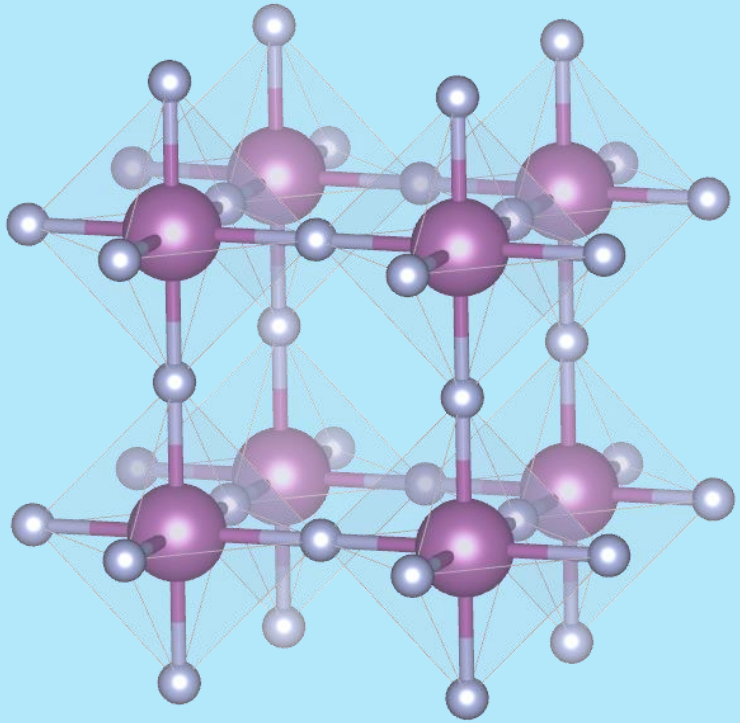
Getting Started with CRYSTAL23: From Geometry to Single-Point Calculations



MSSC2025
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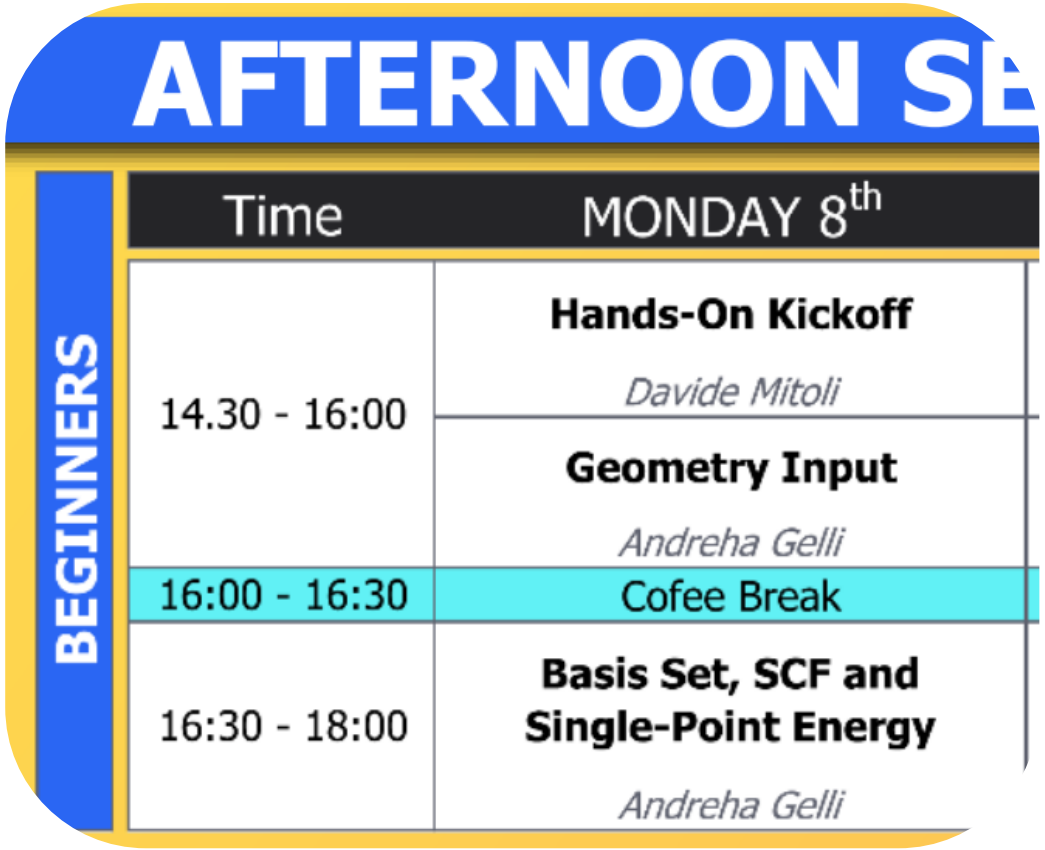
Andreha Gelli – PhD student
andreha.gelli@unito.it

UNIVERSITÀ DI TORINO

UAB
Universitat Autònoma de Barcelona

What you will learn today



- Understand CRYSTAL input structure
- Explore geometry, basis set and functionals initialization
- Run a first single-point calculation

Please note: coffee break from 16:00 to 16:30

Usefull links

General resources:

🌐 Website

📖 Manual

💬 Forum

Tutorials

Getting started:

▶️ A quick tour of CRYSTAL

▶️ Introduction

Tutorials

Input details:

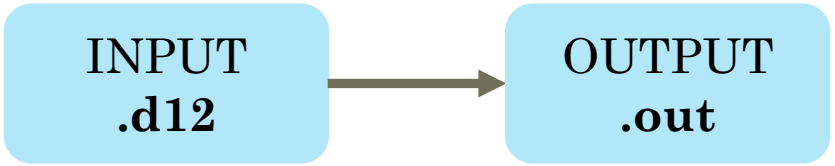
▶️ Geometry

▶️ Basis Set

▶️ Functionals & Others

▶️ Total energy calculation

General structure of a CRYSTAL input



Please log to the Virtual Machine and navigate to the following folder:

📂MSSC2025/Basic/Day1/1_single_point_example

```
$ cd MSSC2025/Basic/Day1/1_single_point_example
$ ls
 diis_Fg    diis_Fia2  fort.10  fort.21  fort.62  fort.9
fort.98       mgo_input.out
diis_Fia1  diis_Sk    fort.11  fort.61  fort.8   fort.95
mgo_input.d12
$ vi mgo_input.d12
```

MgO bulk

```
CRYSTAL
0 0 0
225
4.21
2
12 0.    0.    0.
 8 0.5   0.5   0.5
END
```

Geometry →

Title
Dimensionality of the system
Crystallographic information
Space group
Lattice parameters
Number of atoms in the cell
Atomic position

End of the block

```
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
END
```

Basis set →

For **each atom**: atomic number and the number of shells.
For **each shell**: type of basis set (0-1-2), type of shell (0-1-2-3-4), number of primitives GTF, shell electronic charge, scale factor.

End of the block

```
SHRINK
8 8
END
```

SCF & Co →

Sampling of k points in reciprocal space

End of the block

Deep dive: Geometry block

```
MgO bulk
CRYSTAL
0 0 0
225
4.21
2
12 0.    0.    0.
 8 0.5   0.5   0.5
END
```

1. Title section.

2. Dimensionality of the system: CRYSTAL, SLAB; POLYMER and MOLECULE, for 3D, 2D, 1D and 0D, respectively.

3. Crystallographic information (3D only), three integer numbers for:
- convention for the space group identification: sequential number (0) or alphanumeric code (1).
- type of cell for rhombohedral groups: hexagonal (0) or rhombohedral (1).
- setting of the origin.

4. Space group, check Symmetry groups p. 418 of the manual.

5. Lattice parameters: the *minimal* set of crystallographic cell parameters is indicated (in Angstrom and degrees). For cubic system a=b=c. Note that CRYSTAL works on the primitive cell.

6. Number of non-equivalent atoms in the cell and **atomic position** (coordinates in fractional units).

7. Closing the geometry input section.

Constructing the geometry

CRYSTAL inputs can be built starting from common structure files. Most used formats: .xyz (molecules) and .cif (crystals).

From .xyz to .d12 :

```
3
Water molecule
O    0.000000   0.000000   0.000000
H    0.758602   0.000000   0.504284
H   -0.758602   0.000000   0.504284
```

```
Water
MOLECULE
15                ! C2v
3
8    0.000000   0.000000   0.000000
1    0.758602   0.000000   0.504284
1   -0.758602   0.000000   0.504284
END
```

Constructing the geometry

From .cif to .d12 :

```
data_MgO
_symmetry_space_group_name_H-M    Fm-3m
_cell_length_a    4.19400279
_cell_length_b    4.19400279
_cell_length_c    4.19400279
_cell_angle_alpha    90.00000000
_cell_angle_beta    90.00000000
_cell_angle_gamma    90.00000000
_symmetry_Int_Tables_number    225
_chemical_formula_structural    MgO
_chemical_formula_sum    'Mg4 O4'
_cell_volume    73.77108036
_cell_formula_units_Z
4loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1    'x, y, z'
2    2  '-x, -y, -z'
…
```

```
…
loop_
_atom_type_symbol
_atom_type_oxidation_number
Mg2+  2.0
O2-  -2.0
loop_
_atom_site_type_symbol
_atom_site_label
_atom_site_symmetry_multiplicity
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
Mg2+  Mg0  4  0.00000000  0.00000000  0.00000000  1
O2-  O1  4  0.00000000  0.00000000  0.50000000  1
```

```
MgO bulk
CRYSTAL
0 0 0
225
4.19400279
2
12 0.    0.    0.
 8  0.    0.    0.5
END
```

Constructing the geometry

From The Materials Project :

Lattice (Conventional)

a	4.19 Å
b	4.19 Å
c	4.19 Å
α	90.00 °
β	90.00 °
ɣ	90.00 °
Volume	73.77 Å³

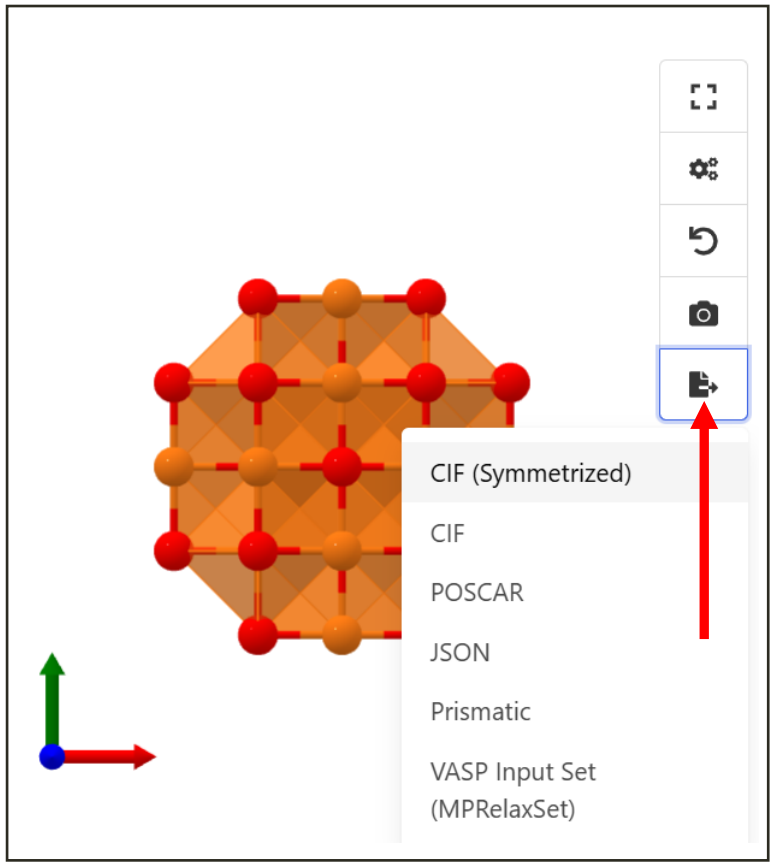
Lattice is given in its conventional crystallographic setting.

Atomic Positions

Wyckoff	Element	x	y	z
4a	Mg	0	0	0
4b	O	0	0	1/2

Symmetry

Crystal System	Cubic
Lattice System	Cubic
Hall Number	-F 4 2 3
International Number	225
Symbol	$Fm\bar{3}m$
Point Group	$m\bar{3}m$



Run a geometry test

Before running a full calculation, it's good practice to check the geometry. CRYSTAL provides the keyword:

TESTGEOM → stops after checking the input geometry

```
$ cd MSSC2025/Basic/Day1/2_first_block_geometry/1_testgeom
$ ls
 0D 1D 2D 3D
$ cd 0D
$ ls
1_benzene  2_methane
$ cd 1_benzene
$ runCRY23 benzene_testgeom
```

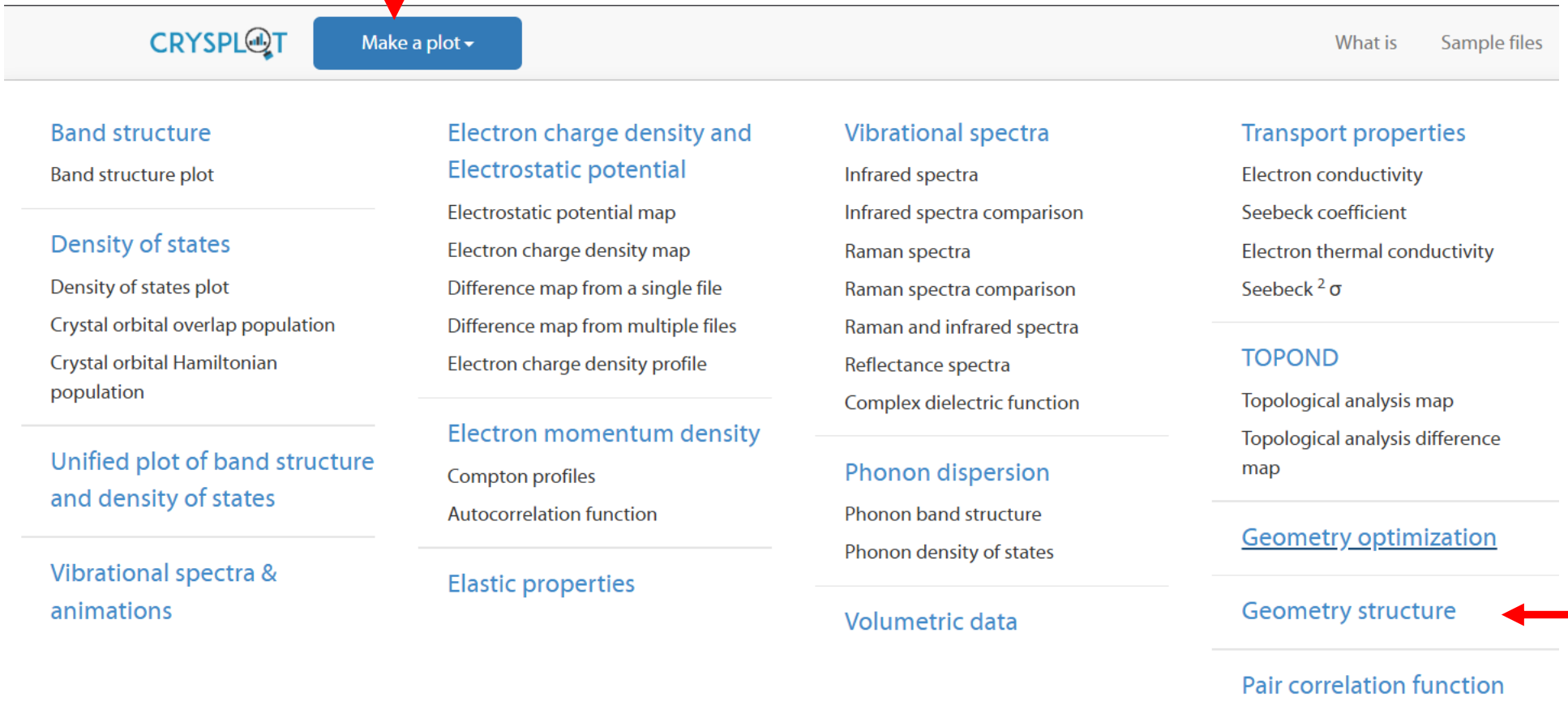
Analyze the .out file

```
$ vi benzene_testgeom.out
```

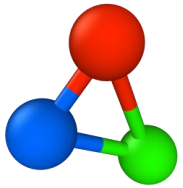
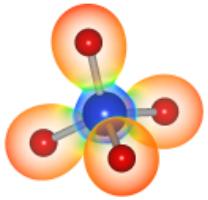
How to visualize

CRYSPLOT

From the file : .out



How to visualize

	File format	PROS	CONS
 Moldraw	.out .f98 .d12	Integrated with CRYSTAL; can visualize MOs and densities	Outdated GUI
 JMol	.cif .xyz .out	Cross-platform, lightweight, Java-based	Limited for advanced density visualization
 OVITO	.cif .xyz	Great for extended systems and animations	Not designed for molecular orbitals
 VESTA	.cif	Excellent for crystals, densities, isosurfaces	Requires some setup

Supercells

The keyword **SUPERCEL** creates a supercell by transforming the lattice vector of the primitive cell, while **SUPERCON** creates a supercell by transforming the lattice vector of the conventional cell.

SUPERCEL

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

```
$ cd MSSC2025/Basic/Day1/2_first_block_geometry/2_supercells
$ ls
1_supercell  2_supercon
$ cd 1_supercell/
$ vi diamond_supercell_testgeom.d12
```

```
...
SUPERCELL
2 0 0
0 2 0
0 0 2
...
```

Other keywords

Geometry keywords

Symmetry information			
ATOMSYMM	printing of point symmetry at the atomic positions	43	–
MAKESAED	printing of symmetry allowed elastic distortions (SAED)	54	–
PRSYMDIR	printing of displacement directions allowed by symmetry.	69	–
SYMMDIR	printing of symmetry allowed geom opt directions	78	–
SYMMOPS	printing of point symmetry operators	78	–
TENSOR	print tensor of physical properties up to order 4	78	I

Symmetry information and control			
BREAKELAS	symmetry breaking according to a general distortion	44	I
BREAKSYM	allow symmetry reduction following geometry modifications	44	–
KEEPSYMM	maintain symmetry following geometry modifications	54	–
MODISYMM	removal of selected symmetry operators	55	I
PURIFY	cleans atomic positions so that they are fully consistent with the group	69	–
SYMMREMO	removal of all symmetry operators	78	–
TRASREMO	removal of symmetry operators with translational components	78	–

Modifications without reduction of symmetry			
ATOMORDE	reordering of atoms in molecular crystals	41	–
NOSHIFT	no shift of the origin to minimize the number of symmops with translational components before generating supercell	64	–
ORIGIN	shift of the origin to minimize the number of symmetry operators with translational components	64	–
PRIMITIV	crystallographic cell forced to be the primitive cell	68	–
ROTCRY	rotation of the crystal with respect to the reference system cell	70	I

Atoms and cell manipulation - possible symmetry reduction (BREAKSYMM)			
ATOMDISP	displacement of atoms	41	I
ATOMINSE	addition of atoms	41	I
ATOMREMO	removal of atoms	42	I
ATOMROT	rotation of groups of atoms	42	I
ATOMSUBS	substitution of atoms	43	I
ELASTIC	distortion of the lattice	47	I
POINTCHG	point charges input	68	I
SCELCONF	generation of supercell for configuration counting	73	I
SCELPHONO	generation of supercell for phonon dispersion	73	I
SUPERCEL	generation of supercell - input refers to primitive cell	75	I
SUPERCON	generation of supercell - input refers to conventional cell	75	I
USESAED	given symmetry allowed elastic distortions, reads δ	78	I

From crystals to slabs (3D→2D)			
SLABINFO	definition of a new cell, with $xy \parallel$ to a given plane	72	I
SLABCUT	generation of a slab parallel to a given plane (3D→2D)	71	I

From slabs to single and multi-wall nanotubes (2D→1D)			
NANOTUBE	building a nanotube from a slab	59	I
SWCNT	building a nanotube from an hexagonal slab	77	I
NANOMULTI	building a multi-wall nanotube from a slab	62	I

From periodic structures to clusters			
CLUSTER	cutting of a cluster from a periodic structure (3D→0D)	45	I
CLUSTSIZE	maximum number of atoms in a cluster	46	I
FULLE	building a fullerene from an hexagonal slab (2D→0D)	52	I
HYDROSUB	border atoms substituted with hydrogens (0D→0D)	54	I

• • •

Deep dive: Basis set block

CRYSTAL performs ab initio calculations on periodic systems within the linear combination of atomic orbitals (LCAO) approximation. That is, the crystalline orbitals (CO) are treated as linear combinations of Bloch functions (BF):

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

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

defined in terms of local functions, hereafter indicated as atomic orbitals (AO). Those local functions are expressed as linear combination of a certain number of Gaussian type functions

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

The AOs belonging to a given atom are grouped into **shells**.

Goal: define AO expansions grouped in **shells**

For **each atom**: atomic number and the number of shells.

For **each shell**: type of basis set, type of shell, number of primitives GTF, shell electronic charge, scale factor.

Basis set types	
0	general: exponent and contraction coefficients defined in input
1	Pople STO-nG type
2	Pople 3(6)-21G type

Shells				
Code	Type	AO	AO order	Max charge
0	s	1	s	2
1	sp	4	s, x, y, z	8
2	p	3	x, y, z	6
3	d	5	$2z^2$-x^2-y^2, xz, yz, x^2-y^2, xy	10
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, $(x^2-3y^2)x$, $(3x^2-y^2)y$	0 - polarization only

The formal **shell electronic charge** is the number of electrons attributed to each shell as initial electronic configuration.

Goal: define AO expansions grouped in **shells**

Back to our first example - MgO

```
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
END
```

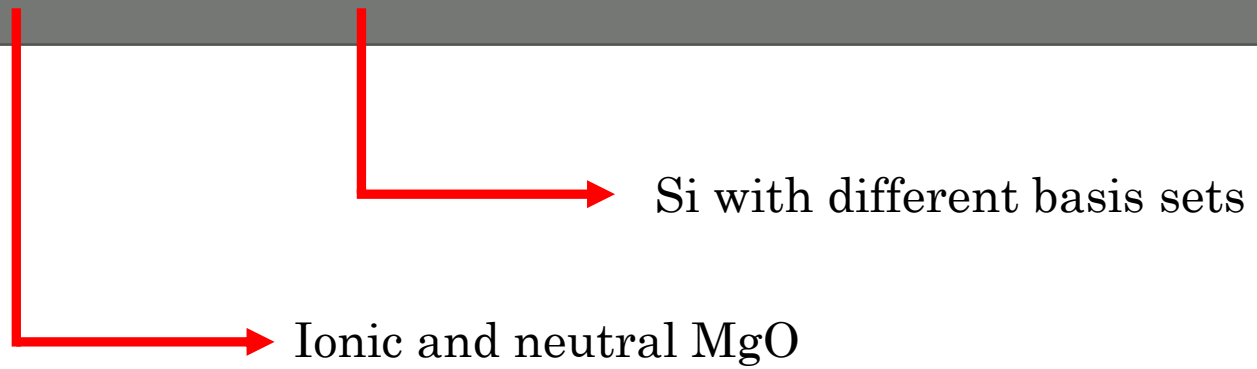
Magnesium – 3 shells
Pople STO-nG bs – shell s – 3 primitives GTF – $2e^-$ – scale factor
Pople STO-nG bs – shell sp – 3 primitives GTF – $8e^-$ – scale factor
Pople STO-nG bs – shell sp – 3 primitives GTF – $2e^-$ – scale factor
standard Pople value for STO-nG is used when the scale factor value is 0
Oxygen – 2 shells
Pople STO-nG bs – shell s – 3 primitives GTF – $2e^-$ – scale factor
Pople STO-nG bs – shell sp – 3 primitives GTF – $6e^-$ – scale factor

Using this basis set we have:
3 shells for Mg -> s (1AO), sp (4AO), sp(4AO) => 9 AO for Mg atom in MgO
2 shells for O -> s (1AO), sp (4AO) => 5 AO for O in MgO
For a total of 14 AO.

Info on the BS in the .out file

```
$ cd MSSC2025/Basic/Day1/1_single_point_example
$ vi mgo_input.out
```

```
$ cd MSSC2025/Basic/Day1/3_second_block_basis_set
$ ls
1_MgO_bs  2_Si_bs
```



Other options

A set of pre-defined basis sets are available by using the keyword **BASISSET**. Note that when specifying this keyword, the **END** to close the GEOMETRY input section and the keywords **99 0** and **END** are no more necessary.

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

The shell charge may correspond to a neutral atom, as in this case, or to an ion (for MgO, Mg and O, or Mg^{++} and O^{--}), but the net charge in the cell must be zero, the cell must be neutral.

Remember:

- Basis for each element in the geometry ✓
- Balanced across species ✓
- End with 99 0 and END ✓

Where to look for BS

Reliable sources for ready-to-use basis sets in CRYSTAL format or easily convertible formats:

1. EMS Database (Stuttgart/Cologne)
   - Wide selection of Pseudopotentials for many elements.
2. Basis Set Exchange (BSE)
   - Modern, comprehensive database; export in various formats.
3. CRYSTAL Basis Set Library (CRYSTAL Solutions)
   - Official database with basis sets already in CRYSTAL format.

Deep dive: Method block

The third input section allows choice of Hamiltonian, of truncation criteria of Coulomb and exchange infinite sums, and of the type of run. All the choices of the third input block are **optional**, but the **END** keyword must be inserted in the input stream to close the section.

The simplest case:

```
END
```

, for 3D:

```
SHRINK
n n
END
```

corresponds to a **Hartree-Fock** energy calculation (default).

Anyway an Unrestricted Hartree-Fock Hamiltonian can be defined adding UHF.

```
UHF
END
```

For Density Functional Theory simulations the keyword **DFT** must be used followed by the chosen functional and the END keyword to close the DFT block.

```
DFT
B3LYP
END
END
```

```
DFT
B3LYP
END
SHRINK
n n
END
```

Hamiltonian

Summary of available Hamiltonian:

Single particle Hamiltonian		
RHF	Restricted Hartree Fock	(Default)
UHF	Unrestricted Hartree-Fock	
ROHF	Restricted Open Shell Hartree-Fock	
DFT	DFT Hamiltonian	
	SPIN spin-polarized solution	

DFT functionals

Some of the available functionals for DFT calculations are:

Global Hybrid functionals

Standalone keywords

B3PW	B3PW parameterization
B3LYP	B3LYP parameterization
PBE0	Adamo and Barone [5]
PBESOL0	Derived from PBE0
B1WC	see [25]
WC1LYP	see [60]
B97H	see [4, 101]
PBE0-13	see [42]
SOGGA11X	see [215]
mPW1PW91	see [6]
mPW1K	see [175]

Range-Separated Hybrid functionals

Short-range Corrected RSH functionals

HSE06	Screened-Coulonb PBE XC functi
HSESOL	Screened-Coulomb PBESOL XC
SC-BLYP	SC-RSH BLYP functional based

271]

Middle-range Corrected RSH functionals

HISS	MC based on PBE XC functional

Long-range Corrected RSH functionals

RSHXLDA	LC LDA XC functional [1, 151]
wB97	Chai/Head-Gordon LC functional
wB97X	Chai/Head-Gordon SC/LC functi
LC-wPBE	LC hybrid based on PBE XC fun
LC-wPBESOL	LC hybrid based on PBESOL XC
LC-wBLYP	LC hybrid based on BLYP XC fu

...

You can loook for a specific functional in the CRYSTAL manual.

Keywords to control the simulation

SHRINK

Defines how the Brillouin Zone is sampled with k-points.

rec	variable	value	meaning
			if the system is periodic insert II
•	*	IS	Shrinking factor in reciprocal space (Section 18.7, page 406)
		ISP	Shrinking factor for a denser k point net (Gilat net) in the evaluation of the Fermi energy and density matrix.

- **IS** → Pack–Monkhorst shrinking factor: controls the k-point grid used to diagonalize the Hamiltonian.
- **ISP** → Gilat shrinking factor: denser grid used to compute the density matrix and Fermi energy (important for metals).

In short: *SHRINK controls the accuracy vs. cost of reciprocal space integration.*

Keywords to control the simulation

TOLINTEG

The 5 ITOL parameters control the accuracy of the calculation of the bielectronic Coulomb and exchange integrals. 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.

	rec	variable	meaning
•	*	ITOL1	overlap threshold for Coulomb integrals- page 402 7
		ITOL2	penetration threshold for Coulomb integrals-page 403 7
		ITOL3	overlap threshold for HF exchange integrals-page 403 7
		ITOL4	pseudo-overlap (HF exchange series-page 403) 7
		ITOL5	pseudo-overlap (HF exchange series-page 403) 14

Keywords to control the simulation

TOLDEE

By default the SCF iterations stop when the change in the absolute value of the total energy is less than $1 \cdot 10^{-6}$ Ha, or the number of cycles exceeds 50. In geometry optimization the tolerance on total energy change is set to $1 \cdot 10^{-7}$ Ha by default. You can change it through TOLDEE.

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

Keywords to control the simulation

FMIXING

Can be used to facilitate the convergence of the SCF iteration. Represents the % of Hamiltonian matrix mixing. The Hamiltonian matrix (Fock/KS matrix) at cycle *i* is defined as :

(F_i matrix computed from the eigenvectors and density matrix of cycle *i*-1)

$$F'_i = (1 - p)\, F_i + p\, F'_{i-1}$$

IPMIX = *p* = 30 by default.

rec		variable	meaning	
•	*	IPMIX	percent of Fock/KS matrices mixing	30

Running a single-point calculation

```
$ cd MSSC2025/Basic/Day1/4_third_block_method
$ ls
1_HF  2_PBE  3_B3LYP  4_other_parameters
$ cd 4_other_parameters
$ ls
1_shrink  2_tolinteg  3_toldee  4_fmixing
```

```
$ runCRY23 input
```

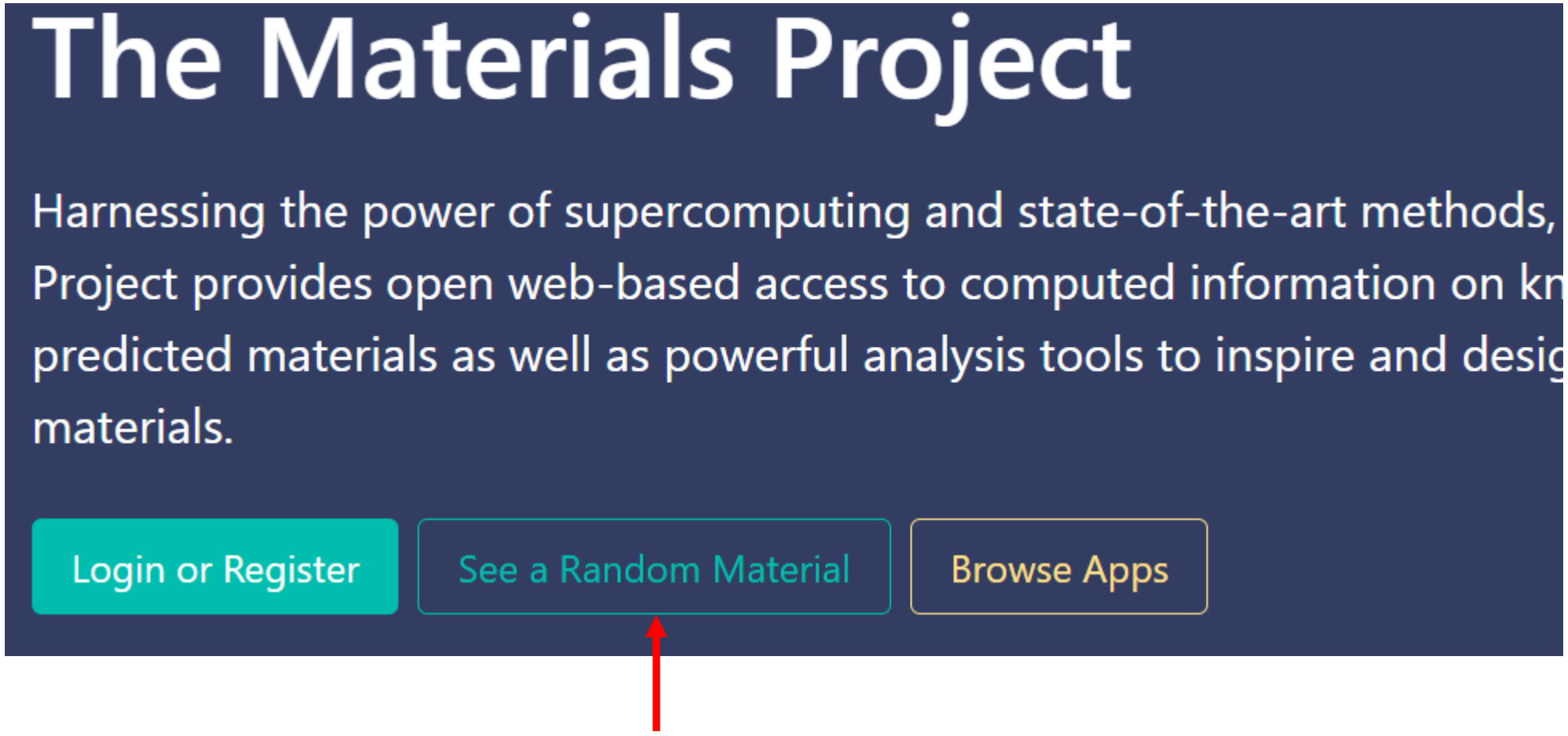
STOP	execution stops immediately	73
TESTPDIM	stop after symmetry analysis	129
TEST[RUN]	stop after integrals classification and disk storage estimate	130

Wrap-up

Take-home messages:

- Inputs in CRYSTAL are modular
- You need all 3 blocks to run a calculation (Geometry + Basis + Method)
- You can already run your first job!

DIY



Click here