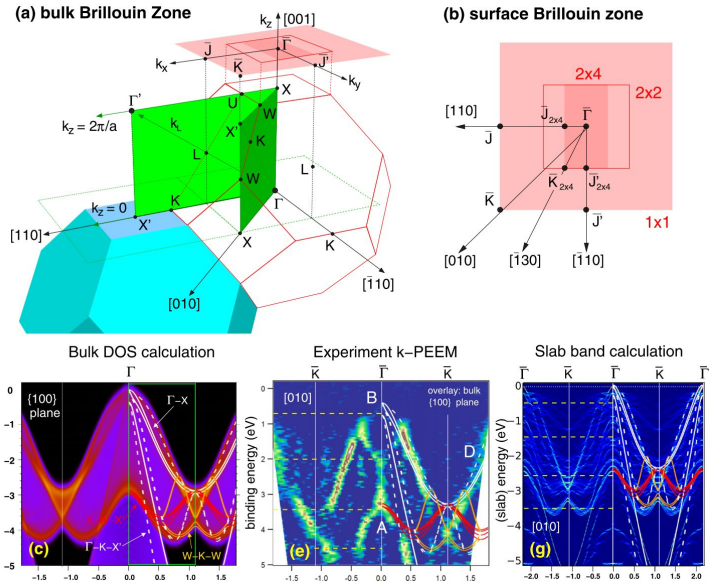

Density Functional Theory:
Part 2. Practical concepts & Basic Tutorials with Quantum Espresso

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Input file: Advanced topics

1. Metals and fractional occupations
2. Structural optimization
3. Low-dimensional systems
4. Spin polarization & magnetism (not examined here)

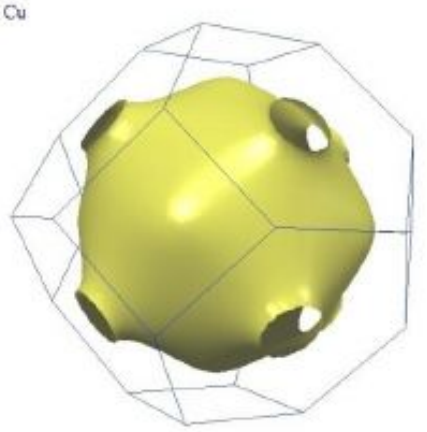
```
&CONTROL
 calculation  = "relax",
 etot_conv_thr = 1.0D-4
 forc_conv_thr = 1.0D-3
  prefix       = "CO",
  pseudo_dir   = "./",
/
&SYSTEM
 ibrav     = 0,
  nat  = 2, ntyp  = 2,
  nbnd  = 6,
  ecutwfc   = 50,
 nspin     = 2,
 starting_magnetization(1)=0.1
 occupations ='smearing',
 degauss     =0.001,
/
&ELECTRONS
/
&IONS
/
CELL_PARAMETERS {bohr}
 30.0    0.0     0.0
   0.0   12.0     0.0
   0.0     0.0   12.0
ATOMIC_SPECIES
O  1.00  O.pw-mt_fhi.UPF
C  1.00  C.pw-mt_fhi.UPF
ATOMIC_POSITIONS {bohr}
C  5.0  0.0  0.0   1 0 0
O  0.0  0.0  0.0   0 0 0
K_POINTS {Gamma}
```

1. Metals and fractional occupations

- Recall:

$$\langle P \rangle = \frac{\Omega}{(2\pi)^3} \sum_{n\ occ} \int_{BZ} P_n(\mathbf{k}) d^3k$$

- For metals, at T=0, this corresponds to (for highest band) an integral over all wave-vectors contained within the Fermi surface, i.e., for highest band, sharp discontinuity in k-space between occupied and unoccupied states…need many k-points to reproduce this accurately.
- Also can lead to scf convergence problems because of band-crossings above/below Fermi level.
- Solve by "smearing".



Fermi Surface of Cu
iramis.cea.fr

Smearing in Quantum-ESPRESSO

```
occupations 'smearing'
```

Instruction: use smearing

```
smearing 'gaussian'
         'methfessel-paxton'
         'marzari-vanderbilt'
         'fermi-dirac'
```

Type of smearing

```
degauss
```

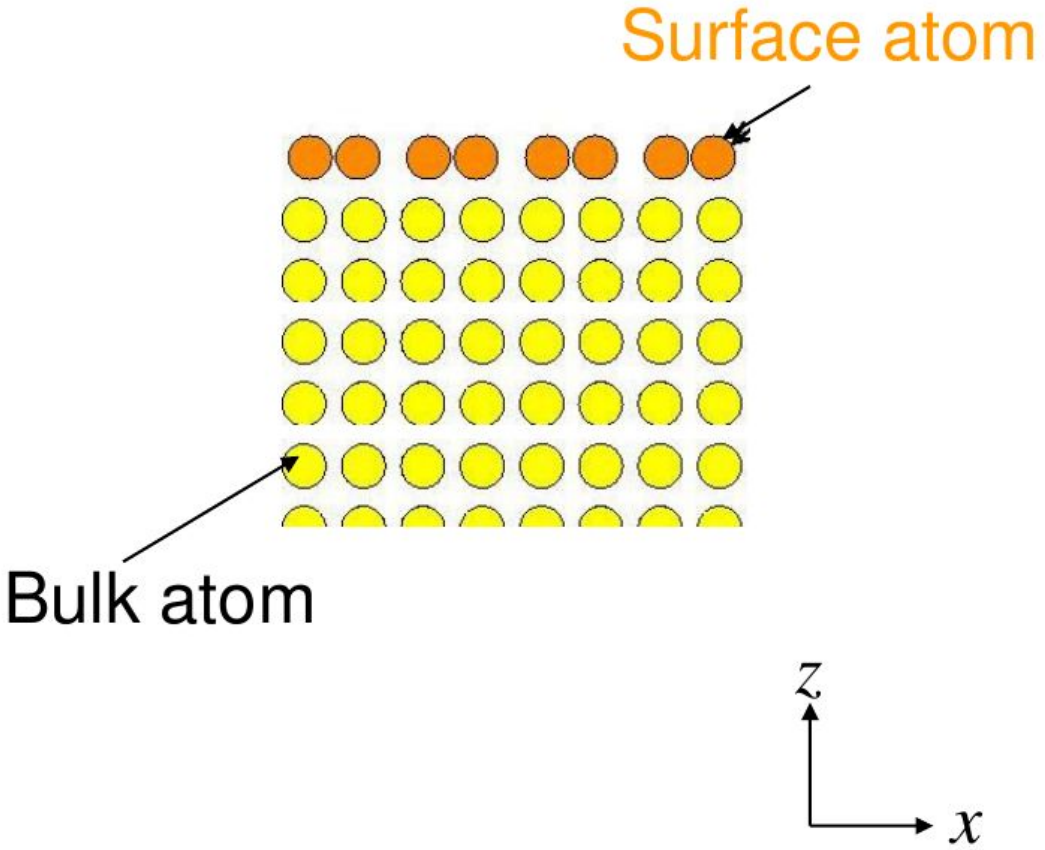
Smearing width

In Ry typical 0.01

Methfessel & Paxton, Phys. Rev. B 40, 3616 (1989).
Marzari & Vanderbilt, Phys Rev. Lett. 82, 3296 (1999).

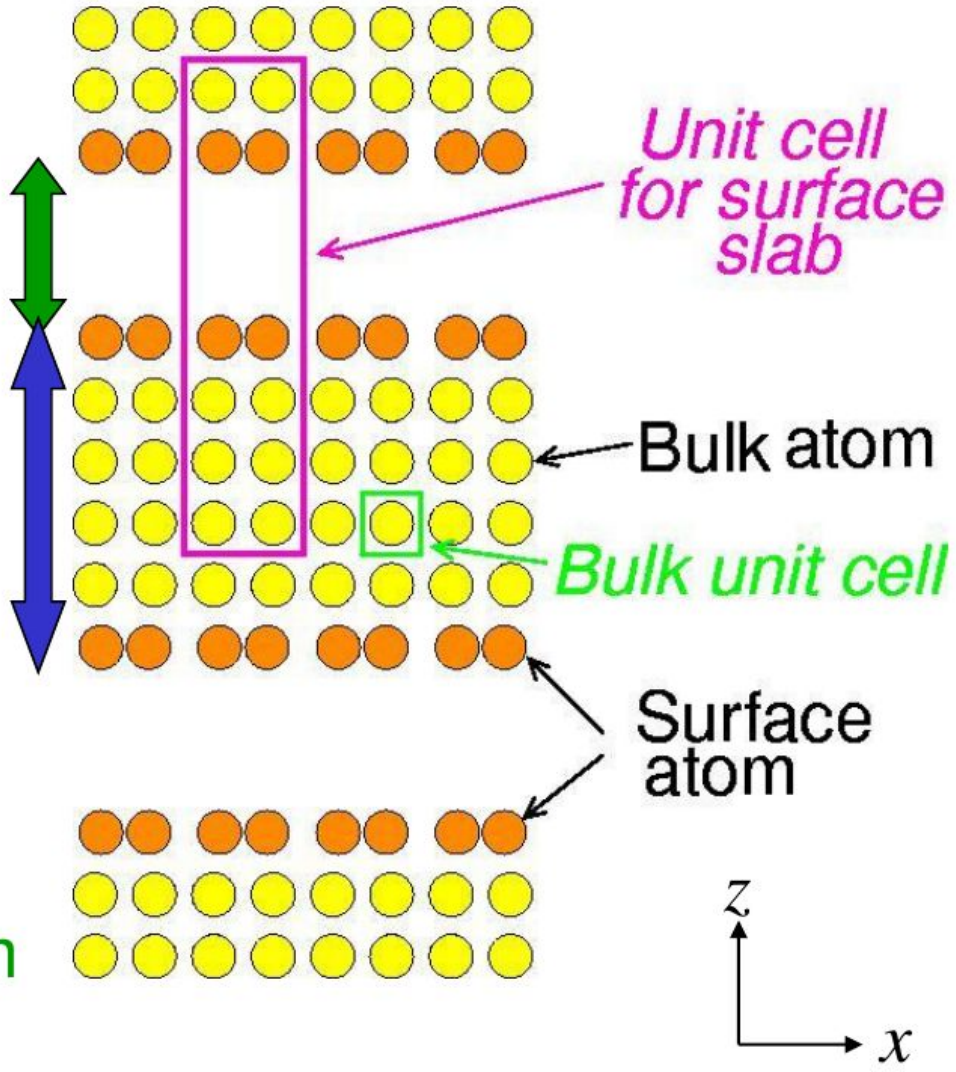
2 What if the system is not periodic?

- Example 1: Want to study properties of a system with a surface.
- Presence of surface $\Rightarrow$ No periodicity along z.



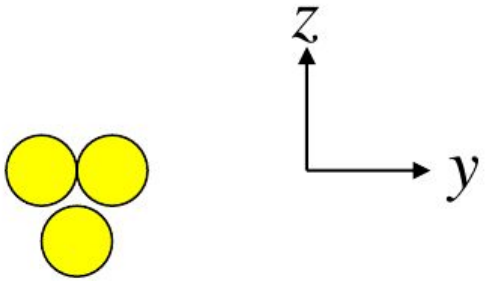
What if the system is not periodic?

- Example 1: Want to study properties of a system with a surface.
- Presence of surface $\Rightarrow$ No periodicity along z.
- Use a supercell: artificial periodicity along z by repeating slabs separated by vacuum.
- Have to check convergence w.r.t. slab thickness & vacuum thickness.



What if the system is not periodic?

- Example 2: Want to study properties of a nanowire.

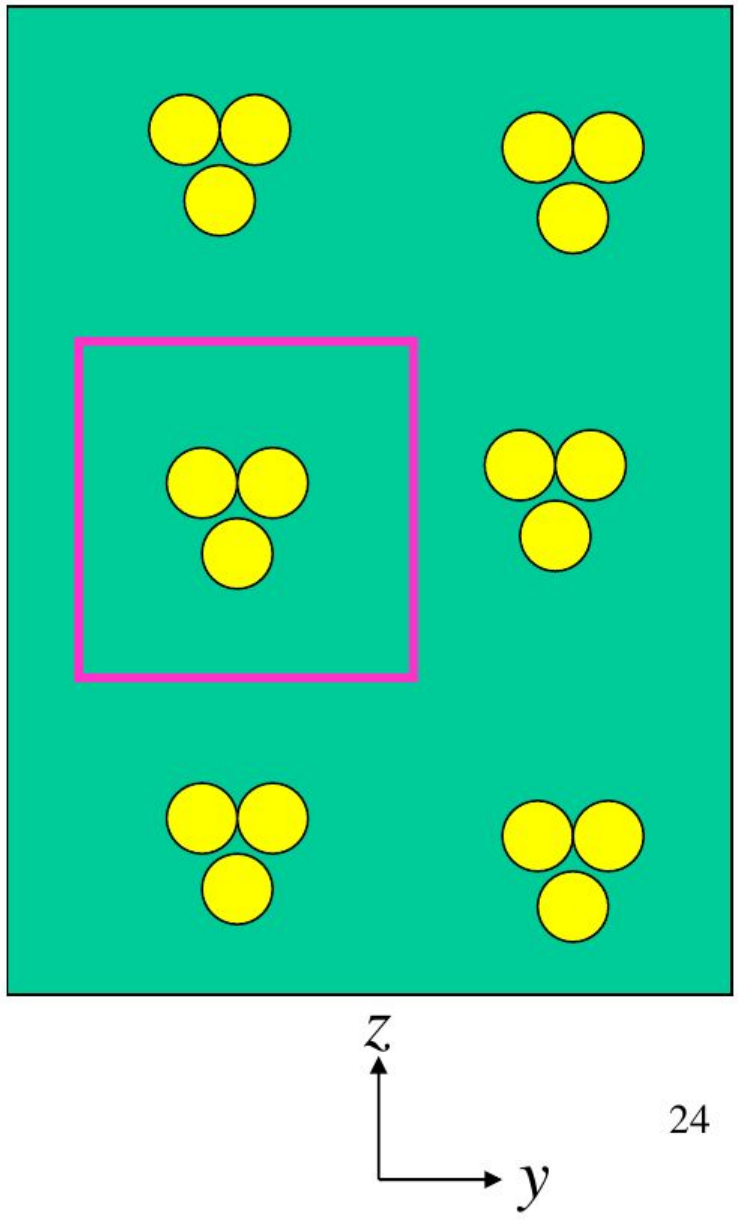


- Example 3: Want to study properties of a cluster

What if the system is not periodic?

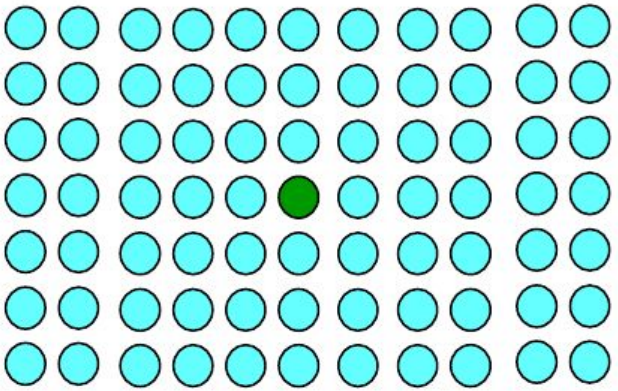
- Example 2: Want to study properties of a nanowire $\Rightarrow$ introduce artificial periodicity along y & z.

- Example 3: Want to study properties of a cluster $\Rightarrow$ introduce artificial periodicity along x, y & z.



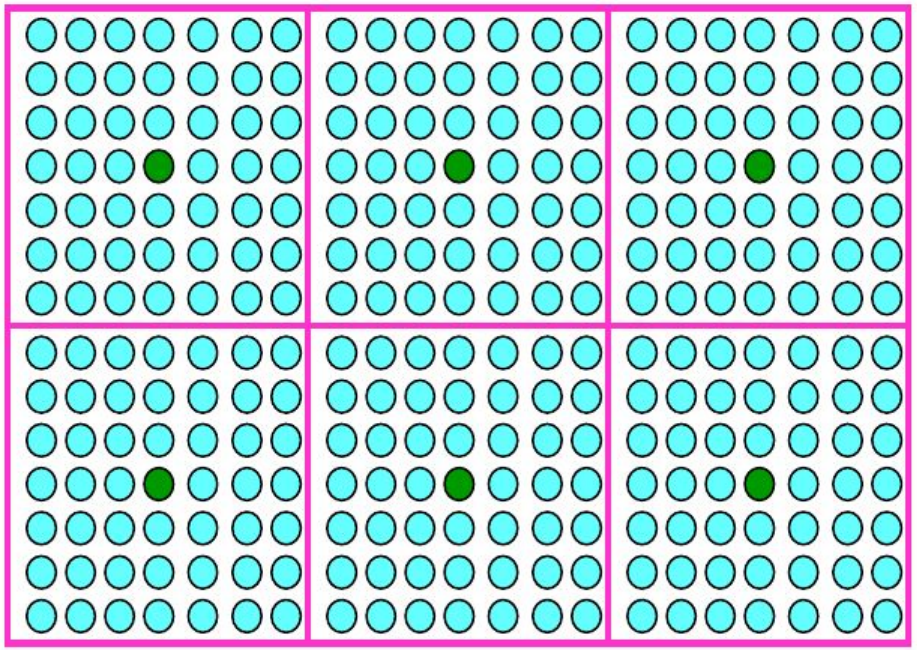
What if the system is not periodic?

- Example 4: Want to study a system with a defect, e.g., a vacancy or impurity:



What if the system is not periodic?

- Example 4: Want to study a system with a defect, e.g., a vacancy or impurity:



Artificially Periodic Systems ⇒ Large Unit Cells

- *Note*: In all these cases, to minimize the effects of the artificially introduced periodicity, need a large unit cell.

⇓

- Long $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ (primitive lattice vectors)

⇓

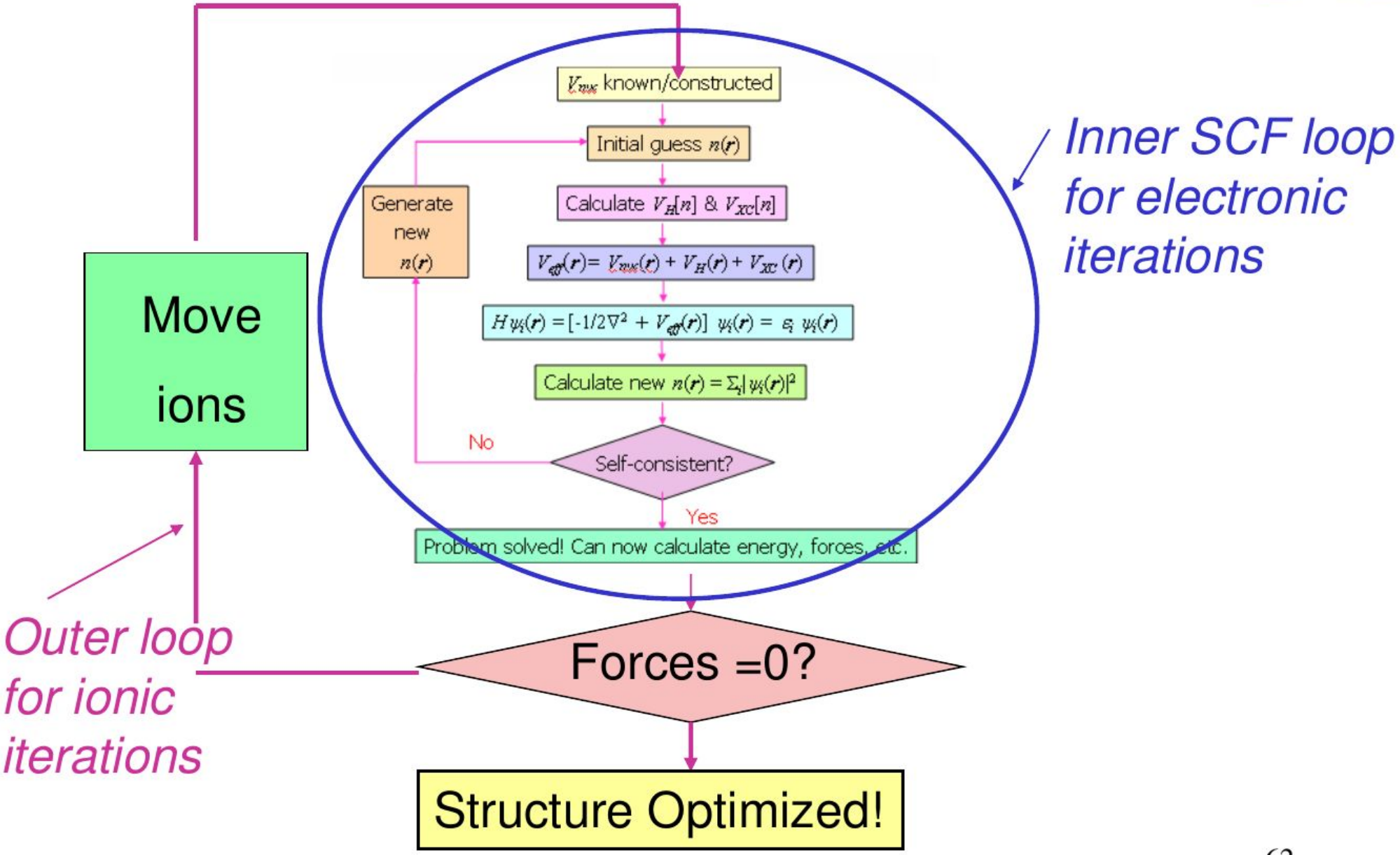
- Short $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ (primitive reciprocal lattice vectors)

⇓

- Many **G**'s will fall within E_{cut} sphere!

=> Many G-vectors (for the same cutoff)
=> Fewer k-points (2D grid, 1D grid, or Gamma point only)

3 An Outer Loop: Ionic Relaxation



Forces

- Need for geometry optimization and molecular dynamics.
- Could get as finite differences of total energy - too expensive!
- Use force (Hellmann-Feynman) theorem:

  - Want to calculate the force on ion I:

$$\mathbf{F}_I = -\frac{d}{d\mathbf{R}_I}\langle\Psi|H|\Psi\rangle$$

  - Get three terms:

$$\mathbf{F}_I = -\langle\Psi|\frac{\partial H}{\partial \mathbf{R}_I}|\Psi\rangle - \langle\frac{\partial\Psi}{\partial \mathbf{R}_I}|H|\Psi\rangle - \langle\Psi|H|\frac{\partial\Psi}{\partial \mathbf{R}_I}\rangle$$

When $|\Psi\rangle$ is an eigenstate, $H|\Psi\rangle = E|\Psi\rangle$

-Substitute this...

Forces (contd.)

- The force is now given by

$$\mathbf{F}_I = -\langle\Psi|\frac{\partial H}{\partial \mathbf{R}_I}|\Psi\rangle - E\langle\frac{\partial \Psi}{\partial \mathbf{R}_I}|\Psi\rangle - E\langle\Psi|\frac{\partial \Psi}{\partial \mathbf{R}_I}\rangle$$

$$= -\langle\Psi|\frac{\partial H}{\partial \mathbf{R}_I}|\Psi\rangle - E\frac{\partial}{\partial \mathbf{R}_I}\langle\Psi|\Psi\rangle$$

$\langle\Psi|\Psi\rangle \rightarrow 0$

- Note that we can now calculate the force from a calculation at ONE configuration alone – huge savings in time.
- If the basis depends upon ionic positions (not true for plane waves), would have extra terms = Pulay forces.
- $|\Psi\rangle$ should be exact eigenstate, i.e., scf well-converged!

Input parameter `tprnfor`

Geometry Optimization With Forces

- Especially useful for optimizing internal degrees of freedom, surface relaxation, etc.

```
calculation = 'relax'
```

- Choice of algorithms for ionic relaxation, e.g., steepest descent, BFGS.

```
NAMELIST &IONS
```

Input parameter `ion_dynamics`