of run			
ATOMHF	Atomic wave functions	72	I
SCFDIR	SCF direct (mono+biel int computed)	96	–
EIGS	S(k) eigenvalues - basis set linear dependence check	81	–
FIXINDEX	Reference geometry to classify integrals	86	–
Basis set - AO occupancy			
FDAOSYM	f and d degeneracies analysis	83	I
FDAOCCUP	f and d orbital occupation guess	84	I
GUESDUAL	Density matrix guess - different Basis set	89	I
Integral file distribution			
BIESPLIT	writing of bielectronic integrals in <i>n</i> files <input type="text" value="n = 1"/> ,max=10	73	I
MONSPLIT	writing of mono-electronic integrals in <i>n</i> file <input type="text" value="n = 1"/> , max=10	93	I
Numerical accuracy control and convergence tools			

ANDERSON	Fock matrix mixing	71	I
BROYDEN	Fock matrix mixing	73	I
FMIXING	Fock/KS matrix (cycle i and $i-1$) mixing <input type="text" value="0"/>	87	I
LEVSHIFT	level shifter <input type="text" value="no"/>	92	I
MAXCYCLE	maximum number of cycles <input type="text" value="50"/>	93	I
SMEAR	Finite temperature smearing of the Fermi surface <input type="text" value="no"/>	99	I
TOLDEE	convergence on total energy <input type="text" value="5"/>	101	I
TOLDEP	convergence on density matrix <input type="text" value="16"/>	102	I
Initial guess			
EIGSHIFT	alteration of orbital occupation before SCF <input type="text" value="no"/>	82	I
EIGSHROT	rotation of the reference frame <input type="text" value="no"/>	82	I
GUESSP	density matrix from a previous run	91	–
GUESSPAT	superposition of atomic densities	91	–
Spin-polarized system			
ATOMSPIN	setting of atomic spin to compute atomic densities	72	I
BETALOCK	beta electrons locking	73	I
SPINLOCK	spin difference locking	100	I
SPINEDIT	editing of the spin density matrix used as SCF guess	100	I
Auxiliary and control keywords			
END	terminate processing of block3 input		–
KSMMPT	printing of Bloch functions symmetry analysis	92	–
NEIGHBOR	number of neighbours to analyse in PPAN	51	I
PARAMPT	output of parameters controlling code dimensions	52	–
PRINTOUT	setting of printing options	53	I
NOSYMADA	No Symmetry Adapted Bloch Functions	95	–
SYMADAPT	Symmetry Adapted Bloch Functions (default)	101	–
SETINF	setting of inf array options	54	I
SETPRINT	setting of printing options	54	I
STOP	execution stops immediately	56	–
TESTPDIM	stop after symmetry analysis	101	–
TEST[RUN]	stop after integrals classification and disk storage estimate	101	–
Output of data on external units			
NOFMWF	wave function formatted output not written in file fort.98.	95	–
SAVEWF	wave function data written every two SCF cycles	96	–
Post SCF calculations			
POSTSCF	post-scf calculations when convergence criteria not satisfied	96	–
EXCHGENE	exchange energy evaluation (spin polarized only)	83	–
GRADCAL	analytical gradient of the energy	87	–
PPAN	population analysis at the end of the SCF <input type="text" value="no"/>	96	

Computational parameters, hamiltonian, SCF control optional keywords

ANDERSON

Anderson's method [62], as proposed by Hamann [63], 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 [7]. 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 179), 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 β electrons at all \mathbf{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.

BIESPLIT - Splitting of large bielectronic integral files

rec	variable	meaning	
• *	NFILE	number of files to be used <table border="1" style="display: inline-table; vertical-align: middle;"><tr><td>1</td></tr></table> (max 10)	1
1			

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	14
*	ITEXCH overlap threshold for exchange	10

The bipolar approximation is applied in the evaluation of the Coulomb and exchange integrals (page 224). ITCOUL and ITEXCH can be assigned any intermediate value between the default values (14 and 10) (see page 224) and the values switching off the bipolar expansion (20000 and 20000).

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 100000. 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 [64]
	* 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 [65] scheme, following the method proposed by Johnson [64], 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.

END

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

DFT

The Kohn-Sham [66, 67] DFT code is controlled by keywords, that must follow the general keyword **DFT**, in any order. These keywords can be classified into four groups:

- 1 Choice of the exchange-correlation functionals
- 2 *Integration grid and numerical accuracy control (optional)*
- 3 *DF energy gradient (optional)*
- 4 *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 functionals

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.

CORRELAT	Correlation Potential (default: no correlation).	
	Insert one of the following keywords	II
LYP	GGA. Lee-Yang-Parr [46]	
P86	GGA. Perdew 86 [47]	
PBE	GGA. Perdew-Burke-Ernzerhof [48]	
PBESOL	GGA. PBE functional revised for solids [49]	
PWLSL	LSD. Perdew-Wang parameterization of the Ceperley-Alder free electron gas correlation results [52]	
PWGGA	GGA. Perdew-Wang [68]	
PZ	LSD. Perdew-Zunger parameterization of the Ceperley-Alder free electron gas correlation results [53]	
VBH	LSD. von Barth-Hedin [54]	
WL	GGA - Wilson-Levy [55]	
VWN	LSD. Vosko-Wilk-Nusair parameterization of the Ceperley-Alder free electron gas correlation results [56]	

EXCHANGE	Exchange potential (default: Hartree-Fock exchange).	
	Insert one of the following keywords	II
BECKE	GGA. Becke [57]	
LDA	LSD. Dirac-Slater [58]	
PBE	GGA. Perdew-Becke-Ernzerhof [48]	
PBESOL	GGA. PBE functional revised for solids [49]	
PWGGA	GGA. Perdew-Wang [68]	
SOGGA	second order GGA. [59]	
VBH	LSD. von Barth-Hedin [54]	
WCGGA	GGA - Wu-Cohen [60]	

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)

It is also possible to incorporate part of the exact Hartree-Fock exchange into the exchange functional through the keyword **HYBRID**. Any mixing (0-100) of exact Hartree-Fock and DFT exchange can be used.

NONLOCAL allows modifying the relative weight of the local and non-local part both in the exchange and the correlation potential with respect to standard definition of GGA type potentials.

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

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

B3PW	Becke's 3 parameter functional [69] combined with the non-local correlation PWGGA [70, 50, 51, 52]
-------------	--

B3LYP	Becke's 3 parameter functional [69] combined with the non-local correlation LYP
--------------	---

PBE0	Adamo and Barone [61]
-------------	-----------------------

SOGGAXC	see [59]
----------------	----------

B3PW, **B3LYP**, **PBE0** and **SOGGAXC** are global keywords, defining hybrid exchange-correlation functionals completely. They replace the following sequences:

B3PW corresponds to the sequence: EXCHANGE BECKE CORRELAT PWGGA HYBRID 20 NONLOCAL 0.9 0.81	B3LYP corresponds to the sequence: EXCHANGE BECKE CORRELAT LYP HYBRID 20 NONLOCAL 0.9 0.81
PBE0 corresponds to the sequence: EXCHANGE PBE CORRELAT PBE HYBRID 25	SOGGAXC corresponds to the sequence: EXCHANGE SOGGA CORRELAT PBE

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 [56]) it is reported as functional V, which is used to extract the 'local' part of the LYP correlation potential. The Becke's 3 parameter functional can be written as:

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

A , B , and C are the input data of **HYBRYD** and **NONLOCAL**.

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

exchange	correlation	
—	PWGGA	Hartree-Fock exchange, non local Perdew-Wang correlation.
LDA	VWN	probably the most popular LDA formulation
VBH	VBH	was the most popular LDA scheme in the early LDA solid state applications (1975-1985).
PWGGA	PWGGA	-----
BECKE	LYP	-----

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 [71] for molecular systems and then extended to periodic systems [72]. 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 [73]. Default choice.

SAVIN Savin weights [74]

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 77) [default 13]

The *default grid* 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

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=          40728
BECKE WEIGHT FUNCTION
RADSAFE =          2.00
TOLERANCES - DENSITY:10**- 6; POTENTIAL:10**- 9; GRID WGT:10**-14

RADIAL INTEGRATION - INTERVALS (POINTS,UPPER LIMIT):          1( 55,  4.0*R)

ANGULAR INTEGRATION - INTERVALS (ACCURACY LEVEL [N. POINTS] UPPER LIMIT):
  1(  1[ 38]   0.4)  2(  2[ 50]   0.6)  3(  5[ 110]   0.8)  4(  8[ 194]   0.9)
  5( 11[ 302]   1.1)  6( 13[ 434]   2.3)  7( 11[ 302]   2.4)  8(  8[ 194]   2.6)
  9(  5[ 110]   2.8) 10(  1[ 38]9999.0)

```

Two more pre-defined grids are available which can be selected to improve accuracy by inputting the following global keywords:

LGRID Large grid

Global keyword to choose a larger 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. [75]. Due to a larger number of radial points and less aggressive pruning, this grid gives more accurate results than the default grid. It is recommended for high-accuracy energy calculations and geometry optimizations. It is also recommended for periodic systems containing second-row and third-row atoms (transition metals).

XLGRID Extra large grid

Global keyword to choose an even larger integration grid, corresponding to the sequence:

```
RADIAL
1
4.0
75
ANGULAR
5
0.1667 0.5 0.9 3.5 9999.0
4 8 12 16 12
```

The *extra-large grid* is a pruned (75,974) grid, consisting of 75 radial points and 974 angular points in the region of chemical interest. This is a very accurate grid and is recommended 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 is also recommended for heavy atoms (fourth-row and heavier).

XXLGRID Extra extra large grid

Very large grid use 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
```

DISTGRID developers only

This forces the code to distribute the DFT grid across the available processors. Only parallel jobs are affected.

REPLGRID developers only

This forces the code to replicate the DFT grid on the available processors. Only parallel jobs are affected.

(This directive at present has no effect - the default is a replicated grid. However I am thinking of changing the default for MPP jobs to distgrid, and then replgrid will have a use for certain medium sized jobs where load balancing is an issue).IJB

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 11.11 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]
-

Default value of BATCH is 100. In the calculation of the exchange-correlation contribution to the Kohn-Sham hamiltonian matrix elements and energy gradients, the grid is partitioned into batches of points as suggested by Ahlrichs [76]. However, in CRYSTAL the number of points per batch is not constant, as it depends on point density, so that BATCH does not correspond to the maximum number of points in a batch. As a consequence, in special cases, memory requirement may become huge and cause problems in dynamic allocation at running time.

When the program runs out of memory, it stops with the following error message:

```
ERROR *** sub_name *** array_name ALLOCATION
```


DF0 KSXC1 KSXC2 KSXC2Y KSXC2Z DFXH DFYH DFZZ DFXH DFYH DFXZ
RHO FRHO AXJ,AYJ,AZJ,VGRID GRAZ GRAY GRAZ

CHUNKS

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

3. DF energy gradient

The current default when computing DFT analytical gradients in CRYSTAL is to include weight derivatives. Weight derivatives are mandatory when low quality grids are adopted.

The radius attributed to each atom for the integration is computed from the nuclear charge and the net charge. It is possible to enter for selected atoms a given atomic radius or a formal charge.

- A RADIUS

• *	NUMAT	number of atoms selected	
		insert NUMAT records	II
• *	LB	<i>label</i> of the atom	
	RAD(LB)	radius (Å) attributed to the atom	

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

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 \mathbf{k} -points generated in the irreducible part of the Brillouin zone, and diagonalized. The eigenvalues are printed.

The Cholesky reduction scheme [77], adopted in the standard SCF route, requires linearly independent basis functions.

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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 21).
	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: KCoF₃ (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 21 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 34) prints information on the atoms symmetry related in the cell.

EIGSHROT

Consider now the case of CoF₂. The first six neighbors of each Co²⁺ 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 CoF₆ 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 82) _____		

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

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 11.19, page 223.
No input data are required. See tests 29, 30, 31, 38.

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 100000).
The size of the buffer is printed in the message:

EXCH. BIPO BUFFER: WORDS USED = XXXXXXX

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> II
	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 11) 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). 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:

GEOM	restart with new geometrical parameters
_____	insert geometry input, page 13 _____
<div style="border: 1px solid black; padding: 2px; display: inline-block;">or</div>	
BASE	restart with new basis set
_____	insert basis set input, page 19 _____
<div style="border: 1px solid black; padding: 2px; display: inline-block;">or</div>	
GEBA	restart with new basis set and new geometrical parameters
_____	insert geometry input, page 13 _____
_____	insert basis set input, page 19 _____

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:

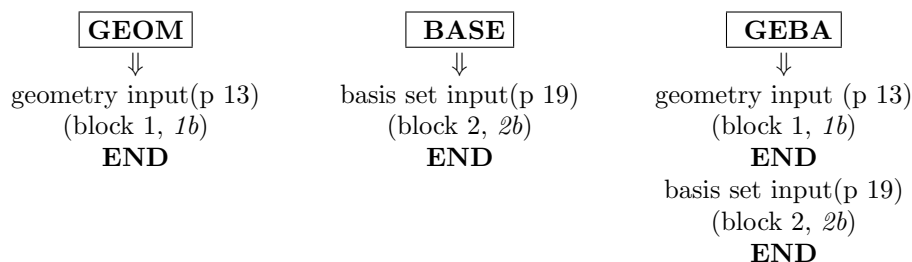
```

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 (smbfOPTGEOM, page 105) FIXINDEX is automatically set, with input geometry as reference geometry. See keyword **FINALRUN**, page 112 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

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.

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 114; **NUMGRATO**, page 114; **NUMGRCEL**, page 114;), 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 [78], 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 20).
• *	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 20) 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 [79, 80, 81], 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. [78]) 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

$$E_{disp} = -s_6 \sum_{i=1}^{N_{at}-1} \sum_{j=i+1}^{N_{at}} \sum_{\mathbf{g}} \frac{C_6^{ij}}{R_{ij,\mathbf{g}}} f_{dump}(R_{ij,\mathbf{g}})$$

The summation is over all atom pairs and **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 [79, 80].

A damping function is used to avoid near-singularities for small interatomic distances:

$$f_{dump}(R_{ij,\mathbf{g}}) = \frac{1}{1 + \exp\left(-d(R_{ij,\mathbf{g}}/R_{vdw} - 1)\right)}$$

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. [78]. 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 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 6 2.0 1.0		0 0 6 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.

GUESSF - Fock/KS matrix from a previous run

Obsolete - See **GUESSP**, page 91.

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 100.

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
crystal	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
crystal	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 86).

Warning When wave function information are stored formatted in file fort.98, the data must be converted to binary by the keyword **RDFMWF**, page 166 of the *properties* program).

Warning SCF guess from a density matrix computed with a different basis set is allowed by the keyword **GUESDUAL**, page 89.

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 19). 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 19).

INTGPACK - Choice of bielectronic integrals package

rec	variable	value	meaning
• *	IPACK	[0]	s , sp shells \rightarrow POPLE; p , d shells \rightarrow 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 [8], if s and sp shells are involved, and by routines derived from ATMOL [10] 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.

KSMMMPRT

Symmetry Adapted Bloch Functions [82, 83] (page 101) 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 54) before **KSMMMPRT**.

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 KSMMMPRT.

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.

The eigenvalue level shifting technique is well known in molecular studies [84, 85], 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 87). 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.

See tests 29, 30, 31, 32, 38.

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".

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.

MPP - Massive Parallel Execution - Programmers only

No input data required.

This option is available only with *MPPcrystal*, the massively parallel version of CRYSTAL09, where Massive Parallel Libraries are linked, and matrices in the reciprocal space are distributed over the processors.

MPPcrystal is designed to compute the total energy and wavefunction of large unit cell systems with large memory requirements. In particular, The MPP option is eligible when n_k/n_{procs} , i.e. the ratio between n_k , the number of k points sampled in the reciprocal space and n_{procs} , the number of processors used, is small.

In choosing n_{procs} , the user should consider that MPP 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.

Advantages of MPP:

- matrix diagonalization is well balanced because many processors are involved in the diagonalization of one matrix (use of standard linear algebra libraries for massively parallel calculation)
- 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.

Warnings.

- The following options are not available with MPP:

	keyword	block
CPHF	CPHF	1
Frequency calculation - IR intensities	FREQCALC/INTENS	1
Bloch Functions Symmetry Adapted	SYMADAPT	3
Printing of eigenvalues of overlap matrix in k space	EIGS	3

- use of option NOBIPOLA (page 95) is recommended for very large systems, because data distribution has not been implemented for the bipolar approximation of two-electron integrals (such approximation becomes less efficient with large unit-cell systems so that switching to NOBIPOLA does generally not affect performance significantly)
- MPP calculations run with NOSYMADA (page 95) active (no use of symmetry in the reciprocal space)
- keyword DCDIAG may activate Divide&Conquer diagonalization strategy (not default) which improves performance; however, it must be used with caution as one failure was reported in one case where eigenvectors and eigenvalues were not determined correctly (with no other clear symptom)
- SCF convergence may proceed along slightly different paths with and without MPP, particularly in sensitive cases, and 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 be either effective or ineffective when using MPP or not. However, a proper choice of the parameters will always result into achievement of the SCF cycle convergence.

If keyword MPP is not part of the input deck, *MPPcrystal* will run as *Pcrystal* (replicated data storage in memory, matrix diagonalization by k-point with one full matrix diagonalization per processor, no link to external libraries).

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 224). 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 224) 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 51

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.

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.

PARAMPRT - - printing of parametrized dimensions

See input block 1, page 52.

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 11.3, page 222.

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 51, 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 262.

PRINTOUT - Setting of printing environment

See input block 1, page 53.

RHF [default]

A restricted closed-shell hamiltonian calculation is performed ([86, 23], Chapter 8 of ref. [13]). Default choice.

ROHF

Obsolete. See **UHF**

SCFDIR

No input data required.

In the SCF step monoelectronic and bielectronic integrals are evaluated at each cycle. No screening of the integrals is performed.

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 54

SETPRINT - Setting of printing options

See input block 1, page 54.

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 11.7, page 226)	
	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:

$$H_k = \sum_g H_g e^{i\mathbf{g}\mathbf{k}}$$

$$H_k A_k = S k A_k E_k$$

A second shrinking factor, ISP, defines the sampling of k points, "Gilat net" [21, 22], 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:

$$b1/is1, b2/is2, b3/is3 \quad is1=is2=is3=IS, \text{ unless otherwise stated}$$

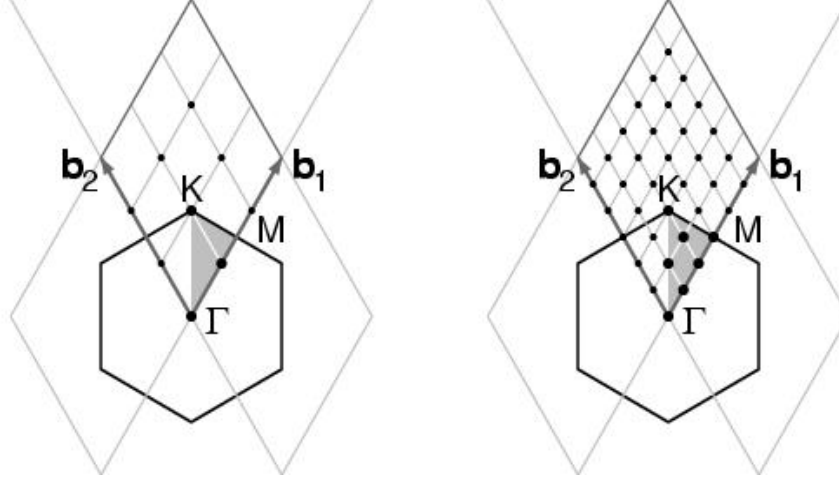
where b1, b2, b3 are the reciprocal lattice vectors, and is1, is2, is3 are integers "shrinking factors".

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 11.7, page 226. 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 [23], 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.

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 $ISP = IS * NINT(MAX(ISP, IS) / IS)$, 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 k points in the Pack-Monkhorst net, and 2920 in the Gilat net.

IS	points in IBZ fcc	points in IBZ hcp	points BZ
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 95.

Some tools for accelerating convergence are given through the keywords **LEVSHIFT** (page 92 and tests 29, 30, 31, 32, 38), **FMIXING** (page 87), **SMEAR** (page 99), **BROYDEN** (page 73) and **ANDERSON** (page 71).

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 101;

TOLDEP (tolerance on SQM in density matrix elements) page 102;

MAXCYCLE (maximum number of cycles) page 93.

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 11.9, page 221) to the Fermi function;

$$f_j = (1 + e^{\frac{(\epsilon_j - \epsilon_F)}{k_b T}})^{-1} \quad (2.20)$$

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 [87]. In this case the “free energy” of the system may be computed as:

$$\begin{aligned} F &= E(T) - k_b T S(T) \\ &= E - k_b T \sum_i^{N_{states}} f_i \ln f_i + (1 - f_i) \ln(1 - f_i) \end{aligned} \quad (2.21)$$

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:

$$\begin{aligned} E(T) &= E(0) + \alpha T^2 \\ S(T) &= 2\alpha T \end{aligned} \quad (2.22)$$

and so the quantity

$$E0 = \frac{F(T) + E(T)}{2} = E(0) + O(T^3) \quad (2.23)$$

may be used as an estimate of $E(0)$.

Figure 2.4 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 J/M² significantly above that obtained by extrapolating $E(T)$ to the $T=0$ limit (0.573 J/M²). The

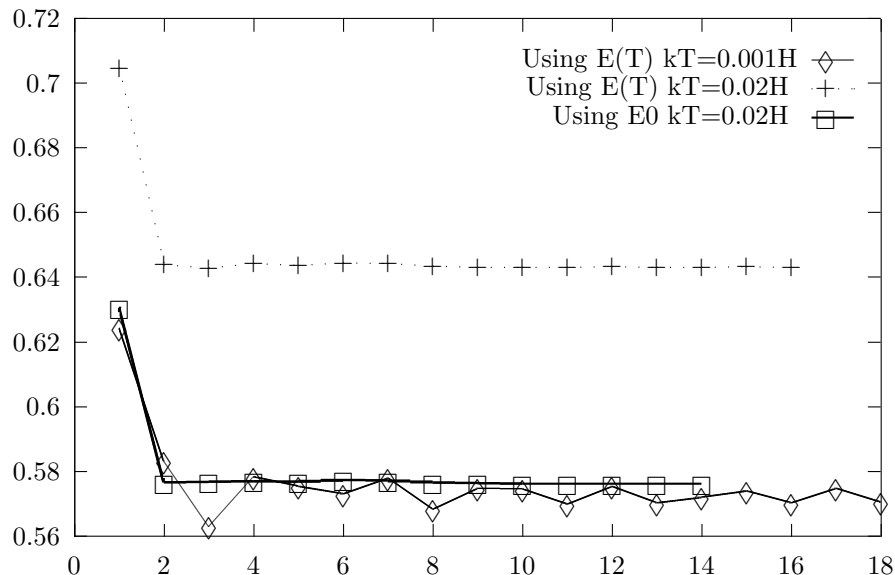


Figure 2.4: The surface energy (J/M²) of Li(100) for various numbers of layers in a slab model showing the effects of WIDTH (0.02H and 0.001H) and the use of E(T) or E0

use of E0 at WIDTH=0.02H results in an excellent estimate of the surface energy - 0.576 J/M².

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 113). 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	<i>atom labels</i>

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 102) or **DFT/SPIN** (input block 3, page 75) and **GUESSP**.

Example: the anti ferromagnetic solution for the spinel MnCr₂O₄ 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 **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 inequivalent. 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	$\uparrow \uparrow \uparrow \uparrow$

See tests 29, 30, 32, 33, 37, 38.

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 [82, 83].

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 51).

TEST[RUN] - Integrals classification and selection

Full input (geometry, basis set, general information, SCF) is processed.

The symmetry analysis is performed, and the monoelectronic and bielectronic integrals classified and selected, according to the the truncation criteria adopted. The size of the Fock/KS and density matrices (direct lattice) and the disk space required to store the bielectronic are printed. The value printed as "disk space for monoelectronic 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

TOLDEP - SCF convergence threshold on density matrix

	rec	variable	meaning
• *		ITOL	10^{-ITOL} threshold for convergence on ΔP

For developers only.

TOLINTEG - Truncation criteria for bielectronic integrals (Coulomb and HF exchange series)

	rec	variable	meaning
• *		ITOL1	overlap threshold for Coulomb integrals- page 222 6
		ITOL2	penetration threshold for Coulomb integrals-page 223 6
		ITOL3	overlap threshold for HF exchange integrals-page 223 6
		ITOL4	pseudo-overlap (HF exchange series-page 223) 6
		ITOL5	pseudo-overlap (HF exchange series-page 223) 12

The five ITOL parameters control the accuracy of the calculation of the bielectronic 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 11.

TOLPSEUD - Truncation criteria for integrals involving ECPs

	rec	variable	meaning
• *		ITPSE	overlap threshold for ECP integrals 6

The program evaluates only those integrals for which the overlap between the charge distribution $\varphi_\mu^0 \varphi_\nu^g$ (page 220) 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) ([23, 88], Chapter 6 of ref. [13]).

In the Restricted Open Shell [86] 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 [89]. 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. 2.5.

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

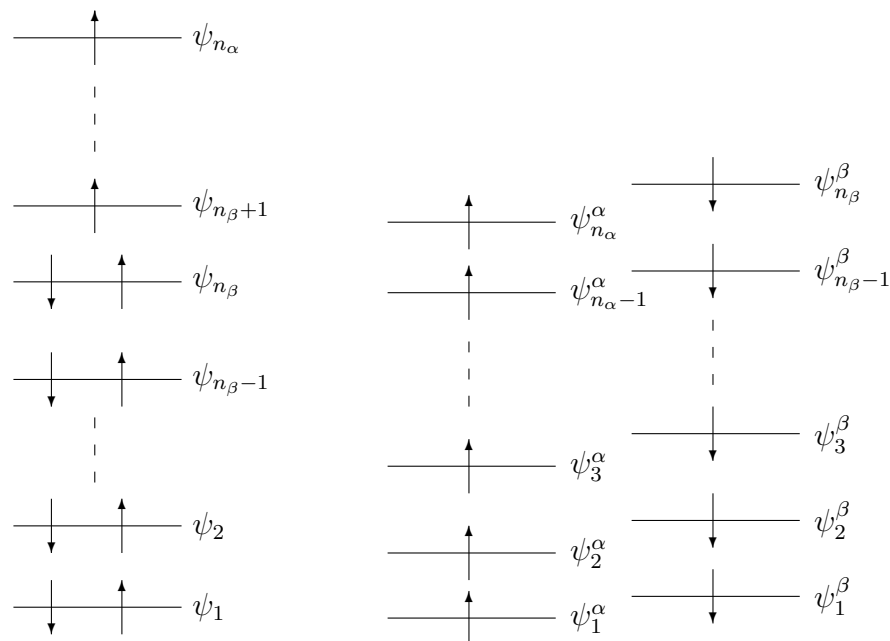


Figure 2.5: Molecular Orbitals diagram for the Restricted Open Shell method (ROHF, left) and for the Unrestricted Open Shell method (UHF, right)

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.

Developers only

FULLTIME - Detailed timing report

A more detailed report of the timing data is generated:

```
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT 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.

DCDIAG - "divide and conquer" diagonalization

This directive is ONLY for MPP jobs. It instructs the code to use the divide and conquer algorithm for the diagonalization stage. This algorithm can be up to four times quicker than the standard, but it has been found very, very, occasionally to generate incorrect results.

CMPLXFAC - Detailed timing report

This directive is ONLY for MPP jobs. For load balancing reasons the MPP code must know how many times more expensive a calculation on a complex k point is relative to a real one. This allows the user to specify a value for this. The default value is 2.333333.

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.

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 symmetrized fractional coordinates [default] or redundant internal coordinates (optional choice, page 115).

OPTGEOM sub keywords can be classified as follow:

1. *General sub keywords:*

- A - Optimization type (page 109)
- B - Initial Hessian (page 109)
- C - Hessian updating technique (page 107)
- D - Convergence criteria (page 106)
- E - Step control (page 110)
- F - Coordinate system related options (page 111)
- G - Optimization procedure control (page 112)
- H - Numerical (first) derivatives (page 113)
- I - Printing options (page 114)

2. *Geometry optimization in redundant coordinates* (page 115).

3. *Geometry optimization with constraints* (page 117).

- A - Constant volume optimization (page 117)
- B - Fixing lattice deformations (page 118)
- C - Linear constraints between atomic coordinates (page 119)
- D - Partial optimization of atomic positions (page 119)
- E - Fixing internal coordinates (page 120)

4. *Geometry optimization with application of an external stress* (page 121)

5. *Searching a transition state* (page 123)

Default values are supplied for all computational parameters.

By default an unconstrained geometry optimization of the atomic positions at fixed cell is performed.

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[90, 91, 92, 93, 94].

By default the step considered is the Newton step (direction and length) controlled by the Trust Radius scheme (see **ALLOWTRUSTR** page 111). **NOTRUSTR** to remove trust radius control (CRYSTAL06 default choice).

HF and DFT (pure and hybrid functionals) analytical gradients 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 99) is used. In that case, *numerical* first derivatives should be computed (see page 113).

For very small value of smearing (around 0.001 hartree) analytical gradients can be used.

For atomic positions, 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 53) 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, unless **FULLOPTG** or **CELLONLY** is requested (see page 109).

To optimize the lattice parameters a set of symmetry preserving cell deformations (see Symmetry Allowed Elastic Distortions, **USESSED**, page 61) 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 normalized combined set of symmetrized directions and deformations is adopted.

Optional choice (keyword **INTREDUN**, page 115) 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 the nuclear coordinates at fixed lattice parameters in symmetrized fractional coordinates.

Optional choices: see page 109.

- 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. 123), 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 53) is used. For ionic systems it may be necessary to modify the default values (see **RAYCOV**, page 53).

- Hessian updating technique

BFGS Broyden-Fletcher-Goldfarb-Shanno scheme [90, 91, 92, 93, 94].

Optional choices:

1. Schlegel's updating scheme [95], (**OLD CG**, page 110), optimization scheme as in CRYSTAL03
2. Powell's updating scheme (**POWELL**, page 110)

- 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 91 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 261). 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 263).

The file can be read to define the basic geometry input. See **EXTERNAL**, page 15

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 263). 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 113).

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 109)
- B - Initial Hessian (page 109)
- C - Hessian updating technique (page 110)
- D - Convergence criteria (page 106)
- E - Step control (page 110)
- F - Coordinate system related options (page 111)
- G - Optimization procedure control (page 112)
- H - Numerical first derivatives (page 113)
- I - Printing options (page 114)

A - Type of optimization

Optional choices:

FULLOPTG	full optimization, atom coordinates and cell parameters. The cell volume may change (see CVOLOPT to optimize at constant volume)
<hr/>	
CELLONLY	only cell parameters are optimized. Default: the cell volume may change (see CVOLOPT, page 117, to optimize at constant volume)
<hr/>	
ITATOCEL	full optimization, iterative procedure optimization: atoms-cell-atoms-cell-
<hr/>	
INTREDUN	full optimization of atomic positions and cell parameters in redundant internal coordinates (page 115).

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)
<hr/>	
HESSIDEN	initial guess: identity matrix
<hr/>	
HESSOPT	external guess (read from file HESSOPT.DAT)
<hr/>	
HESSMOD1	initial guess: Lindh's model Hessian [96]

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 [97, 98] [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 53) is used. For ionic systems it may be necessary to modify the default values (see **RAYCOV**, page 53).

HESSNUM initial guess: numerical estimate

C - Hessian updating technique

Different Hessian updating schemes are available for minimization:

BFGS	Hessian update - Broyden-Fletcher-Goldfarb-Shanno scheme [90, 91, 92, 93, 94] - [default]
-------------	---

OLDCG	Hessian updating - old Schlegel updating scheme[95] (CRYSTAL03)
--------------	---

POWELL	Hessian update - symmetric Powell scheme [99]
---------------	---

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, while the length is determined by linear minimization along an extrapolated quadratic polynomial.

MAXTRADIUS optional

- * TRMAX maximum value allowed for the trust radius - default [16]

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: ∞ ; 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, according to the quadraticity of the surface in the actual region.

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 118) - 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 122
• * ICODE	Action type code:
0	the program stops (default)
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

FIXDELTE	
• * IE	10^{-ie} hartree: threshold on the total energy change for redefining the geometry to which integral classification is referred - see FIXINDEX , page 86 - [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]
<hr/>	
FITDEGR	
• * N	degree of polynomial fitting function for linear search:
	2 parabolic fit [default]
	3 cubic polynomial function
	4 constrained quartic fitting
<hr/>	
HESEVLIM	limits for the allowed region of hessian eigenvalues (hartree)
• * VMIN	lower limit [default 0.001]
VMAX	upper limit [default 1000.]
<hr/>	
ITACCONV	
• * DE	energy difference threshold for ITATOCEL [default 0.1 * TOLDEE between 2 optimization cycles]
<hr/>	
MAXITACE	
• * MAXI	max number of iteration cycles in atom/cell iterative optimization [default 100]
<hr/>	
MAXCYCLE	
• * MAX	maximum number of optimization steps [default 100]
<hr/>	
NOGUESS	SCF guess at each geometry point: superposition of atomic densities at each SCF calculation (default choice in geometry optimization: GUESSP)
<hr/>	
NRSTEPS	
• * DE	number of stored steps to be used in the OLDCG Hessian updating scheme [default: number of degrees of freedom]
<hr/>	
RESTART	restart geometry optimization from a previous run. See page 123
<hr/>	
SORT	sorting of the previous optimization steps information when the OLDCG scheme is active [default:nosort]
<hr/>	

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 metals) 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 defined, which contains 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 53) is used. For ionic systems it may be necessary to reduce the default values (see **RAYCOV**, page 53). In case of systems constituted by unconnected fragments (*ie* some molecular crystals or adsorption complexes), fragments are 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 (under development).

By default, optimization of internal redundant coordinates involves both atomic positions and cell parameters. To avoid optimizing cell parameters the keyword **FIXCELL** page 116 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. The double angles are defined by the angles obtained by projection of the vectors onto two suitable perpendicular planes, in order to avoid 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 [165⁰]

The default value is set to 165⁰. This means that all angles larger than 165⁰ 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 150⁰.

A list of angle 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).

Adding internal coordinates - bonds and angles

When some relevant internal coordinates are missing (e.g. intermolecular bonds) they can be added 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 |

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)
<hr/>	
TESTREDU	request test run for checking automatic definition of internal coordinates
.	
<hr/>	
TOLREDU	tolerance used to eliminate redundancies (developers only)
• * I	tolerance 10^{-I} (default: 7, 10^{-7})
.	
<hr/>	

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 3
- B - Fixing lattice deformations 3
- C - Linear constraints between atomic coordinates 3
- D - Partial optimization of atomic positions 3
- E - Fixing internal coordinates 3

All constraining strategies 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 115).

The examples at 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) or **FULLOPTG** (atom coordinates and cell parameters 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**, that sets crystallographic-like cell deformations (i.e. $a, b, c, \alpha, \beta, \gamma$) 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		a					
hexagonal		$a,$	c				
rhombohedral	hexagonal cell	$a,$	c				
	rhombohedral cell	$a,$	α				
tetragonal		$a,$	c				
orthorhombic		$a,$	$b,$	c			
monoclinic		$a,$	$b,$	$c,$	β		
		$a,$	$b,$	$c,$	γ		
		$a,$	$b,$	$c,$	α		
triclinic		$a,$	$b,$	$c,$	$\alpha,$	$\beta,$	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. 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 9.4, page 205.

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	label of the atom A (it must be in the reference cell)	
LB	label 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	label of the atom A (it must be in the reference cell)	
LB	label of the atom B	
I1, I2, I3	indices of the cell where the atom B is located	
LC	label 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**.

Constraint 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 cartesian coordinate systems)

and the fixed values may be affected by some small changes (in general of the order of 10^{-4} au).

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 SiO_4 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 117).

After using **FREEZINT** (page 120) 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**) or a general external stress. The choice of the external stress is controlled by keywords.

EXTPRESS to apply external, hydrostatic pressure
• * pres pressure in hartree/bohr³

EXTSTRESS to apply a general external stress - stress matrix follows

- * D11 D12 D13 first row of the stress matrix.
- * D21 D22 D23 second row of the stress matrix.
- * D31 D32 D33 third row of the stress matrix.

The stress matrix, input by row - must be a symmetric 3x3 matrix, all elements in hartree/bohr³)

EXTSTRESS may require to reduce the symmetry, e.g. when you apply uniaxial pressure to a cubic system, then you have to break the symmetry. The keyword **BREAKELAS** (geometry input, input block 1, page 35) breaks the symmetry according to a general distortion, but does not perform the distortion.'

EXTPRESS

0.001 hydrostatic pressure of hartree/bohr³ s applied

EXTSTRESS the distortion matrix allows for instance a

0.001 0. 0. cubic lattice to become tetragonal'

0. 0. 0.

0. 0. 0.

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 11.11), 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=3 in FINALRUN input). This is strongly recommended.

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 **MAXRADIUS** [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 of the last step is written in file optc.number_of_step, and can be read by EXTERNAL (see page 15).

If optimization ended successfully, the optimized geometry is written in file fort.34 (EXTERNAL format).

Information on optimization is read from file OPTINFO.DAT, and saved 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 FREQCALC input block.

The reference to be quoted is:

C. M. Zicovich-Wilson, M. L. San-Romn, A. Ramrez-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, 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 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. (Improvements still in progress)

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 coordinate.

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 valence coordinate, 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.

CHNGTTSFOL 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 the lowest eigenvalue. Once this occurs, 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.

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**).

Not compatible with **INTREDUN**.

This directive must be used associated with **FRAGMENT**. The atom to be scanned together with an other atom that belongs to other moiety of the system must be kept fixed using **FRAGMENT** (the remainder atoms can be relaxed).

SCANREDU- To be used with **INTREDUN** only

- * IREDSCA (integer): type of valence coordinate to be scanned (1, bond length, 2 angle, 3 dihedral)
 - ENDSCA (real): last value taken by the chosen coordinate along the scan
 - for MAXSCA initial value is the current one with the geometry defined
 - the number of points considered in the scan
 - struc-
 - ture.
-

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 120), **FREEZDIH** (page 121), **ANGSFROZEN** (page 120), **LNGSFROZEN** (page 120)).

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 *IREDS*CA.

SCANREDU may be requested at maximum twice so as to carry out a bidimensional scan.

Chapter 4

Vibration calculations at Γ point

FREQCALC - Frequency harmonic calculation

Harmonic frequency calculation at Γ is invoked by the keyword **FREQCALC** in input block 1 (geometry). FREQCALC must be the last keyword in geometry input. FREQCALC input block admits several options (subkeywords), and terminates with keyword **END** (or **END[FREQ]**, **END[—]**: the first three characters only 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 frequency calculation at Γ [default] it allows:

1. Calculation of IR intensities (keyword (**INTENS**, page 132).
2. Scanning of geometry along selected normal modes (**SCANMODE**, page 135).
3. Calculation of the IR reflectance spectrum (**REFLECTANCE**, page 139).
4. Anharmonic calculation of frequencies of X-H (X-D) bond stretching (**ANHARM**, page 141).
5. Harmonic calculation of phonon dispersion (**DISPERSION**, page 143).

The second derivatives of the energy are computed numerically by using the analytical first derivatives. 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 calculation 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 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 controlled by two keywords:

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 open that must finish with keyword **END** . The numerical conditions for the optimization are controlled by means of the same keywords as documented in page 105 (keyword **OPTGEOM**).

The conditions adopted by default in geometry optimization before frequency calculation are different than those considered for normal optimizations, 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	0.00015 (si devono cambiare ancora sul codice)
TOLDEX	0.00060 (si devono cambiare ancora sul codice)
FINALRUN	4
MAXRADIUS	0.5
TRUSRADIUS	0.5

Default choices

SCF guess for wave function calculation for all subsequent geometries defined to compute numerical second derivatives is the density matrix obtained at equilibrium geometry.

The default value for SCF convergence criterion on total energy is set to 10^{-9} (**TOLDEE** in block3 input to modify it - expert users only).

The default choice for DFT grid, when DFT hamiltonian is used, corresponds to **XLGRID** (page 79).

Longitudinal optical (LO) frequencies and IR intensities are not evaluated by default. If the **INTENS** (page 132) keyword is used, intensities are evaluated.

The frequency input block must be closed by the keyword **END** (or **ENDFREQ**). All the keywords are optional.

Output files

Files written during frequency calculation, to be saved 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 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, they are read from file fort.20, as 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. Necessary to restart a frequency calculation with IR intensities.

Optional keywords

• A **ANALYSIS** Analysis of the vibrational modes

• A **DIELISO** Calculation of the LO/TO shifts by using the dielectric tensor. The isotropic dielectric tensor (dielectric constant) should be calculated previously with options (SUPERCELL/FIELD) and (DIEL) applied for each axis of the system.

• * **DIEL** dielectric constant

• A **DIELTENS** Calculation of the LO/TO shifts by using the dielectric tensor.

• * **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 with CRYSTAL using SUPERCELL/FIELD (page 41).
It must be computed in order to obtain LO modes. See keyword **INTENS** (page 132).

• 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 in a fragment there are atoms symmetry related, 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 NOANALYSIS	No analysis of the vibrational modes [default]
-----------------------	--

• 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 NOUSESYMM	Symmetry is removed, the space group is set to P_1
----------------------	--

• A NUMBERIV	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: $h(x)=(g(x+t)-g(x))/t$ $t=0.001 \text{ \AA}$ 2 Central-difference formula: $h(x)=(g(x+t)-g(x-t))/2t$ $t=0.001 \text{ \AA}$

• 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 (GPa) [1,0.101325,0.101325]

• A PRINT	Extended printing active (hessian and hessian eigenvectors)
------------------	---

• A RESTART	Restart frequency calculation from a previous run. See page 132.
--------------------	--

• A STEPSIZE	Modify the step size of displacement along each cartesian axis
• * STEP	step (Å) 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 must be present in the first frequency calculation, it can not be inserted in restart only.

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** 129).

1 - IR intensities

Calculation of IR intensities is invoked by the keyword **INTENS** in **FREQCALC** input block.

Two different techniques can be adopted:

- IR intensities through Berry phase - keyword **INTPOL** [default choice in CRYSTAL09]
- IR intensities through Wannier functions - keyword **INTLOC** [default choice in CRYSTAL06]

In order to obtain the LO modes, the high frequency dielectric tensor must be provided. See keyword **DIETENS**, page 129.

The dielectric tensor elements can be obtained from the literature or computed with CRYSTAL using **SUPERCEL/FIELD** (page 41).

- IR intensities through Berry phase [default CRYSTAL09]

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.

Born charges are the key quantities for the calculation of the IR intensities, the longitudinal optical (LO) frequencies and the static dielectric tensor. The Berry phase approach consists in evaluating the Born charges, 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 [default CRYSTAL06]

Calculation of IR intensities through Wannier functions (default of CRYSTAL06) is invoked by the keyword **INTLOC** following **INTENS** in **FREQCALC** input block.

Many keywords are related to the Wannier functions calculation, and should be used by developers and very experienced users only.

If keyword **LOCALINT** is activated in **FREQCALC** input block, IR intensities, Born charges and LO-TO split 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 (WnF) 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 WnFs, but to an approximation contained into a cyclic space. In the mapping (unfolding) that permits to convert cyclic to real WnFs, 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 cases tested, 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 WnFs, 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 localisation process (see *properties* input, keyword **LOCALWF**, page 168) 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 168
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 170
 - A **CAPTURE** see **LOCALWF**, page 171
 - A **WANDM** see **LOCALWF**, page 174
 - A **FULLBOYS** see **LOCALWF**, page 174
 - A **MAXCYCLE** see **LOCALWF**, page 170
 - A **CYCTOL** see **LOCALWF**, page 169
 - A **ORTHNDIR** see **LOCALWF**, page 174
 - A **CLUSPLUS** see **LOCALWF**, page 173
 - A **PHASETOL** see **LOCALWF**, page 169
 - A **RESTART** see **LOCALWF**, page 169
 - A **IGSSBND** see **LOCALWF**, page 171
 - A **IGSSVCTS** see **LOCALWF**, page 170
 - A **IGSSCTRL** see **LOCALWF**, page 170
-

2 - Scanning of geometry along selected normal modes

R. Dovesi, J. Torres, L. Valenzano

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_i Δ " (see below), in a format suitable to be read by the keyword **EXTERNAL** (geometry input, page 15).

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 211).

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		EIGV	FREQUENCIES		IRREP	IR	RAMAN
		(HARTREE**2)	(CM**-1)	(THZ)			
1-	3	-0.1863E-11	-0.2995	-0.0090	(F2)	A	A
4-	6	0.7530E-07	60.2270	1.8056	(F1)	I	I
7-	9	0.4821E-04	1523.8308	45.6833	(F2)	A	A
10-	11	0.6302E-04	1742.3056	52.2330	(E)	I	A
12-	12	0.2099E-03	3179.3763	95.3153	(A)	I	A
13-	15	0.2223E-03	3272.4193	98.1047	(F2)	A	A

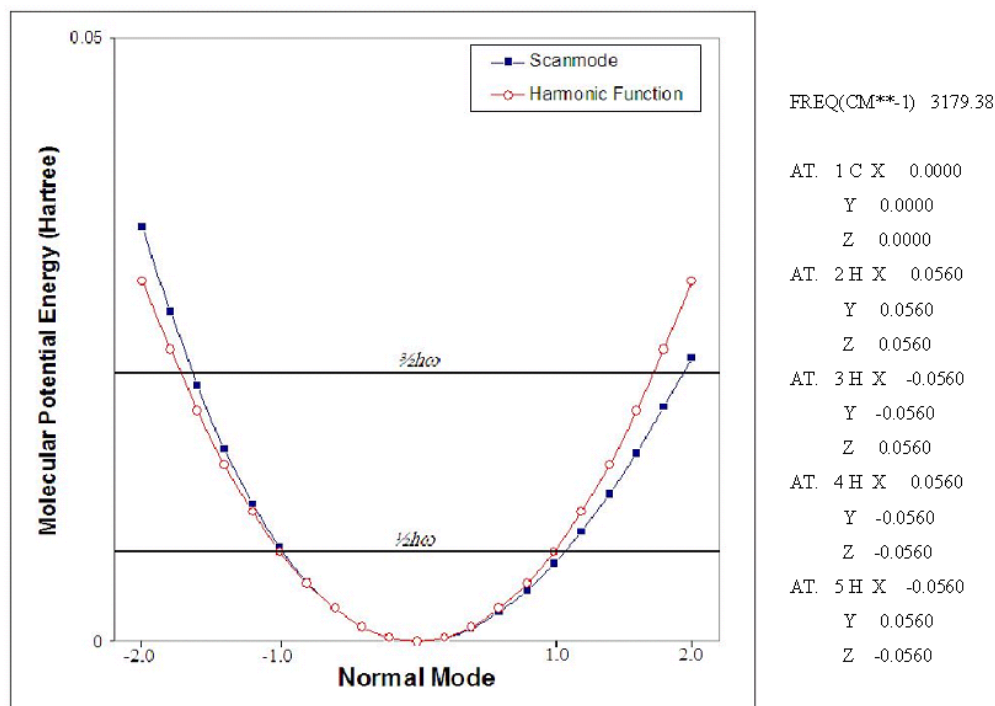
Third run: Scanning of a selected mode.

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 10, $\nu=3179.3763 \text{ cm}^{-1}$, corresponding to C-H symmetric stretching



Example 2 - PbCO₃

The spacegroup of this carbonate, as it can be found in the literature [ICSD database], is *Pmcn* (orthorhombic lattice).

First run: full optimization of the geometry in *Pmcn* space group (full input at page 211).

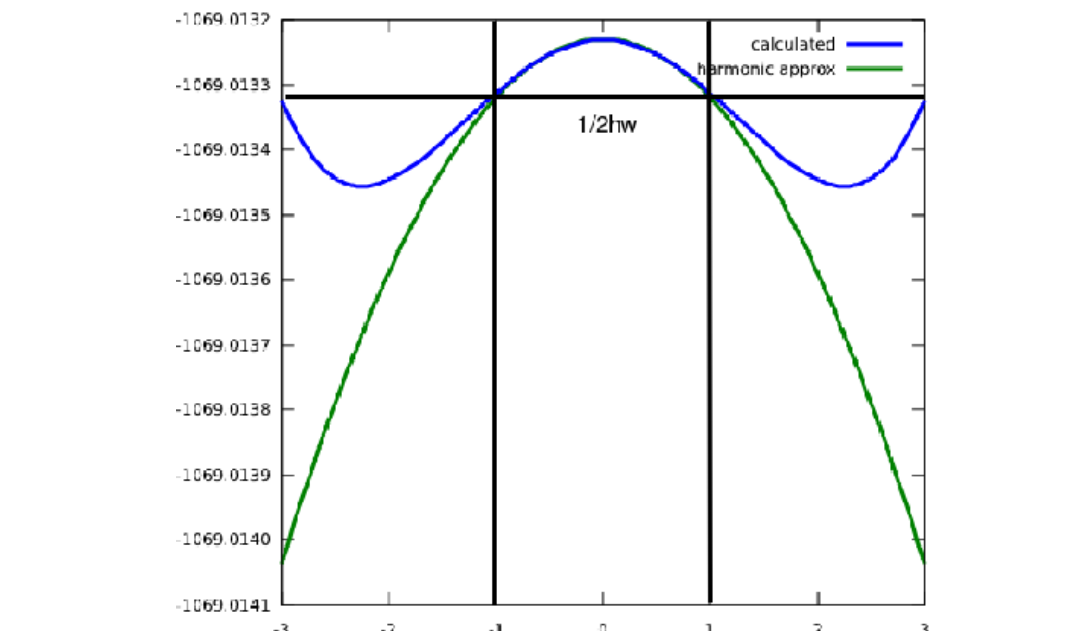
Second run: frequency calculation. The output would look as follows:

MODES		EIGV	FREQUENCIES		IRREP	IR	RAMAN
		(HARTREE**2)	(CM**-1)	(THZ)			
1-	1	-0.3212E-07	-39.3362	-1.1793	(AU)	I	I
2-	2	-0.1388E-09	-2.5858	-0.0775	(B3U)	A	I
3-	3	-0.6924E-10	-1.8262	-0.0547	(B2U)	A	I
4-	4	-0.2405E-11	-0.3404	-0.0102	(B1U)	A	I
5-	5	0.4141E-07	44.6637	1.3390	(AG)	I	A
6-	6	0.4569E-07	46.9137	1.4064	(B3G)	I	A
7-	7	0.5304E-07	50.5476	1.5154	(B1G)	I	A
.							
53-	53	0.4245E-04	1429.9950	42.8702	(AU)	I	I
54-	54	0.4338E-04	1445.5993	43.3380	(B1G)	I	A
55-	55	0.4340E-04	1445.8649	43.3459	(AG)	I	A
56-	56	0.4401E-04	1455.9714	43.6489	(B1U)	A	I
57-	57	0.4408E-04	1457.1539	43.6844	(B3G)	I	A
58-	58	0.4417E-04	1458.5583	43.7265	(B3U)	A	I
59-	59	0.4475E-04	1468.2070	44.0157	(B2U)	A	I
60-	60	0.5007E-04	1553.0286	46.5586	(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 [100]); 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 $Pmcn$ 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 ($Pmcn$). The geometry, with correct reduced symmetry, is read (EXTERNAL, page 15) from one of the files written during the scan, for instance SCAN1.-39.3361_DISP.-2.400 (scan of mode 1, frequency -39.3361 cm^{-1} , displacement -2.4 the classical amplitude).

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	FREQUENCIES		IRREP	IR	INTENS	RAMAN
		(HARTREE**2)	(CM**-1)	(THZ)			(KM/MOL)	
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.

3 - Calculation of the IR reflectance spectrum

Keyword **REFLECTANCE**, inserted in the **FREQCALC** input block, activates the calculation of the IR reflectance spectrum. Prior calculation of IR intensities is required (keyword **INTENS**, page 132) and definition of the dielectric tensor matrix (keyword **DIELTENS**, page 129) or of the isotropic dielectric constant (keyword **DIELISO**, page 129).

For each desired direction 3 quantities are calculated (for a given frequency range):

1. Reflectance (R)
2. Imaginary part of the inverse dielectric function ($Im(1/\epsilon)$). The maxima provide the Longitudinal Optical frequencies (LO)
3. Imaginary part of the dielectric function ($Im(\epsilon)$)

The keyword **REFLECTANCE** defines an input block (closed by **END**).

rec	variable	meaning
•	REFLDIR	keyword to define directions
• *	NDIR	Number of directions along which the spectrum is computed [1]
• *	IDIR(I),I=1,NDIR	Directions are labeled from 1 to 6 as in Voigt notation (see Chapter 11.11, page 229)
	END	

REFLECTANCE is at the moment limited to:

- 3D systems
- directions 1,2 and 3 only ($\epsilon_{11}, \epsilon_{22}, \epsilon_{33}$, according to Voigt notation, page 229))
- dielectric tensor in diagonal form (all crystal systems, apart from monoclinic and triclinic, can be oriented in order to have diagonal dielectric tensor)

Generalization is in progress.

REFLECTANCE data are written in file REFLECTANCE.DAT and can be directly plotted with *gnuplot* (<http://www.gnuplot.info>, appendix D, page 265).

Once the dielectric tensor and the vibrational spectrum are calculated, the reflectance spectrum 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]
REFLECTANCE
REFLDIR
...
...
[other optional keywords]
END           [end REFLECTANCE]
END           [end FREQCALC]
```

To be modified by developers only.

There are several keywords which allow to modify the **default** values.

rec	variable	meaning
• A	REFLNSTEP	.
• *	N	Number of points used for the reflectance spectrum [1000].
• A	REFLSTEPS	
• *	X	Step size used for the reflectance spectrum [no default]. To be used as an alternative to REFLNSTEP
• A	REFLRANGE	
• *	X1,X2	Frequency range used for the reflectance spectrum Default: [0., 1.3 ν_{max}], where ν_{max} is the frequency of the highest calculated mode .
• A	REFLDAMP	
• *	GAMMA	Damping factor (related to peak width) used for the reflectance spectrum [8.0]
• A	REFLANGLE	
• *	ALPH	Angle of incidence used for the reflectance spectrum (degrees) [10.0]
		.

,

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

Anharmonic calculation of frequencies of X-H (X-D) bond stretching is invoked by the keyword **ANHARM** in FREQCALC input block.

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 [101]. 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
<hr/>		
KEEPSYMM	all atoms symmetry equivalent to the selected one are displaced	
<hr/>		
NOGUESS	scf guess at each geometry point: superposition of atomic densities at each scf calculation	
<hr/>		
POINTS26	26 points: d_{X-H} range: $d_0 - 0.2 \div d_0 + 0.3$ with a step of 0.02 Å.	
<hr/>		
PRINT	extended printing	
<hr/>		
PRINTALL	printing for programmers	
<hr/>		
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

5 - Harmonic calculation of phonon dispersion

Keyword **DISPERSION**, inserted in the **FREQCALC** input block, activates the calculation of phonon dispersion on the reciprocal points, compatible with the supercell given in input. The supercell must be generated using the keyword **SCELPHONO** (page 58). in order to perform a dispersion calculation.

The program finds the symmetry irreducible set of points in the first Brillouin zone corresponding to the supercell. The frequencies and symmetry adapted modes are computed for these points, allowing a better description of thermodynamic and other related properties.

NOKSYMDISP

Active if **DISPERSION** is active. Do not factorize the Dinamic Matrices in reciprocal space according to the irreducible representations of the Space Groups. The symmetry properties of the phonons are not recognized.

Chapter 5

Coupled Perturbed HF/KS calculation

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

This keyword performs Coupled Perturbed HF/KS calculation up to the second order. It must be the last keyword in geometry input block.

Users of this module are 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)

rec variable	meaning
• A END[CPHF]	end of CPHF input block
• A FMIXING	permits to mix the Fock/KS matrix derivatives between CPHF-SCF1 cycles n and $n - 1$
* IPMIX	percentage of cycle $n - 1$ [IPMIX=0, no mixing]
• A TOLALPHA	threshold on energy first derivative change between CPHF-SCF1 cycles
* ITOL	$ \Delta E < 10^{-ITOL}$ [default: 4]
* ITOL	$ \Delta E < 10^{-ITOL}$ [default: 4]
• A MAXCYCLE	permits to modify the max number of CPHF-SCF1 cycles [default: 100]
* NMAX	maximum number of SCF cycles
• A TOLUDIK	maximum allowed difference between degenerate eigenvalues
• * ITOL	$ \Delta E < 10^{-ITOL}$ [default: 6]

CPHF-SCF1 is the self consistent field that calculates the $U^{[1]}$ matrix, the polarizability tensor (α) and, through the $2n + 1$ formula, the first hyperpolarizability tensor (β).

CPHF-SCF2 is the self consistent field that calculates the $U^{[2]}$ matrix, the first hyperpolarizability tensor (β).

The keyword TOLUDIK may be useful for calculations extended above the first order (CPHF-SCF1). In this case, in fact, the *non - canonical* approach leads to the problem of calculating

the difference between eigenvalues to obtain the $\partial U_{ij}^{[cb]}/\partial k_a$ matrix derivative. The latter is defined as a function of $Q_{ij}^{k_a}$, the derivative of the density matrix with respect to the k_a point

$$Q_{ij}^{k_a}(\vec{k}) = \frac{K_{ij}^{k_a}(\vec{k}) - E_j R_{ij}^{k_a}(\vec{k})}{E_j - E_i} \quad (5.1)$$

where $K_{ij}^{k_a}(\vec{k})$ and $R_{ij}^{k_a}(\vec{k})$ are, respectively, the Fock matrix and the overlap matrix derivatives with respect to k_a . $Q_{ij}^{k_a}$ can be conveniently redefined in terms of the equivalent hermitian matrix

$$\tilde{Q}_{ij}^{k_a} = Q_{ij}^{k_a} + \frac{1}{2} R_{ij}^{k_a}$$

that, as can be shown, leads to

$$\tilde{Q}_{ii}^{k_a} = 0$$

and to

$$Q_{ij}^{k_a}(\vec{k}) = \frac{K_{ij}^{k_a}(\vec{k}) - \frac{1}{2} R_{ij}^{k_a}(\vec{k})(E_j + E_i)}{E_j - E_i} \quad i \neq j$$

Thus, it becomes necessary to define a threshold value (10^{-ITOL}) as the maximum difference allowed between degenerate eigenvalues, in order to separate these two cases.

RESTART

A CPHF/CPKS run can be started from the results of an analogous previous run (even an incomplete run). Every CPHF/CPKS run dumps the necessary information for a restart to file fort.31. This file must be copied to file fort.32 before running a calculation with the RESTART directive. GUESSP (SCF guess from density matrix of a previous run, input block 3, page 91) is not applied by default, but its use is recommended.

For computational detail on the implementation of CPHF method see [102]. For applications see [103, 104, 105].

Chapter 6

Mapping of CRYSTAL calculations to model Hamiltonians

CONF CNT - Configuration counting and cluster expansion

The CONF CNT environment can be used to study possible configurations within a given cell if one or more than one sites are activated, i. e. atoms lying in this site can be substituted or its spin flipped. If DUMMYFIT keyword is inserted a subsequent mapping to two body Hamiltonian is performed. This method is usually indicated as cluster expansion method and can be applied to solid solutions (elemental substitution within the given cell) or magnetic configurations (Ising model to map different anti ferromagnetic and ferrimagnetic ordering). In this manual section the allowed keywords are described, for a longer explanation of the use of this part of the code, please refer to the tutorial page:

<http://www.crystal.unito.it> → tutorials → Combinatorial mapping of solid solutions and

magnetic configurations..

For the use and implementation of this scheme in the CRYSTAL code see:

A. Meyer, R. Orlando, R. Dovesi

Andradite - grossular solid solution: an hybrid functional all electron calculation and cluster expansion scheme approach.

For a discussion concerning the cluster expansion method see:

M. H. F. Sluiter, Y. Kawazoe

Cluster expansion method for adsorption: Application to hydrogen chemisorption on graphene.,
Phys. Rev. B 68 (2003) 085410

Default choices

CONF CNT

- * N number of active sites
- ST number of analyzed stars of neighbors of N sites
- * NA(L),L=1,N *label* of the active atoms

CONF CNT as such is an information keyword. A symmetry and neighbors analysis of N irreducible atoms is performed. ST stars of neighbors of the N activated atoms are printed. Note that only atoms symmetry equivalent to the activated ones are reported as neighbors.

Atom pair neighbors characterized by the same distance but symmetry in-equivalent are split in subsets. Each one of the N atoms is specified with the label NA (CRYSTAL output). Atoms symmetry related to all NA atoms are printed. Let us indicate the sum of all atoms equivalent to the activated sites as IALL. The number of in-equivalent configurations that can be obtained by substituting from one to IALL/2 (or IALL/2 plus one if IALL is odd) is printed increasing the number of substitutions that take place. Symmetry analysis is performed and in-equivalent configurations only are printed. The number of in-equivalent configurations for a fixed number of substitutions as well as the total number of configurations including all possible number of substitutions is reported. After the CONFCNT analysis the program stops except if DUMMYFIT keyword is inserted.

Example

```
CONFCNT
1 2
13
END
```

One site (N=1) is analyzed, two (ST=2) stars of neighbors of the activated site are printed. The atom label (CRYSTAL output) of the activated atom is 13.

Optional keywords

END indicates that CONFCNT environment input is concluded and no more optional keywords will be inserted.

JDIST stars of neighbors of atom pairs characterized by the same distance are not split even though they are not symmetry equivalent

PRTCONF all configurations are printed, equivalent configuration subsets are distinguished

SETCOMP

- * IX the whole configurational analysis is performed for a subset of possible configurations, the ones referring to IX substitutions (or spin flipping). IX must be higher than zero and lower equal to IALL/2
-

DUMMYFIT

- * SOLSOL dummy keyword to be inserted for activate the cluster expansion scheme the cluster expansion scheme is applied to solid solutions with reference to end-members.
- * MAGNET the cluster expansion scheme is applied in order to construct Ising Hamiltonian to map magnetic configurations.

II _____ if MAGNET _____ II

- * SP The formal spin SP is assigned to each spin site. Both symmetry equivalent and symmetry in-equivalent atoms will have the same formal spin.
-

RDIST

- * RD Only if DUMMYFIT is inserted
A tolerance in the definition of pair distances is inserted. Stars of neighbors that differ by less than RD Angstrom are treated as equivalent.
-

DATAFORFIT	Only if DUMMYFIT is inserted
• * ND	number of CRYSTAL energies introduced that will be used for the fitting in order to extract the J coupling parameters.
II	<i>insert ND records</i> II
• * X	number of substitutions (spin flipped)
C	configuration label (class), in agreement with the classification of the CONFCNT environment
ENE	energy in a.u. as written by the CRYSTAL code of configuration X,C

Chapter 7

Calculation of elastic constants

ELASTCON - 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). **EOS** must be the last keyword in geometry input.

```
. . . geometry input . . . .  
ELASTCON  
END[ELAS]   close ELASTCON input block  
END         close geometry input block
```

ELASTCON input block admits several options (optional sub keywords), and terminates with keyword **END** (or **END[ELAS]**, **END[—]**: the first three characters only are processed).

The procedure for calculating the second-order elastic constants takes maximum advantage of the capabilities of the CRYSTAL09 according to the following steps:

1. Determine the minimum number of deformations required to calculate the entire set of elastic constants.
2. Make a deformation followed by full optimization of the geometry.
3. When optimization has been achieved for a given deformation, the 3x3 force matrix is calculated using the analytic first derivative.
4. Steps 2 and 3 are repeated in order to obtain numerical second derivatives of the total energy, which give the second-order elastic constants.

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 module are requested to cite the following papers:

W.F. Perger, J. Criswell, B. Civalleri and R. Dovesi
Ab-initio calculation of elastic constants of crystalline systems with the CRYSTAL code
Comp. Phys. Comm. 180, 1753-1759 (2009)

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 101.

Default choices can be modified by optional keywords (in any order):

rec variable	meaning
• <i>A</i> 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]
• <i>A</i> 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]

For example, if *NUMDERIV* = 5 and *STEPSIZE* = 0.002, then the displacements will be -0.004, -0.002, 0.002, and 0.004.

rec variable	meaning
• <i>A</i> PRINT	This option turns on a higher level of diagnostic printing and will generally not be necessary for the typical user. [<i>default</i> minimal printing]
• <i>A</i> RESTART	Allows for a RESTART using file <i>ELASINFO.DAT</i> from a previous run.
• <i>A</i> 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:

• <i>A</i> TOLDEG	EOS default [0.00006] - see OPTGEOM , page 110
• <i>A</i> TOLDEX	EOS default [0.00012] - see OPTGEOM , page 110
• <i>A</i> TOLDEE	EOS default [8] - see OPTGEOM , page 110
• <i>A</i> MAXCYCLE	see OPTGEOM , page 113
• <i>A</i> NOTRISTR	see OPTGEOM , page 111
• <i>A</i> TRUSTRADIUS	see OPTGEOM , page 111
• <i>A</i> MAXTRADIUS	see OPTGEOM , page 111

Example (the following lines are inserting into the ‘geometry’ section):

```
...
ELASTCON
NUMBERIV    modify default choice of n. points [3]
5
STEPSIZE    modify step size for numerical gradient [0.001]
0.002
PRINT       extended printing - Warning: may be very large!!!!
END[ELAST]  ELASTCON input
END         geometry input
```

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.

As a second diagnostic, the optimized total energy for each deformation is tested to see if it is within *TOLDEE* * 100 of the equilibrium value. If it is, a warning is printed for the user to try decreasing *TOLDEE* or increasing *STEPSIZE*.

Chapter 8

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 166).

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 255, for information on printing.

8.1 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 | <i>stored on Fortran unit 13 (2nd record)</i> |
| c.3 | valence electron | <i>stored on Fortran unit 13 (3rd record)</i> |
| d. | reducible overlap matrix | stored on Fortran unit 3 |
| e. | Fock/KS eigenvectors | <i>stored on Fortran unit 10</i> |
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 fortan 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 180) reads the MP2 correction to the valence density matrix. Properties can then be computed from a MP2 corrected density matrix.

8.2 Properties keywords

RDFMWF wave function data conversion formatted-binary (fort.98 → fort.9)

Preliminary calculations			
NEWK	Eigenvectors calculation	178	I
NOSYMADA	No symmetry Adapted Bloch Functions	95	–
PATO	Density matrix as superposition of atomic (ionic) densities	179	I
PBAN	Band(s) projected density matrix (preliminary NEWK)	179	I
PGEOMW	Density matrix from geometrical weights (preliminary NEWK)	180	I
PDIDE	Energy range projected density matrix (preliminary NEWK)	180	I
PSCF	Restore SCF density matrix	186	–
Properties computed from the density matrix			
ADFT	Atomic density functional correlation energy	154	I
BAND	Band structure	156	I
BIDIERD	Reciprocal form factors	157	I
CLAS	Electrostatic potential maps (point multipoles approximation)	158	I
ECHG	Charge density and charge density gradient - 2D grid	163	I
ECH3	Charge density - 3D grid	162	I
EDFT	Density functional correlation energy (HF wave function only)	163	I
EMDLPG	Electron momentum distribution from density matrix	165	I
PMP2	MP2 correction to the Valence Density Matrix	180	
POLI	Atom and shell multipoles evaluation	181	I
POTM	Electrostatic potential - 2D grid	184	I
POT3	Electrostatic potential - 3D grid	182	I
POTC	Electrostatic properties	183	I
PPAN	Mulliken population analysis	96	
XFAC	X-ray structure factors	187	I
Properties computed from the density matrix (spin-polarized systems)			
ANISOTRO	Hyperfine electron-nuclear spin tensor	155	I
ISOTROPIC	Hyperfine electron-nuclear spin interaction - Fermi contact	167	I
POLSPIN	Atomic spin density multipoles	181	I
Properties computed from eigenvectors (after keyword NEWK)			

ANBD	Printing of principal AO component of selected CO	154	I
BWIDTH	Printing of bandwidth	158	I
DOSS	Density of states	161	I
EMDL	Electron momentum distribution - line	164	I
EMDP	Electron momentum distribution - plane maps	165	I
PROF	Compton profiles and related quantities	185	I
New properties			
POLARI	Berry phase calculations	189	I
SPOLBP	Spontaneous polarization (Berry phase approach)	191	–
SPOLWF	Spontaneous polarization (localized CO approach)	192	–
PIEZOBP	Piezoelectricity (Berry phase approach) preliminary	188	–
PIEZOWF	Piezoelectricity (localized CO approach) - preliminary	188	–
LOCALWF	Localization of Wannier functions	168	I
DIEL	Optical dielectric constant	159	I
Auxiliary and control keywords			
ANGSTROM	Set input unit of measure to Ångstrom	31	–
BASISSET	Printing of basis set, Fock/KS, overlap and density matrices	156	–
BOHR	Set input unit of measure to bohr	34	–
CHARGED	Non-neutral cell allowed (PATO)	62	–
END	Terminate processing of properties input keywords		–
FRACTION	Set input unit of measure to fractional	44	–
MAPNET	Generation of coordinates of grid points on a plane	176	I
NEIGHBOR	Number of neighbours to analyse in PPAN	51	I
PRINTOUT	Setting of printing options	53	I
RAYCOV	Modification of atomic covalent radii	53	I
SETINF	Setting of inf array options	54	I
SETPRINT	Setting of printing options	54	I
STOP	Execution stops immediately	56	–
SYMMOPS	Printing of point symmetry operators	60	–
Info - Output of data on external units			
ATOMIRR	Coordinates of the irreducible atoms in the cell	155	–
ATOMSYMM	Printing of point symmetry at the atomic positions	34	–
COORDPRT	Coordinates of all the atoms in the cell	37	–
CRYAPI_OUT	geometry, BS, direct lattice information	159	–
EXTPRT	Explicit structural/symmetry information	41	–
FMWF	Wave function formatted output in file fort.98. Section 8.2	166	–
INFOGUI	Generation of file with wf information for visualization	167	–
CRYAPI_OUT	Reciprocal lattice information + eigenvalues	159	–

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.
_____ if $NK > 0$ insert _____ II			
• *	IK(J),J=1,NK		Sequence number of the k points chosen (printed at the top of NEWK output)
_____ if $NB > 0$ insert _____ 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-Shamm 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] [73]
		_____ or _____
SAVIN		Savin weights [74]
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 53)
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 31.

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	<i>label</i> 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 [106]

$$\mathbf{T}[\text{mT}] = \frac{1000}{(0.529177 \cdot 10^{-10})^3} \frac{1}{4\pi} \mu_0 \beta_N g_N \mathbf{T} = 3.4066697 g_N \mathbf{T}$$

(see **ISOTROPIC** for the units and conversion factors). The elements of the \mathbf{T} tensor at nucleus A are defined as follows:

$$T_{ij}^A = \sum_{\mu\nu} \sum_g P_{\mu\nu g}^{\text{spin}} \int \varphi_{\mu}(\mathbf{r}) \left(\frac{r_A^2 \delta_{ij} - 3r_{Ai} r_{Aj}}{r_A^5} \right) \varphi_{\nu}^g(\mathbf{r}) d\mathbf{r}$$

where $r_A = |\mathbf{r} - \mathbf{A}|$ and $r_{Ai} = (\mathbf{r} - \mathbf{A})_i$ (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 34

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 259
	LPR66	≠ 0	printing of eigenvalues
_____ add NLINE records _____			
• *			coordinates of the line extremes in units of $ b_i /ISS$
	I1,I2,I3		first point coordinates.
	J1,J2,J3		last point coordinates.

The band structure along a given path in 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 Crga2006) and in file BAND.DAT (processed by DLV; see <http://www.cse.clrc.ac.uk/cmng/DLV>). See Appendix D, page 259).

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 [23] and in Chapter 2 of reference [13], 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.
3. 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.
4. 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.
5. 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.

See tests 3, 4, 6, 7, 8, 9, 11, 12 and 30.

BASISSET - Printing of basis set and data from SCF

rec	variable	value	meaning
• *	NPR		number of printing options.
_____ if NPR ≠ 0 insert prtrec (see page 54) _____			

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).

BIDIERD - 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. The starting auto-correlation function must be of good quality in order to get good CPs. Both RFFs and CPs can be convoluted 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 pedices identify quantities in coordinates and momentum space, respectively. The anisotropies of the RFFs and the CPs can be evaluated via the **DIFF** keyword. This block must be ended by **ENDB**. It works also for open-shell systems.

By using the **PROF** keyword, followed by the **BR** keyword, it is possible to obtain the same quantity by Fourier transforming the Compton profiles. As the latter implies numerical integration, the **BIDIERD** keyword is expected to provide more accurate results.

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 $B(r)$
• *	STPC		step along each direction (a.u.)
• A4	DIFF		$B(r)$ and CPs anisotropies are computed
• A3	DIR		The directions are specified
			<i>if IMODO=0, insert NDIR records</i>
• *	X Y Z		the explored direction is defined by the straight line going from the origin to (X,Y,Z)
			<i>if IMODO≠0, insert NDIR records</i>
• *	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 34.

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 62.

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
<i>if IFOR \neq 0 insert _____ II</i>			
• *	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)
<i>insert MAPNET input records (page 176) _____</i>			

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 176). The potential values are written formatted in file fort.25. (see Appendix D, page 258).
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 37.

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$\neq 0$, 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 $\text{NPU} \times \text{NPU}$ 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 168) are appended to file GRED.DAT

k points coordinates (Monkhorst sampling net) and eigenvectors (if computed by **NEWK** page 178) 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 266.

DIEL/DIELECT - Optical dielectric constant

rec	variable	meaning
•	A END/ENDDIEL	end of DIEL input block
		<i>optional keywords</i>
•	A PRINT	extended output

The electron density must be obtained by applying an electric field (keyword **FIELD**, page 41). The dielectric constant is calculated by using the concept of macroscopic average of the total charge density (see for example Fu *et al.* [26]) and Poisson's equation. The charge density is first averaged with respect to the (infinite) plane orthogonal to the field

$$\bar{\rho}(z) = \frac{1}{A} \int_A \rho(z) dA \quad (8.1)$$

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:

$$\bar{\rho}(z) = \frac{1}{V} \sum_{\ell=-\infty}^{+\infty} F_{00\ell} e^{-i \frac{2\pi\ell z}{C}} \quad (8.2)$$

$F_{00\ell}$ 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

$$\bar{\bar{\rho}}(z) = \frac{1}{\Delta z} \int_{z-\Delta z/2}^{z+\Delta z/2} \bar{\rho}(z') dz' \quad (8.3)$$

that is

$$\bar{\bar{\rho}}(z) = \frac{1}{V} \sum_{\ell=-\infty}^{+\infty} F_{00\ell} \text{sinc} \left(\ell\pi \frac{\Delta z}{C} \right) e^{-i \frac{2\pi\ell z}{C}} \quad (8.4)$$

where the *sinc* function is the *cardinal sinus* ($\text{sinc}(u) = \frac{\sin(u)}{u}$) and Δz has been chosen equal to c ; we can now apply Poisson's equation to $\bar{\bar{\rho}}(z)$:

$$\frac{\partial^2 \bar{\bar{V}}(z)}{\partial z^2} = -4\pi \bar{\bar{\rho}}(z) \quad (8.5)$$

or

$$\frac{\partial \bar{\bar{E}}(z)}{\partial z} = 4\pi \bar{\bar{\rho}}(z) \quad (8.6)$$

because

$$\frac{\partial \bar{\bar{V}}(z)}{\partial z} = -\bar{\bar{E}}(z) \quad (8.7)$$

$\bar{\bar{V}}(z)$, $\bar{\bar{E}}(z)$ and $\bar{\bar{\rho}}(z)$ 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:

$$F_{00\ell} = F_{00\ell}^{\Re} + i F_{00\ell}^{\Im} \quad (8.8)$$

Exploiting the following properties of the structure factors:

$$\begin{aligned} F_{000} &= N_e \quad (\text{number of electrons in the supercell}) \\ F_{00\ell}^{\Re} &= F_{00-\ell}^{\Re} \\ F_{00\ell}^{\Im} &= -F_{00-\ell}^{\Im} \end{aligned} \quad (8.9)$$

the real and imaginary parts of $\bar{\bar{\rho}}$ take the following form:

$$\Re [\bar{\bar{\rho}}(z)] = \frac{N_e}{V} + \frac{2}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \cos \left(\frac{2\pi\ell z}{C} \right) + F_{00\ell}^{\Im} \sin \left(\frac{2\pi\ell z}{C} \right) \right] \text{sinc} \left(\ell\pi \frac{\Delta z}{C} \right) \quad (8.10)$$

$$\Im [\bar{\bar{\rho}}(z)] = 0 \quad (8.11)$$

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 8.7, the local macroscopic field corresponds to minus the slope of $\bar{\bar{V}}(z)$, it has opposite sign with respect to the imposed outer field, according to the Lenz law, and is obtained from $\bar{\bar{\rho}}(z)$ (eq. 8.6):

$$\bar{\bar{E}}(z) = \frac{8\pi}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \frac{\sin \left(\frac{2\pi\ell z}{C} \right)}{\left(\frac{2\pi\ell}{C} \right)} - F_{00\ell}^{\Im} \frac{\cos \left(\frac{2\pi\ell z}{C} \right)}{\left(\frac{2\pi\ell}{C} \right)} \right] \text{sinc} \left(\ell\pi \frac{\Delta z}{C} \right) \quad (8.12)$$

The corresponding macroscopic electric potential can be written as follows:

$$\bar{\bar{V}}(z) = \frac{-8\pi}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \frac{\cos\left(\frac{2\pi\ell z}{C}\right)}{\left(\frac{2\pi\ell}{C}\right)^2} + F_{00\ell}^{\Im} \frac{\sin\left(\frac{2\pi\ell z}{C}\right)}{\left(\frac{2\pi\ell}{C}\right)^2} \right] \text{sinc}\left(\ell\pi \frac{\Delta z}{C}\right) \quad (8.13)$$

Since $-\bar{\bar{E}}$ and E_0 have opposite sign, the ratio $E_0/(E_0 + \bar{\bar{E}})$ is larger than one, and characterizes the relative dielectric constant of the material along the direction of the applied field:

$$\epsilon = \frac{E_0}{E_0 + \bar{\bar{E}}} \quad (8.14)$$

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 259.

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 on Fortran unit 25 for plotting (Appendix D, page 259).	
		2	formatted output on file DOSS.DAT (Fortran unit 24) for plotting (Appendix D, page 260).	
	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 54)</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:

$$\rho_\mu(\epsilon) = 2/V_B \sum_j \sum_\nu \sum_{\underline{g}} \int_{BZ} d\underline{k} S_{\mu\nu}(\underline{k}) a_{\mu j}(\underline{k}) a_{\nu j}^*(\underline{k}) e^{i\underline{k} \cdot \underline{g}} \delta[\epsilon - \epsilon_j(\underline{k})] \quad (8.15)$$

$$\rho_A(\epsilon) = \sum_{\mu \in A} \rho_\mu(\epsilon) \quad (8.16)$$

$$\rho_{tot}(\epsilon) = \sum_A \rho_A(\epsilon) \quad (8.17)$$

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!

2. 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 11.7, page 226). 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.
3. DOSS are calculated according to the Fourier-Legendre technique described in Chapter II.6 of reference 1, and in C. Pisani et al, ([107, 108]). Three computational parameters must be defined: NPOL, IS, ISP. IS and ISP are entered in the **NEWK** option input.
4. 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.
5. **Warning NEWK** with IFE=1 must be run when spin-polarized solutions (**SPIN-LOCK**, page 100) or level shifter (**LEVSHIFT**, page 92) were requested in SCF, to obtain the correct Fermi energy and eigenvalues spectra.
6. 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

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 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 in fortran unit 31 (function value at the grid points) in the format required by the visualization program DLV.

See Appendix D, page 264, 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 8.2, page 176)			

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 176). The electron density values (electron bohr⁻³) are written formatted in file fort.25 (see Appendix D, page 258).
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 ($A \equiv B$ or $B \equiv C$), function data are written in file RHOLINE.DAT. (see Appendix D, page 258)
4. When IDER $\neq 0$, 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 258).
5. The electron charge density is computed from the density matrix stored in fortran unit 13. 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] [73]
	or
SAVIN	Savin weights [74]
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 53)
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 260).
		2	formatted output to file LINEA.DAT for plotting (Appendix D, page 260).
	LPR113	$\neq 0$	printing of EMD before interpolation
• *	(K(I,J),		directions in oblique coordinates
	I=1,3),J=1,N		
• *	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 (**NEWK keyword with IFE = 1**).

The Electron Momentum Density is calculated along given directions (equation 11.22, page 227). 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. $\rho(0)$ 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.

EMDLPG - Electron Momentum Density from Density Matrix - line path

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 260).
		2	formatted output to file LINEA.DAT for plotting (Appendix D, page 260).
	LPR113	$\neq 0$	printing of EMD before interpolation
• *	(K(I,J), I=1,3),J=1,N		directions in oblique coordinates
• *	ICASO	1:	the total density matrix is used
		2:	the core density matrix is used
		3:	the valence density matrix is used

The Electron Momentum Density is calculated along given directions (equation 11.23, page 227) directly from the Density Matrix. The Electron Momentum Density, EMD, is a non-periodic function; it falls rapidly to zero outside the first Brillouin zone. $\rho(0)$ gives the number of electrons at rest. For Open-Shell systems the $\alpha + \beta$ and the $\alpha - \beta$ EMD are computed. The oblique coordinates directions given in input refer to the conventional cell, *not* to the primitive cell, for 3D systems.

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 (**NEWK keyword with IFE = 1**)

Calculation of electron momentum density on definite planes (equation 11.22, page 227). 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	<i>properties</i>	FMWF	wave function formatted to file fort.98
ftp file fort.98 from platform 1 to platform 2			
2	<i>properties</i>	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 44.

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, in fortran unit 31. See Appendix D, page 264, 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 264, 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

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 [106]

$$a_N[\text{mT}] = \frac{1000}{(0.529177 \cdot 10^{-10})^3} \frac{2}{3} \mu_0 \beta_N g_N \langle \rho^{\text{spin}}(\mathbf{r}_N) \rangle = 28.539649 g_N \langle \rho^{\text{spin}}(\mathbf{r}_N) \rangle$$

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 [106]. 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.

KNETOUT - Reciprocal lattice information - Fock/KS eigenvalues

Obsolete. See **CRYAPIOUT**, page 159.

LOCALWF - Localization of Wannier Functions (WnF)

Wannier functions are computed from Bloch functions, and then localized, following the method described in [109] and [110]. 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 fortran unit 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: $10^{-\text{ITDP0}}$ 2
	ITDP	> 0	Final tolerance used to calculate the DM matrix elements: $10^{-\text{ITDP}}$ 5
	ICONV	> 0	Convergence criterion to finish a large cycle: $\text{ABS}(\text{ADI}(\text{N}) - \text{ADI}(\text{N}-1)) < 10^{-\text{ICONV}}$, where ADI is the atomic delocalization index and N is the short cycle number 5

PHASETOL

rec	variable	value	meaning
• *	ITPH0	> 0	$10^{-\text{ITPH0}}$ is the initial tolerance on the atomic charge population to attribute the phase to atoms in the wannierization step 2
	ITPH	> 0	$10^{-\text{ITPH}}$ is the final tolerance used to attribute this phase 3
	ICHTOL	> 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 unit 81 (same format as unit 80) 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 the unit 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 86), 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 [111]) 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]

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) [112].

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 53). An inter-atomic distance lower than the capture indicates that I and J can be covalently bonded. Default value [2.0].
	MPMAXIT		Maximum number of iterations in the pre-localization process [200]
	ICNVMP		$10^{-\text{ICNVMP}}$ is the convergence threshold for the Magnasco-Perico pre-localization [8]
	IOVPOP		Just those pairs of atoms whose overlap population are greater than $10^{-\text{IOVPOP}}$ are considered covalently bonded [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 × 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 $\text{CAPTURE} * (\text{RAYCOV}(\text{I}) + \text{RAYCOV}(\text{J}))$ (RAYCOV, covalent radius (default value table page 53). 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 [113], 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 < \text{tolb}$ 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 $\langle \omega_j R \omega_i \rangle > \text{TOLSYM}$ - 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 \mathbf{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

PRINTPLO

rec	variable	value	meaning
• *	IPRT	0 > 0	Does not print Wannier coefficients [default] Prints Wannier coefficients at each cycle up to the IPRT-th star of direct lattice vectors [0]
	IPRP	0 ≠0	Prints population analysis only at the end of the localization. Prints analysis at each W-B cycle [0]
	ITPOP		Only atomic population larger than 10^{-ITPOP} are printed [2]
	IPLOT	0 ≠ 0	WnFs are not computed for plot WnFs are computed in a grid of points, IPLOT being the number of stars of direct lattice vectors taken into account for WnF coefficients. Data are written in file fort.25 [0]

If IPLOT ≠ 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 8.2, page 176)</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**, 176. 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.

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 RO 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 $ABS(ALOCLEN(ISTAR)-ALOCLEN(ISTAR-1)) \leq 10^{**}(-ABS(INEIGH))$, where $ALOCLEN(ISTAR)$ 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**(-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**(-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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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 8.1)
		_____ <i>optional keyword</i> _____ II
•	MARGINS	definition of a new A'',B'',C'',D'' window including ABCD (or A'B'C'D') (see Fig 8.2)
• *	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 258).
- 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 31)
 - 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).

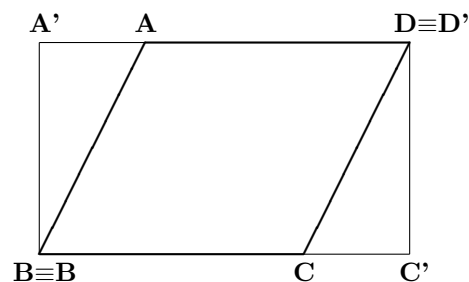


Figure 8.1: Definition of the window where the function F is mapped Effect of optional keyword RECTANGU.

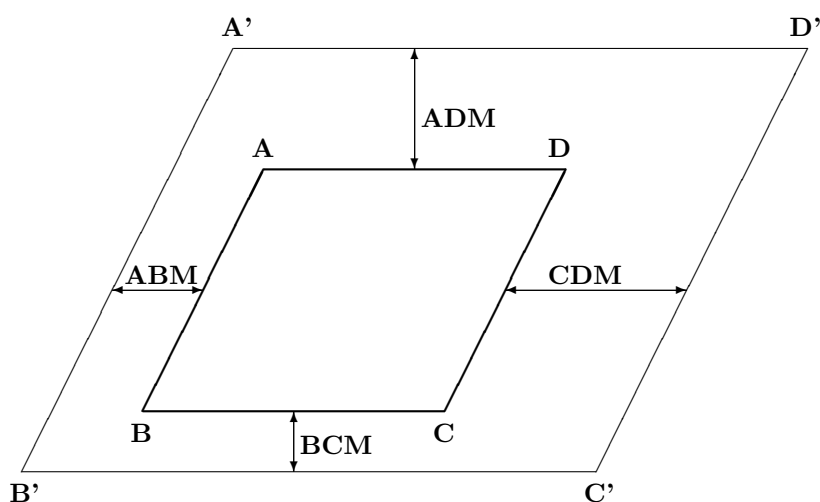


Figure 8.2: Definition of frame around the original window where the function F is mapped. Effect of optional keyword MARGINS.

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 51

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 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 23).	
	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 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 ≠ 0 insert prtrec (see page 54)</i>	II

The Fock/KS eigenvectors are computed at a number of **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 **k** points in reciprocal lattice, weights etc) are written in file KIBZ.DAT by inserting the keyword **CRYAPI.OUTPUT** (page 159).

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 11.7, page 226) 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 11, equation 11.5).
3. A Fermi energy calculation must be performed (IFE=1) to run **PROF** the Compton profiles option, **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 92; **SPINLOCK**, page 100; **BETALOCK**, 73.
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 95

PARAMPRT - - printing of parametrized dimensions

See input block 1, page 52.

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 19)</i>
			II

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 density matrix is written in fortran unit 13.
2. The atomic wave function is computed by the atomic program [7], 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 72, and **CHARGED**, input block 2, page 62.

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 ($N_s=n_\alpha - n_\beta$ 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 ($N_s=n_\alpha - n_\beta$ 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 fortran unit 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 [114] within the Tersoff-Haman approximation [115].

PMP2 - Reads the MP2 correction to the Valence Density Matrix

rec	variable	value	meaning
• *	IMP2	0	The HF+MP2 Density Matrix is used
		1	The MP2 Density Matrix is used

1. The MP2 correction to the Valence Density Matrix, as computed by the CRYSCOR program, is read from the external and unformatted fortran unit 63 (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 (IMP2=0) or the pure MP2 one (IMP2=1), where the former choice is the recommended one and can be used in order to compute any DM-related quantity, while the latter can be used just for plotting electron charge density maps (**ECHG** keyword).
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* (**BIDIERD**) The ICASO variable must be 1 or 3
- *Electron Momentum Density* (**EMDLPG**) The ICASO variable must be 1 or 3
- *Electron Charge Density* (**ECHG**) This is the only keyword that can be used if IMP2=1
- *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 [23]) 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 184)

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 264, for description of the format.

Function data computed at 3D grid points are written according to GAUSSIAN CUBE format in file POT.CUBEDAT

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
<hr/>		
<i>if ICA = 0 then</i>		
<i>if NPU > 0 insert NPU records</i>		
• *	X,Y,Z	point coordinates (cartesian, bohr) <i>if NPU < 0 data are read from file POTC.INP</i>
<hr/>		
<i>if ICA = 2 insert</i>		
• *	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) <i>if ICA = 3 insert</i>
<hr/>		
• *	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

$$\rho(z) = -\frac{1}{4\pi} \frac{d^2 V(z)}{dz^2} = \frac{-E'(z)}{4\pi}$$

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:

$$V_{field}(z) = V(z) - E_0 z$$

where $V(z)$ is the potential of the slab itself and $-E_0 z$ 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 261.

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 176)_____			

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 176). The electrostatic potential values are written formatted in file fort.25 (see Appendix D, page 258).
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 258).
3. The electrostatic potential at \mathbf{r} is evaluated [116] 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 $\rho_\lambda(\underline{r} - \underline{h})$ [117]. 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 [116, 117].

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 96.

PRINTOUT - Setting of printing environment

See input block 1, page 53.

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 260)
		2	formatted CP data stored in Fortran unit 24 (Appendix D, page 260)
<hr/>			
• A2	CP		calculation of Compton profiles (J(q)) along selected directions (eq. 11.27). II
• *	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.
<hr/>			
• A2	BR		auto-correlation function B(r) calculation (eq. 11.30).
• *	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) (eq. 11.29)
• *	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. 11.27). 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, equation 11.25); the valence contribution is computed numerically (IVIA=0) by integrating the EMD (equation 11.23). 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 $\text{ICORE} \neq 2$ (valence electron CP's are required) the **NEWK** option, with $\text{IFE}=1$, 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 $\text{ICORE} \neq 2$ and $\text{IVIA} = 0$ 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 $\text{ICORE} = 2$ or $\text{IVIA} = 1$ 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 $\text{ICORE}=1$, 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 53

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 82)

SETINF - Setting of INF values

See input block 1, page 54

SETPRINT - Setting of printing options

See input block 1, page 54.

STOP

Execution stops immediately. Subsequent input records are not processed.

SYMADAPT

See input block 3, page 101

XFAC - X-ray structure factors

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
			<i>if ISS > 0 insert ISS records</i>
● *	H,K,L		Miller indices of the reflection (conventional cell) .

The Fourier transform of the ground state charge density of a crystalline system provides the static structure factors 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:

$$F_{\underline{k}} = \int \rho(\underline{r}) e^{i\mathbf{k} \cdot \underline{r}} d\mathbf{r}$$

where $\underline{k} \equiv h \underline{b}_1 + k \underline{b}_2 + l \underline{b}_3$. *The Miller indices refer to the conventional cell.* The structure factors are integrated over the primitive cell volume.

8.3 Spontaneous polarization and piezoelectricity

Y. Noel, September 2002 - not fully updated to CRYSTAL09

PIEZOBP - Piezoelectricity (Berry phase approach)

The calculation the piezoelectric constants of a system, can be decompose in few steps. A preliminary run must be performed for the undistorted system ($\lambda = 0$) with the keyword **POLARI**. Then, for a first distorted system ($\lambda = 1$), a second preliminary run (with the keyword **POLARI**) must be performed, followed by third run with the keyword **PIEZOBP** that calculates a approximated value of the piezoelectric constants. The evaluation of the slope $\frac{d\varphi_\alpha}{d\epsilon_{jk}}$ is computed with a single point. For more accuracy, other runs must be done for other distortions (one run with the keyword **POLARI** of the new system, followed by a second run with the keyword **PIEZOBP** with the undistorted and the new distorted systems). Then the mean value of the obtained piezoelectric constants must be performed.

1. First run: preliminary calculation related to system $\lambda = 0$ (undistorted)

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 undistord.f27		

2. Second run: preliminary calculation related to system $\lambda = 1$ (distorted)

Program	Keyword	comments
crystal		see deck 1 for input blocks 1 and 1b
properties	NEWK	same input as in first run
	POLARI	
save Fortran unit 27 as distord1.f27		

3. Third run: merging of previous data.

copy undistord.f27 to Fortran unit 28		
copy distord1.f27 to fortran unit 29		
Program	Keyword	comments
properties	PIEZOBP	

4. Refine the computed value

Repeat 2. and 3. for several distortions.		
Then compute the mean value of the piezoelectric constants obtained in each case.		

PIEZOWF - Piezoelectricity (localized CO approach)

The calculation the piezoelectric constants of a system, can be decompose in few steps. A preliminary run must be performed for the undistorted system ($\lambda = 0$) with the keyword **LOCALWF**. Then, for a first distorted system ($\lambda = 1$), a second preliminary run (with the keyword **LOCALWF**) must be performed, followed by third run with the keyword **PIEZOWF** that calculates a approximated value of the piezoelectric constants. The evaluation of the slope $\frac{d\varphi_\alpha}{d\epsilon_{jk}}$ is computed with a single point. For more accuracy, other runs must be done for other distortions (one run with the keyword **LOCALWF** of the new system, followed by a second run with the keyword **PIEZOWF** with the undistorted and the new distorted systems). Then the mean value of the obtained piezoelectric constants must be performed.

1. First run: preliminary calculation related to system $\lambda = 0$ (undistorted)

Program	Keyword	comments
crystal		see deck 1 for input blocks 1 and 1b
properties	NEWK LOCALWF	additional keywords allowed see above
save Fortran unit 37 as undistord.f37		

2. Second run: preliminary calculation related to system $\lambda = 1$ (distorted)

Program	Keyword	comments
crystal		see deck 1 for input blocks 1 and 1b
properties	NEWK LOCALWF	same input as in first run
save Fortran unit 37 as distord1.f37		

3. Third run: merging of previous data.

copy undistord.f37 to Fortran unit 38		
copy distord1.f37 to Fortran unit 39		
Program	Keyword	comments
properties	PIEZOWF	

4. Refine the computed value

Repeat 2. and 3. for several distortions.
Then compute the mean value of the piezoelectric constants obtained in each case.

POLARI - Spontaneous polarization (steps 1 and 2)

PHASE - Spontaneous polarization (step 3)

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 the Berry phase approach [118, 119] as the polarization difference between one of the two enantiomorphic structures ($\lambda=+1$ or $\lambda=-1$) and the intermediate geometric structure ($\lambda=0$).

The fortran unit 70 is defined as direct access:

```
OPEN(UNIT=I070,ACCESS='DIRECT',RECL=LREC)
```

Three subsequent runs are required.

1. First run: preliminary calculation related to $\lambda=0$ structure

Program	Keyword	comments
crystal		see deck
properties	NEWK POLARI	see page 178 no input data required
move fortran unit 27 to zero.f27		

2. Second run: preliminary calculation related to $\lambda=+1$ (or $\lambda=-1$) structure

Program	Keyword	comments
crystal		see deck 2
properties	NEWK POLARI	same input as in first run no input data required
move fortran unit 27 to one.f27		

3. Third run: merging of previous data

fortran unit 9 of previous calculation must be present copy zero.f27 to fortran unit 28 copy one.f27 to fortran unit 29		
Program	Keyword	comments
properties	PHASE END	no input data required terminate processing of polari keywords

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

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 178 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 keyword **POLARI** in the first two runs do not have any physical meaning if considered independently. Only the output produced choosing the keyword **PHASE** 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 the Berry phase 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.

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 1 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 **SPOLBP** 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 1 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	

Chapter 9

Input examples

9.1 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 (2^{nd} 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 (1^{st} 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, $P6_3mc$, hexagonal
3.81 6.23	a, c (Å)
2	2 non equivalent atoms
30 .6666666667 .3333333333 .0	Zinc, (2/3, 1/3, 0.)
16 .6666666667 .3333333333 .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 .25

IFLAG 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 .087

IFLAG (1, SPGR symbol) IFHR IFSO

space group $Pmcn$, 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 .0

IFLAG 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 .0

IFLAG 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 .0

IFLAG IFHR IFSO

space group 136, $P4_2/mnm$, 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 .333333333333 .666666666667 .25

IFLAG IFHR IFSO

space group 194, $P6_3/mmc$, 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 .386

IFLAG 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, <i>rhombohedral representation</i>) 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, <i>rhombohedral cell</i>) 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, <i>standard shift of origin</i>)
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, <i>standard shift of origin</i>)
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, <i>standard shift of origin</i>)
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	IFLAG IFHR (=1, <i>rhombohedral representation</i>) IFSO
166	space group 166 $R\bar{3}m$, hexagonal
9.42 94.47	a (Å), β°
5	5 non equivalent atoms (36 atoms in the primitive cell)
14 .1045 .334 .8755	Silicon (multiplicity 12)
8 .262 -.262 .0	Oxygen (multiplicity 6)
8 .1580 -.1580 .5000	Oxygen (multiplicity 6)
8 .2520 .2520 .8970	Oxygen (multiplicity 6)
8 .0250 .0250 .3210	Oxygen (multiplicity 6)

SiO₂, Siliceous Faujasite

CRYSTAL

0 0 0	IFLAG IFHR IFSO
227	space group 227, $Fd\bar{3}m$, cubic
21.53	a (Å)
5	5 non equivalent atoms (144 atoms in the primitive cell)
14 .1265 -.0536 .0370	Silicon (multiplicity 48)
8 .1059 -.1059 .0	Oxygen (multiplicity 24)
8 -.0023 -.0023 .1410	Oxygen (multiplicity 24)
8 .1746 .1746 -.0378	Oxygen (multiplicity 24)
8 .1785 .1785 .3222	Oxygen (multiplicity 24)

SiO₂, Siliceous Edingtonite

CRYSTAL

0 0 0	IFLAG IFHR IFSO
115	space group 115, $P\bar{4}m2$, tetragonal
6.955 6.474	a, c (Å)
5	5 non equivalent atoms (15 atoms in the primitive cell)
14 .0 .0 .5000	Silicon (multiplicity 1)
14 .0 .2697 .1200	Silicon (multiplicity 4)
8 .0 .189 .3543	Oxygen (multiplicity 4)
8 .50000 .0 .8779	Oxygen (multiplicity 2)
8 .189 .189 .0	Oxygen (multiplicity 4)

SiO₂, Siliceous Sodalite

CRYSTAL

0 0 0	IFLAG IFHR IFSO
218	space group 218, $P\bar{4}3n$, cubic
8.950675	a (Å)
3	3 non equivalent atoms (36 atoms in the primitive cell)
14 .25000 .50000 .0	Silicon (multiplicity 6)
14 .25000 .0 .50000	Silicon (multiplicity 6)
8 .14687 .14687 .50000	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 55), 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 -0.3333333333 0.3333333333 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 0.3333333333 0.6666666667 0.	Z=4, Beryllium; $1/3, 2/3, z$
4 0.6666666667 0.3333333333 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 0.3333333333 0.6666666667 0.897499	Z=4, Beryllium; x,y,z
4 0.6666666667 0.3333333333 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 19, 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

9.2 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.		

9.3 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 23)
SPINLOCK	n_α - n_β 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) -7.072808080821E+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			

9.4 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 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:

```

OPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPTOPT
*****
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 15).

▷ 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 15).

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 -Al ₂ O ₃ - (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	(<i>h, k, l</i>) 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 10

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.

10.1 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) [120, 121, 122, 123].

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 [124, 125]. 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.

10.2 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.

10.3 Valence functions

Molecular crystals

Molecular BSs, minimal and split-valence, are perfectly adequate. Tests have been performed on bulk urea [126] 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 10.1. The last entry of Table 10.1 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 [127] 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 [128, 129].

Table 10.1: 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 [25, 19].

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) [19].

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 ($\Delta E \leq 1$ m hartree 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 [25]. 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 10.1; 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 [130]).

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 10.2: 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 10.2. Finally, the most diffuse gaussian can be optimized; in the two cases the minimum has not been found owing to numerical instabilities.

See [131] for a more extensive discussion of the metallic lithium case.

10.4 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 10.1 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 $e^{-\alpha r^2}$ 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 10.1 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 10.2), 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).

10.5 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 81). 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 [77] requires basis functions linearly independent. A symptom of numerical dependence may produce an error message in RHOLSK or CHOLSK while running **scf**.

Chapter 11

Theoretical framework

11.1 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).

$$\psi_i(\mathbf{r}; \mathbf{k}) = \sum_{\mu} a_{\mu,i}(\mathbf{k}) \phi_{\mu}(\mathbf{r}; \mathbf{k}) \quad (11.1)$$

$$\phi_{\mu}(\mathbf{r}; \mathbf{k}) = \sum_{\mathbf{g}} \varphi_{\mu}(\mathbf{r} - \mathbf{A}_{\mu} - \mathbf{g}) e^{i\mathbf{k} \cdot \mathbf{g}} \quad (11.2)$$

\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:

$$\varphi_{\mu}(\mathbf{r} - \mathbf{A}_{\mu} - \mathbf{g}) = \sum_j^{n_G} d_j G(\alpha_j; \mathbf{r} - \mathbf{A}_{\mu} - \mathbf{g}) \quad (11.3)$$

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} :

$$\mathbf{F}(\mathbf{k})\mathbf{A}(\mathbf{k}) = \mathbf{S}(\mathbf{k})\mathbf{A}(\mathbf{k})\mathbf{E}(\mathbf{k}) \quad (11.4)$$

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:

$$\mathbf{F}(\mathbf{k}) = \sum_{\mathbf{g}} \mathbf{F}^{\mathbf{g}} e^{i\mathbf{k} \cdot \mathbf{g}} \quad (11.5)$$

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:

$$F_{12}^{\mathbf{g}} = H_{12}^{\mathbf{g}} + B_{12}^{\mathbf{g}} \quad (11.6)$$

The one electron contribution is the sum of the kinetic and nuclear attraction terms:

$$H_{12}^{\mathbf{g}} = T_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = \langle \varphi_1^0 | \hat{T} | \varphi_2^{\mathbf{g}} \rangle + \langle \varphi_1^0 | \hat{Z} | \varphi_2^{\mathbf{g}} \rangle \quad (11.7)$$

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:

$$B_{12}^{\mathbf{g}} = C_{12}^{\mathbf{g}} + X_{12}^{\mathbf{g}} = \sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^0 \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}}) - \frac{1}{2}(\varphi_1^0 \varphi_3^{\mathbf{h}} | \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (11.8)$$

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),

$$P_{3,4}^{\mathbf{n}} = 2 \int_{BZ} d\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{n}} \sum_j a_{3j}^*(\mathbf{k}) a_{4j}(\mathbf{k}) \theta(\epsilon_F - \epsilon_j(\mathbf{k})) \quad (11.9)$$

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:

$$E^{elec} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} (H_{12}^{\mathbf{g}} + F_{12}^{\mathbf{g}}) \quad (11.10)$$

A discussion of the different contributions to the total energy is presented in [132, 116] and in Chapter 11 of reference [13].

$$E^{coul} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^0 \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (11.11)$$

$$E^{exch} = -\frac{1}{4} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^0 \varphi_3^{\mathbf{h}} | \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (11.12)$$

11.2 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).

11.3 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 [133] and by Saunders et al. [116]. It may be summarized as follows.

Consider the Coulomb bielectronic contribution to the Fock matrix ($C_{12}^{\mathbf{g}}$) and to the total energy :

$$E_{ee}^{coul} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{3,4} \sum_{\mathbf{n}} P_{34}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^0 \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (11.13)$$

Seven indices are involved in equation 11.13; 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 11.13 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 :

$$\rho_{\lambda}(\mathbf{r} - \mathbf{h}) \equiv \{\lambda\}' \equiv \{\lambda\} - Z_{\lambda} = \sum_{3 \in \lambda} \sum_{4\mathbf{n}} P_{34}^{\mathbf{n}} \varphi_3(\mathbf{r} - \mathbf{h}) \varphi_4(\mathbf{r} - \mathbf{h} - \mathbf{n}) - Z_{\lambda} \quad (11.14)$$

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:

$$C_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = \sum_{\lambda} \sum_{\mathbf{h}} \int d\mathbf{r} d\mathbf{r}' \varphi_1^0(\mathbf{r}) \varphi_2^{\mathbf{g}}(\mathbf{r}) |\mathbf{r} - \mathbf{r}' - \mathbf{h}|^{-1} \rho_{\lambda}(\mathbf{r}' - \mathbf{h}) \quad (11.15)$$

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 [116].

The resulting expression for the Coulomb contribution to the Fock matrix is:

$$\begin{aligned} C_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = & \sum_{\lambda} \{ \sum_{\mathbf{h}}^{B_{\lambda}} [\sum_{3 \in \lambda} \sum_{4\mathbf{n}} P_{34}^{\mathbf{n}} (\varphi_1^0 \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}}) + \\ & - \sum_{\ell, m} \gamma_{\ell}^m(\mathbf{A}_{\lambda}; \{\lambda\}) \Phi_{\ell}^m(12\mathbf{g}; \mathbf{A}_{\lambda} + \mathbf{h})] + \\ & + \sum_{\mathbf{h}} \sum_{\ell, m} \gamma_{\ell}^m(\mathbf{A}_{\lambda}; \{\lambda\}') \Phi_{\ell}^m(12\mathbf{g}; \mathbf{A}_{\lambda} + \mathbf{h}) \} \end{aligned} \quad (11.16)$$

where:

$$\gamma_{\ell}^m(\mathbf{A}_{\lambda}; \{\lambda\}) = \int d\mathbf{r} \rho_{\lambda}(\mathbf{r} - \mathbf{A}_{\lambda}) N_{\ell}^m X_{\ell}^m(\mathbf{r} - \mathbf{A}_{\lambda}) \quad (11.17)$$

$$\Phi_{\ell}^m(12\mathbf{g}; \mathbf{A}_{\lambda} + \mathbf{h}) = \int d\mathbf{r} \varphi_1^0(\mathbf{r}) \varphi_2^{\mathbf{g}}(\mathbf{r}) X_{\ell}^m(\mathbf{r} - \mathbf{A}_{\lambda} - \mathbf{h}) |\mathbf{r} - \mathbf{A}_{\lambda} - \mathbf{h}|^{-2\ell-1} \quad (11.18)$$

The Ewald term in eq. 11.16 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 11.16 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 95).

11.4 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 [134]. The exchange contribution to the total energy can be written as follows:

$$E^{ex} = \frac{1}{2} \sum_{12} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \left[-\frac{1}{2} \sum_{34} \sum_{\mathbf{n}} P_{34}^{\mathbf{n}} \sum_{\mathbf{h}} (\varphi_1^0 \varphi_3^{\mathbf{h}} | \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h}+\mathbf{n}}) \right] \quad (11.19)$$

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 $\{\varphi_1^0 \varphi_3^{\mathbf{h}}\}$ 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 $\mathbf{n} = \mathbf{g}$:

$$e_{12}^{\mathbf{g}} = -1/4 (P_{12}^{\mathbf{g}})^2 (10 \ 10 | 2\mathbf{g} \ 2\mathbf{g}) = -(p^{\mathbf{g}})^2 / (4|\mathbf{g}|) \quad (11.20)$$

(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 [108], 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 $\int d\mathbf{r} \varphi_1^0 \varphi_2^{\mathbf{g}}$ 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 $\int d\mathbf{r} \varphi_3^0 \varphi_4^{\mathbf{n}}$ 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 [23] for a discussion of this point). In order to overcome this problem, the threshold, $P_{ex}^{\mathbf{n}}$ (**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 $\int d\mathbf{r} \varphi_3^0 \varphi_4^{\mathbf{n}}$ is larger than $P_{ex}^{\mathbf{n}}$ 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.

11.5 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 11.13. Consider one contribution to the charge distribution of electron 1, centred in the reference cell: $\rho^0 = \varphi_1^0 \varphi_2^{\mathbf{g}}$; now consider the charge distribution $\rho_\lambda(\mathbf{h})$ of shell λ centred in cell \mathbf{h} (equation 11.14). 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 $\varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}}$ contributions to ρ_λ are external to $\rho^0 = \varphi_1^0 \varphi_2^{\mathbf{g}}$; 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 [23] 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 $\lambda_1^0 \lambda_2^{\mathbf{g}}$, shell $\lambda_3^{\mathbf{h}}$ is attributed to the B (*bielectronic*) zone, the penetration between the products of adjoined Gaussians $G_1^0 G_2^{\mathbf{g}}$ and $G_3^{\mathbf{h}} G_4^{\mathbf{h}+\mathbf{n}}$ 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 $\rho^0 = \{12\mathbf{g}\}$ and $\rho_\lambda \equiv \{\lambda_3\}$ is then split into two subsets, which are specific for each partner $\lambda_4^{\mathbf{l}}$ 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 [133, 116]. 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.

11.6 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 [135] 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:

$$D_{1,2T;3,4Q} = \sum_{\mathbf{n}} [(\varphi_1^{\mathbf{0}} \varphi_2^{\mathbf{g}} | \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h}+\mathbf{n}}) - 1/2(\varphi_1^{\mathbf{0}} \varphi_3^{\mathbf{h}} | \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h}+\mathbf{n}})] \quad (11.21)$$

- 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

11.7 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 11.9. The technique adopted to compute ϵ_F and the P matrix in the SCF step is described in reference [136]. The Fourier-Legendre technique presented in Chapter II.6 of reference [23] is adopted in the calculation of total and projected DOS. The Fermi energy and the integral in equation 11.9 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*, [20]) 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 11.9 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* [21, 22] 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.

11.8 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, $\rho(\mathbf{p})$ or EMD; the Compton profile function, $J(\mathbf{p})$ or CP; the autocorrelation function, or reciprocal space form factor, $B(\mathbf{r})$ 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:

$$\rho(\underline{p}) = 1/V_{BZ} \sum_j \int_{BZ} d\underline{k} |\psi_j(\underline{k}, \underline{p})|^2 \theta[\epsilon_F - \epsilon_j(\underline{k})] = \quad (11.22)$$

$$= \sum_j \sum_{\mu\nu} e^{-i\underline{p} \cdot (\underline{s}_\mu - \underline{s}_\nu)} a_{\mu j}(\underline{p}^0) a_{\nu j}^*(\underline{p}^0) \chi_\mu(\underline{p}) \chi_\nu^*(\underline{p}) \theta[\epsilon_F - \epsilon_j(\underline{p}^0)] \quad (11.23)$$

$$\rho(\underline{p}) = N^{-1} \int d\underline{r} d\underline{r}' e^{-i\underline{p} \cdot (\underline{r}' - \underline{r})} \rho(\underline{r} - \underline{r}') \quad (11.24)$$

$$= \sum_{\mu\nu} \sum_{\underline{g}} P_{\mu\nu}^g e^{-i\underline{p} \cdot (\underline{g} + \underline{s}_\mu - \underline{s}_\nu)} \chi_\mu(\underline{p}) \chi_\nu^*(\underline{p}) \quad (11.25)$$

In the above equations \underline{p}^0 is the value of momentum in the Brillouin zone (BZ), which is related to \underline{p} by a reciprocal lattice vector \underline{K} , \underline{s}_μ is the fractional coordinate of the χ_μ centre, and $\chi_\mu(\underline{p})$ is the Fourier transform of $\chi_\mu(\underline{r})$, calculated analytically:

$$\chi_\mu(\underline{p}) = \int d\underline{r} \chi_\mu(\underline{r}) e^{i\underline{p} \cdot \underline{r}} \quad (11.26)$$

Equation 11.25 is used by default to compute the core band contribution, and equation 11.23 the valence band contribution.

The CPs are obtained by 2D integration of the EMD over a plane through \underline{p} and perpendicular to the \underline{p} direction. After indicating with \underline{p}_\perp the general vector perpendicular to \underline{p} , we have:

$$J(\underline{p}) = \int d\underline{p}'_\perp \rho(\underline{p} + \underline{p}'_\perp) \quad (11.27)$$

It is customary to make reference to CPs as functions of a single variable p , with reference to a particular direction $\langle hkl \rangle$ identified by a vector

$$\mathbf{e} = (h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3) / |(h\mathbf{a}_1 + k\mathbf{a}_2 + l\mathbf{a}_3)|$$

We have:

$$J_{\langle hkl \rangle}(p) = J(p \mathbf{e}) \quad (11.28)$$

The function $J_{\langle hkl \rangle}(p)$ will be referred to as directional CPs.

The weighted average of the directional CPs over all directions is the average CP.

In the so called impulse approximation, $J_{\langle hkl \rangle}(p)$ may be related to the experimental CPs, after correction for the effect of limited resolution as a convolution of the "infinite resolution" results, $J_{\langle hkl \rangle}^0(p)$, with a normalized function characterized by a given standard deviation σ :

$$J_{\langle hkl \rangle}^\sigma(p) = \int_{-\infty}^{+\infty} dp' J_{\langle hkl \rangle}^0(p') g_\sigma(p - p') \quad (11.29)$$

In CRYSTAL g_σ is a gaussian function with standard deviation σ . Once the directional CPs are available, the numerical evaluation of the corresponding autocorrelation function, or reciprocal space form factor, $B(\underline{r})$ is given by the 1D Fourier Transform:

$$B_{\langle hkl \rangle}(\underline{r}) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dp J_{\langle hkl \rangle}(p) e^{i \underline{p} \cdot \underline{r}} \quad (11.30)$$

The average Compton profile can be evaluated from the average EMD:

$$\overline{J(q)} = \int_0^q \rho(\underline{p}) p d\underline{p} \quad (11.31)$$

and can be used for the evaluation of the kinetic energy:

$$KE = \int_0^\infty p^2 \overline{J(p)} dp \quad (11.32)$$

11.9 Elastic Moduli of Periodic Systems

The elastic constants are *second* derivatives of the energy density with respect to strain components:

$$C_{ij} = 1/V \cdot \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \quad (11.33)$$

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 86; **OPTGEOM**, page 105).

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 34) is useful in finding the atomic coordinates to be relaxed. Examples of deformation strategies are discussed in references [25, 137].

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 :

$$\mathbf{L}_p = \begin{bmatrix} \mathbf{l}_1 \\ \mathbf{l}_2 \\ \mathbf{l}_3 \end{bmatrix} = \begin{bmatrix} l_{1x} & l_{1y} & l_{1z} \\ l_{2x} & l_{2y} & l_{2z} \\ l_{3x} & l_{3y} & l_{3z} \end{bmatrix} \quad (11.34)$$

$$V = \det(\mathbf{L}_p)$$

$\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$ 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:

$$\begin{aligned} \mathbf{r}' &= \mathbf{h} \mathbf{L}'_p \\ \mathbf{L}'_p &= (\mathbf{I} + \epsilon) \mathbf{L}_p \end{aligned} \quad (11.35)$$

or:

$$\mathbf{L}'_p = \mathbf{L}_p + \mathbf{Z} \quad (11.36)$$

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:

$$\mathbf{L}_p' = \mathbf{L}_p (V/V')^{1/3} \quad (11.37)$$

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:

$$\epsilon = (\eta + \eta^+)/2$$

$$\omega = (\eta - \eta^+)/2$$

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:

$$E(\epsilon) = E(\mathbf{0}) + \sum_i^6 \frac{\partial E}{\partial \epsilon_i} \epsilon_i + 1/2 \sum_{i,j}^6 \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \epsilon_i \epsilon_j \quad (11.38)$$

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 Fm3m 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 11.38)

$$E(\epsilon_4) = E(0) + 1/2 \frac{\partial^2 E}{\partial \epsilon_4^2} \delta^2 + \dots = E(0) + 2 \frac{\partial^2 E}{\partial \epsilon_4^2} x^2 + \dots = a + bx^2 + \dots$$

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:

$$E(\epsilon) = E(0) + 3/2 \frac{\partial^2 E}{\partial \epsilon_1^2} \delta^2 + 3 \frac{\partial^2 E}{\partial \epsilon_1 \partial \epsilon_2} \delta^2 = \quad (11.39)$$

$$= E(0) + \frac{3V}{2} [C_{11} + 2C_{12}] \delta^2 \quad (11.40)$$

so that $B = \frac{2}{9V} b$

N.B. Conversion factors:

1 hartree $\text{\AA}^{-3} = 4359.74812 \text{ GPa}$

1 GPa = 1 GN m^{-2} = 1 GJ m^{-3} = 10^{10} dyne cm^{-2} = 10^{-2} Mbar.

11.10 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:

$$\varphi_{el}^{(\lambda,1)} = \frac{1}{s2s3} \sum_{j2,j3} \sum_{j1} \Delta\varphi_{j1,j2,j3}^{(\lambda,1)}(\mathbf{k}) \quad (11.41)$$

The electronic contribution to the polarization of a system λ can be written as :

$$\mathbf{P}_{el}^{(\lambda)} = \frac{1}{\Omega^{(\lambda)}} \left(B^{(\lambda)} \right)^{-1} \varphi_{el}^{(\lambda)} \quad (11.42)$$

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:

$$\mathbf{P}_{nuc}^{(\lambda)} = \frac{1}{\Omega^{(\lambda)}} \sum_A \mathbf{R}_A^{(\lambda)} \cdot Z_A \quad (11.43)$$

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

$$\mathbf{P}_{tot}^{(\lambda)} = \mathbf{P}_{nuc}^{(\lambda)} + \mathbf{P}_{el}^{(\lambda)} \quad (11.44)$$

The spontaneous polarization is the difference between the systems $\lambda = 1$ and $\lambda = 0$

$$\mathbf{P} = \mathbf{P}_{tot}^{(\lambda)} - \mathbf{P}_{tot}^{(0)} \quad (11.45)$$

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

$$\mathbf{P}_{el}^{(\lambda)} = \frac{e}{\Omega^{(\lambda)}} \sum_{\mu} \langle \mathbf{r}_{\mu} \rangle \quad (11.46)$$

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

$$\mathbf{P}_{nuc}^{(\lambda)} = \frac{1}{\Omega^{(\lambda)}} \sum_A \mathbf{R}_A \cdot Z_A \quad (11.47)$$

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

$$\mathbf{P}_{tot}^{(\lambda)} = \mathbf{P}_{nuc}^{(\lambda)} + \mathbf{P}_{el}^{(\lambda)} \quad (11.48)$$

The spontaneous polarization is the difference between the both systems $\lambda = 1$ and $\lambda = 0$:

$$\mathbf{P} = \mathbf{P}_{tot}^{(1)} - \mathbf{P}_{tot}^{(0)} \quad (11.49)$$

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 $\lambda = 0$.

11.11 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

$$\varphi_{nuc}^{(\lambda)} = \Omega^{(\lambda)} B^{(\lambda)} \mathbf{P}_{nuc}^{(\lambda)} \quad (11.50)$$

Where $B^{(\lambda)}$ reciprocal lattice vectors components matrix. The last equation can be simplified thanks to (11.43):

$$\varphi_{nuc}^{(\lambda)} = B^{(\lambda)} \sum_A \mathbf{R}_A^{(\lambda)} \cdot \mathbf{Z}_A \quad (11.51)$$

So the phase vector of a system λ , $\varphi^{(\lambda)}$ is:

$$\varphi^{(\lambda)} = \varphi_{nuc}^{(\lambda)} + \varphi_{el}^{(\lambda)} \quad (11.52)$$

The proper piezoelectric constants can be obtained by:

$$\tilde{e}_{ijk} = -\frac{1}{2\pi} \frac{1}{\Omega} \sum_{\alpha} \frac{d\varphi_{\alpha}}{d\epsilon_{jk}} a_{\alpha,i} \quad (11.53)$$

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 be done:

$$e_{ijk} = \tilde{e}_{ijk} + \delta_{ij} P_k - \delta_{jk} P_i \quad (11.54)$$

In the piezoelectric constants calculations the $\frac{d\varphi_{\alpha}}{d\epsilon_{jk}}$ term is evaluated numerically. The calculated term is:

$$\frac{d\varphi_{\alpha}}{d\epsilon_{jk}} \simeq \frac{\Delta\varphi_{\alpha}}{\Delta\epsilon_{jk}} = \frac{\varphi_{\alpha}^{(1)} - \varphi_{\alpha}^{(0)}}{\epsilon_{jk}^{(1)} - \epsilon_{jk}^{(0)}} \quad (11.55)$$

Piezoelectricity through the localized crystalline orbitals approach

The electronic phase vector of a system λ , is given by:

$$\varphi_{el}^{(\lambda)} = \Omega^{(\lambda)} B^{(\lambda)} \mathbf{P}_{el}^{(\lambda)} \quad (11.56)$$

Where $B^{(\lambda)}$ reciprocal lattice vectors components matrix. The nuclear phase vector of a system λ , $\varphi_{nuc}^{(\lambda)}$, can be written as

$$\varphi_{nuc}^{(\lambda)} = \Omega^{(\lambda)} B^{(\lambda)} \mathbf{P}_{nuc}^{(\lambda)} \quad (11.57)$$

The last equation can be simplified thanks to 11.43:

$$\varphi_{nuc}^{(\lambda)} = B^{(\lambda)} \sum_A \mathbf{R}_A^{(\lambda)} \cdot \mathbf{Z}_A \quad (11.58)$$

So the phase vector of a system λ , $\varphi^{(\lambda)}$ is:

$$\varphi^{(\lambda)} = \varphi_{nuc}^{(\lambda)} + \varphi_{el}^{(\lambda)} \quad (11.59)$$

The proper piezoelectric constants can be obtained by:

$$\tilde{e}_{ijk} = -\frac{1}{2\pi} \frac{1}{\Omega} \sum_{\alpha} \frac{d\varphi_{\alpha}}{d\epsilon_{jk}} a_{\alpha,i} \quad (11.60)$$

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 be done:

$$e_{ijk} = \tilde{e}_{ijk} + \delta_{ij} P_k - \delta_{jk} P_i \quad (11.61)$$

In the piezoelectric constants calculations the $\frac{d\varphi_\alpha}{d\epsilon_{jk}}$ term is evaluated numerically. The calculated term is:

$$\frac{d\varphi_\alpha}{d\epsilon_{jk}} \simeq \frac{\Delta\varphi_\alpha}{\Delta\epsilon_{jk}} = \frac{\varphi_\alpha^{(1)} - \varphi_\alpha^{(0)}}{\epsilon_{jk}^{(1)} - \epsilon_{jk}^{(0)}} \quad (11.62)$$

Appendix A

Symmetry groups

A.1 Labels and symbols of the space groups

The labels are according to the International Tables for Crystallography [14]. The symbols are derived by the standard SHORT symbols, as shown in the following examples:

Symbol		Input to CRYSTAL
P $\bar{6}$ 2 m	→	P ₁ -6 ₁ 2 ₁ M ;
P 6 ₃ m	→	P ₁ 63 ₁ 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. → P m 3 m ; 1982 ed. → 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>Pmmn</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	$P31m$	202	$Fm\bar{3}$
121	$I4_2m$	163	$P31c$	203	$Fd\bar{3}$
122	$I4_2d$	164	$P3m1$	204	$Im\bar{3}$
123	$P4/mmm$	165	$P3c1$	205	$Pa\bar{3}$
124	$P4/mcc$	166	$R3m$	206	$Ia\bar{3}$
125	$P4/nbm$	167	$R3c$	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	$P6$	215	$P43m$
134	$P4_2/nmm$	175	$P6/m$	216	$F43m$
135	$P4_2/mbc$	176	$P6_3/m$	217	$I43m$
136	$P4_2/mnm$	177	$P622$	218	$P43n$
137	$P4_2/nmc$	178	$P6_122$	219	$F43c$
138	$P4_2/ncm$	179	$P6_522$	220	$I43d$
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	$P6m2$	228	$Fd\bar{3}c$
146	$R3$	188	$P6c2$	229	$Im\bar{3}m$
147	$P\bar{3}$	189	$P62m$	230	$Ia\bar{3}d$
148	$R\bar{3}$	190	$P62c$		
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)					
1 $P1$	C_1^1	1	41 $Pbam$	D_{2h}^9	55
2 $P\bar{1}$	C_i^1	2	42 $Pmaa$	D_{2h}^3	(49)
3 $P112$	C_2^1	(3)	43 $Pman$	D_{2h}^7	(53)
4 $P11m$	C_s^1	(6)	44 $Pbma$	D_{2h}^1	(57)
5 $P11a$	C_s^2	(7)	45 $Pbaa$	D_{2h}^8	(54)
6 $P112/m$	C_{2h}^1	(10)	46 $Pban$	D_{2h}^4	50
7 $P112/a$	C_{2h}^4	(13)	47 $Cmmm$	D_{2h}^9	65
			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}^2	$P4/mcc$	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}^2	$P6_3/m$	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

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).

$$\begin{array}{ll}
P \rightarrow A \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{1}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{pmatrix} & P \rightarrow B \quad \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} & A \rightarrow P \quad \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix} & B \rightarrow P \quad \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} \\
P \rightarrow C \quad \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & P \rightarrow F \quad \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix} & C \rightarrow P \quad \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & F \rightarrow P \quad \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \\
P \rightarrow I \quad \begin{pmatrix} \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{pmatrix} & R \rightarrow H \quad \begin{pmatrix} \frac{2}{3} & \frac{1}{3} & \frac{1}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{2}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} & I \rightarrow P \quad \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} & H \rightarrow R \quad \begin{pmatrix} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}
\end{array}$$

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. [14]).

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	34	–	
MAKESAED	printing of symmetry allowed elastic distortions (SAED)	45	–	
PRSYMDIR	printing of displacement directions allowed by symmetry.	53	–	
SYMMDIR	printing of symmetry allowed geom opt directions	60	–	
SYMMOPS	printing of point symmetry operators	60	–	
TENSOR	print tensor of physical properties up to order 4	60	I	
Symmetry information and control				
BREAKELAS	symmetry breaking according to a general distortion	35	I	
BREAKSYMM	allow symmetry reduction following geometry modifications	34	–	
KEEPSYMM	maintain symmetry following geometry modifications	44	–	
MODISYMM	removal of selected symmetry operators	45	I	
PURIFY	cleans atomic positions so that they are fully consistent with the 53 group		–	
SYMMREMO	removal of all symmetry operators	60	–	
TRASREMO	removal of symmetry operators with translational components	60	–	
Modifications without reduction of symmetry				
ATOMORDE	reordering of atoms in molecular crystals	32	–	
NOSHIFT	no shift of the origin to minimize the number of symmops with 52 translational components before generating supercell		–	
ORIGIN	shift of the origin to minimize the number of symmetry operators 52 with translational components		–	
PRIMITIV	crystallographic cell forced to be the primitive cell	52	–	
ROTCRY	rotation of the crystal with respect to the reference system cell	54	I	
Atoms and cell manipulation (possible symmetry reduction (BREAKSYMM))				

ATOMDISP	displacement of atoms	32	I
ATOMINSE	addition of atoms	32	I
ATOMREMO	removal of atoms	32	I
ATOMROT	rotation of groups of atoms	33	I
ATOMSUBS	substitution of atoms	34	I
ELASTIC	distortion of the lattice	38	I
POINTCHG	point charges input	52	I
SCELPHONO	generation of supercell for phonon dispersion	58	I
SUPERCEL	generation of supercell - input refers to primitive cell	56	I
SUPERCON	generation of supercell - input refers to conventional cell	56	I
USESAED	given symmetry allowed elastic distortions, reads δ	61	I
From crystals to slabs (3D→2D)			
SLABINFO	definition of a new cell, with $xy \parallel$ to a given plane	56	I
SLABCUT	generation of a slab parallel to a given plane (3D→2D)	55	I
From slabs to nanotubes (2D→1D)			
NANOTUBE	building a nanotube from a slab	47	I
SWCNT	building a nanotube from an hexagonal slab	50	I
From periodic structure to clusters			
CLUSTER	cutting of a cluster from a periodic structure (3D→0D)	36	I
HYDROSUB	border atoms substituted with hydrogens (0D→0D)	44	I
Molecular crystals			
MOLECULE	extraction of a set of molecules from a molecular crystal (3D→0D)	46	I
MOLEXP	variation of lattice parameters at constant symmetry and molecular geometry (3D→3D)	46	I
MOLSPLIT	periodic structure of non interacting molecules (3D→3D)	47	–
RAYCOV	modification of atomic covalent radii	53	I
BSSE correction			
MOLEBSSE	counterpoise method for molecules (molecular crystals only) (3D→0D)	45	I
ATOMBSSE	counterpoise method for atoms (3D→0D)	31	I
Auxiliary and control keywords			
ANGSTROM	sets input units to Ångstrom	31	–
BOHR	sets input units to bohr	34	–
BOHRANGS	input bohr to Å conversion factor (0.5291772083 default value)	34	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	44	–
NEIGHBOR	number of neighbours in geometry analysis	51	I
PARAMPR	printing of parameters (dimensions of static allocation arrays)	52	–
PRINTCHG	printing of point charges coordinates in geometry output	52	
PRINTOUT	setting of printing options by keywords	53	–
SETINF	setting of inf array options	54	I
SETPRINT	setting of printing options	54	I
STOP	execution stops immediately	56	–
TESTGEOM	stop after checking the geometry input	60	–
Output of data on external units			

COORPRT	coordinates of all the atoms in the cell	37	–
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	56	–

External electric field - modified Hamiltonian
--

FIELD	electric field applied along a periodic direction	41	I
FIELDCON	electric field applied along a non periodic direction	43	I

Geometry optimization - see index for keywords full list
--

OPTGEOM	Geometry optimization input block - closed by END	105	I
----------------	--	-----	---

Type of optimization (default: atom coordinates)
--

FULLOPTG	full geometry optimization	–
CELLONLY	cell parameters optimization	–
INTREDUN	optimization in redundant internal coordinates	115
ITATOCEL	iterative optimization (atom/cell)	–
CVOLOPT	full geometry optimization at constant volume	117

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	119	I
RESTART	data from previous run	—	
FINALRUN	Wf single point with optimized geometry		I

Gradient calculation control

NUMGRATO	numerical atoms first derivatives	114	–
NUMGRCEL	numerical cell first derivatives	114	–
NUMGRALL	numerical atoms and cell first derivatives	114	–

External stress

EXTSTRESS	apply external stress	121	I
EXTPRESS	apply external hydrostatic pressure	121	I

Printing options

PRINTFORCES	atomic gradients	–
PRINTHESS	Hessian	–
PRINTOPT	optimization procedure	–
PRINT	verbose printing	–

Frequencies at Γ - Harmonic calculation
--

FREQCALC	Frequencies at Γ (harmonic calculation) input block - closed by END	127	I
ANALYSIS			—
[NOANALYSIS]			—
DIELISO			I
DIETENS			I
END[FREQ]			—
FRAGMENT			I
INTENS			—
INTLOC	- IR intensities through Wannier functions	133	—
[INTPOL]	- IR intensities through Berry phase [default]	133	—
ISOTOPES		129	I
[MODES]			—
[NOINTENS]			—
NOMODES			—
NORMBORN			—
NOUSESMM			—
NUMBERIV			I
PRESSURE			I
PRINT			—
RESTART			—
SCANMODE			I
STEPSIZE			I
TEMPERAT			I
TESTFREQ			—
[USESMM]			—
ANHARM	Frequency at Γ (anharmonic calculation) input block - closed by END	141	I
END[ANHA]			—
ISOTOPES	modification of atomic mass	142	I
KEEPSMM		44	—
NOGUESS		142	—
POINTS26		142	—
PRINT			—
TEST[ANHA]			—

CONFCONT - Configuration counting and cluster expansion	146
--	-----

CPHF - Coupled Perturbed Hartree-Fock	144
--	-----

ELASTCON - Second order elastic constants	149
--	-----

EOS - Equation of state	144
--------------------------------	-----

Basis set input (Input block 2)

Symmetry control	
------------------	--

ATOMSYMM	printing of point symmetry at the atomic positions	34	—
-----------------	--	----	---

Basis set modification	
------------------------	--

CHEMOD	modification of the electronic configuration	62	I
GHOSTS	eliminates nuclei and electrons, leaving BS	64	I

Auxiliary and control keywords

CHARGED	allows non-neutral cell	62	–
NOPRINT	printing of basis set removed	64	–
PARAMPRT	printing of parameters controlling code dimensions	52	–
PRINTOUT	setting of printing options	53	I
SETINF	setting of inf array options	54	I
SETPRINT	setting of printing options	54	I
STOP	execution stops immediately	56	–
SYMMOPS	printing of point symmetry operators	60	–
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	64	–
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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	96	–
UHF	Unrestricted Open Shell	102	–

DFT	DFT Hamiltonian	102	–
	SPIN spin-polarized solution	75	–
	Choice of the exchange-correlation functionals		
	CORRELAT correlation functional	74	I
	LYP Lee-Yang-Parr [46] (GGA)		
	P86 Perdew 86 [47] (LDA)		
	PBE Perdew-Becke-Ernzerhof [48] (GGA)		
	PBESOL GGA. PBE functional revised for solids [49]		
	PWGGA Perdew-Wang 91 (GGA)		
	PWLS Perdew-Wang 92 [50, 51, 52] (GGA)		
	PZ Perdew-Zunger [53] (LDA)		
	VBH von Barth-Hedin [54] (LDA)		
	WL GGA - Wilson-Levy [55]		
	VWN Vosko,-Wilk-Nusair [56] (LDA)		
	EXCHANGE exchange functional	75	I
	BECKE Becke [57] (GGA)		
	LDA Dirac-Slater [58] (LDA)		
	PBE Perdew-Becke-Ernzerhof [48] (GGA)		
	PBESOL GGA. PBE functional revised for solids [49]		
	PWGGA Perdew-Wang 91 (GGA)		
	SOGGA second order GGA. [59]		
	VBH von Barth-Hedin [54] (LDA)		
	WCGGA GGA - Wu-Cohen [60]		
	Global keywords: exchange+correlation		
	B3PW B3PW parameterization	76	–
	B3LYP B3LYP parameterization	76	–
	PBE0 Adamo and Barone [61]	76	
	SOGGAXC see [59]	76	
	Custom made dft exchange-local exchange		
	HYBRID hybrid mixing	76	I
	NONLOCAL local term parameterization	76	I
	Numerical accuracy control		
	ANGULAR definition of angular grid		I
	BATCHPNT grid point grouping for integration		I
	[BECKE] selection of Becke weights (default)		–
	[CHUNKS] max n. points in a batch for numerical int.		I
	LGRID "large" predefined grid		I
	RADSAFE safety radius for grid point screening		I
	RADIAL definition of radial grid		I
	SAVIN selection of Savin weights		–
	TOLLDENS density contribution screening [6]		I
	TOLLGRID grid points screening [14]		I
	XLGRID "extra large" predefined grid		I
	XXLGRID "extra extra large" predefined grid		I
	Atomic parameters control		
	RADIUS customized atomic radius	81	I
	FCHARGE customized formal atomic charge	81	I
	Auxiliary		
	PRINT extended printing		
	END close DFT input block		

Numerical accuracy and computational parameters control

BIPOLAR	Bipolar expansion of bielectronic integrals	73	I
BIPOSIZE	size of coulomb bipolar expansion buffer	73	I
EXCHSIZE	size of exchange bipolar expansion buffer	73	I
INTGPACK	Choice of integrals package <input type="text" value="0"/>	92	I
NOBIPCOU	Coulomb bielectronic integrals computed exactly	95	–
NOBIPEXCH	Exchange bielectronic integrals computed exactly	95	–
NOBIPOLA	All bielectronic integrals computed exactly	95	–
POLEORDR	Maximum order of multipolar expansion <input type="text" value="4"/>	95	I
TOLINTEG	Truncation criteria for bielectronic integrals <input type="text" value="6 6 6 6 12"/>	102	I
TOLPSEUD	Pseudopotential tolerance <input type="text" value="6"/>	102	I
Type of execution			
MPP	MPP execution	93	
Type of run			
ATOMHF	Atomic wave functions	72	I
SCFDIR	SCF direct (mono+biel int computed)	96	–
EIGS	S(k) eigenvalues - basis set linear dependence check	81	–
FIXINDEX	Reference geometry to classify integrals	86	–
Basis set - AO occupancy			
FDAOSYM	f and d degeneracies analysis	83	I
FDAOCCUP	f and d orbital occupation guess	84	I
GUESDUAL	Density matrix guess - different Basis set	89	I
Integral file distribution			
BIESPLIT	writing of bielectronic integrals in n files <input type="text" value="n = 1"/> , max=10	73	I
MONSPLIT	writing of mono-electronic integrals in n file <input type="text" value="n = 1"/> , max=10	93	I
Numerical accuracy control and convergence tools			
ANDERSON	Fock matrix mixing	71	I
BROYDEN	Fock matrix mixing	73	I
FMIXING	Fock/KS matrix (cycle i and $i-1$) mixing <input type="text" value="0"/>	87	I
LEVSHIFT	level shifter <input type="text" value="no"/>	92	I
MAXCYCLE	maximum number of cycles <input type="text" value="50"/>	93	I
SMEAR	Finite temperature smearing of the Fermi surface <input type="text" value="no"/>	99	I
TOLDEE	convergence on total energy <input type="text" value="5"/>	101	I
TOLDEP	convergence on density matrix <input type="text" value="16"/>	102	I
Initial guess			
EIGSHIFT	alteration of orbital occupation before SCF <input type="text" value="no"/>	82	I
EIGSHROT	rotation of the reference frame <input type="text" value="no"/>	82	I
GUESSP	density matrix from a previous run	91	–
GUESSPAT	superposition of atomic densities	91	–
Spin-polarized system			
ATOMSPIN	setting of atomic spin to compute atomic densities	72	I
BETALOCK	beta electrons locking	73	I
SPINLOCK	spin difference locking	100	I
SPINEDIT	editing of the spin density matrix used as SCF guess	100	I
Auxiliary and control keywords			

END	terminate processing of block3 input		–
KSYMMPT	printing of Bloch functions symmetry analysis	92	–
NEIGHBOR	number of neighbours to analyse in PPAN	51	I
PARAMPT	output of parameters controlling code dimensions	52	–
PRINTOUT	setting of printing options	53	I
NOSYMADA	No Symmetry Adapted Bloch Functions	95	–
SYMADAPT	Symmetry Adapted Bloch Functions (default)	101	–
SETINF	setting of inf array options	54	I
SETPRINT	setting of printing options	54	I
STOP	execution stops immediately	56	–
TESTPDIM	stop after symmetry analysis	101	–
TEST[RUN]	stop after integrals classification and disk storage estimate	101	–

Output of data on external units

NOFMWF	wave function formatted output not written in file fort.98.	95	–
SAVEWF	wave function data written every two SCF cycles	96	–

Post SCF calculations

POSTSCF	post-scf calculations when convergence criteria not satisfied	96	–
EXCHGENE	exchange energy evaluation (spin polarized only)	83	–
GRADCAL	analytical gradient of the energy	87	–
PPAN	population analysis at the end of the SCF no	96	

Properties

RDFMWF wave function data conversion formatted-binary (fort.98 → fort.9)

Preliminary calculations

NEWK	Eigenvectors calculation	178	I
NOSYMADA	No symmetry Adapted Bloch Functions	95	–
PATO	Density matrix as superposition of atomic (ionic) densities	179	I
PBAN	Band(s) projected density matrix (preliminary NEWK)	179	I
PGEOMW	Density matrix from geometrical weights (preliminary NEWK)	180	I
PDIDE	Energy range projected density matrix (preliminary NEWK)	180	I
PSCF	Restore SCF density matrix	186	–

Properties computed from the density matrix

ADFT	Atomic density functional correlation energy	154	I
BAND	Band structure	156	I
BIDIERD	Reciprocal form factors	157	I
CLAS	Electrostatic potential maps (point multipoles approximation)	158	I
ECHG	Charge density and charge density gradient - 2D grid	163	I
ECH3	Charge density - 3D grid	162	I
EDFT	Density functional correlation energy (HF wave function only)	163	I
EMDLPG	Electron momentum distribution from density matrix	165	I
PMP2	MP2 correction to the Valence Density Matrix	180	
POLI	Atom and shell multipoles evaluation	181	I
POTM	Electrostatic potential - 2D grid	184	I
POT3	Electrostatic potential - 3D grid	182	I
POTC	Electrostatic properties	183	I
PPAN	Mulliken population analysis	96	
XFAC	X-ray structure factors	187	I

Properties computed from the density matrix (spin-polarized systems)
--

ANISOTRO	Hyperfine electron-nuclear spin tensor	155	I
ISOTROPIC	Hyperfine electron-nuclear spin interaction - Fermi contact	167	I
POLSPIN	Atomic spin density multipoles	181	I
Properties computed from eigenvectors (after keyword NEWK)			
ANBD	Printing of principal AO component of selected CO	154	I
BWIDTH	Printing of bandwidth	158	I
DOSS	Density of states	161	I
EMDL	Electron momentum distribution - line	164	I
EMDP	Electron momentum distribution - plane maps	165	I
PROF	Compton profiles and related quantities	185	I
New properties			
POLARI	Berry phase calculations	189	I
SPOLBP	Spontaneous polarization (Berry phase approach)	191	–
SPOLWF	Spontaneous polarization (localized CO approach)	192	–
PIEZOBP	Piezoelectricity (Berry phase approach) preliminary	188	–
PIEZOWF	Piezoelectricity (localized CO approach) - preliminary	188	–
LOCALWF	Localization of Wannier functions	168	I
DIEL	Optical dielectric constant	159	I
Auxiliary and control keywords			
ANGSTROM	Set input unit of measure to Ångstrom	31	–
BASISSET	Printing of basis set, Fock/KS, overlap and density matrices	156	–
BOHR	Set input unit of measure to bohr	34	–
CHARGED	Non-neutral cell allowed (PATO)	62	–
END	Terminate processing of properties input keywords		–
FRACTION	Set input unit of measure to fractional	44	–
MAPNET	Generation of coordinates of grid points on a plane	176	I
NEIGHBOR	Number of neighbours to analyse in PPAN	51	I
PRINTOUT	Setting of printing options	53	I
RAYCOV	Modification of atomic covalent radii	53	I
SETINF	Setting of inf array options	54	I
SETPRINT	Setting of printing options	54	I
STOP	Execution stops immediately	56	–
SYMMOPS	Printing of point symmetry operators	60	–
Info - Output of data on external units			
ATOMIRR	Coordinates of the irreducible atoms in the cell	155	–
ATOMSYMM	Printing of point symmetry at the atomic positions	34	–
COORDPRT	Coordinates of all the atoms in the cell	37	–
CRYAPI_OUT	geometry, BS, direct lattice information	159	–
EXTPRT	Explicit structural/symmetry information	41	–
FMWF	Wave function formatted output in file fort.98. Section 8.2	166	–
INFOGUI	Generation of file with wf information for visualization	167	–
CRYAPI_OUT	Reciprocal lattice information + eigenvalues	159	–

Appendix C

Printing options

Extended printing can be obtained by entering the keywords **PRINTOUT** (page 53) or **SET-PRINT** (page 54).

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.

<i>crystal</i>	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 wheight: 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>	–
<i>crystal</i> - <i>properties</i>		
• 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>KSMMMPRT</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	$\neq 0$	crystal symmetry operators	SYMMOPS	
3	EQUPOS	$\neq 0$	equivalent positions in the reference cell	EQUIVAT	
4	CRYSTA	$\neq 0$	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	$\neq 0$	information on shells symmetry related		
7	GV	N>0	stars of g associated to the first n couples		
7		N<0	stars of g associated to the n-th couple		
8	GORDSH	$\neq 0$	information on couples of shells symmetry related		
9	GSYM11	$\neq 0$	intermediates for symmetrized quantities		
10	GMFCAL	$\neq 0$	nstatg, idime, idimf, idimcou		
11	MAIN2U	$\neq 0$	exchange energy	EXCHGENE	
	MAIND			EXCHGENE	
12	IRRPR	$\neq 0$	symmops (reciprocal lattice)	SYMMOPSR	
13	MATVIC	N	n stars of neighbours in cluster definition		
14	GSLAB	$\neq 0$	coordinates of the atoms in the slab		
15	symdir	$\neq 0$	print symmetry allowed directions	PRSYMDIR	
18	TENSOR	$\neq 0$	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	$\neq 0$	Madelung parameters		
29					
30	CRYSTA	$\neq 0$	write file FINDSYM.DAT		
31		$\neq 0$	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	\neq	properties - exchange correlation printing		
37					
38					
39					
40					
41	SHELL*	$\neq 0$	printing of bipolar expansion parameters		
47	KSYMBA	n	Symmetry Adapted Bloch Functions printing level		
48	KSYMBA	$\neq 0$	Symmetry Adapted Bloch Functions printing active	KSYMPRT	
51	AB	$\neq 0$	B functions orthonormality check		
52	DIF	> 0	Fermi energy - Warning !!!! Huge printout !!!		
53	SCFPRT	$\neq 0$	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	$\neq 0$	mvlu, ksh, idp4		
59	RROTA	N > 0	P(g) matrices - first N vectors at the end of SCF, if PPAN present	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	$\neq 0$	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	
70	FINE2	≠ 0	Mulliken population analysis		
	NEIGHB		at the end of scf cycles		
	POPAN		calls PPBOND, to perform Mulliken analysis		
	PDIBAN				
71	PATIRR	≠ 0	atomic wave function	ATOMICWFF	
	PATIR1	≠ 0	" "	ATOMICWFF	
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 berny 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
<i>crystal</i>	OPTGEOM	34	optaxxx	Geometry input - opt atoms coord. only - 41 See EXTPRT
	OPTGEOM	34	optcxxx	Geometry input - opt cell [atoms] - See 41 EXTPRT
		66	HESSOPT.DAT	Hessian matrix
		68	OPTINFO.DAT	Information to restart optimization
	GAUSS98	92	GAUSSIAN.DAT	Input for GAUSS98 64
	FINDSYM	26	FINDSYM.DAT	data in crystallographic format - read by 37 program findsym(IUCR)
	STRUCPRT	33	STRUC.INCOOR	Cell parameters, coordinates of atoms 56
	COORPRT	33	fort.33	Coordinates of the atoms in the cell 37
	EXTPRT	34	fort.34	Geometry input 41
	PPAN	24	PPAN.DAT	Mulliken population analysis 96
<i>crystal properties</i>	BAND	25	fort.25	Bands (Crgra2006) 156
		24	BAND.DAT	Bands data 156
	CLAS	25	fort.25	Classical potential 158
	DIEL	24	DIEL.DAT	Dielectric constant 159
	DOSS	25	fort.25	Density of states (IPLOT=1) 161
		24	DOSS.DAT	Density of states (IPLOT=2) 161
	ECHG	25	fort.25	Electronic charge density - 2D grid 163
		25	RHOLINE.DAT	Electronic charge density - 1 grid 163
	ECH3	31	—	Electronic charge density - 3D grid 162
			DENS.CUBE.DAT	Electronic charge density - 3D grid CUBE 162 format
			SPIN.CUBE.DAT	Spin density - 3D grid CUBE format 162
	POT3		POT.CUBE.DAT	Electrostatic potential - 3D grid CUBE for- 182 mat
	EMDL	25	fort.25	EMD line (IPLOT=1) 164
		24	EMDL.DAT	EMD line(IPLOT=2) 164
	EMDP	25		EMD - 2D grid 260
	INFOGUI	32		Data for the graphical user interface 167
	POTC	24	POTC.DAT	Electrostatic potential V, Electric field, 183 Electric field gradient
	POTM	25	fort.25	Electrostatic potential - 2D grid 184
	PROF	25	fort.25	Compton profile and related quantities 185 (IPLOT=1)
		24	PROF.DAT	Compton profile and related quantities 185 (IPLOT=2)

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 - Isovalue maps

The value of the function chosen (classic electrostatic potential (CLAS), charge(+spin) density (ECHG), electrostatic potential (POTM)) 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** 8.2 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/cmg/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/cmg/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; total energy, 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** [24] 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)
  0.0000000000000000  3.97787351190423  3.97787351190423
  3.97787351190423  0.0000000000000000  3.97787351190423
  3.97787351190423  3.97787351190423  0.0000000000000000
$coordinates          cartesian coordinates of atoms (bohr)
MG  0.0000000000000000  0.0000000000000000  0.0000000000000000  12
O   0.0000000000000000  0.0000000000000000  -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 -0.3333333333 0.3333333333 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 162), **POT3** (page 182), **GRID3D** (page 166) 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,npc, 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* npc 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 167). 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

```

REFLECTANCE.DAT

Written by **REFLECTANCE** in **FREQCALC** input block.

REFLECTANCE.DAT contains: 1 column reporting frequencies and 3 columns for each explored direction, containing R , $Im(1/\epsilon)$ and $Im(\epsilon)$, respectively.

Suppose we have the following reflectance input block

```

. . . . .
FREQCALC
INTENS
[options for INTENS]
DIELTENS or DIELISO
. . . . .
[optional FREQCALC keywords]
. . . . .
REFLECTANCE
REFLDIR
2
1 2
END

```

The first column in the generated REFLECTANCE.DAT contains frequencies, from column 2 to 4 R , $Im(1/\epsilon)$ and $Im(\epsilon)$ corresponding to reflection direction 1 are listed, and from column 5 to 7 the same quantities corresponding to reflection direction 2 are reported.

Suppose we want to plot R in the two directions. Once *gnuplot* is opened on the terminal (type *gnuplot*), it is sufficient to type

```
plot 'REFLECTANCE.DAT' using 1:2
```

where 1 stands for "first column assigned to x axis and second column to y axis". The plot of R corresponding to the first direction 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

```

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>.

In a similar way, we can type

```
plot 'REFLECTANCE.DAT' using 1:5
```

in order to obtain R along the second reflection direction.

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 inpfname.GRED and inpfname.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** 8.2) 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:

$$\begin{aligned} G(\alpha; \mathbf{r} - \mathbf{A})G(\beta; \mathbf{r} - \mathbf{B}) &= \exp(-\alpha_i(\mathbf{r} - \mathbf{A})^2) \exp(-\alpha_j(\mathbf{r} - \mathbf{B})^2) \\ &= \exp(-\alpha(\mathbf{r}^2 + \mathbf{A}^2 + 2\mathbf{r}\mathbf{A}) - \beta(\mathbf{r}^2 + \mathbf{B}^2 + 2\mathbf{r}\mathbf{B})) \\ &= \exp\left[-\xi\left((\mathbf{r} - \mathbf{P})^2 + \mathbf{P}^2 - \frac{\alpha\mathbf{A}^2 + \beta\mathbf{B}^2}{\xi}\right)\right]. \end{aligned} \quad (\text{E.6})$$

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 [138] 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 , [139] 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 $-\ell \leq m \leq \ell$. [140]

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*, [139] 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; [140]

$$\begin{aligned}
\Xi_\vartheta &= \int_0^\pi d\vartheta \left(P_\ell^{|m|}(\cos \vartheta) \right)^2 \sin \vartheta \\
&= \frac{2(\ell+|m|)!}{(2\ell+1)(\ell-|m|)!}, \tag{E.34}
\end{aligned}$$

where the Legendre polynomials' properties have been used, [140] 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, [140] 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. [138] 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 $\pi^{5/8} 2^{1/4}$; [23] therefore, in the code, pre-Gaussian factors are not stored, but the following quantities, that we shall call *code pre-Gaussian constants*:

$$S_i^{\lambda} = \pi^{5/8} 2^{1/4} n_{\lambda,i}^{00} \quad (\text{E.76})$$

$$P_i^{\lambda} = \pi^{5/8} 2^{1/4} n_{\lambda,i}^{1m} \forall m = 0, 1, -1 \quad (\text{E.77})$$

$$D_i^{\lambda} = \pi^{5/8} 2^{1/4} \sqrt{\frac{(2 + |m|)!}{(2 - \delta_{m0})(2 - |m|)!}} n_{\lambda,i}^{2m} \forall m = 0, 1, -1, 2, -2. \quad (\text{E.78})$$

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 s (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:

$$P_i^{\lambda} = \frac{\pi^{5/8} 2^{1/4}}{2\alpha_i} n_{\lambda,i}^{1m} \forall m = 0, 1, -1 \quad (\text{E.79})$$

$$D_i^{\lambda} = \frac{\pi^{5/8} 2^{1/4}}{(2\alpha_i)^2} \sqrt{\frac{(2 + |m|)!}{(2 - \delta_{m0})(2 - |m|)!}} n_{\lambda,i}^{2m} \forall m = 0, 1, -1, 2, -2. \quad (\text{E.80})$$

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 15) 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 47).

Geometry optimization

- Default choice modified: TRUSRADIUS scheme active.
Use keyword **NOTRUSTR** in **OPTGEOM** input block (page 111) 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**
- 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
- **FDOCCUP** (input block3, page 84) 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

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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