The Kohn-Sham problem

- Want to solve the Kohn-Sham equations:

$$\underbrace{\left[-\frac{1}{2}\nabla^2 + V_{nuc}(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{XC}[n(\mathbf{r})]\right]}_{H}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})$$

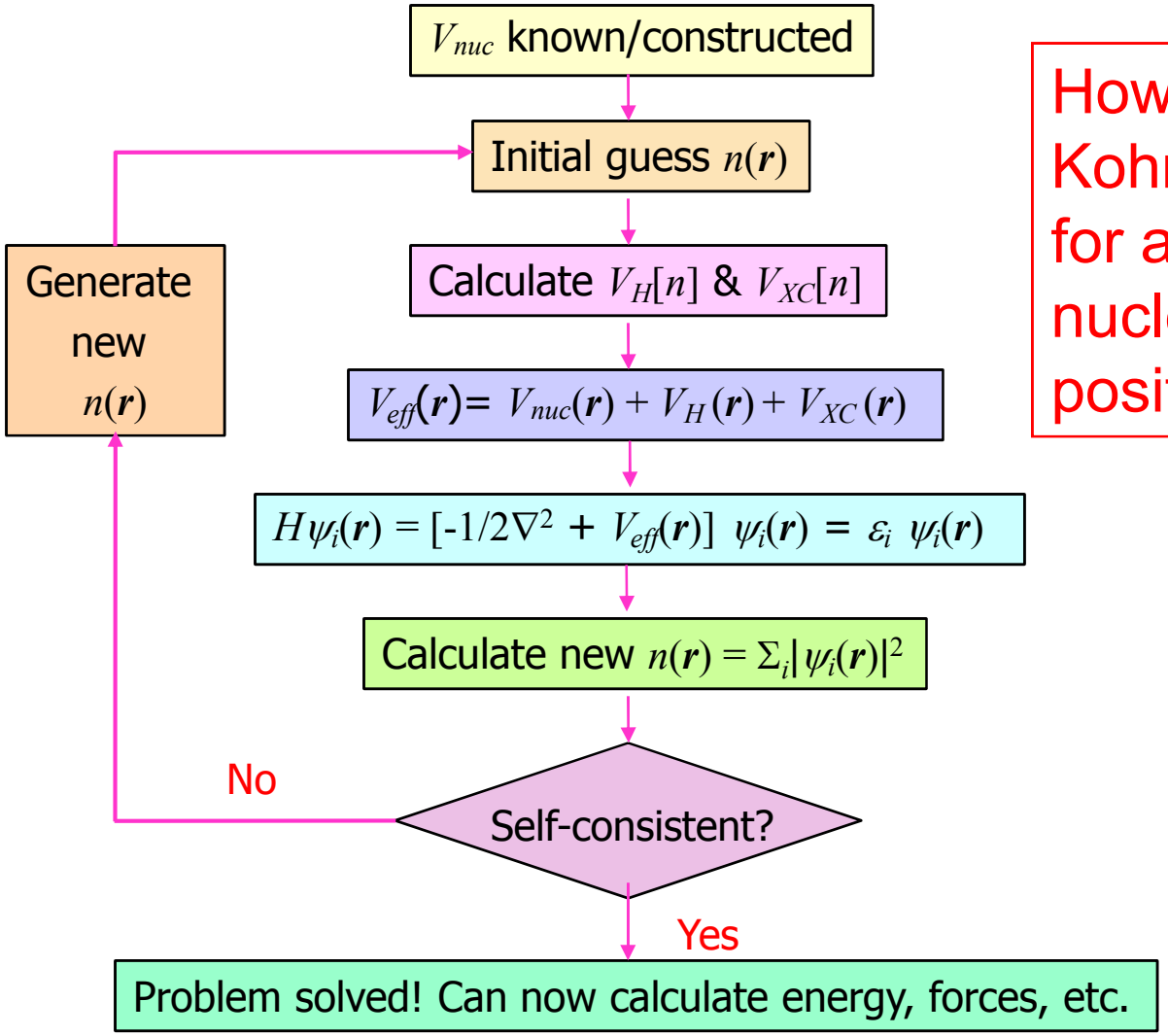
- Note that self-consistent solution necessary, as H depends on solution:

$$\{\psi_i\} \rightarrow n(r) \rightarrow H$$

- Convention:

$$e = \hbar = m_e = 1$$

Self-consistent Iterative Solution



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

Kohn-Sham Equations in a Basis

- Can choose to expand wavefunctions in a basis set:

$$\psi_i(\mathbf{r}) = \sum_{\alpha=1}^{N_b} c_{i\alpha} f_\alpha(\mathbf{r})$$

- Eigenvalue equation then becomes:

$$\Sigma_\beta \; H_{\alpha\beta} \; c_{i\beta} = \varepsilon_i \; c_{i\alpha}$$

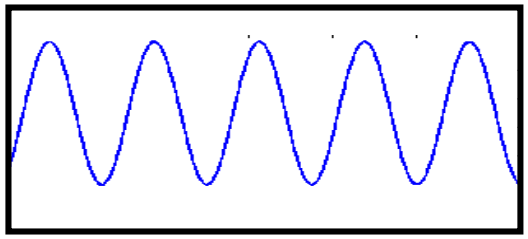
Matrix element *Eigenvalue* *Eigenvector*

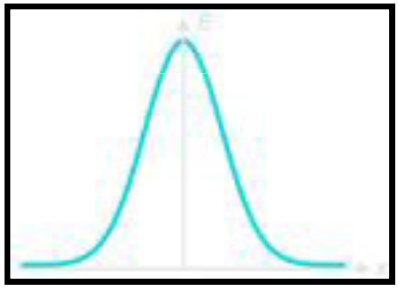
- Solving $\Leftrightarrow$ Have to diagonalize a matrix of size N_b x N_b

Size of basis

Some possible basis sets

- Various possible choices of basis:
  - Plane waves $e^{iK \bullet r}$
  - Localized sets:
    e.g., Gaussians
  - Mixed basis





- Choose so that calculation is fast, accurate, convenient.
- Would like N_b to be small?
- Would like form of $\mathbf{f}_\alpha(\mathbf{r})$ to be simple?

Advantages of a Plane Wave Basis

- Simple: Easy to take derivatives, etc.$\Rightarrow$ Coding is easy!
- Orthonormal: No overlap integrals.
- Independent of atomic positions $\Rightarrow$ No "Pulay forces"; easy to calculate forces for structural relaxation & molecular dynamics.
- Unbiased: No assumption about where charge concentrated. (But $\therefore$ also wasteful?)

- Easy to control convergence w.r.t. size of basis: only one parameter $E_{cut.}$
- Can take advantage of FFT's : r-space $\leftrightarrow$ k-space

Disadvantages of a Plane Wave Basis

- The set of plane waves is discrete only if the system is periodic!

  (Will discuss…solution = introduction of artificial supercell or periodic approximant.)

- Recall:

  - for free electrons, wavefunction = plane wave.

  - for nearly free electrons, wavefunction = superposition of small number of plane waves.

  - for tightly bound electrons, need a HUGE number of plane waves to get an adequate expansion, i.e., N_b very large!

  (Will discuss…solution = introduction of pseudopotentials.)

- Sometimes interpretation harder.

Periodic Systems & Bloch's Theorem

- For a periodic system, recall Bloch's Theorem:

$$\psi_{\mathbf{k}}(r) = e^{i\mathbf{k}\bullet\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$$

- $u_{\mathbf{k}}(\mathbf{r})$ has the periodicity of the system, i.e.,

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}),$$ where $\mathbf{R}$ = lattice vector

- As for all lattice-periodic functions, only certain plane waves will appear in the Fourier expansion of $u_{\mathbf{k}}(\mathbf{r})$:

$$u_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega}\sum_{\mathbf{G}} c_{\mathbf{k},\mathbf{G}} e^{i\mathbf{G}\bullet\mathbf{r}}$$ where $\mathbf{G}$ = reciprocal lattice vector

using plane waves

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{n\mathbf{k}}(\mathbf{G}) \mathrm{e}^{i\mathbf{G}\cdot\mathbf{r}}$$

$$-\nabla^2 \psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto |\mathbf{k}+\mathbf{G}|^2 c_{n\mathbf{k}}(\mathbf{G})$$

$$V(\mathbf{r})\psi_{n\mathbf{k}}(\mathbf{r}) \longmapsto \frac{1}{\Omega} \int \mathrm{e}^{-i\mathbf{G}\cdot\mathbf{r}} V(\mathbf{r}) u_{n\mathbf{k}}(\mathbf{r}) d\mathbf{r}$$

$$\rho(\mathbf{r}) = \sum_{v\mathbf{k}} |u_{v\mathbf{k}}(\mathbf{r})|^2$$

$$\begin{aligned} V_{xc}(\mathbf{r}) &= \mu_{xc}\big(\rho(\mathbf{r})\big) \\ V_H(\mathbf{r}) &= e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' \\ &= e^2 \sum_{\mathbf{G}\neq 0} \mathrm{e}^{i\mathbf{G}\cdot\mathbf{r}} \frac{4\pi}{G^2} \tilde{\rho}(\mathbf{G}) \end{aligned}$$

the fast Fourier transform

$$\tilde{f}_k = \sum_{l=0}^{N-1} f_l \mathrm{e}^{-2\pi i \frac{lk}{N}} \qquad \mathcal{O}\left(N^2\right) \text{ ops}$$

$$= \sum_{l=0}^{N/2-1} f_{2l} \mathrm{e}^{-2\pi i \frac{2lk}{N}} + \sum_{l=0}^{N/2-1} f_{2l+1} \mathrm{e}^{-2\pi i \frac{(2l+1)k}{N}}$$

$$= \sum_{l=0}^{N/2-1} f_{2l} \mathrm{e}^{-2\pi i \frac{lk}{N/2}} + \mathrm{e}^{-2\pi i \frac{k}{N}} \sum_{l=0}^{N/2-1} f_{2l+1} \mathrm{e}^{-2\pi i \frac{lk}{N/2}}$$

$$\mathcal{O}\left(N^2\right) \longrightarrow \mathcal{O}\left(N \log(N)\right)$$

for k≤N/2-1, this is the linear combination of two FFTs of order N/2

for k≥N/2, use:

$$\begin{aligned} \tfrac{N}{2} \tilde{f}_{k+\frac{N}{2}} &= \tfrac{N}{2} \tilde{f}_k \\ \mathrm{e}^{-2\pi i \frac{k+N/2}{N}} &= -\mathrm{e}^{-2\pi i \frac{k}{N}} \end{aligned}$$

multivariate FFTs (II)

$$F(k,l,m) = \sum_{pqs} \mathrm{e}^{i2\pi \frac{pk+ql+sm}{N}} \tilde{F}(p,q,s)$$

$$= \underbrace{\sum_{p} \mathrm{e}^{i2\pi \frac{pk}{N}} \underbrace{\sum_{q} \mathrm{e}^{i2\pi \frac{ql}{N}} \underbrace{\sum_{s} \mathrm{e}^{i2\pi \frac{sm}{N}} \tilde{F}(p,q,s)}_{N^2 \ \mathrm{FFT}(N)}}_{N^2 \ \mathrm{FFT}(N)}}_{N^2 \ \mathrm{FFT}(N)}$$

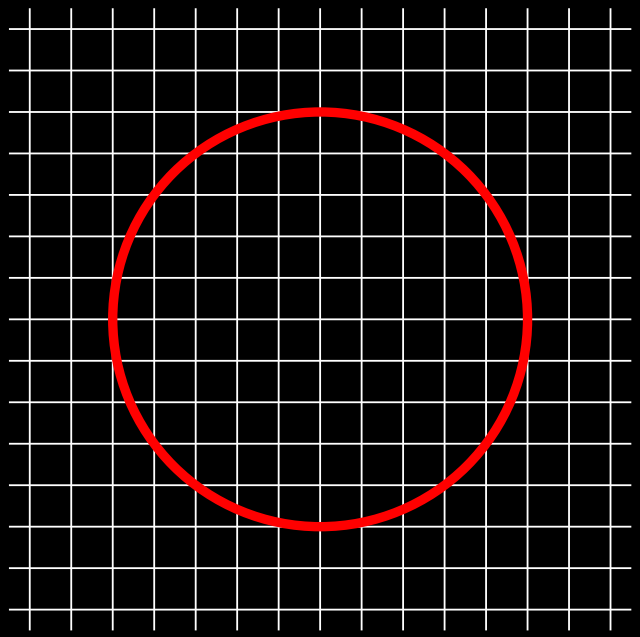
$$3N^2 \times N \log N = N^3 \log\left(N^3\right)$$

solving the Poisson equation

$$\Delta V(\mathbf{r}) = 4\pi\rho(\mathbf{r})$$

$$V(\mathbf{r}) = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}'$$

$$\tilde{V}(\mathbf{G}) = \frac{4\pi}{G^2}\tilde{\rho}(\mathbf{G}) \qquad \tilde{V}(\mathbf{G}=0) = 0$$



$$\rho(\mathbf{r}) \rightarrow \tilde{\rho}(\mathbf{G})$$

$$\mathbf{G}_{max} \sim \frac{2\pi}{h}$$

$$h \lesssim \frac{2\pi}{G_{max}}$$

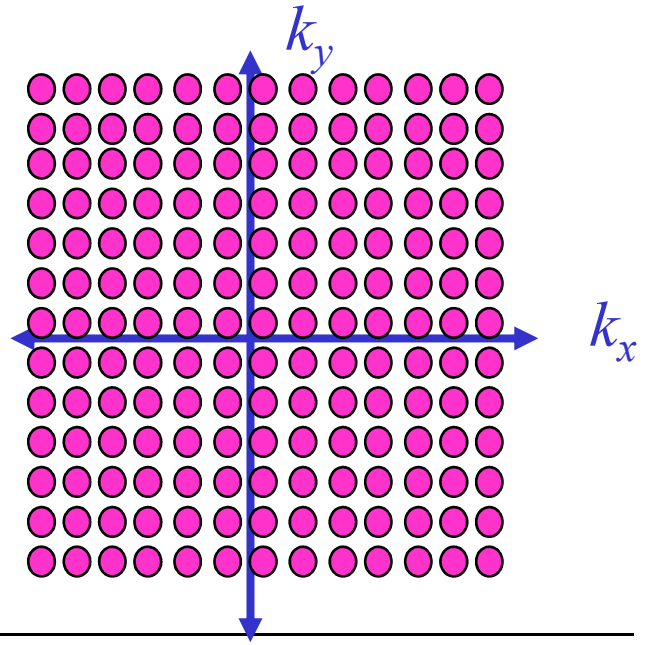
Plane Waves & Periodic Systems

- 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 **G** = reciprocal lattice vector

- The plane waves that appear in this expansion can be represented as a grid in k-space:



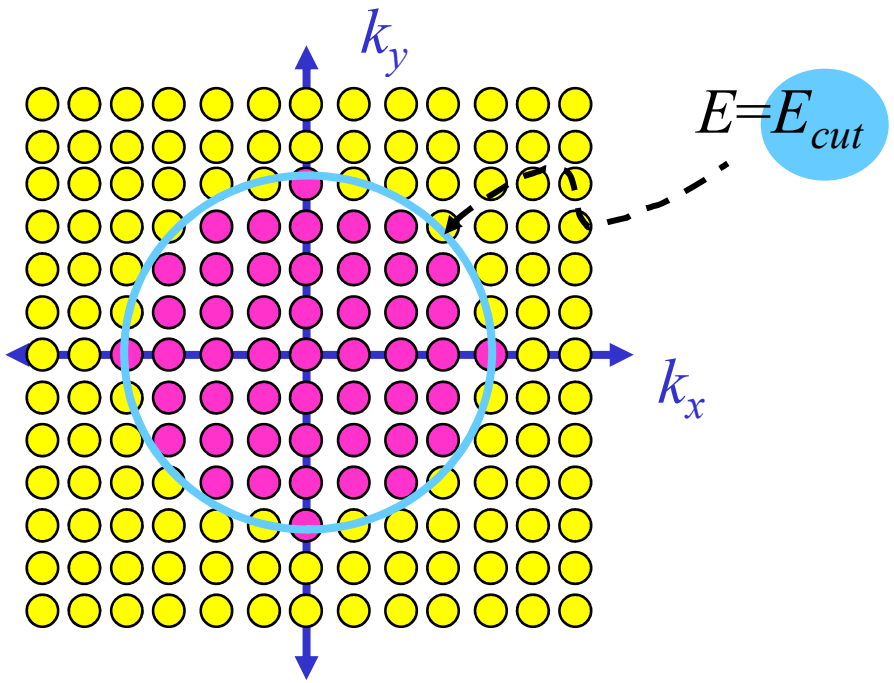
- Only true for periodic systems that grid is discrete.
- In principle, still need infinite number of plane waves.

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:

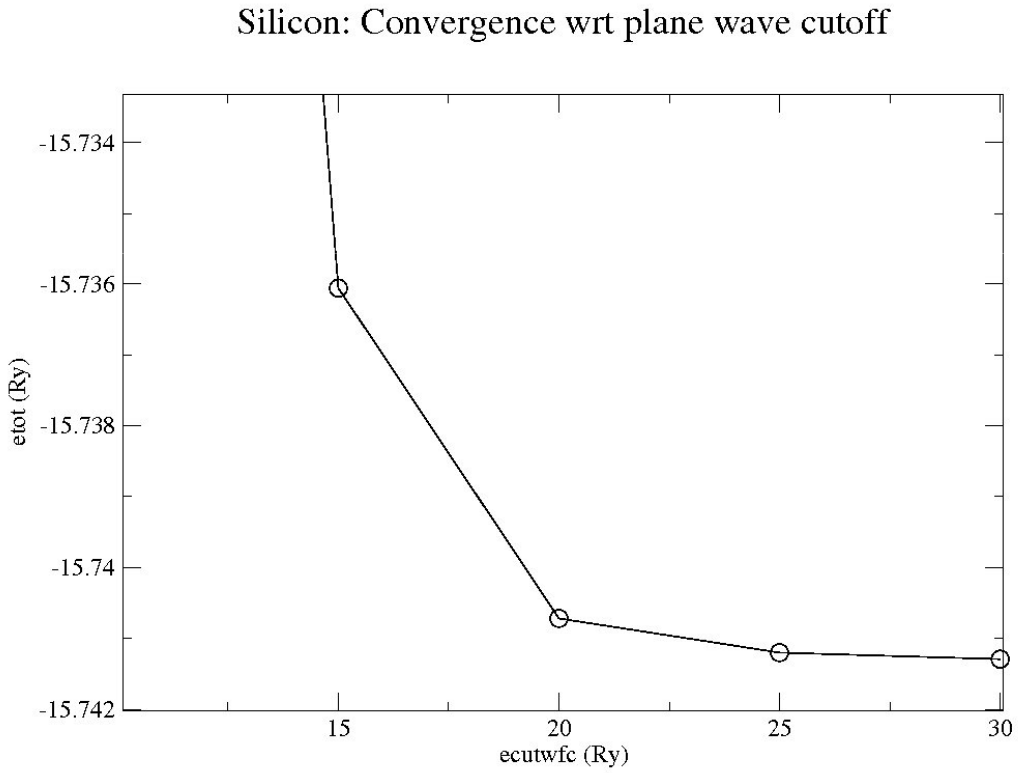
$$\frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m} \leq E_{cut}$$

Input parameter **`ecutwfc`**



Checking Convergence wrt ecutwfc

- Must always check.
- Monotonic (variational).

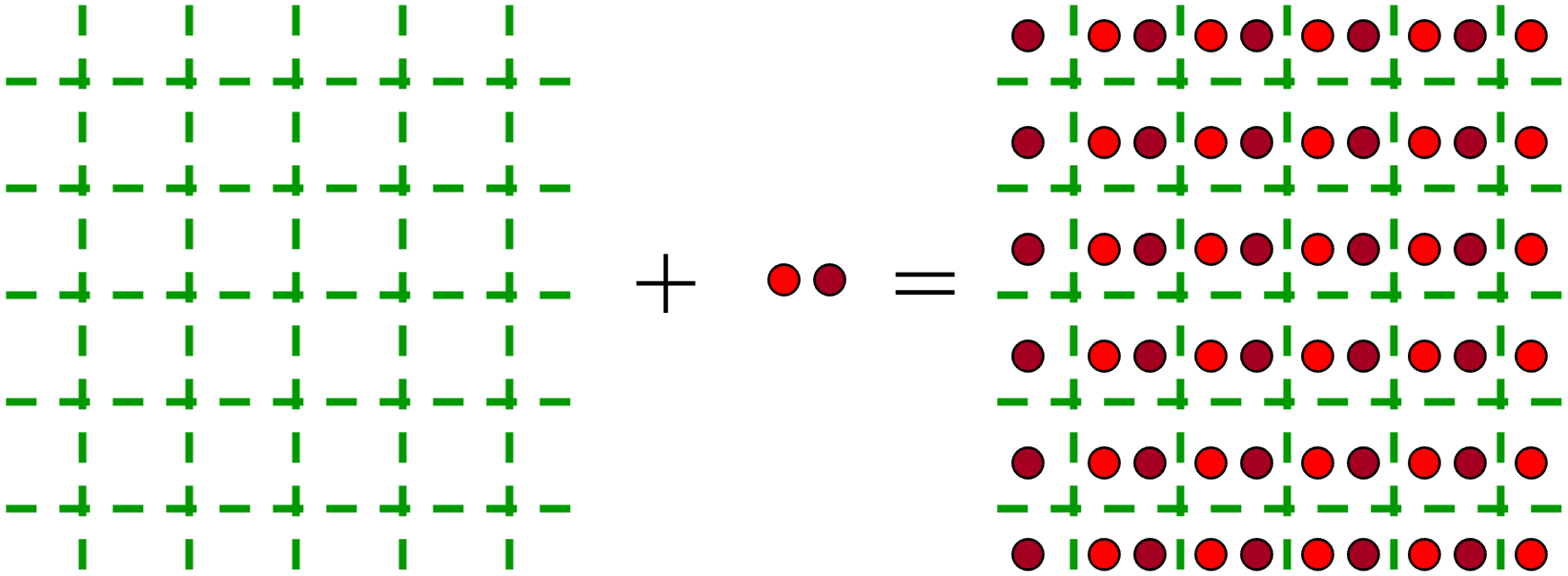


Step 0:
Defining the (periodic) system

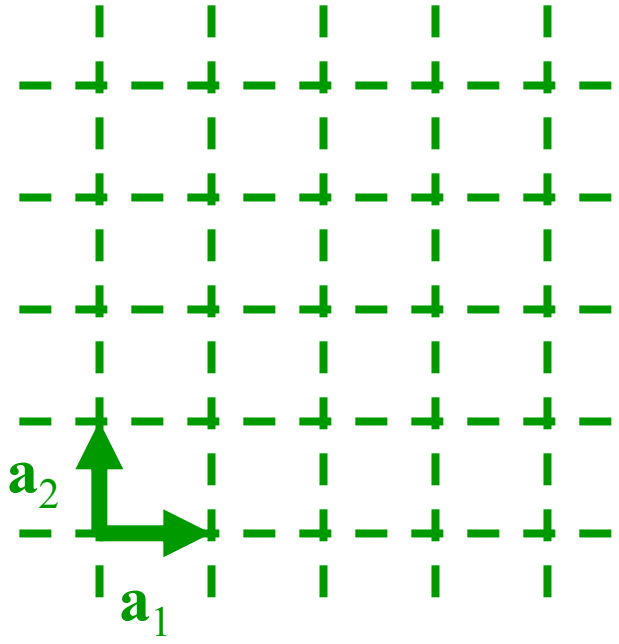
Namelist '**SYSTEM**'

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



Input parameter **`ibrav`**

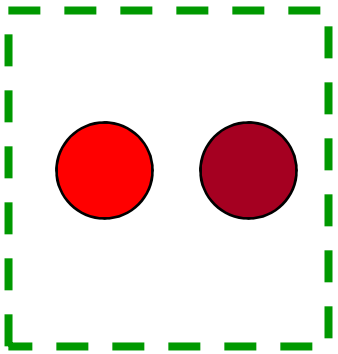
- Gives the type of Bravais lattice (SC, BCC, Hex, etc.)

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

- Give the lengths [& directions, if necessary] of the lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$

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

Atoms Within Unit Cell – How many, where?



Input parameter **`nat`**

- Number of atoms in the unit cell

Input parameter **`ntyp`**

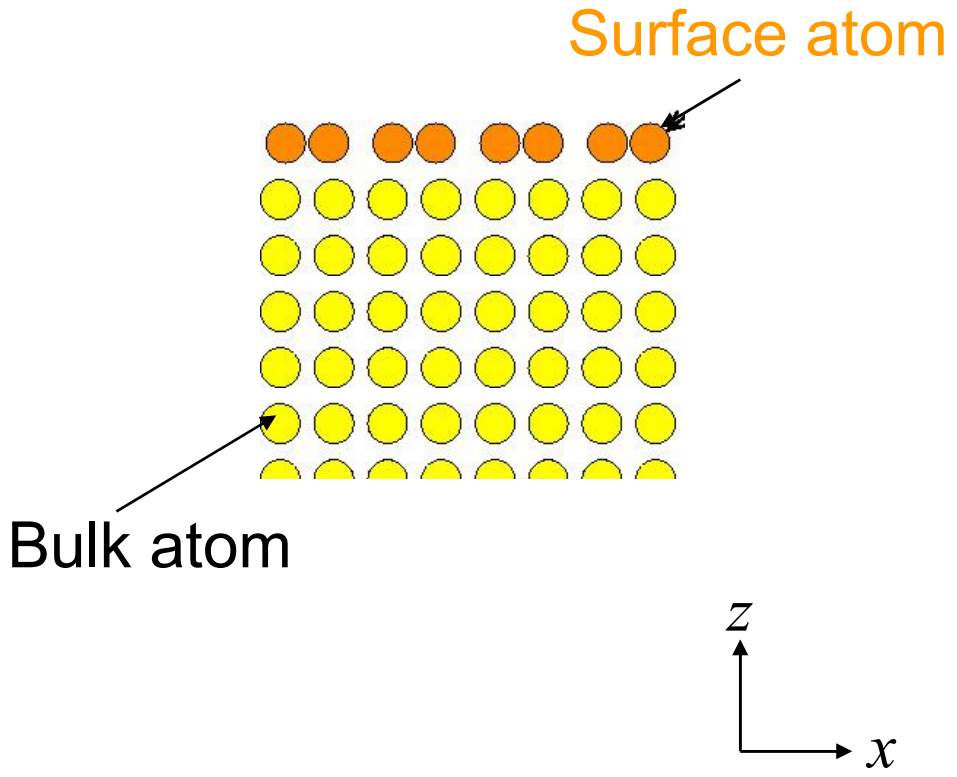
- Number of types of atoms

Card: **`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`**")

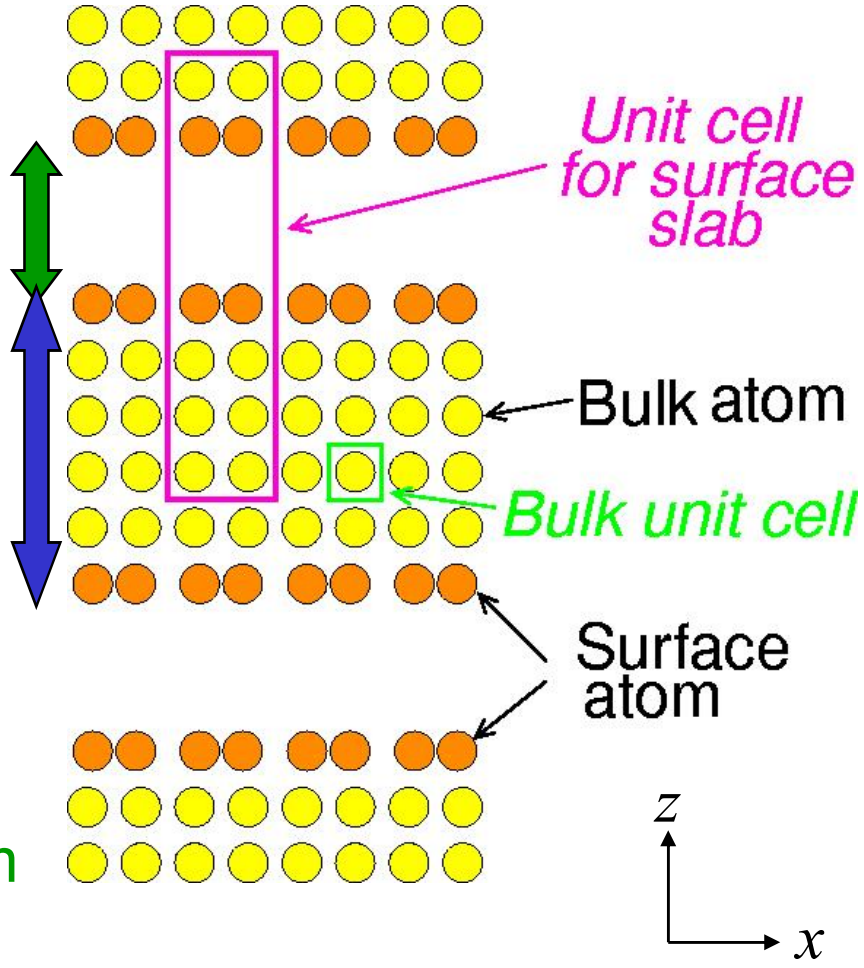
What if the system is not periodic?

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



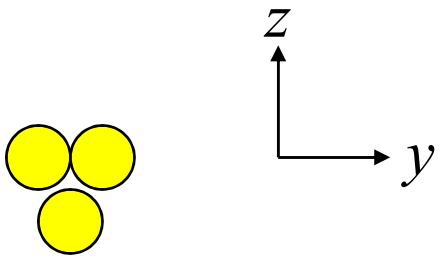
What if the system is not periodic?

- Example 1: Want to study properties of a system with a surface.
- Presence of surface ⇒ 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.

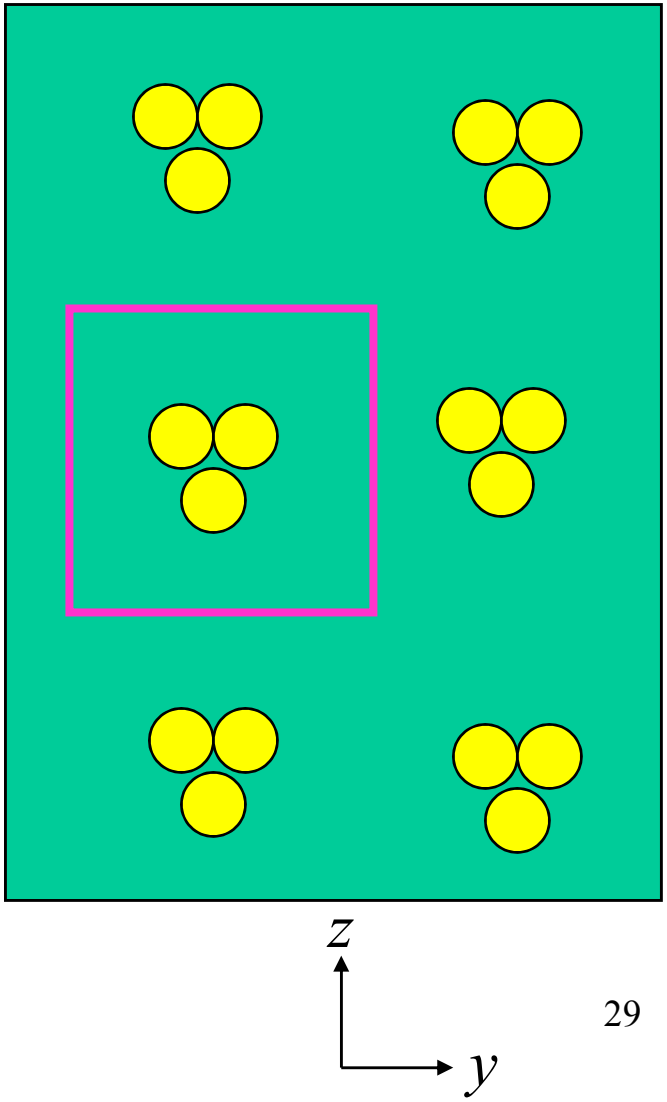


- Example 3: Want to study properties of a cluster

What if the system is not periodic?

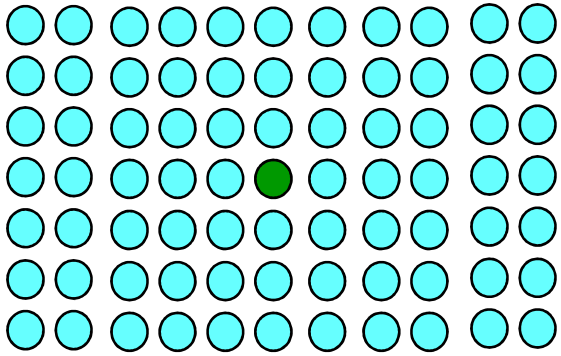
- Example 2: Want to study properties of a nanowire $\Rightarrow$ introduce artificial periodicity along y & z.

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



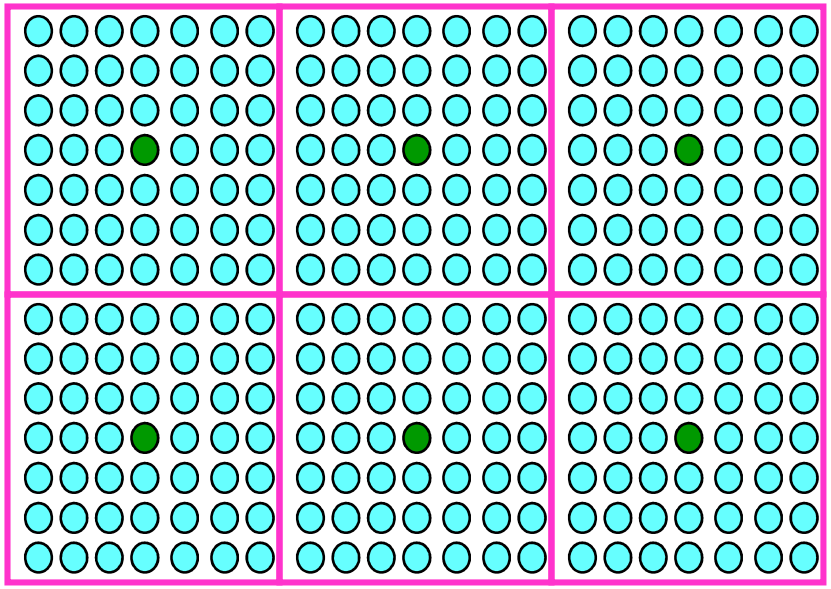
What if the system is not periodic?

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



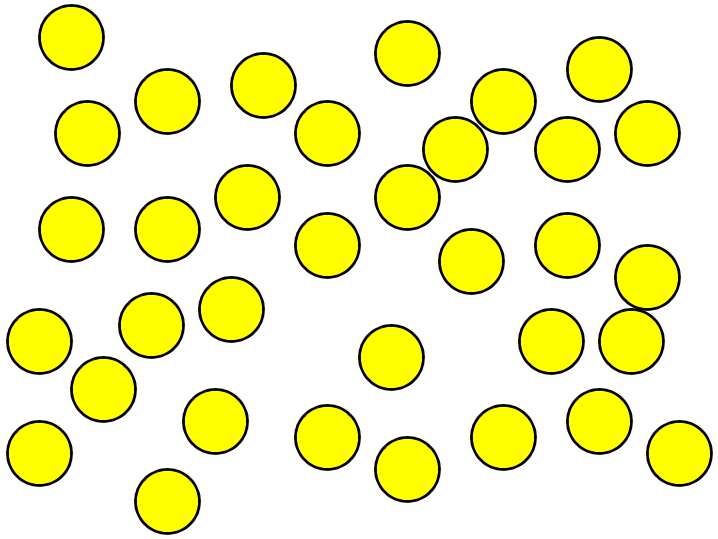
What if the system is not periodic?

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



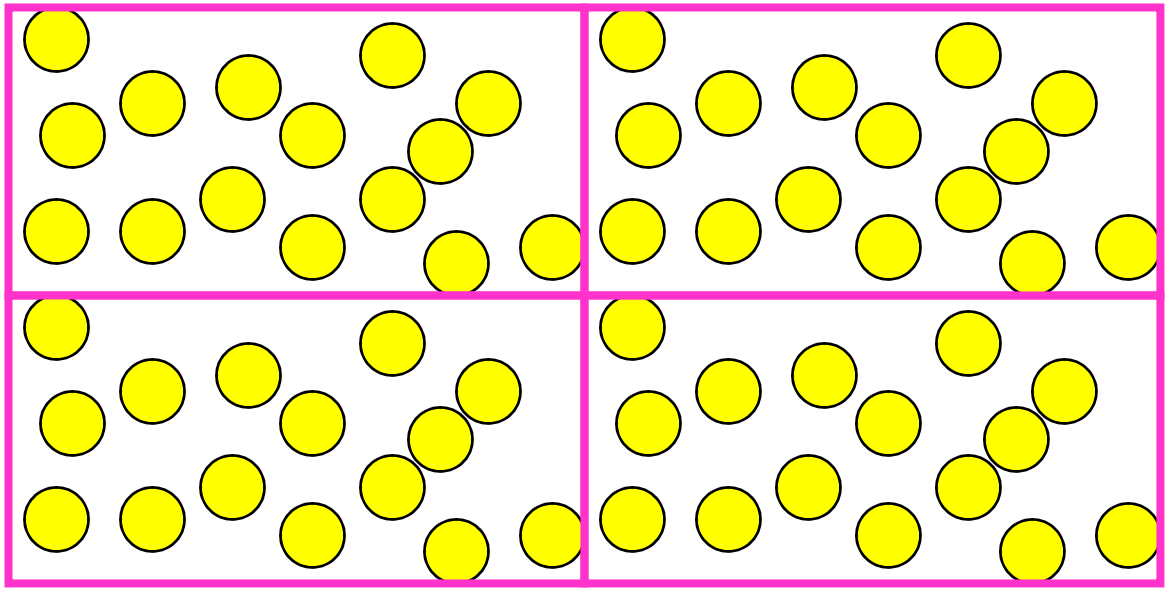
What if the system is not periodic?

- Example 5: Want to study an amorphous or quasicrystalline system.



What if the system is not periodic?

- Example 5: Want to study an amorphous or quasicrystalline system: approximate by a periodic system (with large unit cell).



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)

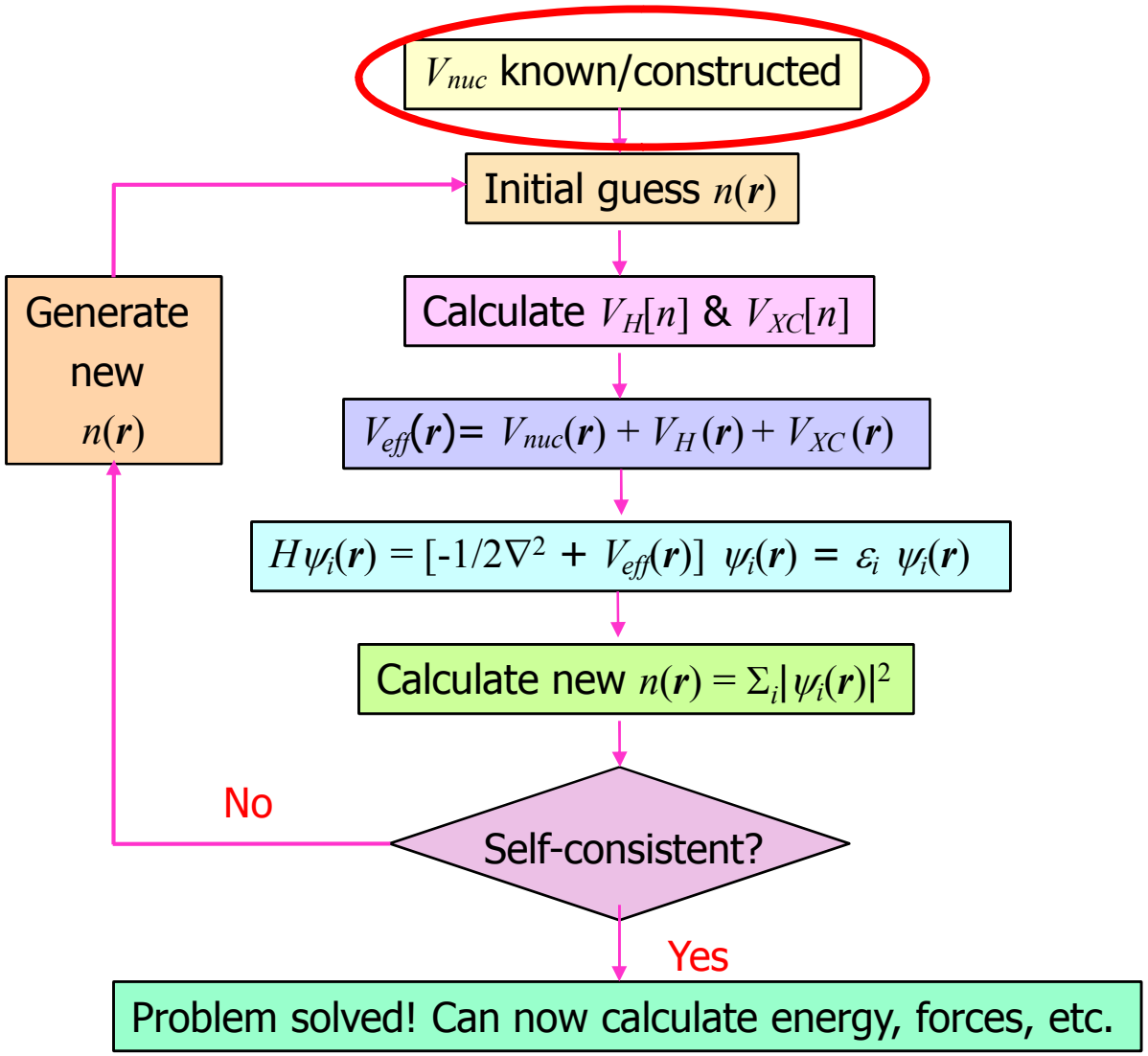
⇓

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

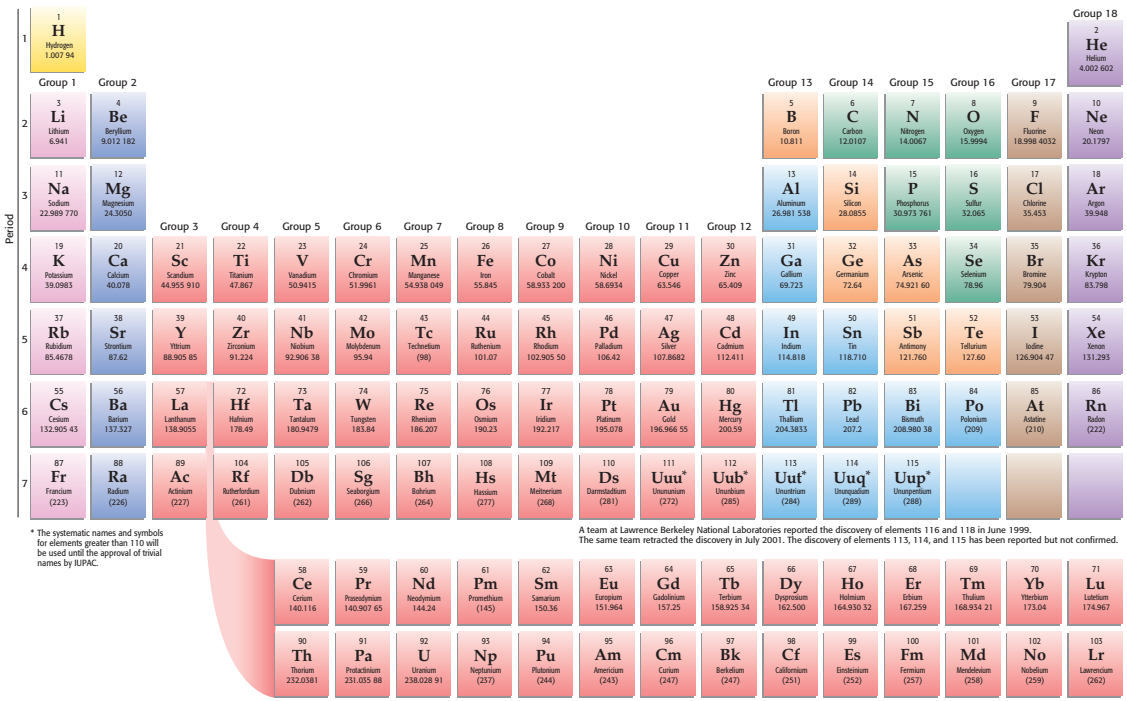
⇓

- Many $\mathbf{G}$'s will fall within E_{cut} sphere!

Step 1: Obtaining V_{nuc}



treating core states



$$\epsilon_{1s} \sim Z^2 \quad a_{1s} \sim \frac{1}{Z}$$

$$E_{cut} \sim Z^2$$

$$N_{PW} = \frac{4\pi}{3} k_{cut}^3 \frac{\Omega}{(2\pi)^3}$$

$$\sim Z^3$$

Nuclear Potential

- Electrons experience a Coulomb potential due to the nuclei.

- This has a known and simple form:

$$V_{nuc} = -\frac{Z}{r}$$

- But this leads to computational problems!

Problem for Plane-Wave Basis

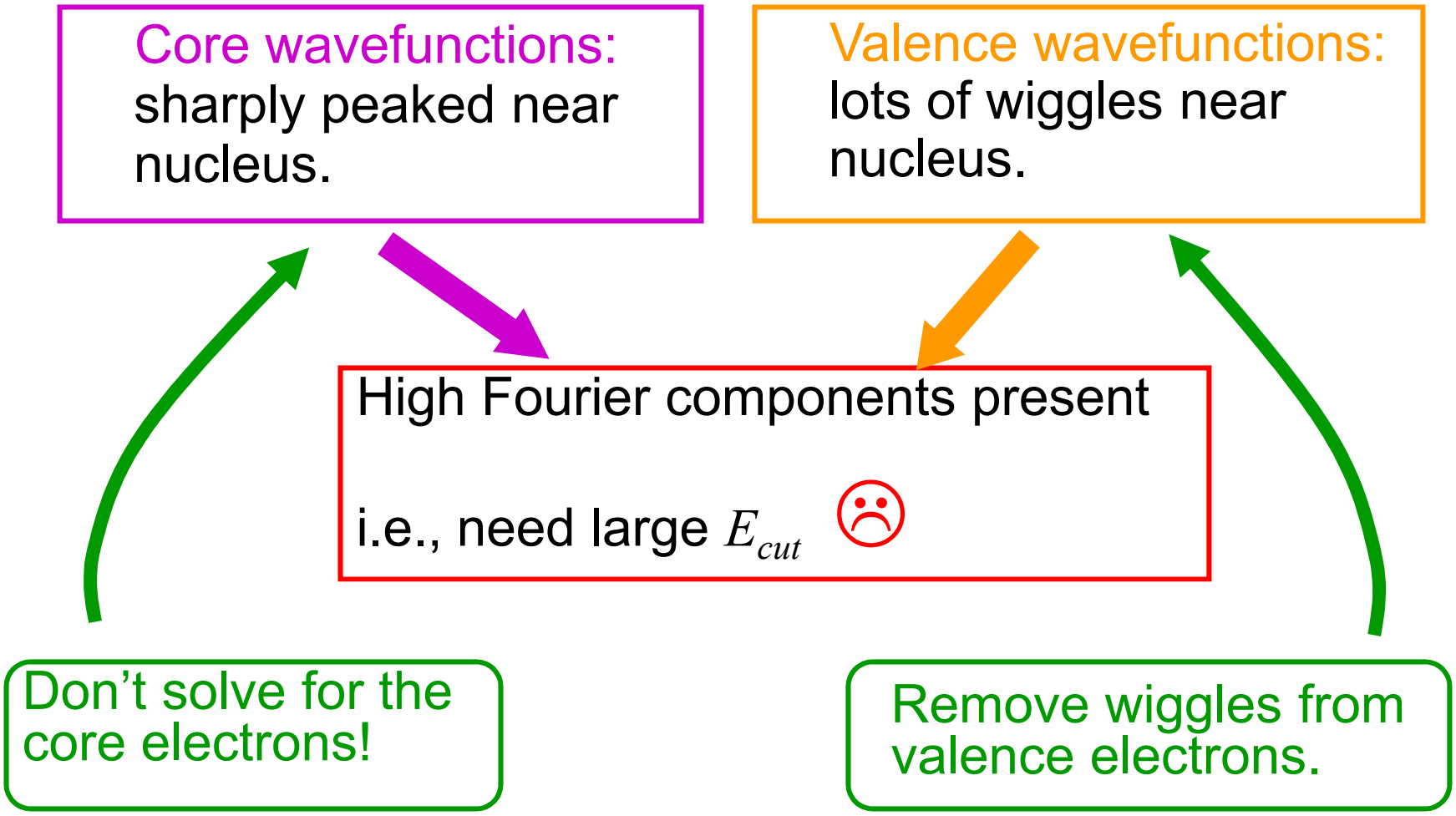
Core wavefunctions: sharply peaked near nucleus.

Valence wavefunctions: lots of wiggles near nucleus.

High Fourier components present

i.e., need large E_{cut} ☹

Solutions for Plane-Wave Basis



trashing core states: pseudopotentials

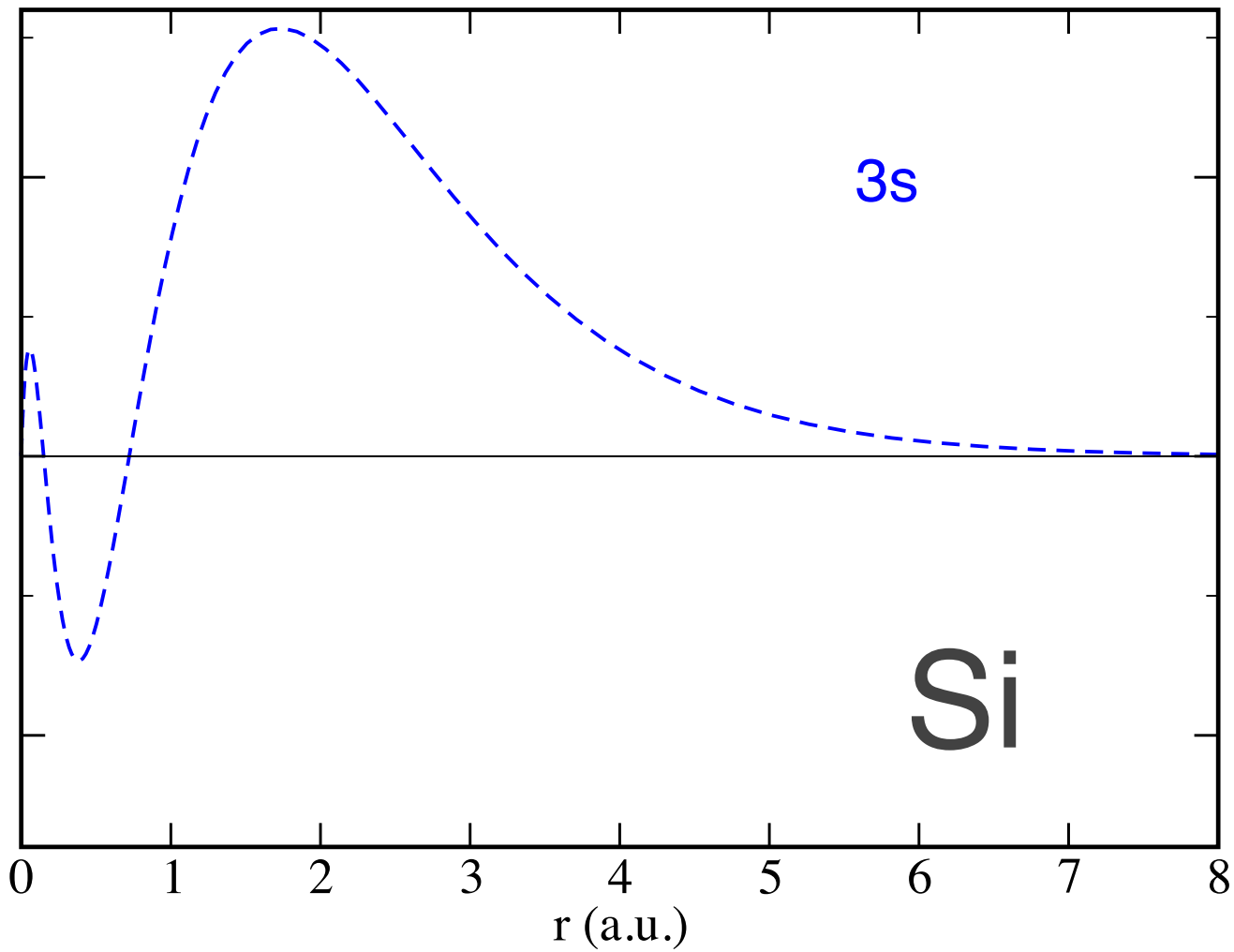
pseudo-atoms do not have core states: valence states of any given angular symmetry are the lowest-lying states of that symmetry:

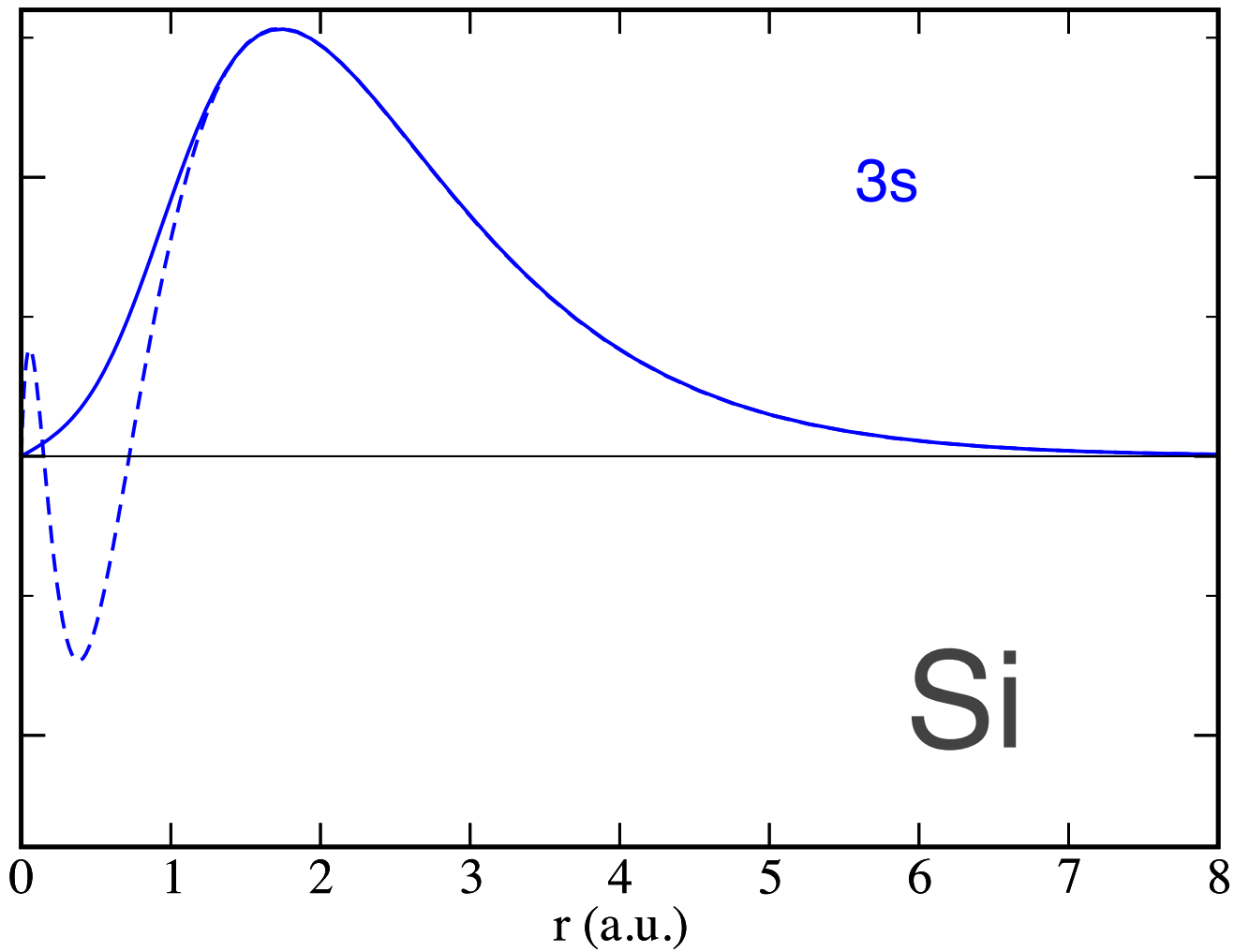
ϕ_{val}^{ps} is nodeless and smooth

the chemical properties of the pseudo-atom are the same as those of the true atom:

$$\epsilon_{val}^{ps} = \epsilon_{val}^{ae}$$

$$\phi_{val}^{ps}(r) = \phi_{val}^{ae}(r) \quad \text{for} \quad r > r_c$$


3s
Si
0
1
2
3
4
5
6
7
8
r (a.u.)


3s
Si
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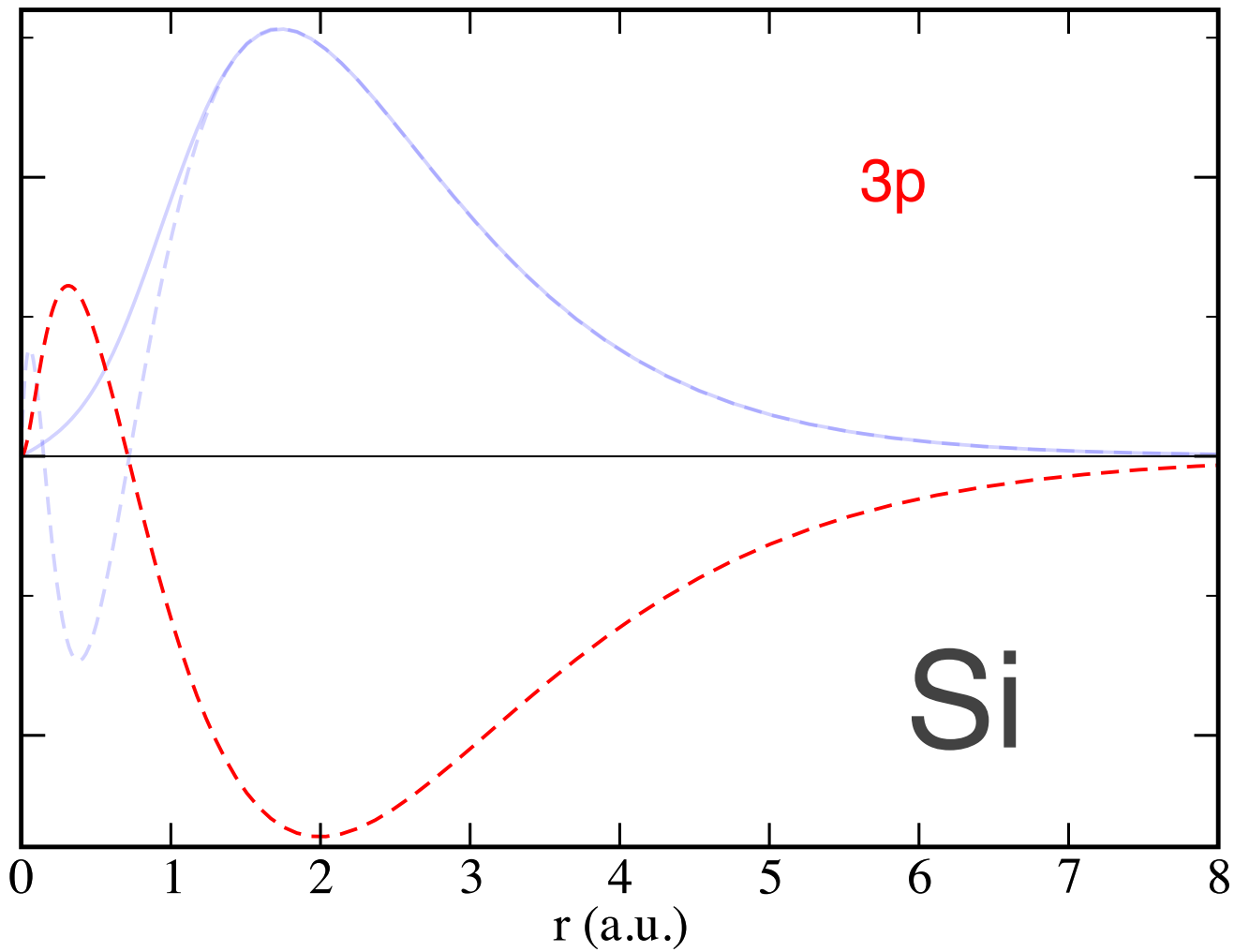
r (a.u.)


3p
Si
0
1
2
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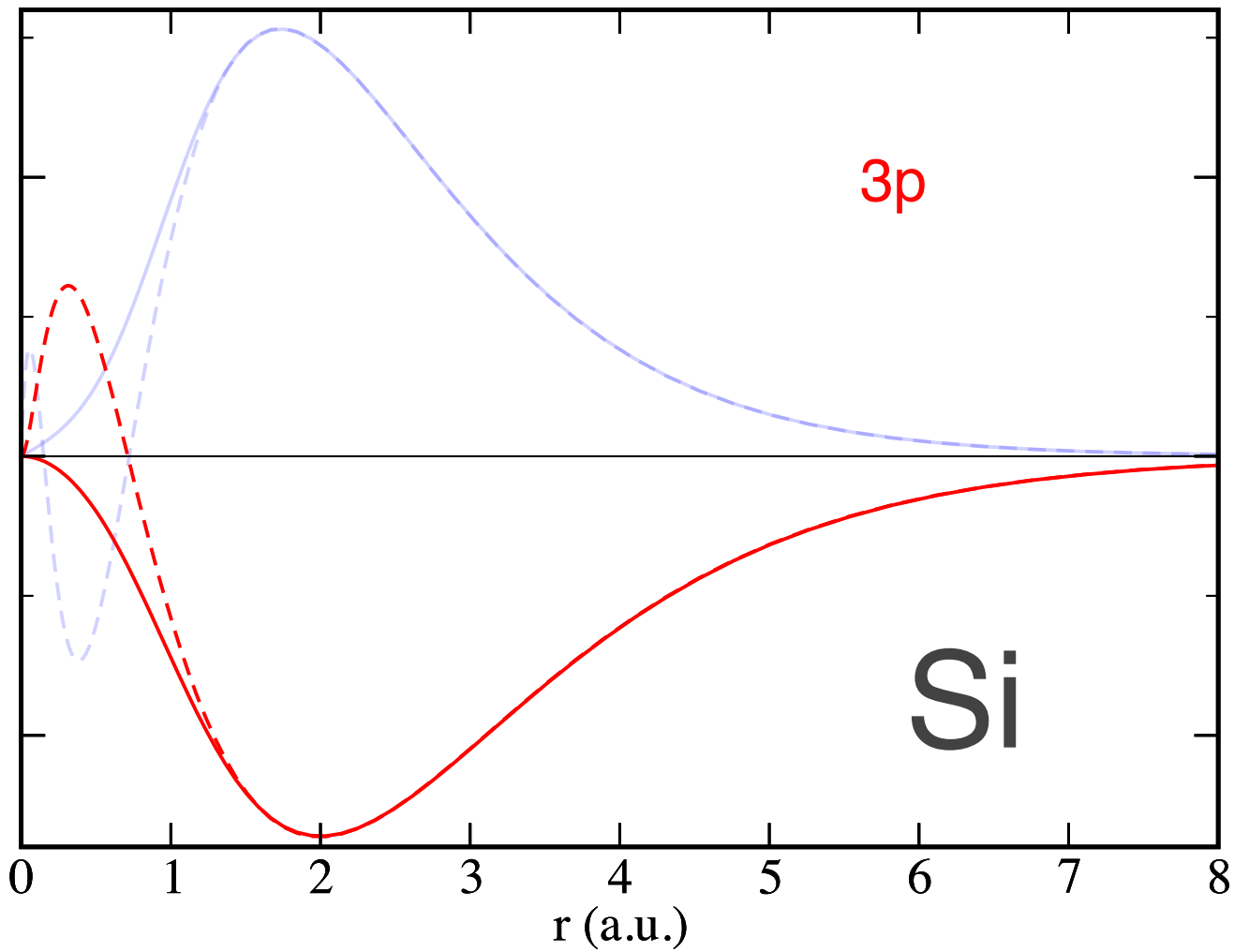
7
8
r (a.u.)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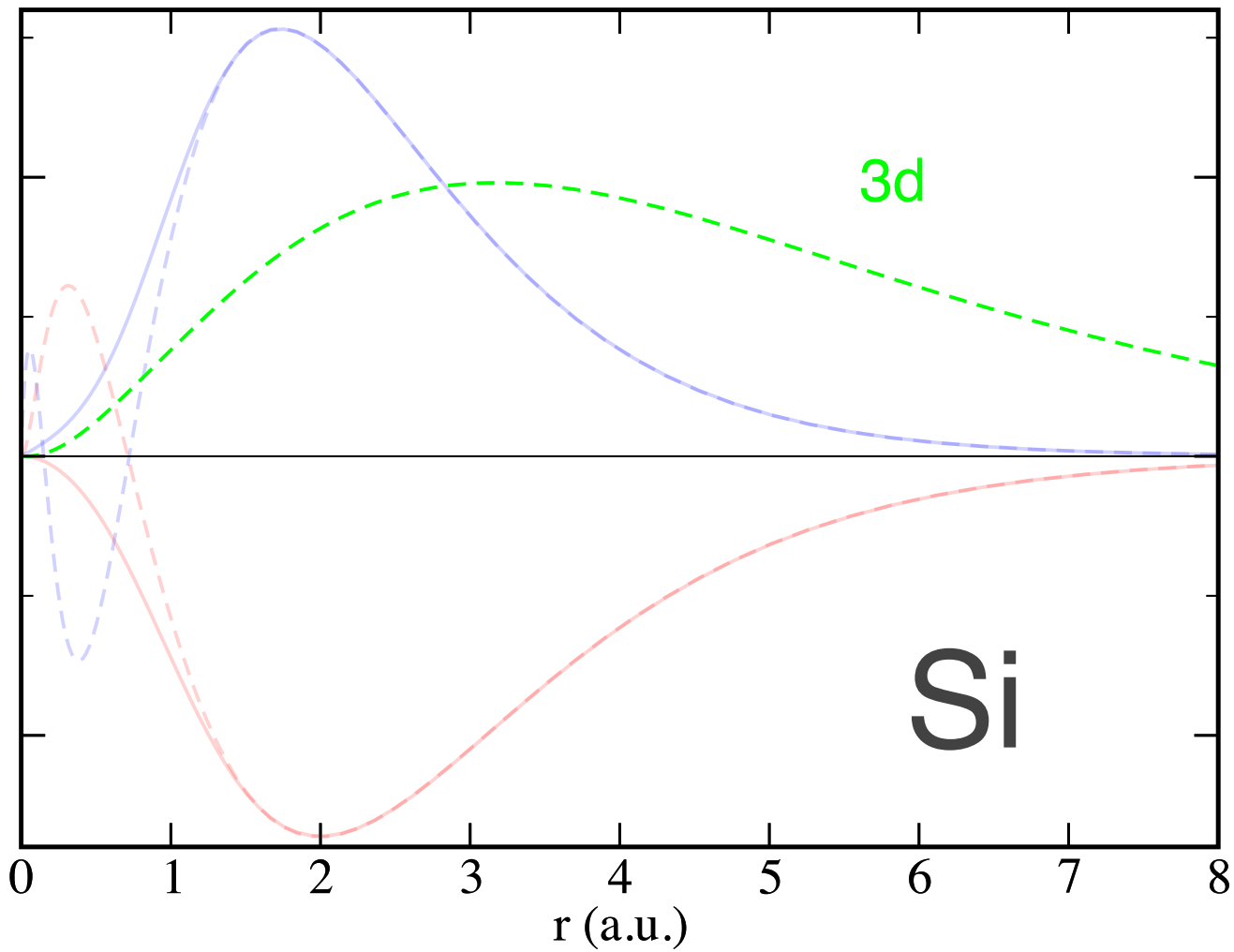
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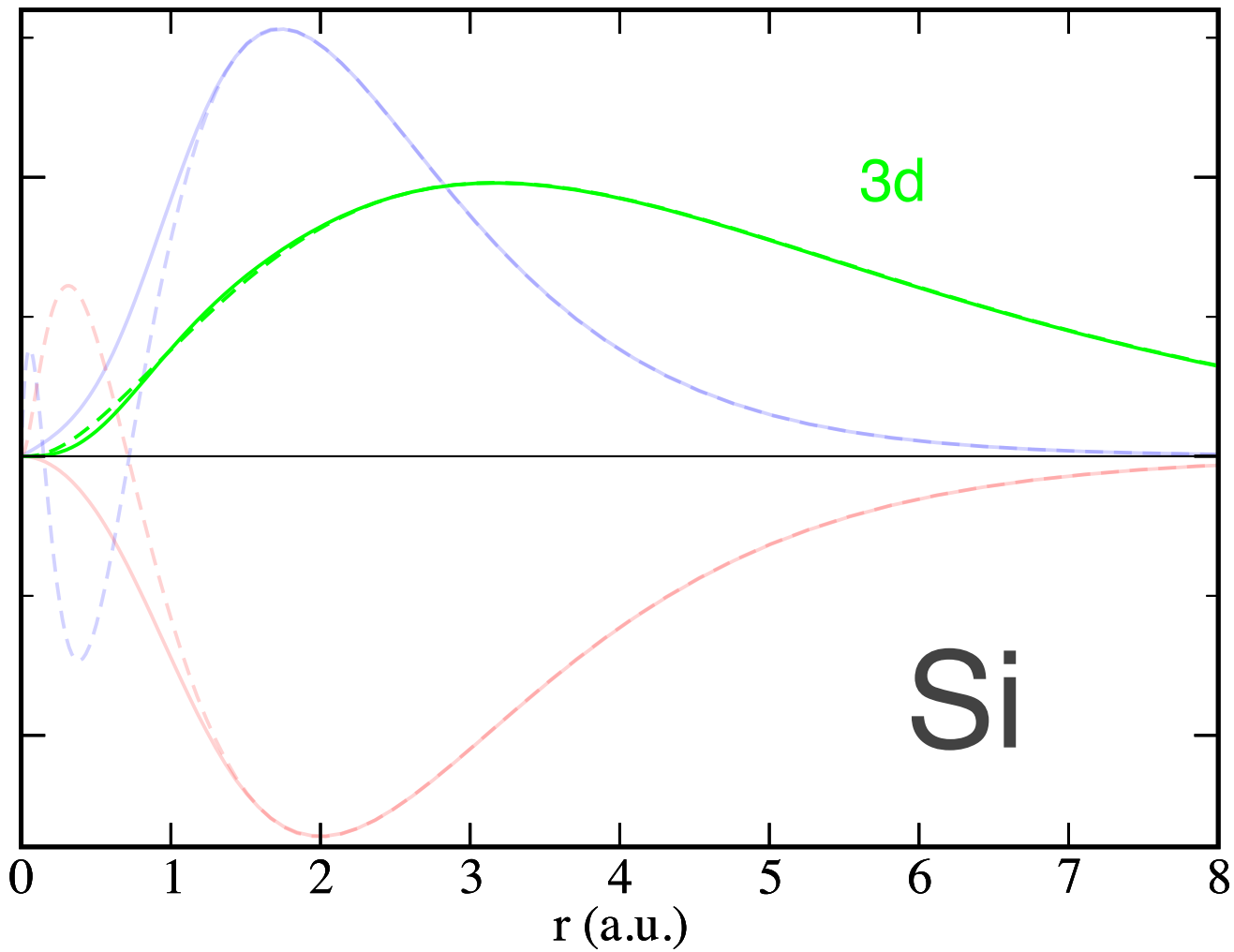
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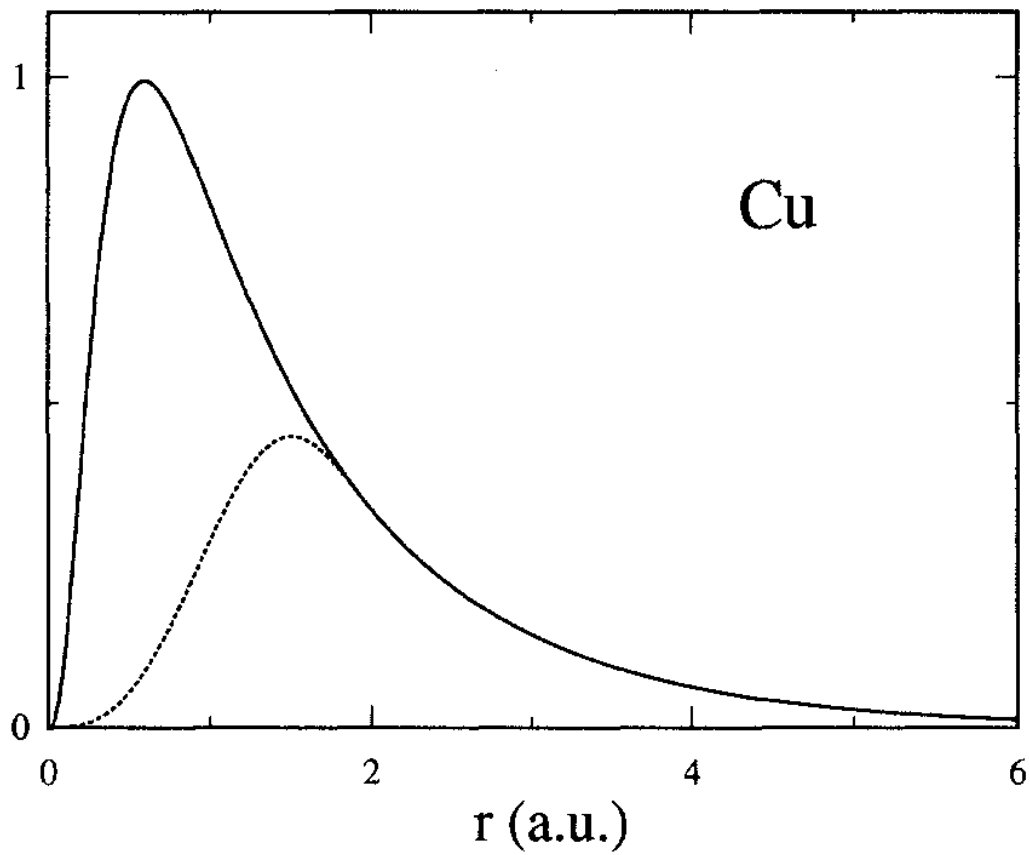
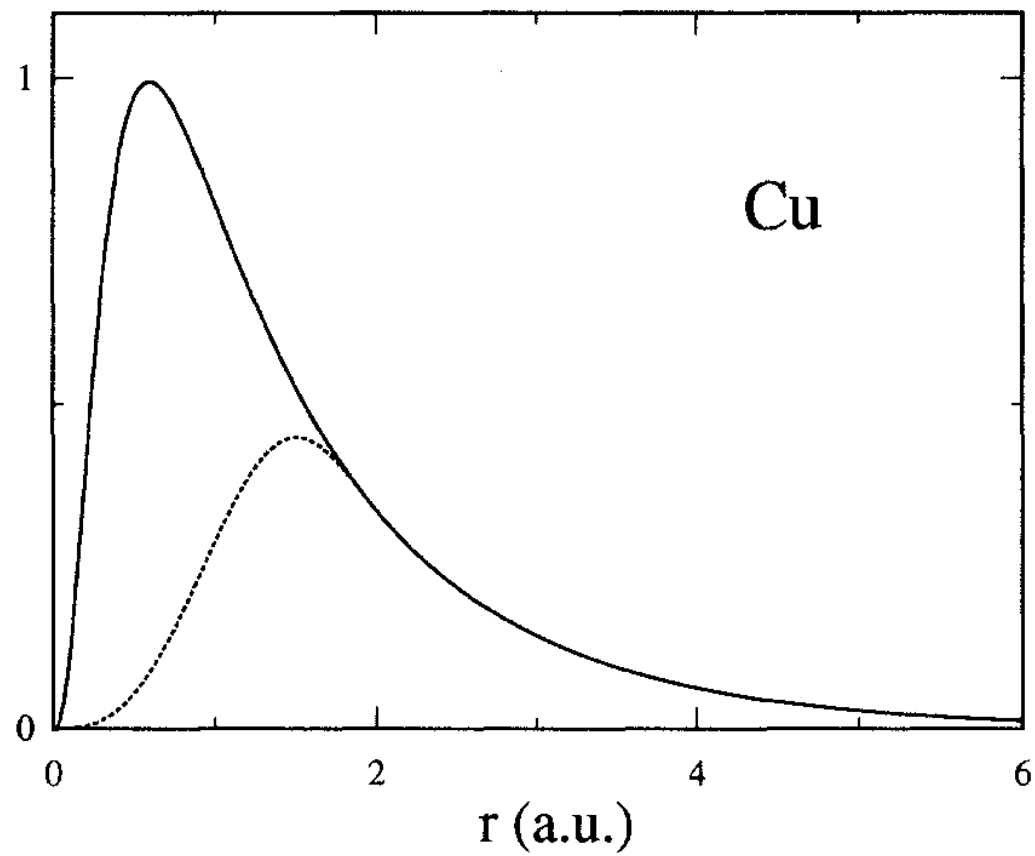
US pseudopotentials



US pseudopotentials



$$H_{US}\phi_n = \epsilon_n S\phi_n \qquad \langle\phi_n|S|\phi_m\rangle = \delta_{nm}$$

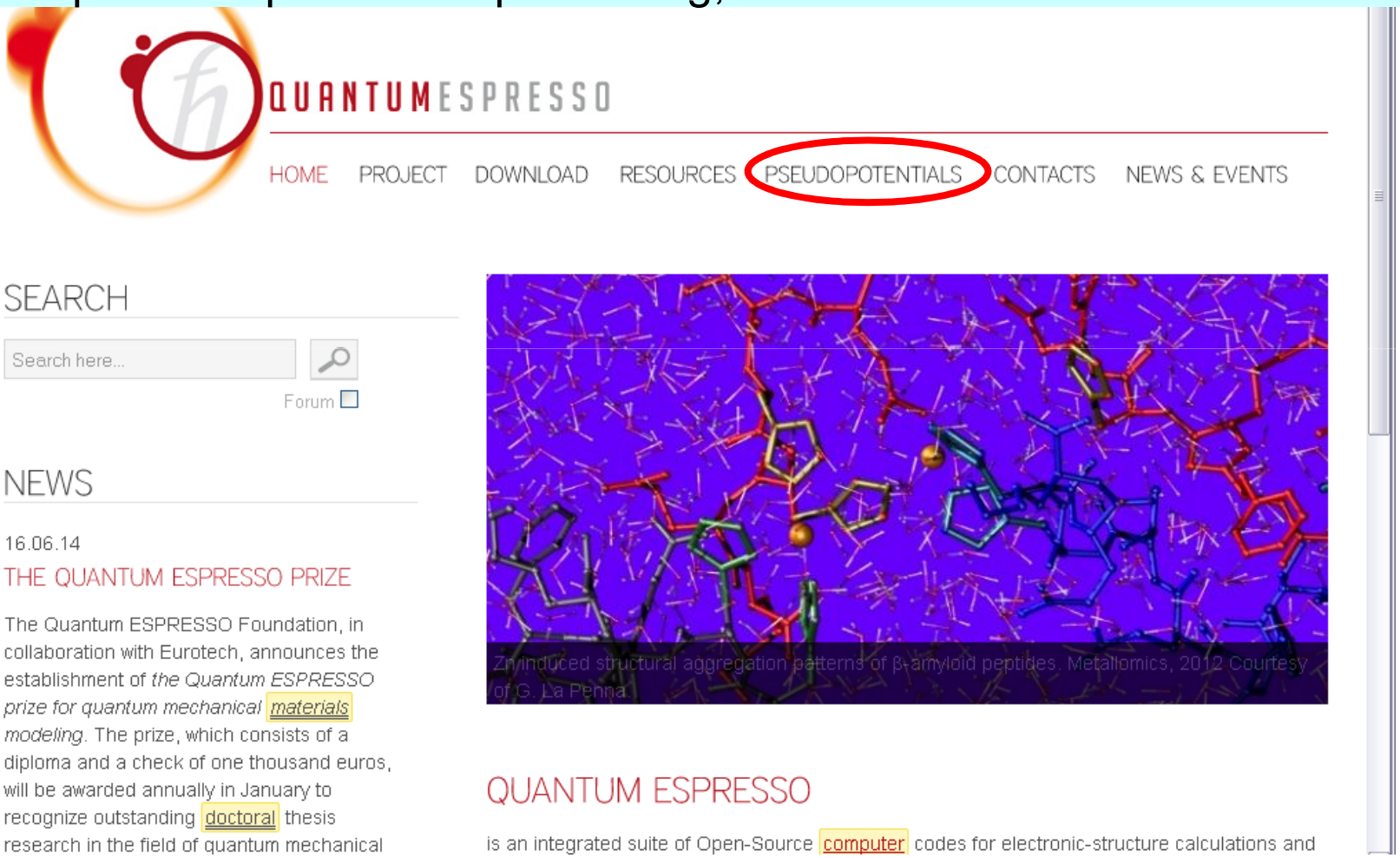
Pseudopotentials

- Replace nuclear potential by pseudopotential
- This is a numerical trick that solves these problems
- There are different kinds of pseudopotentials (Norm conserving pseudopotentials, ultrasoft pseudopotentials, etc.)
- Which kind you use depends on the element.

Will discuss in much greater detail on July 1 (tomorrow).

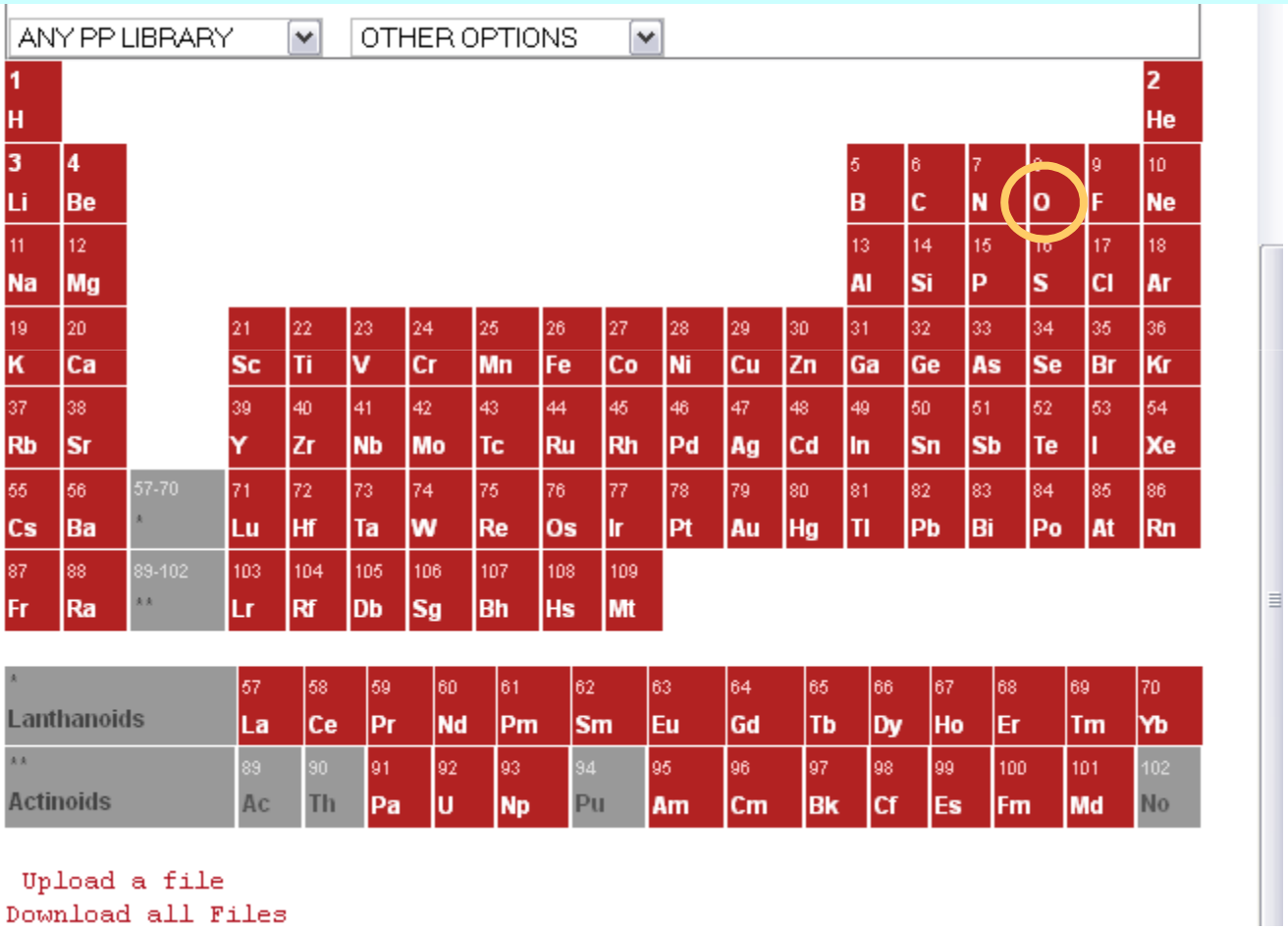
Pseudopotentials for Quantum Espresso - 1

- Go to http://www.quantum-espresso.org; Click on “PSEUDOPOTENTIALS”



Pseudopotentials for Quantum Espresso - 2

- Click on element for which pseudopotential wanted.



Pseudopotentials for Quantum-ESPRESSO

O.pbe-rrkjus.UPF

```
Pseudopotential type: ULTRASOFT
Method: Rappe Rabe Kaxiras Joannopoulos
Functional type: Perdew-Burke-Ernzerhof (PBE) exch-corr
scalar relativistic

Origin: Original QE PP library
Author: Andrea Dal Corso
Generated by Andrea Dal Corso code (rrki3)
Uploaded by Layla Martin-Samos
Classification controlled by Paolo Giannozzi
```

O.pbe-van_ak.UPF

```
Pseudopotential type: ULTRASOFT
Method: Vanderbilt ultrasoft
Functional type: Perdew-Burke-Ernzerh
scalar relativistic

Origin: Original QE PP library
Generated by Vanderbilt code version 7.3.4
More Information: O.pbe-van_ak.txt
Uploaded by Layla Martin-Samos
Classification controlled by Paolo Giannozzi
```

Pseudopotential's name gives information about :

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

Element & V_{ion} for Quantum-ESPRESSO

e.g, for calculation on $BaTiO_3$:

```
ATOMIC_SPECIES
Ba 137.327 Ba.pbe-nsp-van.UPF
Ti 47.867 Ti.pbe-sp-van_ak.UPF
O  15.999 O.pbe-van_ak.UPF
```

- **`ecutwfc, ecutrho`** depend on type of pseudopotentials used (should test).

- When using ultrasoft pseudopotentials, set **`ecutrho`** = 8-12 × **`ecutwfc`** !!

Element & V_{ion} for Quantum-ESPRESSO

- Should have same exchange-correlation functional for all pseudopotentials.

input

```
    diagonalization = 'cg' , mixing_mo
    mixing_beta = 0.7, conv_thr = 1.0
/
ATOMIC_SPECIES
 Fe   55.85 Fe.pz-nd-rrkjus.UPF
 Co   58.93 Co.pbe-nd-rrkjus.UPF
ATOMIC_POSITIONS {crystal}
 Fe 0.00  0.00  0.00
```

oops!

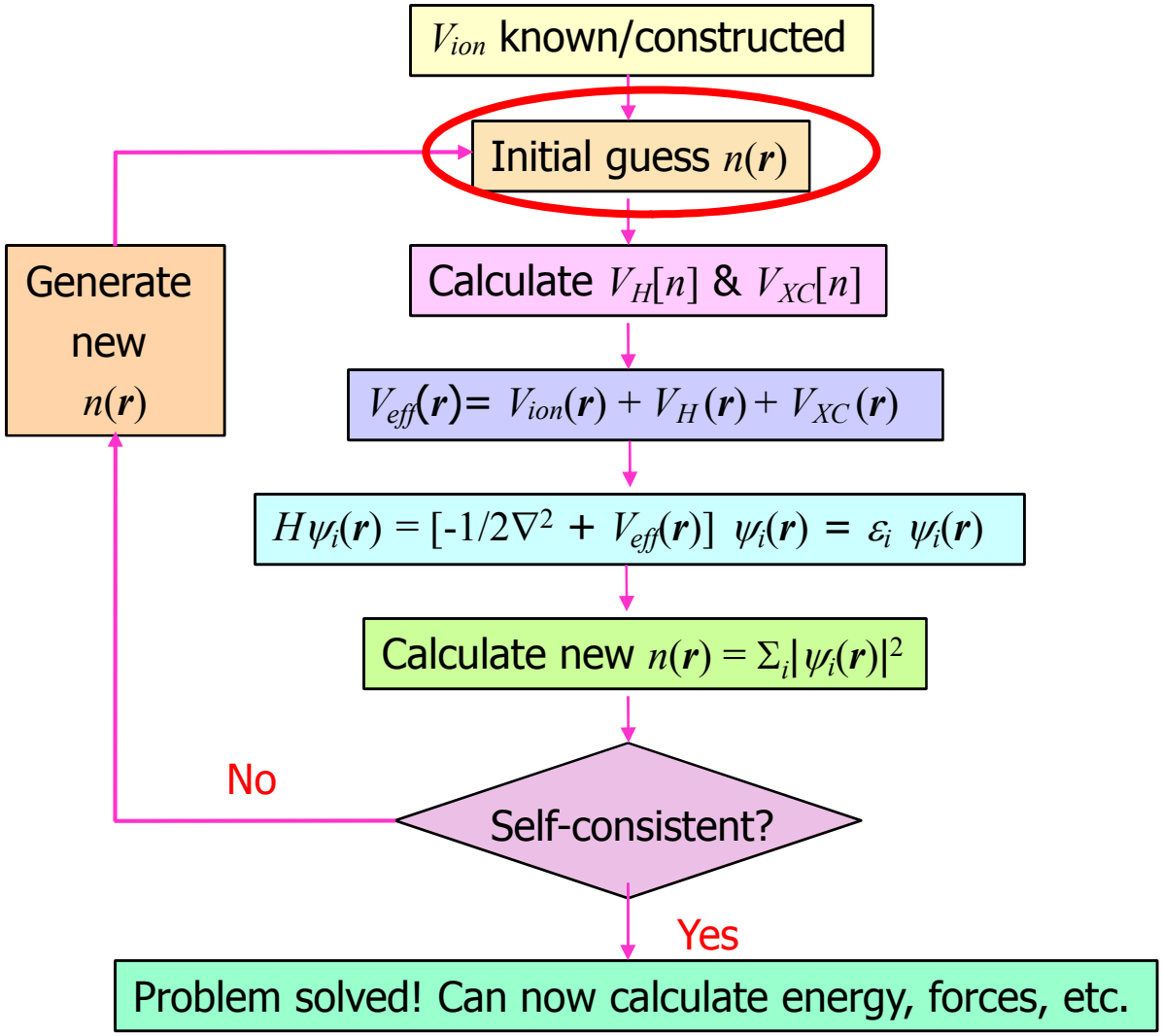
output

```
     Max angular momentum in pseudopotentials

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
     from readpp : error #         2
     inconsistent DFT read
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

     stopping ...
```

Step 2: Initial Guess for $n(\mathbf{r})$



Starting Wavefunctions

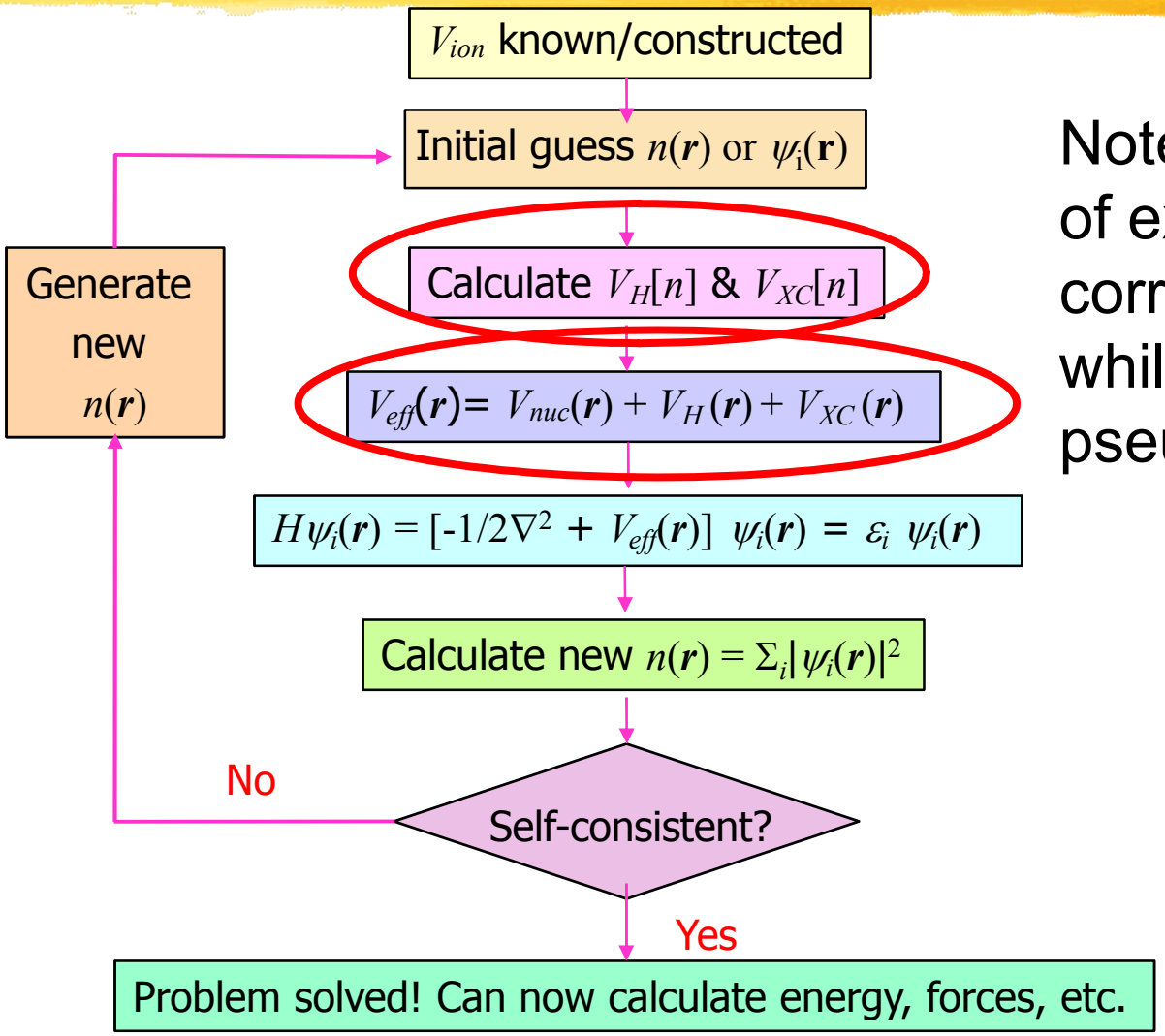
The closer your starting wavefunction is to the true wavefunction (which, of course, is something you don't necessarily know to start with!), the fewer the scf iterations needed.

```
startingwfc  'atomic'
             'atomic+random'
             'random'
             'file'
```

Superposn of atomic orbitals

"The beginning is the most important part of the work" - Plato

Steps 3 & 4: Effective Potential



Note that type of exchange-correlation chosen while specifying pseudopotential

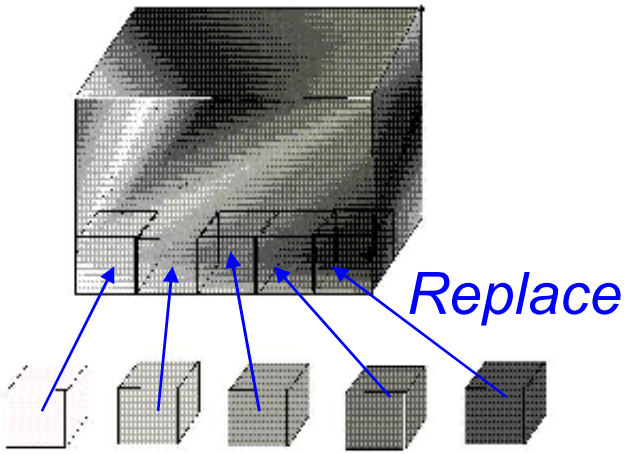
Exchange-Correlation Potential

- $V_{XC} \equiv \delta E_{XC}/\delta n$ contains all the many-body information.
- Known [numerically, from Quantum Monte Carlo ; various analytical approximations] for homogeneous electron gas.
- Local Density Approximation:

$$E_{xc}[n] = \int n(\mathbf{r})\, V_{xc}^{\mathrm{HOM}}[n(\mathbf{r})]\, d\mathbf{r}$$

-surprisingly successful!

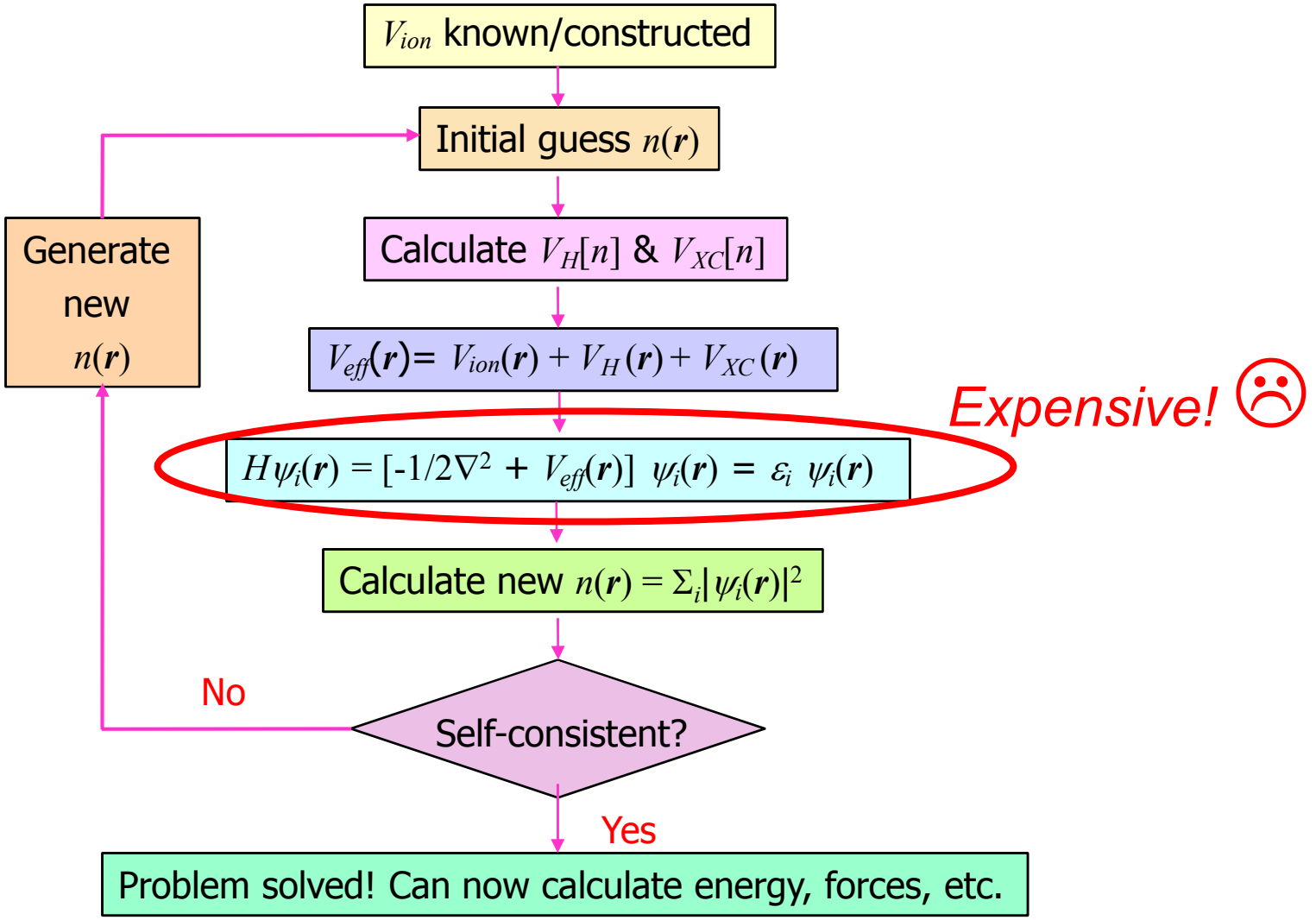
pz (in name of pseudopotential)



- Generalized Gradient Approximation(s): Include terms involving gradients of $n(\mathbf{r})$

pw91, pbe (in name of pseudopotential)

Step 5: Diagonalization



Diagonalization

- Need to diagonalize a matrix of size $N_{PW} \times N_{PW}$
- N_{PW} **>>** N_b = number of bands required = $N_e/2$ or a little more (for metals).
- OK to obtain lowest few eigenvalues.
- Exact diagonalization is expensive!
- Use iterative diagonalizers that recast diagonalization as a minimization problem.

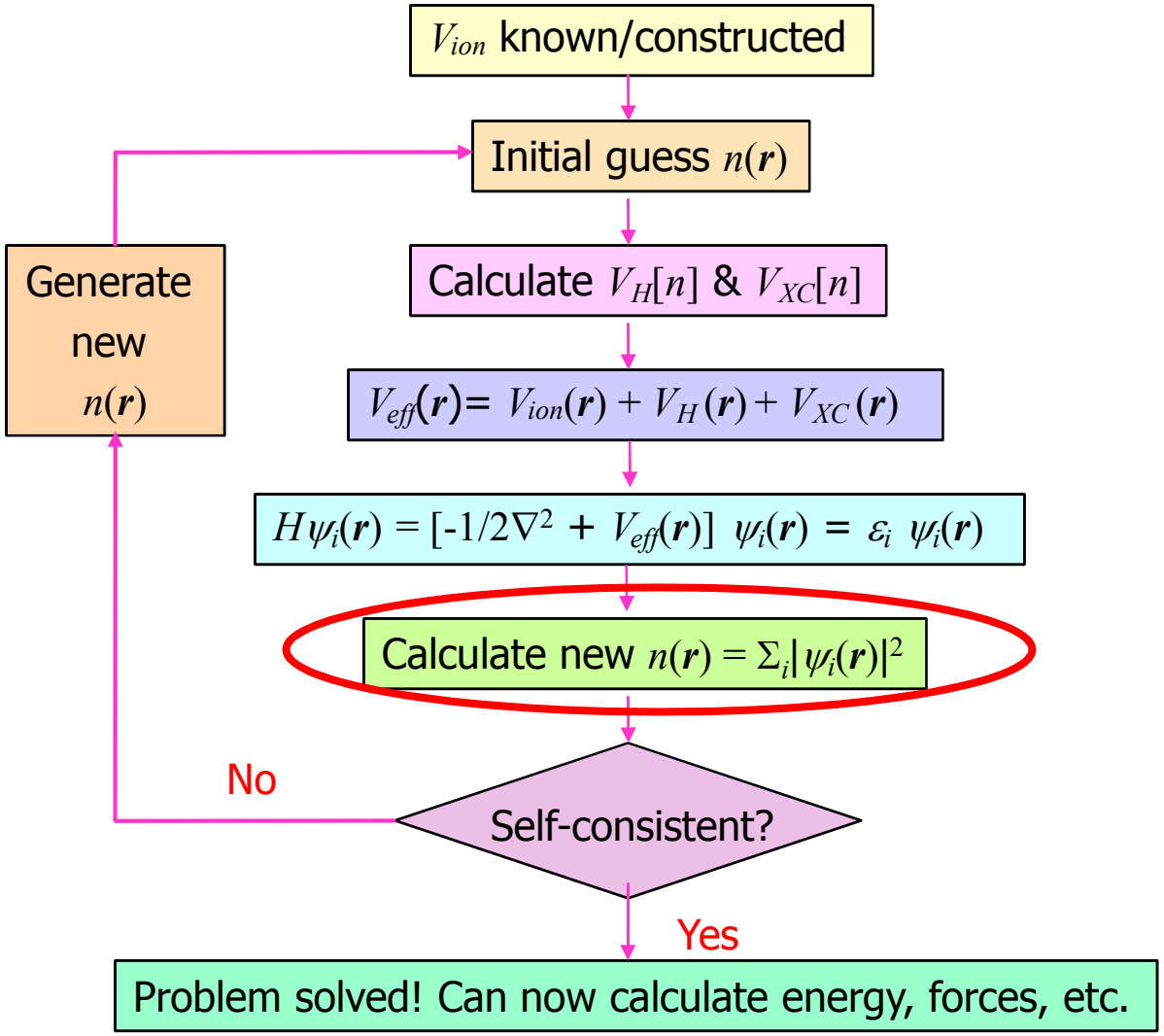
Input parameter **`diagonalization`**

-which algorithm used for iterative diagonalization

Input parameter **`nbnd`**

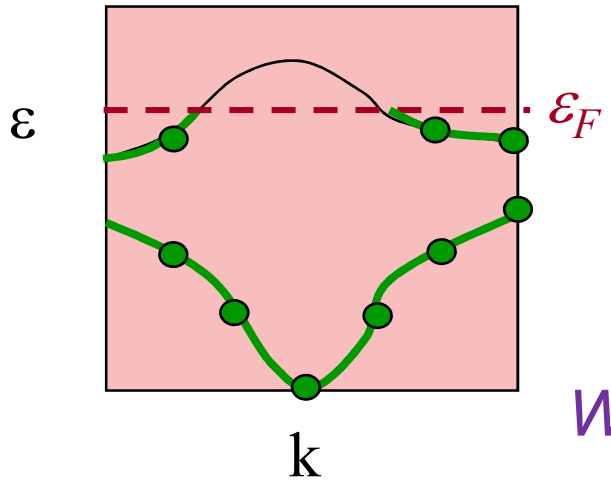
-how many eigenvalues computed
for metals, choose depending on value of **`degauss`**

Step 6: New Charge Density



Brillouin Zone Sums

- Many quantities (e.g., n, E_{tot}) involve sums over **k.**
- In principle, need infinite number of **k**'s.
- In practice, sum over a finite number: BZ "Sampling".
- Number needed depends on band structure.
- Typically need more **k**'s for metals.
- Need to test convergence wrt k-point sampling.

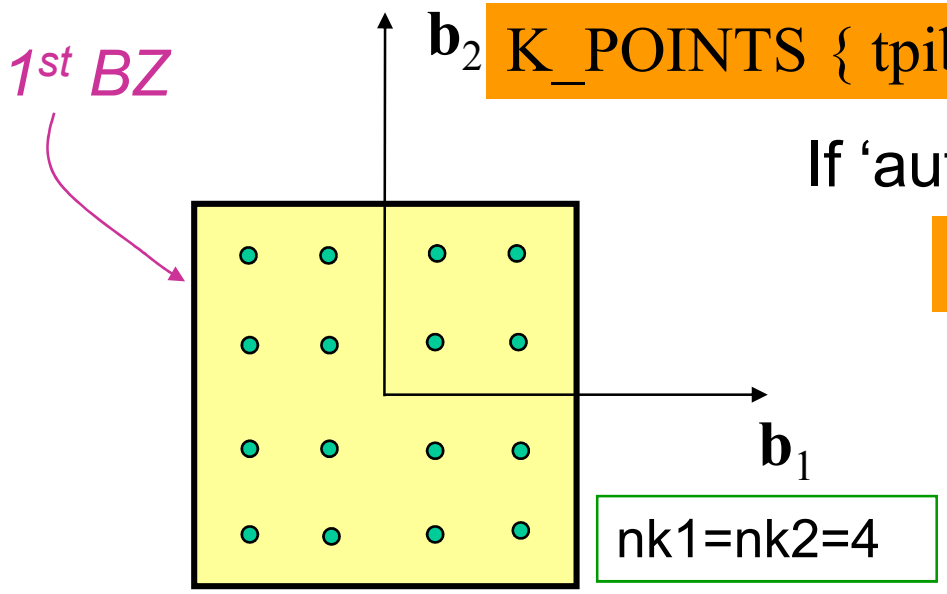


$$\langle P \rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k} \in BZ} P(\mathbf{k}) w_{\mathbf{k}}$$

Will discuss in greater detail tomorrow

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']



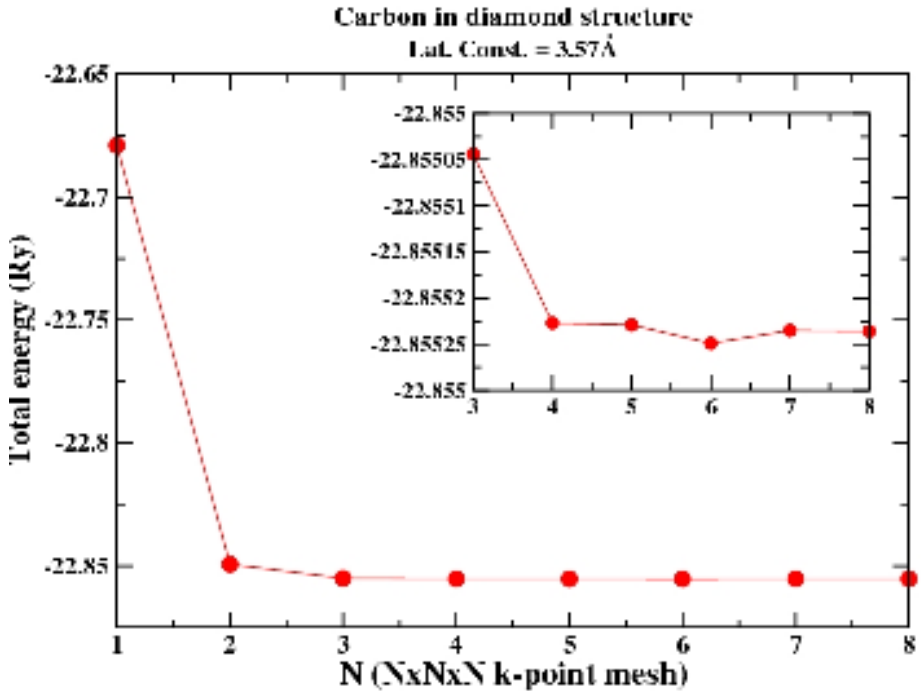
K_POINTS { tpiba | automatic | crystal | gamma }

If 'automatic', use M-P mesh:

nk1, nk2, nk3, k1, k2, k3

shift

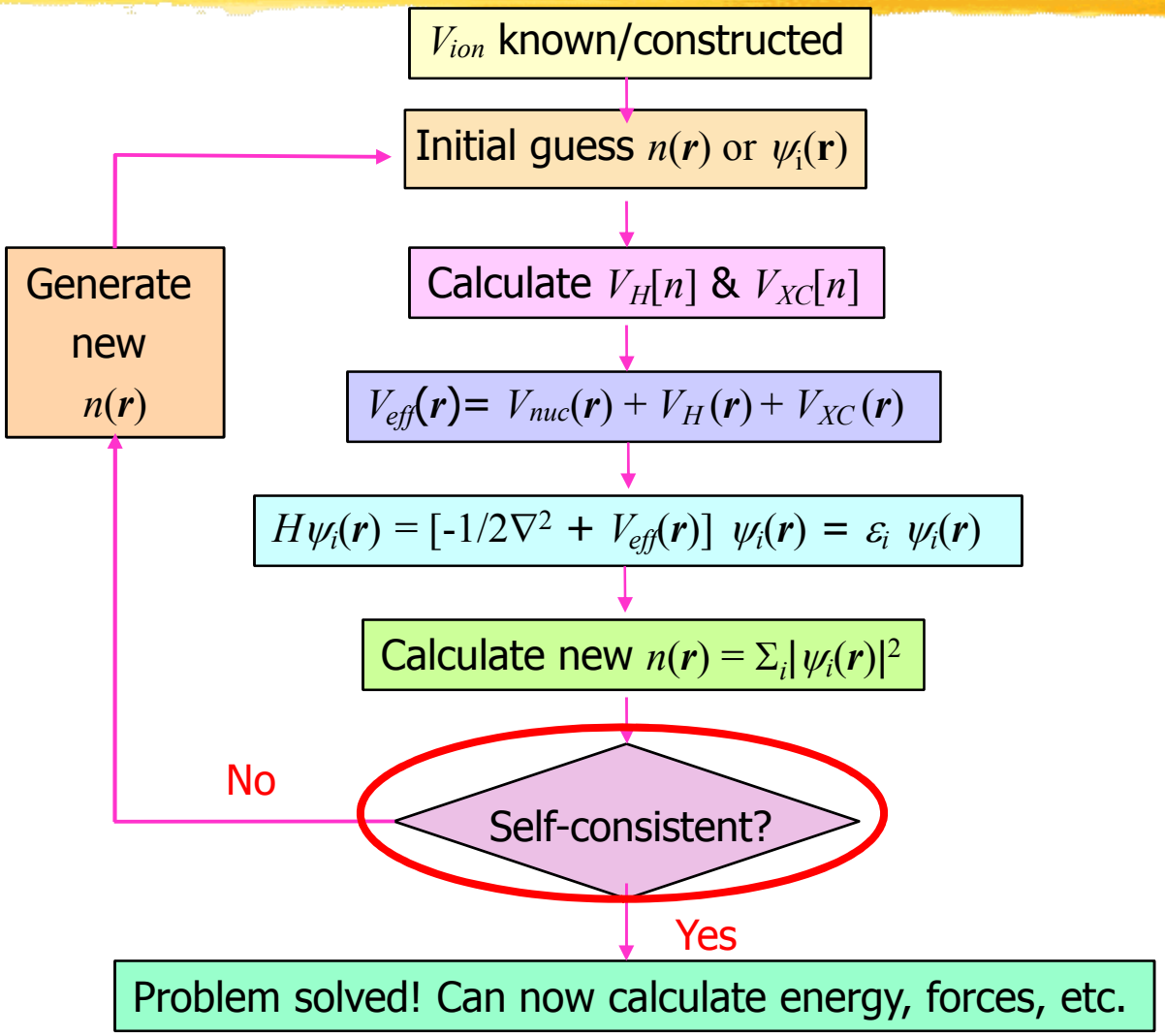
Convergence wrt BZ sampling



Madhura Marathe

Note: Differences in energy usually converge faster than absolute value of total energy because of error cancellation (if supercells & k-points are identical or commensurate).

Step 7: Check if Convergence Achieved



Testing for scf convergence

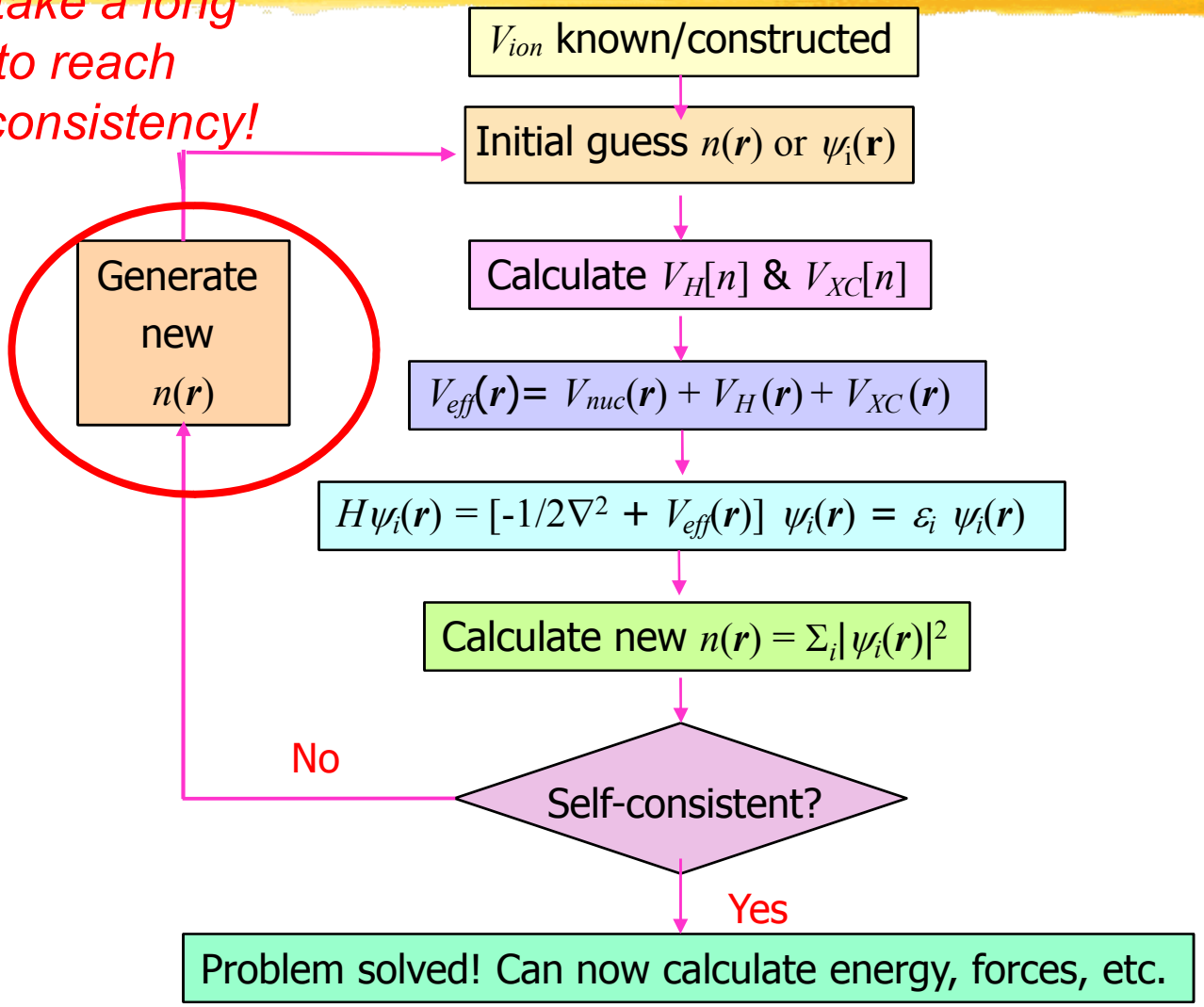
- Compare nth and (n-1)th approximations for density, and see if they are close enough that self-consistency has been achieved.

Input parameter **`conv_thr`**

Step 8: Mixing

Can take a long time to reach self-consistency!

☹



Mixing

- Iterations n of self-consistent cycle:
- Successive approximations to density:

  $n_{in}(n) \rightarrow n_{out}(n) \rightarrow n_{in}(n+1).$
- $n_{out}(n)$ fed directly as $n_{in}(n+1)$?? No, usually doesn't converge.
- Need to mix, take some combination of input and output densities (may include information from several previous iterations).
- Goal is to achieve self consistency ($n_{out} = n_{in}$) in as few iterations as possible.

Mixing in Quantum-ESPRESSO

Input parameter **`mixing_mode`**

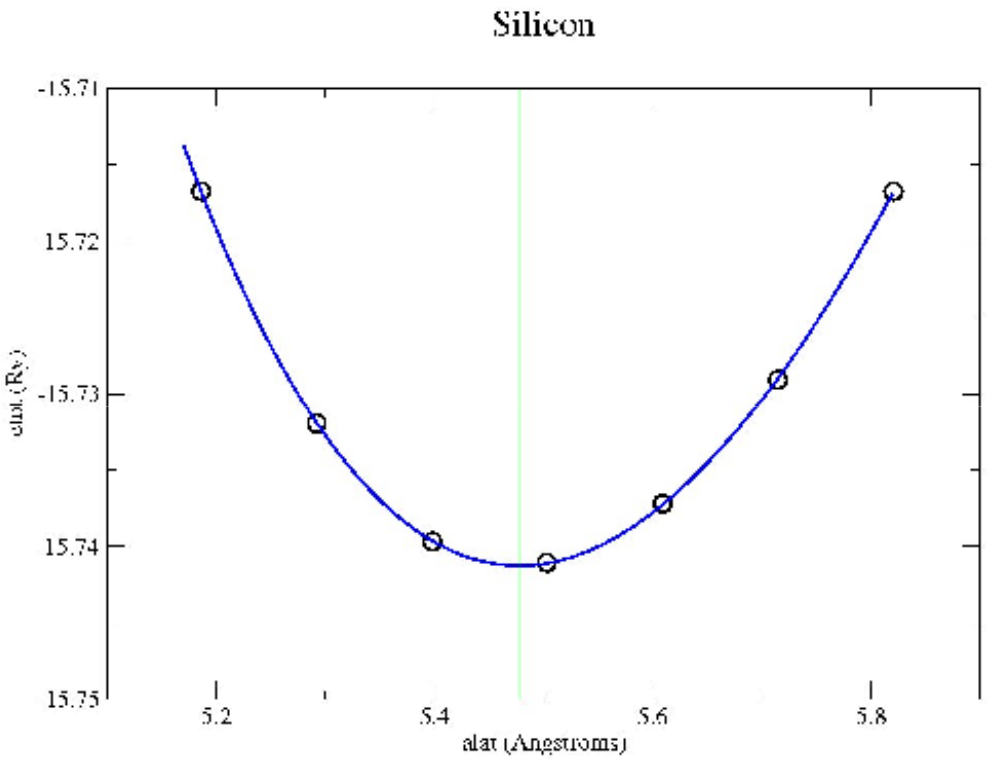
-Prescription used for mixing.

Input parameter **`mixing_beta`**

-How much of new density is used at each step
-Typically use value between 0.1 & 0.7

Output Quantities: Total Energy

- Perhaps the most important output quantity is the TOTAL ENERGY
- Can use, e.g., to optimize structure
- e.g., for a cubic crystal, where the structure can be specified by a single parameter (side of cube):



Energy vs. lattice constant or volume is given by "Equation of State"

IV. Structure of PWscf Input Files

PWscf input file

- For documentation about input parameters for PWscf, read **`INPUT_PW.html`** in the **`Doc`** subdirectory.

- The PWscf input file is structured into **`NAMELISTS`** and **`INPUT_CARDS.`**

PWscf NAMELISTs in Input File

- There are three mandatory **NAMELISTs**:
- **&CONTROL** input variables that control the type of calculation performed and the amount of I/O.
- **&SYSTEM** input variables that specify the system.
- **&ELECTRONS** input variables that control the algorithms used to reach a self-consistent solution of the Kohn-Sham equations.
- There are other (optional) namelists...

PWscf CARDs in Input File

- There are three mandatory **CARDs**:
- **ATOMIC_SPECIES** name, mass and pseudopotential used for each species in system.
- **ATOMIC_POSITIONS** coordinates of each atom in unit cell.
- **K_POINTS** coordinates and weights of the k-points used for BZ sums..
- There are other (optional) CARDs...

Other Features / Types of Calculations

- Spin Polarized Calculations (Magnetism)
- Density Functional Perturbation Theory (Phonons)
- Nudged Elastic Band (Barriers)
- Molecular Dynamics
- …and much, much more!

It's not a bird…

It's not Superman…

It's a Plane Wave !

The End!

Have fun with Quantum-ESPRESSO!