Density Functional Theory:
Practical concepts &
Basic Tutorials with Quantum Espresso

Dr. Conor Hogan
Istituto di Struttura della Materia (ISM-CNR) and Dip. Fisica Univ. Roma "Tor Vergata"
conor.hogan@ism.cnr.it or conor.d.hogan@gmail.com Corridoio C0, C002 bis, x4894

quantum-ESPRESSO

QE is a powerful density functional theory code that uses planewaves and pseudopotentials.

A wide range of **Documentation** is available at

quantum-espresso.org

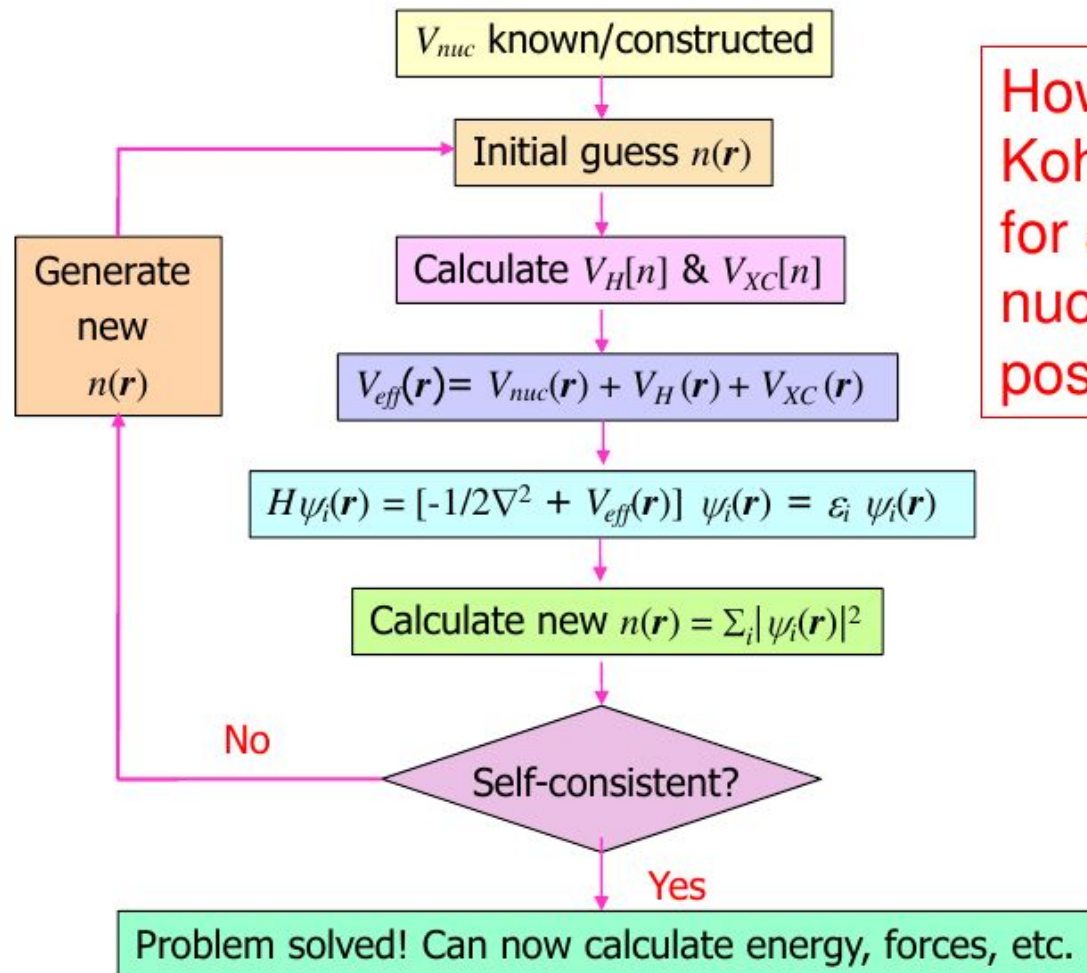including links to video lectures and tutorials, links to pseudopotentials and external PP databases, etc.

Input file variables are explained in quantum-espresso.org/Doc/INPUT_PW.html

also found in the distributed code in QEDIR/**Doc/INPUT_PW.txt**

Executables

 pw.x   main code

 pp.x   data analysis

 ph.x   phonons & electron-phonon coupling

 dos.x   density of states

 bands.x   plot band structure

 projwfc.x projection onto atomic orbitals

 pwcond.x transmittance

 cp.x   molecular dynamics

 more tools available:

 x-ray spectra, optics ,EELS, superconductivity,

 magnetic resonance (NMR) etc..

Self-consistent iterative solution of Kohn-Sham equations

V_{nuc} known/constructed

Initial guess $n(r)$

Calculate $V_H[n]$ & $V_{XC}[n]$

$V_{eff}(r) = V_{nuc}(r) + V_H(r) + V_{XC}(r)$

$H\psi_i(r) = [-1/2\nabla^2 + V_{eff}(r)]\ \psi_i(r) = \varepsilon_i\ \psi_i(r)$

Calculate new $n(r) = \Sigma_i |\psi_i(r)|^2$

Self-consistent?

Generate new $n(r)$

No

Yes

Problem solved! Can now calculate energy, forces, etc.

How to solve the Kohn-Sham eqns. for a set of fixed nuclear (ionic) positions.

Input file structure

```
&control
   calculation = 'scf'
   prefix = 'silicon',
   pseudo_dir = './'
   outdir = './',
/
&system
   ibrav=  2,
   celldm(1) =10.2,
   nat=  2,
   ntyp= 1,
   ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
 Si  28.086  Si.vbc.UPF
ATOMIC_POSITIONS {crystal}
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
2 2 2 0 0 0
```

NAMELIST
Variables in any order
If not given, default values are used

NAMELIST

The 3 NAMELISTS and INPUT_CARDS shown here are **always** present

NAMELIST

INPUT_CARD
Fixed format inside each INPUT_CARD

INPUT_CARD
Order of INPUT_CARDS is not crucial

INPUT_CARD

1. CONTROL namelist

```
&control
   calculation = 'scf'
   prefix = 'silicon',
   pseudo_dir = './'
   outdir = './',
/
&system
   ibrav=  2,
   celldm(1) =10.2,
   nat=  2,
   ntyp= 1,
   ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
 Si  28.086  Si.vbc.UPF
ATOMIC_POSITIONS {crystal}
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
2 2 2 0 0 0
```

- Used to specify what kind of calculation to be run: calculation = scf/relax/bands/nscf

- Location of pseudopotential, output, temporary directories

- Convergence parameters on forces and energies

- Controls writing of data to disk or memory

2. SYSTEM namelist

```
&control
   calculation = 'scf'
   prefix = 'silicon',
   pseudo_dir = './'
   outdir = './',
/
&system
   ibrav=  2,
   celldm(1) =10.2,
   nat=  2,
   ntyp= 1,
   ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
 Si  28.086  Si.vbc.UPF
ATOMIC_POSITIONS {crystal}
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
2 2 2 0 0 0
```

Define the periodic system:

- Bravais lattice

- Lattice parameters
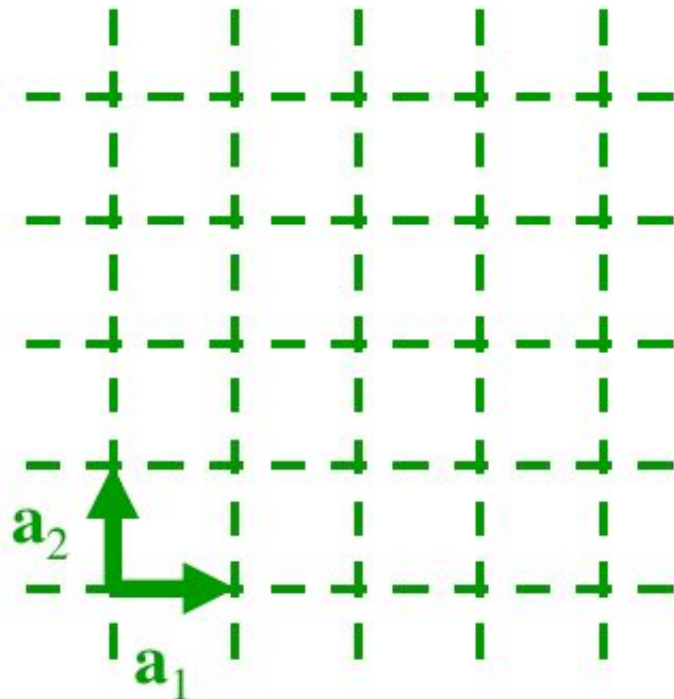
- Number of atoms

- Number of elements

- Expansion over planewaves

How to Specify the System

- All periodic systems can be specified by a Bravais Lattice and an atomic basis.
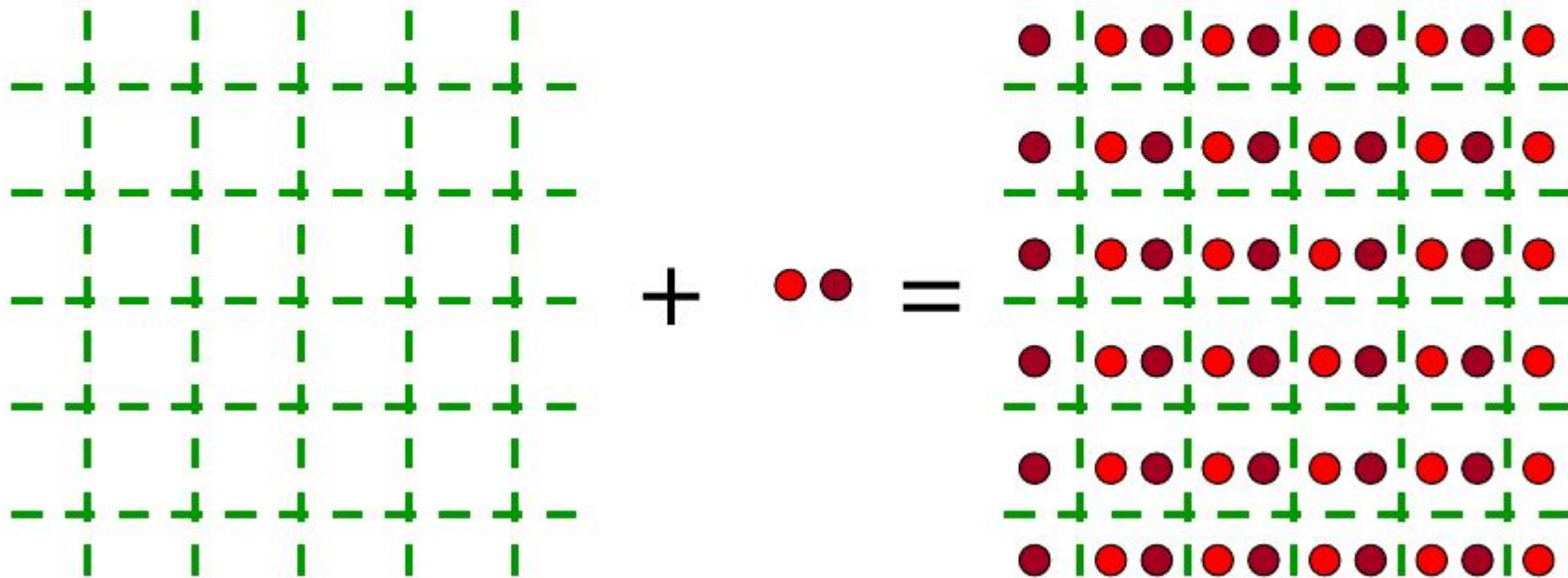
How to Specify the Bravais Lattice / Unit Cell

- Gives the type of Bravais lattice (SC, BCC, Hex, etc.)

Input parameters {**celldm(i)**}

- Give the lengths [& directions, if necessary] of the lattice vectors a_1, a_2, a_3

- Note that one can <u>choose</u> a non-primitive unit cell (e.g., 4 atom SC cell for FCC structure).

Bravais Lattices: ibrav flag

https://en.wikipedia.org/wiki/Bravais_lattice

ibrav =1,3,2

ibrav =6, 7

ibrav =8, 9, 10, 11

ibrav =4, 5, -5

ibrav =12, -12, 13

ibrav =14
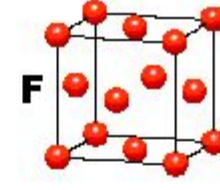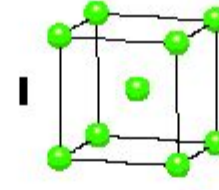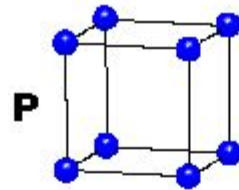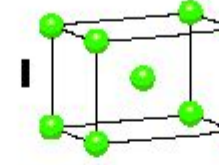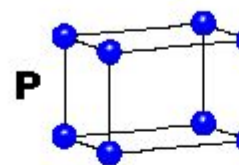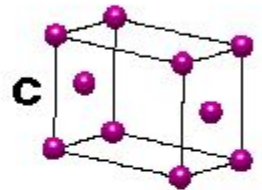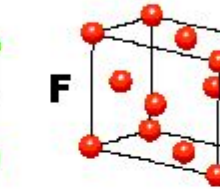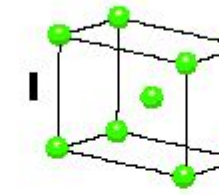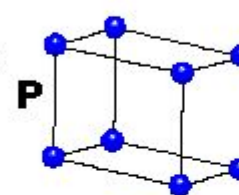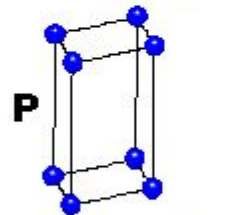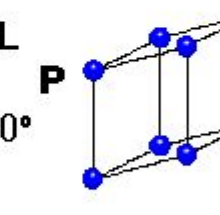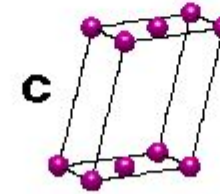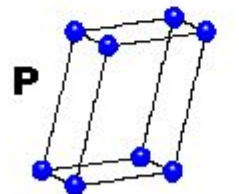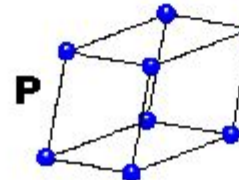
Atoms Within Unit Cell – How many, where?
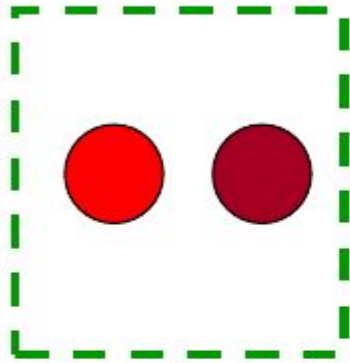
Input parameter **nat**

- Number of atoms in the unit cell

Input parameter **ntyp**

- Number of types of atoms

FIELD **ATOMIC_POSITIONS**

- Initial positions of atoms (may vary when "**relax**" done).
- Can choose to give in units of lattice vectors ("**crystal**") or in Cartesian units ("**alat**" or "**bohr**" or "**angstrom**")

Plane Waves & Periodic Systems

- For a periodic system:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} \sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i(\mathbf{k}+\mathbf{G})\bullet\mathbf{r}}$$

where $\mathbf{G}$ = reciprocal lattice vector

- The plane waves that appear in this expansion can be represented as a grid in k-space:
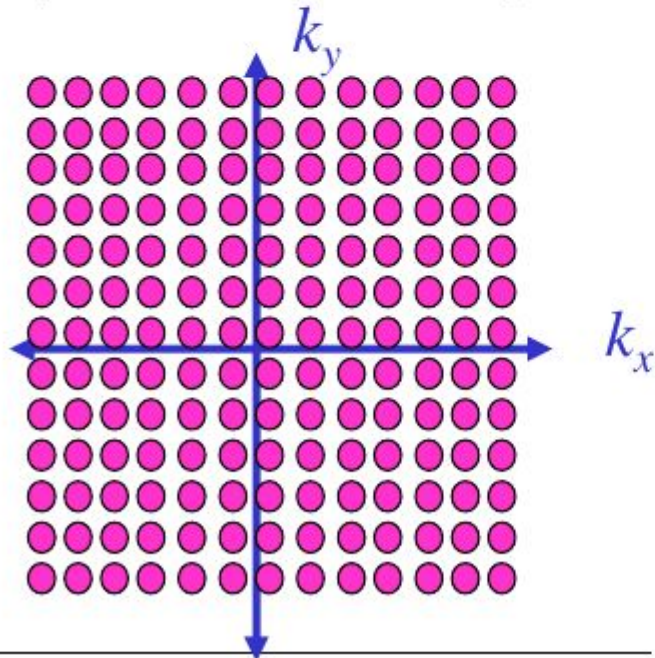
- Only true for periodic systems that grid is discrete.

- In principle, still need infinite number of plane waves.

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Truncating the Plane Wave Expansion

- In practice, the contribution from higher Fourier components (large $|\mathbf{k}+\mathbf{G}|$) is small.

- So truncate the expansion at some value of $|\mathbf{k}+\mathbf{G}|$.

- Traditional to express this cut-off in energy units:

$$\frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m} \leq E_{cut}$$

Input parameter **ecutwfc**

k_y

$E = E_{cut}$

k_x
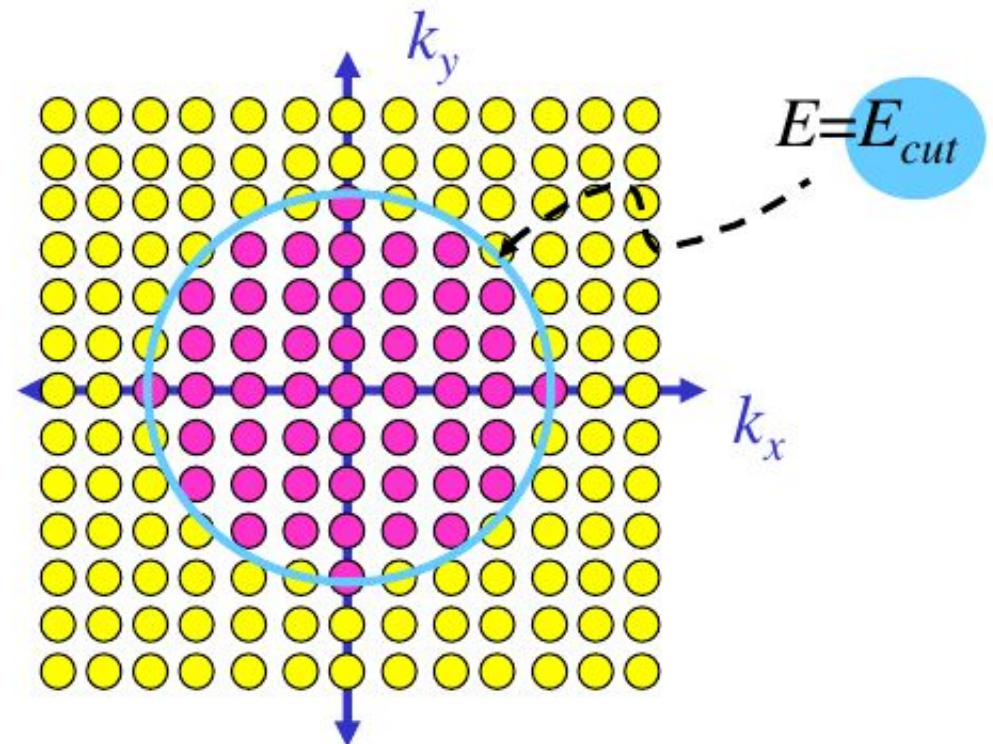
3. ELECTRONS namelist

```
&control
   calculation = 'scf'
   prefix = 'silicon',
   pseudo_dir = './'
   outdir = './',
/
&system
   ibrav=  2,
   celldm(1) =10.2,
   nat=  2,
   ntyp= 1,
   ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
 Si  28.086  Si.vbc.UPF
ATOMIC_POSITIONS {crystal}
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
2 2 2 0 0 0
```

Parameters that define the self consistent iterative solution

For typical use, the default parameters are sufficient

4. ATOMIC_SPECIES input card

```
&control
   calculation = 'scf'
   prefix = 'silicon',
   pseudo_dir = './'
   outdir = './',
/
&system
   ibrav=  2,
   celldm(1) =10.2,
   nat=  2,
   ntyp= 1,
   ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
 Si  28.086  Si.vbc.UPF
ATOMIC_POSITIONS {crystal}
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
2 2 2 0 0 0
```

- Element symbols

- Atomic weights (only used in molecular dynamics)

- Pseudopotentials...

PSEUDOPOTENTIALS

More about pseudopotentials

SSSP on Materials Cloud

Pseudo DoJo

ONCV Potentials

SCAN pseudopotentials

PSlibrary table

Original QE PP table

Hartwigesen-Goedecker-Hutter PP table

Old FHI PP table

PSLIBRARY

Ready-to-use pseudopotentials from PSlibrary (*recommended*). For other ready-to-use tables, follow the links of the menu at the left. For more info, see here.

Please cite the pseudopotentials used and give proper credit to their authors (see this page for a rather complete list of acknowledgments).

Pseudopotentials for Quantum-ESPRESSO

Name: **Oxygen**
Symbol: **O**
Atomic number: **8**
Atomic configuration: **[He] 2s2 2p4**
Atomic mass: **15.9994 (3)**

Available pseudopotentials:

O.blyp-mt.UPF (details)
  Becke-Lee-Yang-Parr (BLYP) exch-corr
  Martins-Troullier

O.pbe-rrkjus.UPF (details)
  Perdew-Burke-Ernzerhof (PBE) exch-corr
  Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

O.pbe-van_bm.UPF (details)
  Perdew-Burke-Ernzerhof (PBE) exch-corr
  Vanderbilt ultrasoft
        author: bm

O.pz-mt.UPF (details)
  Perdew-Zunger (LDA) exch-corr
  Martins-Troullier

O.pz-rrkjus.UPF (details)
  Perdew-Zunger (LDA) exch-corr
  Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

O.blyp-van_ak.UPF (details)
  Becke-Lee-Yang-Parr (BLYP) exch-corr
  Vanderbilt ultrasoft
        author: ak

Pseudopotential's name gives information about :

- type of exchange-correlation functional
- type of pseudopotential
- e.g.:

O.pbe-rrkjus.UPF (details)
  Perdew-Burke-Ernzerhof (PBE) exch-corr
  Rabe Rappe Kaxiras Joannopoulos (ultrasoft)

- We will use only norm-conserving pseudo types: mt, vbc, hgh, dojo

- NB: Use the same XC type for all elements!

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5. ATOMIC_POSITIONS input card

```
&control
   calculation = 'scf'
   prefix = 'silicon',
   pseudo_dir = './'
   outdir = './',
/
&system
   ibrav=  2,
   celldm(1) =10.2,
   nat=  2,
   ntyp= 1,
   ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
 Si  28.086  Si.vbc.UPF
ATOMIC_POSITIONS {crystal}
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
 2 2 2 0 0 0
```

Card: ATOMIC_POSITIONS { alat | bohr | angstrom | crystal | crystal_sg }

IF `calculation == 'bands' OR calculation == 'nscf'` :

> Specified atomic positions will be IGNORED and those from the previous scf calculation will be used instead !!!

ELSE

Syntax:

ATOMIC_POSITIONS { alat | bohr | angstrom | crystal | crystal_sg }
X(1)   x(1)   y(1)   z(1)   { if_pos(1)(1)   if_pos(2)(1)   if_pos(3)(1)   }
X(2)   x(2)   y(2)   z(2)   { if_pos(1)(2)   if_pos(2)(2)   if_pos(3)(2)   }
. . .
X(nat) x(nat) y(nat) z(nat) { if_pos(1)(nat) if_pos(2)(nat) if_pos(3)(nat) }

List of **nat** atoms in terms of some choice of units (see INPUT_PW.html)

The best choice depends on the system being studied, e.g. Angstrom for molecules, alat for slabs, crystal for bulk

6. K_POINTS input card

```
&control
   calculation = 'scf'
   prefix = 'silicon',
   pseudo_dir = './'
   outdir = './',
/
&system
   ibrav=  2,
   celldm(1) =10.2,
   nat=  2,
   ntyp= 1,
   ecutwfc = 12.0,
/
&electrons
/
ATOMIC_SPECIES
 Si  28.086  Si.vbc.UPF
ATOMIC_POSITIONS {crystal}
 Si 0.00 0.00 0.00
 Si 0.25 0.25 0.25
K_POINTS automatic
2 2 2 0 0 0
```

Possibilities are:

- Ask the code to generate a regularly spaced grid
- Specify a list of k-point coordinates by hand
- Use the gamma point only
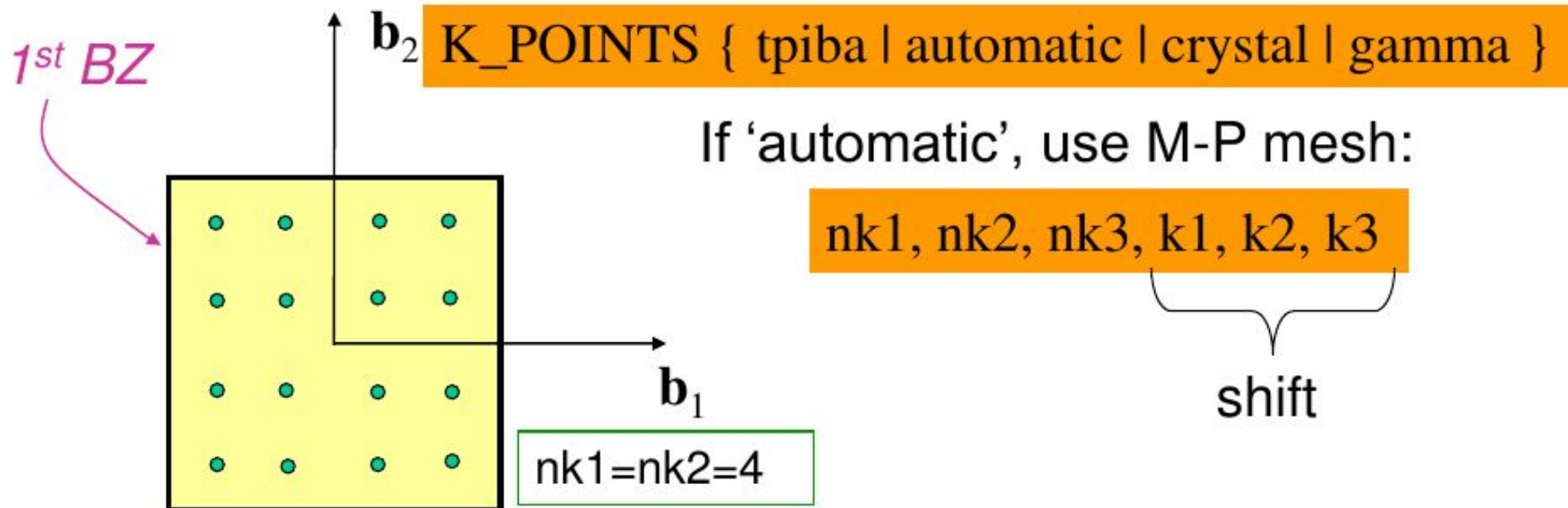
Types of k-point meshes

- **Special Points:** *[Chadi & Cohen]*
  Points designed to give quick convergence for particular crystal structures.
- **Monkhorst-Pack:**
  Equally spaced mesh in reciprocal space.
  May be centred on origin ['non-shifted'] or not ['shifted']

1st BZ

$\mathbf{b}_2$

K_POINTS { tpiba | automatic | crystal | gamma }

If 'automatic', use M-P mesh:

nk1, nk2, nk3, k1, k2, k3

shift

$\mathbf{b}_1$

nk1=nk2=4

Irreducible Brillouin Zone

- **IBZ** depends on symmetries of system.
- Can save computational time by using appropriately weighted k-points from IBZ alone.
- For 'automatic' k-points, code will 'reduce' to IBZ.
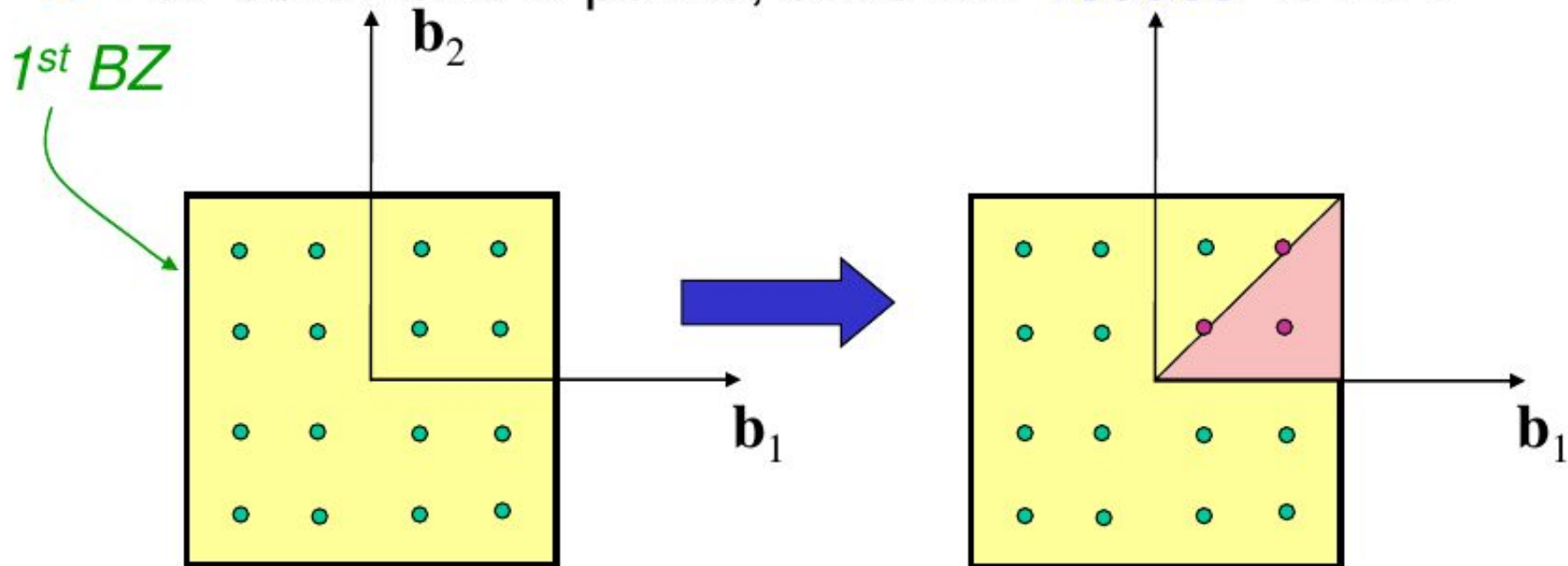
- May not want to maintain symmetries in relaxation/MD.

Input parameter `nosym`