

The Kohn-Sham problem

- Want to solve the Kohn-Sham equations:

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

H

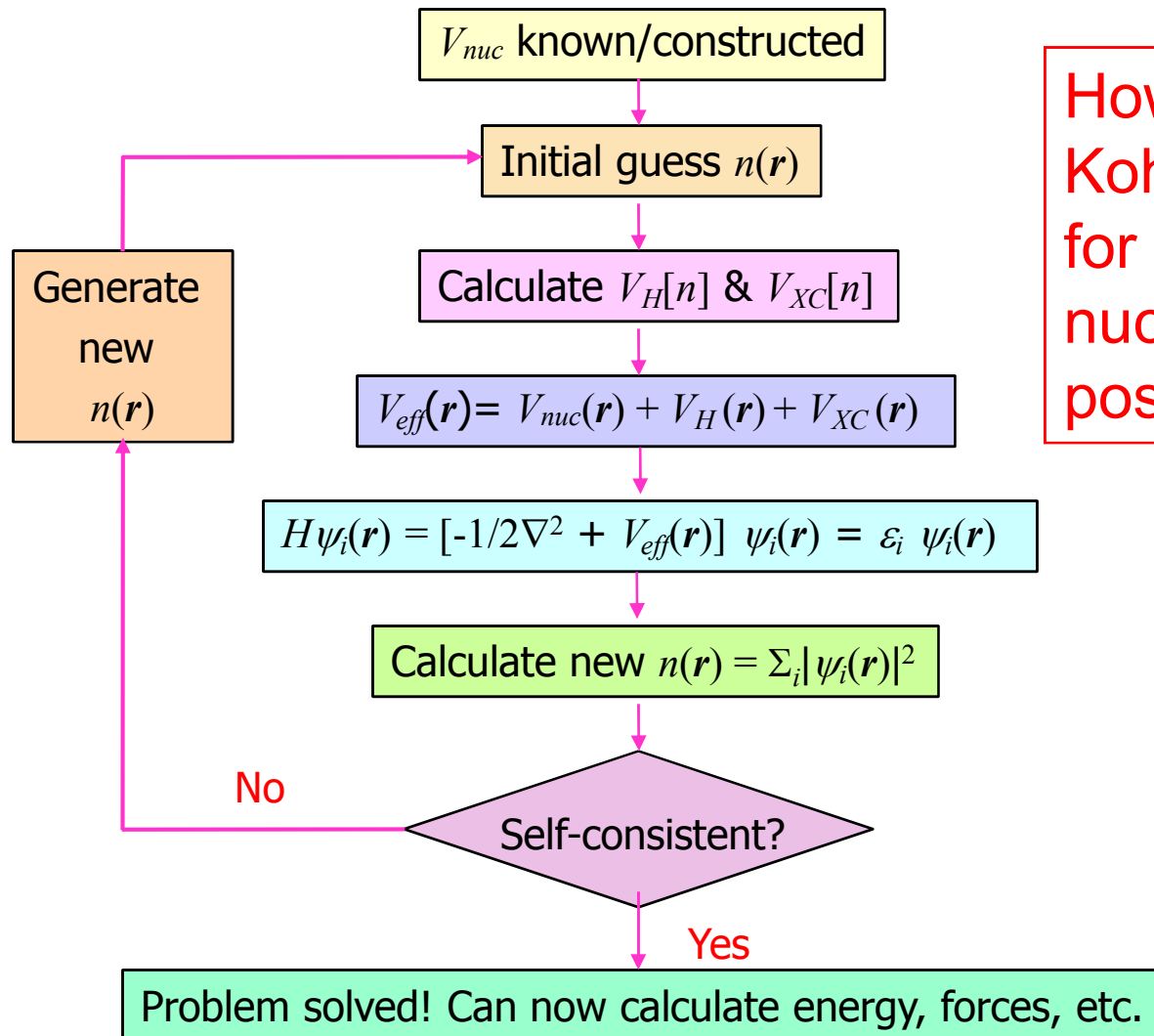
- Note that **self-consistent solution** necessary, as H depends on solution:

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

- 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.

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:

$$\sum_{\beta} H_{\alpha\beta} c_{i\beta} = \epsilon_i c_{i\alpha}$$

Matrix element *Eigenvalue* *Eigenvector*

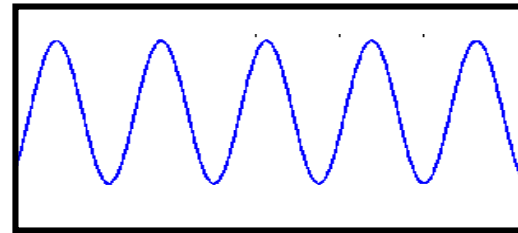
- Solving $\Leftrightarrow$ Have to diagonalize a matrix of size $N_b \times N_b$

Size of basis

Some possible basis sets

- Various possible choices of basis:

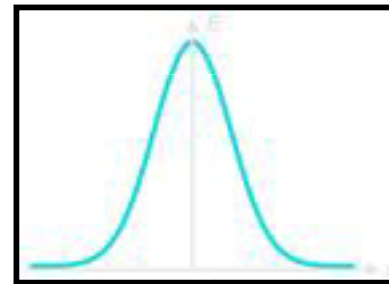
- Plane waves $e^{i\mathbf{K}\cdot\mathbf{r}}$



- 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:

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

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

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

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

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

using plane waves

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

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

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

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

$$V_{xc}(\mathbf{r}) = \mu_{xc}(\rho(\mathbf{r}))$$

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

the fast Fourier transform

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

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

$$\mathcal{O}(N^2) \rightarrow \mathcal{O}(N \log(N))$$

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

for $k \geq N/2$, use:

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

multivariate FFTs (II)

$$\begin{aligned} F(k, l, m) &= \sum_{pqs} e^{i2\pi \frac{pk+ql+sm}{N}} \tilde{F}(p, q, s) \\ &= \sum_p e^{i2\pi \frac{pk}{N}} \underbrace{\sum_q e^{i2\pi \frac{ql}{N}} \underbrace{\sum_s e^{i2\pi \frac{sm}{N}} \tilde{F}(p, q, s)}_{N^2 \text{ FFT}(N)}}_{N^2 \text{ FFT}(N)} \end{aligned}$$

$N^2 \text{ FFT}(N)$

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

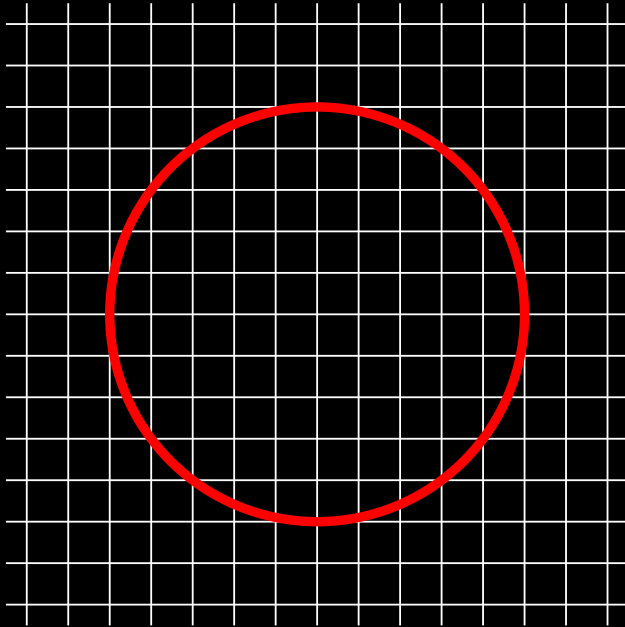
solving the Poisson equation

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

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

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

$$\tilde{V}(\mathbf{G} = 0) = 0$$



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

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

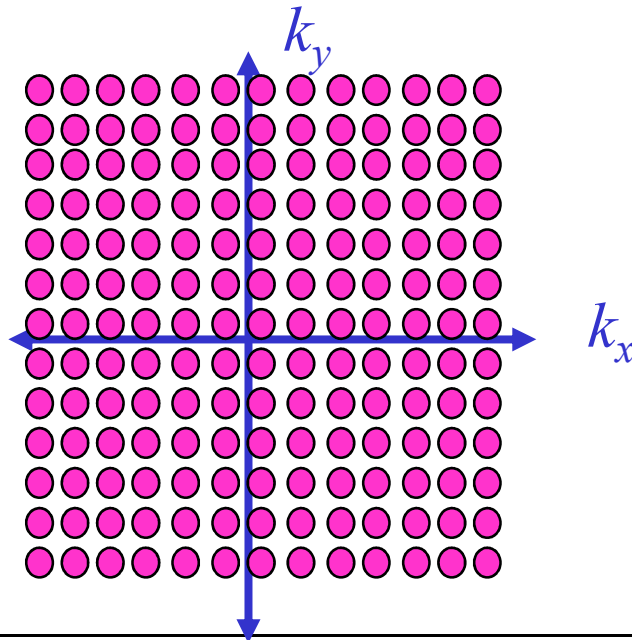
Plane Waves & Periodic Systems

- For a periodic system:

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

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

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



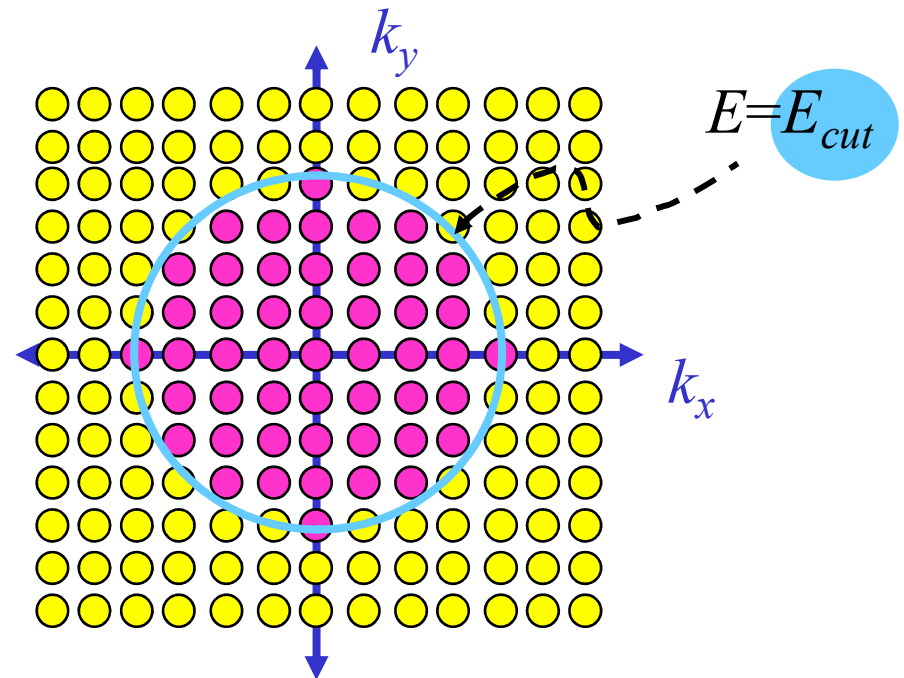
- Only true for periodic systems that grid is discrete.
- In principle, still need infinite number of plane waves.

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:

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

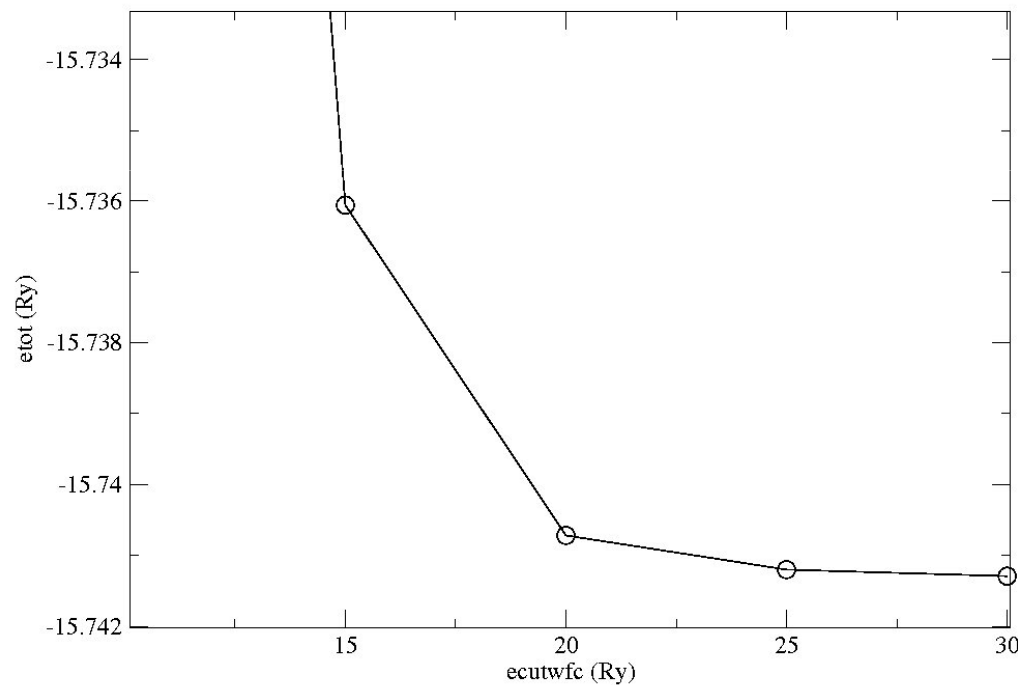
Input parameter **ecutwfc**



Checking Convergence wrt $ecutwfc$

- Must always check.
- Monotonic (variational).

Silicon: Convergence wrt plane wave cutoff



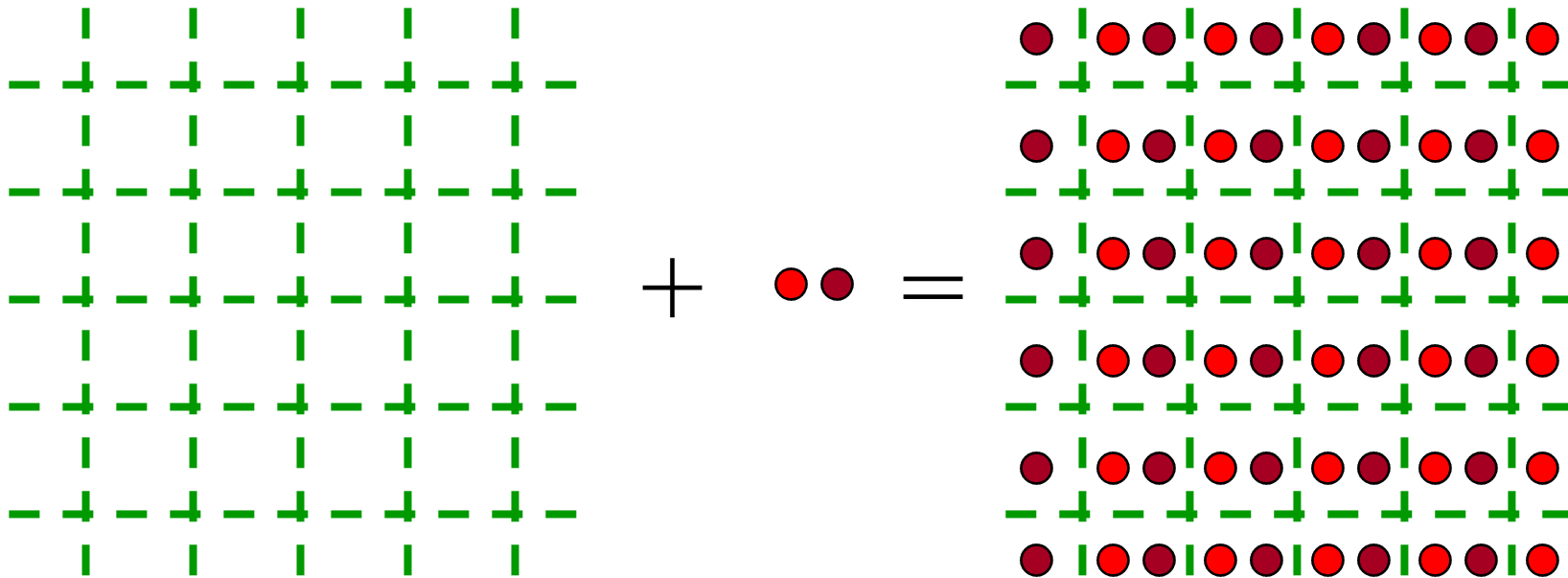
Step 0: Defining the (periodic) system



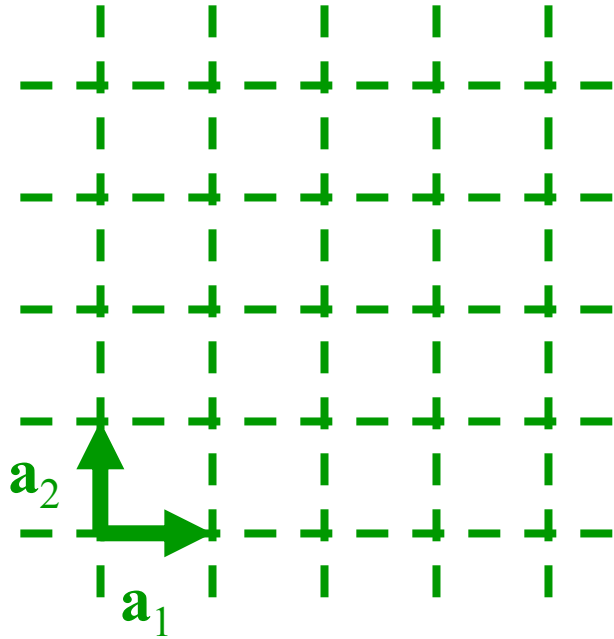
Namelist '**SYSTEM**'

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**

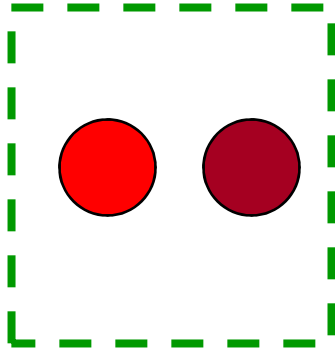
- Gives the type of **Bravais lattice** (SC, BCC, Hex, etc.)

Input parameters {**cell_{dm}(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**

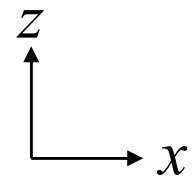
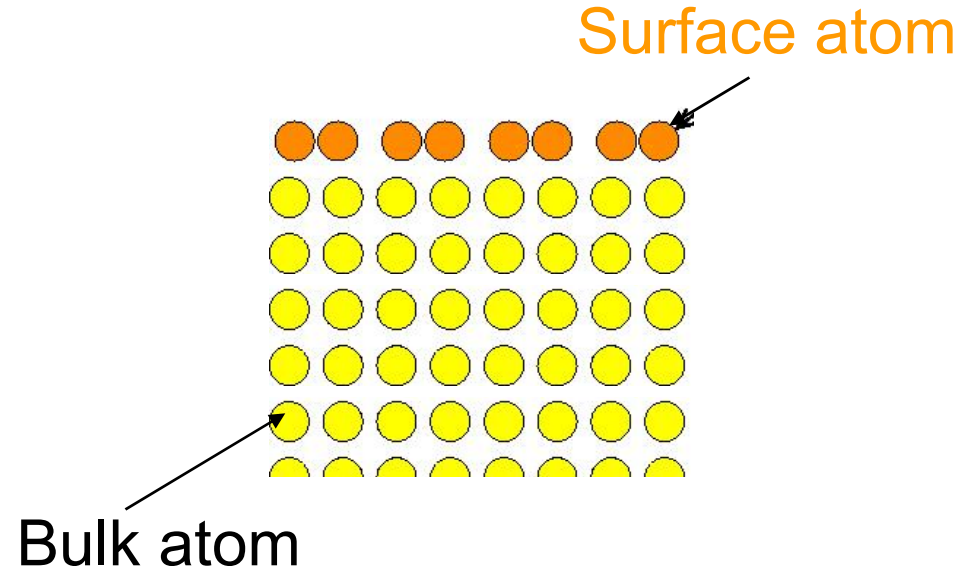
- Number of types of atoms

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**”)

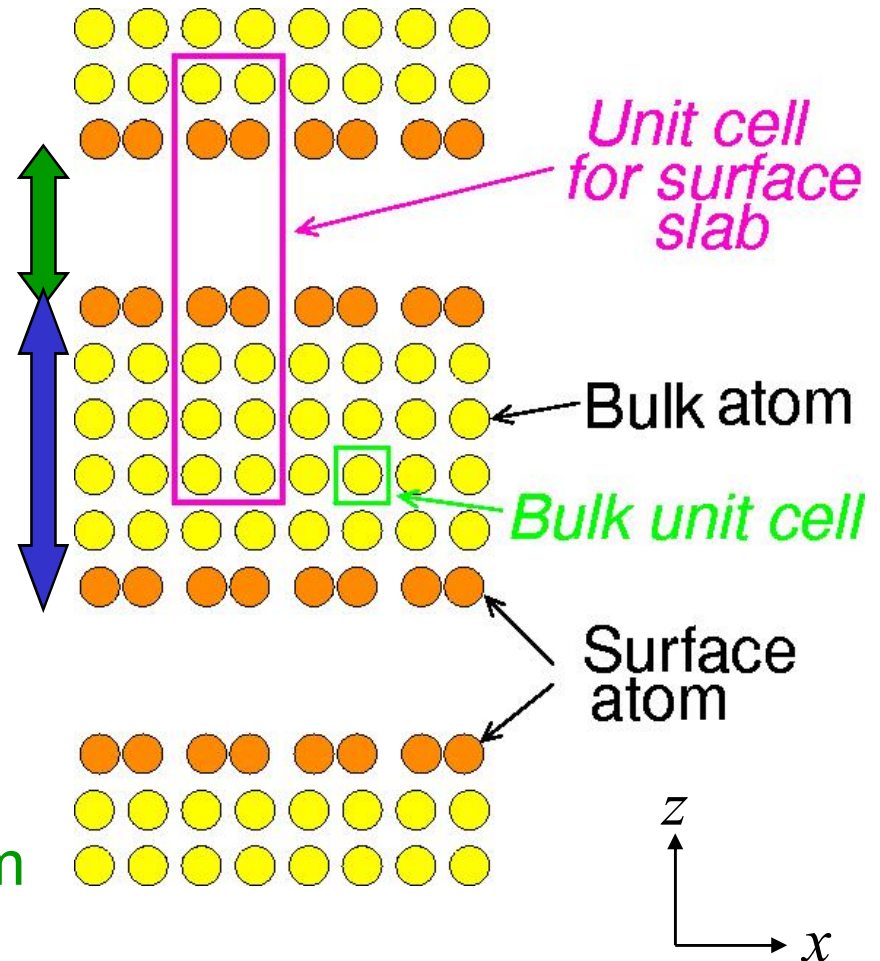
What if the system is not periodic?

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



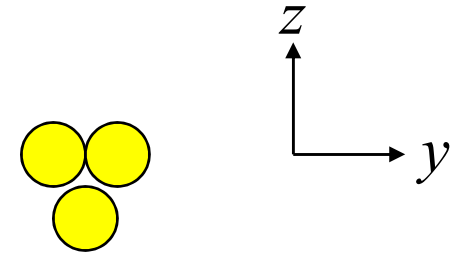
What if the system is not periodic?

- Example 1: Want to study properties of a system with a **surface**.
- Presence of surface $\Rightarrow$ 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?

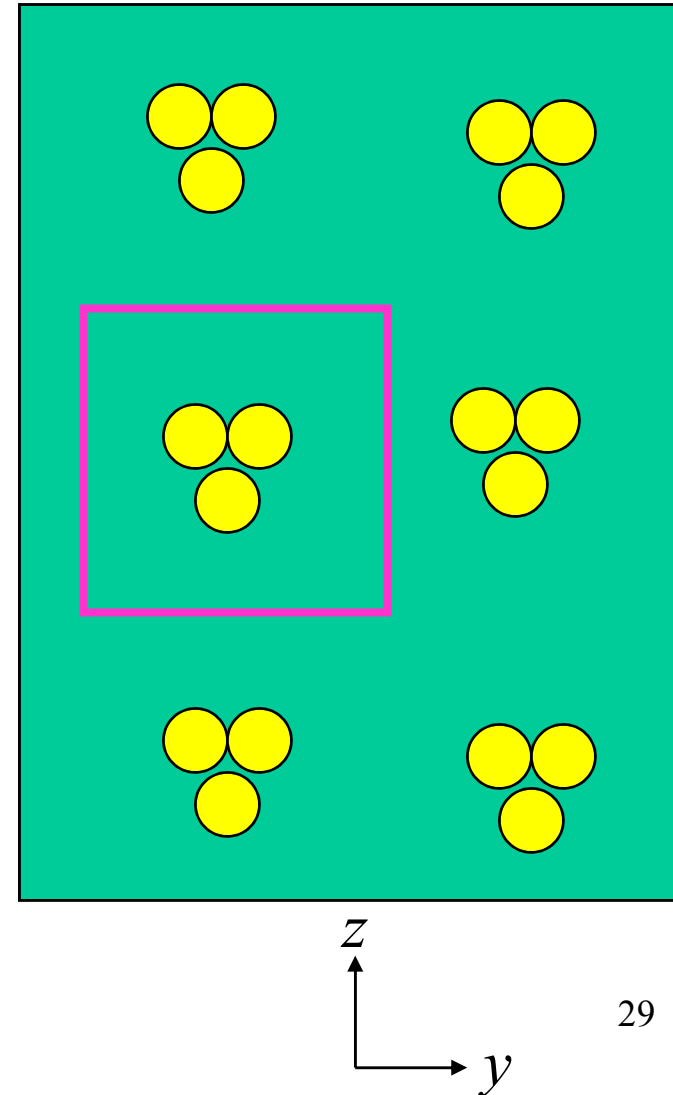
- Example 2: Want to study properties of a nanowire.



- Example 3: Want to study properties of a cluster

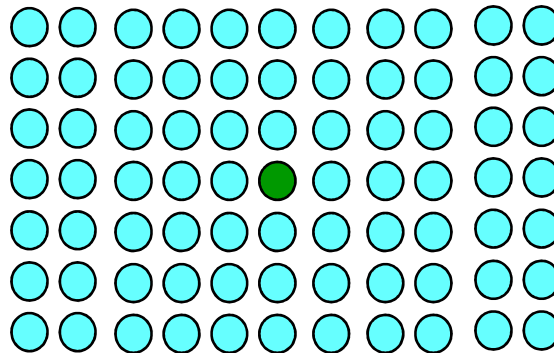
What if the system is not periodic?

- 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** .



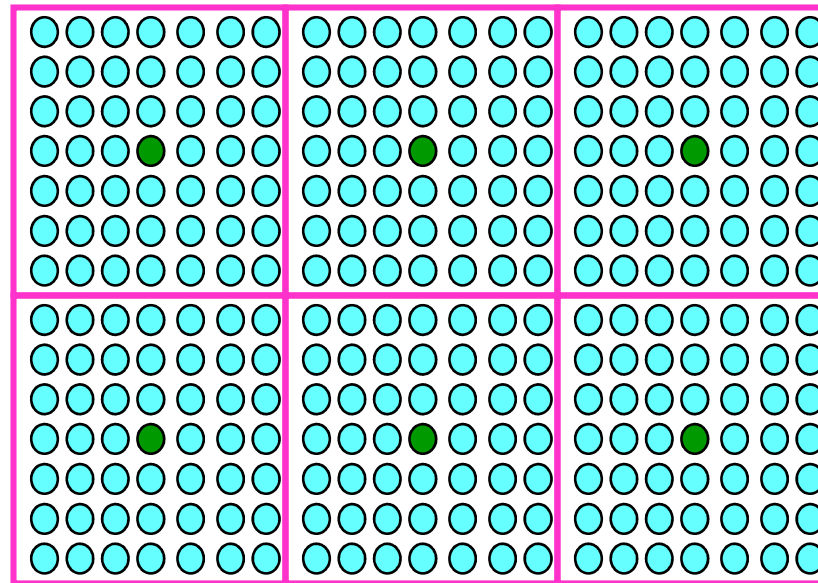
What if the system is not periodic?

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



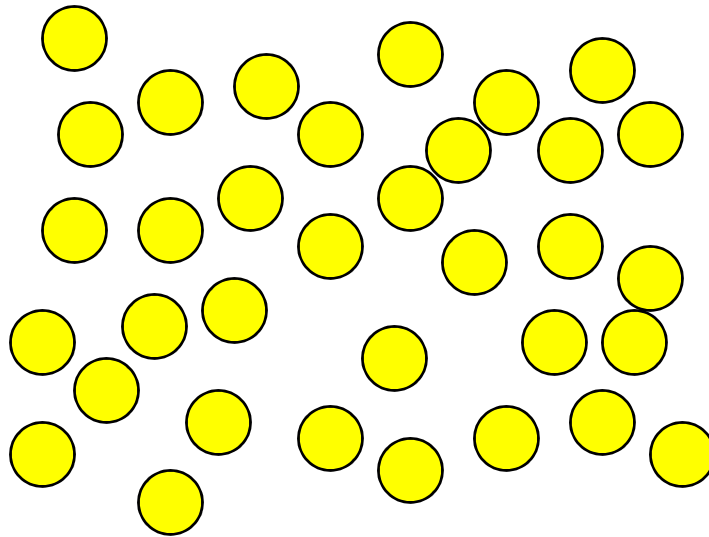
What if the system is not periodic?

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



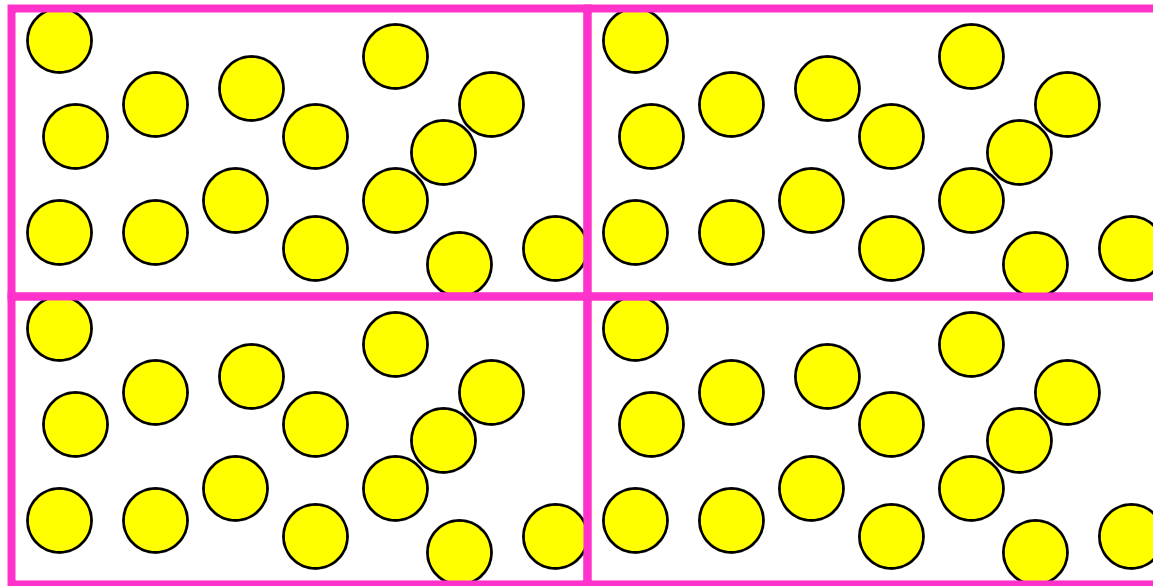
What if the system is not periodic?

- 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 $\Rightarrow$ 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)

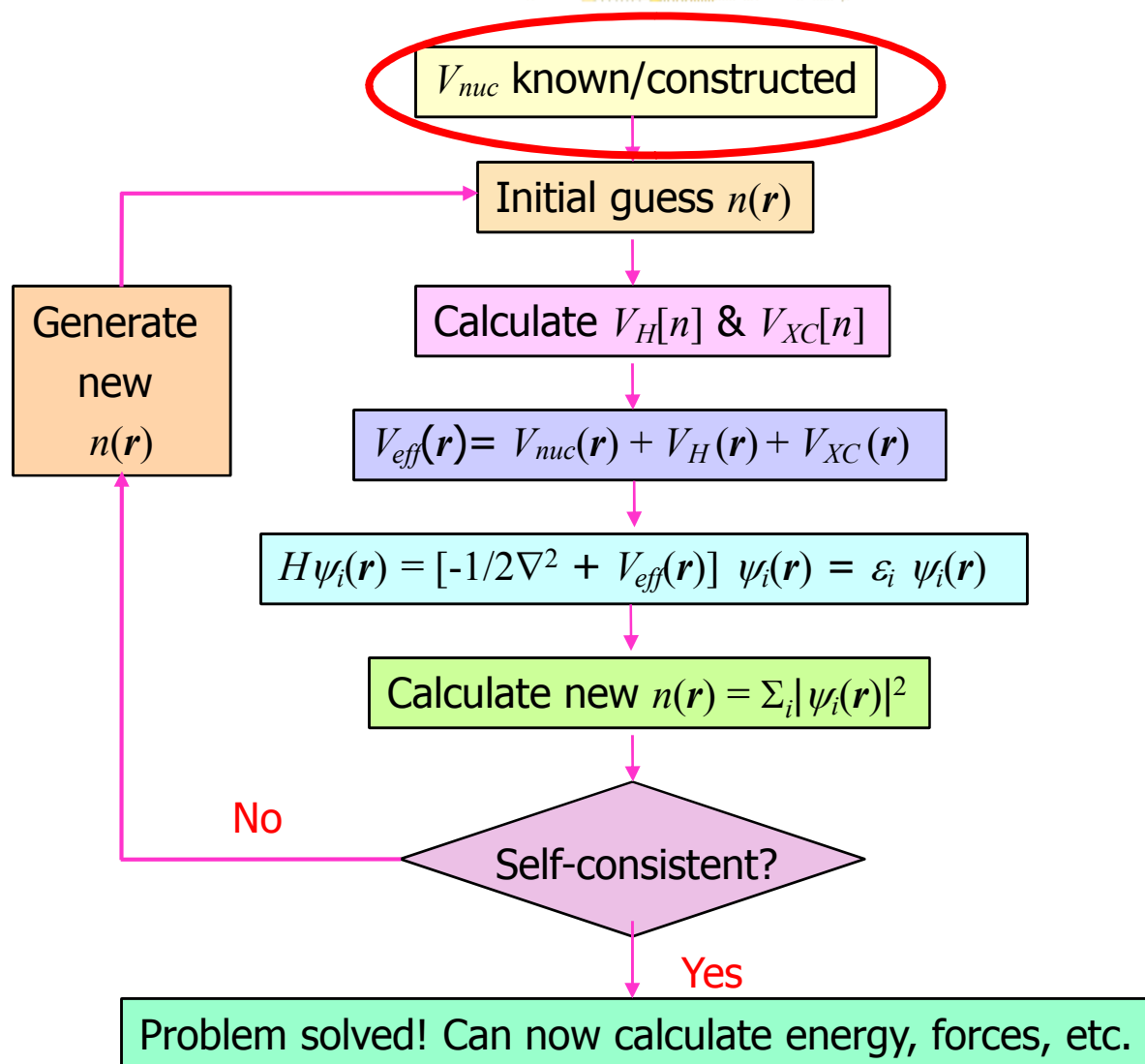


- Short $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$ (primitive reciprocal lattice vectors)



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

Step 1: Obtaining V_{nuc}



treating core states

Period	1	1 H Hydrogen 1.007 94																2 He Helium 4.002 602																			
	2	Group 1 3 Li Lithium 6.941		Group 2 4 Be Beryllium 9.012 182																		Group 13 5 B Boron 10.811		Group 14 6 C Carbon 12.0107		Group 15 7 N Nitrogen 14.0067		Group 16 8 O Oxygen 15.9994		Group 17 9 F Fluorine 18.998 4032		Group 18 10 Ne Neon 20.1797					
	3	11 Na Sodium 22.989 770		12 Mg Magnesium 24.3050																13 Al Aluminum 26.981 538		14 Si Silicon 28.0855		15 P Phosphorus 30.973 761		16 S Sulfur 32.065		17 Cl Chlorine 35.453		18 Ar Argon 39.948							
	4	19 K Potassium 39.0983		20 Ca Calcium 40.078		Group 3 21 Sc Scandium 44.955 910		Group 4 22 Ti Titanium 47.867		Group 5 23 V Vanadium 50.9415		Group 6 24 Cr Chromium 51.9961		Group 7 25 Mn Manganese 54.938 049		Group 8 26 Fe Iron 55.845		Group 9 27 Co Cobalt 58.933 200		Group 10 28 Ni Nickel 58.6934		Group 11 29 Cu Copper 63.546		Group 12 30 Zn Zinc 65.409		31 Ga Gallium 69.723		32 Ge Germanium 72.64		33 As Arsenic 74.921 60		34 Se Selenium 78.96		35 Br Bromine 79.904		36 Kr Krypton 83.798	
	5	37 Rb Rubidium 85.4678		38 Sr Strontium 87.62		39 Y Yttrium 88.905 85		40 Zr Zirconium 91.224		41 Nb Niobium 92.906 38		42 Mo Molybdenum 95.94		43 Tc Technetium (98)		44 Ru Ruthenium 101.07		45 Rh Rhodium 102.905 50		46 Pd Palladium 106.42		47 Ag Silver 107.8682		48 Cd Cadmium 112.411		49 In Indium 114.818		50 Sn Tin 118.710		51 Sb Antimony 121.760		52 Te Tellurium 127.60		53 I Iodine 126.904 47		54 Xe Xenon 131.293	
	6	55 Cs Cesium 132.905 43		56 Ba Barium 137.327		57 La Lanthanum 138.9055		72 Hf Hafnium 178.49		73 Ta Tantalum 180.9479		74 W Tungsten 183.84		75 Re Rhenium 186.207		76 Os Osmium 190.23		77 Ir Iridium 192.217		78 Pt Platinum 195.078		79 Au Gold 196.966 55		80 Hg Mercury 200.59		81 Tl Thallium 204.3833		82 Pb Lead 207.2		83 Bi Bismuth 208.980 38		84 Po Polonium (209)		85 At Astatine (210)		86 Rn Radon (222)	
	7	87 Fr Francium (223)		88 Ra Radium (226)		89 Ac Actinium (227)		104 Rf Rutherfordium (261)		105 Db Dubnium (262)		106 Sg Seaborgium (266)		107 Bh Bohrium (264)		108 Hs Hassium (277)		109 Mt Meitnerium (268)		110 Ds Darmstadtium (281)		111 Uuu* Ununium (273)		112 Uub* Unbium (285)		113 Uut* Untrium (284)		114 Uuq* Unquadrium (289)		115 Uup* Unpentium (288)							
* The systematic names and symbols for elements greater than 110 will be used until the approval of final names by IUPAC.																																					
A team at Lawrence Berkeley National Laboratories reported the discovery of elements 116 and 118 in June 1999. The same team retracted the discovery in July 2001. The discovery of elements 113, 114, and 115 has been reported but not confirmed.																																					
58 Ce Cerium 140.116 59 Pr Praseodymium 140.907 65 60 Nd Neodymium 144.24 61 Pm Promethium (145) 62 Sm Samarium 150.36 63 Eu Europium 151.964 64 Gd Gadolinium 157.25 65 Tb Terbium 158.925 34 66 Dy Dysprosium 162.500 67 Ho Holmium 164.930 32 68 Er Erbium 167.259 69 Tm Thulium 168.934 21 70 Yb Ytterbium 173.04 71 Lu Lutetium 174.967																																					
90 Th Thorium 232.0381 91 Pa Protactinium 231.036 88 92 U Uranium 238.028 91 93 Np Neptunium (237) 94 Pu Plutonium (244) 95 Am Americium (243) 96 Cm Curium (247) 97 Bk Berkelium (247) 98 Cf Californium (251) 99 Es Einsteinium (252) 100 Fm Fermium (257) 101 Md Mendelevium (258) 102 No Nobelium (259) 103 Lr Lawrencium (262)																																					

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

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

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

$$\sim Z^3$$

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

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.

trashing core states: pseudopotentials

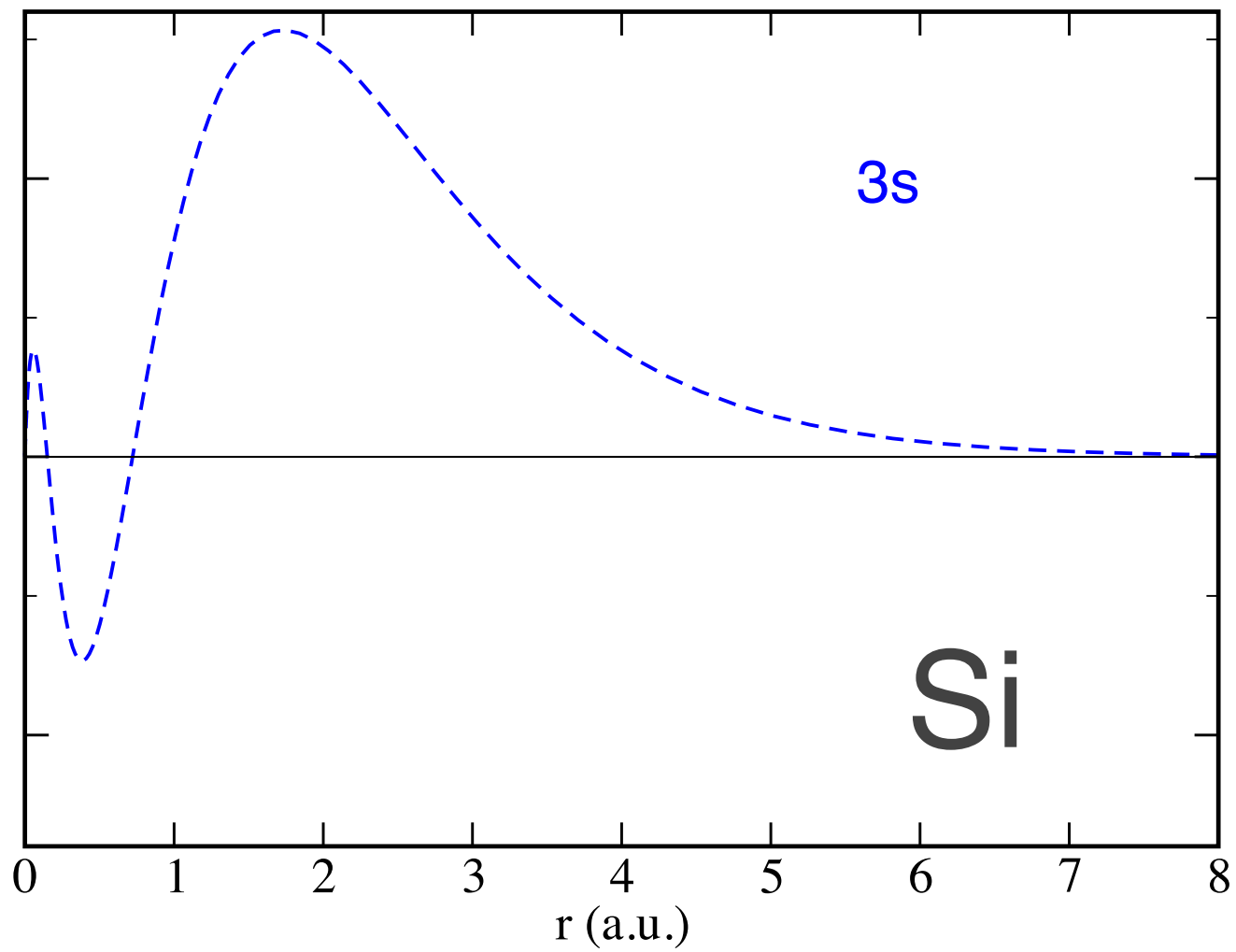
pseudo-atoms do not have core states: valence states of any given angular symmetry are the lowest-lying states of that symmetry:

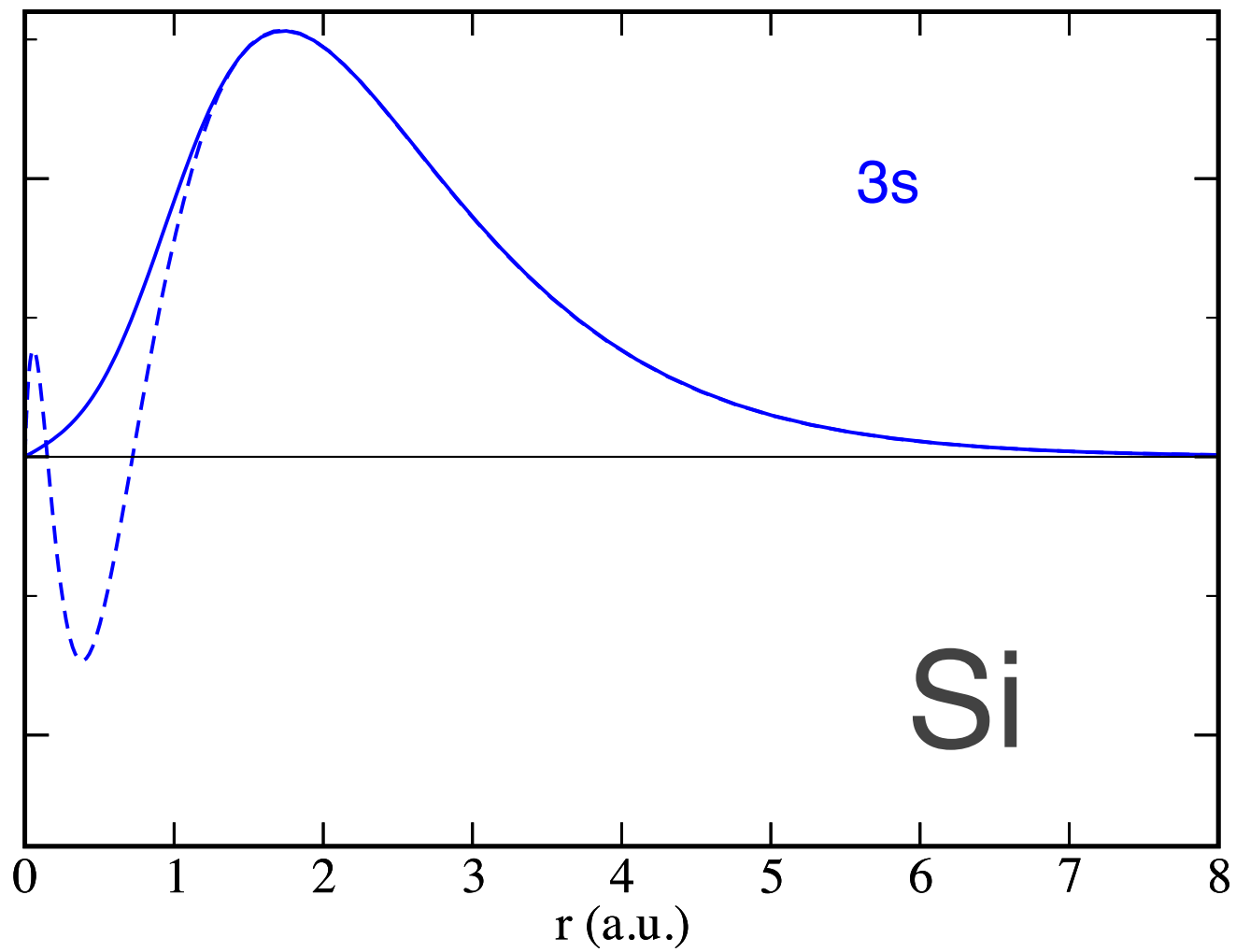
ϕ_{val}^{ps} is nodeless and smooth

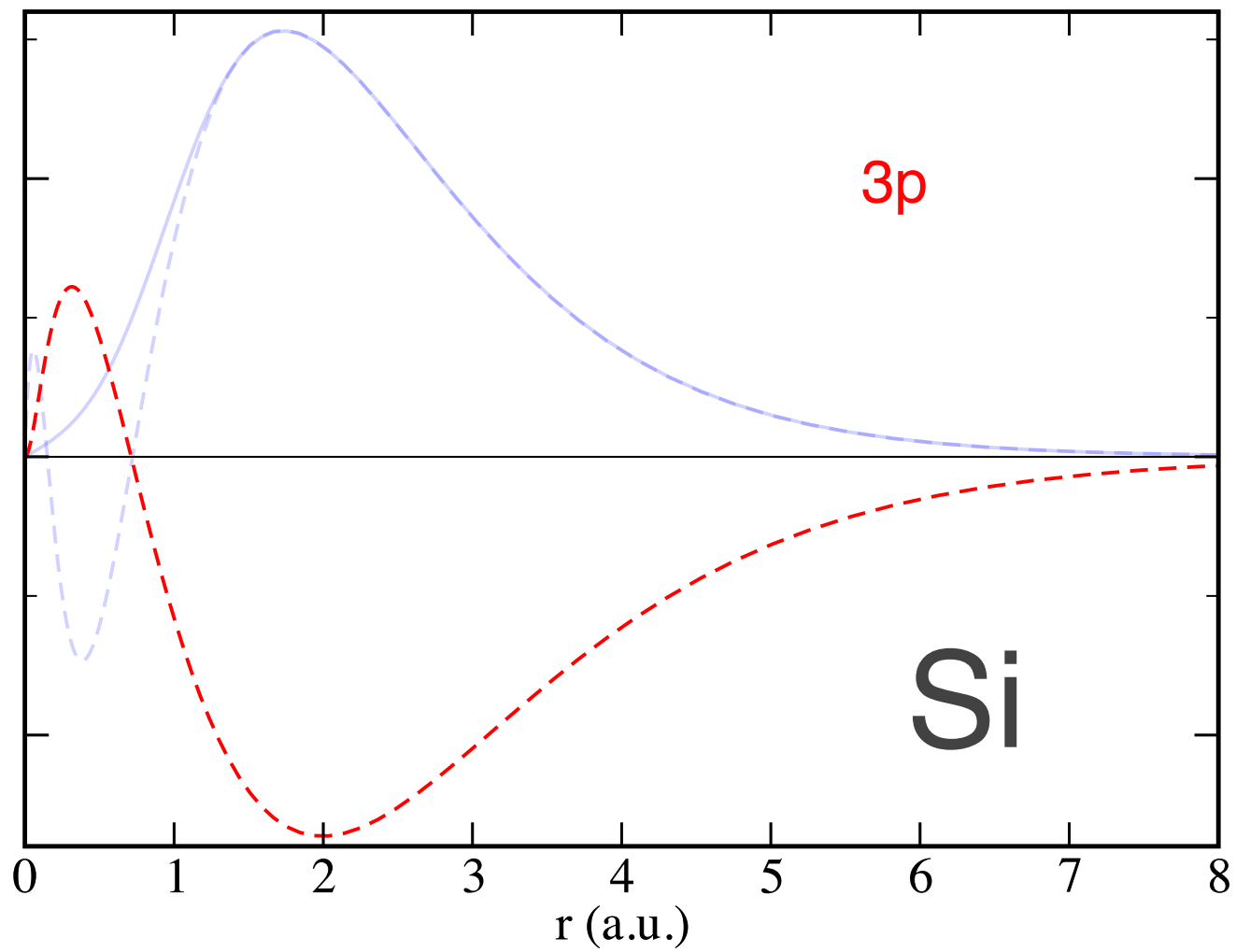
the chemical properties of the pseudo-atom are the same as those of the true atom:

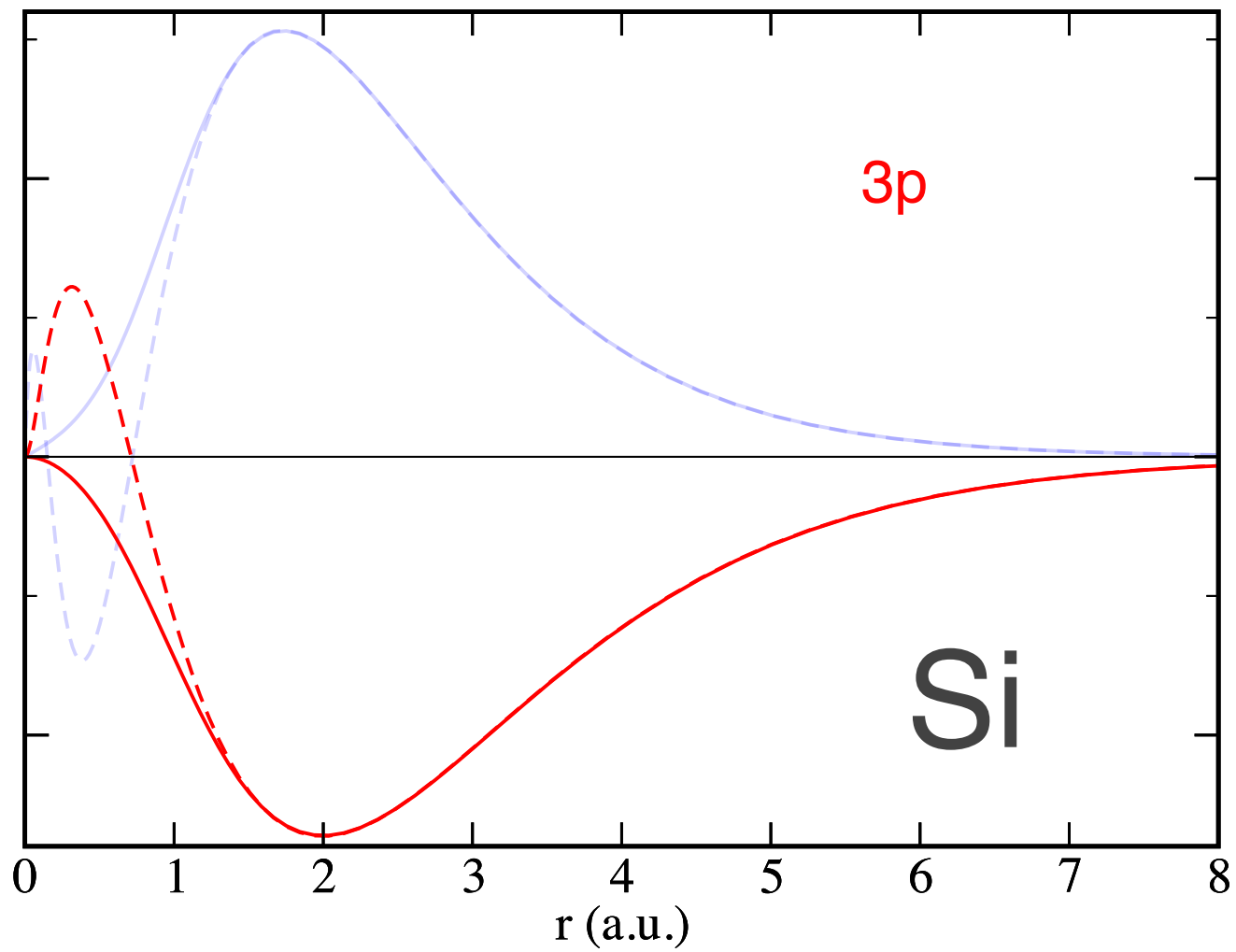
$$\epsilon_{val}^{ps} = \epsilon_{val}^{ae}$$

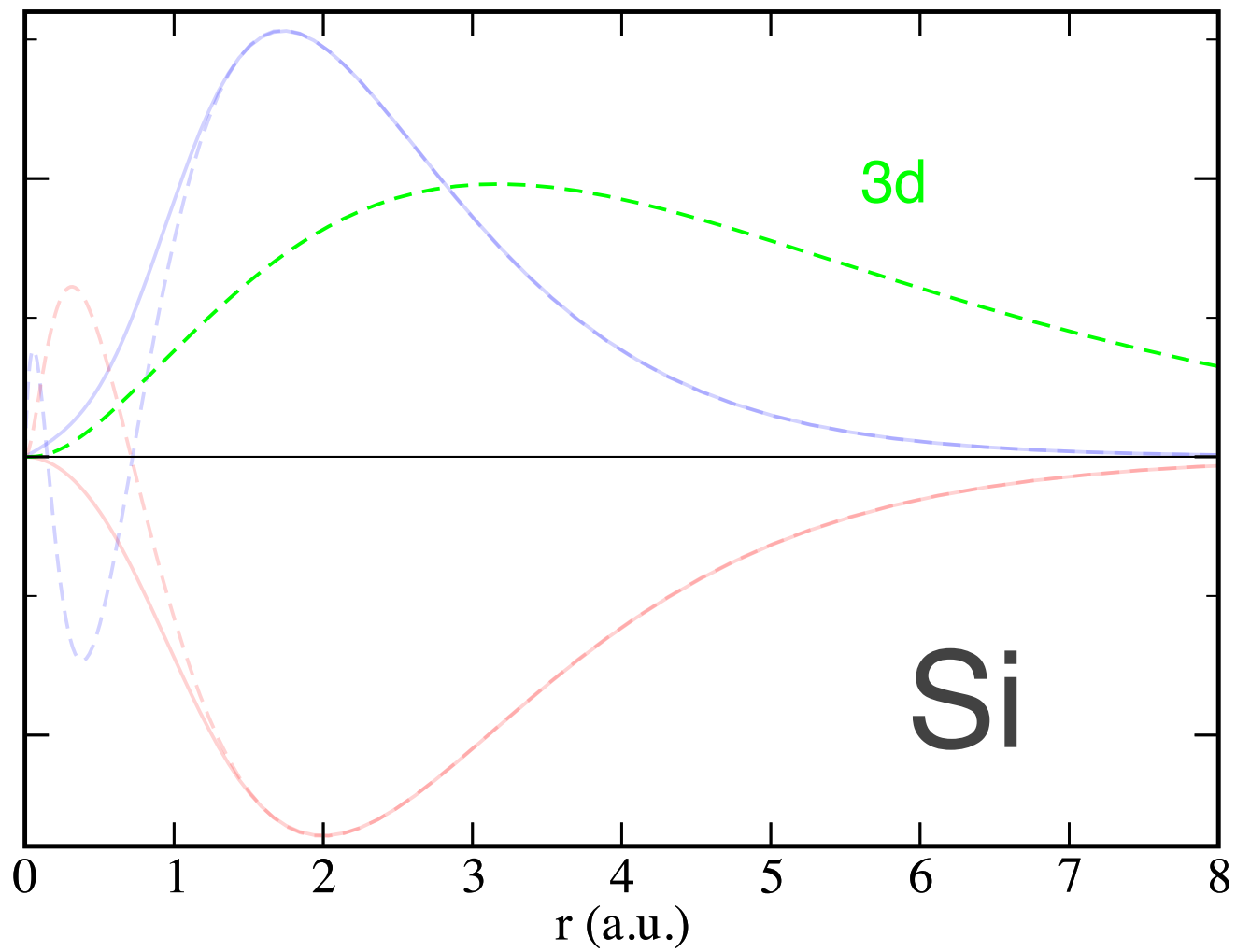
$$\phi_{val}^{ps}(r) = \phi_{val}^{ae}(r) \quad \text{for} \quad r > r_c$$

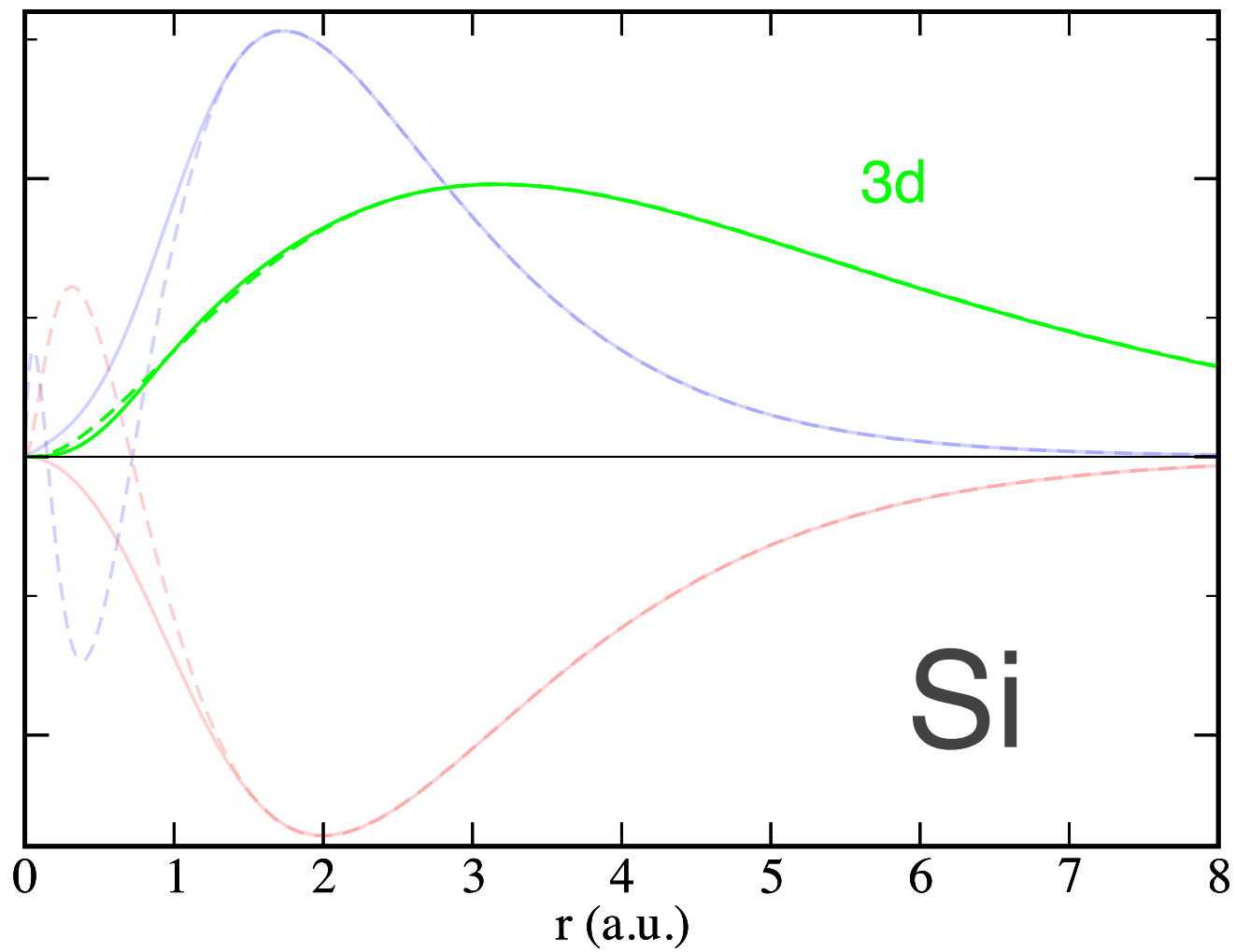




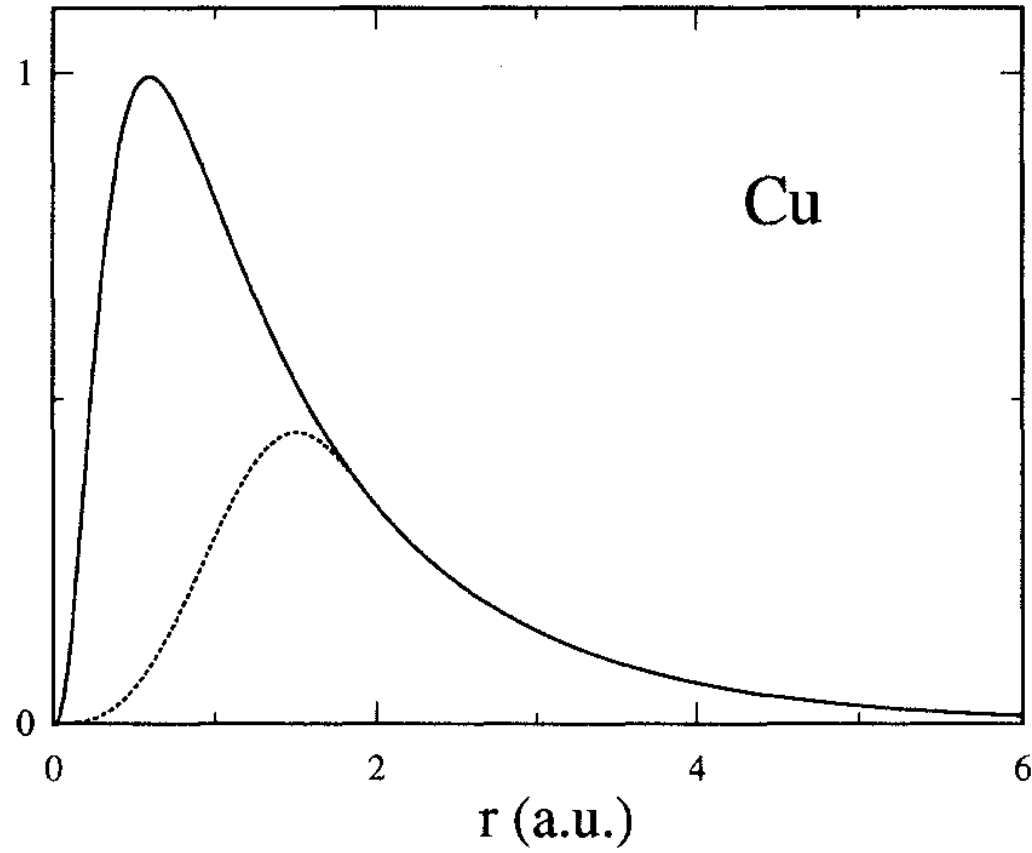




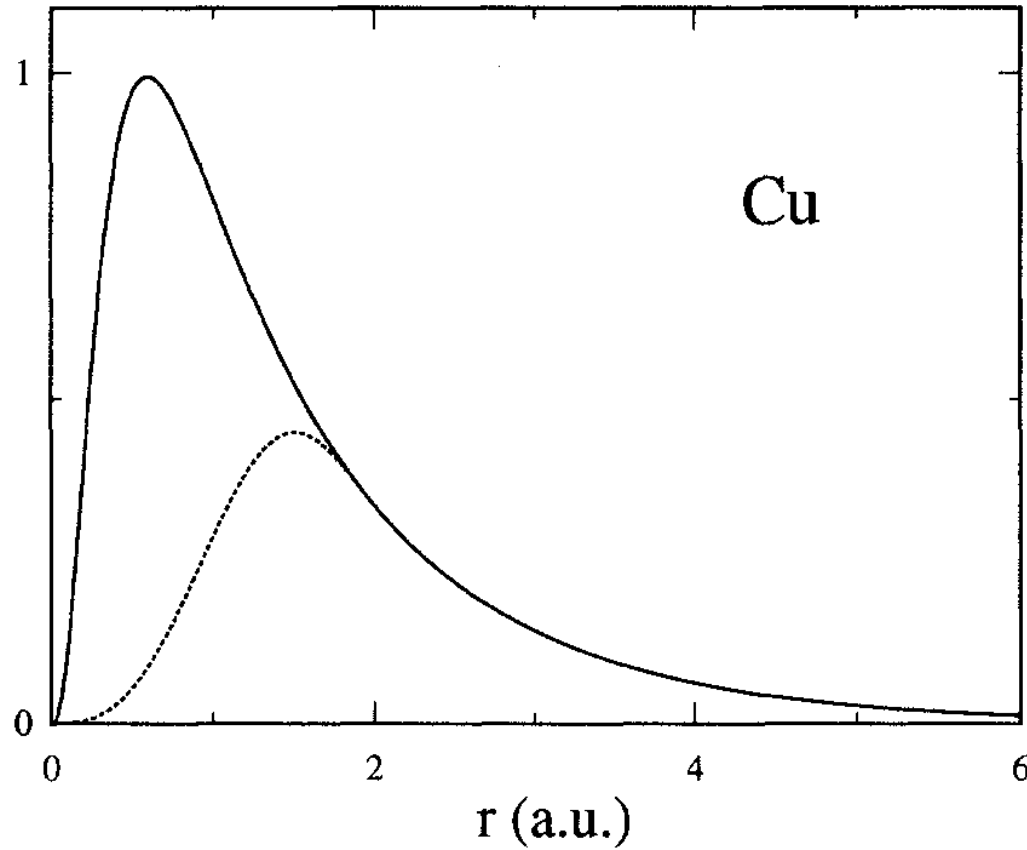




US pseudopotentials



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”



QUANTUM ESPRESSO

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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.

ANY PP LIBRARY		OTHER OPTIONS																			
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 A	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 A A	103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt												
A 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					
A A 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					

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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 (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-Ernzerhof (PBE) exch-corr
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** = $8-12 \times \text{ecutwfc}$!!

Element & V_{ion} for Quantum-ESPRESSO

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

input

```
diagonalization = cg, 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
```

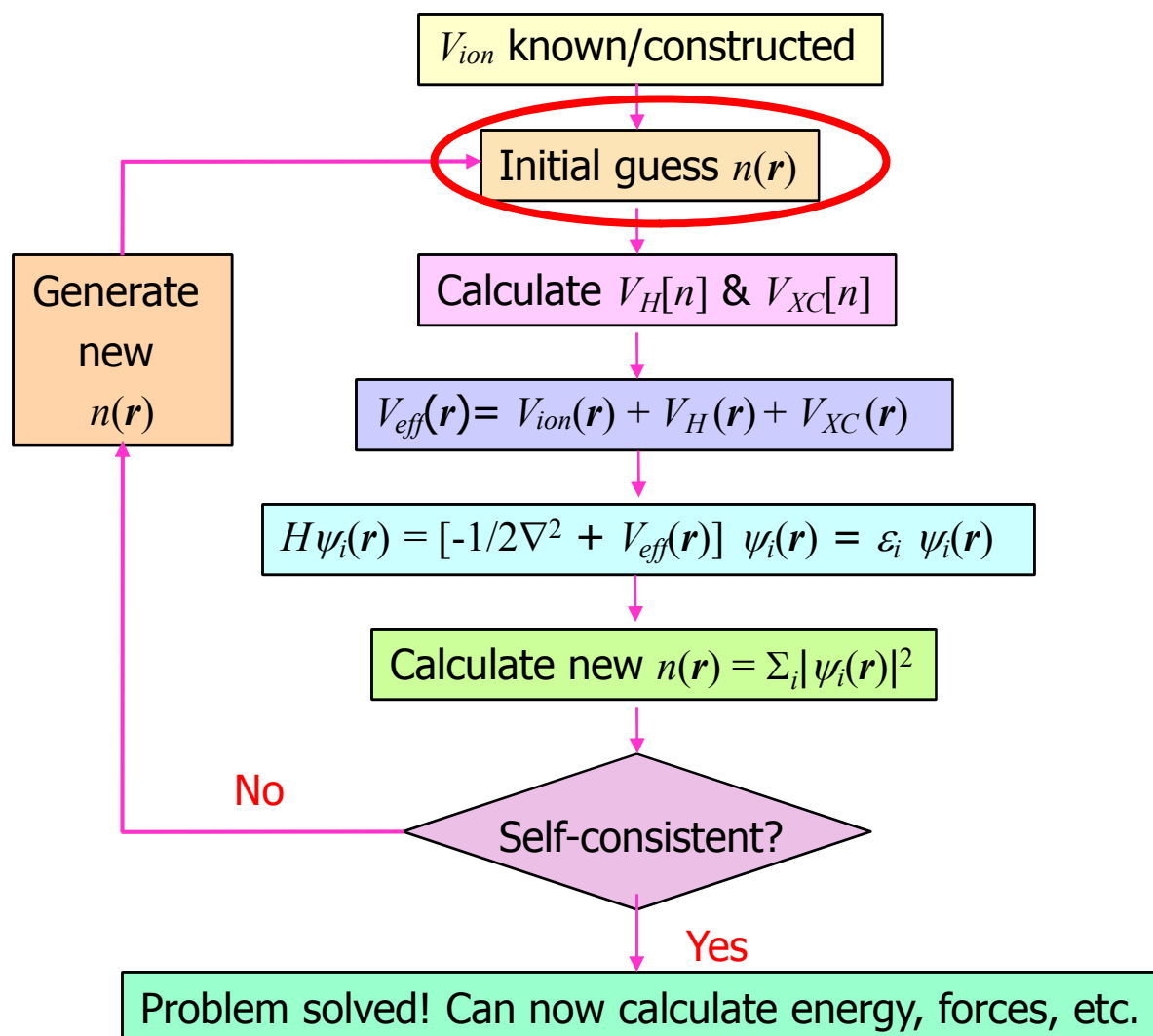
oops!

output

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

stopping ..█
```

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



Starting Wavefunctions

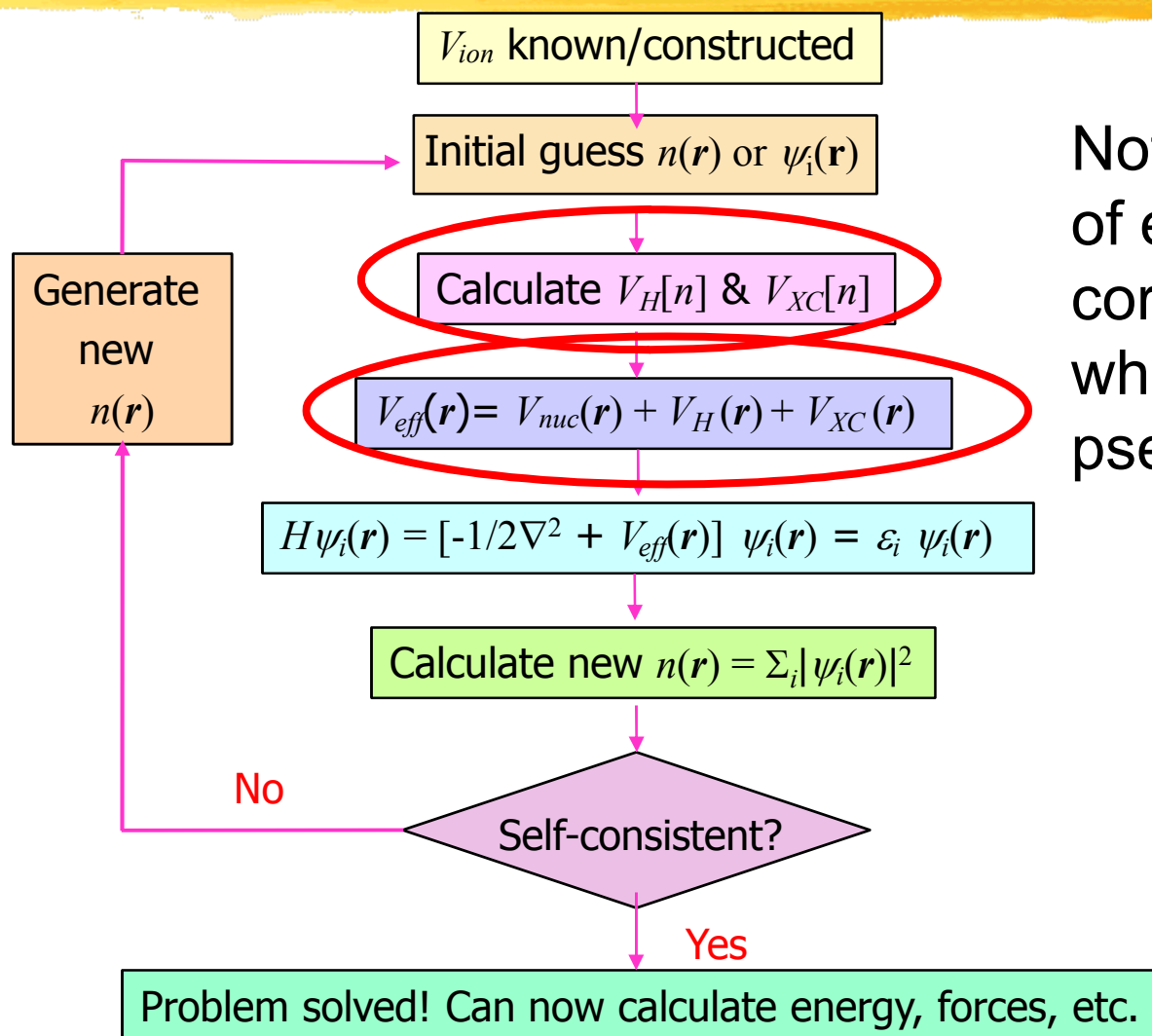
The closer your starting wavefunction is to the true wavefunction (which, of course, is something you don't necessarily know to start with!), the fewer the scf iterations needed.

```
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**.

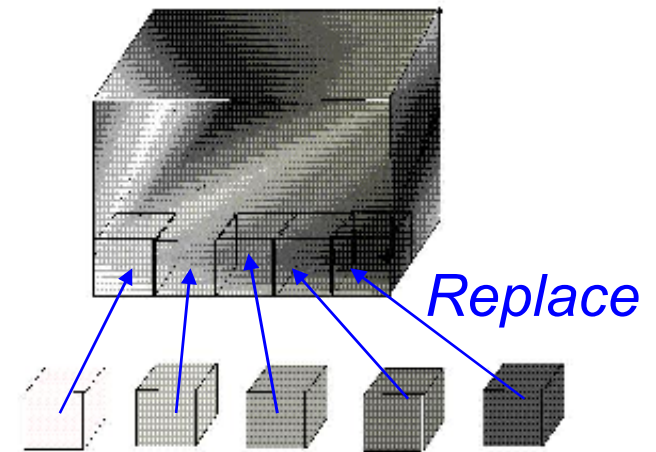
- Local Density Approximation:

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

-surprisingly successful!

pz

(in name of pseudopotential)

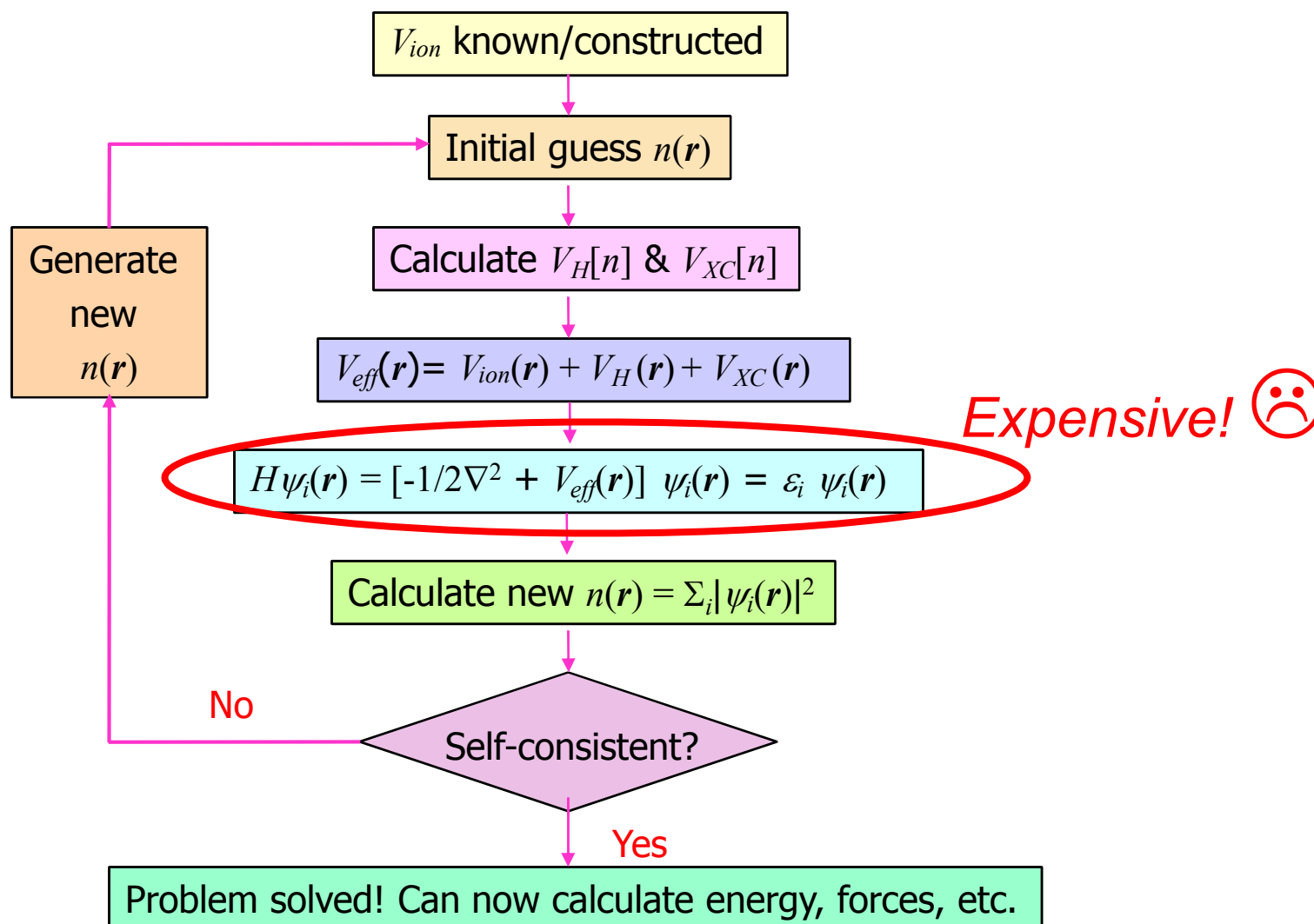


- Generalized Gradient Approximation(s): Include terms involving gradients of $n(\mathbf{r})$

pw91, pbe

(in name of pseudopotential)

Step 5: Diagonalization



Diagonalization

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

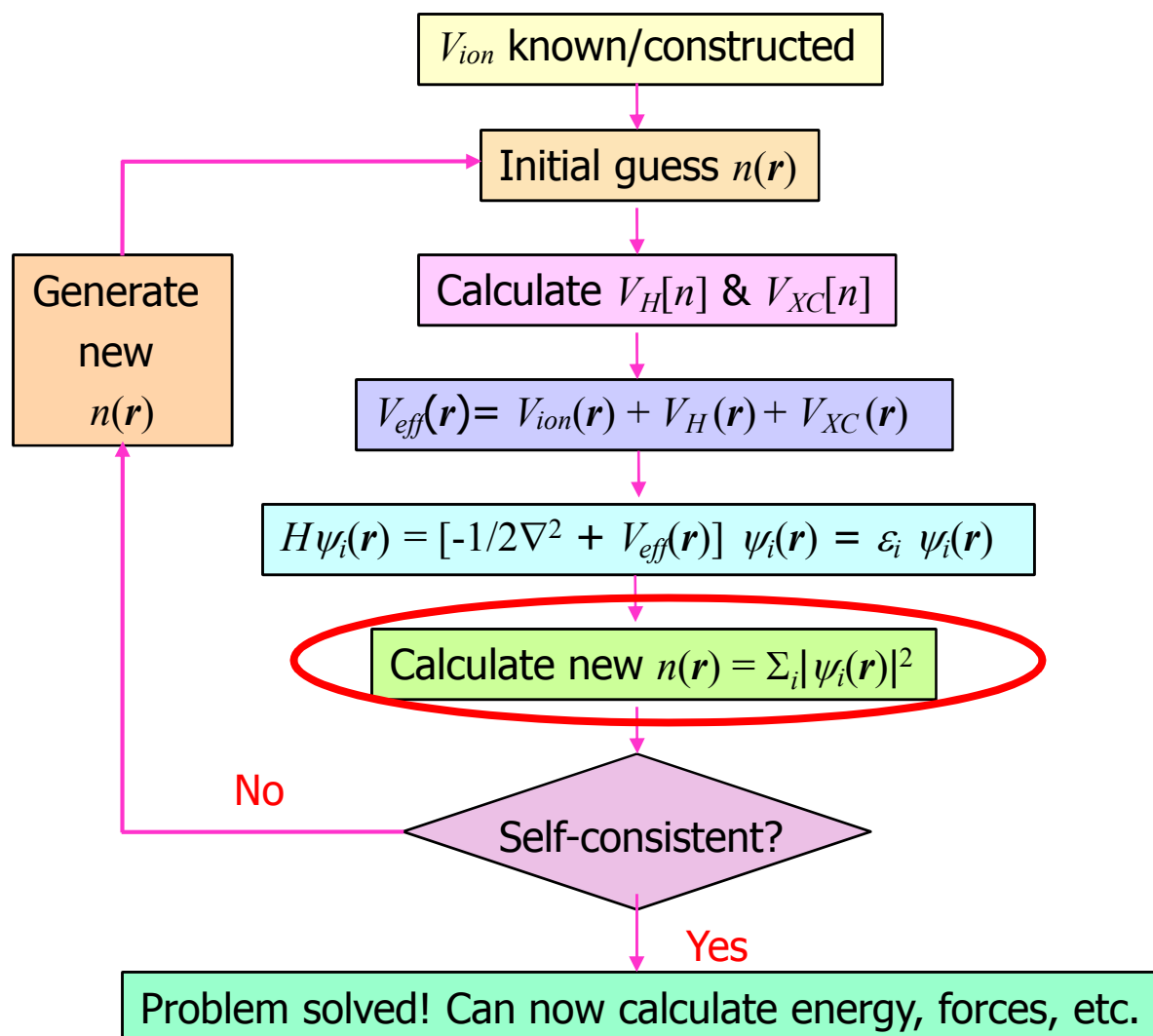
Input parameter **diagonalization**

-which algorithm used for iterative diagonalization

Input parameter **nbnd**

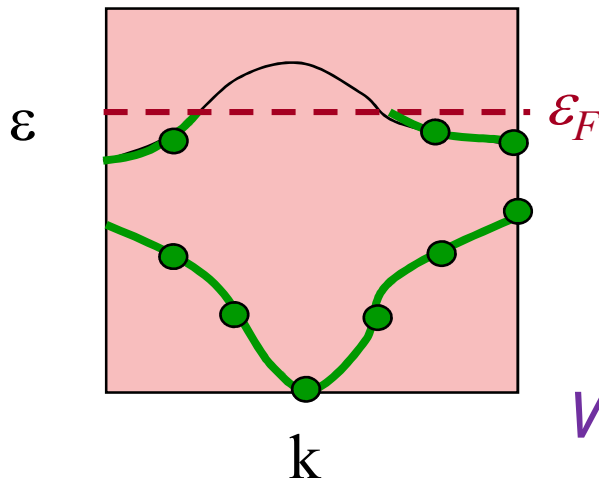
*-how many eigenvalues computed
for metals, choose depending on value of **degauss***

Step 6: New Charge Density



Brillouin Zone Sums

- Many quantities (e.g., n , E_{tot}) involve sums over $\mathbf{k}$.
- 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.

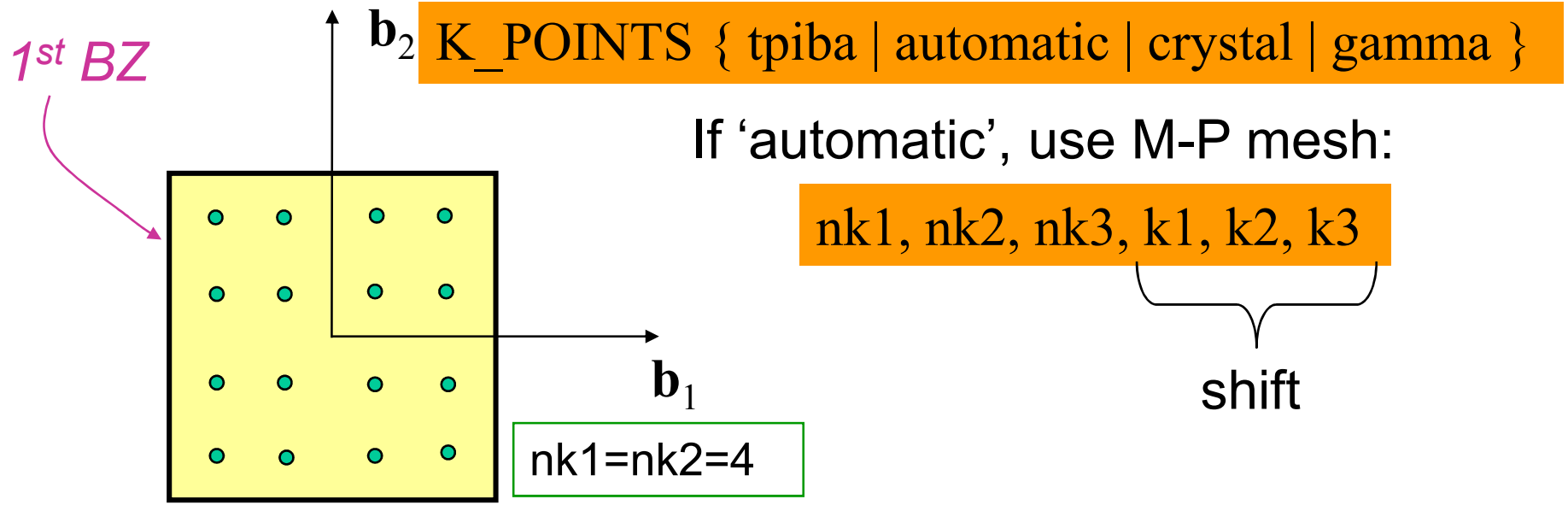


$$\langle P \rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\mathbf{k} \in BZ} P(\mathbf{k}) w_{\mathbf{k}}$$

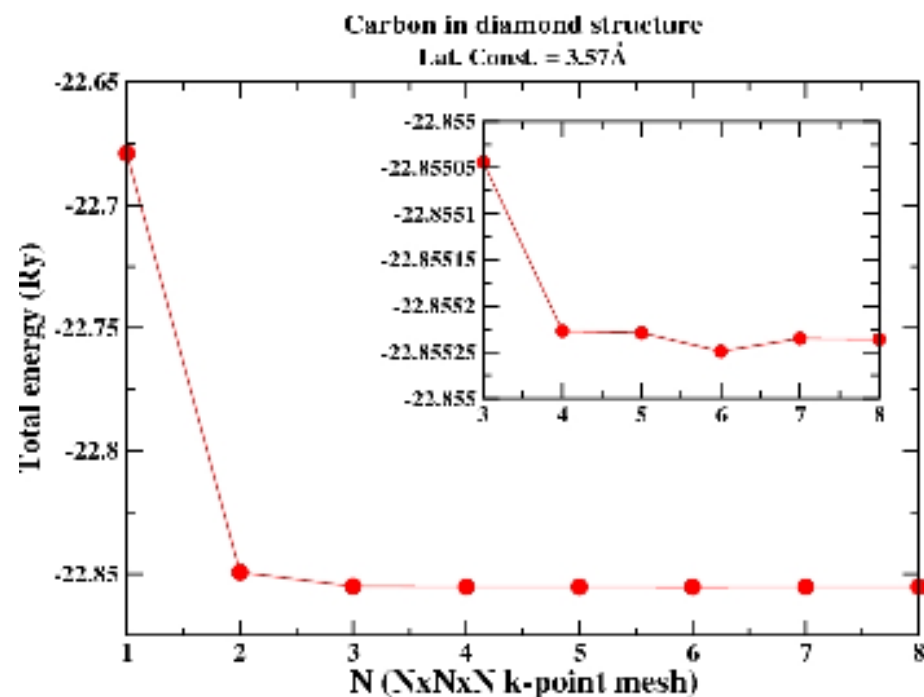
Will discuss in greater detail tomorrow

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']



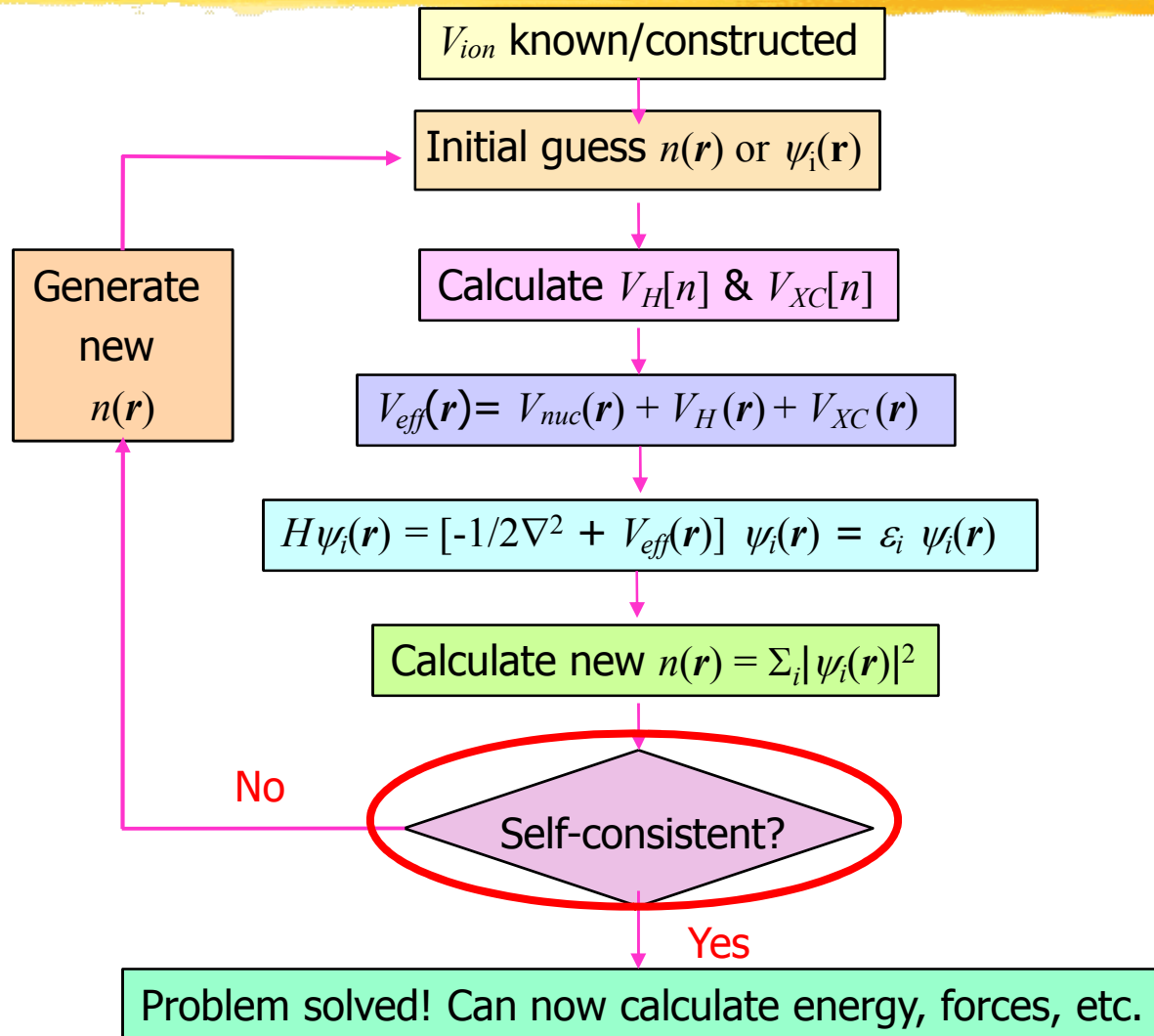
Convergence wrt BZ sampling



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

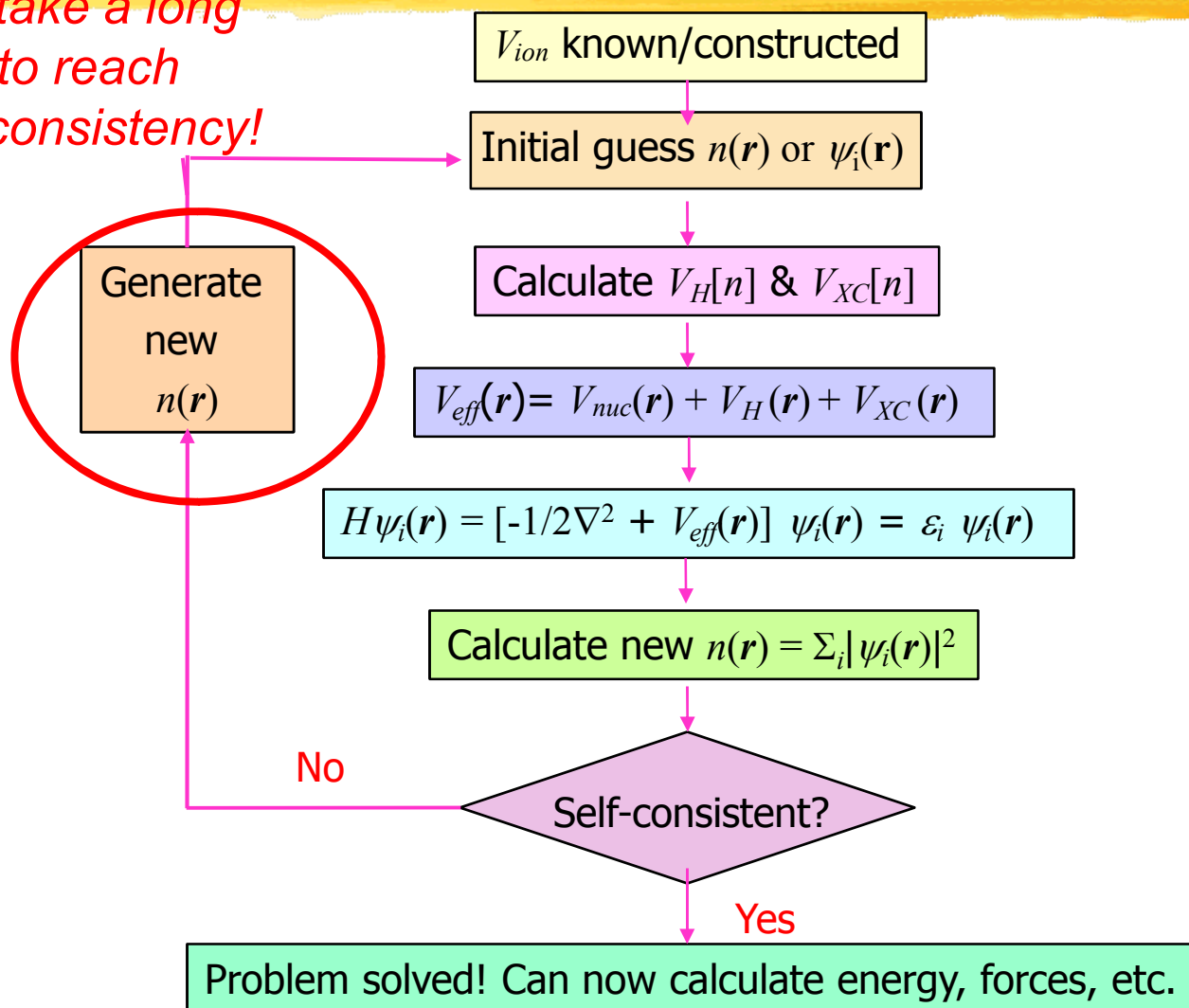
- Compare n th and $(n-1)$ th approximations for density, and see if they are close enough that self-consistency has been achieved.



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**

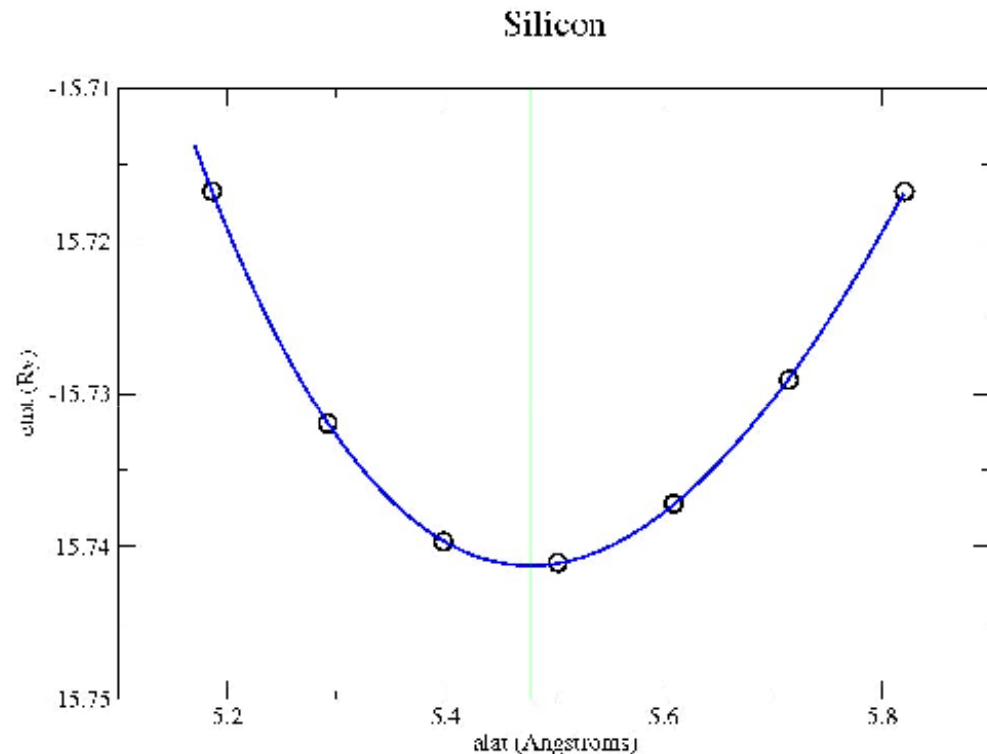
-Prescription used for mixing.

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!

