



The Abdus Salam
International Centre for Theoretical Physics



2221-5

Hands-on Tutorial on Electronic Structure Computations

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**The "Self Consistent Field" (SCF) Loop
and Some Relevant Input Parameters for Quantum-ESPRESSO**

Shobhana Narasimhan
*Jawaharlal Nehru Centre for Advanced Scientific Research
Bangalore
India*

The “Self Consistent Field” (SCF) Loop and Some Relevant Input Parameters for Quantum-ESPRESSO



Shobhana Narasimhan
Theoretical Sciences Unit
JNCASR, Bangalore
shobhana@jncasr.ac.in

First Some Very Personal Questions...

- Are you an experienced Quantum Espresso user?

Yes

- Are you an extraordinarily nice person?

No.

PLEASE GO AWAY!



First Some Very Personal Questions...

- Are you an experienced Quantum Espresso user?

Yes

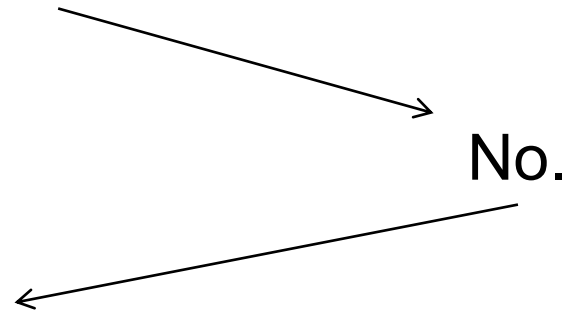
- Are you an extraordinarily nice person?

Yes

It would be really nice if you could stick around here and help with the hands-on session....

First Some Very Personal Questions...

- Are you an experienced Quantum Espresso user?



Then this session is aimed at YOU!

(But we are assuming that you are familiar with electronic structure calculations, linux commands, etc., etc.)

The Kohn-Sham problem

- Want to solve the Kohn-Sham equations:

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

H

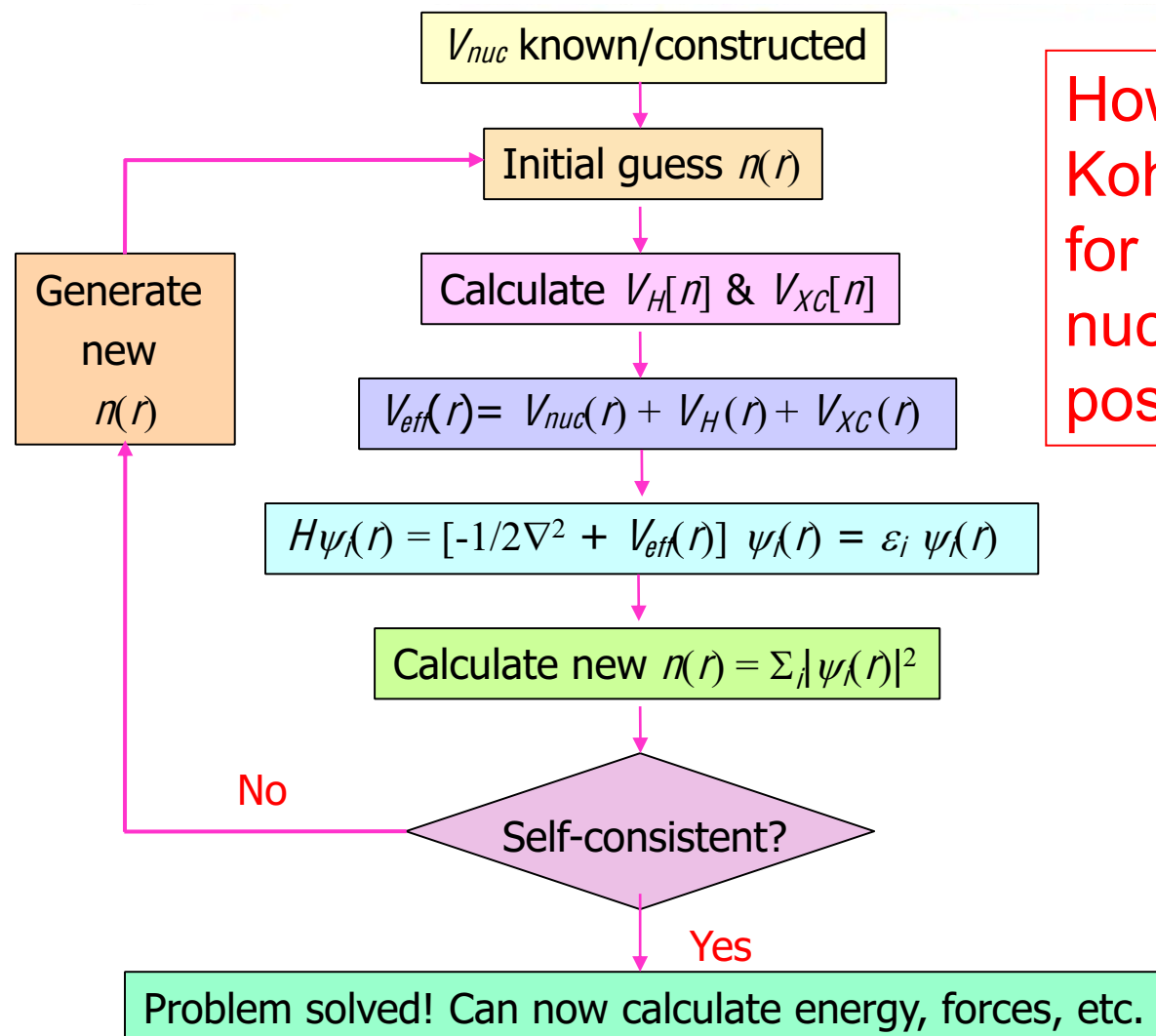
- Note that **self-consistent solution** necessary, as H depends on solution:

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

- 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.

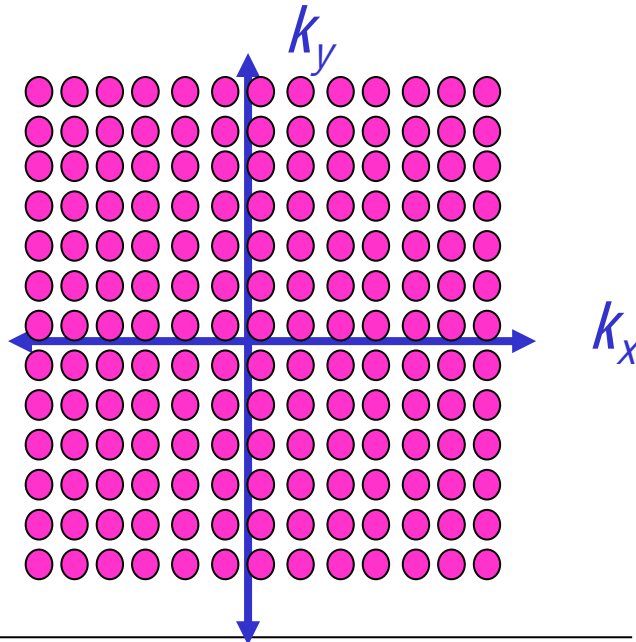
Plane Waves & Periodic Systems

- For a periodic system:

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

where \mathbf{G} = reciprocal lattice vector

- The **plane waves** that appear in this expansion can be represented as a grid in \mathbf{k} -space:



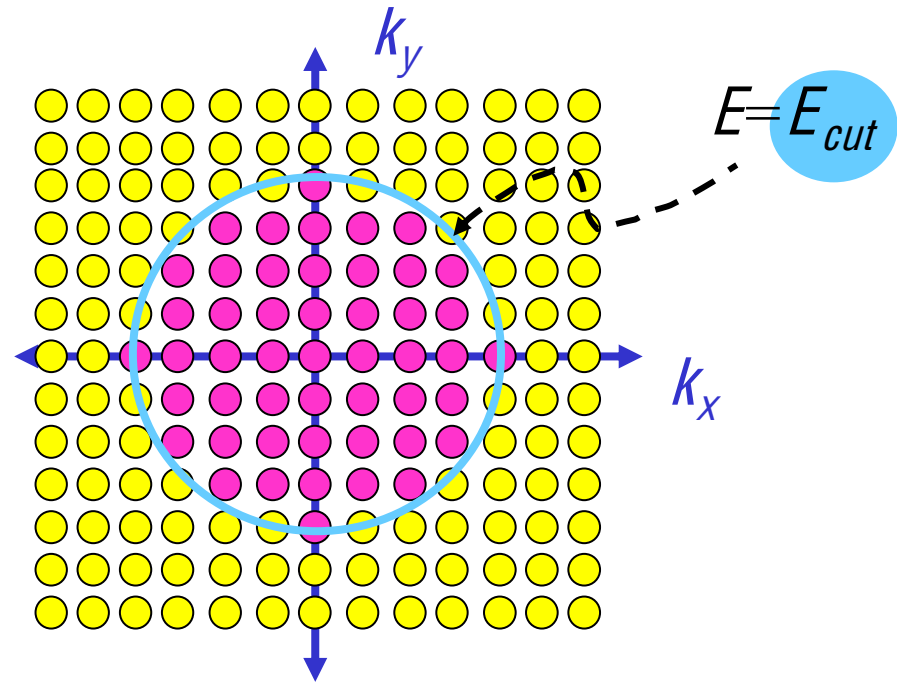
- Only true for periodic systems that grid is discrete.
- In principle, still need **infinite number of plane waves**.

Truncating the Plane Wave Expansion

- In practice, the contribution from higher Fourier components (large $|k+G|$) is small.
- So truncate the expansion at some value of $|k+G|$.
- Traditional to express this cut-off in energy units:

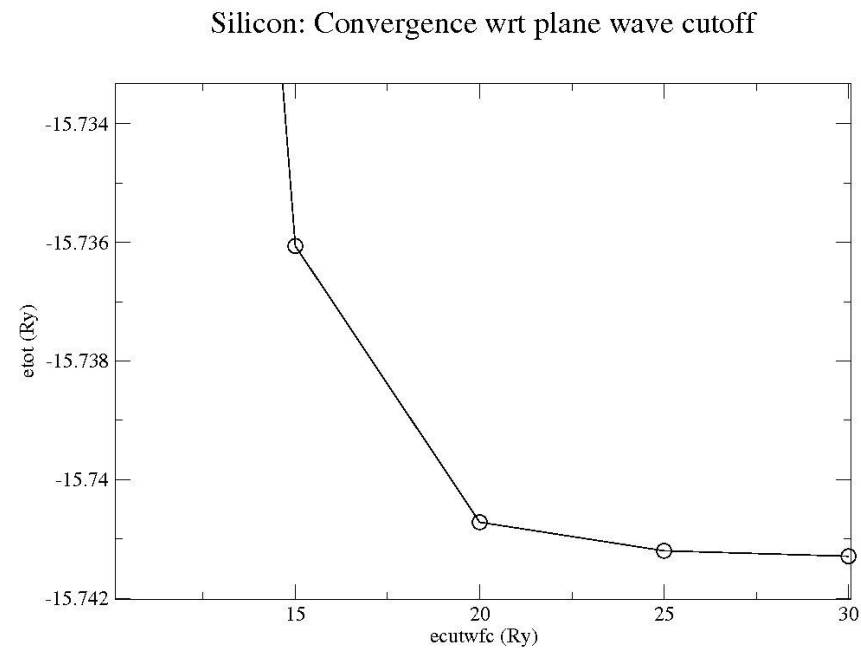
$$\frac{\hbar^2 |k + G|^2}{2m} \leq E_{cut}$$

Input parameter **ecutwfc**




Checking Convergence wrt ecutwfc

- Must always check.
- Monotonic (variational).



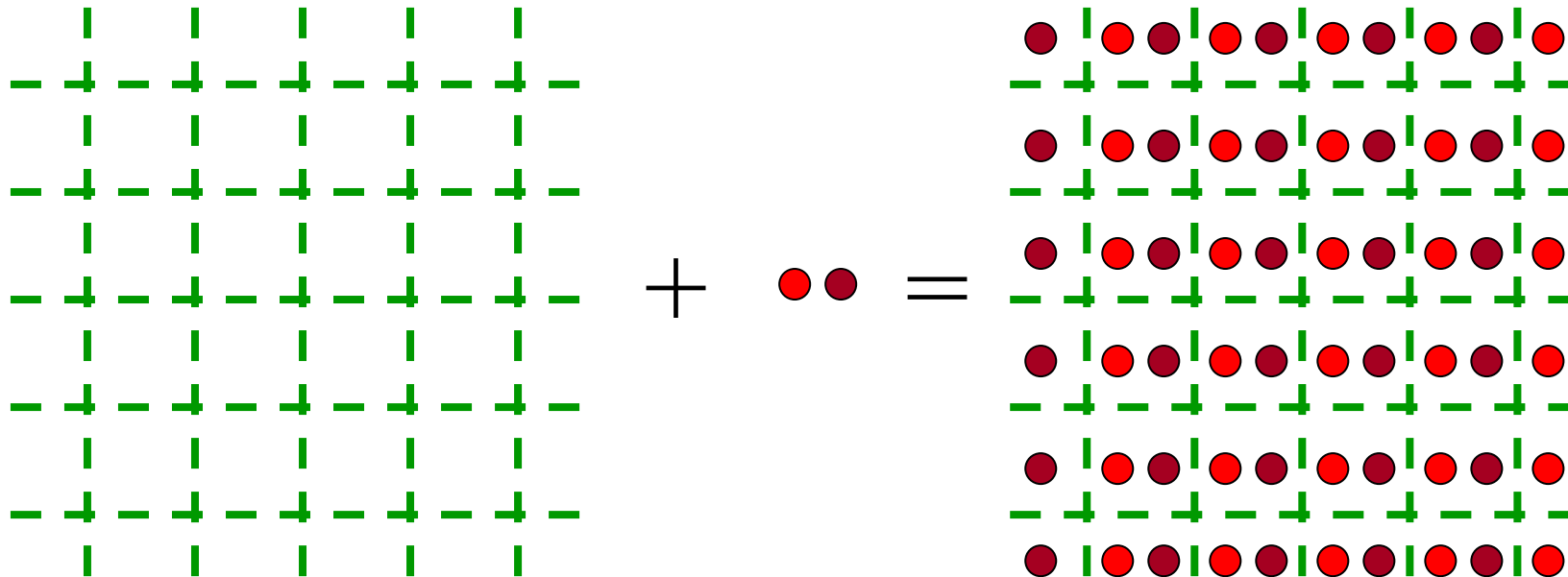
Step 0: Defining the (periodic) system



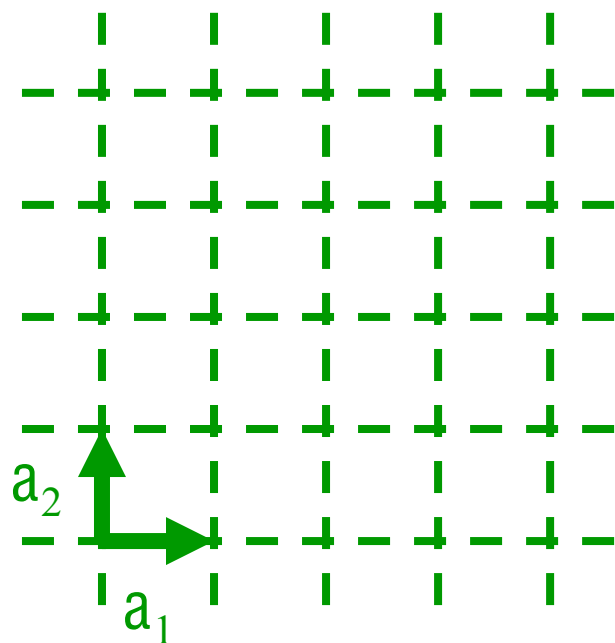
Namelist '**SYSTEM**'

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**

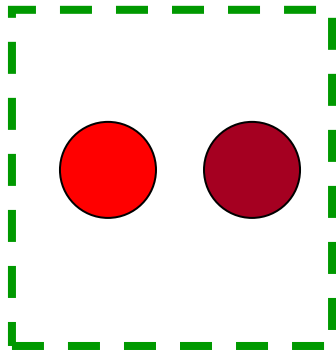
- Gives the type of **Bravais lattice** (SC, BCC, Hex, etc.)

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

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

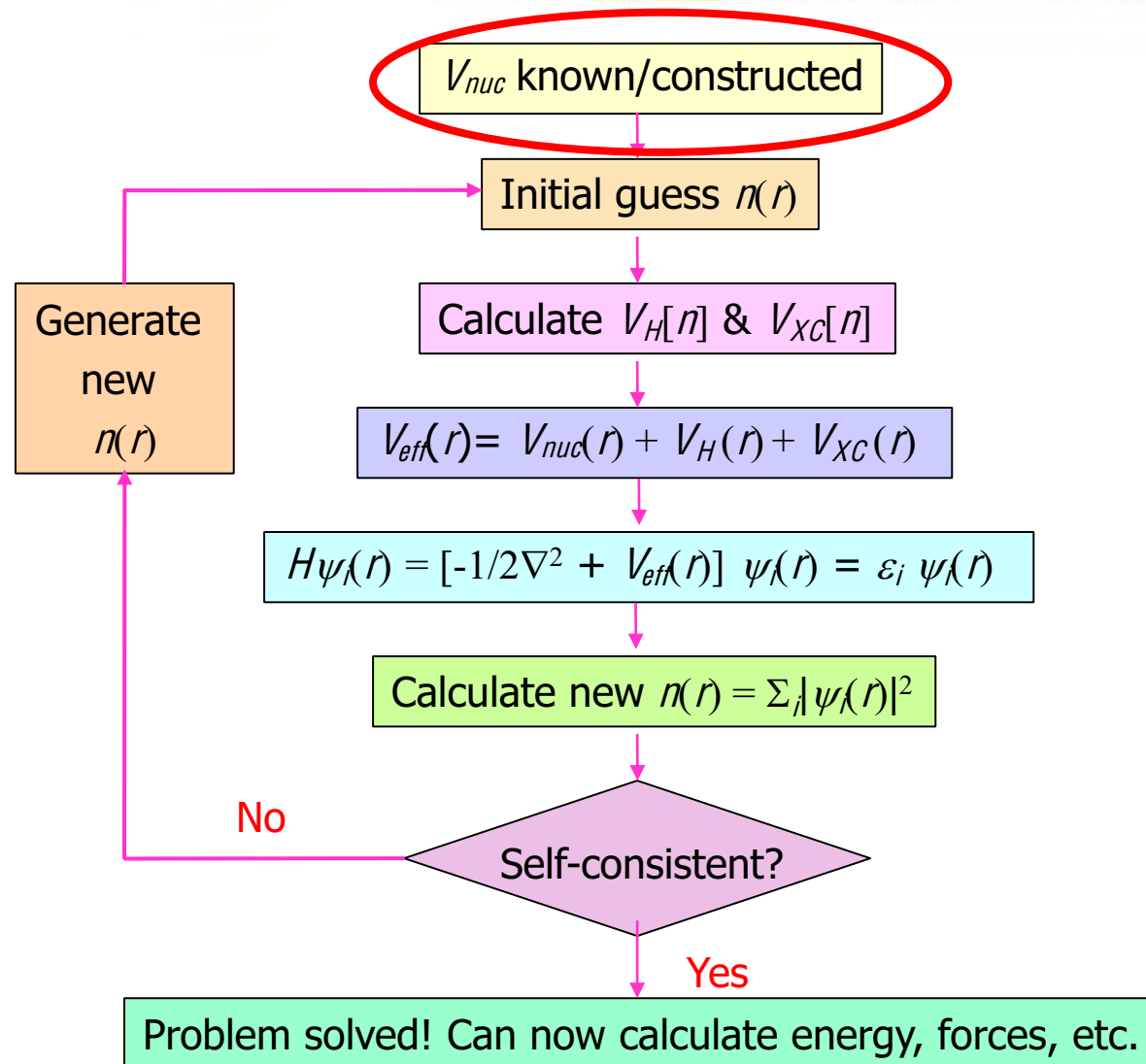
Input parameter **ntyp**

- Number of types of atoms

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**”)

Step 1: Obtaining V_{nuc}



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

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.

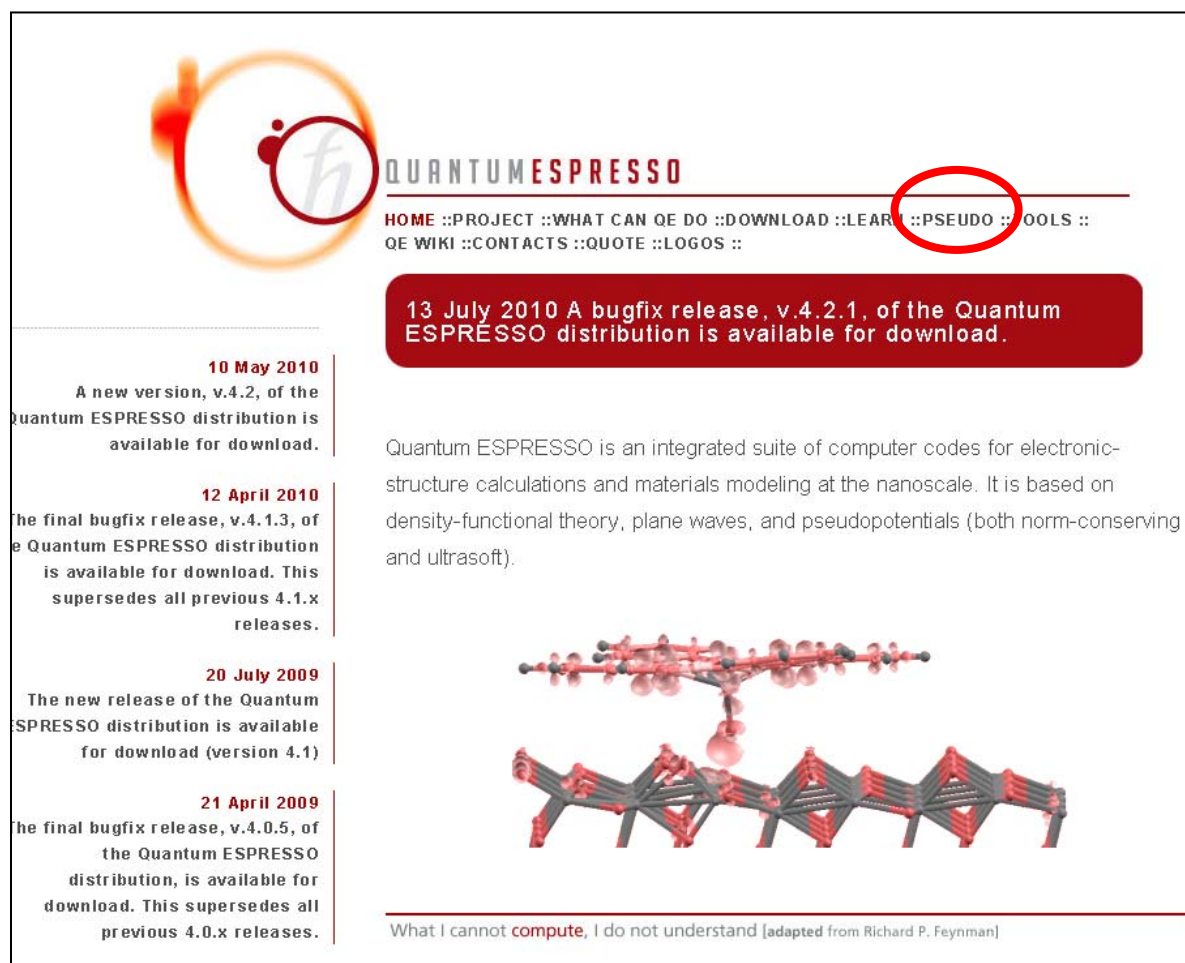
Pseudopotentials




- 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.

Pseudopotentials for Quantum Espresso - 1

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



 **QUANTUM ESPRESSO**

HOME :: PROJECT :: WHAT CAN QE DO :: DOWNLOAD :: LEARN :: **PSEUDO** :: TOOLS ::
QE WIKI :: CONTACTS :: QUOTE :: LOGOS ::

13 July 2010 A bugfix release, v.4.2.1, of the Quantum ESPRESSO distribution is available for download.

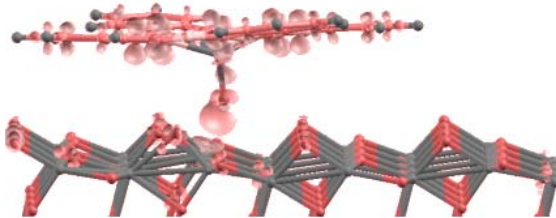
10 May 2010
A new version, v.4.2, of the Quantum ESPRESSO distribution is available for download.

12 April 2010
The final bugfix release, v.4.1.3, of the Quantum ESPRESSO distribution is available for download. This supersedes all previous 4.1.x releases.

20 July 2009
The new release of the Quantum ESPRESSO distribution is available for download (version 4.1)

21 April 2009
The final bugfix release, v.4.0.5, of the Quantum ESPRESSO distribution, is available for download. This supersedes all previous 4.0.x releases.

Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling at the nanoscale. It is based on density-functional theory, plane waves, and pseudopotentials (both norm-conserving and ultrasoft).



What I cannot compute, I do not understand [adapted from Richard P. Feynman]

Pseudopotentials for Quantum Espresso - 2

- Click on element for which pseudopotential wanted.

QUANTUM ESPRESSO

HOME :: PROJECT :: WHAT CAN QE DO :: DOWNLOAD :: LEARN :: **PSEUDO** :: TOOLS ::
QE WIKI :: CONTACTS :: QUOTE :: LOGOS ::

PSEUDOPOTENTIALS

Updated: Sat, 14 Aug 2010 21:16:03 CEST

◦ About
◦ Notes

| | | | | | | | | | | | | | | | | | | |
|------------------|----------|--------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|----------|----------|----------|-----------|-----------|-----------|----------|----------|
| 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 | | |

[Download the full archive \(~30MB\)](#)

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)

Element & V_{ion} for Quantum-ESPRESSO

e.g, for calculation on BaTiO₃:

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

```
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
```

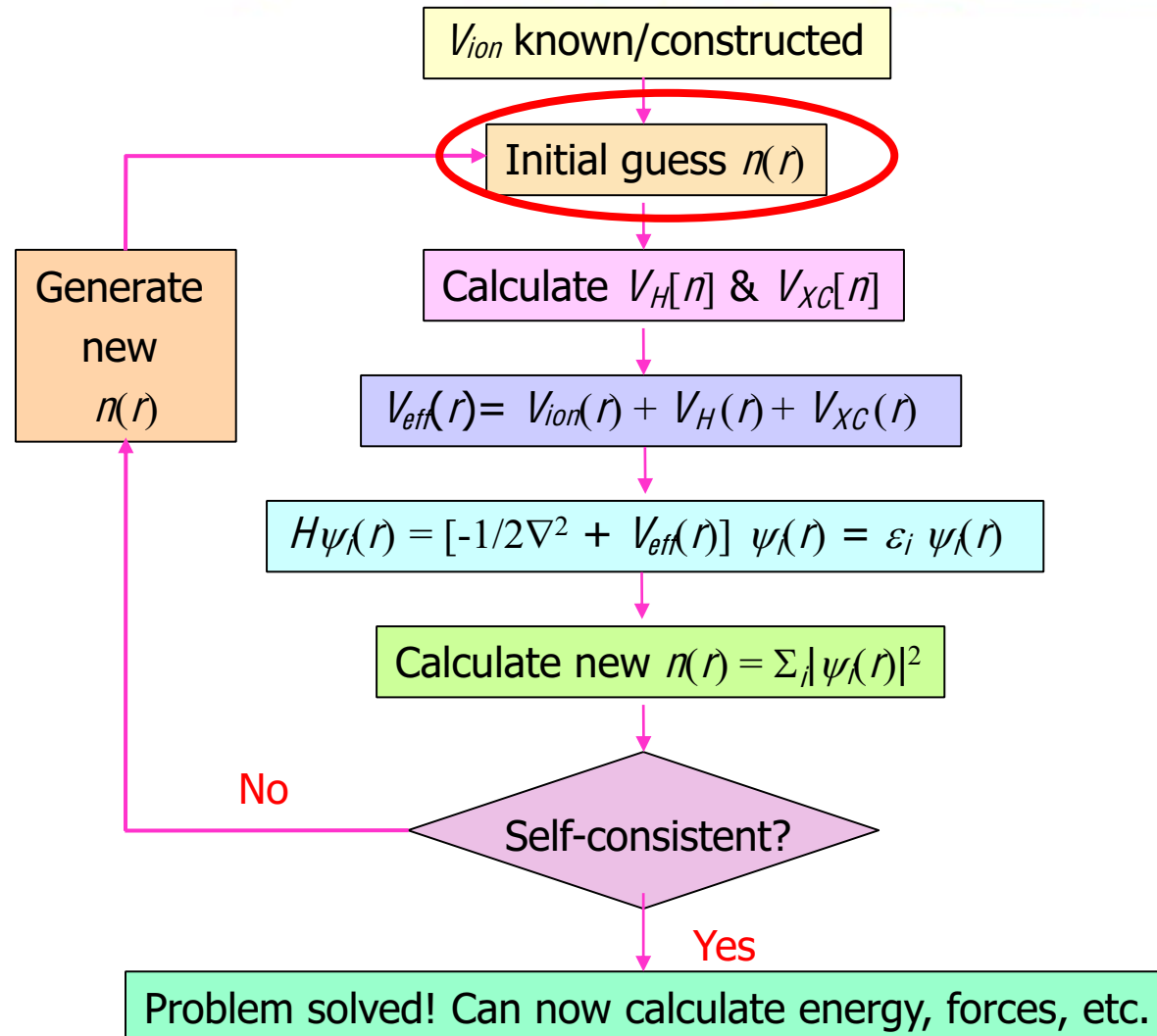
oops!

output

```
Max angular momentum in pseudopotentials
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
from readpp : error #          2
inconsistent DFT read
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

stopping ..█
```


Step 2: Initial Guess for $n(r)$



Starting Wavefunctions

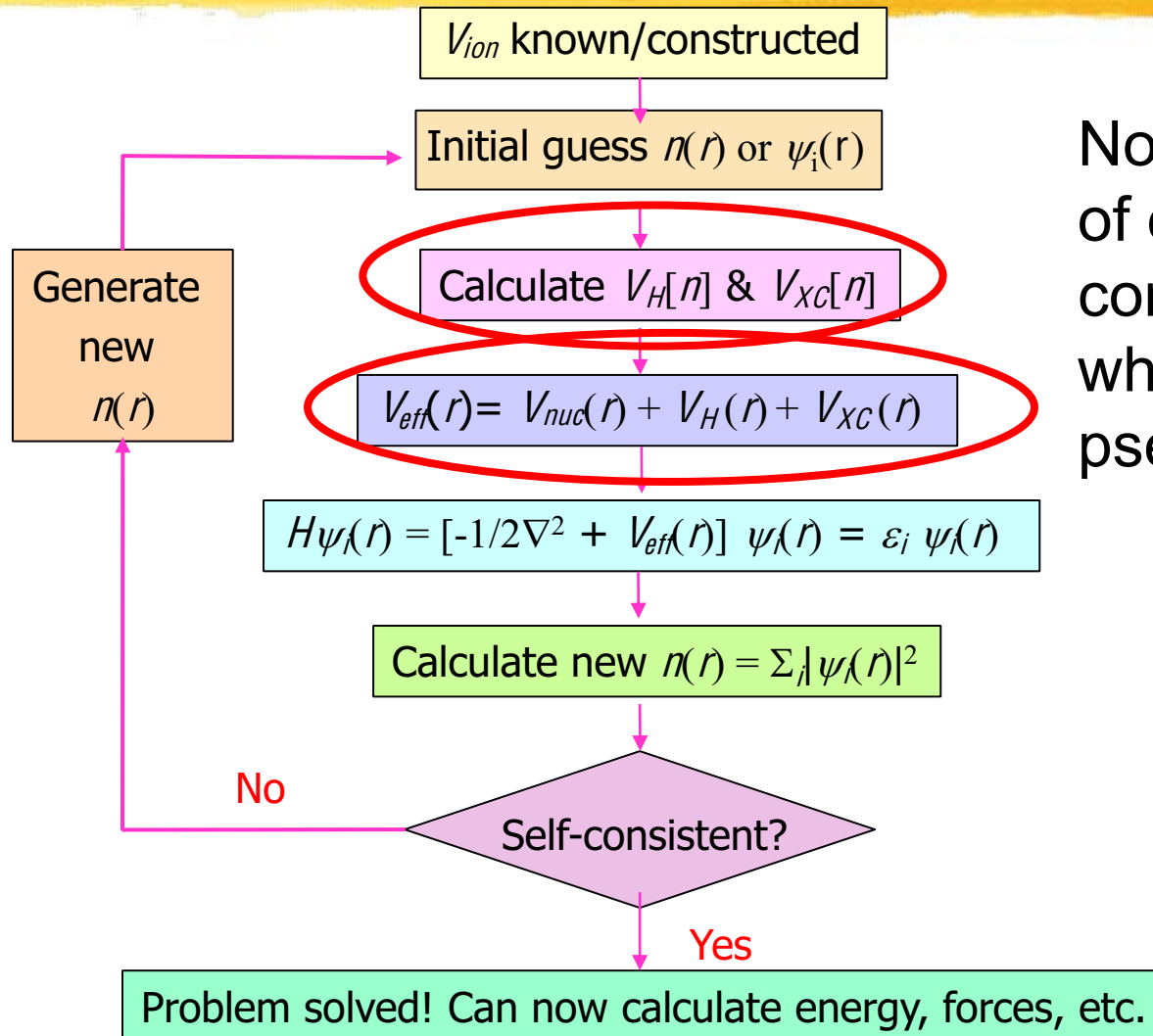
The closer your starting wavefunction is to the true wavefunction (which, of course, is something you don't necessarily know to start with!), the fewer the scf iterations needed.

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

Superposition 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:

$$E_{xc}[n] = \int n(r) V_{xc}^{\text{HOM}}[n(r)] dr$$

-surprisingly successful!

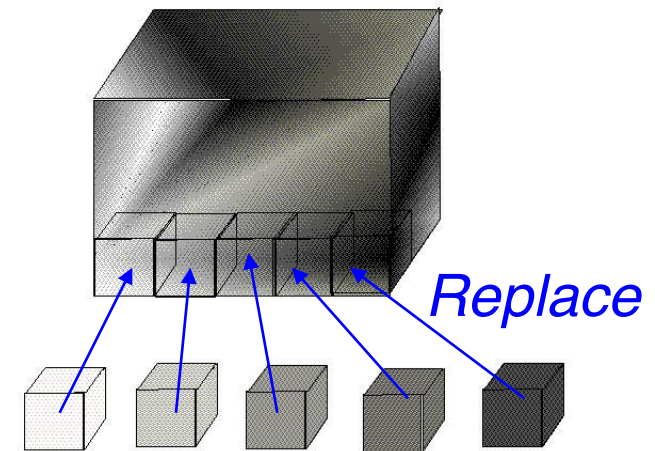
pz

(in name of pseudopotential)

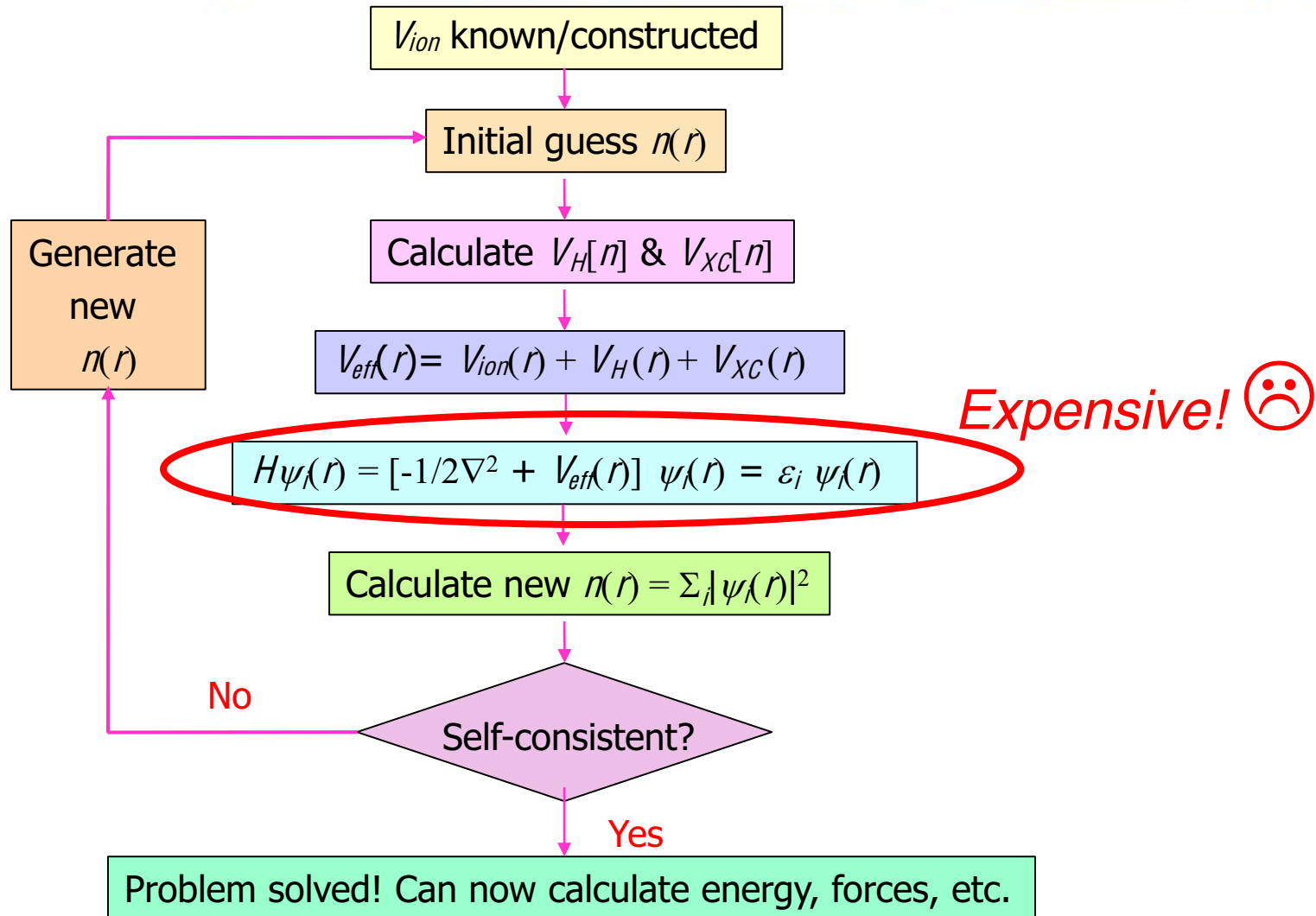
- Generalized Gradient Approximation(s): Include terms involving gradients of $n(r)$

pw91, pbe

(in name of pseudopotential)



Step 5: Diagonalization



Diagonalization

- Need to diagonalize a matrix of size $N_{PW} \times N_{PW}$
- $N_{PW} \gg N_b$ = 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.

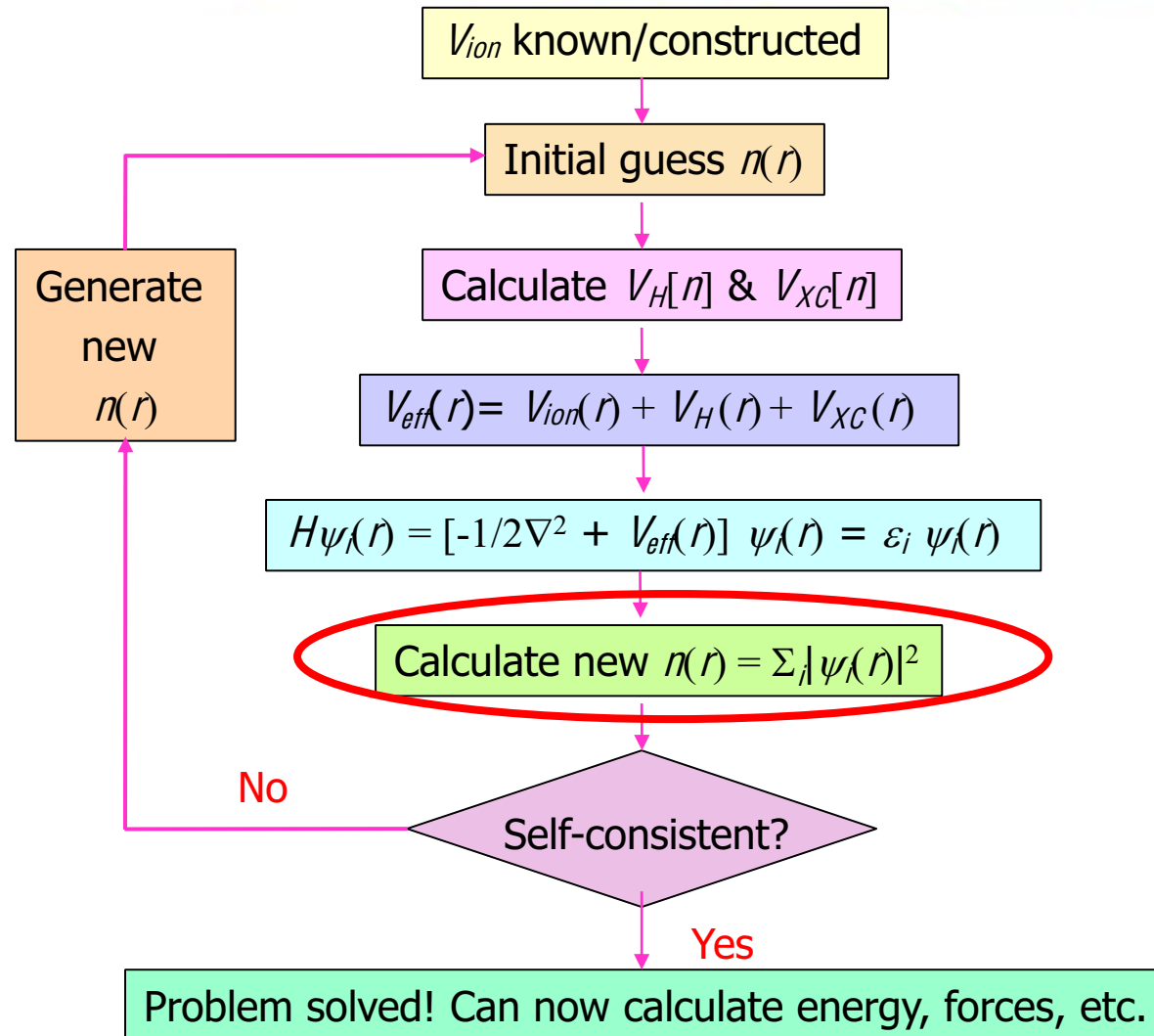
Input parameter **diagonalization**

-which algorithm used for iterative diagonalization

Input parameter **nbnd**

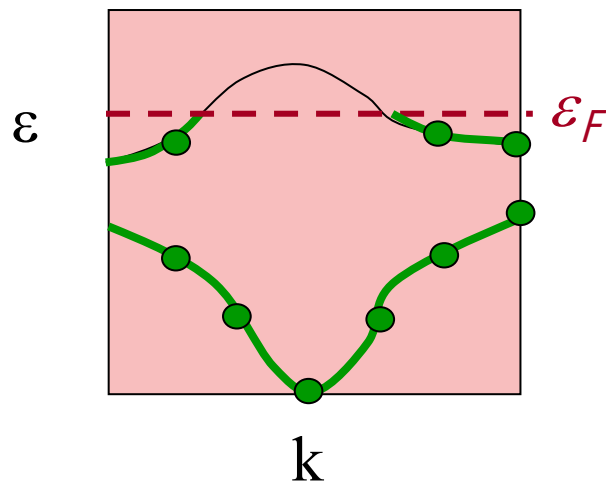
*-how many eigenvalues computed
for metals, choose depending on value of **degauss***

Step 6: New Charge Density



Brillouin Zone Sums

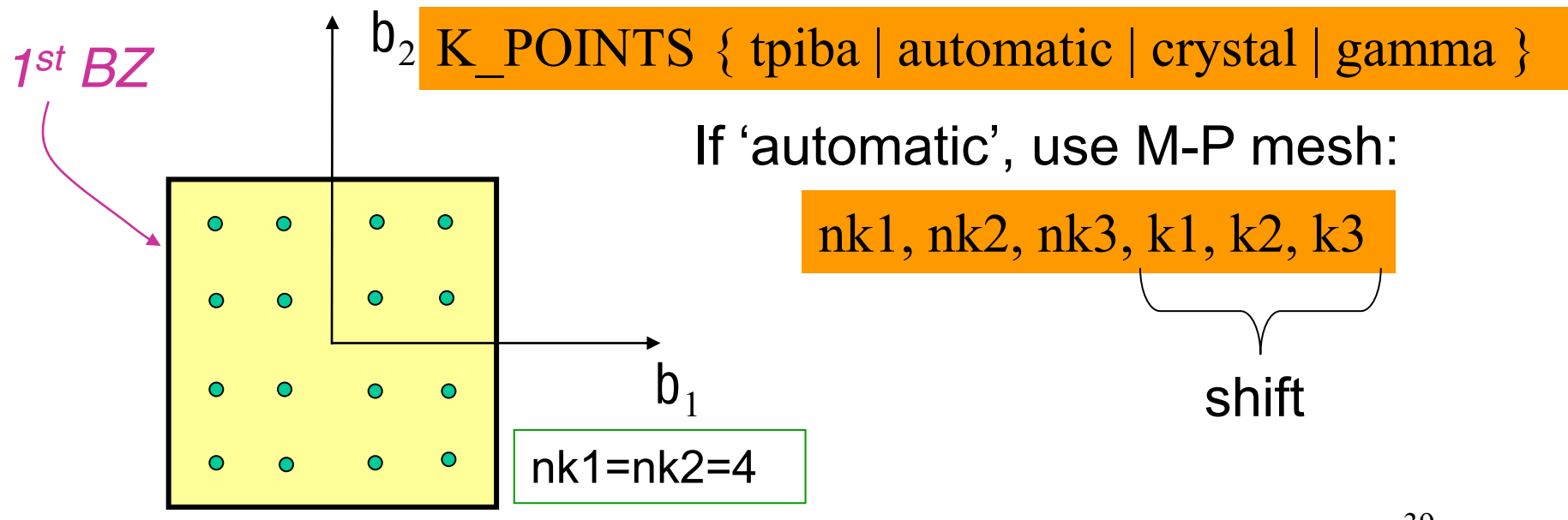
- Many quantities (e.g., n , E_{tot}) involve sums over k .
- In principle, need infinite number of k 's.
- In practice, sum over a finite number: **BZ "Sampling"**.
- Number needed depends on band structure.
- Typically need more k 's for metals.
- Need to test convergence wrt k -point sampling.



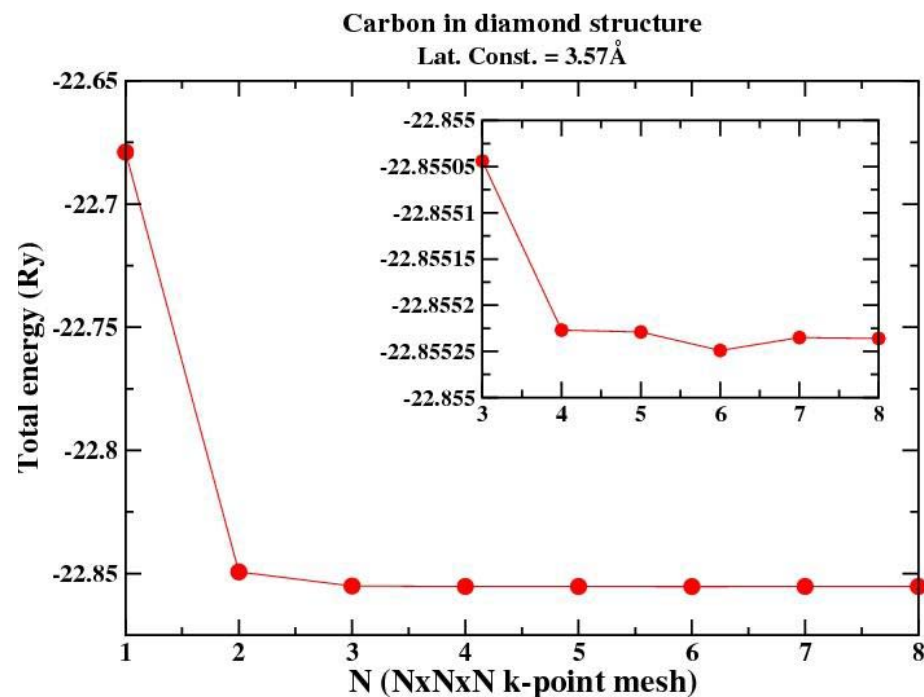
$$\langle P \rangle = \frac{1}{N_k} \sum_{k \in BZ} P(k) W_k$$

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']



Convergence wrt BZ sampling



Madhura Marathe

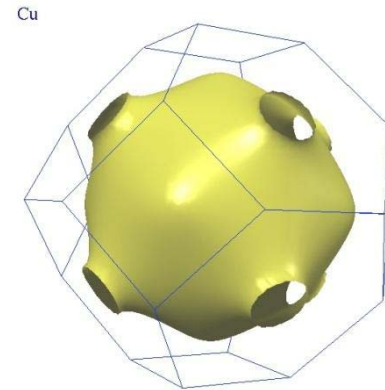
Note: Differences in energy usually converge faster than absolute value of total energy because of error cancellation (if supercells & k-points are identical or commensurate).

Problems with Metals

- Recall:

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

- 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.



Fermi Surface of Cu
iramis.cea.fr

A Smear Campaign!

- Problems arise because of **sharp discontinuity** at Fermi surface / Fermi energy.
- **“Smear”** this out using a smooth operator!
- Will now converge faster w.r.t. number of k-points (but not necessarily to the right answer!)
- The larger the smearing, the quicker the convergence w.r.t. number of k-points, but the greater the error introduced.
- The trick is to use a clever smearing function so that the error is small.



PhD Comics

Smearing in Quantum-ESPRESSO

`occupations 'smearing'`

Instruction: use smearing

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

Type of
smearing

`degauss`

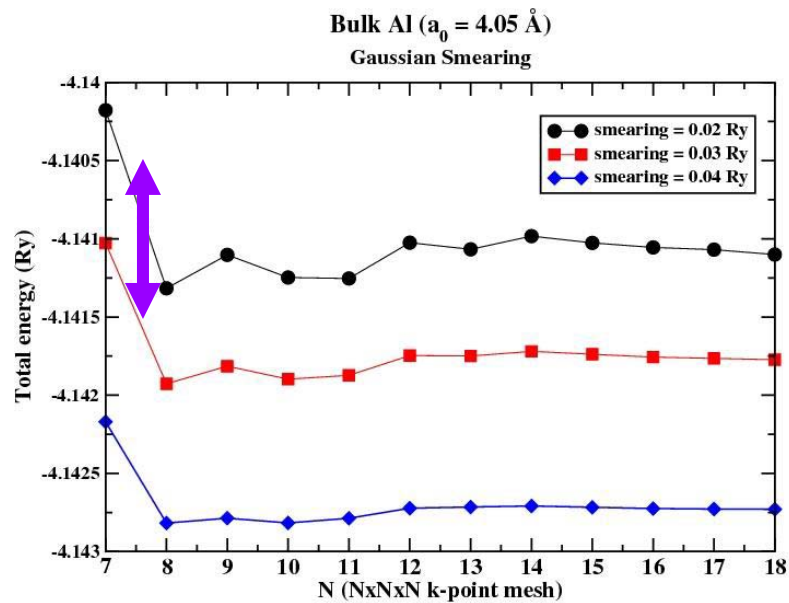
Smearing width

Methfessel & Paxton, Phys. Rev. B 40, 3616 (1989).

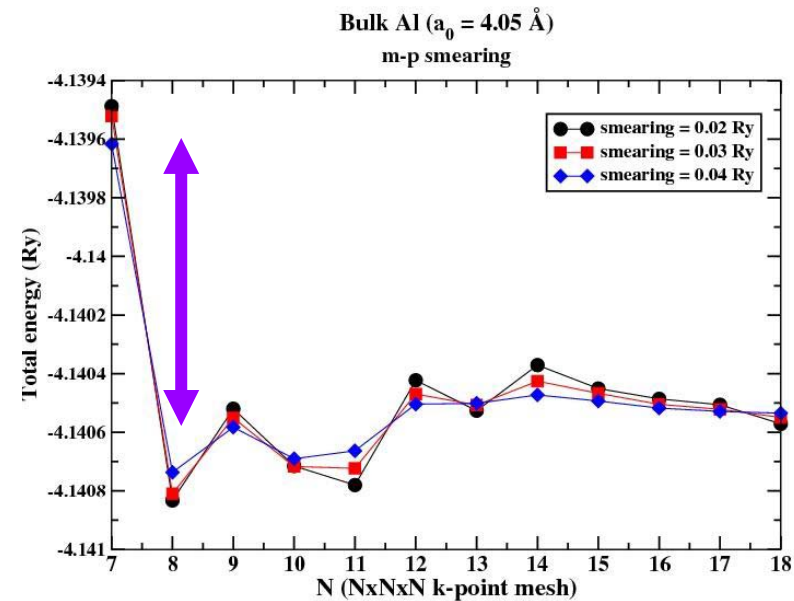
Marzari & Vanderbilt, Phys Rev. Lett. 82, 3296 (1999).

Convergence wrt grid & smearing

- Gaussian:



- Methfessel-Paxton:

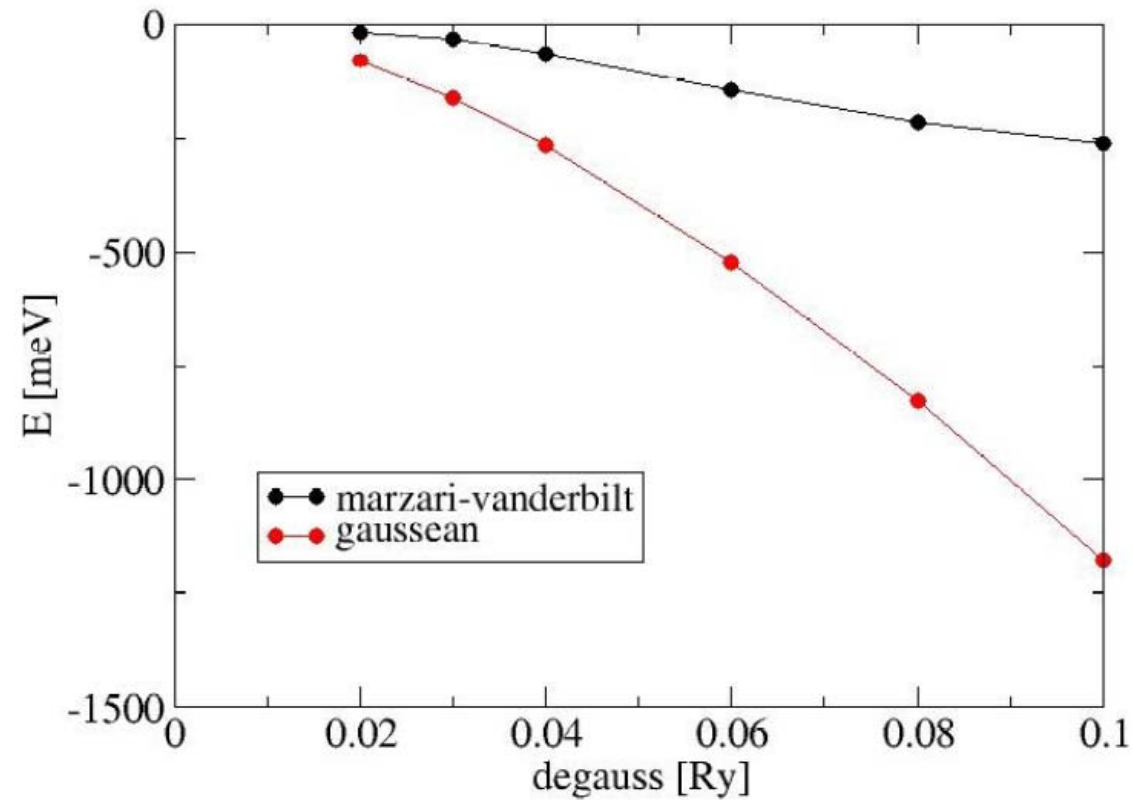


represents an energy difference of 1 mRy

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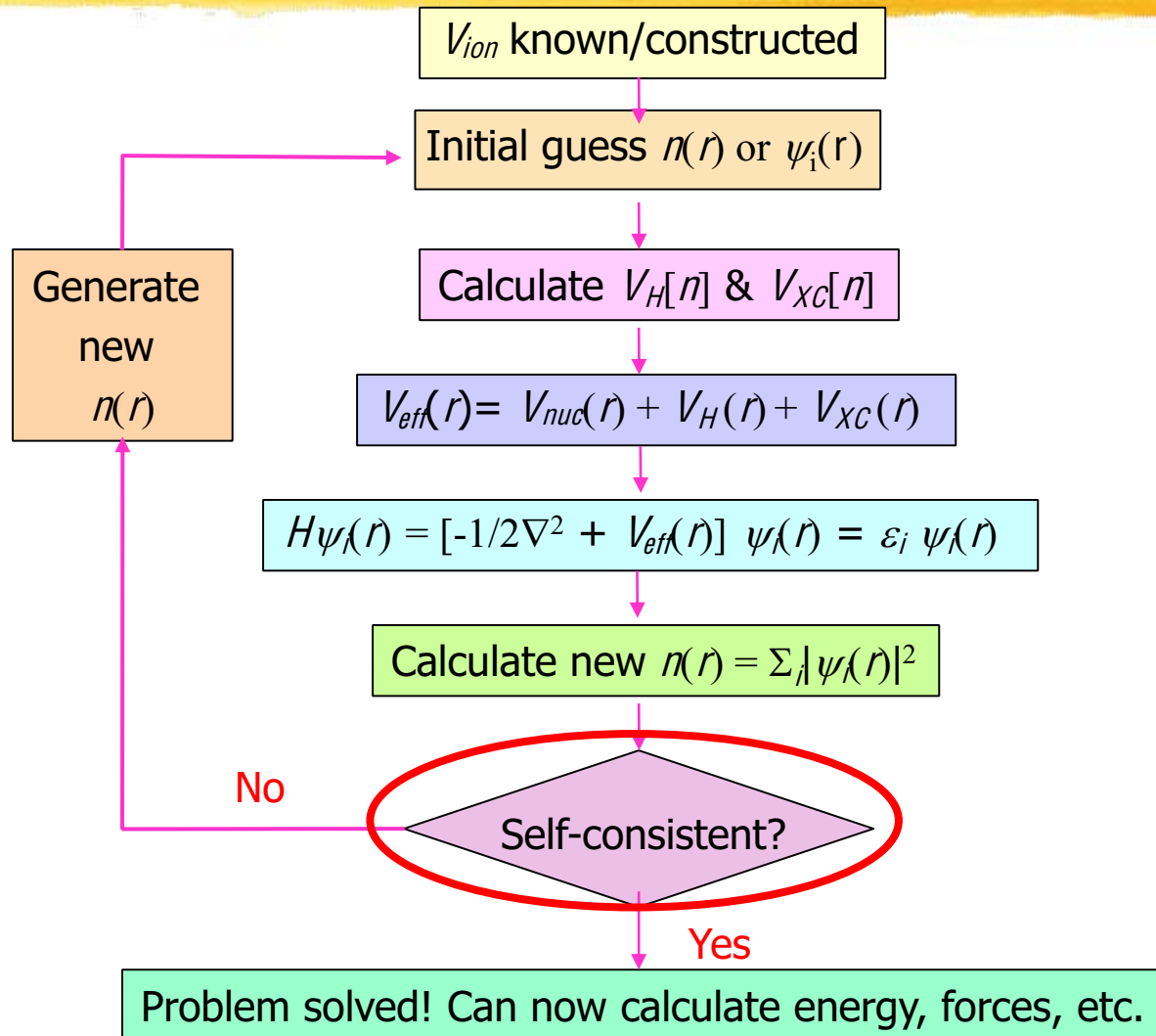
Convergence wrt k-points & smearing width

e.g., for bcc Fe, using $14 \times 14 \times 14$ grid:



R. Gebauer

Step 7: Check if Convergence Achieved



Testing for scf convergence

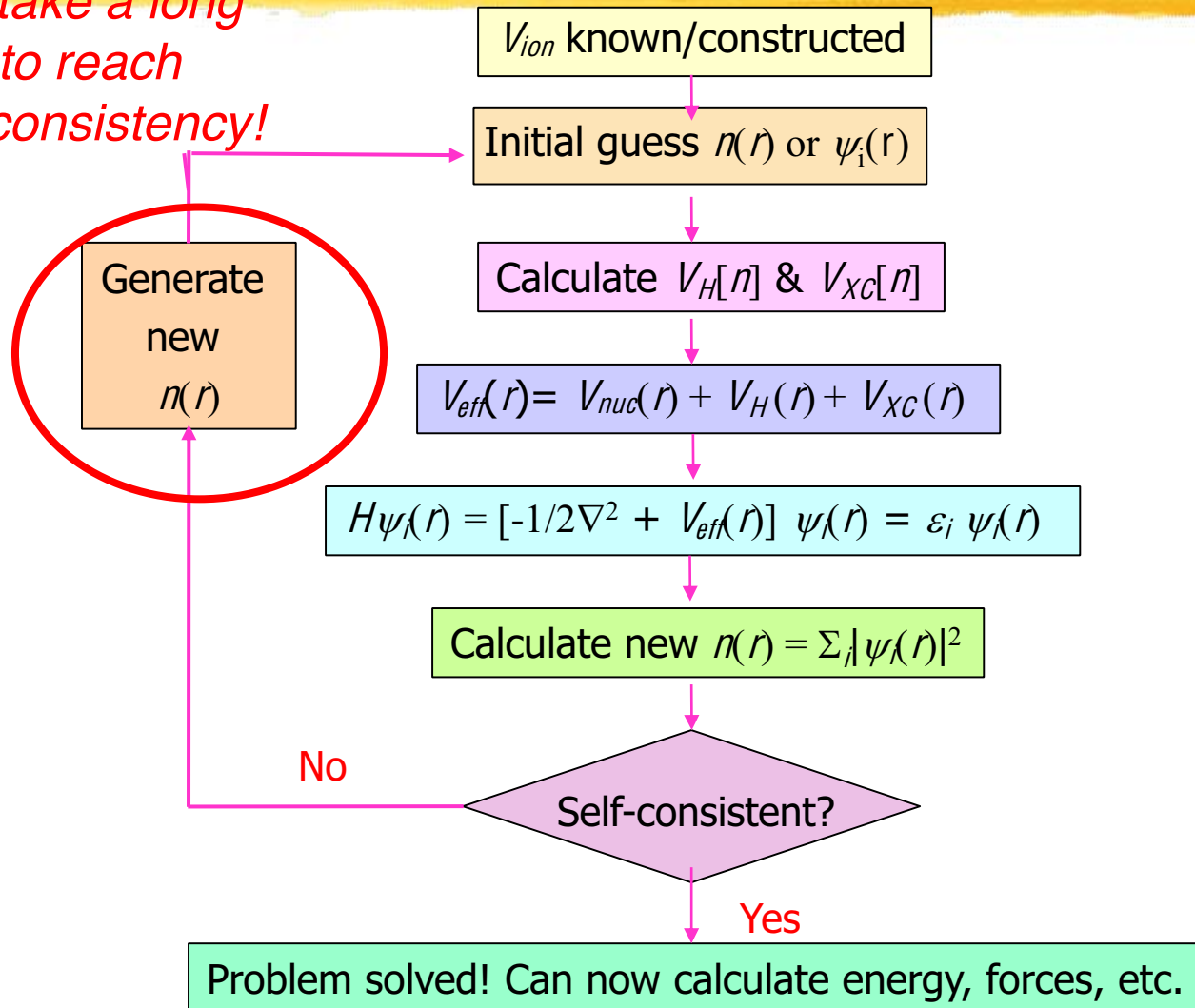
- Compare n th and $(n-1)$ th approximations for density, and see if they are close enough that self-consistency has been achieved.
- Examine squared norm of difference between the charge density in two successive iterations...should be close to zero.



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):

