CRYSTAL2003

1.0

User's Manual

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Contents

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 6.

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 18. 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 cannot treat helical structures (translation followed by a rotation around the periodic axis). However, when commensurate rotations are involved, a suitably large unit cell can be adopted.

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 supercell with a defect and a large variety of structure editing. See Section 2.1

Previous releases of the software in 1988 (CRYSTAL88, [1]), 1992 (CRYSTAL92, [2]), 1996 (CRYSTAL95, [3]) and 1998 (CRYSTAL98, [4]), 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.

The CRYSTAL package has been developed over a number of years. Many of the algorithms developed and reviews of the applications of the code have been previously published (for instance, [5, 6, 7, 8, 9, 10, 11, 12, 13]).

The required citation for this work is:

V.R. Saunders, R. Dovesi, C. Roetti, R. Orlando, C. M. Zicovich-Wilson,
N.M. Harrison, K. Doll, B. Civalleri, I. Bush, Ph. D'Arco, M. Llunell
CRYSTAL2003 User's Manual, University of Torino, Torino, 2003

CRYSTAL2003 output will display the references relevant to the property computed, when necessary.
The following sites will supply updated information on the CRYSTAL code:

http://www.cse.dl.ac.uk/Activity/CRYSTAL

http://www.crystal.unito.it

Functionality

The basic functionality of the code is outlined below.

The single particle potential	
Restricted Hartree-Fock Theory	
Unrestricted Open Shell Hartree-Fock Theory	
Density Functional Theory for Exchange and Correlation	
Spin Density Functional Theory	
Hybryds HF-DFT (B3LYP-B3PW)	
Effective Core Pseudopotentials	
Finite field perturbation added to the Hamiltonian	*
Algorithms	
Parallel processing (replicated data)	
Massive Parallel Processing (distributed data)	*
Traditional SCF	
Full Direct SCF	*
Structural Editing	
Use of space, layer, rod and point group symmetry	
Deformation of the crystallographic cell	
Removal, insertion, deletion and substitution of atoms	
Displacement of atoms	
Rotation of groups of atoms	
Extraction of surface models from a 3D crystal structure	
Cluster generation from a 3D crystal	
Cluster of molecules from molecular crystal	
Properties	
Band structure	
Density of states	
Electronic charge density maps	
Electronic charge density on a 3D grid	
Mulliken population analysis	
Spherical harmonic atom and shell multipoles	
X-ray structure factors	
Electron momentum distributions	
Compton profiles	
First order density matrix	*
Reciprocal form factors	*
Electrostatic potential, field and field gradients	
Spin polarized generalization of properties	
Hyperfine electron-nuclear spin tensor	
A posteriori Density Functional correlation energy	
Localization of Crystalline Orbitals	*
Spontaneous polarization through Berry phase approach	
Spontaneous polarization through localized orbitals approach	*
Piezoelectricity through Berry phase approach	*
Piezoelectricity through localized orbitals approach	*
Optical dielectric constant	*
Analytic nuclear coordinates gradient of the energy	*
Geometry optimizer	*

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.

- *italic*   optional input

- ——————*optional input records follow*——————II

- ——————additional input records follow——————II

Part of the code is written in fortran 77. The name of the variables is associated with the type of data, following the fortran 77 convention: if the first letter of the name is I, J, K, L, M or N, the type is integer. Otherwise the type is real.

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 25): `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 be typed left-justified, with no leading blanks.

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conventional atomic number (usually callet NAT) is used to associate a given basis set with an atom. The real atomic number is the remainder of the division NAT/100.

Acknowledgements

Getting Started

See $\boxed{\text{http://www.crystal.unito.it}}$ $\rightarrow$ documentation $\rightarrow$ README.

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 CRYSTAL2003. 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) or to the Daresbury team (crystal@dl.ac.uk).

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
SLAB   2D system
POLYMER   1D system
MOLECULE   0D system
EXTERNAL   geometry from external file
DLVINPUT   geometry from DLV [18] Graphical User Interface.

Three input schemes are used. The first is for crystalline systems, and is specified by the keyword **CRYSTAL**. The second is for slabs, polymers and molecules as specified by the keywords **SLAB**, **POLYMER** or **MOLECULE** respectively. In the third scheme, with keyword **EXTERNAL** or **DLVINPUT**, the unit cell, atomic positions and symmetry operators may be provided directly (see Appendix F, page 181). Such an input file can be prepared by the keyword **EXTPRT** (input block 1, page 31; **properties**). Sample input decks for a number of structures are provided in section 4.1, page 115.

Geometry input for crystalline compounds

rec	variable	value	meaning
● ∗	IFLAG		convention for space group identification (Appendix A.1, page 155):
		0	space group sequential number(1-230)
		1	Hermann-Mauguin alphanumeric code
	IFHR		type of cell for rhombohedral groups (meaningless for non-rhombohedral crystals):
		0	hexagonal cell
		1	rhombohedral cell
	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
● ∗			space group identification code (following IFLAG value):
	IGR		space group sequence number (IFLAG=0)
	or		
A	AGR		space group alphanumeric symbol (IFLAG=1)
			if IFSO > 1 insert ─────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],		**minimal** set of crystallographic cell parameters:
	$[\alpha]$,$[\beta]$		translation vector[s] length [Ångstrom],
	$[\gamma]$		crystallographic angle[s] (degrees)
● ∗	NATR		number of atoms in the asymmetric unit.
			insert NATR records ─────II
● ∗	NAT		conventional atomic number [1]
	X,Y,Z		atom coordinates in fractional units of crystallographic lattice vectors
			optional keywords terminated by **END/ENDGEOM** or **STOP** ─────II

Geometry input for molecules, polymers and slabs

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, fractionary (direction with translational symmetry) or Ångstrom (non periodic direction).

translational	unit of measure of coordinates		
symmetry	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 162)
		1D - polymers (Appendix A.3, page 159)
		2D - slabs (Appendix A.2, page 158)
		──────────── *if polymer or slab, insert*────────────II
● *	a,[b],	minimal set of lattice vector(s)- length in Ångstrom
		(b for rectangular lattices only)
	[γ]	$\widehat{AB}$ angle (degrees) - triclinic lattices only
● *	NATR	number of non-equivalent atoms in the asymmetric unit
		──────────── insert NATR records ────────────II
● *	NAT	conventional atomic number
	X,Y,Z	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
		──────── optional keywords terminated by **END or STOP** ────────**II**

Geometry input from external geometry editor

The keywords **EXTERNAL** and **DLVINPUT** select the third input scheme. They work for molecules, polymers, slabs and crystals. The input data are read from Fortran unit 34. The unit cell, atomic positions and symmetry operators are provided directly according to the format described in Appendix F, page 181. Coordinates in Ångstrom. Such an input file is written when OPTBERNY route for geometry optimization is chosen, and can be prepared by the keyword **EXTPRT** (input block 1, page 31; **properties**).

The geometry so defined can be modified by inserting any geometry editing keyword (page 22) after EXTERNAL.

Comments on geometry input

1. All coordinates in Ångstrom. In geometry editing the unit of measure of coordinates may be modified by entering the keywords **FRACTION** (page 31) or **BOHR** (page 27).

2. The geometry of a system is defined by the crystal structure ([19], Chapter 1 of ref. [20]). Reference is made to the International Tables for Crystallography [21] 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
rhombohedral	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 163, and are taken from table 5.1 of the International Tables [21].

   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 38, 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 1-4), 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
2nd (default)	1/8	1/8	1/8	36
1st	0.	0.	0.	24

   NB With 2nd setting, the position 0., 0., 0. has multiplicity 4.

   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 34) 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 that 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 $\overline{3}$. See Appendix A.1, page 155.

    Examples:

Group number	input symbol	
137 (tetragonal)	P␣42/N␣M␣C	
10 (monoclinic)	P␣1␣2/M␣1	(unique axis *b*, standard setting)
	P␣1␣1␣2/M	(unique axis *c*)

	P␣2/M␣1␣1	(unique axis a)
25 (orthorhombic)	P␣M␣M␣2	(standard setting)
	P␣2␣M␣M	
	P␣M␣2␣M	

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. 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.

14. The conventional atomic number NAT is used to associate a given basis set with an atom (see Basis Set input, Section 1.2, page 16). 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 (all electron basis set for carbon atom); 206, 306 (core pseudo-potential for carbon atom, Section 2.2, page 51).

    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 [22], 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 50).

15. The keyword **SLAB** (Geometry editing input, page 37) 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.

16. 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.

17. Conventional orientation of slabs and polymers: Polymers are oriented along the x axis. Slabs are parallel to the xy plane.

18. The keywords **MOLECULE** (for molecular crystals only; page 33) and **CLUSTER** (for any n-D structure; page 28) 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 number
		<200	all-electron basis set
		>200	valence electron basis set. ECP (Effective Core Pseudopotential) must be defined (page 51)
		=99	end of basis set input section
	NSHL	n	number of shells
		0	end of basis set input (when NAT=99)
			if NAT > 200 insert ECP input (page 51) ——————————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)
	NG		Number of primitive Gaussian Type Functions (GTF) in the contraction for the basis functions (AO) in the shell
		$1 \leq NG \leq 10$	for ITYB=0 and LAT $\leq$ 2
		$1 \leq NG \leq 6$	for ITYB=0 and LAT = 3
		$2 \leq NG \leq 6$	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.
			if ITYB=0 (general basis set insert NG records ——————————II
● ∗	EXP		exponent of the normalized primitive GTF
	COE1		contraction coefficient of the normalized primitive GTF:
			LAT=0,1 $\rightarrow$ s function coefficient
			LAT=2 $\rightarrow$ p function coefficient
			LAT=3 $\rightarrow$ d function coefficient
	COE2		LAT=1 $\rightarrow$ 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 3.2. When an effective core pseudo-potential is used, the basis set **must** be optimized with reference to that potential (Section 2.2, page 51).

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 25), the corresponding basis set input can remain in the input stream.

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 6, page 139).

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: 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 > 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 51, for information on core pseudo-potentials.

Suppose we have four non-equivalent carbon atoms in the unit cell. Conventional atomic numbers 6 106 206 306 mean that carbon atoms (real atomic number 6) unrelated by symmetry are to be associated with different basis sets: the first two (6, 106) 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.
The optional keywords may follow.

In summary:

1. *CRYSTAL* can use the following all electrons basis sets:

   a)   general basis sets, including *s,p,d* functions (given in input);
   b)   standard Pople basis sets [23] (internally stored)
        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	$(2z^2 - 3x^2 - 3y^2)z, (4z^2 - x^2 - y^2)x, (4z^2 - x^2 - y^2)y,$ $(x^2 - y^2)z, xyz, (x^2 - 3y^2)x, (3x^2 - y^2)y$

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 3: Mulliken population analysis (**PPAN**, page 78), electrostatic multipoles (**POLI**, page 105), projected density of states (**DOSS**,page 91) and to provide an input for some options (**EIGSHIFT**, input block 4, page 74).

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

6. 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 to S functions
1	SP	8.	if CHE>2, 2 to S and (CHE−2) to P functions, if CHE≤2, CHE to S function
2	P	6.	CHE to P functions
3	D	10.	CHE to D functions
4	F	14.	CHE to F functions
5	G	18.	CHE to G functions

7. 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.

8. 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.*

9. 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 built as a superposition of atomic (or ionic) density matrices (default option, **GUESS-PAT** 2.4). When a different guess is required (**GUESSF** or **GUESSP**), the shell charges are not used, but checked for electron neutrality when the basis set is entered.

10. 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 [24]. This is obtained by entering the keyword **CHARGED** (page 48) after the standard basis set input.

11. 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 48).

12. 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 and adequate description of the tails of the isolated atom charge density [25] (keyword **ATOMHF**, input block 3, page 57).

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

http://www.crystal.unito.it

1.3 General information, computational parameters, hamiltonian

No input is required if the default values are used. Note however that **END/ENDM** or **STOP**, to close the section, are always needed. If no Hamiltonian is specified, RHF (Restricted Hartree-Fock Hamiltonian) is assumed.

1.4 SCF input

rec	variable	value	meaning
			if the system is periodic insert ————II
• *	IS		Shrinking factor in reciprocal space (Section 6.7, page 145)
	IDUM		not used.
	ISP		Shrinking factor for a denser k point net (Gilat net) in the evaluation of the Fermi energy and density matrix.
			if IS = 0 insert ————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 **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 **k** value, and diagonalized, to obtain eigenvectors and eigenvalues:

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

$$H_k A_k = Sk A_k E_k$$

A second shrinking factor, ISP, defines the sampling of k points, i "Gilat net", used for the calculation of the density matrix and the determination of Fermi energy in the case of conductors, when bands are not fully occupied.

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

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

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

In 2D crystals, IS3 is set equal to 1; in 1D crystals both IS2 and IS3 are set equal to 1. Only points ki 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 6.7, page 145. 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 **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). The **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 gray), and the coordinates of the $\mathbf{k}_i$ points according to a Monkhorst-Pack sampling, with shrinking factor 3 and 6.

ISP shrinking factor of reciprocal lattice vectors in the Gilat net (see [7], 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.
Note. The value used in the calculation is ISP=IS*NINT(MAX(ISP,IS)/IS)

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 78.

Some tools for accelerating convergence are given through the keywords **LEVSHIFT** (page 77 and tests 29, 30, 31, 32, 38), **FMIXING** (page 75), **SMEAR** (page 79), **BROYDEN** (page 73) and **ANDERSON** (page 72).
At each SCF cycle the total atomic charges, following a Mulliken population analysis scheme, and the total energy are printed.
The defaulty 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:
TOLSCF (tolerance on change in eigenvalues and total energy),
TOLENE (tolerance on change in total energy),
TOLDEP (tolerance on SQM in density matrix elements),
MAXCYCLE (maximum number of cycles).

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** and **BETALOCK**.

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 **TESTGEOM**.

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** and **BREAKSYM**, 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 is written. 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	27	–
MAKESAED	printing of symmetry allowed elastic distortions (SAED)	32	–
PRSYMDIR	printing of displacement directions allowed by symmetry.	35	–
SYMMDIR	printing of symmetry allowed geom opt directions	40	–
SYMMOPS	printing of point symmetry operators	40	–
TENSOR	tensor of physical properties	40	I

Symmetry information and control

BREAKSYM	allow symmetry reduction following geometry modifications	28	–
KEEPSYMM	maintain symmetry following geometry modifications	32	–
MODISYMM	removal of selected symmetry operators	32	I
PURIFY	cleans atomic positions so that they are fully consistent with the group	35	–
SYMMREMO	removal of all symmetry operators	40	–
TRASREMO	removal of symmetry operators with translational components	40	–

Modifications without reduction of symmetry

ATOMORDE	reordering of atoms in molecular crystals	25	–
NOSHIFT	no shift of the origin to minimize the number of symmops with translational components before generating supercell	34	–
ORIGIN	shift of the origin to minimize the number of symmetry operators with translational components	34	–
PRIMITIV	crystallographic cell forced to be the primitive cell	35	–
REDEFINE	definition of a new cell, with $xy \parallel$ to a given plane	36	I

Atoms and cell manipulation (possible symmetry reduction (BREAKSYMM)

ATOMDISP	displacement of atoms	25	I
ATOMINSE	addition of atoms	25	I
ATOMREMO	removal of atoms	25	I
ATOMROT	rotation of groups of atoms	26	I
ATOMSUBS	substitution of atoms	27	I
ELASTIC	distortion of the lattice	30	I
USESAED	given symmetry allowed elastic distortions, reads δ	41	I
SUPERCEL	generation of supercell - input refers to primitive cell	38	I
SUPERCON	generation of supercell - input refers to conventional cell	38	I

From crystals to slabs

SLABCUT	generation of a slab parallel to a given plane (3D→2D)	37	I

From periodic structure to clusters

CLUSTER	cutting of a cluster from a periodic structure (3D→0D)	28	I
HYDROSUB	border atoms substituted with hydrogens (0D→0D)	31	I

Molecular crystals

MOLECULE	extraction of a set of molecules from a molecular crystal (3D→0D)	33	I
MOLEXP	variation of lattice parameters at constant symmetry and molecular geometry (3D→3D)	33	I
MOLSPLIT	periodic structure of non interacting molecules (3D→3D)	34	–
RAYCOV	modification of atomic covalent radii	35	I

BSSE correction

MOLEBSSE	counterpoise method for molecules (molecular crystals only) (3D→0D)	32	I
ATOMBSSE	counterpoise method for atoms (3D→0D)	25	I

Auxiliary and control keywords

ANGSTROM - unit of measure

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

ATOMBSSE - counterpoise for closed shell atoms and ions

rec	variable	meaning
● *	IAT	*label* 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 neighbours, 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 1.4, page 19).

ATOMDISP

rec	variable	meaning
● *	NDISP	number of atoms to be displaced
		———————— insert NDISP records ———————— II
● *	LB	*label* 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 28). Increments are in Ångstrom, unless otherwise requested (keyword **BOHR**, **FRACTION**, page 24). 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 24). Remember that the original symmetry of the system is maintained, applying the symmetry operators to the added atoms if the keyword **KEEPSYMM** (page 28) was previously entered. The default is **BREAKSYM** (page 28). Attention should be paid to the neutrality of the cell (see **CHARGED**, page 48). 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 33) and **MOLSPLIT** (page 34). No input data are required.

ATOMREMO

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

Selected atoms, and related basis set, are removed from the primitive cell (see test 16). A vacancy is created in the lattice. The symmetry can be maintained (**KEEPSYMM**), by removing all the atoms symmetry-related to the selected one, or reduced (**BREAKSYM**). Attention should be paid to the neutrality of the cell (see **CHARGED**, page 48).

NB. The keyword **GHOSTS** (basis set input, page 50) allows removal of selected atoms, leaving the related basis set.

ATOMROT

rec	variable	value	meaning
● *	NA	0	all the atoms of the cell are rotated and/or translated
		>0	only NA selected atoms are rotated and/or translated.
		<0	the atom with *label* |NA| belongs to the molecule to be rotated. The program selects all the atoms of the molecule on the base of the sum of their atomic radii (Table on page 35).
			if NA > 0, insert NA data ⎯⎯⎯⎯⎯⎯ II
● *	LB(I),I=1,NA		*label* of the atoms to be rotated and/or translated.
● *	ITR	>0	translation performed. The selected NA atoms are translated by -**r**, where **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.
			if ITR<0 insert ⎯⎯⎯⎯⎯⎯ II
● *	X,Y,Z		Cartesian components of the translation vector [Å]
			if ITR=0 insert ⎯⎯⎯⎯⎯⎯ II
● *	N1,N2		*label* of the atoms defining the axis.
	DR		translation along the axis defined by the atoms N1 and N2, in the direction N1 → N2 [Å].
			if IRO<0 insert ⎯⎯⎯⎯⎯⎯ II
● *	A,B,G		Euler rotation angles (degree).
	IPAR		defines the origin of the Cartesian system for the rotation
		0	the origin is the barycentre of the NAT atoms
		>0	the origin is the atom of *label* IPAR
			if IRO>0 insert ⎯⎯⎯⎯⎯⎯ II
● *	N1,N2		*label* of the atoms that define the axis for the rotation
	ALPHA	≠ 0.	rotation angle around the N1–N2 axis (degrees)
		0.	the selected atoms are rotated anti-clockwise in order to orientate the N1–N2 axis parallel to the z axis.

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

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

1. Cartesian components of the translation vector (ITR < 0);

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

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

The rotation can be performed in three different ways:

1. by defining the Euler rotation angles α, β, γ and the origin of the rotating system (IRO < 0). The axes of the rotating system are parallel to the axes of the Cartesian reference system. (The rotation is given by: $R^{\alpha z} R^{\beta x} R^{\gamma z}$, where R are the rotation matrices).

2. by defining the rotation angle α around an axis defined by two atoms A and B. The origin is at A, the positive direction A→B.

3. by defining a z' axis (identified by two atoms A and B). The selected atoms are rotated, in such a way that the A–B z' axis becomes parallel to the z Cartesian axis. The origin is at A and the positive rotation anti clockwise (IRO>0, α=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	*label* 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**). 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 48.

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 30).

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 (**ATOMSPI**, block4, page 73) 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 25, keyword **ATOMINSE**).

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 then 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
				if NNA $\neq$ 0 insert 1 record ————————————————II
●	∗	RNNA		radius of sphere in which to search for neighbours of a given atom in order to print the nearest neighbour analysis
				if NCN $\neq$ 0 insert NCN records ————————————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
				if NMO > 0 insert NMO records —— II
●	*	IPAD		*label* of the atom to be modified *(cluster sequence)*
		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).
				if NMO < 0 insert —— II
●	*	IMIN		*label* of the first atom to be saturated *(cluster sequence)*
		IMAX		*label* of the last atom to be saturated *(cluster sequence)*
		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 1.4, page 19). See test 16.

COORPRT

Geometry information is printed: cell parameters, fractionary coordinates of all atoms in the reference cell, symmetry operators.
A formatted file is written (in append mode) in fortran unit 33. See Appendix F, page 181.
No input data are required.
Fortran unit 33 has the right format for the program Xmol [26].
Download from `http://biotech.icmb.utexas.edu/mime/xmol.html`

or by the program **MOLDEN** [27] which can be downloaded from:
`www.cmbi.kun.nl/ schaft/molden/molden.html`

ELASTIC

An elastic deformation of the lattice may be defined in terms of the Z or ϵ strain tensors defined in section 6.9, page 147.

rec	variable	value	meaning
● *	IDEF	± 1	deformation through equation 6.36, Z matrix.
		± 2	deformation through equation 6.35: ϵ matrix.
		> 0	volume conserving deformation (equation 6.37).
		< 0	not volume conserving (equation 6.36 or 6.35).
● *	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 $V^{-1}\frac{\partial^2 E}{\partial \epsilon_i^2}\mid_{\epsilon_i=0}$, 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 24). The suggested value for IDEF is -2 (deformation through equation 6.35, *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 150) elastic constants of Li_2O [28].

```
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 6.35
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 defor-
                 | mation
. . . . . . .     |
```

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 27). See test 20 for complete input deck, including shift of the Li atoms.

END

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

EXTPRT

A formatted input deck with explicit structural/symmetry information is written in fortran unit 34. If the keyword is entered many times, the data are overwritten. The last geometry is recorded. The deck may be used as input of the crystal geometry to CRYSTAL through the EXTERNAL keyword (final optimized geometry, geometry obtained by editing who modified the original space group). See Appendix F, page 181. No input data are required.

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.

HYDROSUB - substitution with hydrogen atoms

rec	variable	meaning	
● *	NSOST	number of atoms to be substituted with hydrogen	
		insert NSOST records	II
● *	LA	*label* of the atom to substitute	
	LB	*label* 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

n 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 25, 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

This generates symmetry allowed elastic distortions. No input data are required.

MODISYMM

rec	variable	meaning
● ∗	N	number of atoms to be attached a flag
● ∗	LA,LF(LA),L=1,N	atom *labels* 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

A formatted input deck for the visualization program **MOLDRAW** [29] is written on fortran unit 93. If the keyword is entered many times, the data are overwritten. The last geometry can be visualized.

No input data are required. See:

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

MOLEBSSE - counterpoise for molecular crystals

rec	variable	meaning
● ∗	NMOL	number of molecules to be isolated
		———— insert NMOL records ————
● ∗	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
● ∗	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 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 33). The molecule is reconstructed on the basis of the covalent radii reported in Table on page 35.

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

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

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

   | and |

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

Warning. The system obtained is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.4, page 19). See test 19.

MOLECULE - Extraction of n molecules from a molecular crystal

rec	variable	meaning
● *	NMOL	number of molecules to be isolated
		———— insert NMOL records ————II
● *	ISEED	*label* of one atom in the nth 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 35).

The program stops after printing full neighbouring analysis of the non-equivalent atoms, up to n neighbours (default value 3; keyword **NEIGHBOR**, page 34 to modify it).

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 25). 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 16).

The keyword **GAUSS98**, entered in input block 2 (basis set input), writes an input deck to run Gaussian 98 (see page 49)

Warning. The system is 0D. No reciprocal lattice information is required in the **scf** input (Section 1.4, page 19).

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
● *	δa,[δb],[δc],	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 13) 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 35)

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 1.4, page 19).
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).
See test 21.

NEIGHBOR/NEIGHPRT

rec	variable	meaning
● ∗	INEIGH	number of neighbours of each non-equivalent atom to be printed

The option is active when analyzing the crystal structure (bond lengths and bond angles) and when printing the bond populations following Mulliken analysis. Full input deck must be given (block 1-2-3-4),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

To 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.

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 37) 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.

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 163) is set to the identity. No effect on the CPU time: CRYSTAL always refers to the primitive cell. No input data are 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 179.
Extended printing request can be entered in any input block. Printing requests are not transferred from wave function to properties calculation.
See Appendix E, page 177.

PRSYMDIR

Printing of displacement directions allowed by symmetry. The printing is done after the neighbor analysis, before computing the wave function. Full input must be supplied (4 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). 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 ($0 \leq NAT \leq 92$)
	RAY	covalent radius of the atom with atomic number NAT ([Å], default,
		or bohr, if the keyword **BOHR** precedes in the deck)

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

```
                        Table of covalent radii (Angstrom)
 H                                                                               He
 0.68                                                                            1.47
 ---------                                   ----------------------------
 Li   Be                                     B    C    N    O    F    Ne
 1.65 1.18                                   0.93 0.81 0.78 0.78 0.76 1.68
 ---------                                   ----------------------------
 Na   Mg                                     Al   Si   P    S    Cl   Ar
 2.01 1.57                                   1.50 1.23 1.15 1.09 1.05 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.

REDEFINE - 3D unit cell redefinition

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 **SLAB** option.

5. After neighboring analysis, the program stops.

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 **SLAB** (page 37).

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 E, page 179. 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 34).

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 **REDEFINE** (page 36) option. This information can be obtained by a test run, inserting in the geometry input block the keyword **TESTGEOM** (page 40). 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 **SLAB** option run:

1. keyword **REDEFINE**: Rotation of the 3D cell, to have the z axis perpendicular to the (hkl) place, with numbering of the atomic layers in the rotated reference cell, according to their z coordinate of the atoms (insert **STOP** after **REDEFINE** 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 25), **ATOMDISP** (page 25), 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.

STOP

Execution stops immediately. Subsequent input records are not processed.

STRUCPRT

A formatted deck with cell parameters and atoms coordinates in cartesian reference is written in the file STRUC.INCOOR. See appendix F.

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 (use **SUPERCON** for conventional 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 14). To avoid this operation, insert **NOSHIFT** before **SUPERCEL**

Atoms that are related by translational symmetry in the unit cell are considered inequivalent 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 25), **ATOMSUBS** (page 27), **ATOMINSE** (page 25), **ATOMDISP** (page 25), **SLAB** (page 37).

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 4, page 73). See tests 17, 30, 31, 34, 37.

Example.   Construction of supercells of face-centred cubic 3D system ($a = 5.42$ Å).

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 14).

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                       DIRECT LATTICE VECTORS
E1     1.000    -1.000      .000     B1     4.122    -2.380      .000
E2      .000     1.000    -1.000     B2      .000     4.760      .000
E3     1.000     1.000     1.000     B3      .000      .000    12.993

LATTICE PARAMETERS (ANGSTROM AND DEGREES)
```

```
      A       B       C      ALPHA    BETA    GAMMA    VOLUME
   4.76020  4.76020 12.99330  90.000   90.000  120.000   254.97670
```

SUPERCON

A supercell is obtained by defining the new unit cell vectors as linear combinations of the conventional cell vectors. The point symmetry is defined by the number of symmetry operators in the new cell. It may be reduced, not increased. See **SUPERCEL**, page 38 for input instructions.

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.

SYMMDIR

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

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 **NEIGH-BOR**, 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 34), 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,nsaed	δ for each distortion

Given the symmetry allowed elastic distortion (SAED), (printed by the keyword **MAKE-SAED**, page 32) δ for the allowed distortion are given in input.

FIELD- Electric field in the hamiltonian

rec	variable	value	meaning
● ∗	E0MAX		electric field intensity E_0 (in atomic units)
			——— *if* **CRYSTAL 3D** *calculation insert* ———II
● ∗	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

A perturbation due to a finite periodic electric field ($\vec{E}$) is added to the Hamiltonian (Fock or Kohn-Sham):

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

where $\hat{H}_0$ is the unperturbed Hamiltonian and $\hat{H}_1(\vec{E})$ the electric-dipole interaction.
The crystalline orbitals are relaxed under the effect of the field, leading to a perturbed wave function and charge density.

In the three-dimensional case, the applied electric field is periodic, in order to maintain the translational symmetry. The corresponding electric potential has a triangular form ("saw-tooth").
When the field is along the z direction, the perturbation $\hat{H}_1(\vec{E})$ takes the form:

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

where the f^+ or the f^- function is developed in a Fourier series and is chosen according to the symmetry of the supercell in the direction of the applied field:

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

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

C is the cell size in the field direction.
Not implemented fo 0-D (molecules) and 1-D (polymers) systems.

1. A supercell approach (see keywords **SUPERCEL/SUPERCON**, page 38 allows to minimize edge effect and obtain a better convergence of results.

2. The direction of electric field is along z axis, In 2D systems (slab) it is always perpendicular to the slab. The symmetry of the system can be reduced due to the anti-symmetric nature of the field, even if intensity $E_0 = 0$.

3. In 3D systems, as the direction of electric field is always along the z axis, the keyword **ROTATE** (page 36 allows definition of a new crystallographic cell, where in the new Cartesian reference system the z axis is perpendicular to a selected (hkl) plane.

4. In 3D-crystal, 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 supercell, along z axis. Use this option if there is a symmetry plane orthogonal to z axis.

    b) ISYM=−1, triangular potential is anti-symmetric. This option can be used when the supercell does not have a symmetry plane orthogonal to z axis.

5. MUL, the number of term in Fourier expansion, can take values between 1 and 60 (LIM060).

    MUL=40 is sufficient to perfectly reproduce the triangular shape of the potential.
    Note - CPU time is not MUL-dependent.

6. When $|E_0|$ takes high value, the system can reach a non converged conducting state during the SCF process. The threshold $|E_0^{max}|$ value depends on the dielectric susceptibility of the system and on the gap width. For very narrow gap cases, the eigenvalue level shifting technique (keyword **LEVSHIFT**, page 77) can be useful to avoid the SCF fall in a spurious conducting state

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× IS, where IS is the Monkhorst net shrinking factor (see SCF input, page 19.

Conversion factors for electric field
1 AU = 1.71527E+07 ESU·CM^{-2} = 5.72152E+01 C ·M^{-2} = 5.14226E+11 V·M^{-1}

OPTCOORD - Atom coordinates optimization

A modified conjugate gradient algorithm (H.B. Schlegel, J. Comp. Chem. **3**, 214, 1982) is used [30] to optimize the atomic coordinates and locate minima on the potential energy surface (PES). A cell fixed unconstrained optimization of the atomic coordinates can be carried out. Lattice parameters must be optimized numerically point by point.

HF and DFT (pure and hybrid functionals) analytical gradients are used for insulators, both for all-electron and ECP calculations. For conducting systems numerical first derivatives must be computed (keyword **NUMGRAD**).

Geometry optimization can be performed on systems with any periodicity: molecules, polymers, slabs, and crystals.

Gradients are evaluated every time the total energy is computed; the second derivative matrix is built from the gradients. At each step, a one dimensional minimization using a quadratic polynomial is carried out, followed by an n-dimensional search using the Hessian matrix.

The **OPTCOORD** keyword must be the last keyword in the geometry input section. The optimization input block must be closed by the keyword **END** (or **ENDOPT**).

No input data are required, as default values for all parameters controlling the optimization are supplied. The default value for SCF convergence criteria on total energy is set to 10^{-7}.

Geometry optimization is performed in symmetrized cartesian coordinates, in order to exploit the point group symmetry of the lattice. The keyword **PRSYMDIR** (input block 1, page 35), may be used to print the symmetrized directions adopted in the geometry optimization. If there are no symmetry allowed directions, the program prints a warning message and stops.

The output from the wave function and gradient calculation is printed at the first step only. The output from the other steps is routed to fortran unit 65.

The fortran unit 33 contains the cartesian coordinates of the atoms in the unit cell for each geometry optimization step in a simple *xyz* format (see keyword **COORPRT**, input block1 1, page 29). This file is suitable to be read by molecular graphics programs (e.g. Molden, XMol, ...) to display the animation of the geometry optimization run.

Fortran unit 34 contains complete geometry input deck, with the last defined geometry. To run **crystal** with that geometry, insert **EXTERNAL** keyword to define the geometry in the input stream (see keyword **EXTPRT**, input block 1, page 31, for explanation of the format).

Fortran unit 68 contains information to restart optimization. (see keyword **RESTART** in OPTCOORD input block).

ATOMFREE	Partial geometry optimization (default: global optimization)
• * NL	number of atoms "free"
• * LB(L),L=1,NL	*label* of the atoms to move

This keyword allows partial geometry optimization, limited to an atomic fragment rather than the whole system. 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.

FINALRUN	action after geometry optimization - integrals classification is based on the last geometry
● ∗ 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

Truncation of infinite series (Coulomb, exchange, etc.), based on the overlap between two atomic functions (see chapter 6.11), depends on the geometry of a crystal. With default setting of thresholds slightly different truncation levels correspond to different geometries that often introduce small discontinuities in the PES, producing artificial noise in the optimization process. To avoid noise in interpolation of PES, **FIXINDEX** option is always active during optimization. The adopted truncation pattern refers to the starting geometry.

If equilibrium geometry is significantly different from 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 geometry, to calculate correct total energy and gradients.

If the convergence test on the forces is not satisfied, optimization has to be restarted, keeping the integrals classification based on the new geometry.

The three 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.

If the starting and final geometry are not far away, the energy and gradient calculated from the final geometry, but the integrals classification based on the initial geometry, and the values computed with integrals classification based on the final geometry are not very different. 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).

HESGUESS	defines the initial guess for the Hessian
● ∗ ICODE	Initial guess code:
-1	identity matrix (default)
0	numerical estimate (two-points formula)
1	external guess (read from fort.66

By default a unit matrix is adopted as initial Hessian. The Hessian matrix is stored in fortran unit 66 during the optimization at each 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, but this process is very expensive.

MAXOPTC	
● ∗ MAX	maximum number of optimization steps (default 100)

NOGUESS scf guess at each geometry point: superposition of atomic densities at each scf calculation

At each geometry point the default guess for scf is the density matrix calculated at the end of the previous run. If the solution does not correpond at real convergence, but to an energy stabilization due to the techiques applied to help convergence (LEVSHIFT, FMIXING, BROYDEN..) when the final density matrix, obtained from the last cycle eigenvectors, is used to build the first hamiltonian matrix, the hamiltonian eigenvalues can be unphysical, no chances to recover the scf process. In those cases it may be better an atomic guess.

NUMGRAD numerical first-derivatives are used during the geometry optimization

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 atom coordinates.

PRINTFORCES printing atomic gradients

PRINTHESS printing Hessian inormation

PRINTOPT prints information on optimization process

PRINT verbose printing

RESTART restart geometry optimization from a previous run

Full 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. Needed information is read from fortran unit 68, and saved in the same file at each step .

The same input deck as for the initial geometry optimization must be used when the RESTART keyword is added.

Convergence criteria

A stationary point on the potential energy surface is found when the forces acting on atoms are zero. So, a 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 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 the current implementation the following defaults are used (in a.u.):

```
TOLDEG   RMS GRADIENT     0.000300 default value - MAX GRADIENT 1.5*TOLDEG
TOLDEX   RMS DISPLAC.     0.001200 default value - MAX DISPLAC. 1.5*TOLDEX
```

The maximum gradient and the maximum displacement threshold are defined as 1.5 times TOLDEG and TOLDEX, respectively.

In case of flat surfaces (e.g. a system formed by two weakly-interacting moieties, a molecule adsorbed on a surface at large distance) it may happen that the convergence criteria on displacements are not satisfied, though the energy does not change. Additional combined test on gradient and energy has been adopted:

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.

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 4, 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)

Full optimization: cell parameters and atomic coordinates

A full optimization of a crystalline structure includes also the optimization of the lattice parameters. However, analytical gradients for the cell constants are not yet implemented; thus, a two-step iterative process must be adopted:

1. the cell parameters are optimized at fixed atomic positions. This must be accomplished by hand or by means of external drivers (e.g. the LoptCG script).

2. atomic positions are relaxed by keeping the lattice parameters fixed at the previously optimum values.

The process is then iterated until convergence is attained, that is cell constants no longer change and convergence criteria on nuclear forces are satisfied.

Notes - From periodic structure to molecules and clusters

The geometry editing described in this section allow the generation of finite (non-periodic) systems, derived from periodic structures: clusters, molecules, groups of molecules (for example, dimers), functional groups. The atoms in a molecular crystal are assigned to the same molecule when their distance is shorter than the sum of the covalent radii, according to table at page 35.

The possibility of computing the wave function of a finite cluster allows the comparison of data with those computed for the original periodic structure. In this way the exact nature of the 'border effect' introduced by the cluster approximation in solid-state calculations may be analyzed [31, 32].

The default value of covalent radii can be modified for selected atoms by the option **RAYCOV** (page 35). This modification may be necessary to force the correct definition of a fragment in the **MOLECULE** and **CLUSTER** options, as well as in the **MOLEBSSE** option (page 47).

Warning
The result of the geometry editing: **CLUSTER, MOLECULE**, **ATOMBSSE** and **MOLEBSSE** is a 0D system. No reciprocal lattice information is required in the **scf** input (Section 1.4, page 19).

ATOMORDE can be applied to molecular crystals only. The *molecules* ordered in the lattice are defined as groups of atoms with a separation less than the sum of their covalent radii (Table on page 35). 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 35)

Notes - From 3D periodic structure to 2D Slab model for surfaces

```
to be written
at least:
test on thickness of the slab
non-polar surfaces,
calculation of surface energy
```

Notes - BSSE correction - counterpoise scheme

The counterpoise method [33] is applied to correct the Basis Set Superposition Error for atoms, ions or molecules. An atom or cluster of atoms surrounded by the basis functions of the neighbours are extracted from the periodic structure.

A BSSE estimate, maintaining the periodic symmetry of the system, can be obtained transforming into ghosts selected atoms in the lattice (keyword **GHOSTS**, page 50, test 36).

```
example: urea bulk
```

2.2 Basis set input

Symmetry control			
ATOMSYMM	printing of point symmetry at the atomic positions	27	–

Basis set modification			
CHEMOD	modification of the electronic configuration	48	I
GHOSTS	eliminates nuclei and electrons, leaving BS	50	I

Auxiliary and control keywords			
CHARGED	allows non-neutral cell	48	–
PARAMPRT	printing of parameters controlling code dimensions	35	–
PRINTOUT	setting of printing options	35	I
SETINF	setting of inf array options	36	I
SETPRINT	setting of printing options	37	I
STOP	execution stops immediately	38	–
SYMMOPS	printing of point symmetry operators	40	–
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	49	–

ATOMSYMM

See input block 1, page 27

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.

CHEMOD - modification of electronic configuration

rec		variable	meaning
●	∗	NC	number of configurations to modify
●	∗	LA	*label* 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 32).

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 on fortran unit 92 an input deck to run Gaussian 94 (or Gaussian 98) [34, 35]. The deck can be prepared without the calculation of the wave function by entering the keyword **TESTPDIM** in input block 3 (page 69). For periodic systems, coordinates and basis set for all the atoms in the reference cell are written.
If the keyword is entered many times, the data are overwritten. The fortran file fort.92 contains the data corresponding to the last call.
No input data required.

1. The route card specifies:

method	HF
basis set	GEN
type of job	SP
geometry	UNITS=AU

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)

To compare molecular energies obtained with GAUSSIAN and CRYSTAL, default computational parameters of CRYSTAL must be modife by inserting the keywords:
NOBIPOLA remove bipolar exoansio to compute coulomb interaction of non overlapping pseudo-charge distributions;
BOHRANGS follwed by the value adopteb by GAUSSIAN for the conversion factor bohr/ Ångstrom
Warning: Only for 0D systems! The programs does not stop when the keyword **GAUSS94** is entered for 1-2-3D systems. Coordinates and basis set of all the atoms in the primitive cell are written, formatted, on fortran unit 92, following Gaussian 94 scheme.

GHOSTS

rec	variable	meaning
● ∗	NA	number of atoms to be transformed into ghosts
● ∗	LA(L),L=1,NA	*label* 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.

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 test 36.

Warning Do not use with ECP

Warning The keyword **ATOMREMO** (input block 1, page 25) 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.

PARAMPRT - Printing of parametrized dimensions

See input block 1, page 35.

PRINTOUT - Setting of printing environment

See input block 1, page 35.

SETINF - Setting of INF values

See input block 1, page 36.

SETPRINT - Setting of printing options

See input block 1, page 37.

STOP

Execution stops immediately. Subsequent input records are not processed.

SYMMOPS

See input block 1, page 40

Effective core pseudo-potentials.

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.
			if PSN = INPUT insert ————— II
• *	ZNUC		effective core charge (ZN in eq. 2.6).
	M		Number of terms in eq. 2.7
	M0		Number of terms in eq. 2.8 for $\ell = 0$.
	M1		Number of terms in eq. 2.8 for $\ell = 1$.
	M2		Number of terms in eq. 2.8 for $\ell = 2$.
	M3		Number of terms in eq. 2.8 for $\ell = 3$.
			insert M+M0+M1+M2+M3 records ————— 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):

$$W_{ps} = C + W0 + SL \tag{2.5}$$

where:

$$C = -Z_N/r \tag{2.6}$$

$$W0 = \sum_{k=1}^{M} r^{n_k} C_k e^{-\alpha_k r^2} \tag{2.7}$$

$$SL = \sum_{\ell=0}^{3} [\sum_{k=1}^{M_\ell} r^{n_{k\ell}} C_{k\ell} e^{-\alpha_{k\ell} r^2}] P_\ell \tag{2.8}$$

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 ([36, 37]) are of the general form 2.5. In this case, the NKL value given in the tables of ref. [36, 37] must be decreased by 2 ($2 \rightarrow 0$, $1 \rightarrow$ -1, $0 \rightarrow$ -2).

2. Durand and Barthelat (DB) ([38] - [39], [40], [41]), and Stuttgart-Dresden [42] 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).

$$SL = \sum_{\ell=0}^{3} e^{-\alpha_\ell r^2} [\sum_{k=1}^{M_\ell} r^{n_{k\ell}} C_{k\ell}] P_\ell \tag{2.9}$$

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 139) 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. The f terms have not yet been implemented. The program stops when an ECP including f terms ($\ell=3$, M=3) is entered.

```
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 where 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 [36, 43]. 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 ([36, 43]) 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 57), or any atomic package with effective core pseudopotentials. See Chapter 3.2 for general comments on atomic basis function optimization. Bouteiller *et al* [44] have published a series of basis sets optimized for Durand and Barthelat ECPs.

Stuttgart-Dresden ECP (formerly STOLL and PREUSS ECP)

These pseudopotentials are under constant development and the CRYSTAL database is not up to date in all cases (for example, improved pseudopotentials exist for many of the main group elements, and pseudopotentials are also available for 5d and other heavier elements). The most recent pseudopotential parameters, optimized basis sets, a list of references and guidelines for the choice of the pseudopotentials can be found at *http://www.theochem.uni-stuttgart.de/*

These can be used in CRYSTAL via the INPUT keyword (see below).

The format of the pseudopotential data in the database is as follows:

The local term

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

always vanishes ($C_k = 0.000000$), leaving only the semilocal term:

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

Note the different convention for the factor $r^{n_{k\ell}-2}$ compared to equation 2.8

The pseudopotential parameters are given in a table like this:

```
Cl ECP ECP10MWB : 10 3 0 22
Q=7., MEFIT, WB, Ref 17.                              nuclear charge 7
1  2  1.000000    0.000000                             one local term, $n_1$=2, $\alpha_1$ = 1.000000,
                                                      $C_1$=0.000000
2  2  6.394300   33.136632   2  3.197100   16.270728  2    s-projectors   ($M_0$=2),      $n_{1,0}$=2,
                                                      $\alpha_{1,0}$=6.394300, $C_{1,0}$=33.136632 and $n_{2,0}$=2,
                                                      $\alpha_{2,0}$=3.197100, $C_{2,0}$=16.270728
2  2  5.620700   24.416993   2  2.810300   7.683050    2    p-projectors   ($M_1$=2),      $n_{1,1}$=2,
                                                      $\alpha_{1,1}$=5.620700, $C_{1,1}$=24.416993, and $n_{2,1}$=2,
                                                      $\alpha_{2,1}$=2.810300, $C_{2,1}$=7.683050
1  2  5.338100   -8.587649                             1    d-projector    ($M_2$=1),      $n_{1,2}$=2,
                                                      $\alpha_{1,2}$=5.338100, $C_{1,2}$=-8.587649
```

The corresponding basis set (optimized for the free atom) looks like this:

```
Cl s ECP10MWB : 4 1 1.3                           4 primitives, 1 group of them contracted, contracted
                                                  are exponents 1-3
(4s5p)/[2s3p]-Basissatz fuer PP. von Ref 17.
14.0730760 2.3315650  0.5071000  0.1824330    | 4 s-exponents
0.0203450   -0.2892230 0.6303670              | contraction coefficients
```

and

```
Cl p ECP10MWB : 5 1 1.3                           5 primitives, 1 group of them contracted, con-
                                                  tracted exponents are 1-3
(4s5p)/[2s3p]-Basissatz fuer PP. von Ref 17.
3.3531290   0.7856860   0.2674540   0.0782750 | 4 p-exponents
0.0154770                                     | 1 p-exponent
-0.0415520  0.3997480   0.5918290             | contraction coefficients
```

In CRYSTAL, this pseudopotential and basis set is entered as follows:

```
Free input
217 5                              Z=17, chlorine basis set - 5 shells (valence only)
INPUT                              keyword: free ECP - input follows
7.            0 2 2 1 0            nuclear charge 7; number of terms in eq. 2.7 and 2.8
6.394300      33.136632    0       eq. 2.8, 5 records:
3.197100      16.270728    0       α, C, n
5.620700      24.416993    0
2.810300      7.683050     0
5.338100      -8.587649    0       ———————basis set input follows - valence only ——————
0 0 3 2.0 1                        1st shell: s type; 3 GTF; CHE=2; scale fact.=1
14.0730760    0.0203450
2.3315650     -0.2892230
0.5071000     0.6303670
0 0 1 0.0 1                        2nd shell: s type; 1 GTF; CHE=0; scale fact.=1
0.1824330     1.000000
0 2 3 5.0 1                        3rd shell: p type; 3 GTF; CHE=5; scale fact.=1
3.3531290     -0.0415520
0.7856860     0.3997480
0.2674540     0.5918290
0 2 1 0.0 1                        4th shell: p type; 1 GTF; CHE=0; scale fact.=1
0.0782750     1.000000
0 2 1 0.0 1                        5th shell: p type; 1 GTF; CHE=0; scale fact.=1
0.0154770     1.000000
```

The Hartree-Fock energy of the atomic ground state with this choice of pseudopotential and basis set is -1.472982977E+01 hartree.

RCEP Stevens et al.

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. [45, 46]. 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   General information, computational parameters, hamiltonian

Single particle Hamiltonian			

RHF	Restricted Closed Shell	68	–
UHF	Unrestricted Open Shell	70	–
ROHF	Restricted Open Shell	70	–
DFT DFT Hamiltonian		70	–
SPIN	spin-polarized solution	59	–

Choice of the exchange-correlation functionals			
EXCHANGE exchange functional		59	I
LDA	Dirac-Slater [47] (LDA)		
VBH	von Barth-Hedin [48] (LDA)		
BECKE	Becke [49] (GGA)		
PWGGA	Perdew-Wang 91 (GGA)		
PBE	Perdew-Becke-Ernzerhof [50] (GGA)		
CORRELAT correlation functional		59	I
VBH	von Barth-Hedin [48] (LDA)		
PWGGA	Perdew-Wang 91 (GGA)		
PBE	Perdew-Becke-Ernzerhof [50] (GGA)		
PZ	Perdew-Zunger [51] (LDA)		
PWLSD	Perdew-Wang 92 [52, 53, 54] (GGA)		
VWN	Vosko,-Wilk-Nusair [55] (LDA)		
P86	Perdew 86 [56] (LDA)		
LYP	Lee-Yang-Parr [57] (GGA)		
HYBRID	hybrid mixing	60	I
NONLOCAL	local term parameterization	60	I
B3PW	B3PW parameterization	60	–
B3LYP	B3LYP parameterization	60	–

Integration method			
[**NUMERICA**] numerical integration (default)			–
RADSAFE	safety radius for grid point screening		I
BATCHPNT	grid point grouping for integration		I
FITTING	integration through auxiliary basis set fitting	172	I:
BASIS	Auxiliary basis set input	172	I
TOLLPOT 9			–
LINEQUAT		173	I

Numerical accuracy control			
[**BECKE**]	selection of Becke weights (default)		–
SAVIN	selection of Savin weights		–
RADIAL	definition of radial grid		I
ANGULAR	definition of angular grid		I
LGRID	”large” predefined grid		I
XLGRID	”extra large” predefined grid		I
TOLLDENS	density contribution screening 6		I
TOLLGRID	grid points screening 14		I

Auxiliary and control			
PRINT	**END**		

Numerical accuracy and computational parameters control			

BIPOLAR	Bipolar expansion of bielectronic integrals	58	I
BIPOSIZE	size of coulomb bipolar expansion buffer	58	I
EXCHSIZE	size of exchange bipolar expansion buffer	58	I
INTGPACK	Choice of integrals package $\boxed{0}$	67	I
NOBIPOLA	All bielectronic integrals computed exactly	67	–
POLEORDR	Maximum order of multipolar expansion $\boxed{4}$	68	I
TOLINTEG	Truncation criteria for bielectronic integrals $\boxed{6\ 6\ 6\ 6\ 12}$	69	I
TOLPSEUD	Pseudopotential tolerance $\boxed{6}$	69	I

Type of run			
ATOMHF	Atomic wave functions	57	I
MPP	MPP execution - see makefile	67	I
SCFDIR	SCF direct (mono+biel int computed)	68	–
SEMIDIR	integrals in memory	68	I
NOMONDIR	SCF semidirect (mono on disk, biel computed)	67	–
EIGS	S($\mathbf{k}$) eigenvalues - basis set linear dependence check	64	–
FIXINDEX	Reference geometry to classify integrals	65	–

Integral file distribution			
BIESPLIT	writing of bielectronic integrals in n files $\boxed{n=1}$,max=10	58	I
MONSPLIT	writing of mono-electronic integrals in n file $\boxed{n=1}$, max=10	67	I

Auxiliary and control keywords			
PARAMPRT	output of parameters controlling code dimensions	35	–
PRINTOUT	setting of printing options	35	I
SETINF	setting of inf array options	36	I
SETPRINT	setting of printing options	37	I
TESTPDIM	stop after symmetry analysis	69	–
TESTRUN	stop after integrals classification and disk storage estimate	69	–
STOP	execution stops immediately	38	–
END/ENDM	terminate processing of general information keywords		

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 [14]. 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 104), 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.

BIESPLIT - Splitting of large bielectronic integral files

rec	variable	meaning
● ∗	NFILE	number of files to be used $\boxed{1}$ (max 10)

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

BIPOLAR - Bipolar expansion approximation control

rec	variable	meaning
● ∗	ITCOUL	overlap threshold for Coulomb $\boxed{14}$
∗	ITEXCH	overlap threshold for exchange $\boxed{10}$

The bipolar approximation is applied in the evaluation of the Coulomb and exchange integrals (page 143). ITCOUL and ITEXCH can be assigned any intermediate value between the default values (14 and 10) (see page 143) 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
```

DFT

The Kohn-Sham [58, 59] 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 $\boxed{\text{Choice of the exchange-correlation functionals}}$

2 $\boxed{\textit{Integration method}}$

3 $\boxed{\textit{Integration grid and numerical accuracy control}}$

4 $\boxed{\textit{DF energy gradient}}$

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
PZ	LSD. Perdew-Zunger parameterization of the Ceperley-Alder free electron gas correlation results [51]
PWLSD	LSD. Perdew-Wang parameterization of the Ceperley-Alder free electron gas correlation results [52, 53, 54]
VWN	LSD. Vosko-Wilk-Nusair parameterization of the Ceperley-Alder free electron gas correlation results [55]
VBH	LSD. von Barth-Hedin [48]
P86	GGA. Perdew 86 [56]
PWGGA	GGA. Perdew-Wang [60, 52, 53, 54]
LYP	GGA. Lee-Yang-Parr [57]
PBE	GGA. Perdew-Burke-Ernzerhof [50]

EXCHANGE	Exchange potential (default: Hartree-Fock exchange).
	Insert one of the following keywords ————————II
LDA	LSD. Dirac-Slater [47]
VBH	LSD. von Barth-Hedin [48]
BECKE	GGA. Becke [49]
PWGGA	GGA. Perdew-Wang [52, 53, 54]
PBE	GGA. Perdew-Becke-Ernzerhof [50]

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 [61] combined with the non-local correlation PWGGA [60, 52, 53, 54]

B3LYP	Becke's 3 parameter functional [61] combined with the non-local correlation LYP

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

B3PW	**B3LYP**
corresponds to the sequence:	corresponds to the sequence:
EXCHANGE	EXCHANGE
BECKE	BECKE
CORRELAT	CORRELAT
PWGGA	LYP
HYBRID	HYBRID
20	20
NONLOCAL	NONLOCAL
0.9 0.81	0.9 0.81

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 [55]) 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 method

The exchange-correlation contribution to the Kohn-Sham matrix and to gradients is computed through the same quadrature used to compute the exchange-correlation energy [62, 63]. The alternative method of fitting the exchange-correlation potential to an auxiliary basis set of gaussian functions (see Appendix C) is not available for gradients. Therefore, numerical integration is the default choice in CRYSTAL2003.

3. 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 [64] for molecular systems and then extended to periodic systems [65]. 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	
4		15	86		19		71	1730	
5	3	17	110		20		77	2030	
6		19	146		21		83	2354	
7		21	170		22		89	2702	
8	4	23	194		23		95	3074	
9		25	230	*	24		101	3470	
10	5	27	266	*	25		107	389	
11	6	29	302		26		113	4334	
12		31	350		27		119	4802	
13	7	35	434		28		125	5294	
14		41	590		29		131	5810	
15		47	770						

Index of Lebedev accuracy levels

LEV : Lebedev accuracy level
CR98 : corresponding index in CRYSTAL 98
ℓ : maximum quantum number of spherical harmonics used in Lebedev derivation
N_{ang} : number of angular points generated per radial point
* : sets with negative weights, to be avoided

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 [66]. Default choice.

SAVIN Savin weights [67]

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 61) [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 inputing 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. [63]. 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).

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 6.11 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	[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 [68]. 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 maximun 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
```

where `array_name` is one of the following:

```
DFO KSXC1 KSXC2 KSXC2Y KSXC2Z DFXX DFYY DFZZ DFXY DFYZ DFXZ
RHO FRHO AXJ,AYJ,AZJ,VGRID GRAZ GRAY GRAZ
```

In these cases it is recommended that the value of BATCH be reduced, although this may result in some degree of inefficiency (minimum value: 1).

4. DF energy gradient

[NEWTON]

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.

NONEWTON

Calculation of DF gradient can also be performed without weight derivatives by specifying the keyword NONEWTON. In this case the gradients relative to nuclear coordinates do not rigorously sum to 0, and the accuracy of the gradient is more strongly influenced by the quality of the integration grid.

EIGS - Check of basis set linear dependence

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

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

The Cholesky reduction scheme [69], adopted in the standard SCF route, requires linearly independent basis functions.

MPP doesn' support EIGS.

END

Terminate processing of block3, general information, input. Execution continues. Subsequent input records are processed, if required.

EXCHSIZE -Size of buffer for exchange integrals bipolar expansion

rec	variable	meaning
● ∗	ISIZE	size of the buffer in words

Size (words) of the buffer for bipolar expansion of exchange integrals (default value 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
```

FIXINDEX - Geometry and basis set optimization tools

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 6) can lead to the selection of different numbers of bielectronic 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 reference geometry must correspond to the most compact structure, and 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 1.4), 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 11

<div align="center">

or

</div>

BASE	restart with new basis set
	insert basis set input, page 16

<div align="center">

or

</div>

GEBA	restart with new basis set and new geometrical parameters
	___ insert geometry input, page 11 ___
	___ insert basis set input, page 16 ___

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 | *General information keywords* |

3 **FIXINDEX**

    END

4 | **scf** input. Section 1.4 |

4b | **scf** *related keywords (optional; Section 2.4)* |

    END

GEOM	**BASE**	**GEBA**
⇓	⇓	⇓
geometry input(p 11)	basis set input(p 16)	geometry input (p 11)
(block 1, *1b*)	(block 2, *2b*)	(block 1, *1b*)
END	**END**	**END**
		basis set input(p 16)
		(block 2, *2b*)
		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 a file linked to fortran unit 34, the wave function geometry in a file linked to fortran unit 35.

See tests 5 and 20.

INTGPACK - Choice of bielectronic integrals package

rec	variable	value	meaning
● ∗	IPACK	[0]	*s, sp* shells→ POPLE; *p, d* shells → ATMOL
		1	ATMOL for Coulomb integrals;
			POPLE for exchange integrals
		2	POPLE for Coulomb integrals;
			ATMOL for exchange integrals
		3	ATMOL for Coulomb integrals;
			ATMOL for exchange integrals

By default the bielectronic integrals are computed using a set of routines derived from Pople's GAUSSIAN 70 package [15], if *s* and *sp* shells are involved, and by routines derived from ATMOL [17] 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.

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

No input data required.
Massive Parallel Libraries are linked, and matrices in K space are distributed over the processors. MPP doesn't support:

Anderson mixing	**ANDERSON**	4
Broyden mixing	**BROYDEN**	4
Symmetry analysis of Bloch Functions	**KSYMMPRT**	4
Bloch Functions Symmetry Adapted	**SYMADAPT**	4
Printing of eigenvalues of overlap matrix in k space	**EIGS**	3
Restricted open shell wave function	**ROHF**	3
DFT fitting	**DFT/FITTING**	3

NOBIPOLA - Bipolar expansion approximation suppression

All the bielectronic integrals are evaluated exactly. No input data are required. The CPU time in the **integrals** program can increase up to a factor 3.

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.

PARAMPRT - - printing of parametrized dimensions

See input block 1, page 35.

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 6.3, page 141.

PRINTOUT - Setting of printing environment

See input block 1, page 35.

RHF [default]

A restricted closed-shell hamiltonian calculation is performed ([70, 7], Chapter 8 of ref. [20]). Default choice.

ROHF

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.

SEMIDIR

rec	variable	meaning
• ∗	IBUF	number of integral buffers PER PROCESSOR to store in memory (a buffer is about 4 Mbytes)
	IWHAT	flag telling the code what to do with the rest of the integrals
		1 store on disk
		0 recalculate at each cycle

This keyword allows Crystal to run in a semidirect mode. Some of the integrals are calculated only once at the start of the calculation and held in memory, while the others can either be stored on disk or recalculated each cycle. The code also orders the integral evaluation so that the most expensive ones are preferentially stored in memory (and this will also help load balancing in the parallel stuff).

Example

```
SEMIDIR
5 0
```

means: store the first 5 buffers worth of integrals in memory and recalculate the rest each cycle. SEMIDIR should work with both MPP and SCFDIR as well so this means given enough memory you can do a 'conventional' calculation AND use the distributed memory portion of the MPP code.
It can not be used with **BIESPLIT**.

SETINF - Setting of INF values

See input block 1, page 36

SETPRINT - Setting of printing options

See input block 1, page 37.

STOP

Execution stops immediately. Subsequent input records are not processed.

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 34).

TESTRUN - Integrals classification and selection

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 (not *shell* multipolar expansion as in CRYSTAL95) reduces the required space to about 1/3 of the printed value.

Full input (geometry, basis set, general information, SCF) is processed. No input data after the keyword are required. This type of run is fast, and allows an estimate of the resources to allocate for the traditional SCF wave function calculation.

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

	rec	variable	meaning	
●	*	ITOL1	overlap threshold for Coulomb integrals- page 141	6
		ITOL2	penetration threshold for Coulomb integrals-page 142	6
		ITOL3	overlap threshold for HF exchange integrals-page 142	6
		ITOL4	pseudo-overlap (HF exchange series-page 142)	6
		ITOL5	pseudo-overlap (HF exchange series-page 142)	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 6.

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 139) 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).
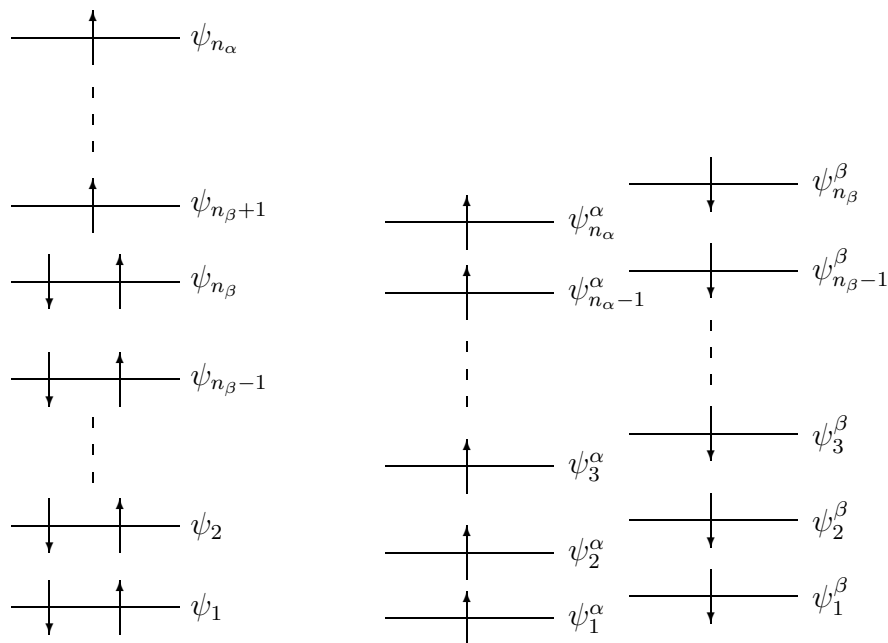
Figure 2.1: Molecular Orbitals diagram for the Restricted Open Shell method (ROHF, left) and for the Unrestricted Open Shell method (UHF, right)

UHF/ROHF - 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) ([7, 71], Chapter 6 of ref. [20]).

In the Restricted Open Shell (**ROHF**) [70] 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. This particular mono-determinantal approach can be used in the open-shell part of CRYSTAL. The correct spin state must be defined by the keyword **SPINLOCK**.

Another mono-determinantal approach for the study of open-shell systems is the UHF method [72]. 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. 2.1.

The double occupancy constraint allows the ROHF approach to obtain solutions that are eigenfunctions of the spin operator, $\widehat{S^2}$, whereas UHF solutions are formed by a mixture of spin states. The greater variational freedom allows the UHF method to produce wave-functions that are energetically more stable than the corresponding ROHF ones; another advantage of the UHF method is that it allows solutions with locally negative spin density (i.e. anti ferromagnetic systems), a feature that ROHF solutions can never exhibit.

To run ROHF with a conducting system does not make much sense. This is because tha aufbau principle is only very roughly obeyed, and when one uses it (say for non-conductors or molecules) it is usual to establish the requisit occupation pattern by carefull use of level shifting.

To use ROHF for a conductor is extremely risky, as the converged state (if there is one) will

rarely be the ground state, and it will converge to different points with the smallest change in numerical conditions (such as diagonalizer accuracy ....).

MPP doesn' support ROHF.

Related keywords

SPINLOCK definition of (n_α - n_β electrons)

BETALOCK definition of n_β electrons.

2.4 SCF input

Numerical accuracy control and convergence tools		
ANDERSON	Fock matrix mixing	72	I
BROYDEN	Fock matrix mixing	73	I
FMIXING	Fock/KS matrix (cycle i and i-1) mixing $\boxed{0}$	75	I
LEVSHIFT	level shifter $\boxed{\text{no}}$	77	I
MAXCYCLE	maximum number of cycles $\boxed{50}$	78	I
SMEAR	Finite temperature smearing of the Fermi surface $\boxed{\text{no}}$	79	I
TOLDEE	convergence on total energy $\boxed{5}$	81	I
TOLDEP	convergence on density matrix $\boxed{?}$	81	I
TOLSCF	convergence on eigenvalues $\boxed{6}$ and total energy $\boxed{5}$	81	I

Initial guess		
EIGSHIFT	alteration of orbital occupation before SCF $\boxed{\text{no}}$	74	I
EIGSHROT	rotation of the reference frame $\boxed{\text{no}}$	74	I
GUESSF	Fock/KS matrix from previous run	76	–
GUESSP	density matrix from a previous run	76	–
$\boxed{\textbf{GUESSPAT}}$	superposition of atomic densities	76	–

Spin-polarized system		
ATOMSPIN	setting of atomic spin to compute atomic densities	73	I
BETALOCK	beta electrons locking	73	I
SPINLOCK	spin difference locking	80	I
SPINEDIT	editing of the spin density matrix	80	I

Auxiliary and control keywords		
END/ENDSCF	terminate processing of scf I keywords		–
KSYMMPRT	printing of Bloch functions symmetry analysis	77	–
NEIGHBOR	number of neighbours to analyse in **PPAN**	34	I
PARAMPRT	output of parameters controlling code dimensions	35	–
PRINTOUT	setting of printing options	35	I
NOSYMADA	No Symmetry Adapted Bloch Functions	78	–
SYMADAPT	Symmetry Adapted Bloch Functions (default)	81	–
SETINF	setting of inf array options	36	I
SETPRINT	setting of printing options	37	I
STOP	execution stops immediately	38	–

Output of data on external units		
NOFMWF	wave function formatted output not written to fortran unit 98.	78	–
KNETOUT	Reciprocal lattice information + eigenvalues	77	–
SAVEWF	wave function data written every two SCF cycles	79	–

Post SCF calculations		
POSTSCF	post-scf calculations when convergence criteria not satisfied	78	–
EXCHGENE	exchange energy evaluation (spin polarized only)	75	–
GRADCAL	analytical gradient of the energy	76	–
PPAN	population analysis at the end of the SCF $\boxed{\text{no}}$	78	

ANDERSON

Anderson's method [73], as proposed by Hamann [74], is applied. No input data are required. MPP doesn't support Anderson mixing.

ATOMSPIN - Setting of atomic spin

rec		variable	meaning
●	∗	NA	number of atoms to attribute a spin
●	∗	LA,LS(LA),L=1,NA	*atom labels* 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 **GUESSF** or **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.

BROYDEN

rec		variable	meaning
●	∗	W0	*W0* parameter in Anderson's paper [75]
	∗	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 [76] scheme, following the method proposed by Johnson [75], 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
```

MPP doesn't support Broyden mixing.
See test 43, a metallic Lithium 5 layers slab, PWGGA Hamiltonian.

BETALOCK - Spin-polarized solutions

rec		variable	meaning
●	∗	INF97	n_β electrons
	∗	INF98	number of cycles the n_β electrons is maintained

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

unit cell. INF95 must be odd when the number of electrons is odd, even when the number of electrons is even.

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	number of the shell in the selected atom Basis Set
	IORB	number of the AO in the selected shell
	SHIF1	α (or total, if Restricted) Fock/KS matrix shift
	[SHIF2	β Fock matrix shift - spin polarized only]
		───── if NORB < 0 ─────
● ∗	IAT	label of the atom
	ISH	number of the shell in the selected atom Basis Set
	IORB1	number of the AO in the selected shell
	IORB2	number of the AO in the selected shell
	SHIF1	α (or total, if Restricted) Fock/KS matrix shift
	[SHIF2	β Fock matrix shift - spin polarized only]

```
notes on irreducible atoms
```

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 locate the degeneracy in order to allow the system to converge to a stable non-metallic solution. The eigenvalue shift is removed after the first SCF cycle.

Example: $KCoF_3$ (test 38). In the cubic environment, two β electrons would occupy the three-fold degenerate t_{2g} bands. A state with lower energy is obtained if the degeneracy is removed by a tetragonal deformation of the cell (keyword **ELASTIC**), and the d_{xy} orbital (see page 18 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 keyword **ATOMSYMM** prints symmetry information on the atoms in the cell.

EIGSHROT

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

    α: all five d orbitals

    β: d_{xz} and d_{yz}

The principal axis of the CoF_6 octahedron, however, is not aligned along the z direction, but lies in the xy plane, at 45^0 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	*label* 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	*label* 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	*label* 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 2.4, page 74)	

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

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

```
CoF2 example
```

END

Terminate processing of block 4, SCF, input (last input block). Execution continues. Subsequent input records are not processed.

EXCHGENE - Exchange energy calculation

In RHF calculations Coulomb and exchange integrals are summed during their calculation, and there is no way to separate the exchange contribution to the total energy. In UHF/ROHF calculations, this option allows the independent calculation and printing of the exchange contribution to the total energy. See equation 6.19, page 142.
No input data are required. See tests 29, 30, 31, 38.

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 (**NUMGRAD**, page 45), analyical gradient is not computed.

GUESSF - Fock/KS matrix from a previous run

The Fock/KS matrix F^0 (direct lattice) is read from disk (from fortran unit 20), and diagonalized (after Fourier transformation to the reciprocal lattice), to compute the first cycle density matrix. The data set containing F^0 is written on fortran unit 9 at the end of a previous **scf** run. No input data are required. When wave function information are stored formatted on fortran unit 98, the data must be converted to binary (program **convert**, page 95, or keyword **RDFMWF**, page 95 of the **properties** program). The two cases, the present one and that used for the restart, must have the same symmetry, and the 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 Fock/KS matrix

Program	inp. block	section	comments
crystal	0	1	Title
	1	1.1	geometry input
	2	1.2	basis set input
	3	1.3	general information
	4	1.4	scf input
save fortran unit 9 (binary wf) or 98 (formatted wf)			

2. Second run - the Fock/KS matrix is read in as a guess to start scf

copy fortran unit 9 to unit 20 (or convert unit 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	general information input **FIXINDEX**
	4	1.4	scf input (**GUESSF**)
	1b	1.1	geometry input present case

Warning The modification of the geometry may result in a different order in the storage of the Fock/KS 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 65).

GUESSP - Density matrix from a previous run

The density matrix P^0 (direct lattice) is read from disk (from fortran unit 20) to start the SCF cycles. Same procedure as for **GUESSF**. No input data are required.
The denist matrix can be edited to modify the spin state. See **SPINEDIT**, page 80.

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 16). 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 16).

KNETOUT - Reciprocal lattice information - Fock/KS eigenvalues

Reciprocal lattice information and Fock/KS eigenvalues are written on fortran unit 30. No input data required.
NEWK must be called before KNETOUT to compute hamiltonian eigenvelues and FErmi energy.
See Appendix D, page 176.

KSYMMPRT

Symmetry Adapted Bloch Functions [12, 13] (page 81)are used as basis for the Fock matrix diagonalization. The results of the symmetry analysis in reciprocal space are printed. At each **k**-point: number of point symmetry operators, number of active IRs, maximum IR dimension and maximum block dimension in the Fock 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 37) before **KSYMMPRT**.

N	information
0	Basic Symmetry Information - At each **k**-point: list of point symmetry operators, IR dimensions and number of Irreducible Sets.
> 0	Symmetry Information - At each **k**-point $\leq$ N: class structure, character table and IR information concerning the K-Little Group. For the rest of the **k**-point the same information as -1 is printed.
< -1	Full Symmetry Information - At each **k**-point: the same information as N > 0, together with the matrix representatives of the point operators.

MPP doesn't support KSYMMPRT.

LEVSHIFT - Eigenvalue level shifting

rec	variable	value	meaning
• *	ISHIFT		The level shifter is set to ISHIFT *0.1 hartree.
	ILOCK	0	no locking
		1	causes a lock in a particular state (eg non-conducting) even if the solution during the SCF cycles would normally pass through or even converge to a conducting state.

The eigenvalue level shifting technique is well known in molecular studies [77, 78], 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 75). 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 a file linked to fortran unit 9, even if SCF ends before reaching convergence for "too many cycles".

NEIGHBOR/NEIGHPRT

See input block 1, page 34

NOSYMADA

The Symmetry Adapted Functions are not used in the Fock matrix diagonalization. No input data are required. This choice increases the diagonalization CPU time when the system has symmetry operators.

NOFMWF - Wave function formatted output

CRYSTAL is writing the formatted wave function on fortran unit 98 at the end of SCF by default. This keyword deletes this feature.

PARAMPRT - - printing of parametrized dimensions

See input block 1, page 35.

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 34, 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. $b(A^0, B^g) = \sum_{\mu \in A} \sum_{\nu \in B} P^g_{\mu\nu} S^g_{\mu\nu}$ 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.

PRINTOUT - Setting of printing environment

See input block 1, page 35.

SAVEWF

The wave function is written on fortran unit 79 every two cycles. The format is the same as the one used for fortran unit 9 at the end of SCF.
No input data required.

SETINF - Setting of INF values

See input block 1, page 36

SETPRINT - Setting of printing options

See input block 1, page 37.

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 6.9, page 140) to the Fermi function;

$$f_j = (1 + e^{\frac{(\epsilon_j - \epsilon_F)}{k_b T}})^{-1} \tag{2.10}$$

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 [79]. In this case the "free energy" of the system may be computed as;

$$
\begin{aligned}
F &= E(T) - k_b T S(T) \\
&= E - k_b T \sum_i^{N_{states}} f_i \ln f_i + (1 - f_i) \ln(1 - f_i)
\end{aligned}
\tag{2.11}
$$

where S is the electronic entropy. Often we wish to compute properties for the athermal limit (T=0). For the free electron gas the dependencies of the energy and entropy on temperature are;

$$
\begin{aligned}
E(T) &= E(0) + \alpha T^2 \\
S(T) &= 2\alpha T
\end{aligned}
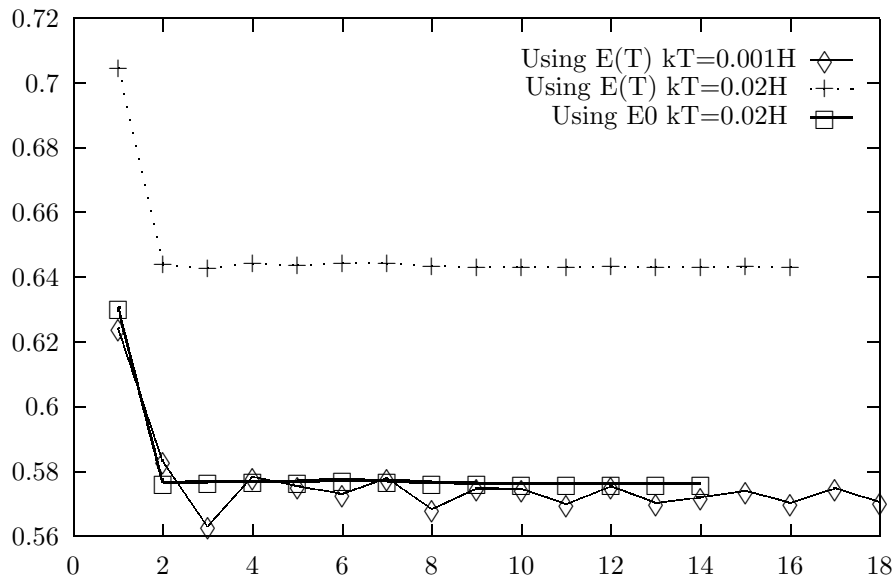\tag{2.12}
$$

and so the quantity

Figure 2.2: The surface energy (J/M^2) of Li(100) for various numbers of layers in a slab model showing the effects of WIDTH (0.02H and 0.001H) and the use of E(T) or E0

$$E0 = \frac{F(T) + E(T)}{2} = E(0) + O(T^3) \tag{2.13}$$

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

Figure 2.2 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/M^2 significantly above that obtained by extrapolating E(T) to the T=0 limit (0.573 J/M^2). The use of E0 at WIDTH=0.02H results in an excellent estimate of the surface energy - 0.576 J/M^2.

SPINEDIT - Editing of the spin density matrix

rec	variable	meaning
● ∗	N	number of atoms for which spin must be reversed
● ∗	LB, L=1,N	*atom labels*

The spin density matrix from a previous run is edited to generate an approximate guess for a new spin configuration. The sign of the elements of the spin density matrix of selected atoms is reversed. The keyword **SPINEDIT** must be combined with **UHF** (input block 3, page 70) and **GUESSP**.

Example: the ferro and anti ferromagnetic solution for the spinel $MnCr_2O_4$ can be obtained by calculating only once the integrals, 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
● ∗	INF95	n_α-n_β electrons
∗	INF96	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 $(N + INF95)/2$, 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.

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	↑ ↓ ↑ ↓
4	ferromagnetic	↑ ↑ ↑ ↑

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

STOP

Execution stops immediately. Subsequent input records are not processed.

SYMADAPT

The Symmetry Adapted Functions are used in the Fock 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.

TOLDEE - SCF convergence threshold on total energy

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

The default value for single point calculation is 5, but 7 in geometry optimization process.

TOLDEP - SCF convergence threshold on density matrix

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

`to be written BC`

TOLSCF - threshold total energy and eigenvalues

rec	variable	meaning
• *	IT1	threshold on eigenvalues RMS $\boxed{6}$
	IT2	threshold on total energy diffference $\boxed{5}$

The SCF ends when the root mean square (RMS) of the change in eigenvalues from cycle $i - 1$ to i is less than 10^{-IT1} **or** the change in the absolute value of the total energy is less than 10^{-IT2}. The energy converges to 10^{-6} hartree/cell in 8-15 cycles in RHF calculation of insulators. The number of cycles may increase for UHF spin polarized systems and can be very high in DFT calculations. The tolerance values to be used depend on the required precision; when IT2=x, IT1=x+2.

Chapter 3

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 on Fortran unit 9, and as formatted data on Fortran unit 98. The wave function data can be transferred formatted from one platform to another (see keyword **RDFMWF**, page 95).
The data set on fortran unit 9 (or 98) is 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 E, page 179, for information on printing.

3.1   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 on fortran unit 9, the keyword **RDFMWF**, entered as 1st record, will read formatted data on fortran unit 98 and convert them in binary on fortran unit 9.
Full information on the system is generated: :

a.	symmetry analysis information	stored in COMMON areas
b.	reducible Fock/KS matrix	stored on Fortran unit 11
c.	reducible density matrix	
c.1	all electron	stored on Fortran unit 13 (1st record)
c.2	core electron	*stored on Fortran unit 13 (2nd record)*
c.3	valence electron	*stored on Fortran unit 13 (3rd record)*
d.	reducible overlap matrix	stored on Fortran unit 3
e.	Fock/KS eigenvectors	*stored on Fortran unit 10*

1. a, b, c1, d, are automatically computed and stored any time you run the **properties** program.

2. in unrestricted calculations, the total electron density matrix $(\alpha+\beta)$ and the spin density matrix $(\alpha - \beta)$ are written as a unique record on fortran unit 13.

3. The core and valence electron density matrices (c.2, c.3) are computed *only* by the **NEWK** option when IFE=1. They are stored as sequential data set on Fortran unit 13, after the all electron density matrix. Calculation of Compton profiles and related quantities requires such information.

4. Properties can be calculated using a new density matrix, projected into a selected range of bands (keyword **PBAN**,**PGEOMW**), range of energy (keyword **PDIDE**), or constructed as a superposition of the atomic density matrices relative to the atoms (or ions) of the lattice (keyword **PATO**). In the latter case a new basis set can be used.

5. Each property is associated with a keyword. The keywords can be entered in any sequence. *When a specific density matrix is calculated* [band projected (**PBAN**), energy projected (**PDIDE**), atomic superposition (**PATO**)], *all the subsequent properties are computed from that density matrix.* The option **PSCF** restores the SCF density matrix.

6. The Fock/KS eigenvectors are computed on request by running the **NEWK** option. The options that need such information are: **PBAN - PDIDE - PGEOMW - ANBD - BWIDTH - DOSS - EMBE - EMDL - EMDP - PROF**.

7. The reciprocal space vectors refer by default to the primitive cell when defining the k-points coordinates to compute the bands (**BAND**). The keyword **CONVCELL** allows entering conventional cell coordinates.

8. The reciprocal space vectors (input and output) in **RODK**, **EMDL**, **EMDP** and **PROF** refer to the conventional cell, *not* to the primitive cell. See Appendix A.5, page 163.

3.2   Properties keywords

RDFMWF   wave function data conversion formatted-binary (fortran unit 98→ 9)

Preliminary calculations			
NEWK	Eigenvectors calculation	103	I
NOSYMADA	No symmetry Adapted Bloch Functions	78	–
PATO	Density matrix as superposition of atomic (ionic) densities	104	I
PBAN	Band(s) projected density matrix (preliminary **NEWK**)	104	I
PGEOMW	Density matrix from geometrical weights (preliminary **NEWK**)	105	I
PDIDE	Energy range projected density matrix (preliminary **NEWK**)	105	I
PSCF	Restore SCF density matrix	110	–
ROTREF	Rotation of the reference frame	110	I

Properties computed from the density matrix			
ADFT	Atomic density functional correlation energy	85	I
BAND	Band structure	87	I
CLAS	Electrostatic potential maps (point multipoles approximation)	88	I
ECHG	Charge density maps and charge density gradient	93	I
ECH3	Charge density 3D maps	92	I
EDFT	Density functional correlation energy	93	I
POLI	Atom and shell multipoles evaluation	105	I
POTM	Electrostatic potential maps	107	I
POTC	Electrostatic properties	107	I
PPAN	Mulliken population analysis	78	
XFAC	X-ray structure factors	111	I

Properties computed from the density matrix (spin-polarized systems)			
ANISOTRO	Hyperfine electron-nuclear spin tensor	86	I
ISOTROPIC	Hyperfine electron-nuclear spin interaction - Fermi contact	96	I
POLSPIN	Atomic spin density multipoles	106	I

Properties computed from eigenvectors (after keyword **NEWK**)			
ANBD	Printing of principal AO component of selected CO	85	I
BWIDTH	Printing of bandwidth	88	I
DOSS	Density of states	91	I
EMDL	Electron momentum distribution - line	94	I
EMDP	Electron momentum distribution - plane maps	95	I
PROF	Compton profiles and related quantities	109	I

New properties			
POLARI	Berry phase calculations	113	I
SPOLBP	Spontaneous polarization (Berry phase approach)	114	–
SPOLWF	Spontaneous polarization (localized CO approach)	114	–
PIEZOBP	Piezoelectricity (Berry phase approach) preliminary	112	–
PIEZOWF	Piezoelectricity (localized CO approach) - preliminary	113	–
LOCALWF	Localization of Wannier functions	97	I
DIELEC	Optical dielectric constant	89	I

Auxiliary and control keywords			
ANGSTROM	Set input unit of measure to Ångstrom	24	–
BASISSET	Printing of basis set, Fock/KS, overlap and density matrices	87	–
BOHR	Set input unit of measure to bohr	27	–
CHARGED	Non-neutral cell allowed (**PATO**)	48	–
CONVCELL	Reference cell for k-points coordinates (**BAND**)	88	–
END	Terminate processing of properties input keywords		–
FRACTION	Set input unit of measure to fractional	31	–
MAPNET	Generation of coordinates of grid points on a plane	100	I
NEIGHBOR	Number of neighbours to analyse in **PPAN**	34	I
PRINTOUT	Setting of printing options	35	I
RAYCOV	Modification of atomic covalent radii	35	I
SETINF	Setting of inf array options	36	I
SETPRINT	Setting of printing options	37	I
STOP	Execution stops immediately	38	–
SYMMOPS	Printing of point symmetry operators	40	–

Output of data on external units			
ATOMIR	Coordinates of the irreducible atoms in the cell	86	–
ATOMSYMM	Printing of point symmetry at the atomic positions	27	–
COORPRT	Coordinates of all the atoms in the cell	29	–
EXTPRT	Explicit structural/symmetry information	31	–
GAUSS98	Printing of an input file for the GAUSS98 package	49	–
FMWF	Wave function formatted output. Section 3.2	95	–
INFOGUI	Generation of file with wf information for visualization	96	–
KNETOUT	Reciprocal lattice information + eigenvalues	77	–
MOLDRAW	generation of input file for the program MOLDRAW	32	–

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 (different from the values set for a full system calculation). 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] [66]
or
SAVIN	Savin weights [67]

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 35)
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 24.

ANISOTRO - anisotropic tensor

	rec	variable	meaning
•	A	keyword	enter one of the following keywords:
•	A3	**ALL**	The anisotropic tensor is evaluated for all the atoms in the cell
			———————— or ————————
•	A6	**UNIQUE**	(alias NOTEQUIV) The anisotropic tensor is evaluated for all the non-equivalent atoms in the cell
			———————— or ————————
•	A6	**SELECT**	The anisotropic tensor is evaluated for selected atoms
•	*	N	number of atoms where to evaluate the tensor
•	*	IA(I),I=1,N	*label* of the atoms
•	A	**PRINT**	extended printing

The anisotropic hyperfine interaction tensor is evaluated. This quantity is given in bohr^{-3} and is transformed into the hyperfine coupling tensor through the relationship [80]

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

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

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

where $\boldsymbol{r}_A = |\boldsymbol{r} - A|$ and $r_{Ai} = (\boldsymbol{r} - A)_i$ (i$^{\text{th}}$ component of the vector).

ATOMIR - coordinates of irreducible atoms

Cartesian and fractional coordinates of the irreducible atoms are printed. No input data required.

ATOMSYMM

See input block 1, page 27

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 on Fortran unit 25 stored for plotting; see Appendix F, page 181
	LPR66	≠ 0	printing of eigenvalues
			———— add NLINE records ————
• *			coordinates of the line extremes in units of $|\underline{b}_i|$/ISS
	I1,I2,I3		first point coordinates.
	J1,J2,J3		last point coordinates.

The band structure along a given path and for a given range of bands is computed. The data are printed on standard output and written on fortran unit 25 as formatted data for plotting (if IPLO = 1) (see Appendix F, page 181).

1. **Warning** : does not run for molecules!! (0D)

2. The coordinates of the line extremes refer to the primitive cell. They can be expressed with reference to the conventional cell by entering the keyword **CONVCELL** before **BAND**.

3. 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 [7] and in Chapter 2 of reference [20], 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.

4. 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.

5. 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.

6. If symmetry adapted Bloch functions are used (default option), **BAND** generates symmetry information in k points different from the ones defined by the Monkhosrt net. Eigenvectors computed by NEWK in k points corresponding to the Monkhosrt 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 37) ———— II

This option allows printing of the basis set and the computational parameters, and, on request (keyword **PRINTOUT** before **BASISSET**), of the Fock/KS matrix (**FGRED**), the

overlap matrix (**OVERLAP**), and the reducible density matrix (**PGRED**), in direct lattice representation.
Printing options:
59 (Density matrix); 60 (Overlap matrix); 64 (Fock/KS matrix).

BOHR - unit of measure

Unit of measure of coordinates (**ECHG**, **POTM**, **CLAS**) See input block 1, page 27.

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 48.

CLAS   - Point charge electrostatic potential maps

rec	variable	value	meaning
• *	IDER	0	potential evaluation
		1	calculation of potential and its first derivatives
	IFOR	0	point multipoles have to be evaluated by **POLI** option
		1	point formal charges given as input
			if IFOR ≠ 0 insert ————————————————II
• *	Q(I),I=1,NAF		formal net charge for all the NAF atoms in the unit cell (equivalent and non equivalent, following the sequence printed at the top of the **properties** printout)
			insert **MAPNET** input records (page 100)

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 100). The potential values are written formatted on fortran unit 25 (see Appendix F, page 181).

2. When IDER ≠ 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.

CONVCELL

When computing the bands, the k-points coordinates are entered with reference to the primitive cell. This option allows entering the coordinates of the k points with reference to the conventional cell.

COORPRT

See input block 1, page 29.

DIEL/DIELECT - Optical dielectric constant

rec	variable	meaning
• *A* **ENDDIEL**		end of **DIELECT** input block
	optional keywords	II
• *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.* [81]) and Poisson's equation. The charge density is first averaged with respect to the (infinite) plane orthogonal to the field

$$\overline{\rho}(z) = \frac{1}{A} \int_A \rho(z) \, dA \tag{3.1}$$

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:

$$\overline{\rho}(z) = \frac{1}{V} \sum_{\ell=-\infty}^{+\infty} F_{00\ell} \, e^{-\imath \frac{2\pi\ell z}{C}} \tag{3.2}$$

$F_{00\ell}$ 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 $\overline{\rho}$ is then averaged with respect to the z coordinate

$$\overline{\overline{\rho}}(z) = \frac{1}{\Delta z} \int_{z-\Delta z/2}^{z+\Delta z/2} \overline{\rho}(z') \, dz' \tag{3.3}$$

that is

$$\overline{\overline{\rho}}(z) = \frac{1}{V} \sum_{\ell=-\infty}^{+\infty} F_{00\ell} \, sinc\left(\ell\pi \frac{\Delta z}{C}\right) e^{-\imath \frac{2\pi\ell z}{C}} \tag{3.4}$$

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

$$\frac{\partial^2 \overline{\overline{V}}(z)}{\partial z^2} = -4\pi \overline{\overline{\rho}}(z) \tag{3.5}$$

or

$$\frac{\partial \overline{\overline{E}}(z)}{\partial z} = 4\pi \overline{\overline{\rho}}(z) \tag{3.6}$$

because

$$\frac{\partial \overline{\overline{V}}(z)}{\partial z} = -\overline{\overline{E}}(z) \tag{3.7}$$

$\overline{\overline{V}}(z)$, $\overline{\overline{F}}(z)$ and $\overline{\overline{\rho}}(z)$ 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:

$$F_{00\ell} = F_{00\ell}^{\Re} + \imath F_{00\ell}^{\Im} \tag{3.8}$$

Exploiting the following properties of the structure factors:

$$
\begin{aligned}
F_{000} &= N_e \quad \textbf{(number of electrons in the supercell)} \\
F_{00\ell}^{\Re} &= F_{00-\ell}^{\Re} \\
F_{00\ell}^{\Im} &= -F_{00-\ell}^{\Im}
\end{aligned} \tag{3.9}
$$

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

$$
\Re\left[\overline{\overline{\rho}}(z)\right] = \frac{N_e}{V} + \frac{2}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \cos\left(\frac{2\pi\ell z}{C}\right) + F_{00\ell}^{\Im} \sin\left(\frac{2\pi\ell z}{C}\right) \right] sinc\left(\ell\pi\frac{\Delta z}{C}\right) \tag{3.10}
$$

$$
\Im\left[\overline{\overline{\rho}}(z)\right] = 0 \tag{3.11}
$$

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 3.7, the local macroscopic field corresponds to minus the slope of $\overline{\overline{V}}(z)$, it has opposite sign with respect to the imposed outer field, according to the Lenz law, and is obtained from $\overline{\overline{\rho}}(z)$ (eq. 3.6):

$$
\overline{\overline{E}}(z) = \frac{8\pi}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \frac{\sin\left(\frac{2\pi\ell z}{C}\right)}{\left(\frac{2\pi\ell}{C}\right)} - F_{00\ell}^{\Im} \frac{\cos\left(\frac{2\pi\ell z}{C}\right)}{\left(\frac{2\pi\ell}{C}\right)} \right] sinc\left(\ell\pi\frac{\Delta z}{C}\right) \tag{3.12}
$$

The corresponding macroscopic electric potential can be written as follows:

$$
\overline{\overline{V}}(z) = \frac{-8\pi}{V} \sum_{\ell=1}^{+\infty} \left[F_{00\ell}^{\Re} \frac{\cos\left(\frac{2\pi\ell z}{C}\right)}{\left(\frac{2\pi\ell}{C}\right)^2} + F_{00\ell}^{\Im} \frac{\sin\left(\frac{2\pi\ell z}{C}\right)}{\left(\frac{2\pi\ell}{C}\right)^2} \right] sinc\left(\ell\pi\frac{\Delta z}{C}\right) \tag{3.13}
$$

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

$$
\epsilon = \frac{E_0}{E_0 + \overline{\overline{E}}} \tag{3.14}
$$

The minimal input for the dielectric calculation is:

```
DIEL
END
```

for an extended output
```
DIEL
PRINT
END
```
In the former case the corresponding output is as follows:

```
*******************************************************************************

DIELECTRIC
MACROSCOPIC AVERAGE OF CHARGE DENSITY, ELECTROSTATIC FIELD AND POTENTIAL

*******************************************************************************

DIRECTION 3

NUMBER OF CONVENTIONAL CELLS (SUPERCELL VOLUME/SLIDING CELL VOL) 5
NUMBER OF FACTORS COMPUTED 300 NUMBER OF SAMPLING POINTS 7592

COORDINATES (A.U.):
SLIDING CELL HEIGHT 7.59103 SLIDING CELL VOLUME 218.71200
MIN SAMPLING POINT -18.97758 MAX SAMPLING POINT 18.97758
SAMPLING INTERVAL 37.95516 SAMPLING STEP 0.00500


                          MINIMUM MAXIMUM DELTA
DENSITY (A.U.) -0.00010 0.00010 0.00021
FIELD (A.U.) -0.00399 0.00399 0.00799
POTENTIAL (A.U.) -0.02950 0.02949 0.05899


POSITION MINIMUM MAXIMUM DISTANCE
DENSITY -18.58258 -0.39750 18.18508
FIELD -6.71753 6.71753 13.43506
POTENTIAL -18.97758 0.00250 18.98008


APPLIED FIELD 0.0100000000
RESPONCE FIELD -0.0039929327
RESULTANT FIELD 0.0060070673
DIELECTRIC CONSTANT 1.6647058467


DDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDDD
```
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 $F_{00\ 300}$.

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 F, page 181).
			2	formatted output on Fortran unit 24 for plotting (Appendix F, page 181).
		NPOL		number of Legendre polynomials used to expand DOSS ($\leq$ 25)
		NPR		number of printing options to switch on
				if INZB and IFNB < 0 insert ———————————————————II
●	*	BMI,BMA		Minimum and maximum energy (hartree) values to span for DOSS. They must be in a band gap
				if NPRO $\neq$ 0, insert NPRO records ———————————————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)
				if NPR $\neq$ 0, insert **prtrec** *(see page 37)* ———————————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:

$$\rho_\mu(\epsilon) = 2/V_B \sum_j \sum_\nu \sum_{\underline{g}} \int_{BZ} d\underline{k} S_{\mu\nu}(\underline{k}) a_{\mu j}(\underline{k}) a_{\nu j}^*(\underline{k}) \ e^{i\underline{k}\cdot\underline{g}} \ \delta[\epsilon - \epsilon_j(\underline{k})] \qquad (3.15)$$

$$\rho_A(\epsilon) = \sum_{\mu \in A} \rho_\mu(\epsilon) \qquad (3.16)$$

$$\rho_{tot}(\epsilon) = \sum_A \rho_A(\epsilon) \qquad (3.17)$$

where the last sum extends to all the atoms in the unit cell.
Bond population density of states are not computed.

1. **Warning:** does 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 6.7, page 145). 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 **OSS**, 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, ([82, 83]). 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 third 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 80) or level shifter (**LEVSHIFT**, page 77) were requested in SCF, to obtain the correct Fermi energy and eigenvalues spectra.

6. Unit of measure: energy: hartree; DOSS: state/hartree/cell.

Printing options: 105 (density of states and integrated density of states); 107 (symmetrized plane waves).

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):

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SCALE	RANGE
length scales for non-periodic dimensions	boundary for non-periodic dimensions (au)
if 2D system	
● * ZSCALE	● * ZMIN
	● * ZMAX
if 1D system	
● * YSCALE,ZSCALE	● * YMIN,ZMIN
	● * YMAX,ZMAX
if 0D system	
● * XSCALE,YSCALE,ZSCALE	● * XMIN,YMIN,ZMIN
	● * XMAX,YMAX,ZMAX

The electronic charge or spin density 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. See Appendix F, page 181, for description of the format.

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 3.2, page 100)

1. When 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 100). The electron density values (electron bohr^{-3}) are written formatted in fortran unit 25 (see Appendix F, page 181).

2. 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 on fortran unit 25 (see Appendix F, page 181).

3. The electron charge density is computed from the density matrix stored on fortran unit 13. The density matrix computed at the last cycle of **SCF** is the default.

4. 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 DF of the 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] [66]

<div align="center">or</div>

		SAVIN	Savin weights [67]

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 35)
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 on Fortran unit 25 for plotting (Appendix F, page 181).
		2	formatted output on Fortran unit 24 for plotting (Appendix F, page181).
	LPR113	$\neq 0$	printing of EMD before interpolation
• ∗	(K(I,J), I=1,3),J=1,N		directions in oblique coordinates
• ∗	NPO		number of orbital projections (≤ 10)
	NPB		number of band projections(≤ 10)
			if NPO ≠ 0 insert NPO sets 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 sequence.
			if NPB ≠ 0 insert NPB sets 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 EMDL does not work for UHF wave functions.

The Electron Momentum Density is calculated along given directions (equation 6.23, page 146). The electron momentum distribution, EMD, is a non-periodic function; it falls rapidly to zero outside the first Brillouin zone. $\rho(\underline{0})$ gives the number of electrons at rest. The oblique coordinates directions given in input refer to the conventional cell, *not* to the primitive cell,

for 3D systems.

Example: in a FCC system the input directions refer to the orthogonal unit cell frame (sides of the cube) not to the primitive non-orthogonal unit cell frame.

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 band projections
			_____ insert NP set of records _____
● ∗	(L1(J),J=1,3),		fractional coordinates of the reciprocal lattice vectors that identify the
	(L2(J),J=1,3)		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 EMDP does not work for UHF wave functions.

Calculation of electron momentum density on definite planes (equation 6.23, page 146).

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 31

FMWF - Wave function formatted output

The keyword **FMWF**, entered in **properties** input, generates formatted wave function data (same data are written on fortran unit 9, unformatted, at the end of SCF) on fortran unit 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 fortran unit 98, and writes unformatted data to fortran unit 9. The key dimensions of the program computing the wave function and the one computing the properties are checked. If the dimensions of the arrays are not compatible, the program stops, after printing the PARAMETER statement used to define the dimension of the arrays in the program

which computed the wave function. The sequence of the operations, when transferring data from one platform to another is the following:

platform	program	input	action
1	**properties**	**FMWF**	wave function formatted to fortran unit 98
			ftp fortran unit 98 file from platform 1 to platform 2
2	**properties**	**RDFMWF**	wf read from fortran unit 98, written to fortran unit 9

FRACTION - unit of measure

Unit of measure of coordinates in the periodic direction (**ECHG**, **POTM**, **CLAS**) See input block 1, page 31.

GAUSS98

See input block 2, page 49

INFOGUI/INFO - output for visualization

Information on the system and the computational parameters are written formatted on fortran unit 32, in a format suitable for visualization programs. No input data required.

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
• A	**PRINT**	extended printing

The spin density at the nuclei ($\langle \rho^{\mathrm{spin}}(\boldsymbol{r}_{\mathrm{N}}) \rangle$) is evaluated. This quantity is given in bohr^{-3} and is transformed into the hyperfine coupling constant $a_{\mathrm{N}}[\mathrm{mT}]$ through the relationship [80]

$$a_{\mathrm{N}}[\mathrm{mT}] = \frac{1000}{(0.529177 \cdot 10^{-10})^3} \frac{2}{3} \, \mu_0 \, \beta_{\mathrm{N}} \, g_{\mathrm{N}} \, \langle \rho^{\mathrm{spin}}(\boldsymbol{r}_{\mathrm{N}}) \rangle = 28.539649 \, g_{\mathrm{N}} \, \langle \rho^{\mathrm{spin}}(\boldsymbol{r}_{\mathrm{N}}) \rangle$$

where

$$\mu_0 = 4\pi \cdot 10^{-7} = 12.566370614 \cdot 10^{-7} [\mathrm{T}^2 \mathrm{J}^{-1} \mathrm{m}^3] \qquad \text{(permeability of vacuum)}$$

$$\beta_{\mathrm{N}} = 5.0507866 \cdot 10^{-27} [\mathrm{JT}^{-1}] \qquad \text{(nuclear magneton)}$$

the nuclear g_{N} factors for most of the nuclei of interest are available in the code and are taken from [80]. Conversion factors:

$$a_{\mathrm{N}}[\mathrm{MHz}] = \frac{a_{\mathrm{N}}[\mathrm{mT}] g_{\mathrm{e}} \beta_{\mathrm{e}}}{10^9 \mathrm{h}[\mathrm{Js}]} = 28.02.6 \cdot a_{\mathrm{N}}[\mathrm{mT}]$$

$$a_{\mathrm{N}}[\mathrm{cm}^{-1}] = \frac{a_{\mathrm{N}} \, [\mathrm{MHz}] 10^8}{c[\mathrm{ms}^{-1}]} = 0.33356410 \cdot 10^{-4} \cdot a_{\mathrm{N}}[\mathrm{MHz}]$$

$$a_N[J] = g_e \ \beta_e \ 10^{-3} a_N[mT] = 1.856954 \cdot 10^{-26} a_N[mT]$$

where:

$$\beta_e = 9.2740154 \cdot 10^{-24} \ [JT^{-1}] \qquad \text{(bohr magneton)}$$

$$g_e = 2.002319304386 \qquad \text{(free-electron g factor)}$$

$$c = 2.99792458 \cdot 10^8 \ [ms^{-1}] \qquad \text{(speed of light in vacuum)}$$

$$h = 6.6260755 \cdot 10^{-34} \ [Js] \qquad \text{(Planck constant)}$$

KNETOUT

See input block 4, page 77

LOCALWF - Localization of Wannier Functions (WnF)

The localization of WnF is controlled by keywords. The **LOCALWF** block is finished by the **END** keyword. The plotting options (when requested) must be in separated blocks immediately following the first block. Each block should consist of the index number of WnF to be plotted followed by the corresponding **MAPNET** block. For UHF calculations two set of blocks must be inserted for the α and β electrons. The final WnF are written on unit 80.

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: $10^{-\text{ITDP0}}$ $\boxed{2}$
	ITDP	> 0	Final tolerance used to calculate the DM matrix elements: $10^{-\text{ITDP}}$ $\boxed{5}$
	ICONV	> 0	Convergence criterion to finish a large cycle: ABS(ADI(N) - ADI(N-1)) $< 10^{-\text{ICONV}}$, where ADI is the atomic delocalization index and N is the short cycle number $\boxed{5}$

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 $\boxed{2}$
	ITPH	> 0	$10^{-\text{ITPH}}$ is the final tolerance used to attribute this phase $\boxed{3}$
	ICHTOL	> 0	DM tolerance of the cycle where ITPH0 changes to ITPH. $\boxed{\text{ITDP0+1}}$

General Keywords:

RESTART

With this option the WnF of a previous job are read from unit 81 (in the same format as output unit 80). The **RESTART** option set the same choice of the active bands as the previous job (and override any other definition) and the tolerances are, by default, the last attained in the previous calculation. The latter can be changed using **CYCTOL** and **PHASETOL**.

MAXCYCLE

rec	variable	value	meaning
● *	NCYC	> 0	maximal number of short cycles for the iterative process $\boxed{30}$

PRINTPLO

rec	variable	value	meaning
● *	IPRT	0	Does not print Wannier coefficients
		> 0	Prints Wannier coefficients at each cycle up to the IPRT-th star of direct lattice vectors $\boxed{0}$
	IPRP	0	Prints population analysis only at the end of the localization.
		$\neq 0$	Print analysis at each W-B cycle $\boxed{0}$
	ITPOP		Only atomic population larger than $10^{-\text{ITPOP}}$ are printed $\boxed{2}$
	IPLOT	0	WnFs are not computed for plot
		$\neq 0$	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 fortran unit 25 $\boxed{0}$

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 [84]) 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}. $\boxed{4}$
	IBFRZ		If for a pair of WnFs st, $|A_{st}| \leq 10^{-\text{IBFRZ}}$, then the corresponding WnFs are not mixed. $\boxed{4}$
	MXBCYC		Maximum number of cycles allowed in the Boys localization process $\boxed{500}$

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 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) [85].

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 CAPTURE ∗ (RAYCOV(I) + RAYCOV(J)). An inter-atomic distance lower than the capture indicates that I and J can be covalently bonded 1.0 RAYCOV, covalent radius (default value page 35).
	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 ways:

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.
			insert 2 × NGUES records
• ∗	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)
			insert:
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.
			insert NBOND records
• ∗	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

Plotting the WnFs

If IPLOT $\neq 0$ insert after the keyword block (terminated by END):

rec	variable	value	meaning
• ∗	NWF		number of WF to plot
		insert NWF blocks of data	
• ∗	NUMBWF		sequence number (output order) of the WF to plot
		MAPNET input data (Section 3.2, page 100)	

The WnFs and the WnF densities (in this order) within the selected regions are given in fortran unit 25.

1. The **NEWK** option must be executed before running **LOCALWF**, to compute the crystalline orbitals.

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, a IS twice 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. However, a necessary condition for the WnFs to be well represented, is that the volume in terms of number of unit cells of the cluster that contains the set of WnFs up to AO coefficients of 10^{-ITDP}, given as output, should be lower than the number of **k**-points in the net (IS**IDIM, being IDIM the dimensionality of the system).

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.

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S. F. Boys Rev. Mod. Phys 32 (1960) 296.

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J. Pipek and P. G. Mezey J. Chem. Phys 90 (1989) 4916.

V. Magnasco and A. Perico, J. Chem. Phys. 47 (1967) 971.

MAPNET - coordinates of grid points on a plane

This is a dummy keyword, to explain the way is generated the grid of points in which is evaluated a given function F: charge density and spin density (**ECHG**), electrostatic potential (**CLAS**, **POTM**). The graphic representation of the resulting 2D function is made by external software.

rec	variable	meaning
● *	NPY	number of points on the B-A segment.
● *A*	keyword	enter a keyword to choose the type of coordinate:
● **COORDINA**		
● *	XA,YA,ZA	cartesian coordinates of point A
● *	XB,YB,ZB	cartesian coordinates of point B
● *	XC,YC,ZC	cartesian coordinates of point C

———————————————— or ————————————————

● **ATOMS**		
● *	IA	*label* of the atom at point A
	AL,AM,AN	indices (direct lattice, input as reals) of the cell where the atom is located
● *	IB	*label* of the atom at point B
	BL,BM,BN	indices (direct lattice, input as reals) of the cell where the atom is located
● *	IC	*label* of the atom at point C
	CL,CM,CN	indices (direct lattice, input as reals) of the cell where the atom is located

———————————— *optional keyword* ————————————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 3.1)

———————————— *optional keyword* ————————————II

● **MARGINS**		definition of a new A",B",C",D" window including ABCD (or A'B'C'D') (see Fig 3.2)
● *	ABM	margins along AB
	CDM	margins along CD
	ADM	margins along AD
	BCM	margins along BC

———————————— *optional keyword* ————————————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 fractionary units
● **END**		end of **MAPNET** input block

1. 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 ≡ B, F is calculated along the line AB.

2. n_{BC} is set by the program such that all points in the net are as equally spaced as possible ($\delta_{AB} \approx \delta_{BC}$).

3. Output for plot on formatted (logical record length 80) fortran unit 25

4. 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 / fractionary units (default Ångstrom; see Section 2.1, page 24)

   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).

5. 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.
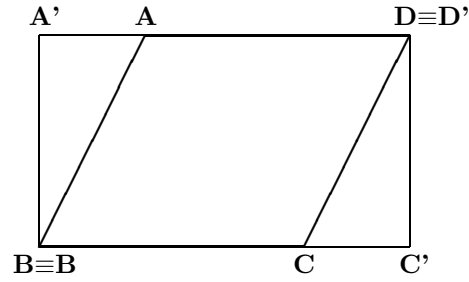
Figure 3.1: Definition of the window where the function F is mapped Effect of optional keyword RECTANGU.
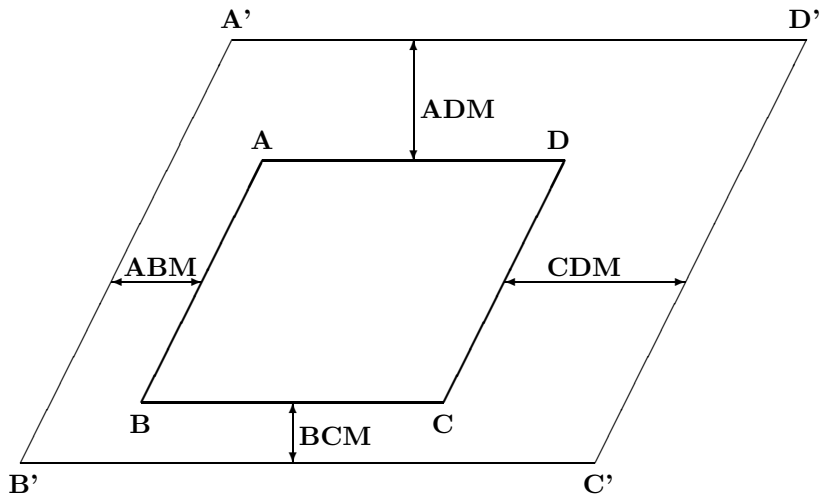
Figure 3.2: Definition of frame around the original window where the function F is mapped. Effect of optional keyword MARGINS.

MOLDRAW

See input block 1, page 32

NEIGHBOR/NEIGHPRT

See input block 1, page 34

NEWK - Fock/KS eigenvectors

rec	variable	value	meaning
			if system is periodic, insert ———————————— 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 19).
	ISHF	n	dummy variable
	ISP		Shrinking factor of the secondary reciprocal space net (Gilat net) for the evaluation of the Fermi energy and density matrix.
			if system is periodic and IS=0, insert ——————— 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
			if NPR ≠ 0 insert **prtrec** *(see page 37)* ————— 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 fortran unit 10 (in the basis of symmetry adapted Bloch functions) and in fortran unit 8 (in the basis of AO). Eigenvalues and related information (coordinates of k points in reciprocal lattice, weights etc) are written on fortran unit 30 by inserting the keyword **KNETOUT** (page 77). See Appendix D, page 176.

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.

2. The shrinking factors IS and ISP (Section 6.7, page 145) 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 6, equation 6.5).

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 77; **SPINLOCK**, page 80; **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 (defaul 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 4, page 78

PARAMPRT - - printing of parametrized dimensions

See input block 1, page 35.

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
			if IBN $\neq$ 0 insert basis set input (page 16) _____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 on fortran unit 13.

2. The atomic wave function is computed by the atomic program [14], 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 on fortran unit 9 at the end of the SCF cycles are not modified. Only the data stored on the temporary data set (reducible density matrix on fortran unit 13 and overlap matrix on 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 57, and **CHARGED**, input block 2, page 48.

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 on 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_α + n_β electrons);

second record, spin density matrix (Ns=n_α - n_β 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_α + n_β electrons);

second record, spin density matrix (Ns=n_α - n_β 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 NOSYMADA 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 on 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 [86] within the Tersoff-Haman approximation [87].

POLI   - Spherical harmonics multipole moments

rec	variable	value	meaning
● ∗	IDIPO		multipole order (maximum order ℓ=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 ($0 \leq$ IDIPO ≤ 6). The first nine terms, corresponding to ℓ=0,1,2 (for the definition of higher terms, see Appendix A1, page 170 in reference [7]) 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 ℓ=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.

POTC   - Electrostatic potential and its derivatives

rec	variable		meaning
• *	ICA	0	calculation of potential (V), its first derivative (E) and second derivatives (E') in one or more points
		1	not implemented
		2	calculation of $V(z)$, $E(z)$, $E'(z)$ and $\rho(z)$ averaged in the plane at z position (2D only)
		3	calculation of $V(z)$, $E(z)$, $E'(z)$ and $\rho(z)$ averaged in the volume between z–ZD and z+ZD (2D only)
	NPU	n	number of points at which these properties are computed
		0	these properties are computed at the atomic positions defined by IPA value
	IPA	0	calculations are performed at each atomic positions in the cell
		1	calculations are performed just for non equivalent atomic positions in the cell
			if ICA = 0 and NPU > 0 insert NPU records —————————II
• *	X,Y,Z		point coordinates (cartesian, bohr)
			if ICA = 2 insert —————————II
• *	ZM,ZP		properties are averaged over NPU planes orthogonal to the z axis from z = ZP to z = ZM by step of (ZP–ZM)/(NPU–1) (bohr)
			if ICA = 3 insert —————————II
• *	ZM,ZP		properties are averaged over NPU volumes centered on planes orthogonal to the z axis, same as ICA = 2
	ZD		half thickness of the volume (bohr)

The exact electrostatic potential V, its derivatives E (electric field) and E' (electric field gradient) are evaluated for molecules (0D), slabs (2D) and crystals (3D). Plane and volume averaged properties can be computed for slabs (2D) only. The plane is orthogonal to the z axis.

For ICA = 3, the volume average is performed around a middle plane at z position, from z–ZD to z+ZD, giving a thickness of 2∗ZD.

According to Poisson's law, the charge density $\rho(z)$ is defined as

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

If an electric field of intensity E_0 is present (keyword **FIELD**, see page 2.1, only for slabs), the total potential $V_{field}(z)$ is calculated:

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

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

Note - When ICA = 0 and NPU $\neq$ 0, it is possible to enter the cartesian coordinates (bohr) of the points where the exact values of the properties must be computed. It is useful when applying fitting procedure to obtain formal point charges.

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 100)

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 100). The electrostatic potential values are written formatted on fortran unit 25 (see Appendix F, page 181).

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, and written formatted on fortran unit 25 (see Appendix F, page 181).

3. The electrostatic potential at $\mathbf{r}$ is evaluated [10] by partitioning the periodic charge density $\rho(r)$ in shell contributions ρ_λ^h:

$$\rho(\underline{r}) = \sum_h \sum_\lambda \rho_\lambda(\underline{r} - \underline{h})$$

(h translation vector).

4. The long range contributions are evaluated through a multipolar expansion of $\rho_\lambda(\underline{r} - \underline{h})$ [11]. 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; $\mathbf{s}_\lambda$ = 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 (input datum to **POTM**) =5 and IDIPO (input datum to **POLI**) =4, and smaller than 0.01% when ITOL=15 and IDIPO=6 [10, 11].

6. The multipoles of shell charges <u>must</u> be computed by running the **POLI** option before **POTM**.

PPAN/MULPOPAN - Mulliken Population Analysis

See input block 4, page 78.

PRINTOUT - Setting of printing environment

See input block 1, page 35.

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 on Fortran unit 25 (Appendix F, page 181)
			2	formatted CP data stored on Fortran unit 24 (Appendix F, page 181)
				if NPR ≠ 0 insert **prtrec** *(see page 37)* ——————II
●	A2		**CP**	calculation of Compton profiles (J(q)) along selected directions (eq. 6.27).
●	*	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),		directions in oblique coordinates; see note 9
		N=1,ND		
●	*	STPJ		interpolation step (in interpolated Compton profiles calculation).
●	A4		**DIFF**	CP difference between all computed directional CPs.
●	A2		**BR**	autocorrelation function B(r) calculation (eq. 6.30).
●	*	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. 6.29)
●	*	FWHM		convolution parameter (a.u.) full width half maximum; $\sigma = \sqrt{(FWHM)^2/(8 \cdot 2log2)}$.
●	A4		**ENDP**	End of input records for CP data

The keyword **PROF** starts the calculation of Compton profiles (J(q)) along selected directions (eq. 6.27). 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 6.25); the valence contribution is computed numerically (IVIA=0) by integrating the EMD (equation 6.23). 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 then 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 then IS. IRAP=IS1/IS is given in INPUT card 2; a reasonable value is IRAP=2. The outer contribution is supposed to be the same for different CP's, and is obtained by integrating the average EMD.

4. If ICORE $\neq$ 2 (valence electron CP's are required) the **NEWK** option, with IFE=1, must be run before the **PROF** option, in order to generate the eigenvectors required for the EMD calculation, as well as the weights associated with each k point.

5. If ICORE $\neq$ 2 and IVIA = 0 the CPs are evaluated at points resulting from the IS partition of the reciprocal lattice translators. The interpolation is performed at STPJ intervals (STPJ is given in input).

   If ICORE = 2 or IVIA = 1 the CPs are, in any case, evaluated at points resulting from STPJ intervals.

   IVIA=0 (numerical integration) produces much more accurate results;

   IVIA=1 (analytical integration) is to be used only for molecular calculations or for non conducting polymers.

6. Total CP's are always obtained by summing core and valence contributions.

7. Reasonable values of the integration parameters depend on the system under investigation. The normalization integral of the CP's is a good check of the accuracy of the calculation. For instance, in the case of the valence electron of beryllium (test 9), good values of RINT and IS are 10. a.u. and 4 respectively. In the case of silicon (test 10), good values of the same variables are 8. a.u. and 8 respectively. Much greater RINT values are required in order to include all the core electrons (70. a.u. in the case of silicon, and 25. a.u. in the case of beryllium).

8. BR (autocorrelation function or reciprocal space form factor) should be calculated only for valence electrons. All electron BR are reliable when the normalization integral, after the analytical integration for core electrons contribution, is equal to the number of core electrons.

9. The oblique coordinates directions given in input refer to the conventional cell, *not* to the primitive cell for 3D systems.

   Example: in a FCC system the input directions refer to the orthogonal unit cell frame (sides of the cube) not to the primitive non-orthogonal unit cell frame.

Printing options: 116 (Compton profiles before interpolation); 117 (average EMD before interpolation); 118 (printing of core, valence etc. contribution). The LPRINT(118) option should be used only if ICORE=1, that is, if core plus valence calculation are chosen.

PSCF   - Restore SCF density matrix

The wave function data computed at the last SCF cycle are restored in common areas and fortran units 3 (overlap matrix), 11 (Fock/KS matrix), 13 (density matrix). The basis set defined in input block 2 is restored. Any modification in the default settings introduced in **properties** is overwritten. No input data required.

RAYCOV - covalent radii modification

See input block 1, page 35

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 45^0 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 74)

SETINF - Setting of INF values

See input block 1, page 36

SETPRINT - Setting of printing options

See input block 1, page 37.

STOP

Execution stops immediately. Subsequent input records are not processed.

SYMADAPT

See input block 4, page 81

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
		if ISS > 0 insert ISS records	II
• *	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:

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

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.

3.3 Spontaneous polarization and piezoelectricity

Y. Noel, September 2002

PIEZOBP - Piezoelectricity (Berry phase approach)

The calculation of the piezoelectric constants of a system, can be decomposed in few steps. A preliminary run must be performed for the undistorted system at the equilibrium geometry (*crystal* followed by *properties* with the keyword **POLARI**). Then, for a distorted system at equilibrium (all internal parameters must be optimized), a second run (*crystal* followed by *properties* with the keyword **POLARI**) must be performed, followed by a third run (only *properties* with the keyword **PIEZOBP** that computes φ_l, the polarization vector component along the reciprocal lattice vector $\mathbf{b}_l$ (φ_l is a phase). Steps 2 and 3 are repeated for other strains. Then, the obtained set of data is fitted and the slope ($\frac{d\varphi_l}{d\epsilon_j}$) at zero strain is computed. The piezoelectric constant is finally deduced from the following equation:

$$e_{ij} = \frac{|e|}{2\pi V^{(0)}} \sum_l a_{li}^{(0)} \frac{d\varphi_l}{d\epsilon_j} \qquad (3.18)$$

Where the prefactor $\frac{|e|}{2\pi V^{(0)}}$ and $a_{li}^{(0)}$ are given in the output of the keyword **PIEZOBP**. In summary:

1. First run: calculation at $\lambda = 0$ (undistorted)

Program	Keyword	comments
crystal		
properties	**NEWK**	additional keywords allowed
	POLARI	see above
save Fortran unit 27 as undistord.f27 for example.		

2. Second run: calculation at $\lambda = 1$ (distorted)

Program	Keyword	comments
crystal		Use OPTBERNY to obtain the system at the equilibrium
properties	**NEWK**	same input as in first run
	POLARI	
save Fortran unit 27 as distord**1**.f27 for example.		

3. Third run: merging previous data.

copy undistord.f27 to Fortran unit 28
copy distord**1**.f27 to Fortran unit 29

Program	Keyword	comments
properties	**PIEZOBP**	

4. Construction of a set of data

Repeat 2. and 3. for several amplitude of the strain.
(Systems labeled distord**2** to distord**n** for example).

5. Evaluation of the slope $\frac{d\varphi_l}{d\epsilon_j}$ and calculation of the related piezoelectric constant

Use an external program as *gnuplot* or *xmgr* to plot and fit the data and evaluate the slope at zero strain.
Deduce e_{ij} from Eq. (3.18).

PIEZOWF - Piezoelectricity (localized CO approach)

The calculation the piezoelectric constants of a system, using localized Wannier functions, follows exactly the same path than in the Berry phase scheme (see **PIEZOBP**).
In summary:

1. First run: calculation at $\lambda = 0$ (undistorted)

Program	Keyword	comments
crystal		
properties	**NEWK**	additional keywords allowed
	LOCALWF	see above
save Fortran unit 37 as undistord.f37 for example.		

2. Second run: calculation at $\lambda = 1$ (distorted)

Program	Keyword	comments
crystal		Use OPTBERNY to obtain the system at the equilibrium
properties	**NEWK**	same input as in first run
	LOCALWF	
save Fortran unit 37 as distord**1**.f37 for example.		

3. Third run: merging previous data.

copy undistord.f37 to Fortran unit 38		
copy distord**1**.f37 to Fortran unit 39		
Program	Keyword	comments
properties	**PIEZOWF**	

4. Construction of a set of data

Repeat 2. and 3. for several amplitude of the strain.
(Systems labeled distord**2** to distord**n** for example).

5. Evaluation of the slope $\frac{d\varphi_l}{d\epsilon_j}$ and calculation of the related piezoelectric constant

Use an external program as *gnuplot* or *xmgr* to plot and fit the data and evaluate the slope at zero strain.
Deduce e_{ij} from Eq. (3.18).

POLARI - Spontaneous polarization/ Piezoelectricity

This keyword is used for the preliminary runs of the computation of spontaneous polarization (see **SPOLBP**) and the piezoelectric constants (see **PIEZOBP**)using the Berry phase scheme.

1. This keyword works for 3D systems only.

2. The unit-cell has to contain an even number of electrons (closed shell system).

3. The geometry must be optimized with very high accuracy. The values of the computational parameters for the calculation of the wave function (**TOLINTEG**, page 69 and **TOLSCF**, page 81) and the optimization of the geometry (**XTOL**, **GTOL** and **ETOL**, page 43) must have high values and be the same for all runs.

4. The option **NEWK** (See page 103 for the input) must be used before running **POLARI**. The shrinking factor IS has to be the same for the first and the second run, and 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 outputs produced choosing the keywords **SPOLBP** and **PIEZOBP** in the third run are significant.

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 structures ($\lambda = 1$ and $\lambda = 0$). Then a third run with the keyword SPOLBP gives the polarization difference between the two systems.
In summary:

1. First run: calculation at $\lambda = 0$

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: calculation at $\lambda = 1$

Program	Keyword	comments
crystal		no input data required
properties	NEWK	same input as in first run
	POLARI	
save Fortran unit 27 as sys1.f27		

3. Third run: merging 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)

The calculation of the spontaneous polarization of a system, using the localized Wannier functions follows exactly the same procedure than in the Berry phase scheme (see **SPOLBP**).
It can be summarized as follow:

1. First run: calculation at $\lambda = 0$

Program	Keyword	comments
crystal		see deck 1 for input blocks 1 and 1b
properties	NEWK	additional keywords allowed
	LOCALWF	see above
save Fortran unit 37 as sys0.f37		

2. Second run: calculation at $\lambda = 1$

Program	Keyword	comments
crystal		see deck 1 for input blocks 1 and 1b
properties	NEWK	same input as in first run
	LOCALWF	
save Fortran unit 37 as sys1.f37		

3. Third run: merging previous data.

copy sys0.f37 to Fortran unit 38		
copy sys1.f37 to Fortran unit 39		
Program	Keyword	comments
properties	SPOLWF	

Chapter 4

Input examples

4.1 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, $Fm3m$, cubic
5.64	a (Å)
2	2 non equivalent atoms
11 .5 .5 .5	Z=11, Sodium, $1/2, 1/2, 1/2$
17 .0 .0 .0	Z=17, Chlorine

Diamond - C (2nd Setting - 48 symmops - 36 with translational component)

CRYSTAL	
0 0 0	IFLAG IFHR IFSO
227	space group, $Fd3m$, cubic
3.57	a (Å)
1	1 non equivalent atom
6 .125 .125 .125	Z=6, Carbon, $1/8, 1/8, 1/8$ (multiplicity 2)

Diamond - C (1st Setting - 48 symmops - 24 with translational component)

CRYSTAL	
0 0 1	IFLAG IFHR IFSO
227	space group 227, $Fd3m$, 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 - Cu_2O
CRYSTAL
0 0 0	IFLAG IFHR IFSO
208	space group 208, $P4_2 32$, cubic
4.27	a (Å)
2	2 non equivalent atoms
8 .0 .0 .0	Z=8, Oxygen
29 .25 .25 .25	Z=29, Copper $(1/4, 1/4, 1/4)$

Aragonite - $CaCO_3$
CRYSTAL
1 0 0	IFLAG (1, SPGR symbol) IFHR IFSO
P M C N	space group $Pmcn$, orthorhombic
4.9616 7.9705 5.7394	a,b,c (Å)
4	4 non equivalent atoms
20 .25 .4151 .2103	Z=20, Calcium
6 .25 .7627 .085	Z=6, Carbon
8 .25 .9231 .0952	Z=8, Oxygen
8 .4729 .6801 .087	Z=8, Oxygen

Fluorite - CaF_2
CRYSTAL
0 0 0	IFLAG IFHR IFSO
225	space group 225, $Fm3m$, cubic
5.46	a (Å)
2	2 non equivalent atoms
9 .25 .25 .25	Fluorine
20 .0 .0 .0	Calcium

Cesium chloride - CsCl
CRYSTAL
0 0 0	IFLAG IFHR IFSO
221	space group 221, $Pm3m$, cubic
4.12	a (Å)
2	2 non equivalent atoms
55 .5 .5 .5	Cesium
17 .0 .0 .0	Chlorine

Rutile - TiO_2
CRYSTAL
0 0 0	IFLAG IFHR IFSO
136	space group 136, $P4_2/mnm$, tetragonal
4.59 2.96	a, c (Å)
2	2 non equivalent atoms
22 .0 .0 .0	Titanium
8 .305 .305 .0	Oxygen

Graphite - C (Hexagonal)
CRYSTAL
0 0 0	IFLAG IFHR IFSO
194	space group 194, $P6_3/mmc$, hexagonal
2.46 6.70	a,c (Å)
2	2 non equivalent atoms
6 .0 .0 .0	Carbon
6 .33333333333 .66666666667 .25	Carbon, $1/3, 2/3, 1/4$

Pyrite - FeS_2
CRYSTAL
0 0 0	IFLAG IFHR IFSO
205	space group 205, $Pa3$, cubic
5.40	a (Å)
2	2 non equivalent atoms
26 .0 .0 .0	Iron
16 .386 .386 .386	Sulphur

Calcite - CaCO$_3$

CRYSTAL	
0 1 0	IFLAG IFHR *(=1, rhombohedral representation)* IFSO
167	space group 167, $R\bar{3}c$, hexagonal
6.36 46.833	a (Å), $\alpha°$
3	3 non equivalent atoms
20 .0 .0 .0	Calcium
6 .25 .25 .25	Carbon
8 .007 .493 .25	Oxygen

Corundum - Al$_2$O$_3$ (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 - Al$_2$O$_3$ (rhombohedral representation)

CRYSTAL	
0 1 0	IFLAG IFHR *(=1, rhombohedral cell)* IFSO
167	space group 167, $R\bar{3}c$, hexagonal
5.12948 55.29155	a (Å), $\alpha°$
2	2 non equivalent atoms
13 0.35216 0.35216 0.35216	Aluminium
8 0.94376 0.25 0.55621	Oxygen

Zirconia - ZrO$_2$ - monoclinic structure

CRYSTAL	
0 0 1	IFLAG IFHR IFSO *(=1, standard shift of origin)*
14	space group 14, $P2_1/c$, monoclinic
5.03177 5.03177 5.258 90.0	a,b,c (Å), $\beta°$
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 - ZrO$_2$ - tetragonal structure

CRYSTAL	
0 0 1	IFLAG IFHR IFSO *(=1, standard shift of origin)*
137	space group 137, $P4_2/nmc$, tetragonal
3.558 5.258	a,c (Å)
3	3 non equivalent atoms
240 0.0 0.0 0.0	Zirconium, Pseudopotential (Z' > 200)
208 0.0 -0.5 0.174	Oxygen, Pseudopotential
208 0.5 0.0 0.326	Oxygen, Pseudopotential

Zirconia - ZrO$_2$ - cubic structure

CRYSTAL	
0 0 1	IFLAG IFHR IFSO *(=1, standard shift of origin)*
225	space group 225, $Fm3m$, 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

SiO$_2$, Chabazite

CRYSTAL
0 1 0	IFLAG IFHR *(=1,rhombohedral representation)* IFSO
166	space group 166 $R\bar{3}m$, hexagonal
9.42 94.47	a (Å), $\beta°$
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)

SiO$_2$, Siliceous Faujasite

CRYSTAL
0 0 0	IFLAG IFHR IFSO
227	space group 227, $Fd3m$, 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)

SiO$_2$, 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)

SiO$_2$, 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 37), entered in the geometry editing section of 3D structure input. In that case the layer group is automatically identified by the program. The input tests 4-24, 5-25, 6-26 and 7-27 show the two different ways to obtain the same 2D structure.

Atom coordinates: z in Ångstrom, x, y in fractional units of the crystallographic cell translation vectors.

Test05 - graphite 2D (see test 25)

SLAB	
77	layer group (hexagonal)
2.47	lattice vector length (Å)
1	1 non equivalent atom
6 -0.33333333333 0.33333333333 0.	Z=6; Carbon; x,y,z

Beryllium - 3 layers slab

SLAB	
78	layer group (hexagonal)
2.29	lattice vector length (Å)
2	2 non equivalent atoms
4 0.333333333333 0.666666666667 0.	Z=4, Beryllium; $1/3, 2/3, z$
4 0.666666666667 0.333333333333 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 0.333333333333 0.666666666667 0.897499	Z=4, Beryllium; x,y,z
4 0.666666666667 0.333333333333 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 (triclinic)
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	lattice vectors length (Å)
4	4 non equivalent atoms
12 0. 0. 1.48846	Z=12, Magnesium; x,y,z
8 0.5 0. 1.48846	Z=8, Oxygen; x,y,z
12 0.5 0.5 0.	Z=12, Magnesium; x,y,z
8 0. 0.5 0.	Z=8, Oxygen; x,y,z

CO on MgO (001) two layers slab - one-side adsorption

SLAB	
55	
2.97692	lattice vector length [$4.21/\sqrt{2}$] (Å)
6	6 non equivalent atoms
108 0. 0. 4.5625	Z=8, Oxygen; x,y,z
6 0. 0. 3.4125	Z=6, Carbon; x,y,z
12 0. 0. 1.0525	Z=12, Magnesium; x,y,z
8 0.5 0.5 1.0525	Z=8, Oxygen; x,y,z
12 0. 0. -1.0525	Z=12, Magnesium; x,y,z
8 0.5 0.5 -1.0525	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 16, and test 36).

CO on MgO (001) two layers slab - two-side adsorption

SLAB	
64	
2.97692	lattice vector length (Å)
4	4 non equivalent atoms
108 0.25 0.25 4.5625	Z=8, Oxygen; x,y,z
6 0.25 0.25 3.4125	Z=6, Carbon; x,y,z
12 0.25 0.25 1.0525	Z=12, Magnesium; x,y,z
8 0.75 0.75 1.0525	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	lattice vector length (Å)
5	5 non equivalent atoms
6 0. 0. 0.	Z=6, Carbon; x,y,z
6 0.5 0. 0.8925	Z=6, Carbon; x,y,z
6 0.5 0.5 1.785	Z=6, Carbon; x,y,z
6 0. 0.5 2.6775	Z=6, Carbon; x,y,z
6 0. 0. 3.57	Z=6, Carbon; x,y,z

Diamond slab parallel to (100) face - ten layers slab

SLAB	
39	layer group
2.52437 2.52437	lattice vectors length (Å)
5	5 non equivalent atoms
6 0.25 0. 0.44625	Z=6, Carbon; x,y,z
6 0.25 0.5 1.33875	Z=6, Carbon; x,y,z
6 0.75 0.5 2.23125	Z=6, Carbon; x,y,z
6 0.75 0 3.12375	Z=6, Carbon; x,y,z
6 0.25 0. 4.01625	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 - CH$_4$ 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(NH$_2$)$_2$ 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

4.2 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			nuclear charge; number of terms in eq. 2.7 and 2.8
344.84100	-18.00000	-1		eq. 2.7, 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. 2.8, 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. 2.8, 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. 2.8, 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.			

4.3   SCF options - SPINEDIT

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 19)
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 (FRACTIONARY 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
==============================================================================
```

4.4   Geometry optimization - OPTCOORD

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 (C₂ᵥ)
        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
        OPTCOORD                Keyword to perform a geometry optimization
        ENDOPT                  End of the geometry optimization input block
        END                     End of the geometry input section
```

The **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
```

On the first step of the optimization, the **Crystal** 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 a few lines on the optimization process are reported, namely: current geometry, total energy and gradients, and convergence test. The output for the urea molecule geometry optimization looks as follows:

```
*******************************************************************************
POINT CALCULATION    2
*******************************************************************************
ATOMS IN THE ASYMMETRIC UNIT    5 - ATOMS IN THE UNIT CELL:     8
     ATOM            X(ANGSTROM)          Y(ANGSTROM)          Z(ANGSTROM)
*******************************************************************************
  1 T    6 C      2.952109148728E-18   2.952109148728E-18   1.112498507543E-01
  2 T    8 O      3.738040356496E-17   3.738040356496E-17   1.408675664831E+00
  3 T    7 N      1.643486040825E-01   1.142475701821E+00  -6.110581854722E-01
  4 F    7 N     -1.643486040825E-01  -1.142475701821E+00  -6.110581854722E-01
  5 T    1 H     -2.742826212941E-01   1.173433830045E+00  -1.525846151428E+00
  6 F    1 H      2.742826212941E-01  -1.173433830045E+00  -1.525846151428E+00
  7 T    1 H      7.072543295810E-02   1.995428931213E+00  -5.916392089218E-02
  8 F    1 H     -7.072543295810E-02  -1.995428931213E+00  -5.916392089218E-02

T = ATOM BELONGING TO THE ASYMMETRIC UNIT

INTRACELL NUCLEAR REPULSION (A.U.)  1.224347549602E+02 (BOHR = 0.529177249)

TOTAL ENERGY(DFT)(AU)( 29) -2.2514275144821E+02 DE-1.4E-08 DP 7.7E-09

SYMMETRY ALLOWED FORCES (ANALYTICAL) (DIRECTION, FORCE)

   1  1.1072258E-01    2 -7.4201763E-02    3 -2.8080699E-03    4  2.3779951E-02
   5 -8.3505121E-03    6  2.6313459E-03    7  3.1574557E-03    8  6.4585908E-03
   9  1.1481013E-03   10 -1.1940670E-02

GRADIENT NORM      0.136422  GRADIENT THRESHOLD      0.500000

MAX GRADIENT      0.110723  THRESHOLD                0.000450 CONVERGED NO
RMS GRADIENT      0.043140  THRESHOLD                0.000300 CONVERGED NO
MAX DISPLAC.      0.081245  THRESHOLD                0.001800 CONVERGED NO
RMS DISPLAC.      0.035270  THRESHOLD                0.001200 CONVERGED NO
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT BERNY        TELAPSE       833.18 TCPU      826.21
```

After the first step, output for SCF and gradient calculations is routed to an external fortran unit fort.65.

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):  -2.251504436450E+02  POINTS   10 *
*****************************************************************

...

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      3.947486080494E-18   3.947486080494E-18   1.487605014533E-01
  2 T    8 O      3.633779934042E-17   3.633779934042E-17   1.369385259723E+00
  3 T    7 N      1.721504570772E-01   1.150654062355E+00  -6.120839819527E-01
```

```
   4 F   7 N    -1.721504570772E-01 -1.150654062355E+00 -6.120839819527E-01
   5 T   1 H    -2.789616513042E-01  1.183857618602E+00 -1.516451281243E+00
   6 F   1 H     2.789616513042E-01 -1.183857618602E+00 -1.516451281243E+00
   7 T   1 H     6.793388863152E-02  1.994529879710E+00 -6.664311739212E-02
   8 F   1 H    -6.793388863152E-02 -1.994529879710E+00 -6.664311739212E-02

 T = ATOM BELONGING TO THE ASYMMETRIC UNIT

 INTRACELL NUCLEAR REPULSION (A.U.)  1.233193031445E+02 (BOHR = 0.529177249)

 SYMMETRY OPERATORS:   2
  IV  INV                   ROTATION MATRIX               TRANSLATOR (ANGSTROM)
   1   1  1.  0.  0.  0.  1.  0.  0.  0.  1.  0.00000000  0.00000000  0.00000000
   2   2 -1.  0.  0.  0. -1.  0.  0.  0.  1.  0.00000000  0.00000000  0.00000000
```

The final geometry is both printed in the **Crystal** output and written on the fortran unit 34. Thus, it can be recovered by reading the geometry from the external unit 34 (keyword **EXTERNAL**, input block1, page 13).

▷ Example

Urea Molecule	Title
EXTERNAL	Geometry read from the external fortran unit 34
optional keywords	
END	End of the geometry input section

To restart an optimization, the same input deck used for the first steps has to be modified by adding the keyword **RESTART**. The file with information on the previous optimization must be defined as fortran unit 68

▷ 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
OPTCOORD	OPTCOORD
ENDOPT	RESTART
END	ENDOPT
	END

Partial optimization

In order to optimize the coordinates of the hydrogens in the molecular crystal of urea, the following input must be entered:

```
Urea Molecule          Title
MOLECULE               Dimension of the system
15                     Point group (C₂ᵥ)
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
OPTCOORD               Keyword to perform a geometry optimization
ATOMFREE               Keyword for a partial optimization
4                      Number of atoms to be optimized
5 6 7 8                Label of the atoms to be optimized
ENDOPT                 End of the geometry optimization input block
END                    End of the geometry input section
```

All the hydrogens are given, the program will detect the symmetry relationship between them.

Final run

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). As a consequence, the total energy computed is not correctly defined, according to the numerical methods applied in CRYSTAL. The correct energy of the optimized geometry, computed with true truncation series, is different in those cases from the one given at the end of the optimization. A second optimization process, with truncation series defined according to the geometry obtained in the first optimization, must be performed to check if that geometry corresponds to a real energy minimum. The keyword **FINALRUN** starts the process automatically.

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 -Al$_2$O$_3$ is reported.

▷ Example - Optimization of surface

```
α -Al₂O₃ - (001) surface  title
CRYSTAL                    dimension of the system
0 0 0
167                        space group
4.7602 12.9933             lattice parameters
2                          number of irreducible atoms
13 0.  0.  0.35216         fractional coordinates of first atom
8 0.30624 0.  0.25         fractional coordinates of second atom
SLABCUT                    3D→ 2D
0 0 1                      (h, k, l) Miller indices of the surface
1 6                        number of layers, starting from the first classified
OPTCOORD                   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 O    0 0 0    3 O    0 0 0    4 O    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 O   -1 0 0    3 O    1 1 0    4 O    0 0 0
   1 AL  3    3.4295    6.4808    7 O    0 1 0    8 O    0 1 0    9 O    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 O    0 0 0    3 O    0 0 0    4 O    0 1 0
   1 AL  1    2.6116    4.9351   10 AL   0 0 0
   1 AL  3    2.8198    5.3286    7 O    0 1 0    8 O    0 1 0    9 O    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 O   -1 0 0    3 O    1 1 0    4 O    0 0 0
```

 Total energy   E = -1400.1148194 hartree

Extensive relaxation occurred, the Aluminum atoms penetrate into the
slab. Total energy and gradients are computed after definition of
the truncation series
with reference to the new geometry (the process is authomatic if keyword
FINALRUN is specified in the input stream). Gradients do not match
the convergence criteria.

 Total energy   E = -1400.1193593 hartree

The keyword FINALRUN was entered with ICODE=3, so geometry optimization restarts
from the first step final geometry, with truncation series defined relative to it.
After 6 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 O    0 0 0    3 O    0 0 0    4 O    0 1 0
   1 AL  1    2.5917    4.8976   10 AL   0 0 0
   1 AL  3    2.8095    5.3092    7 O    0 1 0    8 O    0 1 0    9 O    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 O   -1 0 0    3 O    1 1 0    4 O    0 0 0
```

 Total energy   E = -1400.1194545 hartree

The final geometry is printed, and written in fortran unit 34.

A final check on geometry can be done with the following input:

```
alpha-Al2O3 (corundum) 001 2 LAYERS (3D-->2D)
EXTERNAL
OPTCOORD
ENDOPT
END
```

The keyword EXTERNAL route the basic geometry input stream to fortran unit 34.
The file to be read is written at the end of the first optimization run.

No optimization starts, convergence criteria are already satisfied.

 Total energy   E = -1400.1194544 hartree

Chapter 5

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.

5.1   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) [88, 89, 90, 91].

   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 [92, 93]. 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.

5.2 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.

5.3 Valence functions

Molecular crystals

Molecular BSs, minimal and split-valence, are perfectly adequate. Tests have been performed on bulk urea [94] 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 5.1. The last entry of Table 5.1 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 [95] 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 [96, 97].

Table 5.1: 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 (Li$_2$ O and Li$_3$ N) a 'valence' sp shell with exponent 0.4-0.3 and 0.5-0.6, respectively [28, 25].

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) [25].

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 [28]. 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 (α=0.45 and 0.15 to be compared with α=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 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 α=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 5.1; note too that the cost at α=0.15 is only 50% of the one at α=0.09). On the contrary, the best molecular and crystalline exponent (α=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 (α=0.94 and 0.20 bohr^{-2}, respectively [98]).

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 5.2: 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 5.2. Finally, the most diffuse gaussian can be optimized; in the two cases the minimum has not been found owing to numerical instabilities.

See [99] for a more extensive discussion of the metallic lithium case.

5.4   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 5.1 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 5.1 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 5.2), 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).

5.5 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 64). 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 [69] requires basis functions linearly independent. A symptom of numerical dependence may produce an error message in RHOLSK or CHOLSK while running **scf**.

Chapter 6

Theoretical framework

6.1 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).

$$\psi_i(\mathbf{r}; \mathbf{k}) = \sum_\mu a_{\mu,i}(\mathbf{k})\phi_\mu(\mathbf{r}; \mathbf{k}) \tag{6.1}$$

$$\phi_\mu(\mathbf{r}; \mathbf{k}) = \sum_{\mathbf{g}} \varphi_\mu(\mathbf{r} - \mathbf{A}_\mu - \mathbf{g}) \, e^{i\mathbf{k}\cdot\mathbf{g}} \tag{6.2}$$

$\mathbf{A}_\mu$ 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:

$$\varphi_\mu(\mathbf{r} - \mathbf{A}_\mu - \mathbf{g}) = \sum_j^{n_G} d_j \, G(\alpha_j; \mathbf{r} - \mathbf{A}_\mu - \mathbf{g}) \tag{6.3}$$

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, $\mathbf{k}$:

$$\mathbf{F}(\mathbf{k})\mathbf{A}(\mathbf{k}) = \mathbf{S}(\mathbf{k})\mathbf{A}(\mathbf{k})\mathbf{E}(\mathbf{k}) \tag{6.4}$$

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:

$$\mathbf{F}(\mathbf{k}) = \sum_{\mathbf{g}} \mathbf{F}^{\mathbf{g}} \, e^{i\mathbf{k}\cdot\mathbf{g}} \tag{6.5}$$

The matrix elements of $\mathbf{F^g}$, 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:

$$F_{12}^{\mathbf{g}} = H_{12}^{\mathbf{g}} + B_{12}^{\mathbf{g}} \tag{6.6}$$

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

$$H_{12}^{\mathbf{g}} = T_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = \langle \varphi_1^{\mathbf{0}} \mid \widehat{T} \mid \varphi_2^{\mathbf{g}} \rangle + \langle \varphi_1^{\mathbf{0}} \mid \widehat{Z} \mid \varphi_2^{\mathbf{g}} \rangle \tag{6.7}$$

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:

$$B_{12}^{\mathbf{g}} = C_{12}^{\mathbf{g}} + X_{12}^{\mathbf{g}} =$$

$$\sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^{\mathbf{0}} \varphi_2^{\mathbf{g}} \mid \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h+n}}) - \frac{1}{2} (\varphi_1^{\mathbf{0}} \varphi_3^{\mathbf{h}} \mid \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h+n}})] \tag{6.8}$$

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 $\mathbf{P^n}$ density matrix elements in the AOs basis set are computed by integration over the volume of the Brillouin zone (BZ),

$$P_{3,4}^{\mathbf{n}} = 2 \int_{BZ} d\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{n}} \sum_{j} a_{3j}^{*}(\mathbf{k}) a_{4j}(\mathbf{k}) \theta(\epsilon_F - \epsilon_j(\mathbf{k})) \tag{6.9}$$

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:

$$E^{elec} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} (H_{12}^{\mathbf{g}} + B_{12}^{\mathbf{g}}) \tag{6.10}$$

A discussion of the different contributions to the total energy is presented in [6, 10] and in Chapter 11 of reference [20].

$$E^{coul} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^{\mathbf{0}} \varphi_2^{\mathbf{g}} \mid \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h+n}})] \tag{6.11}$$

$$E^{exch} = -\frac{1}{4} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{34} \sum_{\mathbf{n}} P_{34}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^{\mathbf{0}} \varphi_3^{\mathbf{h}} \mid \varphi_2^{\mathbf{g}} \varphi_4^{\mathbf{h+n}})] \tag{6.12}$$

6.2 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).

6.3 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 [100] and by Saunders et al. [10]. It may be summarized as follows.

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

$$E_{ee}^{coul} = \frac{1}{2} \sum_{1,2} \sum_{\mathbf{g}} P_{12}^{\mathbf{g}} \sum_{3,4} \sum_{\mathbf{n}} P_{3,4}^{\mathbf{n}} \sum_{\mathbf{h}} [(\varphi_1^{\mathbf{0}} \varphi_2^{\mathbf{g}} \mid \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h+n}}) \tag{6.13}$$

Seven indices are involved in equation 6.13; 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: $\{G_{1\mathbf{0}}G_{2\mathbf{g}}\}$ and $\{G_{3\mathbf{h}}G_{4\mathbf{h+n}}\}$, 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 6.13 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 :

$$\rho_\lambda(\mathbf{r} - \mathbf{h}) \equiv \{\lambda\}' \equiv \{\lambda\} - Z_\lambda = \sum_{3\in\lambda} \sum_{4\mathbf{n}} P_{34}^{\mathbf{n}} \ \varphi_3(\mathbf{r} - \mathbf{h}) \ \varphi_4(\mathbf{r} - \mathbf{h} - \mathbf{n}) - Z_\lambda \tag{6.14}$$

   where Z_λ is the fraction of nuclear charge formally attributed to shell λ, and $\{\lambda\}$ is the electron charge distribution of shell λ.

2. Z and C contributions are reordered:

$$C_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = \sum_\lambda \sum_{\mathbf{h}} \int d\mathbf{r} \, d\mathbf{r}' \varphi_1^{\mathbf{0}}(\mathbf{r}) \ \varphi_2^{\mathbf{g}}(\mathbf{r}) \ |\mathbf{r} - \mathbf{r}' - \mathbf{h}|^{-1} \ \rho_\lambda(\mathbf{r}' - \mathbf{h}) \tag{6.15}$$

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 [10].

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

$$\begin{aligned} C_{12}^{\mathbf{g}} + Z_{12}^{\mathbf{g}} = \quad & \sum_\lambda \{\sum_{\mathbf{h}}^{B_\lambda} [\sum_{3\in\lambda} \sum_4 \sum_{\mathbf{n}} P_{34}^{\mathbf{n}} (\varphi_1^{\mathbf{0}} \varphi_2^{\mathbf{g}} \mid \varphi_3^{\mathbf{h}} \varphi_4^{\mathbf{h+n}}) + \\ - \quad & \sum_{\ell,m} \gamma_\ell^m(\mathbf{A}_\lambda; \{\lambda\}) \Phi_\ell^m(12\mathbf{g}; A_\lambda + \mathbf{h})] + \\ + \quad & \sum_{\mathbf{h}} \sum_{\ell,m} \gamma_\ell^m(A_\lambda; \{\lambda\}') \Phi_\ell^m(12\mathbf{g}; \mathbf{A}_\lambda + \mathbf{h})\} \end{aligned} \tag{6.16}$$

where:

$$\gamma_\ell^m(\mathbf{A}_\lambda; \{\lambda\}) = \int d\mathbf{r} \ \rho_\lambda(\mathbf{r} - \mathbf{A}_\lambda) N_\ell^m X_\ell^m(\mathbf{r} - \mathbf{A}_\lambda) \tag{6.17}$$

$$\Phi_\ell^m(12\mathbf{g}; \mathbf{A}_\lambda + \mathbf{h}) = \int d\mathbf{r}\varphi_1^\mathbf{0}(\mathbf{r})\varphi_2^\mathbf{g}(\mathbf{r})X_\ell^m(\mathbf{r} - \mathbf{A}_\lambda - \mathbf{h}) \, |\mathbf{r} - \mathbf{A}_\lambda - \mathbf{h}|^{-2\ell-1} \qquad (6.18)$$

The Ewald term in eq. 6.16 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 6.16 is that many four-centre (long-range) integrals can be replaced by fewer three-centre integrals.

The attribution of the interaction between $\rho_1 = \{\mathbf{1}\mathbf{0}, 2\mathbf{g}\}$ 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 68).

6.4 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 [9]. The exchange contribution to the total energy can be written as follows:

$$E^{ex} = \frac{1}{2}\sum_{12}\sum_{\mathbf{g}} P_{12}^\mathbf{g} \, [-\frac{1}{2}\sum_{34}\sum_{\mathbf{n}} P_{34}^\mathbf{n} \sum_{\mathbf{h}}(\varphi_1^\mathbf{0}\varphi_3^\mathbf{h} \mid \varphi_2^\mathbf{g}\varphi_4^{\mathbf{h}+\mathbf{n}})] \qquad (6.19)$$

where the term in square brackets is the exchange contribution to the 12**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 **h** summation can be truncated after a few terms, since the $\{\varphi_1^\mathbf{0}\varphi_3^\mathbf{h}\}$ overlap distribution decays exponentially as **h** increases. Similar considerations apply to the second charge distribution. In CRYSTAL, the **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 **g** and **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 $\mathbf{n} = \mathbf{g}$:

$$e_{12}^\mathbf{g} = -1/4(P_{12}^\mathbf{g})^2(\mathbf{1}\mathbf{0}\,\mathbf{1}\mathbf{0}|2\mathbf{g}\,2\mathbf{g}) = -(p^\mathbf{g})^2/(4|\mathbf{g}|) \qquad (6.20)$$

(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 [83], 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 **g** summations when the $\int d\mathbf{r}\varphi_1^\mathbf{0}\varphi_2^\mathbf{g}$ overlap is smaller than a given threshold, defined as $P_{ex}^\mathbf{g}$ (where **ITOL4** = $-log_{10}\,(P_{ex}^\mathbf{g})$) and also truncating the **n** summation when $\int d\mathbf{r}\varphi_3^\mathbf{0}\varphi_4^\mathbf{n}$ overlap is smaller than the threshold, $P_{ex}^\mathbf{n}$ (**ITOL5** = $-log_{10}$ $(P_{ex}^\mathbf{n})$).

Despite its partially arbitrary nature, this criterion presents some advantages with respect to other more elaborate schemes: it is similar to the other truncation schemes (ITOL1, ITOL2, ITOL3), and so the same classification tables can be used; it is, in addition, reasonably efficient in terms of space occupation and computer time.

This truncation scheme is symmetric with respect to the **g** and **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 [7] 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 $\int d\mathbf{r}\varphi_3^{\mathbf{0}}\varphi_4^{\mathbf{n}}$ 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.

6.5 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 6.13. Consider one contribution to the charge distribution of electron 1, centred in the reference cell: $\rho^{\mathbf{0}} = \varphi_1^{\mathbf{0}}\varphi_2^{\mathbf{g}}$; now consider the charge distribution $\rho_\lambda(\mathbf{h})$ of shell λ centred in cell $\mathbf{h}$ (equation 6.14). For small $|\mathbf{h}|$ values, ρ_λ and $\rho^{\mathbf{0}}$ 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 $\varphi_3^{\mathbf{h}}\varphi_4^{\mathbf{h+n}}$ contributions to ρ_λ are external to $\rho^0 = \varphi_1^{\mathbf{0}}\varphi_2^{\mathbf{g}}$; 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 [7] 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 $\lambda_1^{\mathbf{0}}\lambda_2^{\mathbf{g}}$, shell $\lambda_3^{\mathbf{h}}$ is attributed to the B (*bielectronic*) zone, the penetration between the products of adjoined Gaussians $G_1^{\mathbf{0}}G_2^{\mathbf{g}}$ and $G_3^{\mathbf{h}}G_4^{\mathbf{h+n}}$ is estimated: the default value of the penetration parameter is 14, and the block of bielectronic integrals is attributed accordingly to the b_e (*exact*) or to the b_b (*bipolar*) zone. The set of $\mathbf{h}$ vectors defining the B zone of $\rho^{\mathbf{0}} = \{12\mathbf{g}\}$ and $\rho_\lambda \equiv \{\lambda_3\}$ is then split into two subsets, which are specific for each partner λ_4^l of λ_3.

A similar scheme is adopted for the selected exchange integrals (see previous section) whose pseudo charges do not overlap appreciably. The default value of the penetration parameter is 10.

The total energy change due to the bipolar expansion approximation should not be greater than 10^{-4} hartree/atom; exact evaluation of all the bielectronic integrals (obtained by setting the penetration parameter value > 20000) increases the computational cost by a factor of between 1.3 and 3. Multipolar expansion is very efficient, because the following two conditions are fulfilled:

1. A general algorithm is available for reaching high ℓ values easily and economically [100, 10]. 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.

6.6 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 [8] 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:

$$D_{1,2T;3,4Q} = \sum_{\mathbf{n}}[(\varphi_1^{\mathbf{0}}\varphi_2^{\mathbf{g}} \mid \varphi_3^{\mathbf{h}}\varphi_4^{\mathbf{h+n}}) - 1/2(\varphi_1^{\mathbf{0}}\varphi_3^{\mathbf{h}} \mid \varphi_2^{\mathbf{g}}\varphi_4^{\mathbf{h+n}})] \qquad (6.21)$$

- 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 $1, 2\mathbf{g}$ 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. 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. 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

6.7 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 6.9. The technique adopted to compute ϵ_F and the P matrix in the SCF step is described in reference [101]. The Fourier-Legendre technique presented in Chapter II.6 of reference [7] is adopted in the calculation of total and projected DOS. The Fermi energy and the integral in equation 6.9 are evaluated starting from the knowledge of the eigenvalues, $\epsilon_n(k)$ 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*, [102]) 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 6.9 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* [103, 104] 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.

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

$$\rho(\underline{p}) = 1/V_{BZ} \sum_j \int_{BZ} d\underline{k} \ |\psi_j(\underline{k},\underline{p})|^2 \ \theta[\epsilon_F - \epsilon_j(\underline{k})] = \tag{6.22}$$

$$= \sum_j \sum_{\mu\nu} e^{-i\underline{p}\cdot(\underline{s}_\mu - \underline{s}_\nu)} a_{\mu j}(\underline{p}^0) a_{\nu j}^*(\underline{p}^0) \chi_\mu(\underline{p}) \chi_\nu^*(\underline{p}) \ \theta[\epsilon_F - \epsilon_j(\underline{p}^0)] \tag{6.23}$$

$$\rho(\underline{p}) = N^{-1} \int d\underline{r} d\underline{r}' e^{-i\underline{p}\cdot(\underline{r}' - \underline{r})} \rho(\underline{r} - \underline{r}') \tag{6.24}$$

$$= \sum_{\mu\nu} \sum_{\underline{g}} P_{\mu\nu}^{\underline{g}} e^{-i\underline{p}\cdot(\underline{g} + \underline{s}_\mu - \underline{s}_\nu)} \chi_\mu(\underline{p}) \chi_\nu^*(\underline{p}) \tag{6.25}$$

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 $\underline{K}$, $\underline{s}_\mu$ 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:

$$\chi_\mu(\underline{p}) = \int dr \chi_\mu(\underline{r}) \ e^{i\underline{p}\cdot\underline{r}} \tag{6.26}$$

Equation 6.25 is used by default to compute the core band contribution, and equation 6.23 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:

$$J(\underline{p}) = \int d\underline{p}'_\perp \rho(\underline{p} + \underline{p}'_\perp) \tag{6.27}$$

It is customary to make reference to CPs as functions of a single variable p, with reference to a particular direction $< hkl >$ 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:

$$J_{<hkl>}(p) = J(p \ \underline{e}) \tag{6.28}$$

The function $J_{<hkl>}(p)$ 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, $J_{<hkl>}(p)$ may be related to the experimental CPs, after correction for the effect of limited resolution as a convolution of the "infinite resolution" results, $J_{<hkl>}^0(p)$, with a normalized function characterized by a given standard deviation σ:

$$J_{<hkl>}^\sigma(p) = \int_{-\infty}^{+\infty} dp' J_{<hkl>}^0(p') g_\sigma(p - p') \tag{6.29}$$

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(r) is given by the 1D Fourier Transform:

$$B_{<hkl>}(r) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dp J_{<hkl>}(p) e^{i\ pr} \tag{6.30}$$

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

$$\overline{J(q)} = \int_0^q \rho(\underline{p}) p dp \tag{6.31}$$

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

$$KE = \int_0^\infty p^2 \overline{J(p)} dp \tag{6.32}$$

6.9 Elastic Moduli of Periodic Systems

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

$$C_{ij} = 1/V \cdot \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j} \tag{6.33}$$

where V is the volume of the cell. The energy derivatives must be evaluated *numerically* (analytical gradients are not implemented in CRYSTAL 95). 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 65, page 65). 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$_2$ O.

The analysis of the point group at the atomic positions (printed by the **ATOMSYMM** option, page 27) is useful in finding the atomic coordinates to be relaxed. Examples of deformation strategies are discussed in references [28, 105].

In a crystalline system a point **r** is usually defined in terms of its fractionary components:

$$\mathbf{r} = \mathbf{h}\ \mathbf{L}_p$$

where :

$$\mathbf{L}_p = \begin{bmatrix} \mathbf{l}_1 \\ \mathbf{l}_2 \\ \mathbf{l}_3 \end{bmatrix} = \begin{bmatrix} l_{1x} & l_{1y} & l_{1z} \\ l_{2x} & l_{2y} & l_{2z} \\ l_{3x} & l_{3y} & l_{3z} \end{bmatrix} \tag{6.34}$$

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

$\mathbf{l}_1, \mathbf{l}_2, \mathbf{l}_3$ are the fundamental vectors of the primitive cell, **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:

$$\mathbf{r}' = \mathbf{h}\ \mathbf{L}'_p$$

$$\mathbf{L}'_p = (\mathbf{I} + \epsilon)\mathbf{L}_p \tag{6.35}$$

or:

$$\mathbf{L}'_p = \mathbf{L}_p + \mathbf{Z} \tag{6.36}$$

where

$$\mathbf{Z} = \epsilon\ \mathbf{L}_p$$

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

The deformation may be constrained to be volume-conserving, in which case the lattice vectors of the distorted cell must be scaled as follows:

$$\mathbf{L}_p" = \mathbf{L}'_p (V/V')^{1/3} \tag{6.37}$$

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:

$$E(\epsilon) = E(\mathbf{0}) + \sum_i^6 \frac{\partial E}{\partial \epsilon_i}\epsilon_i + 1/2\sum_{i,j}^6 \frac{\partial^2 E}{\partial \epsilon_i \partial \epsilon_j}\epsilon_i\epsilon_j \tag{6.38}$$

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$_2$O, 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:

$$
E(\delta) = E(0) + 1/2 \frac{\partial^2 E}{\partial \epsilon_1^2} \delta^2 + \cdots = a + b\delta^2 + c\delta^3 \cdots
$$

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:

$$
\begin{aligned}
E(\epsilon_1, \epsilon_2) &= E(0,0) + 1/2 \frac{\partial^2 E}{\partial \epsilon_1^2} \delta^2 + 1/2 \frac{\partial^2 E}{\partial \epsilon_2^2} \delta^2 - \frac{\partial^2 E}{\partial \epsilon_1 \partial \epsilon_2} \delta^2 + \cdots = \\
&= E(0,0) + V(C_{11} - C_{12})\delta^2 + \cdots = a + b\delta^2 + \cdots
\end{aligned}
$$

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:

$$
\epsilon = \begin{bmatrix} \delta & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & -2\delta \end{bmatrix}
$$

$$E(\epsilon_1, \epsilon_2, \epsilon_3) = E(0,0,0) + 3V(C_{11} - C_{12})\delta^2 + \cdots = a + b\delta^2 + \cdots$$

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 6.38)

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

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 $(\delta = 2x, C_{45} = C_{46} = C_{56} = 0)$

$$E(\epsilon_4, \epsilon_5, \epsilon_6) = E(0) + 3/2\frac{\partial^2 E}{\partial \epsilon_4^2}\delta^2 + \cdots = E(0) + 6\frac{\partial^2 E}{\partial \epsilon_4^2}x^2 + \cdots = a + bx^2 + \cdots$$

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:

$$
\begin{aligned}
E(\epsilon) &= E(\mathbf{0}) + 3/2 \frac{\partial^2 E}{\partial \epsilon_1^2} \delta^2 + 3 \frac{\partial^2 E}{\partial \epsilon_1 \partial \epsilon_2} \delta^2 = & (6.39) \\
&= E(\mathbf{0}) + \frac{3V}{2} [C_{11} + 2C_{12}] \delta^2 & (6.40)
\end{aligned}
$$

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

N.B. Conversion factors:
1 hartree Å^{-3} = 4359.74812 GPa
1 GPa = 1 GN m^{-2} = 1 GJ m^{-3} = 10^{10} dyne cm^{-2} = 10^{-2} Mbar.

6.10 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:

$$\varphi_{el}^{(\lambda,1)} = \frac{1}{s2s3} \sum_{j2,j3} \sum_{j_1} \Delta\varphi_{j_1,j_2,j_3}^{(\lambda,1)}(\mathbf{k}) \tag{6.41}$$

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

$$\mathbf{P}_{el}^{(\lambda)} = \frac{1}{\Omega^{(\lambda)}} \left(B^{(\lambda)}\right)^{-1} \varphi_{el}^{(\lambda)} \tag{6.42}$$

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, $P_{nuc}^{(\lambda)}$ can also be written as:

$$\mathbf{P}_{nuc}^{(\lambda)} = \frac{1}{\Omega^{(\lambda)}} \sum_{A} \mathbf{R}_{A}^{(\lambda)} \cdot Z_A \tag{6.43}$$

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

$$\mathbf{P}_{tot}^{(\lambda)} = \mathbf{P}_{nuc}^{(\lambda)} + \mathbf{P}_{el}^{(\lambda)} \tag{6.44}$$

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

$$\mathbf{P} = \mathbf{P}_{tot}^{(\lambda)} - \mathbf{P}_{tot}^{(\lambda)} \tag{6.45}$$

Spontaneous polarization through the localized crystalline orbitals approach

The electronic contribution to the polarization of a system λ, $P_{el}^{(\lambda)}$, can be written as

$$\mathbf{P}_{el}^{(\lambda)} = \frac{e}{\Omega^{(\lambda)}} \sum_{\mu} \langle \mathbf{r}_\mu \rangle \tag{6.46}$$

Where $\langle \mathbf{r}_\mu \rangle$ is the centroid of the Wannier function μ.
The nuclear contribution to the polarization of a system λ, $P_{nuc}^{(\lambda)}$ can also be written as

$$\mathbf{P}_{nuc}^{(\lambda)} = \frac{1}{\Omega^{(\lambda)}} \sum_{A} \mathbf{R}_A \cdot Z_A \tag{6.47}$$

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

$$\mathbf{P}_{tot}^{(\lambda)} = \mathbf{P}_{nuc}^{(\lambda)} + \mathbf{P}_{el}^{(\lambda)} \tag{6.48}$$

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

$$\mathbf{P} = \mathbf{P}_{tot}^{(1)} - \mathbf{P}_{tot}^{(2)} \tag{6.49}$$

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 $\lambda = 0$.

6.11 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

$$\varphi_{nuc}^{(\lambda)} = \Omega^{(\lambda)} \, B^{(\lambda)} \mathbf{P}_{nuc}^{(\lambda)} \tag{6.50}$$

Where $B^{(\lambda)}$ reciprocal lattice vectors components matrix. The last equation can be simplified thanks to (6.43):

$$\varphi_{nuc}^{(\lambda)} = B^{(\lambda)} \sum_A \mathbf{R}_A^{(\lambda)} \cdot Z_A \tag{6.51}$$

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

$$\varphi^{(\lambda)} = \varphi_{nuc}^{(\lambda)} + \varphi_{el}^{(\lambda)} \tag{6.52}$$

The proper piezoelectric constants can be obtained by:

$$\tilde{e}_{ijk} = -\frac{1}{2\pi}\frac{1}{\Omega} \sum_\alpha \frac{d\varphi_\alpha}{d\epsilon_{jk}} \, a_{\alpha,i} \tag{6.53}$$

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 done:

$$e_{ijk} = \tilde{e}_{ijk} + \delta_{ij}P_k - \delta_{jk}P_i \tag{6.54}$$

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

$$\frac{d\varphi_\alpha}{d\epsilon_{jk}} \simeq \frac{\Delta\varphi_\alpha}{\Delta\epsilon_{jk}} = \frac{\varphi_\alpha^{(1)} - \varphi_\alpha^{(0)}}{\epsilon_{jk}^{(1)} - \epsilon_{jk}^{(0)}} \tag{6.55}$$

Piezoelectricity through the localized crystalline orbitals approach

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

$$\varphi_{el}^{(\lambda)} = \Omega^{(\lambda)} \, B^{(\lambda)} \mathbf{P}_{el}^{(\lambda)} \tag{6.56}$$

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

$$\varphi_{nuc}^{(\lambda)} = \Omega^{(\lambda)} \, B^{(\lambda)} \mathbf{P}_{nuc}^{(\lambda)} \tag{6.57}$$

The last equation can be simplified thanks to 6.43:

$$\varphi_{nuc}^{(\lambda)} = B^{(\lambda)} \sum_A \mathbf{R}_A^{(\lambda)} \cdot Z_A \tag{6.58}$$

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

$$\varphi^{(\lambda)} = \varphi_{nuc}^{(\lambda)} + \varphi_{el}^{(\lambda)} \tag{6.59}$$

The proper piezoelectric constants can be obtained by:

$$\tilde{e}_{ijk} = -\frac{1}{2\pi}\frac{1}{\Omega} \sum_\alpha \frac{d\varphi_\alpha}{d\epsilon_{jk}} \, a_{\alpha,i} \tag{6.60}$$

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 done:

$$e_{ijk} = \tilde{e}_{ijk} + \delta_{ij}P_k - \delta_{jk}P_i \tag{6.61}$$

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

$$\frac{d\varphi_\alpha}{d\epsilon_{jk}} \simeq \frac{\Delta\varphi_\alpha}{\Delta\epsilon_{jk}} = \frac{\varphi_\alpha^{(1)} - \varphi_\alpha^{(0)}}{\epsilon_{jk}^{(1)} - \epsilon_{jk}^{(0)}} \tag{6.62}$$

Appendix A

Symmetry groups

A.1 Labels and symbols of the space groups

The labels are according to the International Tables for Crystallography [21]. The symbols are derived by the standard SHORT symbols, as shown in the following examples:

Symbol		Input to CRYSTAL
P $\bar{6}$ 2 m	$\rightarrow$	P␣-6␣2␣M ;
P 6_3 m	$\rightarrow$	P␣63␣M.

For the groups 221-230 the symbols are according to the 1952 edition of the International Tables, *not* to the 1982 edition. The difference involves the 3 axis: 3 (1952 edition); $\bar{3}$ (1982 edition) (Example group 221: 1952 ed. $\rightarrow$ P m 3 m ; 1982 ed. $\rightarrow$ P m $\bar{3}$ m)

IGR	symbol	IGR	symbol	IGR	symbol
Triclinic lattices		37	$Ccc2$	Tetragonal lattices	
1	$P1$	38	$Amm2$	75	$P4$
2	$P\bar{1}$	39	$Abm2$	76	$P4_1$
Monoclinic lattices		40	$Ama2$	77	$P4_2$
3	$P2$	41	$Aba2$	78	$P4_3$
4	$P2_1$	42	$Fmm2$	79	$I4$
5	$C2$	43	$Fdd2$	80	$I4_1$
6	Pm	44	$Imm2$	81	$P\bar{4}$
7	Pc	45	$Iba2$	82	$I\bar{4}$
8	Cm	46	$Ima2$	83	$P4/m$
9	Cc	47	$Pmmm$	84	$P4_2/m$
10	$P2/m$	48	$Pnnn$	85	$P4/n$
11	$P2_1/m$	49	$Pccm$	86	$P4_2/n$
12	$C2/m$	50	$Pban$	87	$I4/m$
13	$P2/c$	51	$Pmma$	88	$I4_1/a$
14	$P2_1/c$	52	$Pnna$	89	$P422$
15	$C2/c$	53	$Pmna$	90	$P42_12$
Orthoorhombic lattices		54	$Pcca$	91	$P4_122$
16	$P222$	55	$Pbam$	92	$P4_12_12$
17	$P222_1$	56	$Pccn$	93	$P4_222$
18	$P2_12_12$	57	$Pbcm$	94	$P4_22_12$
19	$P2_12_12_1$	58	$Pnnm$	95	$P4_322$
20	$C222_1$	59	$Pmmn$	96	$P4_32_12$
21	$C222$	60	$Pbcn$	97	$I422$
22	$F222$	61	$Pbca$	98	$I4_122$
23	$I222$	62	$Pnma$	99	$P4mm$
24	$I2_12_12_1$	63	$Cmcm$	100	$P4bm$
25	$Pmm2$	64	$Cmca$	101	$P4_2cm$
26	$Pmc2_1$	65	$Cmmm$	102	$P4_2nm$
27	$Pcc2$	66	$Cccm$	103	$P4cc$
28	$Pma2$	67	$Cmma$	104	$P4nc$
29	$Pca2_1$	68	$Ccca$	105	$P4_2mc$
30	$Pnc2$	69	$Fmmm$	106	$P4_2bc$
31	$Pmn2_1$	70	$Fddd$	107	$I4mm$
32	$Pba2$	71	$Immm$	108	$I4cm$
33	$Pna2_1$	72	$Ibam$	109	$I4_1md$
34	$Pnn2$	73	$Ibca$	110	$I4_1cd$
35	$Cmm2$	74	$Imma$	111	$P\bar{4}2m$
36	$Cmc2_1$			112	$P\bar{4}2c$

IGR	symbol	IGR	symbol	IGR	symbol
113	$P\bar{4}2_1m$	155	$R32$		Cubic lattices
114	$P\bar{4}2_1c$	156	$P3m1$	196	$F23$
115	$P\bar{4}m2$	157	$P31m$	197	$I23$
116	$P\bar{4}c2$	158	$P3c1$	198	$P2_13$
117	$P\bar{4}b2$	159	$P31c$	199	$I2_13$
118	$P\bar{4}n2$	160	$R3m$	200	$Pm3$
119	$I\bar{4}m2$	161	$R3c$	201	$Pn3$
120	$I\bar{4}c2$	162	$P\bar{3}1m$	202	$Fm3$
121	$I\bar{4}2m$	163	$P\bar{3}1c$	203	$Fd3$
122	$I\bar{4}2d$	164	$P\bar{3}m1$	204	$Im3$
123	$P4/mmm$	165	$P\bar{3}c1$	205	$Pa3$
124	$P4/mcc$	166	$R\bar{3}m$	206	$Ia3$
125	$P4/nbm$	167	$R\bar{3}c$	207	$P432$
126	$P4/nnc$		Hexagonal lattices	208	$P4_232$
127	$P4/mbm$	168	$P6$	209	$F432$
128	$P4/mnc$	169	$P6_1$	210	$F4_132$
129	$P4/nmm$	170	$P6_5$	211	$I432$
130	$P4/ncc$	171	$P6_2$	212	$P4_332$
131	$P4_2/mmc$	172	$P6_4$	213	$P4_132$
132	$P4_2/mcm$	173	$P6_3$	214	$I4_132$
133	$P4_2/nbc$	174	$P\bar{6}$	215	$P\bar{4}3m$
134	$P4_2/nnm$	175	$P6/m$	216	$F\bar{4}3m$
135	$P4_2/mbc$	176	$P6_3/m$	217	$I\bar{4}3m$
136	$P4_2/mnm$	177	$P622$	218	$P\bar{4}3n$
137	$P4_2/nmc$	178	$P6_122$	219	$F\bar{4}3c$
138	$P4_2/ncm$	179	$P6_522$	220	$I\bar{4}3d$
139	$I4/mmm$	180	$P6_222$	221	$Pm\bar{3}m$
140	$I4/mcm$	181	$P6_422$	222	$Pn\bar{3}n$
141	$I4_1/amd$	182	$P6_322$	223	$Pm\bar{3}n$
142	$I4_1/acd$	183	$P6mm$	224	$Pn\bar{3}m$
	Trigonal lattices	184	$P6cc$	225	$Fm\bar{3}m$
143	$P3$	185	$P6_3cm$	226	$Fm\bar{3}c$
144	$P3_1$	186	$P6_3mc$	227	$Fd\bar{3}m$
145	$P3_2$	187	$P\bar{6}m2$	228	$Fd\bar{3}c$
146	$R3$	188	$P\bar{6}c2$	229	$Im\bar{3}m$
147	$P\bar{3}$	189	$P\bar{6}2m$	230	$Ia\bar{3}d$
148	$R\bar{3}$	190	$P\bar{6}2c$		
149	$P312$	191	$P6/mmm$		
150	$P321$	192	$P6/mcc$		
151	$P3_112$	193	$P6_3/mcm$		
152	$P3_121$	194	$P6_3/mmc$		
153	$P3_212$	195	$P23$		
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
	triclinic lattices (P)			41	$Pbam$	D_{2h}^9	55
1	$P1$	C_1^1	1	42	$Pmaa$	D_{2h}^3	(49)
2	$P\bar{1}$	C_i^1	2	43	$Pman$	D_{2h}^7	(53)
3	$P112$	C_2^1	(3)	44	$Pbma$	D_{2h}^1	(57)
4	$P11m$	C_s^1	(6)	45	$Pbaa$	D_{2h}^8	(54)
5	$P11a$	C_s^2	(7)	46	$Pban$	D_{2h}^4	50
6	$P112/m$	C_{2h}^1	(10)	47	$Cmmm$	D_{2h}^9	65
7	$P112/a$	C_{2h}^4	(13)	48	$Cmma$	D_{2h}^2	67
	rectangular lattices (P or C)				square lattices (P)		
8	$P211$	C_2^1	(3)	49	$P4$	C_4^1	75
9	$P2_111$	C_2^2	(4)	50	$P\bar{4}$	S_4^1	81
10	$C211$	C_2^3	(5)	51	$P4/m$	C_{4h}^1	83
11	$Pm11$	C_s^1	(6)	52	$P4/n$	C_{4h}^3	85
12	$Pb11$	C_s^2	(7)	53	$P422$	D_4^1	89
13	$Cm11$	C_s^3	(8)	54	$P42_12$	D_4^2	90
14	$P2/m11$	C_{2h}^1	(10)	55	$P4mm$	C_{4v}^1	99
15	$P2_1/m11$	C_{2h}^2	(11)	56	$P4bm$	C_{4v}^2	100
16	$C2/m11$	C_{2h}^3	(12)	57	$P\bar{4}2m$	D_{2d}^1	111
17	$P2/b11$	C_{2h}^4	(13)	58	$P\bar{4}2_1m$	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	$P222$	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}^{11}	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	(35)	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.

IGR	Hermann Mauguin	Schoenflies	
1	1	C_1	
2	$\bar{1}$	C_i	
3	2 (x)	C_2 (x)	
4	2 (y)	C_2 (y)	
5	2 (z)	C_2 (z)	
6	m (x)	C_s (x)	
7	m (y)	C_s (y)	
8	m (z)	C_s (z)	
9	2/m (x)	C_{2h} (x)	
10	2/m (y)	C_{2h} (y)	
11	2/m (z)	C_{2h} (z)	
12	222	D_2	
13	2mm	C_{2v} (x)	
14	m2m	C_{2v} (y)	
15	mm2	C_{2v} (z)	
16	mmm	D_{2h}	
17	4	C_4	
18	$\bar{4}$	S_4	
19	4/m	C_{4h}	
20	422	D_4	
21	4mm	C_{4v}	
22	$\bar{4}$2m	D_{2d}	(σ_v planes along x+y and x-y)
23	$\bar{4}$m2	D_{2d}	(σ_v planes along x and y)
24	4/mmm	D_{4h}	
25	3	C_3	
26	$\bar{3}$	C_{3i}	
27	321	D_3	(one C_2 axis along y)
28	312	D_3	(one C_2 axis along x)
29	3m1	C_{3v}	(one σ_v plane along x)
30	31m	C_{3v}	(one σ_v plane along y)
31	$\bar{3}$m1	D_{3d}	(one σ_d plane along x)
32	$\bar{3}$1m	D_{3d}	(one σ_d plane along y)
33	6	C_6	
34	$\bar{6}$	C_{3h}	
35	6/m	C_{6h}	
36	622	D_6	
37	6mm	C_{6v}	
38	$\bar{6}$m2	D_{3h}	(one C_2 axis along x)
39	$\bar{6}$2m	D_{3h}	(one C_2 axis along y)
40	6/mmm	D_{6h}	
41	23	T	
42	m$\bar{3}$	T_h	
43	432	O	
44	$\bar{4}$3m	T_d	
45	m$\bar{3}$m	O_h	

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:

$$W\mathbf{x}_P = \mathbf{x}_C \tag{A.1}$$

Likewise, for a point in the *reciprocal space* the following equation holds:

$$\tilde{W}^{-1}\mathbf{x}_P^* = \mathbf{x}_C^* \tag{A.2}$$

The W transforming matrices adopted in CRYSTAL, and reported below, satisfy the following relation between the two metric tensors $\mathbf{G}_P$ and $\mathbf{G}_C$:

$$\mathbf{G}_P = W\mathbf{G}_C\tilde{W} \tag{A.3}$$

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).

$$
P \to A \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{\bar{1}}{2} \\ 0 & \frac{1}{2} & \frac{1}{2} \end{pmatrix}
\quad
P \to B \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & 1 & 0 \\ \frac{\bar{1}}{2} & 0 & \frac{1}{2} \end{pmatrix}
\quad
A \to P \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}
\quad
B \to P \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix}
$$

$$
P \to C \begin{pmatrix} \frac{1}{2} & \frac{\bar{1}}{2} & 0 \\ \frac{1}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}
\quad
P \to F \begin{pmatrix} 0 & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & 0 & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & 0 \end{pmatrix}
\quad
C \to P \begin{pmatrix} 1 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
\quad
F \to P \begin{pmatrix} -1 & 1 & 1 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix}
$$

$$
P \to I \begin{pmatrix} \frac{\bar{1}}{2} & \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{\bar{1}}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} & \frac{\bar{1}}{2} \end{pmatrix}
\quad
R \to H \begin{pmatrix} \frac{2}{3} & \frac{\bar{1}}{3} & \frac{\bar{1}}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{\bar{2}}{3} \\ \frac{1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix}
\quad
I \to P \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix}
\quad
H \to R \begin{pmatrix} 1 & 0 & 1 \\ -1 & 1 & 1 \\ 0 & -1 & 1 \end{pmatrix}
$$

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. [21]).

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	27	–
MAKESAED	printing of symmetry allowed elastic distortions (SAED)	32	–
PRSYMDIR	printing of displacement directions allowed by symmetry.	35	–
SYMMDIR	printing of symmetry allowed geom opt directions	40	–
SYMMOPS	printing of point symmetry operators	40	–
TENSOR	tensor of physical properties	40	I

Symmetry information and control			
BREAKSYM	allow symmetry reduction following geometry modifications	28	–
KEEPSYMM	maintain symmetry following geometry modifications	32	–
MODISYMM	removal of selected symmetry operators	32	I
PURIFY	cleans atomic positions so that they are fully consistent with the group	35	–
SYMMREMO	removal of all symmetry operators	40	–
TRASREMO	removal of symmetry operators with translational components	40	–

Modifications without reduction of symmetry			
ATOMORDE	reordering of atoms in molecular crystals	25	–
NOSHIFT	no shift of the origin to minimize the number of symmops with translational components before generating supercell	34	–
ORIGIN	shift of the origin to minimize the number of symmetry operators with translational components	34	–
PRIMITIV	crystallographic cell forced to be the primitive cell	35	–
REDEFINE	definition of a new cell, with $xy \parallel$ to a given plane	36	I

Atoms and cell manipulation (possible symmetry reduction (BREAKSYMM)			

ATOMDISP	displacement of atoms	25	I
ATOMINSE	addition of atoms	25	I
ATOMREMO	removal of atoms	25	I
ATOMROT	rotation of groups of atoms	26	I
ATOMSUBS	substitution of atoms	27	I
ELASTIC	distortion of the lattice	30	I
USESAED	given symmetry allowed elastic distortions, reads δ	41	I
SUPERCEL	generation of supercell - input refers to primitive cell	38	I
SUPERCON	generation of supercell - input refers to conventional cell	38	I

From crystals to slabs			
SLABCUT	generation of a slab parallel to a given plane (3D→2D)	37	I

From periodic structure to clusters			
CLUSTER	cutting of a cluster from a periodic structure (3D→0D)	28	I
HYDROSUB	border atoms substituted with hydrogens (0D→0D)	31	I

Molecular crystals			
MOLECULE	extraction of a set of molecules from a molecular crystal (3D→0D)	33	I
MOLEXP	variation of lattice parameters at constant symmetry and molecular geometry (3D→3D)	33	I
MOLSPLIT	periodic structure of non interacting molecules (3D→3D)	34	–
RAYCOV	modification of atomic covalent radii	35	I

BSSE correction			
MOLEBSSE	counterpoise method for molecules (molecular crystals only) (3D→0D)	32	I
ATOMBSSE	counterpoise method for atoms (3D→0D)	25	I

Auxiliary and control keywords			
ANGSTROM	sets inputs unit to Ångstrom	24	–
BOHR	sets input units to bohr	27	–
BOHRANGS	input bohr to Å conversion factor (0.5291772083 default value)	27	I
BOHRCR98	bohr to Å conversion factor is set to 0.529177 (CRYSTAL98 value)	–	
END/ENDG	terminate processing of geometry		–
FRACTION	sets input unit to fractional	31	–
NEIGHBOR	number of neighbours in geometry analysis	34	I
PARAMPRT	printing of parameters controlling dimensions of static allocation arrays	35	–
PRINTOUT	setting of printing options by keywords	35	I
SETINF	setting of inf array options	36	I
SETPRINT	setting of printing options	37	I
STOP	execution stops immediately	38	–
TESTGEOM	stop after checking the geometry	40	–

Output of data on external units			
COORPRT	coordinates of all the atoms in the cell	29	–
EXTPRT	generation of file as CRYSTAL input	31	–
MOLDRAW	generation of file for the program MOLDRAW	32	–
STRUCPRT	cell parameters and coordinates of all the atoms in the cell	38	–

External electric field - modified Hamiltonian			

FIELD	external field applied (2D-3D systems only)	41	I

Geometry optimization

OPTCOORD	Atom coordinates optimization	43	I

Initial Hessian

HESGUESS	initial guess for the Hessian		I

Convergence criteria

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
MAXOPTC	max number of optimization steps		I

Optimization control

ATOMFREE	partial geometry optimization		I
RESTART	data from previous run		–
FINALRUN	Wf single point with optimized geometry		I

Gradient calculation control

NUMGRAD	numerical first deivatives		–

Printing options

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

Basis set input (Input block 2)

Symmetry control

ATOMSYMM	printing of point symmetry at the atomic positions	27	–

Basis set modification

CHEMOD	modification of the electronic configuration	48	I
GHOSTS	eliminates nuclei and electrons, leaving BS	50	I

Auxiliary and control keywords

CHARGED	allows non-neutral cell	48	–
PARAMPRT	printing of parameters controlling code dimensions	35	–
PRINTOUT	setting of printing options	35	I
SETINF	setting of inf array options	36	I
SETPRINT	setting of printing options	37	I
STOP	execution stops immediately	38	–
SYMMOPS	printing of point symmetry operators	40	–
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	49	–

General information, hamiltonian (Input block 3)

All DFT related keyword are collected under the heading "**DFT**".

Single particle Hamiltonian				

RHF		Restricted Closed Shell	68	–
UHF		Unrestricted Open Shell	70	–
ROHF		Restricted Open Shell	70	–
DFT	DFT Hamiltonian		70	–
	SPIN	spin-polarized solution	59	–
	Choice of the exchange-correlation functionals			
	EXCHANGE	exchange functional	59	I
	LDA	Dirac-Slater [47] (LDA)		
	VBH	von Barth-Hedin [48] (LDA)		
	BECKE	Becke [49] (GGA)		
	PWGGA	Perdew-Wang 91 (GGA)		
	PBE	Perdew-Becke-Ernzerhof [50] (GGA)		
	CORRELAT	correlation functional	59	I
	VBH	von Barth-Hedin [48] (LDA)		
	PWGGA	Perdew-Wang 91 (GGA)		
	PBE	Perdew-Becke-Ernzerhof [50] (GGA)		
	PZ	Perdew-Zunger [51] (LDA)		
	PWLSD	Perdew-Wang 92 [52, 53, 54] (GGA)		
	VWN	Vosko,-Wilk-Nusair [55] (LDA)		
	P86	Perdew 86 [56] (LDA)		
	LYP	Lee-Yang-Parr [57] (GGA)		
	HYBRID	hybrid mixing	60	I
	NONLOCAL	local term parameterization	60	I
	B3PW	B3PW parameterization	60	–
	B3LYP	B3LYP parameterization	60	–
	Integration method			
	[NUMERICA] numerical integration (default)			–
	RADSAFE	safety radius for grid point screening		I
	BATCHPNT	grid point grouping for integration		I
	FITTING	integration through auxiliary basis set fitting	172	I:
	BASIS	Auxiliary basis set input	172	I
	TOLLPOT 9			–
	LINEQUAT		173	I
	Numerical accuracy control			
	[BECKE]	selection of Becke weights (default)		–
	SAVIN	selection of Savin weights		–
	RADIAL	definition of radial grid		I
	ANGULAR	definition of angular grid		I
	LGRID	"large" predefined grid		I
	XLGRID	"extra large" predefined grid		I
	TOLLDENS	density contribution screening 6		I
	TOLLGRID	grid points screening 14		I
	Auxiliary and control			
	PRINT **END**			

Numerical accuracy and computational parameters control				

BIPOLAR	Bipolar expansion of bielectronic integrals	58	I
BIPOSIZE	size of coulomb bipolar expansion buffer	58	I
EXCHSIZE	size of exchange bipolar expansion buffer	58	I
INTGPACK	Choice of integrals package $\boxed{0}$	67	I
NOBIPOLA	All bielectronic integrals computed exactly	67	–
POLEORDR	Maximum order of multipolar expansion $\boxed{4}$	68	I
TOLINTEG	Truncation criteria for bielectronic integrals $\boxed{6\ 6\ 6\ 6\ 12}$	69	I
TOLPSEUD	Pseudopotential tolerance $\boxed{6}$	69	I

Type of run			
ATOMHF	Atomic wave functions	57	I
MPP	MPP execution - see makefile	67	I
SCFDIR	SCF direct (mono+biel int computed)	68	–
SEMIDIR	integrals in memory	68	I
NOMONDIR	SCF semidirect (mono on disk, biel computed)	67	–
EIGS	S($\mathbf{k}$) eigenvalues - basis set linear dependence check	64	–
FIXINDEX	Reference geometry to classify integrals	65	–

Integral file distribution			
BIESPLIT	writing of bielectronic integrals in n files $\boxed{n=1}$,max=10	58	I
MONSPLIT	writing of mono-electronic integrals in n file $\boxed{n=1}$, max=10	67	I

Auxiliary and control keywords			
PARAMPRT	output of parameters controlling code dimensions	35	–
PRINTOUT	setting of printing options	35	I
SETINF	setting of inf array options	36	I
SETPRINT	setting of printing options	37	I
TESTPDIM	stop after symmetry analysis	69	–
TESTRUN	stop after integrals classification and disk storage estimate	69	–
STOP	execution stops immediately	38	–
END/ENDM	terminate processing of general information keywords		

SCF (Input block 4)

Numerical accuracy control and convergence tools			
ANDERSON	Fock matrix mixing	72	I
BROYDEN	Fock matrix mixing	73	I
FMIXING	Fock/KS matrix (cycle i and i-1) mixing $\boxed{0}$	75	I
LEVSHIFT	level shifter $\boxed{no}$	77	I
MAXCYCLE	maximum number of cycles $\boxed{50}$	78	I
SMEAR	Finite temperature smearing of the Fermi surface $\boxed{no}$	79	I
TOLDEE	convergence on total energy $\boxed{5}$	81	I
TOLDEP	convergence on density matrix $\boxed{?}$	81	I
TOLSCF	convergence on eigenvalues $\boxed{6}$ and total energy $\boxed{5}$	81	I

Initial guess			
EIGSHIFT	alteration of orbital occupation before SCF $\boxed{no}$	74	I
EIGSHROT	rotation of the reference frame $\boxed{no}$	74	I
GUESSF	Fock/KS matrix from previous run	76	–
GUESSP	density matrix from a previous run	76	–
$\boxed{\textbf{GUESSPAT}}$	superposition of atomic densities	76	–

Spin-polarized system			
ATOMSPIN	setting of atomic spin to compute atomic densities	73	I
BETALOCK	beta electrons locking	73	I
SPINLOCK	spin difference locking	80	I
SPINEDIT	editing of the spin density matrix	80	I

Auxiliary and control keywords			
END/ENDSCF	terminate processing of scf I keywords		–
KSYMMPRT	printing of Bloch functions symmetry analysis	77	–
NEIGHBOR	number of neighbours to analyse in **PPAN**	34	I
PARAMPRT	output of parameters controlling code dimensions	35	–
PRINTOUT	setting of printing options	35	I
NOSYMADA	No Symmetry Adapted Bloch Functions	78	–
SYMADAPT	Symmetry Adapted Bloch Functions (default)	81	–
SETINF	setting of inf array options	36	I
SETPRINT	setting of printing options	37	I
STOP	execution stops immediately	38	–

Output of data on external units			
NOFMWF	wave function formatted output not written to fortran unit 98.	78	–
KNETOUT	Reciprocal lattice information + eigenvalues	77	–
SAVEWF	wave function data written every two SCF cycles	79	–

Post SCF calculations			
POSTSCF	post-scf calculations when convergence criteria not satisfied	78	–
EXCHGENE	exchange energy evaluation (spin polarized only)	75	–
GRADCAL	analytical gradient of the energy	76	–
PPAN	population analysis at the end of the SCF $\boxed{\text{no}}$	78	

Properties

RDFMWF	wave function data conversion formatted-binary (fortran unit 98→ 9)	

Preliminary calculations			
NEWK	Eigenvectors calculation	103	I
NOSYMADA	No symmetry Adapted Bloch Functions	78	–
PATO	Density matrix as superposition of atomic (ionic) densities	104	I
PBAN	Band(s) projected density matrix (preliminary **NEWK**)	104	I
PGEOMW	Density matrix from geometrical weights (preliminary **NEWK**)	105	I
PDIDE	Energy range projected density matrix (preliminary **NEWK**)	105	I
PSCF	Restore SCF density matrix	110	–
ROTREF	Rotation of the reference frame	110	I

Properties computed from the density matrix			

ADFT	Atomic density functional correlation energy	85	I
BAND	Band structure	87	I
CLAS	Electrostatic potential maps (point multipoles approximation)	88	I
ECHG	Charge density maps and charge density gradient	93	I
ECH3	Charge density 3D maps	92	I
EDFT	Density functional correlation energy	93	I
POLI	Atom and shell multipoles evaluation	105	I
POTM	Electrostatic potential maps	107	I
POTC	Electrostatic properties	107	I
PPAN	Mulliken population analysis	78	
XFAC	X-ray structure factors	111	I

Properties computed from the density matrix (spin-polarized systems)			
ANISOTRO	Hyperfine electron-nuclear spin tensor	86	I
ISOTROPIC	Hyperfine electron-nuclear spin interaction - Fermi contact	96	I
POLSPIN	Atomic spin density multipoles	106	I

Properties computed from eigenvectors (after keyword **NEWK**)			
ANBD	Printing of principal AO component of selected CO	85	I
BWIDTH	Printing of bandwidth	88	I
DOSS	Density of states	91	I
EMDL	Electron momentum distribution - line	94	I
EMDP	Electron momentum distribution - plane maps	95	I
PROF	Compton profiles and related quantities	109	I

New properties			
POLARI	Berry phase calculations	113	I
SPOLBP	Spontaneous polarization (Berry phase approach)	114	–
SPOLWF	Spontaneous polarization (localized CO approach)	114	–
PIEZOBP	Piezoelectricity (Berry phase approach) preliminary	112	–
PIEZOWF	Piezoelectricity (localized CO approach) - preliminary	113	–
LOCALWF	Localization of Wannier functions	97	I
DIELEC	Optical dielectric constant	89	I

Auxiliary and control keywords			
ANGSTROM	Set input unit of measure to Ångstrom	24	–
BASISSET	Printing of basis set, Fock/KS, overlap and density matrices	87	–
BOHR	Set input unit of measure to bohr	27	–
CHARGED	Non-neutral cell allowed (**PATO**)	48	–
CONVCELL	Reference cell for k-points coordinates (**BAND**)	88	–
END	Terminate processing of properties input keywords		–
FRACTION	Set input unit of measure to fractional	31	–
MAPNET	Generation of coordinates of grid points on a plane	100	I
NEIGHBOR	Number of neighbours to analyse in **PPAN**	34	I
PRINTOUT	Setting of printing options	35	I
RAYCOV	Modification of atomic covalent radii	35	I
SETINF	Setting of inf array options	36	I
SETPRINT	Setting of printing options	37	I
STOP	Execution stops immediately	38	–
SYMMOPS	Printing of point symmetry operators	40	–

Output of data on external units			

ATOMIR	Coordinates of the irreducible atoms in the cell	86	–
ATOMSYMM	Printing of point symmetry at the atomic positions	27	–
COORPRT	Coordinates of all the atoms in the cell	29	–
EXTPRT	Explicit structural/symmetry information	31	–
GAUSS98	Printing of an input file for the GAUSS98 package	49	–
FMWF	Wave function formatted output. Section 3.2	95	–
INFOGUI	Generation of file with wf information for visualization	96	–
KNETOUT	Reciprocal lattice information + eigenvalues	77	–
MOLDRAW	generation of input file for the program MOLDRAW	32	–

Common keywords

Some keywords may be entered in more then one input block, with the same action. They are summarized in the following table.

		input block				
keyword	page	1-geometry	2-basis set	3-general	4-scf	properties
ANGSTROM	24	X				X
ATOMSYMM	27	X				X
BOHR	27	X				X
CHARGED	48		X			X
COORPRT	29	X				X
COORXXL	29	X				X
END		ENDG	ENDB	ENDM	ENDSCF	ENDP
EXTPRT	31	X				X
FRACTION	31	X				X
GAUSS98	49		X			X
KNETOUT	77				X	X
MOLDRAW	32	X				X
NEIGHBOR	34	X			X	X
PARAMPRT	35	X	X	X	X	X
PPAN	78				X	X
PRINTOUT	35	X	X	X	X	X
RAYCOV	35	X				X
SETINF	36	X	X	X	X	X
SETPRINT	37	X	X	X	X	X
STOP	38	X	X	X	X	X
SYMMOPS	40	X	X			X

Appendix C

DFT integration through an auxiliary basis set fitting

The calculation of the exchange-correlation contribution to the Kohn-Sham matrix through the fitting of the exchange-correlation potential to an auxiliary basis set of gaussian functions, as in CRYSTAL98 is not recommended, as the calculation of energy gradients has been implemented only with numerical quadrature.

FITTING	analytical integration through an auxiliary basis set fitting. An even-tempered auxiliary basis set is generated by default.
	────────────── user defined fitting basis set (optional) ──────────────II
BASIS	Auxiliary basis for the fitting of the exchange correlation potential. Enter the numerical code in the next record:

3	a predefined even–tempered basis set of **12** s-type GTF is used. The largest exponent is 2000., the smallest 0.1. Default choice.
2	a predefined even-tempered basis set of **8** s-type GTF is used. The largest exponent is 2000., the smallest 0.1.
1	A predefined even-tempered basis set with **4** s-type GTF is used. The largest exponent is 2000., the smallest 0.1.
0	general basis set is read from input records as follows:

rec	variable	value	meaning	
● ∗	NAT	n	conventional atomic number.	
		=99	end of auxiliary basis set input section	
	NFIN	n	number of groups of functions	
		0	end of basis set input (when NAT=99)	
			insert NFIN records	II
● ∗	ITYB	0	read general basis set.	
		1	even-tempered basis set is generated from input data.	
	LATD	0	s-type GTF.	
		2	p-type GTF.	
		3	d-type GTF.	
		4	f-type GTF.	
		5	g-type GTF.	
		6	h-type GTF.	
		7	i-type GTF.	
	NFUNC		number of gaussians in the contraction	
			if ITYB = 1 add on the same record	II
	EMIN		minimum exponent of the even-tempered BS	
	EMAX		maximum exponent of the even-tempered BS	
			if ITYB = 0 insert NFUNC records	II
● ∗	EXP		Exponent of the GTF.	
	CX		Coefficient of the GTF.	
PRINT			extended printing	
LINEQUAT			keyword - iterative linear equation solver control	
● ∗ MICRO			number of micro-cycles (default 1)	
∗ MACRO			number of macro-cycles (default 1)	

TOLLPOT

The DFT potential tolerance IP controls the level of accuracy for the integration which yields matrix elements of the Kohn-Sham Hamiltonian. Contributions less than 10^{-IP} will be ignored. The default value is 9.

- MPP does not support DFT fitting.

- A basis set for the DF fitting must be defined for each type of atom in the cell

- A basis set for the fitting can be defined for ghost atoms, that means centres with AO basis set, but without nuclear and electron charge. It can be useful when there is a localized electron in a vacancy

- A given atom may have no basis for the DF fitting assigned. This choice must be explicitly defined by setting the value of NFIN to 0.

C.1 DFT input example - fitting method

The following exemples explain the usage of an auxiliary basis set for the fitting.
Example 1. Urea molecule

geometry input terminated by **END** (page 11)

basis set input terminated by **END** (page 16)

input block 3 - general information input (page 19)

DFT	DFT Hamiltonian selected
FITTING	fitting technique chosen
BASIS	auxiliary basis for the fitting of XC potential
0	general basis set read from the following input records
1 3	Z=1, Hydrogen; 3 groups of functions
1 0 9 0.06 60.	1st: even temp BS; s type; 9 gaussians; 0.06 min. exp; 60. max. exp.
1 2 3 0.08 0.72	2nd: even temp. BS; p-type; 3 gaussians; 0.08 min. exp.; 0.72 max. exp.
1 3 1 0.10 0.10	3rd: even temp. BS; d-type; 1 gaussian; 0.1 exp.
6 3	Z=6, Carbon; 3 groups of functions
1 0 13 0.07 2000.	1st: even temp BS; s type; 13 gaussians; 0.07 min. exp.; 2000. max. exp.
1 2 3 0.10 0.8	2nd: even temp BS; p type; 3 gaussians; 0.10 min. exp.; 0.8 max. exp.
1 3 2 0.12 0.3	3rd: even temp BS; d type; 2 gaussians; 0.12 min. exp.; 0.3 max. exp.
7 3	Z=7, Nitrogen; 3 groups of functions
1 0 13 0.07 2000.	1st: even temp BS; s type; 13 gaussians; 0.07 min. exp.; 2000. max. exp.
1 2 3 0.10 0.8	2nd: even temp BS; p type; 3 gaussians; 0.10 min. exp.; 0.8 max. exp.
1 3 2 0.12 0.3	3rd: even temp BS; d type; 2 gaussians; 0.12 min. exp.; 0.7 max. exp.
8 3	Z=8, Oxygen; 3 groups of functions
1 0 13 0.07 2000.	1st: even temp BS; s type; 13 gaussians; 0.07 min. exp.; 2000. max. exp.
1 2 3 0.10 0.8	2nd: even temp BS; p type; 3 gaussians; 0.10 min. exp.; 0.8 max. exp.
1 3 2 0.12 0.3	3rd: even temp BS; d type; 2 gaussians; 0.12 min. exp.; 0.3 max. exp.
99 0	end of auxiliary basis input
CORRELAT	selection of correlation potential
PZ	GGA Perdew-Zunger LSD
END	end of DFT input
END	end of general information input, block 3

SCF input terminated by **END** (page 19)

Example 2. Nickel (II) Oxide

geometry input terminated by **END** (page 11)

basis set input terminated by **END** (page 16)

input block 3 - general information input (page 19)

DFT	DFT Hamiltonian selected
FITTING	
PRINT	extended printing required
SPIN	spin unrestricted DF calculation
BASIS	auxiliary basis for the fitting of XC potential
0	general basis set read from the following input records
28 2	Z=28, Nickel; 2 groups of functions
1 0 12 0.1 6000.	1st: even temp BS; s type; 12 gaussians; 0.1 min. exp; 6000. max. exp.
1 5 3 0.45 3.3	2nd: even temp. BS; g-type; 3 gaussians; 0.45 min. exp.; 3.3 max. exp.
8 1	Z=8, Oxygen; 1 group of functions
1 0 10 0.1 1000.	even temp BS; s type; 10 gaussians; 0.1 min. exp; 1000. max. exp.
99 0	end of auxiliary basis input
CORRELAT	selection of correlation potential
PWGGA	GGA Perdew-Wang
END	end of DFT input
END	end of general information input, block 3

SCF input terminated by **END** (page 19)

Example 3. Silicon bulk

geometry input terminated by **END** (page 11)

basis set input terminated by **END** (page 16)

input block 3 - general information input (page 19)

```
DFT                DFT Hamiltonian selected
FITTING
RADIAL             radial integration information
1                  one integration interval
3.5                limit of the interval
80                 number of points in the interval
EXCHANGE           selection of the exchange potential
BECKE              GGA Becke potential
CORRELAT           selection of correlation potential
PZ                 LSD Perdew-Zunger potential
BASIS              auxiliary basis for the fitting of XC potential
0                  general basis set read from the following input records
14 3               Z=14, Silicon; 3 groups of functions
1 0 14 0.09 4500.  1st: even temp BS; s type; 14 gaussians; 0.09 min. exp; 4500. max. exp.
1 4 1 0.3 0.3      2nd: even temp BS; f type; 1 gaussian; 0.3 exp;
1 5 1 0.3 0.3      3rd: even temp BS; g type; 1 gaussian; 0.3 exp;
99 0               end of auxiliary basis input
END                end of DFT input
END                end of general information input, block 3
```

> SCF input terminated by **END** (page 19)

Example 4. Quartz

> geometry input terminated by **END** (page 11)

> basis set input terminated by **END** (page 16)

——————— input block 3 - general information input (page 19)———————

```
DFT                DFT Hamiltonian selected
FITTING
RADIAL             radial integration information
1                  one integration interval
3.5                limit of the interval
44                 number of points in the interval
EXCHANGE           selection of the exchange potential
LDA                selection of correlation potential
CORRELAT           selection of correlation potential
PZ                 LSD Perdew-Zunger potential
BASIS              auxiliary basis for the fitting of XC potential
0                  general basis set read from the following input records
14 6               Z=14, Silicon; 6 groups of functions
1 0 15 0.07 14000. 1st: even temp BS; s type; 15 gaussians; 0.07 min.exp; 14000. max. exp.
1 2 6 0.1 5.       2nd: even temp BS; p type; 6 gaussians; 0.1 min.exp; 5. max. exp.
1 3 4 0.2 1.5      3rd: even temp BS; d type; 4 gaussians; 0.2 min.exp; 1.5 max. exp.
1 4 3 0.3 1.5      4th: even temp BS; f type; 3 gaussians; 0.3 min.exp; 1.5 max. exp.
1 5 2 0.25 1.3     5th: even temp BS; g type; 2 gaussians; 0.25 min.exp; 1.3 . max. exp.
1 6 1 0.5 0.5      6th: even temp BS; h type; 1 gaussian; 0.5 exp.
8 6                Z=14, Oxygen; 6 groups of functions
1 0 14 0.07 700.   1st: even temp BS; s type; 14 gaussians; 0.07 min.exp; 700. max. exp.
1 2 6 0.08 2.5     2nd: even temp BS; p type; 6 gaussians; 0.08 min.exp; 2.5 max. exp.
1 3 4 0.4 2.5      3rd: even temp BS; d type; 4 gaussians; 0.4 min.exp; 2.5 max. exp.
1 4 3 0.4 1.3      4th: even temp BS; f type; 3 gaussians; 0.4 min.exp; 1.3 max. exp.
1 5 2 0.25 1.3     5th: even temp BS; g type; 2 gaussians; 0.25 min.exp; 1.3 max. exp.
1 6 1 0.5 0.5      6th: even temp BS; h type; 1 gaussian; 0.5 exp.
99 0               end of auxiliary basis input
END                end of DFT input
END                end of general information input, block 3
```

> SCF input terminated by **END** (page 19)

Appendix D

Reciprocal lattice sampling

The keyword **KNETOUT** entered in the program **crystal** or **properties** generates an unformatted file on fortran unit 30. The structure of the file is as follows:

rec	data type	n. data	content
1	3I, F	3+9	ndf, nkf, iuhf, reciprocal lattice vectors cartesian components (a.u.)
2	I	3*nkf	oblique coordinates of the points in reciprocal lattice
3	I	nkf	k points flag: 0 (complex); 1 (real)
4	I	3x3x48	symmetry operators matrices
5	F	nkf	geometrical weight of k points
6	F	ntot	eigenvalues
7	F	ntot	weight of eigenvalues

where:

ndf		number of basis set functions
nkf		number of k points (Monkhorst sampling)
iuhf		0 (Restricted calculation); 1 (Unrestricted calculation)
ntot	(nkf*ndf*(iuhf+1))	number of eigenvalues

The eigenvectors corresponding to the eigenvalues are written on the fortran unit 10 when computed by **properties** (keyword **NEWK**, page 103), and on fortran unit whose number is printed at the end of the printout, when computed by **crystal**. The two sets of eigenvectors may be slightly different, as the ones computed by **properties** correspond to one SCF cycle more then the one computed by **crystal**.

Symmetry adapted Bloch functions generation must be removed (keyword **NOSYMADA**, page 78),in order to read eigenvectors as nkf*(iuhf+1) matrices of size ndfxndf.

The reciprocal lattice vectors cartesian components and the oblique coordinates of the points in reciprocal lattice are printed when the input block 4, SCF input is processed. Printing of the other data may be obtained by setting the appropriate printing options (see keyword **PRINTOUT**, page 177):

keyword	input	information
KNETCOOR		reciprocal lattice sampling points coordinates
KWEIGHTS		geometrical weight of k points
EIGENVAL	n	eigenvalues at the first n k points
EIGENVEC	n	eigenvectors at the first n k points
EIGENALL		eigenvalues at all k points

Appendix E

Printing options

Extended printing can be obtained by entering the keywords **PRINTOUT** (page 35) or **SETPRINT** (page 37).

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.

crystal	Keyword	inp
• direct lattice - geometry information: 1	GLATTICE	–
• symmetry operators : 4, 2	SYMMOPS	–
• atomic functions basis set : 72	BASISSET	–
• DF auxiliary basis set for the fitting: 79	DFTBASIS	–
• scale factors and atomic configuration: 75	SCALEFAC	–
• k-points geometrical wheight: 53	KWEIGHTS	–
• shell symmetry analysis : 5, 6, 7, 8, 9		
• Madelung parameters: 28		
• multipole integrals: 20		
• Fock/KS matrix building - direct lattice: 63, 64, 74	FGRED FGIRR	N
• Total energy contributions: 69	ENECYCLE	–

crystal - properties	Keyword	inp
• shell and atom multipoles: 68	MULTIPOLE	N
• reciprocal space integration to compute Fermi energy: 51, 52, 53, 54, 55, 78		
• density matrix - direct lattice: irreducible (58); reducible (59)	PGRED PGIRR	N
• Fock/KS eigenvalues : 66	EIGENVAL	N
EIGENALL –		
• Fock/KS eigenvectors : 67	EIGENVEC	N
• symmetry adapted functions : 47	KSYMMPRT	–
• Population analysis: 70, 73, 77	MULLIKEN	N
• Atomic wave-function: 71		

properties	Keyword	inp
• 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 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					
28	MADEL2	$\neq 0$	Madelung parameters		
29					
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 on fortran unit 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	LEGDGS		towards EMBED - see EMBED manual		
38	KROT		towards EMBED - see EMBED manual		
39			towards EMBED - see EMBED manual		
40			towards EMBED - see EMBED manual		
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	KSYMMPRT	
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 - each scf cycle	PGRED	N
		N < 0	P(g) matrices - first N vectors - last scf cycle	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	$\neq 0$	contributions to total energy at each cycle	ENECYCLE	
70	FINE2	$\neq 0$	Mulliken population analysis		
	NEIGHB		at the end of scf cycles		
	POPAN		calls PPBOND, to perform Mulliken analysis		
	PDIBAN				
71	PATIRR	$\neq 0$	atomic wave function	ATOMICWF	
	PATIR1	$\neq 0$	" "	ATOMICWF	
72	INPBAS	$\neq 0$	basis set	BASISSET	
	INPUT2	$\neq 0$	basis set	BASISSET	
	READFG	SET = 1			
73	POPAN	$\neq 0$	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	$\neq 0$	printing of scale factor and	SCALEFAC	
			atomic configuration	CONFIGAT	
76					
77	PPBOND	0	printing of neighbouring relationship		
		$\neq 0$	no printing of neighbours relationship		
78	FERMI	$\neq 0$	informations on Fermi energy calculation		
	EMIMAN	$\neq 0$			
79	DFGPRT	$\neq 0$	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	$\neq 0$	DOSS information		
112	PROFCA	$\neq 0$	projected DOSS coefficients		
116	PROFI	$\neq 0$	Compton profile information		
117	PROFI	$\neq 0$			
118	PROFI	N			
119	INTEG	$\neq 0$	charge density at grid points	MAPVALUES	
	JJTEG	$\neq 0$	charge density at grid points	MAPVALUES	
	MAPNET	$\neq 0$	electrostatic potential at grid points	MAPVALUES	
	NAPNET	$\neq 0$	charge density gradient components	MAPVALUES	
120	LIBPHD	$\neq 0$	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 F

External format

Appendix G

Utility programs

Appendix H

CRYSTAL2003 versus CRYSTAL98

CRYSTAL03 consists of 2 programs:

crystal

reads geometry, basis set, computational parameters and Hamiltonian, scf information (4 input blocks ending with the keyword END), computes the wave function, and writes wave function information in fortran unit 9 (binary) and 98 (formatted).
A unique program, *crystal*, controls scf execution technique, traditional, scf direct, scf semidirect (part of bielectronic integrals in memory), and substitutes the programs *integrals*, *scf* and *scfdir* of CRYSTAL98 package. The choice of SCF technique is controlled by keywords in input block 3.

properties

reads wave function information from fortran unit 9 (default) or 98 (keyword RDFMWF first record in the input deck) and computes the properties defined in the input stream.

New features include:

- Dynamic allocation of the arrays depending on the size of the system. Few arrays have fixed dimensions in Release V1.0.

  Max dimensions allowed:

  ```
  N. of atoms                   1200
  N. of shells                  3200
  N. of AOs                    10000
  N. of Monkhorst net k points   400
  N. of Gilat net k points      2400
  ```

- Fully numerical quadrature of the density for DFT methods (default choice). The fitting technique for the DFT potentials is still present, but not recommended (the choice of the auxiliary basis set for the fitting is critical, and the analytical gradient is implemented for numerical integration only);

- a very accurate McMurchie-Davidson integration scheme for Effective Core Pseudopotentials (ECP) methods, allowing higher angular quantum numbers (in CRYSTAL98

the package for computing integrals involving pseudo potentials was derived from PSHONDO);

- Analytic computation of the nuclear coordinate gradient of the energy: HF, DFT, hybrids HF-DFT;

- Automated geometry optimizer (analytical or numerical gradient);

- Improved techniques for finding the ground state in metallic systems;

- Localization of the Crystalline Orbitals (Wannier functions);

- Dielectric properties.

Main differences between CRYSTAL98 and CRYSTAL03

We tried to maintain compatibility between input deck prepared for CRYSTAL98 and CRYSTAL03. The CRYSTAL98 library of Hartree-Fock test cases can be used to test CRYSTAL03.

- CRYSTAL03 writes wave function infos at the end of SCF (fortran units 9 and/or 98) differently from Crystal98.

- The data written in fortran unit 25 (formatted data for plotting maps, doss, band) are different from the data written by CRYSTAL98. The package Crgra2003 can be downloaded from http://www.crystal.unito.it/Crgra2003 to visualize bands, density of states, isovalue contour maps of charge and spin density, classic and quantum electrostatic potential.

- Change in physical constant definition
  Physical constants values are from "CODATA Recommended values of the fundamental Physical Constants 1998" as reported in
  http://physics.nist.gov/constants .
  CRYSTAL03 adopts for the bohr unit 0.5291772083 (it was 0.529177 in CRYSTAL98, according to "CODATA Recommended values of the fundamental Physical Constants 1992").
  The effect on the total energy of 39 tests is presented in the table
  http://www.crystal.unito.it/cr03vscr98.html .

- The atomic coordinates, as provided in the input file, are re-adjusted to be fully consistent with the symmetry group of the system.

  The effect on the total energy of 39 tests is presented in the table
  http://www.crystal.unito.it/cr03vscr98.html .

- The symmetry operators in fractionary units are printed in compact form after atomic coordinates.

- SCF
  The default value to test convergence on the total energy is 10**-5 as in CRYSTAL98, for single point calculation. This value leads to a poor convergence, it was maintained in release V1.0 for compatibility with CRYSTAL98 data. In geometry optimization the value is set to 10**-7.

DFT

The following input deck:

```
input block 1:   geometry definition
input block 2 :  basis set
input block 3 :  DFT
                 B3LYP    (Exchange/correlation functional choice)
                 END
input block 4 :  scf data
```

submitted to CRYSTAL98 and to CRYSTAL03 gives different results, as the integration method is different.

CRYSTAL03 uses by default a numerical integration technique, and at each scf cycle the correct energy is computed. The same integration grid is used for scf and energy calculation. Analytical energy gradient is implemented for numerical DFT only, so the fitting technique used in CRYSTAL98 is no longer recommended. The documentation is available in an appendix of "CRYSTAL03 Users Manual":

http://www.crystal.unito.it/Manuals/cry2003.pdf .

CRYSTAL98 used by default an auxiliary basis set for fitting the potential; if the basis set was not supplied in input, an event-tempered basis set was authomatically generated. At each cycle a DFT pseudo energy was computed, and used to check convergence. The correct energy was computed a posteriori, by the program *properties*, from the density matrix obtained at the end of SCF procedure. The computational parameters used in scf were different from the parameters (more severe) used to compute energy.

The keyword FITTING allows usage of the fitting technique in CRYSTAL03. In that case the scf convergence is based on a pseudo energy, as in CRYSTAL98, but the correct energy is evaluated at the end of scf, by the program *crystal*, and the grids used in scf and energy calculation can not be modified independently.

CRYSTAL98 and CRYSTAL03 give the same pseudo energy, if the computational parameters are the same, or the same a posteriori correlation energy (in CRYSTAL03 computed by *properties* with an HF hamiltonian only), but there is no way to have both pseudo energy and correct total energy coincident, as it is not possible input different parameters for scf and energy calculation, as before.

Properties

The only difference is the input to PPAN, Mulliken population analysis. No input follows the keyword PPAN. If more neighbors than default (6) are requested, use keyword NEIGHBORS before PPAN to define a higher number of neighbors.

Appendix I

Relevant strings

Selected information can be extracted from CRYSTAL output referring to some strings of characters uniquely linked to the requested information.

```
TOTAL ENERGY(          final SCF energy
TOTAL ENERGY(HF        Hartree-Fock
TOTAL ENERGY(DFT       DFT
TTT END                final elapsed and CPU time (crystal/properties)
 OPT END               energy after geometry optimization
 OPT END - FAILED      failed opt only
 OPT END - CONVERGED   successful opt only
TTT BERNY              cpu time for each opt cycle
GEOMETRY FOR WAVE      printing of the geometry used for wf calculation
                       (after editing)
FINAL OPTIMIZED        printing of geometry at the end of optimization
```

Appendix J

Acronyms

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 – Density Matrix

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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[2] R. Dovesi, C. Roetti and V.R. Saunders, *CRYSTAL92 User's Manual*, Università di Torino and SERC Daresbury Laboratory (1992).

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