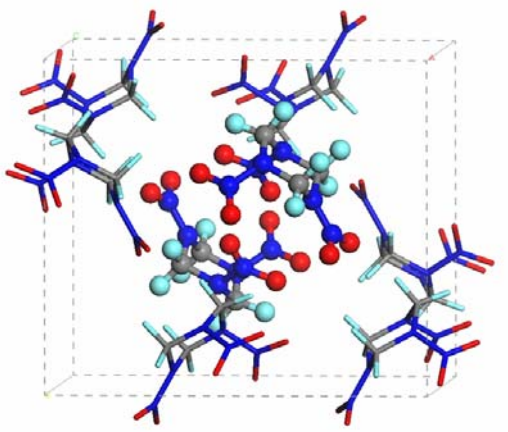

Michigan Tech University - Washington State University - University of Torino

Ab initio Simulation of Crystalline Systems

ASCS2006

September 17-22, 2006 - Spokane, Washington (USA)

Introduction to Tutorial Sessions

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Tutorial sessions

The afternoon sessions are based on the set of tutorials that are part of the CRYSTAL tutorials project.

CRYSTAL tutorials are divided in two levels:

- Basic: to understand the basic features of the code
- Advanced: to show how to use CRYSTAL for applications in solid state chemistry

From the beginning of 2004 CRYSTAL tutorials are available at the CRYSTAL web site

CRYSTAL Tutorials – Web-oriented interface

CRYSTAL Tutorial Project - 2006 - Microsoft Internet Explorer

File Modifica Visualizza Preferiti Strumenti ?

Indietro Cerca Preferiti

Indirizzo D:\mimmo\scuole\mssc2006\mssc2006_cd\tutorials\index.html Vai Collegamenti

How to run CRYSTAL | CRYSTAL06 Manual | Crgra2006 Manual

A quick tour of CRYSTAL input and output:
1. Single point
2. Geometry optimization
3. Harmonic frequencies

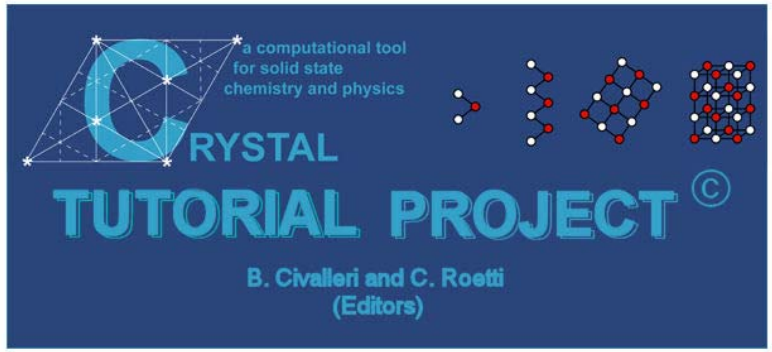
Basic tutorials:
crystal input:
1. Geometry
2. Basis set
3. Hamiltonian, SCF&C

Total energy single point
Geometry optimization
One electron properties
Vibrational frequencies

Surfaces and adsorption
Defects
Magnetic properties

Advanced tutorials:
Phase transitions
Elastic and piezoelectric tensors
Static dielectric constants

Updated 25-08-2006
crystal@unito.it



The "CRYSTAL tutorial project" started in 2000, when the first "Ab initio modeling in solid state chemistry - MSSC2000" school was organized. MSSC2001, MSSC2002, MSSC2003 (Torino), MSSC2004 (London), MASP2004 (Barcelona) followed.

A review article is devoted to a basic introduction to CRYSTAL as a tool for quantum simulation in solid state chemistry :

Roberto Dovesi, Bartolomeo Civalleri, Roberto Orlando, Carla Roetti, and Victor R. Saunders
Ab Initio Quantum Simulation in Solid State Chemistry
Reviews in Computational Chemistry, Chapter 1, Volume 21
Kenny B. Lipkowitz (Editor), Raima Larter (Editor), Thomas R. Cundari (Editor)
John Wiley & Sons, Inc, New York, 2005

Work is in progress: we appreciate suggestions, criticisms, comments, sent to crystal@unito.it

"Basic tutorials" give general information about the main features of the code, "advanced tutorials" show how to use CRYSTAL capabilities in a specific research field (see references).

Refer to "CRYSTAL06 User's Manual" for detailed information.

Background requirements:

- basic concepts of crystallography: direct lattice, reciprocal lattice, space groups;
- basic quantum chemistry: Hartree-Fock and DFT methods;

Risorse del computer

ASCS2006 School tutorials

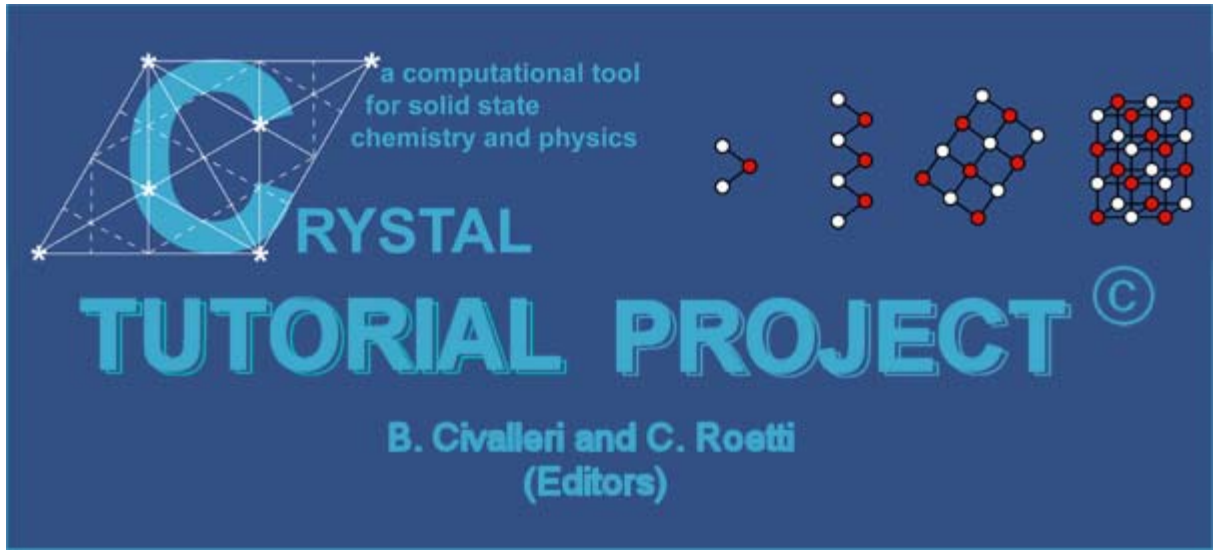
Afternoon Sessions – Center Stage

	Monday 18th	Tuesday 19th	Wednesday 20th	Thursday 21th	Friday 22nd
14.00 15.45	**A.** Geometry input Geometry editing Visualization tools.	**C.** Geometry optimization.	12.30: Travel to ***WSU's Institute for Shock Physics (Pullman).***	Vibrational Frequencies	CRYSCOR
	Break	*Break*			*Break*
16.00 17.30	**B**. Basis sets, Hamiltonians.	**D.** One electron properties.	**13**.The Experimental Connection, ***Y.M. Gupta***	15.45 → *Poster session*	Other Tutorials: surfaces, defects, magnetic properties
					Social hour (18:00)
19.00			Tour of Institute Refreshments		*Dinner*

New features and special sessions:

- Geometry optimization
- Vibrational frequencies calculation → ***Y. Noel - webvib***
- CRYSCOR

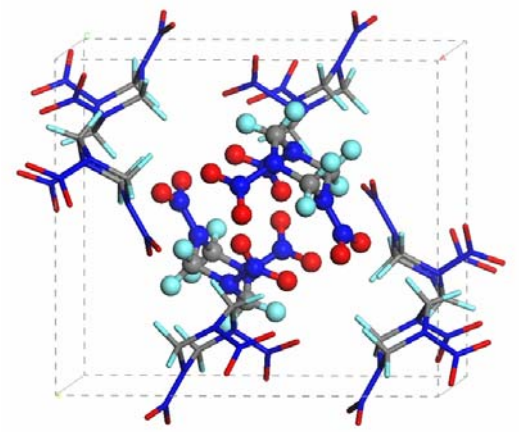
Tutorial sessions - Acknowledgements



Development of the CRYSTAL tutorials

R. Dovesi, R. Orlando, S. Casassa, Y. Noel, G. Mallia, M. Ferrero, I.P.R Moreira, M. Llunell, M. Rerat, C. Darrigan, A. Damin

with contributions by P. Ugliengo and N.M. Harrison



Michigan Tech University - Washington State University - University of Torino

Ab initio Simulation of Crystalline Systems

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CRYSTAL06 input and output

B. Civalleri

Dipartimento di Chimica IFM

Università di Torino

Via Giuria 7, I-10125 Torino, Italy

bartolomeo.civalleri@unito.it

Getting started with CRYSTAL

The CRYSTAL package consists of two executables:

- **crystal**
  - performes integrals calculation and SCF part
  - computes total energy and wavefunction
  - performes geometry optimization
  - calculates vibrational frequencies at Γ point
- **properties**
  - performes the wavefunction analysis

    (e.g. one-electron properties)

CRYSTAL input

CRYSTAL input for the wave function calculation

The CRYSTAL input deck is read by **crystal**

Input deck is an ASCII text file

properties requires an independent input

(see tutorial on “One-electron properties”)

CRYSTAL input scheme

CRYSTAL input is given by *keywords*

It consists of **three sections**:

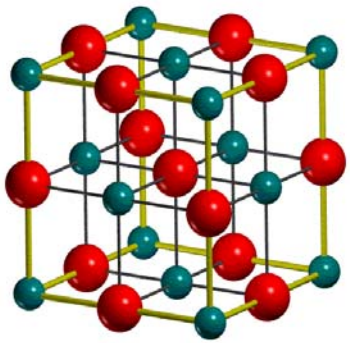
0. Title
1. Geometry input section
2. Basis set input section
3. Method & SCF input section

CRYSTAL input structure

Optional keywords can be specified and each sections ends with the keyword **END**.

0. Title
1. Geometry input section
   - standard geometry input
   - *geometry editing keywords (optional)*
   - *geometry optimization and vibrational frequencies calculation*
2. Basis set input section
   - standard basis set input
   - *optional basis set related keywords*
3. Method & SCF input section
   - Reciprocal space integration parameters
   - *optional general (e.g. Hamiltonian) and SCF related keywords*

CRYSTAL06 input example



MgO bulk
fcc cubic cell
RHF/STO-3G

Title	**MGO BULK**
Geometry input section	**CRYSTAL** **0 0 0** **225** **4.21** **2** **12 0. 0. 0.** **8 0.5 0.5 0.5** ***Optional keywords*** **END**
Basis set input section	**12 3** **1 0 3 2. 0.** **1 1 3 8. 0.** **1 1 3 2. 0.** **8 2** **1 0 3 2. 0.** **1 1 3 6. 0.** **99 0** ***Optional keywords*** **END**
Method & SCF input section	***SHRINK*** ***8 8*** ***Optional keywords*** **END**

CRYSTAL input - Geometry input section

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

```
MGO BULK
CRYSTAL
0 0 0
225
4.21
2
12 0.    0.    0.
8  0.5   0.5   0.5
Optional keywords
END (ENDG)
```

Title
Dimensionality of the system
Crystallographic information (3D only)
Space Group (*Fm3m – 225*)
Lattice parameters (*cubic*)
Number of non equivalent atoms
Atomic number and fractional coordinates

End of geometry input section

The geometry given in input is the asymmetric unit of the *conventional* (or *crystallographic*) unit cell

Several optional keywords are available allowing *geometry editing*:

- modification of the symmetry
- manipulation of atoms (displacement, rotation, insertion, ...)
- reduction of the periodicity (3D ⇒ 2D, 3D ⇒ 0D, …)

➡ ***crystal*** input - Geometry

Geometry optimization and vibrational frequencies calculation keywords are specified in this section

➡ Geometry optimization and vibrational frequencies tutorials

CRYSTAL input - Basis set input section

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

```
12 3
1 0 3  2.  0.
1 1 3  8.  0.
1 1 3  2.  0.
8 2
1 0 3  2.  0.
1 1 3  6.  0.
99   0
Optional keywords
END    (ENDBS)
```

Atomic number and number of shells
Basis set input: code, type, nr. of primitive, formal charge and scale factor of the shell: 0. indicates standard Pople STO-nG value
Here, Mg and O have been described with a minimal STO-3G basis set

End of basis set input section

Basis set and initial electronic configuration are specified for each atom with different *conventional* atomic number

Effective Core Potential must be inserted along with the valence-only basis set

Optional keywords are related to:

- modification of the electronic configuration
- use of ghost functions

→ ***crystal*** input – Basis set

CRYSTAL input – Method & SCF input section

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

SHRINK **8 8** ***Optional keywords*** ***END (ENDSCF)***	Reciprocal space integration parameters End of SCF input section

This section specifies the adopted theoretical method (default: RHF) and controls the SCF part of the calculation

Other information can be indicated including the type of run and computational conditions on integrals calculation.

Reciprocal space integration parameters are the so-called shrinking factors and must be specified for periodic calculations (3D, 2D and 1D)

They are used in the Fermi energy calculation and in the density matrix reconstruction (see R. Orlando's lecture)

Other optional keywords include:

- convergence criteria,
- convergence tools,
- options for spin-polarized systems

➡ ***crystal*** input –Hamiltonians, SCF & C.

CRYSTAL input – DFT input block

E.g.: MgO bulk - fcc cubic cell – SVWN/STO-3G

DFT	DFT input block
EXCHANGE	Keyword to define the exchange functional
LDA	Selected exchange functional
CORRELAT	Keyword to define the correlation functional
VWN	Selected correlation functional
ENDDFT ***(END)***	End of the DFT input block
SHRINK	Reciprocal space integration parameters
8 8	
Optional keywords	
END ***(ENDM)***	End of the Method input section

Other options are available to modify accuracy in DFT calculations (e.g. integration grid)

Other information can be indicated including the type of run and computational conditions on integrals calculation

For spin-polarized systems the keyword **SPIN** must be specified

➡ ***crystal*** input –Hamiltonians, SCF & co.

CRYSTAL output - Header

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

Header of **CRYSTAL**.

It reports the **CRYSTAL** version and the main authors of the code

```
*******************************************************************************
*                                                                             *
*                                  CRYSTAL06                                  *
*                                Release : 1.0                                *
*                              cry06_060822                                   *
*                                                                             *
*                                                                             *
*                                                                             *
*                                MAIN AUTHORS                                 *
*                                                                             *
*        R. DOVESI(1), V.R. SAUNDERS(2), C. ROETTI(1), R. ORLANDO (1,3),      *
*     C.M. ZICOVICH-WILSON(1,4), F. PASCALE(5), B. CIVALLERI(1), K. DOLL(6),  *
*        N.M. HARRISON(2,7), I. J. BUSH(2), Ph. D'ARCO(8), M. LLUNELL(9)      *
*                                                                             *
* (1) THEORETICAL CHEMISTRY GROUP - UNIVERSITA' DI TORINO - TORINO (ITALY)    *
*      http://www.crystal.unito.it                                            *
* (2) COMPUTATIONAL SCIENCE & ENGINEERING DEPARTMENT - CCLRC DARESBURY (UK)   *
*     http://www.cse.clrc.ac.uk/cmg/CRYSTAL/                                  *
* (3) UNIVERSITA' DEL PIEMONTE ORIENTALE - ALESSANDRIA (ITALY)                *
* (4) UNIVERSIDAD AUTONOMA DEL ESTADO DE MORELOS - CUERNAVACA (MEXICO)        *
* (5) UNIVERSITE' HENRI POINCARE' - NANCY (FRANCE)                            *
* (6) TU BRAUNSCHWEIG - BRAUNSCHWEIG (GERMANY)                                *
* (7) IMPERIAL COLLEGE - LONDON (UK)                                          *
* (8) UNIVERSITE' PIERRE ET MARIE CURIE - PARIS (FRANCE)                      *
* (9) UNIVERSIDAD DE BARCELONA - BARCELONA (SPAIN)                            *
*******************************************************************************
```

Date and time.

```
EEEEEEEEEE STARTING  DATE 03 09 2006 TIME 09:25:16.0
```

CRYSTAL output – Geometry part – conventional cell

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

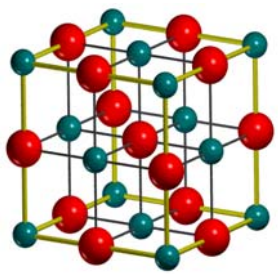
Title section from input

The periodicity of the studied system is indicated as well as a summary of crystallographic information.

The crystal structure specification follows.

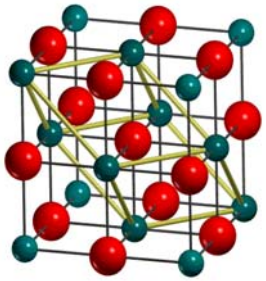
The lattice parameters of the ***conventional cell*** and the atomic positions in the asymmetric unit are reported.

This is the crystal structure given as input.



```
MGO BULK

CRYSTAL CALCULATION
(INPUT ACCORDING TO THE INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY)
CRYSTAL FAMILY                          :  CUBIC
CRYSTAL CLASS  (GROTH - 1921)           :  CUBIC HEXAKISOCTAHEDRAL

SPACE GROUP (CENTROSYMMETRIC)           :  F M 3 M

LATTICE PARAMETERS  (ANGSTROMS AND DEGREES) - CONVENTIONAL CELL
       A           B           C        ALPHA        BETA       GAMMA
    4.21000     4.21000     4.21000    90.00000    90.00000    90.00000


NUMBER OF IRREDUCIBLE ATOMS IN THE CONVENTIONAL CELL:    2

INPUT COORDINATES

ATOM AT. N.                 COORDINATES
  1  12     0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
  2   8     5.000000000000E-01  5.000000000000E-01  5.000000000000E-01
```

CRYSTAL output – Geometry part – primitive cell



E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

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

<< INFORMATION >>: FROM NOW ON, ALL COORDINATES REFER TO THE PRIMITIVE CELL

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

LATTICE PARAMETERS  (ANGSTROMS AND DEGREES) - PRIMITIVE CELL
      A          B          C         ALPHA      BETA     GAMMA        VOLUME
   2.97692    2.97692    2.97692     60.0000   60.0000   60.0000      18.65462

COORDINATES OF THE EQUIVALENT ATOMS (FRACTIONARY UNITS)

N. ATOM EQUIV AT. N.          X                   Y                   Z

  1   1   1   12 MG    0.00000000000E+00  0.00000000000E+00  0.00000000000E+00

  2   2   1    8 O    -5.00000000000E-01 -5.00000000000E-01 -5.00000000000E-01

NUMBER OF SYMMETRY OPERATORS         :   48
*******************************************************************************
* GEOMETRY EDITING - INPUT COORDINATES ARE GIVEN IN ANGSTROM
*******************************************************************************

GEOMETRY NOW FULLY CONSISTENT WITH THE GROUP

GCALCO - MAX INDICES DIRECT LATTICE VECTOR  10  10  10
NO.OF VECTORS CREATED 2999 STARS   59 RMAX    44.65152
```

The lattice parameters of the ***primitive cell*** and all the atomic positions are reported. For each non-equivalent atom the corresponding block of equivalent atoms is displayed.

The number of symmetry operators

CRYSTAL output continues with the geometry editing section

Size of direct lattice

CRYSTAL output – Final geometry printing

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

Here, the final structure for the wave function calculation is reported

The lattice parameters and all the atomic positions of the primitive cell are indicated

When the initial geometry is not primitive, the transformation matrix from the primitive cell to the crystallographic one is reported as well as the lattice parameters and the atomic positions of the conventional unit cell

Irreducible atoms are labelled by T

```
GEOMETRY FOR WAVE FUNCTION - DIMENSIONALITY OF THE SYSTEM    3
(NON PERIODIC DIRECTION: LATTICE PARAMETER FORMALLY SET TO 500)
**********************************************************************
LATTICE PARAMETERS (ANGSTROMS AND DEGREES) - BOHR = 0.5291772083 ANGSTROM
PRIMITIVE CELL - CENTRING CODE 5/0 VOLUME=    18.654615 - DENSITY 3.559 g/cm^3
        A              B              C           ALPHA      BETA       GAMMA
    2.97691955     2.97691955     2.97691955    60.000000  60.000000  60.000000
**********************************************************************
ATOMS IN THE ASYMMETRIC UNIT    2 - ATOMS IN THE UNIT CELL:    2
    ATOM              X/A                 Y/B                 Z/C
**********************************************************************
  1 T  12 MG    0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
  2 T   8 O    -5.000000000000E-01 -5.000000000000E-01 -5.000000000000E-01

TRANSFORMATION MATRIX PRIMITIVE-CRYSTALLOGRAPHIC CELL
-1.0000  1.0000  1.0000  1.0000 -1.0000  1.0000  1.0000  1.0000 -1.0000

**********************************************************************
CRYSTALLOGRAPHIC CELL (VOLUME=         74.61846100)
        A              B              C           ALPHA      BETA       GAMMA
    4.21000000     4.21000000     4.21000000    90.000000  90.000000  90.000000

COORDINATES IN THE CRYSTALLOGRAPHIC CELL
    ATOM              X/A                 Y/B                 Z/C
**********************************************************************
  1 T  12 MG    0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
  2 T   8 O    -5.000000000000E-01 -5.000000000000E-01 -5.000000000000E-01

T = ATOM BELONGING TO THE ASYMMETRIC UNIT
```

CRYSTAL output – Final geometry printing

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

When geometry editing is terminated, residual symmetry operators are printed

```
****  48 SYMMOPS - TRANSLATORS IN FRACTIONARY UNITS
 V INV                    ROTATION MATRICES                        TRANSLATOR
 1  1  1.00  0.00  0.00  0.00  1.00  0.00  0.00  0.00  1.00    0.00  0.00  0.00
 2  2  0.00  1.00 -1.00  1.00  0.00 -1.00  0.00  0.00 -1.00    0.00  0.00  0.00
 3  3 -1.00  0.00  0.00 -1.00  0.00  1.00 -1.00  1.00  0.00    0.00  0.00  0.00
 4  4  0.00 -1.00  1.00  0.00 -1.00  0.00  1.00 -1.00  0.00    0.00  0.00  0.00
 5  6  0.00  1.00  0.00  0.00  0.00  1.00  1.00  0.00  0.00    0.00  0.00  0.00
 6  5  0.00  0.00  1.00  1.00  0.00  0.00  0.00  1.00  0.00    0.00  0.00  0.00
 7  8  1.00  0.00 -1.00  0.00  0.00 -1.00  0.00  1.00 -1.00    0.00  0.00  0.00
 8  7  1.00 -1.00  0.00  0.00 -1.00  1.00  0.00 -1.00  0.00    0.00  0.00  0.00
 9 10 -1.00  0.00  1.00 -1.00  1.00  0.00 -1.00  0.00  0.00    0.00  0.00  0.00
10  9  0.00  0.00 -1.00  0.00  1.00 -1.00  1.00  0.00 -1.00    0.00  0.00  0.00
…
…
…
40 39 -1.00  0.00  1.00 -1.00  0.00  0.00 -1.00  1.00  0.00    0.00  0.00  0.00
41 41  1.00  0.00  0.00  0.00  0.00  1.00  0.00  1.00  0.00    0.00  0.00  0.00
42 42  0.00  0.00  1.00  0.00  1.00  0.00  1.00  0.00  0.00    0.00  0.00  0.00
43 45  0.00  1.00 -1.00  0.00  0.00 -1.00  1.00  0.00 -1.00    0.00  0.00  0.00
44 46 -1.00  1.00  0.00 -1.00  0.00  1.00 -1.00  0.00  0.00    0.00  0.00  0.00
45 43  0.00 -1.00  1.00  1.00 -1.00  0.00  0.00 -1.00  0.00    0.00  0.00  0.00
46 44  0.00  0.00 -1.00  1.00  0.00 -1.00  0.00  1.00 -1.00    0.00  0.00  0.00
47 47 -1.00  0.00  0.00 -1.00  1.00  0.00 -1.00  0.00  1.00    0.00  0.00  0.00
48 48  1.00 -1.00  0.00  0.00 -1.00  0.00  0.00 -1.00  1.00    0.00  0.00  0.00
```

CRYSTAL output – Final geometry printing

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

Finally, lattice vectors and atomic positions of the primitive cell are printed in the Cartesian frame.

```
DIRECT LATTICE VECTORS CARTESIAN COMPONENTS (ANGSTROM)
         X                    Y                    Z
  0.000000000000E+00   0.210500000000E+01   0.210500000000E+01
  0.210500000000E+01   0.000000000000E+00   0.210500000000E+01
  0.210500000000E+01   0.210500000000E+01   0.000000000000E+00


CARTESIAN COORDINATES - PRIMITIVE CELL
*********************************************************************************
*      ATOM          X(ANGSTROM)         Y(ANGSTROM)         Z(ANGSTROM)
*********************************************************************************
  1    12 MG    0.000000000000E+00  0.000000000000E+00  0.000000000000E+00
  2     8 O     2.105000000000E+00  2.105000000000E+00  2.105000000000E+00
```

CRYSTAL output – Basis set

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

Basis set primitive functions of each non equivalent atom

Atom type and cartesian coordinates (Bohr)

Shell type, gaussian exponents and coefficients

```
**********************************************************************
LOCAL ATOMIC FUNCTIONS BASIS SET
**********************************************************************
  ATOM  X(AU)  Y(AU)  Z(AU)    NO. TYPE  EXPONENT  S COEF   P COEF   D/F/G COEF
**********************************************************************
  1 MG  0.000  0.000  0.000
                                   1 S
                                        2.992E+02 1.543E-01 0.000E+00 0.000E+00
                                        5.451E+01 5.353E-01 0.000E+00 0.000E+00
                                        1.475E+01 4.446E-01 0.000E+00 0.000E+00
                                 2-   5 SP
                                        1.512E+01-9.997E-02 1.559E-01 0.000E+00
                                        3.514E+00 3.995E-01 6.077E-01 0.000E+00
                                        1.143E+00 7.001E-01 3.920E-01 0.000E+00
                                 6-   9 SP
                                        1.395E+00-2.196E-01 1.059E-02 0.000E+00
                                        3.893E-01 2.256E-01 5.952E-01 0.000E+00
                                        1.524E-01 9.004E-01 4.620E-01 0.000E+00
  2 O   3.978  3.978  3.978
                                  10 S
                                        1.307E+02 1.543E-01 0.000E+00 0.000E+00
                                        2.381E+01 5.353E-01 0.000E+00 0.000E+00
                                        6.444E+00 4.446E-01 0.000E+00 0.000E+00
                                11-  14 SP
                                        5.033E+00-9.997E-02 1.559E-01 0.000E+00
                                        1.170E+00 3.995E-01 6.077E-01 0.000E+00
                                        3.804E-01 7.001E-01 3.920E-01 0.000E+00
```

CRYSTAL output – General information

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

This section gives computational information concerning the studied system and tolerances for the integrals evaluation

Here the theoretical method is indicated

Information on the computational conditions for the SCF iteration procedure (convergence criteria, shrinking factors and number of k points) are reported

```
*******************************************************************************
N. OF ATOMS PER CELL         2  COULOMB OVERLAP TOL          (T1) 10** -6
NUMBER OF SHELLS             5  COULOMB PENETRATION TOL      (T2) 10** -6
NUMBER OF AO                14  EXCHANGE OVERLAP TOL         (T3) 10** -6
N. OF ELECTRONS PER CELL    20  EXCHANGE PSEUDO OVP (F(G))   (T4) 10** -6
CORE ELECTRONS PER CELL     12  EXCHANGE PSEUDO OVP (P(G))   (T5) 10**-12
N. OF SYMMETRY OPERATORS    48  POLE ORDER IN MONO ZONE                4
*******************************************************************************
TYPE OF CALCULATION :  RESTRICTED CLOSED SHELL
HARTREE-FOCK HAMILTONIAN
*******************************************************************************
MAX NUMBER OF SCF CYCLES      50  CONVERGENCE ON DELTAP        10**-16
NO MIXING OF F MATRICES           CONVERGENCE ON ENERGY        10**- 5
SHRINK. FACT.(MONKH.)    8  8  8  NUMBER OF K POINTS IN THE IBZ     29
SHRINKING FACTOR(GILAT NET)    8  NUMBER OF K POINTS(GILAT NET)     29
*******************************************************************************
```

CRYSTAL output – General information

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

Coordinates of the k-points used in the IBZ sampling are reported

```
*** K POINTS COORDINATES (OBLIQUE COORDINATES IN UNITS OF IS =  8)
  1-R(  0  0  0)   2-C(  1  0  0)   3-C(  2  0  0)   4-C(  3  0  0)
  5-R(  4  0  0)   6-C(  1  1  0)   7-C(  2  1  0)   8-C(  3  1  0)
  9-C(  4  1  0)  10-C(  5  1  0)  11-C(  6  1  0)  12-C(  7  1  0)
 13-C(  2  2  0)  14-C(  3  2  0)  15-C(  4  2  0)  16-C(  5  2  0)
 17-C(  6  2  0)  18-C(  3  3  0)  19-C(  4  3  0)  20-C(  5  3  0)
 21-R(  4  4  0)  22-C(  3  2  1)  23-C(  4  2  1)  24-C(  5  2  1)
 25-C(  4  3  1)  26-C(  5  3  1)  27-C(  6  3  1)  28-C(  5  4  1)
 29-C(  6  4  2)
```

Other information on the direct and reciprocal space follow

```
DIRECT LATTICE VECTORS COMPON. (A.U.)    RECIP. LATTICE VECTORS COMPON. (A.U.)
      X            Y            Z            X            Y            Z
   0.0000000    3.9778735    3.9778735   -0.7897669    0.7897669    0.7897669
   3.9778735    0.0000000    3.9778735    0.7897669   -0.7897669    0.7897669
   3.9778735    3.9778735    0.0000000    0.7897669    0.7897669   -0.7897669
```

Here information about the resource usage are reported. Dimensions of density and Fock matrix in direct space are displayed as well as information on integrals storage and memory usage

```
DISK SPACE FOR EIGENVECTORS (FTN 10)      10780 REALS

SYMMETRY ADAPTION OF THE BLOCH FUNCTIONS ENABLED

DIMENSIONS  P(G)=   13898 F(G)=    2820 P(G),F(G) (IRR)     666
MAX G-VECTOR INDEX FOR 1- AND 2-ELECTRON INTEGRALS 319

INFORMATION **** GENBUF **** COULOMB BIPO BUFFER LENGTH (WORDS) =     66150
TTTTTTTTTTTTTTTTTTTTTTTTTTTTT INPUT      TELAPSE        0.02 TCPU        0.02
```

CRYSTAL output – Neighbors analysis

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

The section labelled `NEIGHBORS OF THE NON-EQUIVALENT ATOMS` reports information on the first neighbours (default: 6).

For each non-equivalent atom: number, type, distance, and position in terms of indices of the direct lattice cell are displayed.

Here the number of internal degrees of freedom of the studied system is indicated

```
NEIGHBORS OF THE NON-EQUIVALENT ATOMS

N = NUMBER OF NEIGHBORS AT DISTANCE R
   ATOM   N      R/ANG      R/AU   NEIGHBORS (ATOM LABELS AND CELL INDICES)
  1 MG    6      2.1050     3.9779   2 O   -1 0 0   2 O    0-1 0   2 O    0 0-1
                                     2 O   -1-1 0   2 O   -1 0-1   2 O    0-1-1
  1 MG   12      2.9769     5.6256   1 MG  -1 0 0   1 MG   1 0 0   1 MG  -1 0 1
                                     1 MG   1 0-1   1 MG  -1 1 0   1 MG   1-1 0
                                     1 MG   0-1 0   1 MG   0 1 0   1 MG   0-1 1
                                     1 MG   0 1-1   1 MG   0 0-1   1 MG   0 0 1
  1 MG    8      3.6460     6.8899   2 O    0 0 0   2 O   -1-1 1   2 O   -1 1-1
                                     2 O    1-1-1   2 O   -2 0 0   2 O    0-2 0
                                     2 O    0 0-2   2 O   -1-1-1
  ...

  2 O     6      2.1050     3.9779   1 MG   1 0 0   1 MG   0 1 0   1 MG   0 0 1
                                     1 MG   1 1 0   1 MG   1 0 1   1 MG   0 1 1
  2 O    12      2.9769     5.6256   2 O   -1 0 0   2 O    1 0 0   2 O   -1 0 1
                                     2 O    1 0-1   2 O   -1 1 0   2 O    1-1 0
                                     2 O    0-1 0   2 O    0 1 0   2 O    0-1 1
                                     2 O    0 1-1   2 O    0 0-1   2 O    0 0 1
  2 O     8      3.6460     6.8899   1 MG   0 0 0   1 MG   1 1-1   1 MG   1-1 1
                                     1 MG  -1 1 1   1 MG   2 0 0   1 MG   0 2 0
                                     1 MG   0 0 2   1 MG   1 1 1
  ...

THERE ARE NO SYMMETRY ALLOWED DIRECTIONS
TTTTTTTTTTTTTTTTTTTTTTTTTTTTT SYMM        TELAPSE        0.03 TCPU      0.03
```

CRYSTAL output – Integrals calc. and SCF initial guess

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

This section reports more information on the integrals evaluation and concludes the first part of a traditional SCF procedure: the integrals calculation

```
INFORMATION **** GENBUF **** COULOMB BIPO BUFFER LENGTH (WORDS) =     66150
INFORMATION **** EXCBUF **** EXCH. BIPO BUFFER: WORDS USED =     97362
TTTTTTTTTTTTTTTTTTTTTTTTTTTTT MONIRR      TELAPSE        0.11 TCPU       0.11

 GAUSS70 FOR COULOMB   GAUSS70 FOR EXCHANGE
**SHELL_ORTHODOX** SPACE FOR BIEL. INTEGRALS     1 BUFFERS
TTTTTTTTTTTTTTTTTTTTTTTTTTTTT SHLC        TELAPSE        1.87 TCPU       1.84
TTTTTTTTTTTTTTTTTTTTTTTTTTTTT MONMAD      TELAPSE        1.99 TCPU       1.92
EEEEEEEEEE INT_CALC TERMINATION  DATE 03 09 2006 TIME 09:25:18.1
```

With this section starts the SCF iteration to compute the total energy

```
********************************************************************************
MGO BULK
CRYSTAL - SCF - TYPE OF CALCULATION :  RESTRICTED CLOSED SHELL
********************************************************************************
TTTTTTTTTTTTTTTTTTTTTTTTTTTTT SDIK        TELAPSE        2.00 TCPU       1.92
```

CRYSTAL output –SCF initial guess

E.g.: MgO bulk - fcc cubic cell – RHF/STO-3G

The SCF starts by defining the initial guess of the density matrix

The default initial guess for the wave function evaluation is obtained from a superposition of atomic densities

The initial electronic configuration of each atomic species is also reported

```
AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
        ATOMIC WAVEFUNCTION(S)


NUCLEAR CHARGE 12.0  SYMMETRY SPECIES            S    P
N. ELECTRONS   12.0  NUMBER OF PRIMITIVE GTOS    9    6
                     NUMBER OF CONTRACTED GTOS   3    2
                     NUMBER OF CLOSED SHELLS     3    1
                     OPEN SHELL OCCUPATION       0    0

 ZNUC SCFIT  TOTAL HF ENERGY   KINETIC ENERGY   VIRIAL THEOREM ACCURACY
 12.0   4   -1.970073545E+02  1.945732082E+02 -2.012510183E+00  2.9E-06

NUCLEAR CHARGE  8.0  SYMMETRY SPECIES            S    P
N. ELECTRONS    8.0  NUMBER OF PRIMITIVE GTOS    6    3
                     NUMBER OF CONTRACTED GTOS   2    1
                     NUMBER OF CLOSED SHELLS     2    0
                     OPEN SHELL OCCUPATION       0    4

 ZNUC SCFIT  TOTAL HF ENERGY   KINETIC ENERGY   VIRIAL THEOREM ACCURACY
  8.0   1   -7.380415026E+01  7.344496710E+01 -2.004890507E+00  0.0E+00

AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA
```

CRYSTAL output – SCF iteration

This section reports information on the SCF iteration.

At each SCF cycle, total charge of the atoms (Mulliken scheme), total energy and values of the convergence criteria are printed

Here, it is also indicated whether the system is an insulator or a conductor and the related Fermi level

```
CHARGE NORMALIZATION FACTOR   1.00000000
TOTAL ATOMIC CHARGES:
 12.0000000   8.0000000
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT QGAM        TELAPSE        2.01 TCPU       1.93
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT BIEL        TELAPSE        2.03 TCPU       1.94
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT TOTENY      TELAPSE        2.03 TCPU       1.94
CYC   0 ETOT(AU) -2.706738561044E+02 DETOT -2.71E+02 tst  0.00E+00 PX 1.00E+00
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT FDIK        TELAPSE        2.03 TCPU       1.94
INSULATING STATE - TOP OF VALENCE BANDS (A.U.) -2.0824792E-01
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT PDIG        TELAPSE        2.04 TCPU       1.95
CHARGE NORMALIZATION FACTOR   1.00000000
TOTAL ATOMIC CHARGES:
 10.9720201   9.0279799
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT QGAM        TELAPSE        2.04 TCPU       1.95
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT BIEL        TELAPSE        2.05 TCPU       1.96
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT TOTENY      TELAPSE        2.05 TCPU       1.96
CYC   1 ETOT(AU) -2.711666415674E+02 DETOT -4.93E-01 tst  0.00E+00 PX 1.00E+00
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT FDIK        TELAPSE        2.05 TCPU       1.96
INSULATING STATE - TOP OF VALENCE BANDS (A.U.) -6.1674907E-02
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT PDIG        TELAPSE        2.06 TCPU       1.97
CHARGE NORMALIZATION FACTOR   1.00000000
TOTAL ATOMIC CHARGES:
 11.3203964   8.6796036
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT QGAM        TELAPSE        2.06 TCPU       1.97
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT BIEL        TELAPSE        2.09 TCPU       1.98
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT TOTENY      TELAPSE        2.09 TCPU       1.98
CYC   2 ETOT(AU) -2.712141249457E+02 DETOT -4.75E-02 tst  2.23E-02 PX 1.35E-01
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT FDIK        TELAPSE        2.10 TCPU       1.99
INSULATING STATE - TOP OF VALENCE BANDS (A.U.) -1.7547943E-01
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT PDIG        TELAPSE        2.10 TCPU       1.99
...
```

… convergence on energy has been achieved
Threshold: $1 \cdot 10^{-5}$

On convergence, each contribution to the total energy is displayed as well as the total energy and the virial coefficient

At the conclusion of the job, the following lines are printed indicating the final energy and the number of cycles needed to reach the convergence.

Finally, the CPU time is reported … only a few seconds …

```
...
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT TOTENY      TELAPSE        2.17 TCPU       2.06
CYC   6 ETOT(AU) -2.712180983825E+02 DETOT -3.38E-06 tst  1.17E-06 PX 1.48E-03
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT FDIK       TELAPSE        2.17 TCPU       2.06
INSULATING STATE - TOP OF VALENCE BANDS (A.U.) -1.4775921E-01
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT PDIG       TELAPSE        2.18 TCPU       2.07
CHARGE NORMALIZATION FACTOR   1.00000000
TOTAL ATOMIC CHARGES:
 11.2223209   8.7776791
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT QGAM       TELAPSE        2.18 TCPU       2.07
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT BIEL       TELAPSE        2.18 TCPU       2.07
+++ ENERGIES IN A.U. +++
::: EXT EL-POLE : L =  0                        -4.6907630069433E+02
::: EXT EL-POLE : L =  1                        -8.4961934766814E-22
::: EXT EL-POLE : L =  2                        -2.4547906991938E-19
::: EXT EL-POLE : L =  3                        -2.4272925970741E-23
::: EXT EL-POLE : L =  4                        -1.0955281259775E-04
::: EXT EL-SPHEROPOLE                           3.9641495581542E+00
::: BIELET ZONE E-E                             5.1160526532334E+02
::: TOTAL E-E                                   4.6493004634354E+01
::: TOTAL E-N + N-E                             -5.1175597833315E+02
::: TOTAL N-N                                   -7.3084276676762E+01
::: KINETIC ENERGY                              2.6712915158680E+02
::: TOTAL   ENERGY                              -2.7121809878875E+02
::: VIRIAL COEFFICIENT                          9.9240462879843E-01
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT TOTENY      TELAPSE        2.19 TCPU       2.08
CYC   7 ETOT(AU) -2.712180987888E+02 DETOT -4.06E-07 tst  1.30E-07 PX 1.48E-03

== SCF ENDED - CONVERGENCE ON ENERGY     E(AU) -2.7121809878875E+02 CYCLES  7

TOTAL ENERGY(HF)(AU)( 7) -2.712180987888E+02 DE-4.1E-07 tst 1.3E-07 PX 1.5E-03
EIGENVECTORS IN FORTRAN UNIT 10
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT END        TELAPSE        2.23 TCPU       2.11
EEEEEEEEEE TERMINATION  DATE 03 09 2006 TIME 09:25:18.3
```

CRYSTAL output – DFT calculations

E.g.: MgO bulk - fcc cubic cell – SVWN/STO-3G

The DFT theoretical method is indicated as

```
********************************************************************************
TYPE OF CALCULATION :  RESTRICTED CLOSED SHELL
KOHN-SHAM HAMILTONIAN

(EXCHANGE)[CORRELATION] FUNCTIONAL:(DIRAC-SLATER LDA)[VOSKO-WILK-NUSAIR]

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

DFT computational parameters on the numerical integration scheme (atomic radii, weights, thresholds and grid information) are also reported in the **CRYSTAL** output

```
DFT PARAMETERS

ATOM       ELECTRONS   NET CHARGE   R(ANGSTROM)
  1  12  MG     12.0000      0.0000     1.60000000
  2   8  O       8.0000      0.0000     0.74000000

SIZE OF GRID=        474
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)
```

CRYSTAL output – DFT calculations

E.g.: MgO bulk - fcc cubic cell – SVWN/STO-3G

On convergence, each contribution to the total energy is displayed as well as the total energy and the virial coefficient

```
...
::: TOTAL E-E                                    6.9971234230499E+01
::: TOTAL E-N + N-E                             -5.0952773870920E+02
::: TOTAL N-N                                   -7.3084276676762E+01
::: KINETIC ENERGY                               2.6580724111130E+02
::: PSEUDO TOTAL   ENERGY                       -2.4683354004417E+02
::: VIRIAL COEFFICIENT                           1.0370116888172E+00
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT TOTENY      TELAPSE        3.42 TCPU       3.40
NUMERICALLY INTEGRATED DENSITY     19.9989148950
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT NUMDFT      TELAPSE        3.53 TCPU       3.52
CYC   8 ETOT(AU) -2.705460373130E+02 DETOT -2.37E-06 tst  4.58E-05 PX 1.44E-03

== SCF ENDED - CONVERGENCE ON ENERGY      E(AU) -2.7054603731298E+02 CYCLES  8
```

At the end of the SCF iteration, the DFT energy expression and the total energy are displayed

```
ENERGY EXPRESSION=HARTREE+FOCK EXCH*0.00000+(LDA   EXCH)*1.00000+VWN   CORR

TOTAL ENERGY(DFT)(AU)(  8) -2.7054603731298E+02 DE-2.4E-06 tst 4.6E-05
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT EDFT        TELAPSE        3.53 TCPU       3.52
EIGENVECTORS IN FORTRAN UNIT  8
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTT END         TELAPSE        3.54 TCPU       3.53
EEEEEEEEEE TERMINATION  DATE 03 09 2006 TIME 09:44:22.7
```

CRYSTAL input - Geometry optimization

E.g.: α-Quartz - hexagonal cell

QUARTZ ALFA	Title
CRYSTAL	Dimensionality of the system
0 0 0	Crystallographic information (3D only)
154	Space Group (*Fm3m – 225*)
4.916 5.4054	Lattice parameters (*cubic*)
2	Number of non equivalent atoms
14 0.4697 0.0000 0.0000	Atomic number and fractional coordinates
8 0.4135 0.2669 0.1191	
OPTGEOM	Geometry optimization input block
Optional keywords	
END	End of the geometry optimization input block
END *(ENDG)*	End of geometry input section

Geometry optimization input block is specified as the **last** part of the geometry input section

Different types of run:

- atomic coordinates only (*default*)
- cell parameters only ⇒ **CELLONLY**
- full geometry optimization (cell param. + atomic positions) ⇒ **FULLOPTG**
- iterative independent optimizations of cell param.s and atomic positions ⇒ **ITATOCEL**
- fragment and constraint (e.g. constant volume)

Geometry optimization in internal redundant coordinates ⇒ **INTREDUN**

CRYSTAL input – Vibrational frequencies at Γ

E.g.: α-Quartz - hexagonal cell

```
QUARTZ ALFA
CRYSTAL
0 0 0
154
4.916 5.4054
2
14 0.4697 0.0000 0.0000
8 0.4135 0.2669 0.1191
FREQCALC
Optional keywords
END
END (ENDG)
```

Title
Dimensionality of the system
Crystallographic information (3D only)
Space Group (*Fm3m – 225*)
Lattice parameters (*cubic*)
Number of non equivalent atoms
Atomic number and fractional coordinates

Vibrational frequencies input block

End of the Vibrational frequencies input block
End of geometry input section

Vibrational frequencies input block is specified as the **last** part of the geometry input section

Optional keywords allow to compute:

- IR intensities
- LO/TO splitting
- Low frequency dielectric constant
- Isotopic substitution
- Vibrational frequencies of an atomic fragment