How To Do Simple Calculations With Quantum ESPRESSO

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I. About The Quantum ESPRESSO Distribution

Quantum ESPRESSO

- www.quantum-espresso.org

The Quantum ESPRESSO Software Distribution

The DEMOCRITOS center of Italian INFM is dedicated to atomistic simulations of materials, with a strong emphasis on the development of high-quality scientific software

Quantum ESPRESSO is the result of a DEMOCRITOS initiative, in collaboration with several other institutions (ICTP, CINECA Bologna, EPF Lausanne, Princeton University, MIT, Paris VI, Oxford, IJS Ljubljana,...)

Quantum ESPRESSO is a distribution of software for atomistic simulations based on electronic structure, using density-functional theory (DFT), a plane waves (PW) basis set and pseudopotentials (PP)

Quantum ESPRESSO stands for *Quantum opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization*

P. Giannozzi

Why “Quantum ESPRESSO”?!

Trieste, Tommaseo (ph. G. Crozzoli)

Licence for Quantum ESPRESSO

Quantum ESPRESSO is distributed under the *GNU (Gnu's Not Unix) General Public License (GPL)*, probably the most common free-software license. Basically:

- The source code is available.
- You can do whatever you want with the sources, but if you distribute any derived work, you have to distribute under the GPL the sources of the derived work.

Advantages:

- Everybody – including commercial entities – can contribute.
- Nobody can "steal" the code and give nothing back to the community.

The most successful example is probably the Linux Kernel.

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Quantum ESPRESSO: Organization

The distribution is maintained as a single CVS (Concurrent Version System) tree. Available to everyone anytime via anonymous (read-only) access.

- *Web site:* `http://www.quantum-espresso.org`
- *Wiki:* `http://www.quantum-espresso.org/index.php/Main_Page` contains the updated documentation
- *Developers' portal:* `http://www.qe-forge.org` integrated developer environment, open to external contributions

Mailing lists:

- `pw_users`: used by developers for announcements about Quantum ESPRESSO
- `pw_forum`: for general discussions (all subscribed users can post)

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Quantum ESPRESSO as a distribution

Quantum ESPRESSO aims at becoming a *distribution* of packages, rather than a single, monolithic, tightly integrated package. Main packages:

- `PWscf`: self-consistent electronic structure, structural relaxation, molecular dynamics
- `CP/FPMD`: variable-cell Car-Parrinello molecular dynamics

They share a common installation method, input format, PP format, data output format, large parts of the basic code. More packages:

- `PHonon`: linear-response calculations (phonons, dielectric properties)
- `PostProc`: graphical and postprocessing utilities (density of states, STM, etc.)
- `atomic`: pseudopotential generation code
- `PWGui`: a Graphical User Interface for production of input files

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Quantum ESPRESSO as a distribution

OTHER PACKAGES

`WANNIER90`: Maximally localized Wannier functions

`Pwcond`: Ballistic conductance

`WanT`: Coherent Transport from Maximally Localized Wannier Functions

`Xspectra`: Calculation of x-ray near edge absorption spectra

`QE-GIPAW`: EPR and NMR Chemical Shifts

`GWL`: GW Band Structure

`TD-DFT`: Time-Dependent Density Functional Pert. Theory

What Can Quantum ESPRESSO Do?

- Both Γ point and k-point calculations.
- Both insulators and metals, with smearing.
- Any crystal structure or supercell form.
- Norm conserving pseudopotentials, ultrasoft PPs, PAW.
- LDA, GGA, DFT+U, hybrid functionals, exact exchange, meta GGA, van der Waals corrected functionals.
- Spin polarized calculations, non-collinear magnetism, spin-orbit interactions.
- Nudged elastic band to find saddle points.
- And much more!

II. Doing a “Total Energy” Calculation with the PWscf Package of QE: The SCF Loop

The Kohn-Sham problem

- Want to solve the Kohn-Sham equations:

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

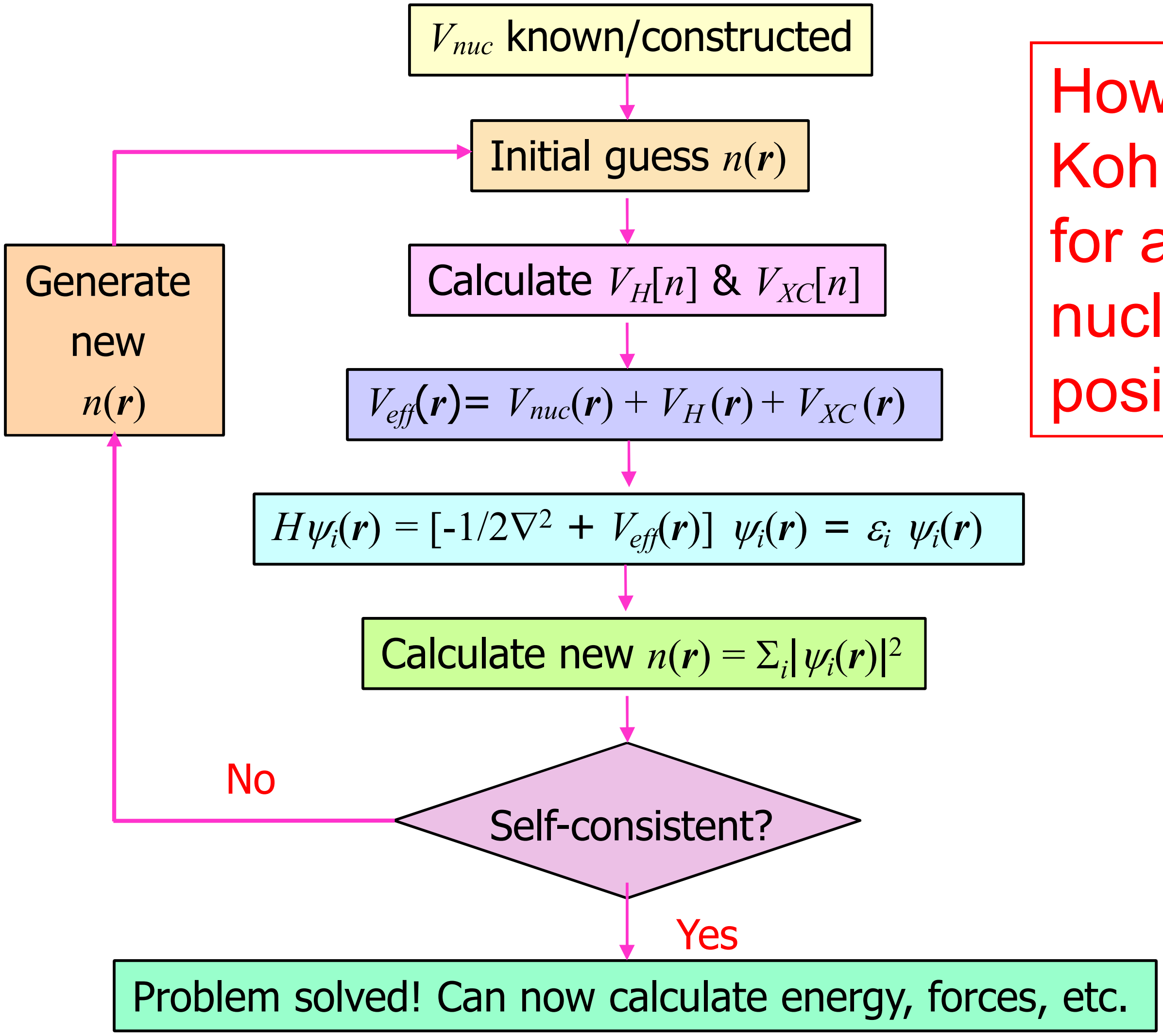
- Note that self-consistent solution necessary, as H depends on solution:

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

- Convention:

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

Self-consistent Iterative Solution



V_{nuc} known/constructed

Initial guess $n(\mathbf{r})$

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

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

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

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

Self-consistent?

No

Generate new $n(\mathbf{r})$

Yes

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

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 ⇔ Have to diagonalize a matrix of size N_b x N_b

Size of basis

Some possible basis sets

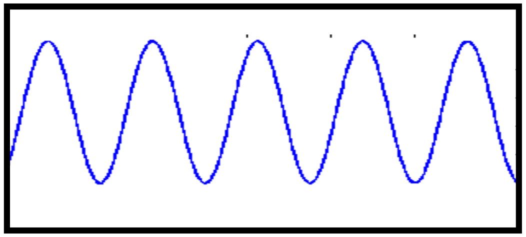
- Various possible choices of basis:

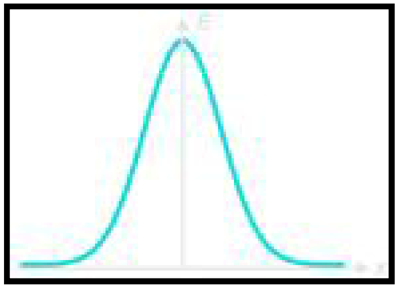
  - Plane waves $e^{iK \bullet r}$

  - 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 $f_\alpha(\mathbf{r})$ to be simple?

Advantages of a Plane Wave Basis

- Simple: Easy to take derivatives, etc.⇒ Coding is easy!
- Orthonormal: No overlap integrals.
- Independent of atomic positions ⇒ No "Pulay forces"; easy to calculate forces for structural relaxation & molecular dynamics.

- Unbiased: No assumption about where charge concentrated. (But ∴ 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 ↔ 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:

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

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

$$\boxed{u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{R}),}$$

where $\mathbf{R} =$ lattice vector

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

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

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

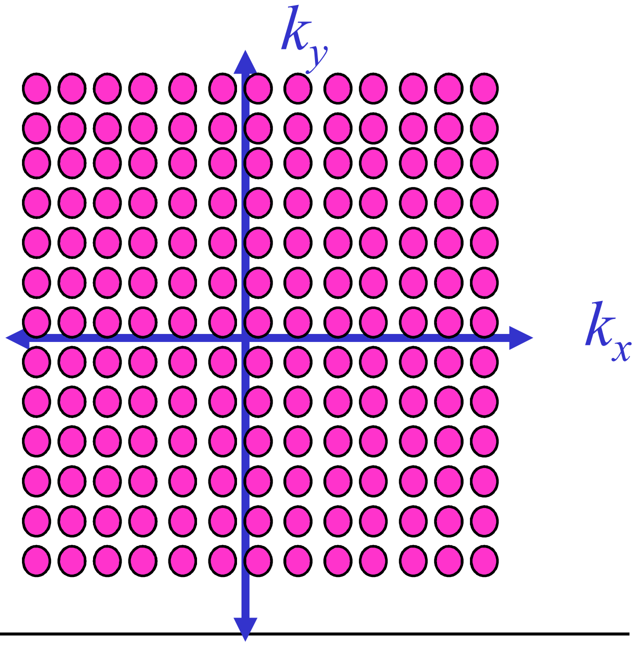
Plane Waves & Periodic Systems

- For a periodic system:

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

where **G** = reciprocal lattice vector

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



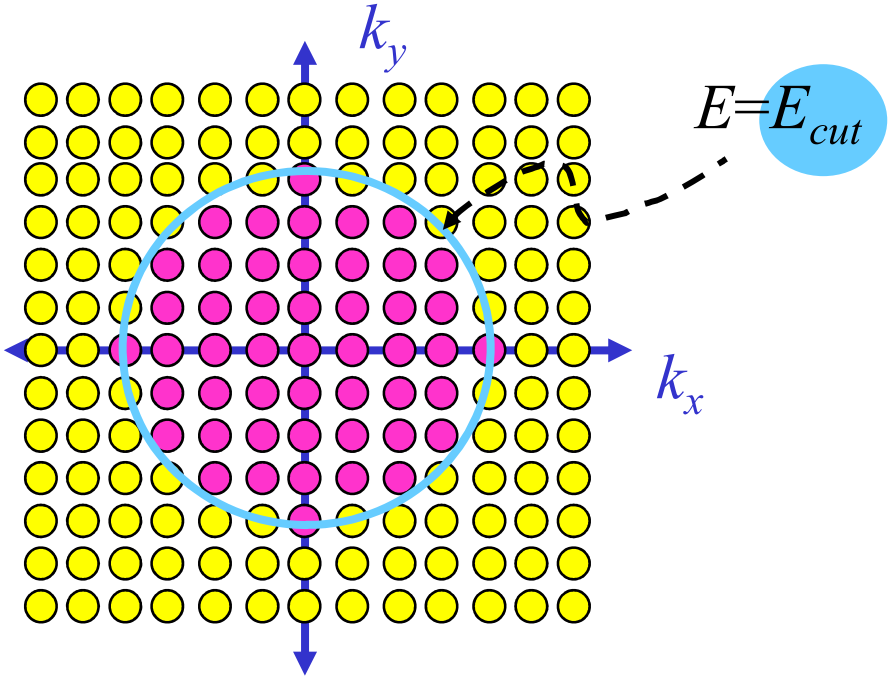
- Only true for periodic systems that grid is discrete.
- In principle, still need infinite number of plane waves.

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:

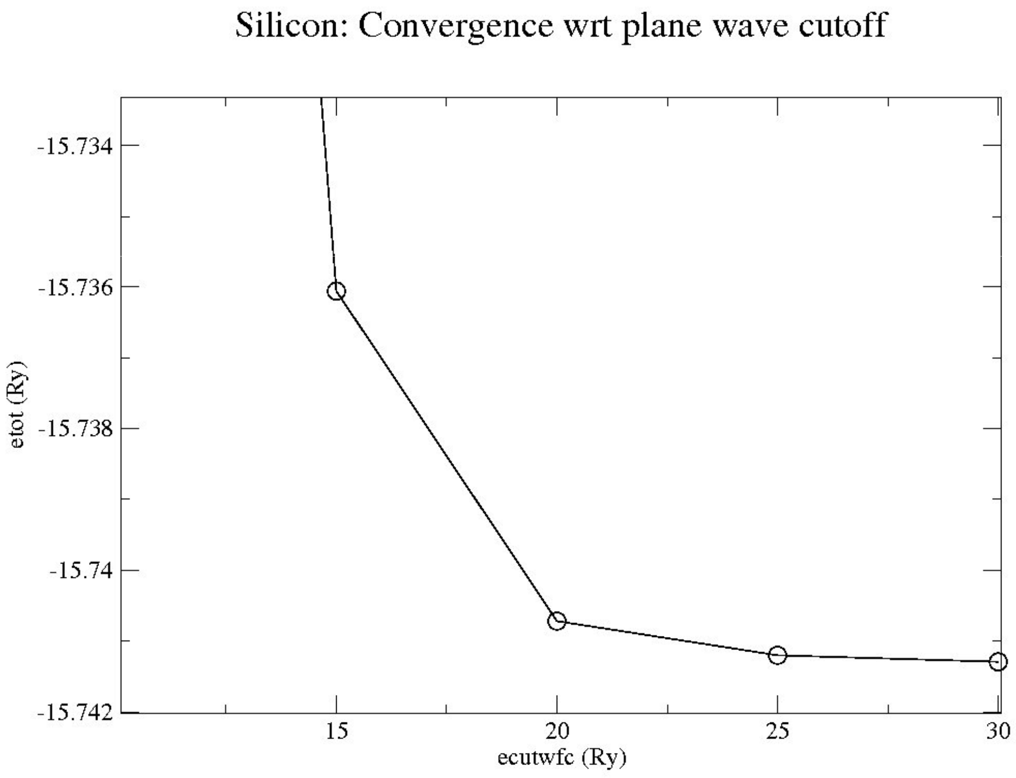
$$\frac{\hbar^2 |\mathbf{k}+\mathbf{G}|^2}{2m} \leq E_{cut}$$

Input parameter **`ecutwfc`**



Checking Convergence wrt ecutwfc

- Must always check.
- Monotonic (variational).

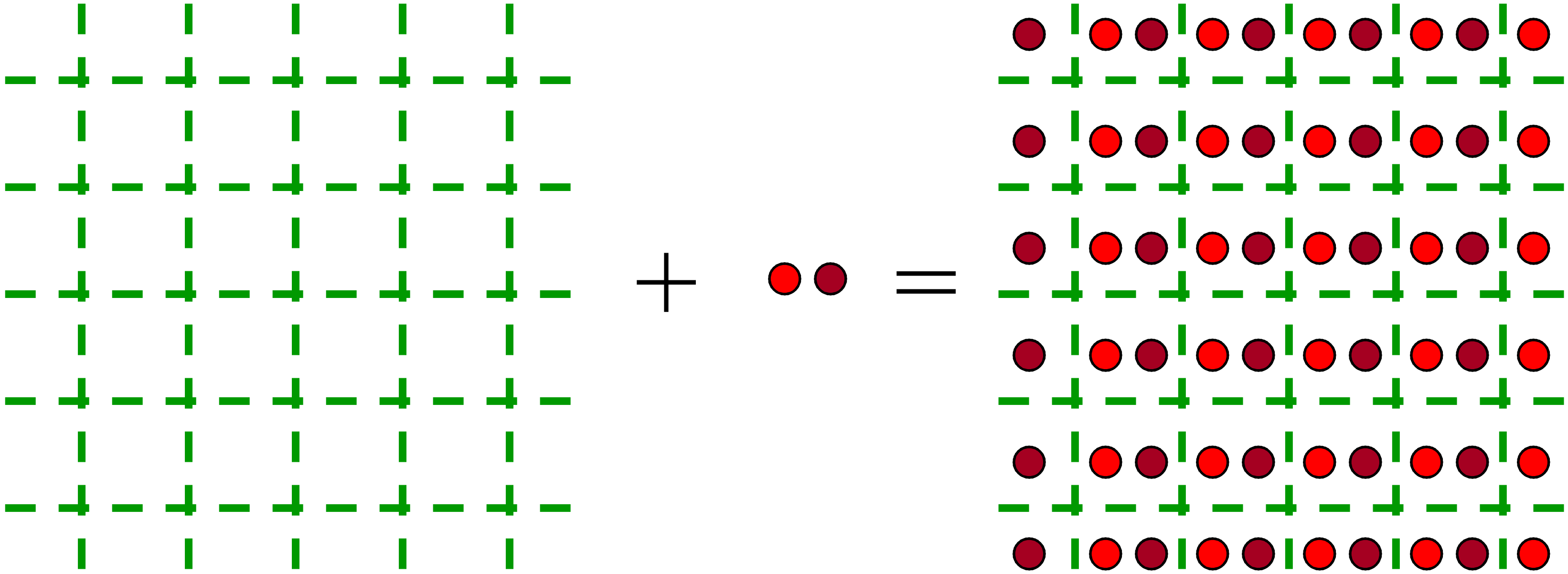


Step 0:
Defining the (periodic) system

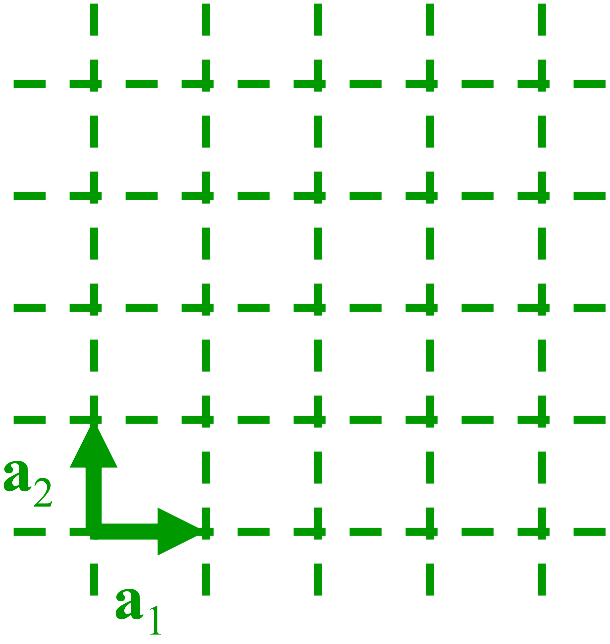
Namelist ‘**`SYSTEM`**’

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`**

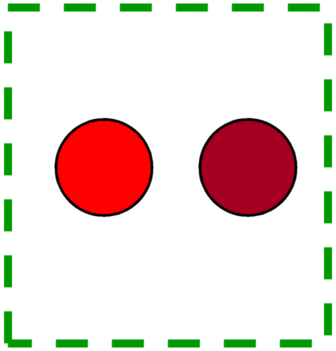
- Gives the type of Bravais lattice (SC, BCC, Hex, etc.)

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

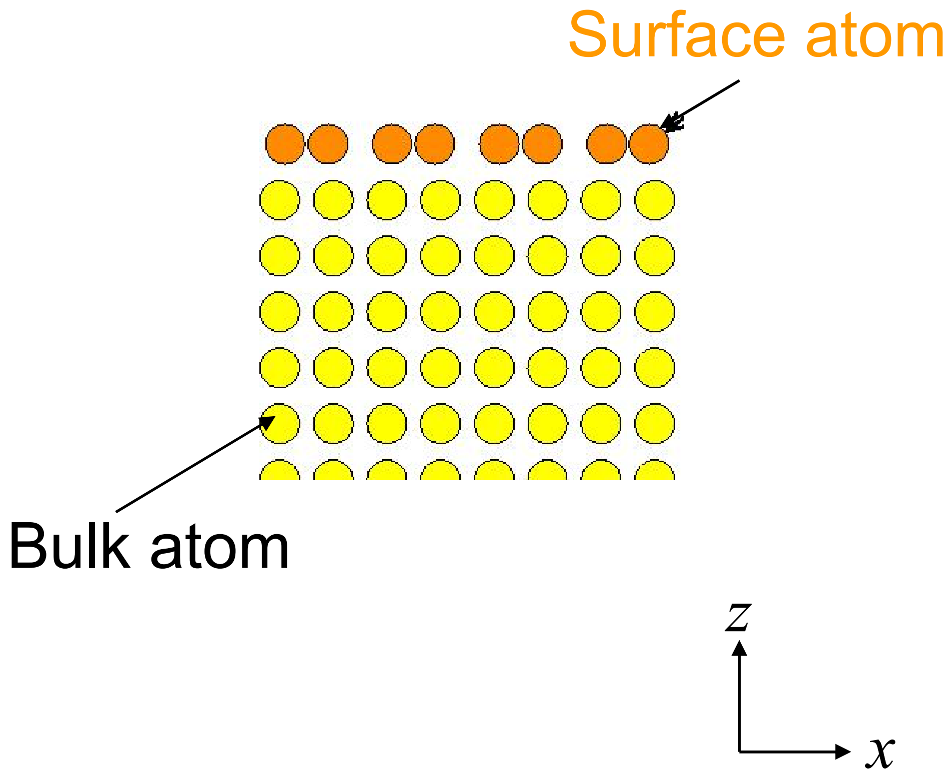
Card : **`ATOMIC_POSITIONS`**

- 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`**")

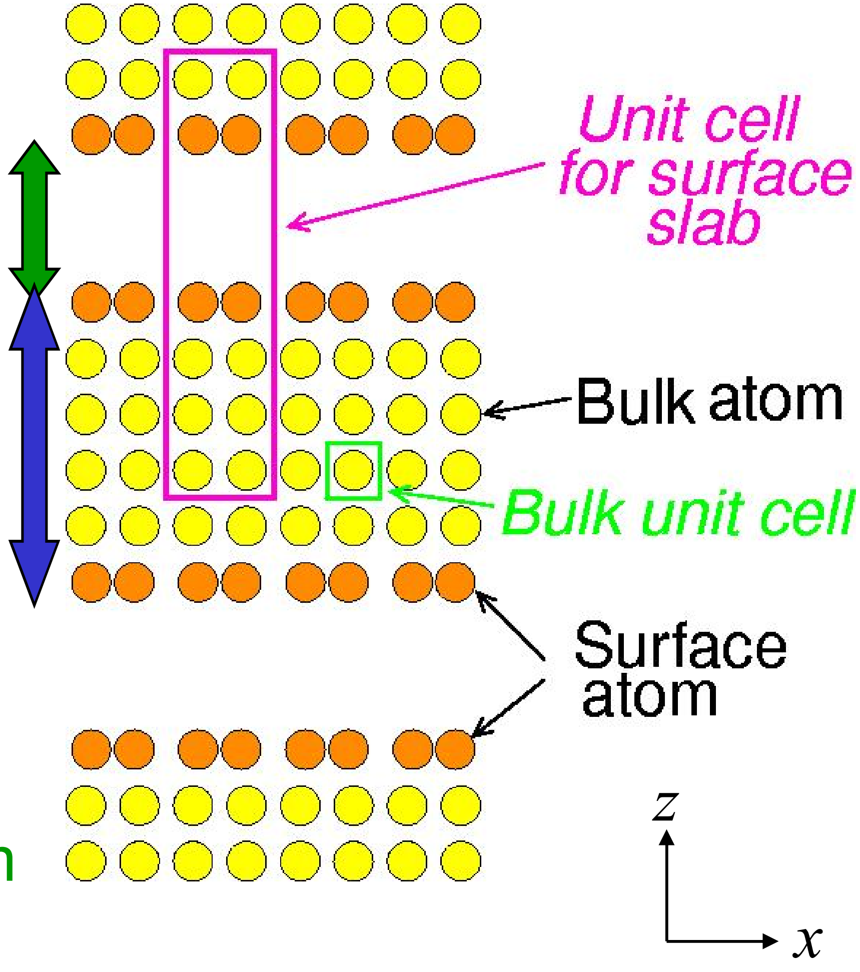
What if the system is not periodic?

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



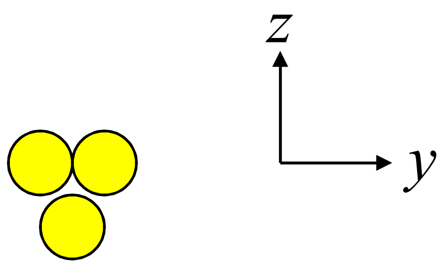
What if the system is not periodic?

- 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.

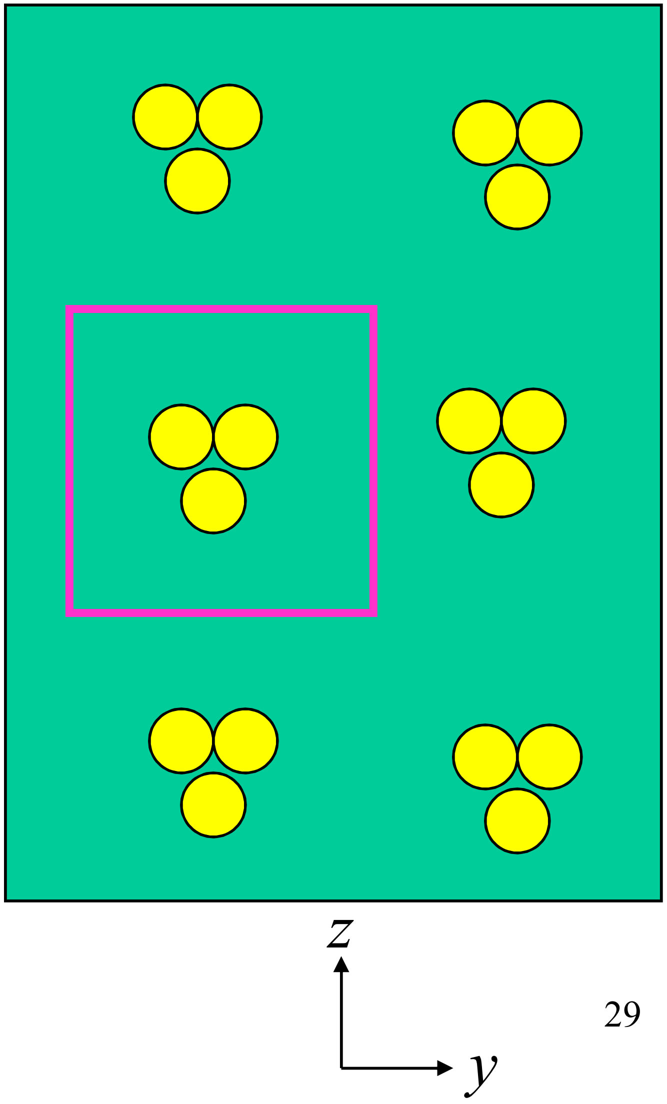


- Example 3: Want to study properties of a cluster

What if the system is not periodic?

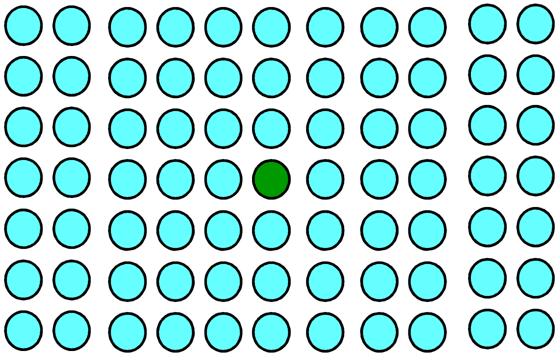
- Example 2: Want to study properties of a nanowire ⇒ introduce artificial periodicity along y & z.

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



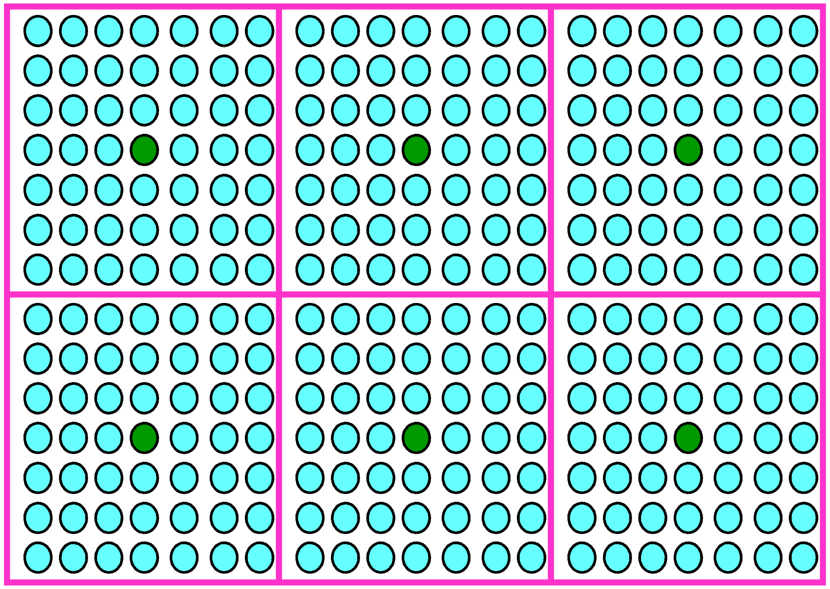
What if the system is not periodic?

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



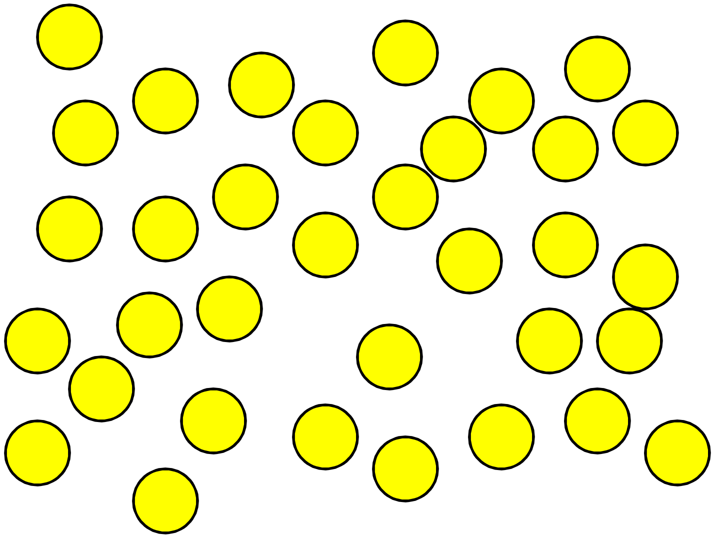
What if the system is not periodic?

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



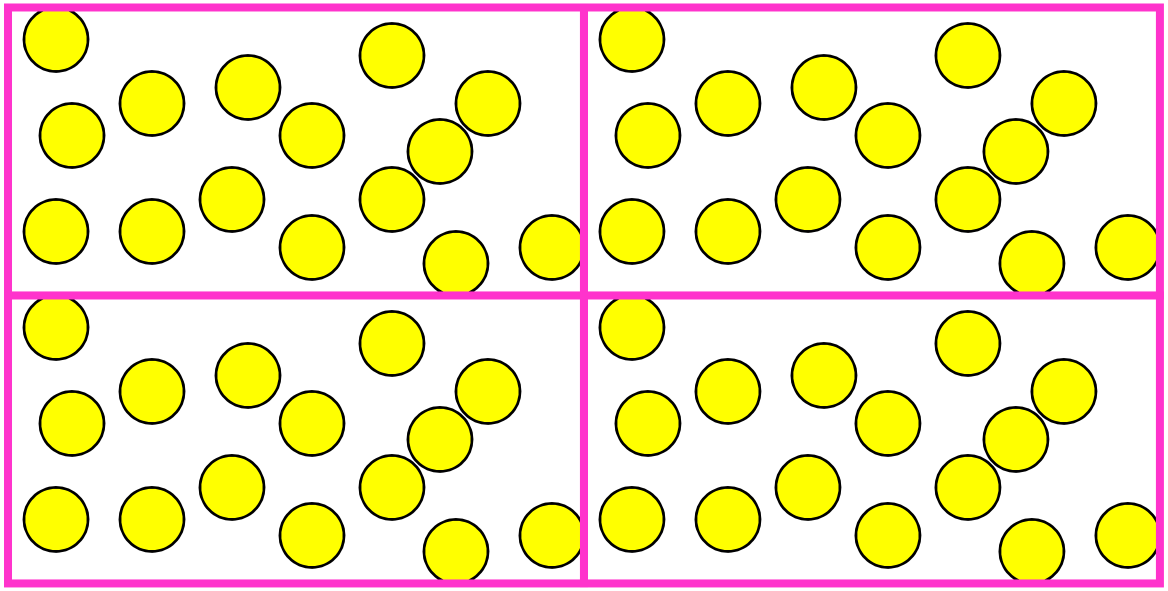
What if the system is not periodic?

- <u>Example 5</u>: 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.

$$\Downarrow$$

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

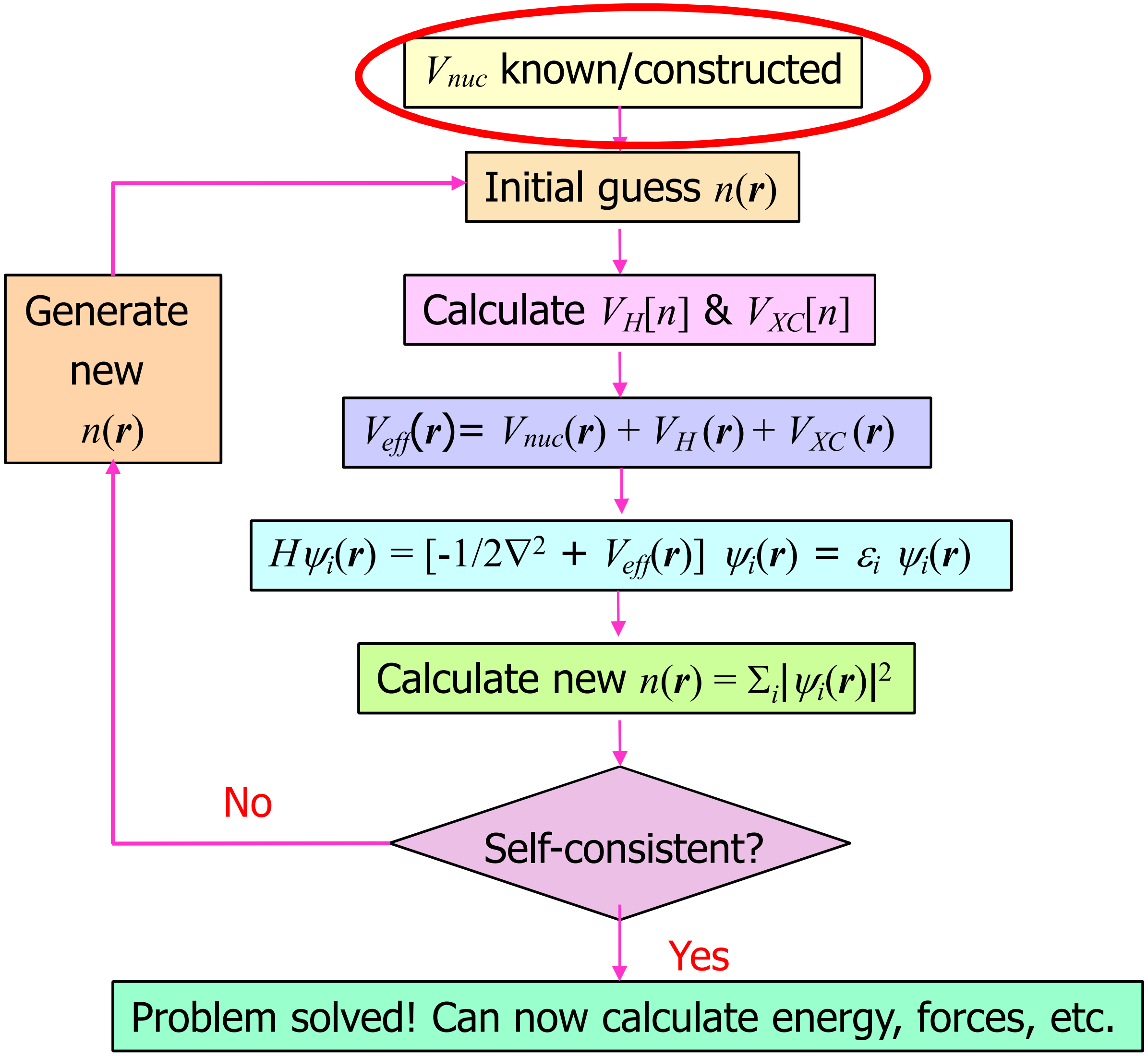
$$\Downarrow$$

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

$$\Downarrow$$

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

Step 1: Obtaining V_{nuc}



V_{nuc} known/constructed

Initial guess $n(\mathbf{r})$

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

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

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

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

Self-consistent?

No

Generate new $n(\mathbf{r})$

Yes

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

Nuclear Potential

- Electrons experience a Coulomb potential due to the nuclei.
- This has a known and simple form:

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

- But this leads to computational problems!

Problem for Plane-Wave Basis

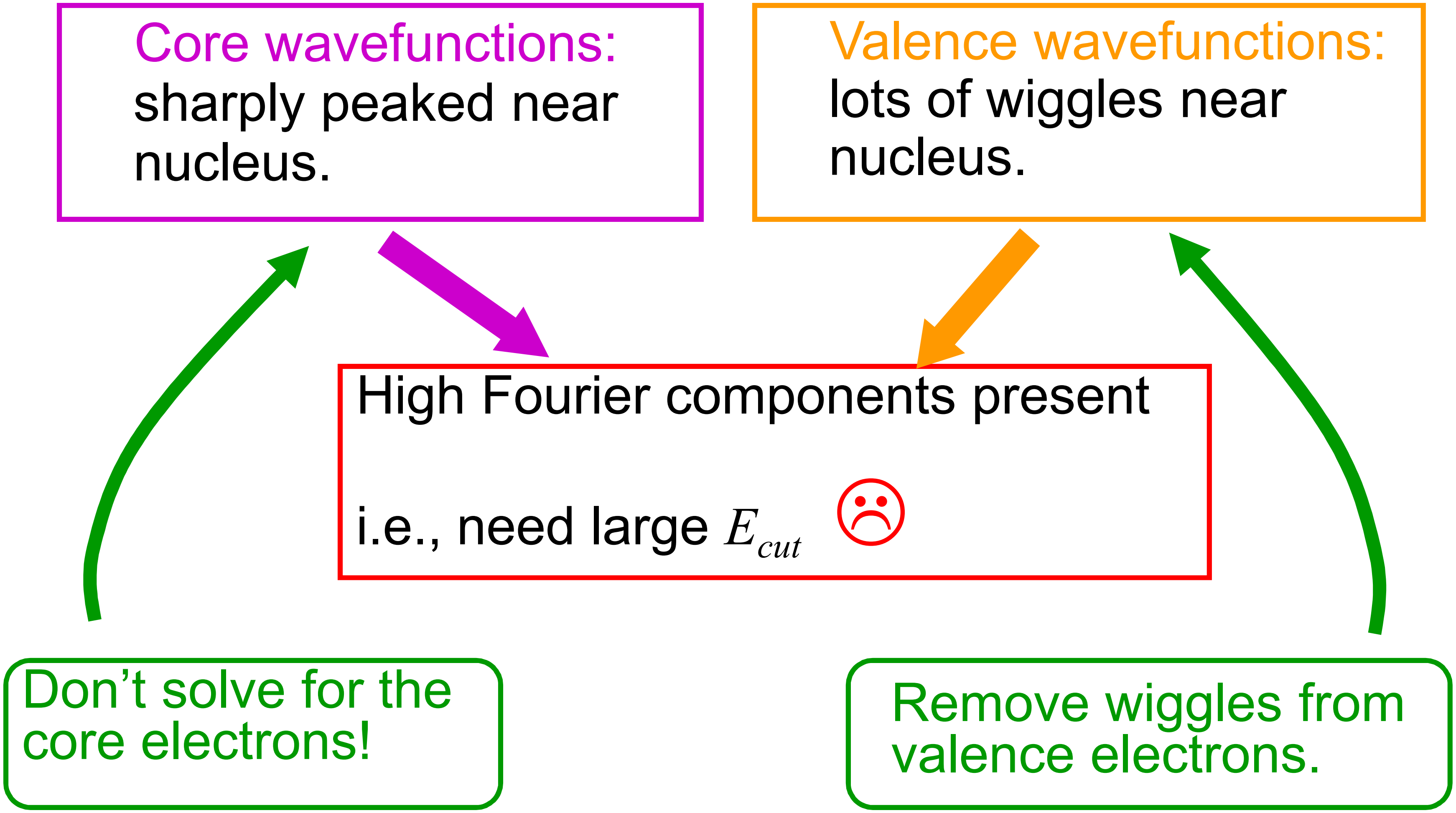
Core wavefunctions:
sharply peaked near
nucleus.

Valence wavefunctions:
lots of wiggles near
nucleus.

High Fourier components present

i.e., need large E_{cut} ☹

Solutions for Plane-Wave Basis



Core wavefunctions: sharply peaked near nucleus.

Valence wavefunctions: lots of wiggles near nucleus.

High Fourier components present

i.e., need large E_{cut} ☹

Don't solve for the core electrons!

Remove wiggles from valence electrons.

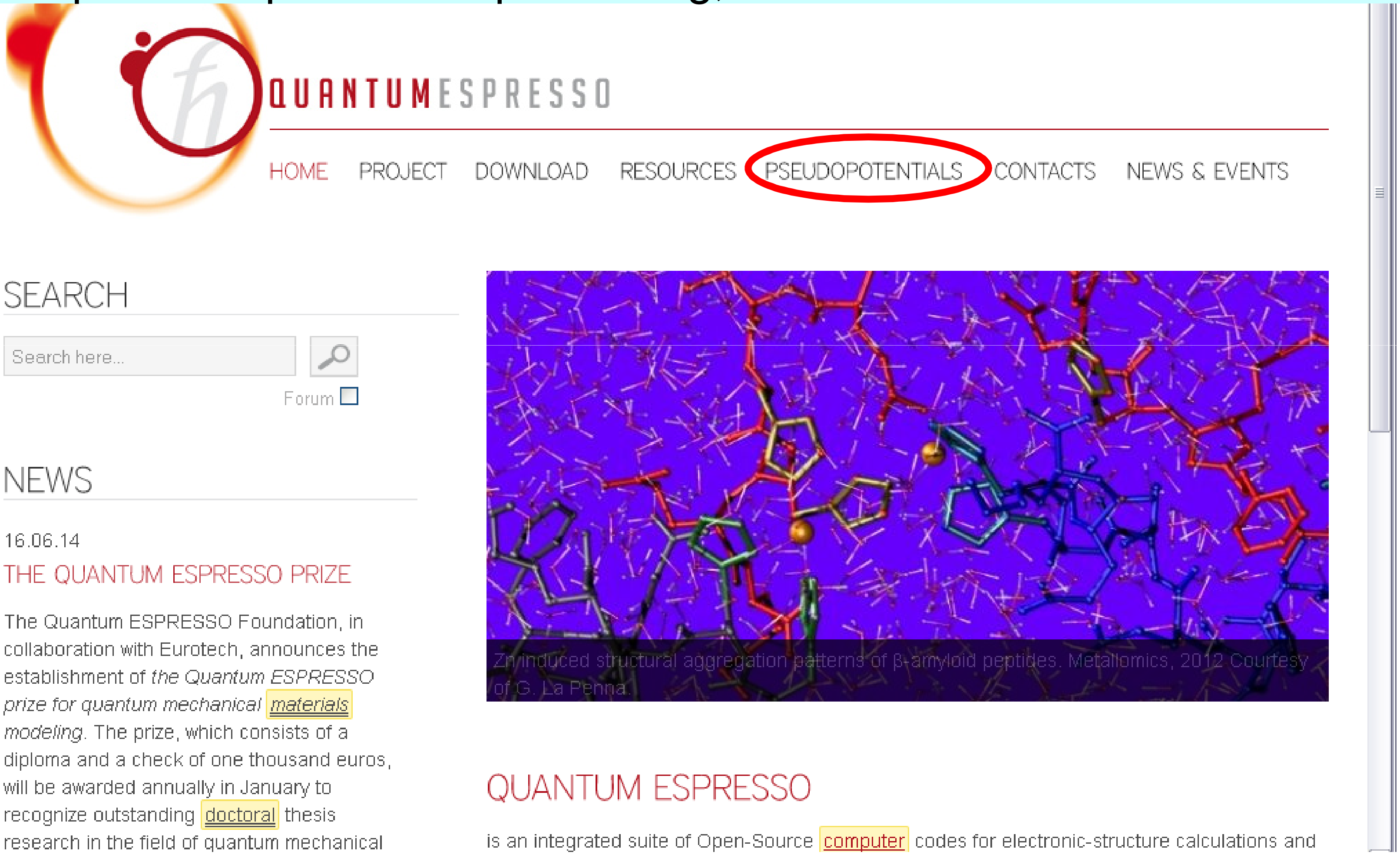
Pseudopotentials

- 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”



NEWS

16.06.14

THE QUANTUM ESPRESSO PRIZE

The Quantum ESPRESSO Foundation, in collaboration with Eurotech, announces the establishment of *the Quantum ESPRESSO prize for quantum mechanical materials modeling*. The prize, which consists of a diploma and a check of one thousand euros, will be awarded annually in January to recognize outstanding doctoral thesis research in the field of quantum mechanical

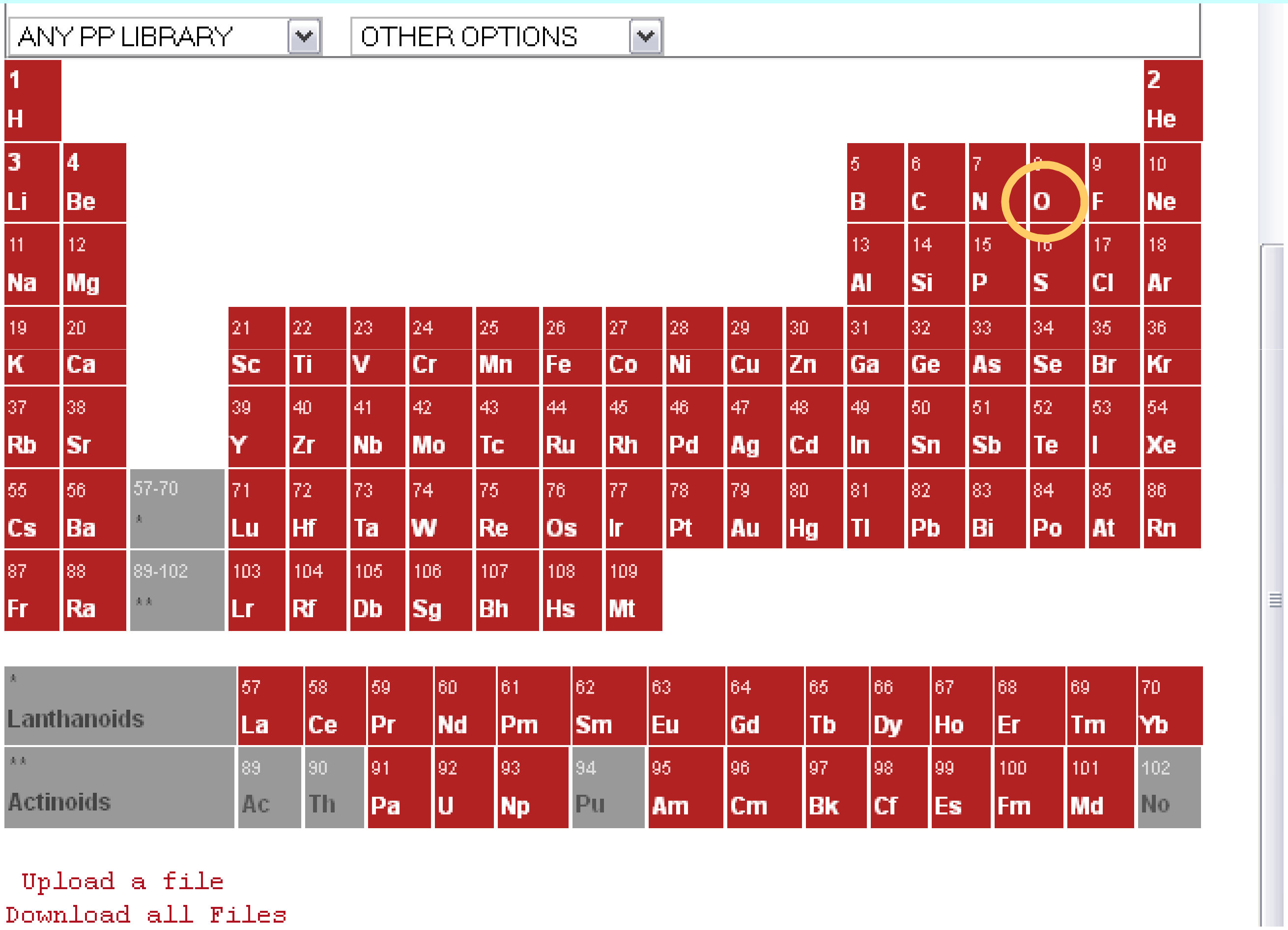
Zn induced structural aggregation patterns of β-amyloid peptides. Metallomics, 2012 Courtesy of G. La Penna

QUANTUM ESPRESSO

is an integrated suite of Open-Source computer codes for electronic-structure calculations and

Pseudopotentials for Quantum Espresso - 2

- Click on element for which pseudopotential wanted.



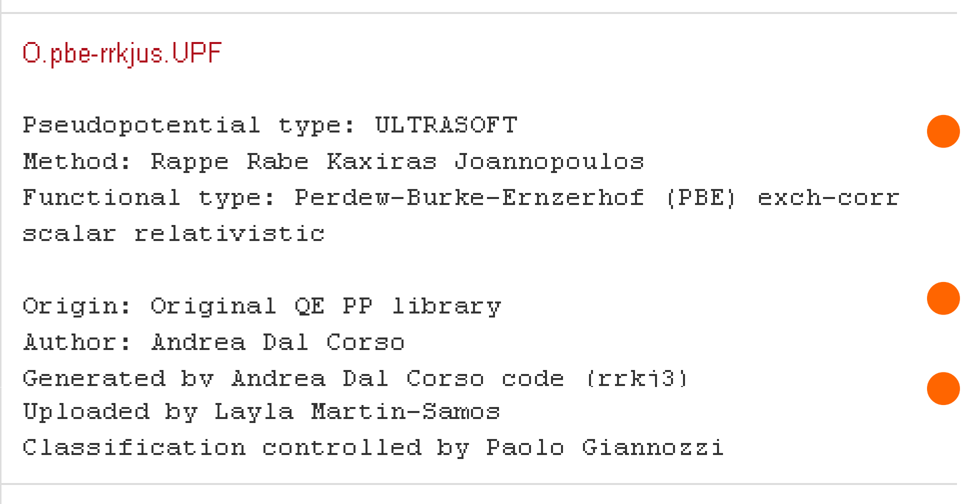
1 H																		2 He
3 Li	4 Be												5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg												13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca		21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr		39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-70 *	71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-102 **	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

* Lanthanoids	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb
** Actinoids	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No

Pseudopotentials for Quantum-ESPRESSO

Pseudopotential's name gives information about :

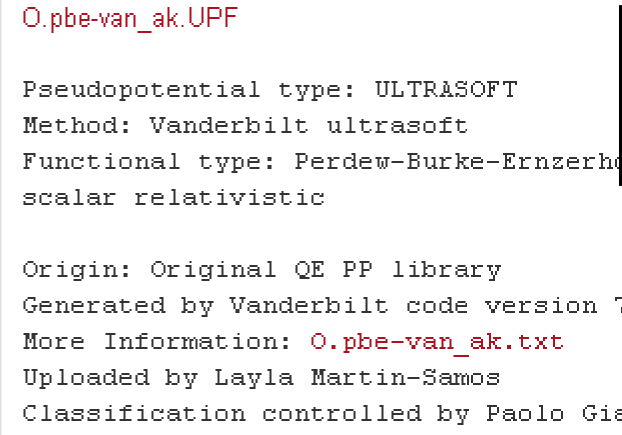
- type of exchange-correlation functional
- type of pseudopotential
- e.g.:



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 (rrkj3)
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-Ernzerho
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

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

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
```

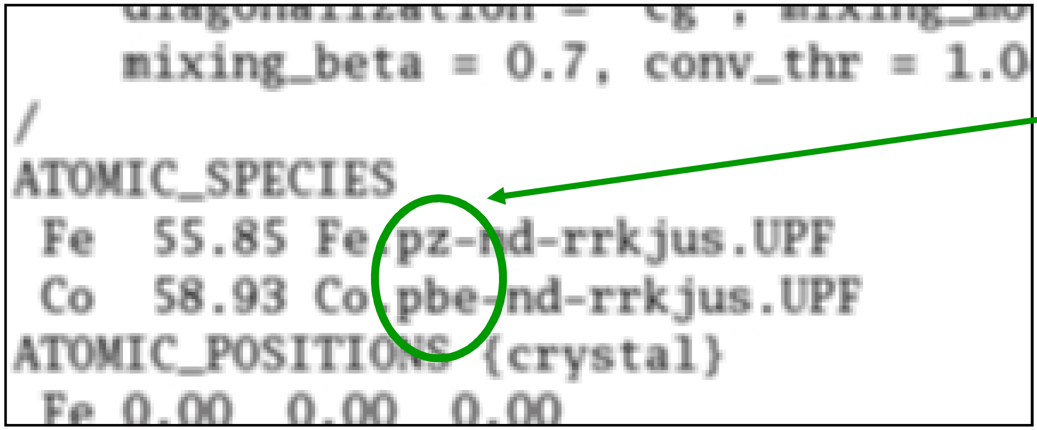
- **`ecutwfc, ecutrho`** depend on type of pseudopotentials used (should test).

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

Element & V_{ion} for Quantum-ESPRESSO

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

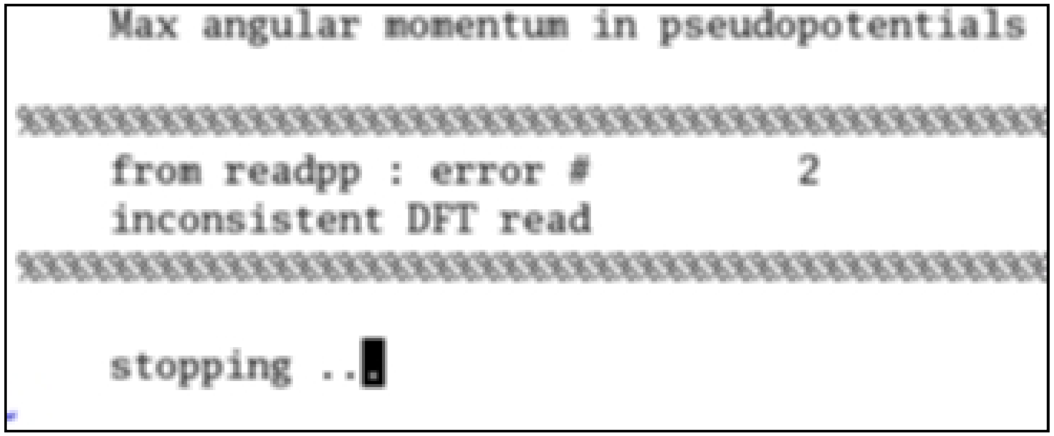
input



```
    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

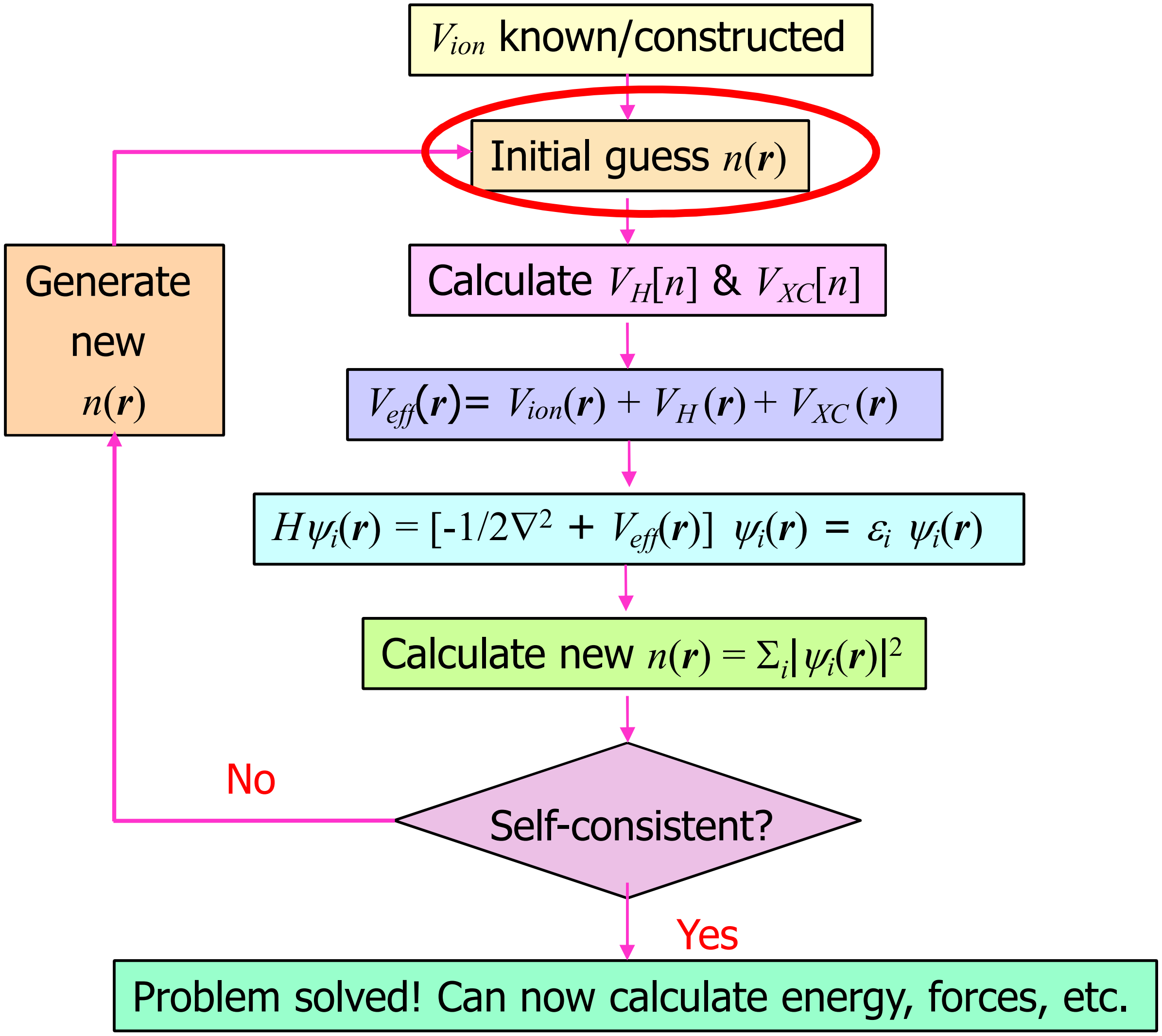


```
     Max angular momentum in pseudopotentials

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

     stopping ...
```

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



V_{ion} known/constructed

Initial guess $n(\mathbf{r})$

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

$V_{eff}(\mathbf{r}) = V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})$

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

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

Self-consistent?

No

Generate new $n(\mathbf{r})$

Yes

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

Starting Wavefunctions

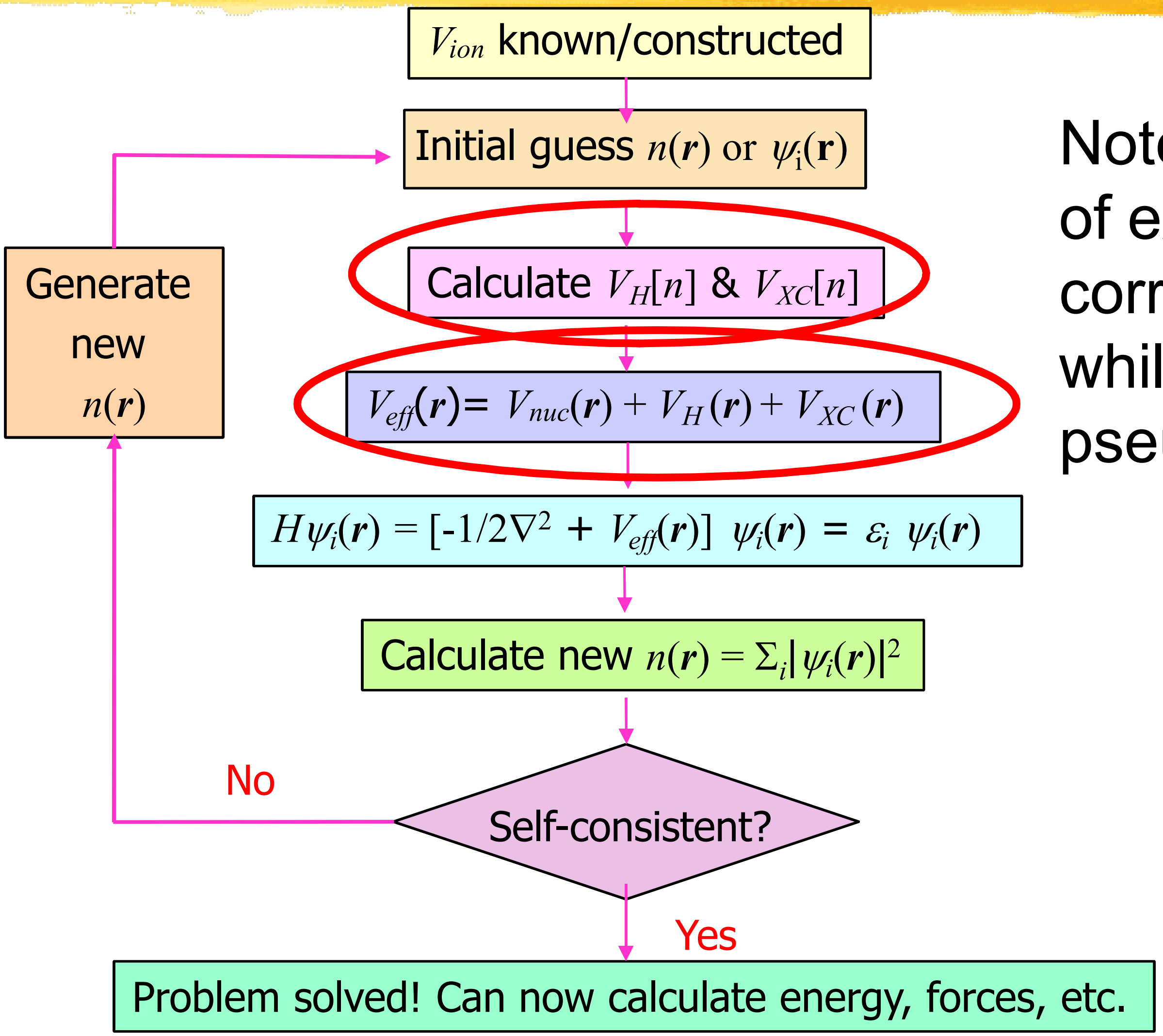
The closer your starting wavefunction is to the true wavefunction (which, of course, is something you don't necessarily know to start with!), the fewer the scf iterations needed.

```
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



V_{ion} known/constructed

Initial guess $n(\mathbf{r})$ or $\psi_i(\mathbf{r})$

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

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

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

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

Self-consistent?

No

Generate new $n(\mathbf{r})$

Yes

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

Note that type of exchange-correlation chosen while specifying pseudopotential

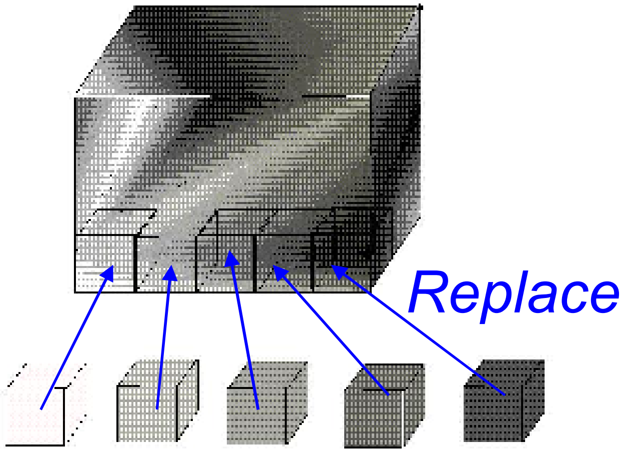
Exchange-Correlation Potential

- $V_{XC} \equiv \delta E_{XC}/\delta n$ 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!

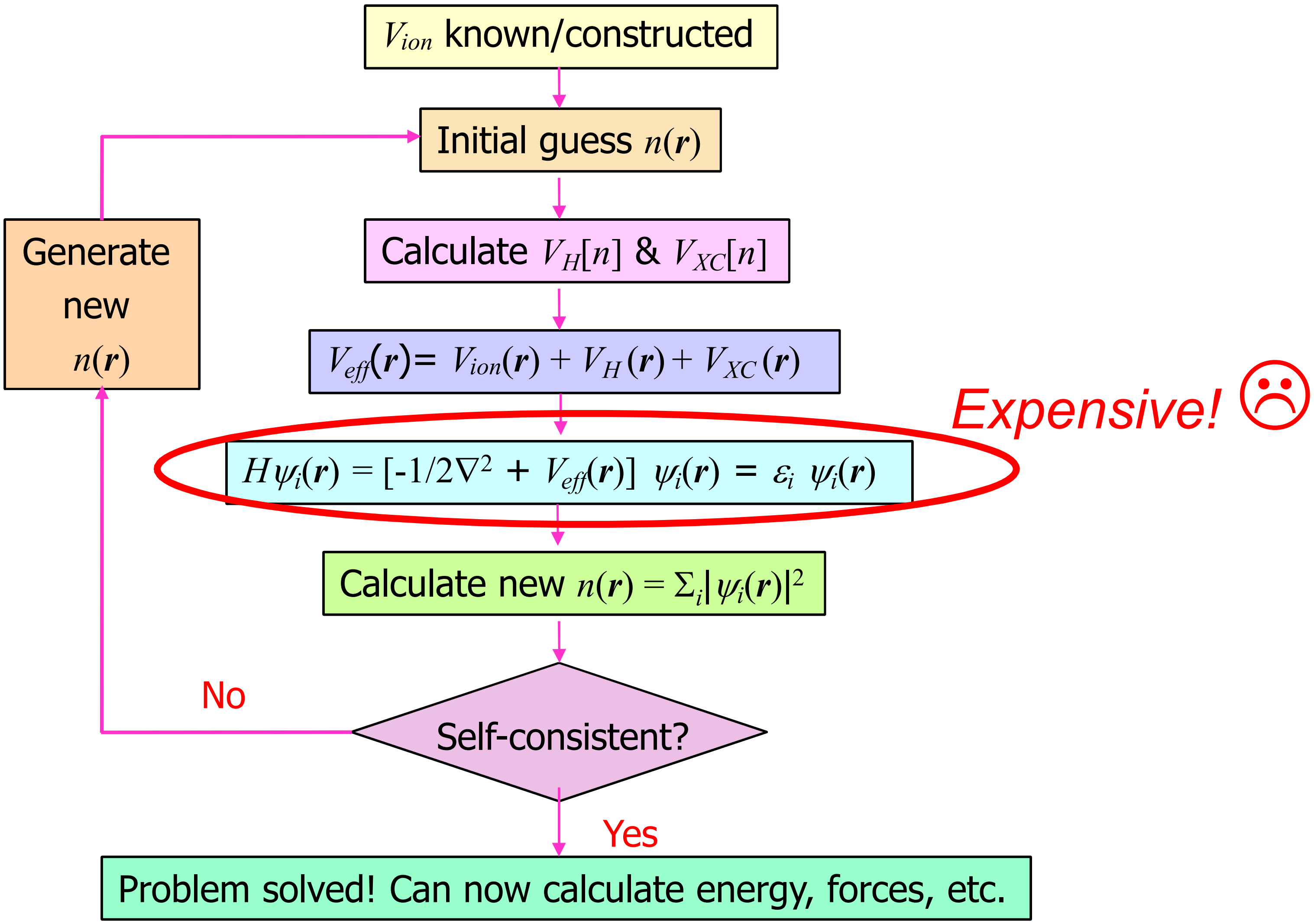
`pz` (in name of pseudopotential)



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

`pw91, pbe` (in name of pseudopotential)

Step 5: Diagonalization



V_{ion} known/constructed

Initial guess $n(\mathbf{r})$

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

$V_{eff}(\mathbf{r}) = V_{ion}(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})$

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

Expensive! ☹

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

Self-consistent?

No

Generate new $n(\mathbf{r})$

Yes

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

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.

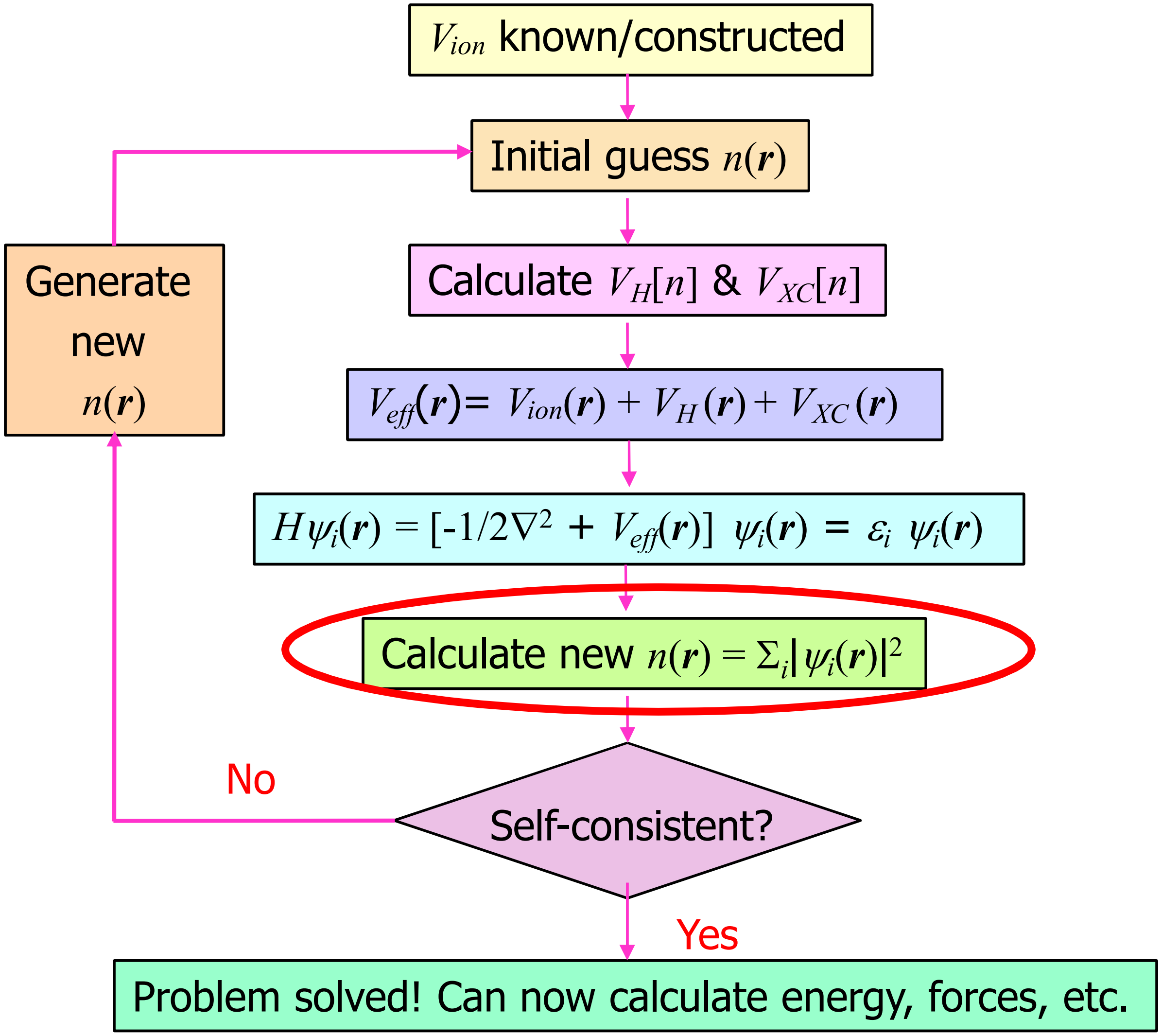
Input parameter **`diagonalization`**

-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



V_{ion} known/constructed

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

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No

Generate new $n(\mathbf{r})$

Yes

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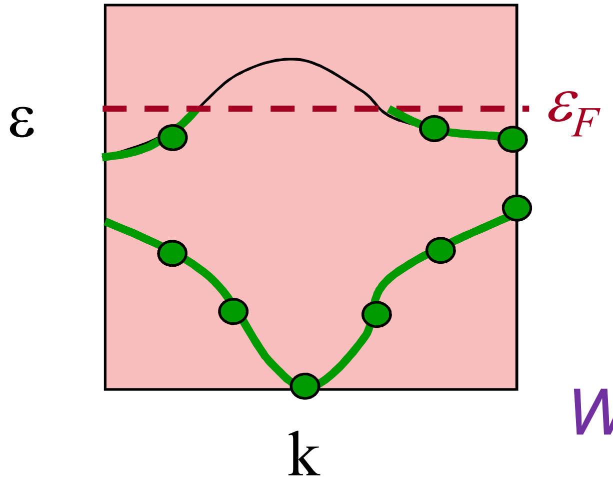
Brillouin Zone Sums

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

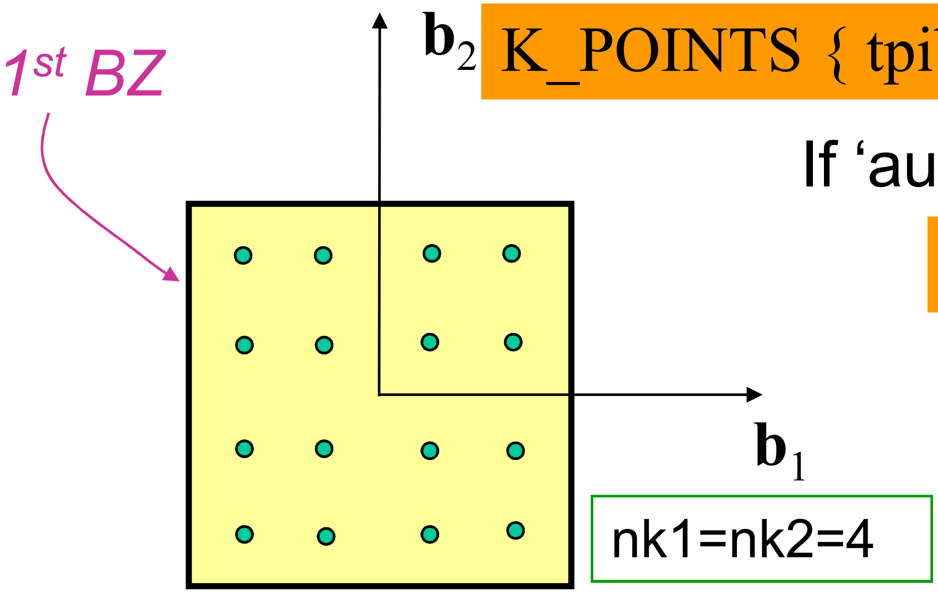


$$\langle P \rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k} \in BZ} P(\mathbf{k}) w_{\mathbf{k}}$$

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']

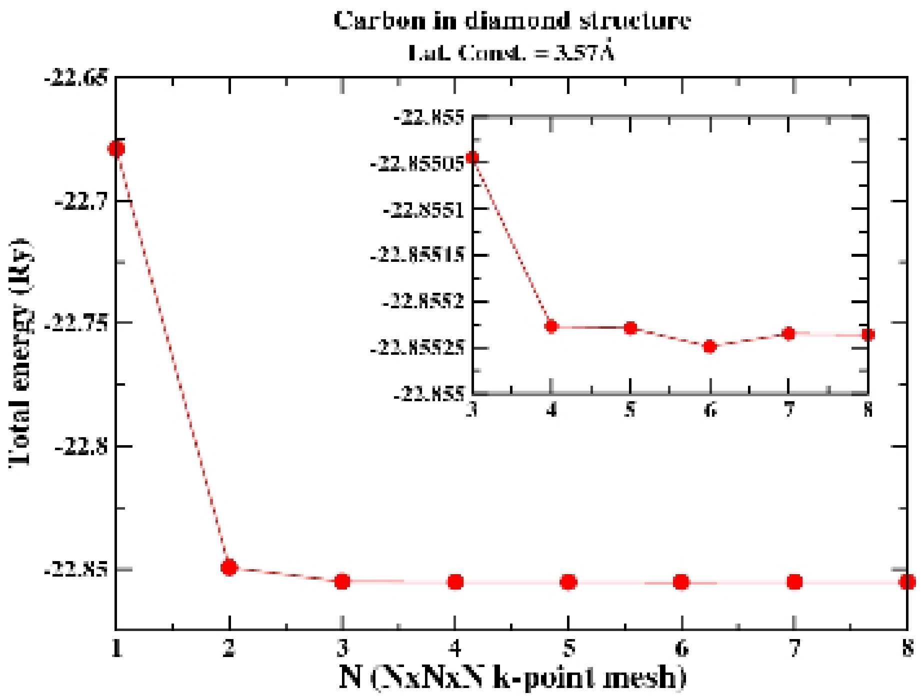


K_POINTS { tpiba | automatic | crystal | gamma }

If 'automatic', use M-P mesh:

$$\text{nk1, nk2, nk3, }\underbrace{\text{k1, k2, k3}}_{\text{shift}}$$

Convergence wrt BZ sampling

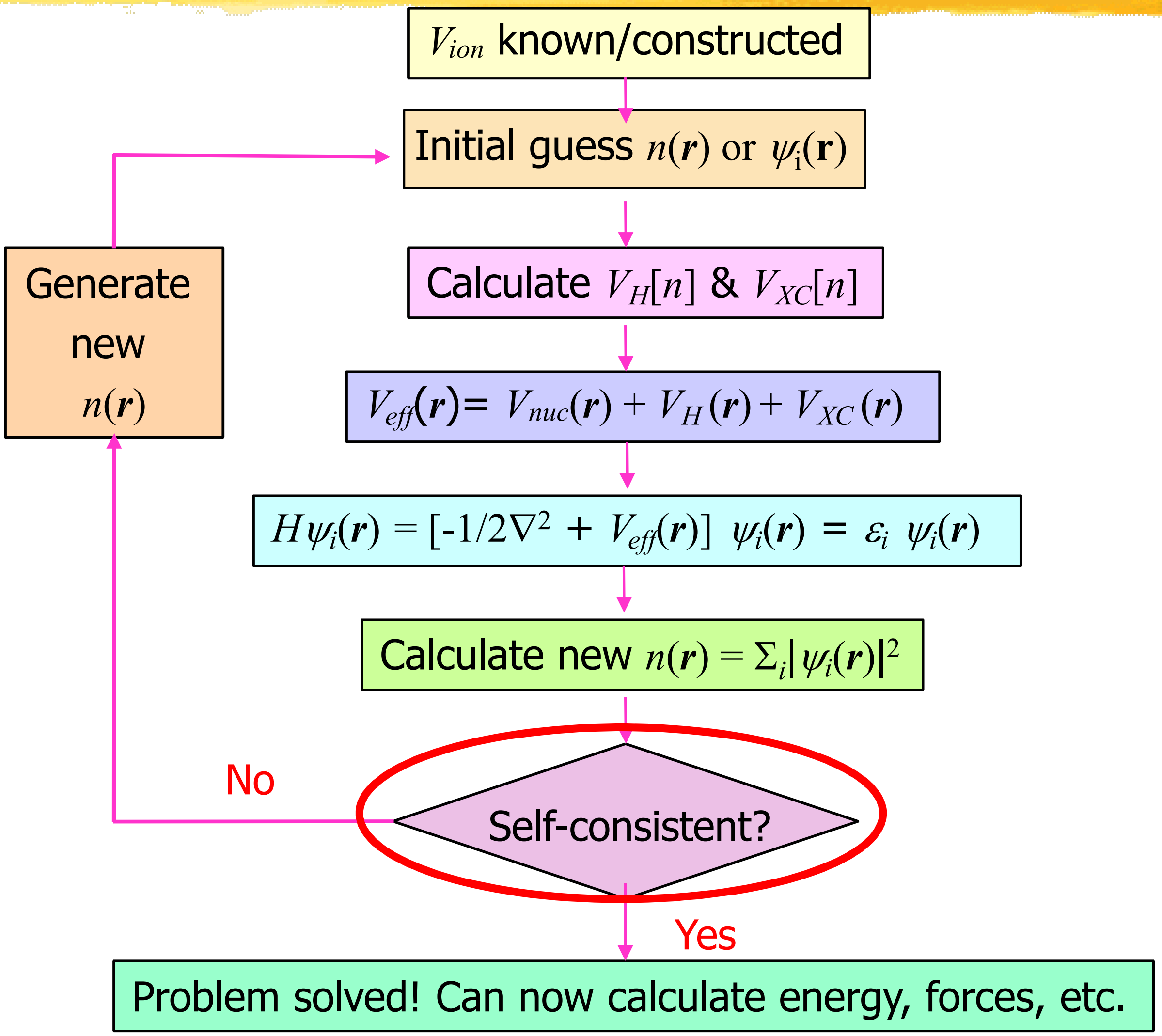

Carbon in diamond structure

Lat. Const. = 3.57Å

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



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

Self-consistent?

No

Generate new $n(\boldsymbol{r})$

Yes

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

Testing for scf convergence

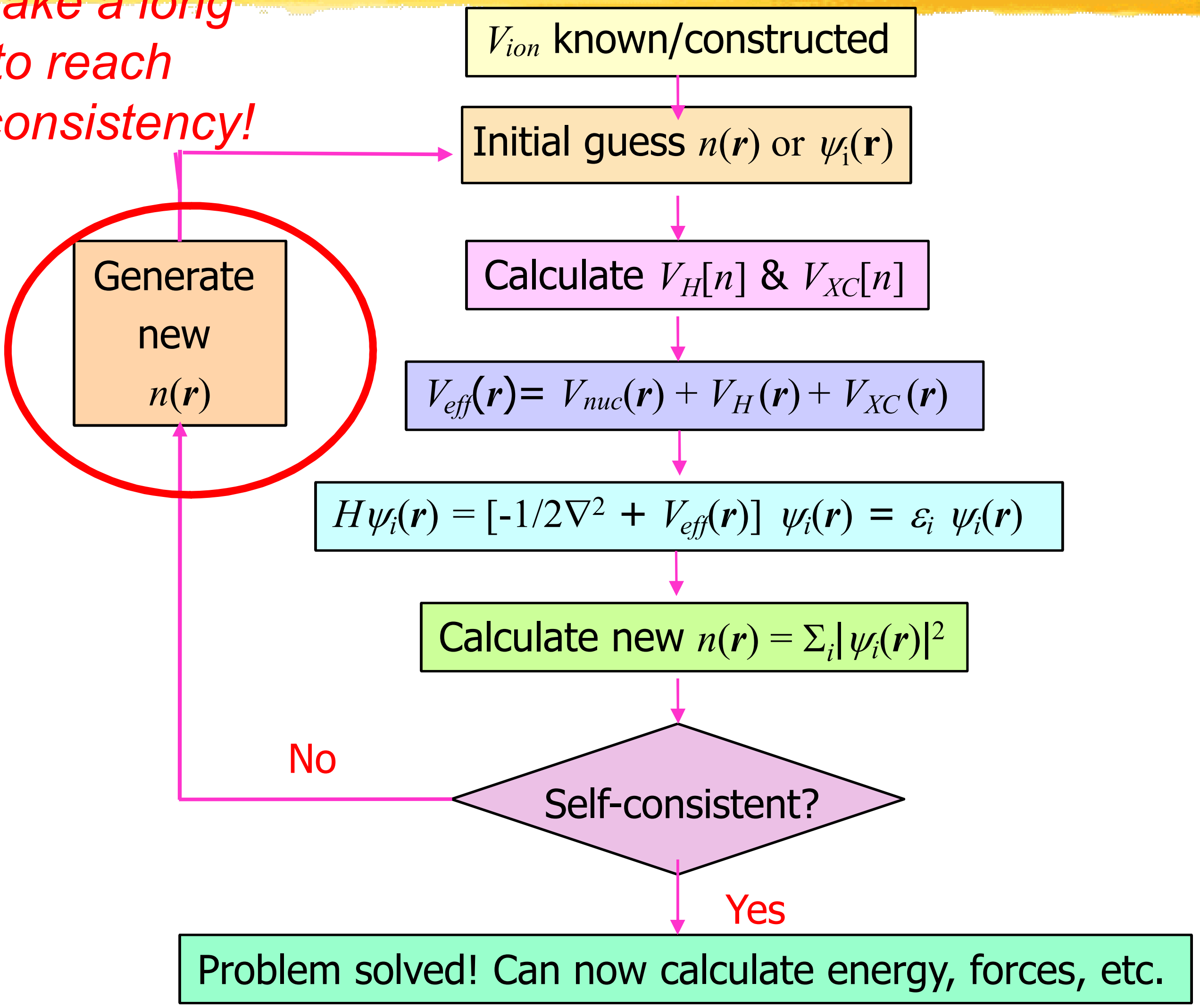
- Compare nth and (n-1)th approximations for density, and see if they are close enough that self-consistency has been achieved.

Input parameter **`conv_thr`**

Step 8: Mixing

Can take a long time to reach self-consistency!

☹



V_{ion} known/constructed

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

Self-consistent?

No

Generate new $n(\boldsymbol{r})$

Yes

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

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`**

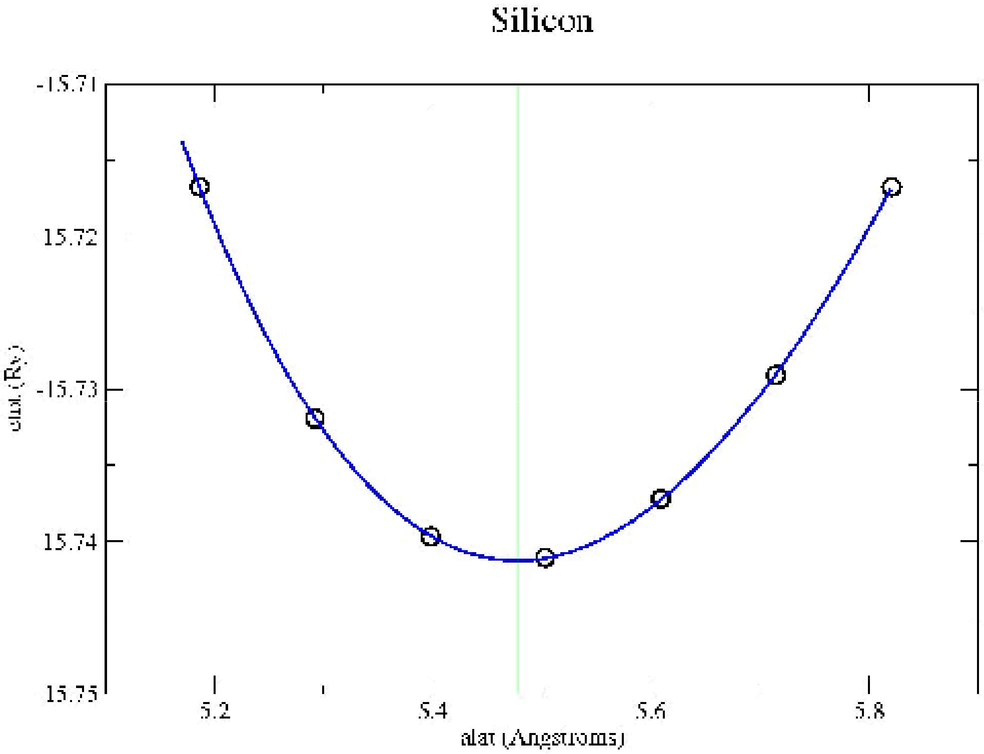
-Prescription used for mixing.

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!