How to Solve the Kohn-Sham Eqns. For Electrons in a Periodic Potential

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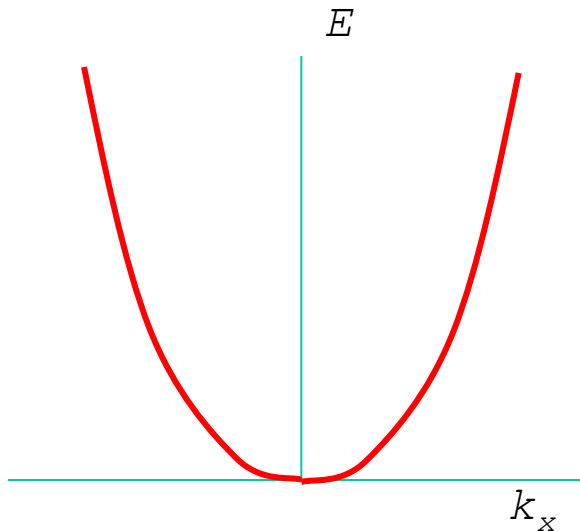
I.   First Let's Quickly Recall What Happens for Free Electrons

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Free Electrons: Energies

- For free electrons, $H_E = T_E + V_{N\text{-}E} + V_{E\text{-}E}$ (last two terms crossed out)
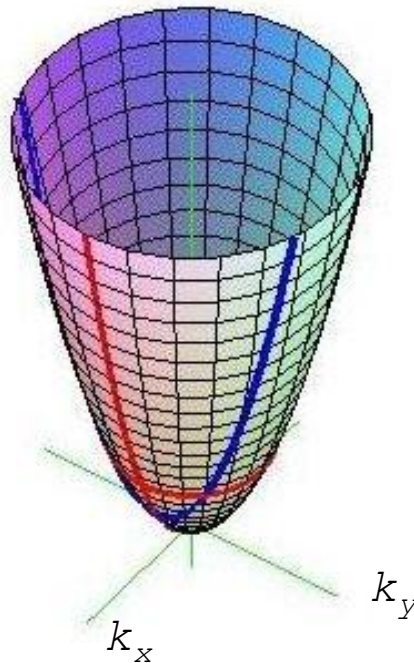
1-D

$$E = \frac{\hbar^2 |\mathbf{k}|^2}{2m} = \frac{\hbar^2 k_x^2}{2m}$$

E

k_x

2-D

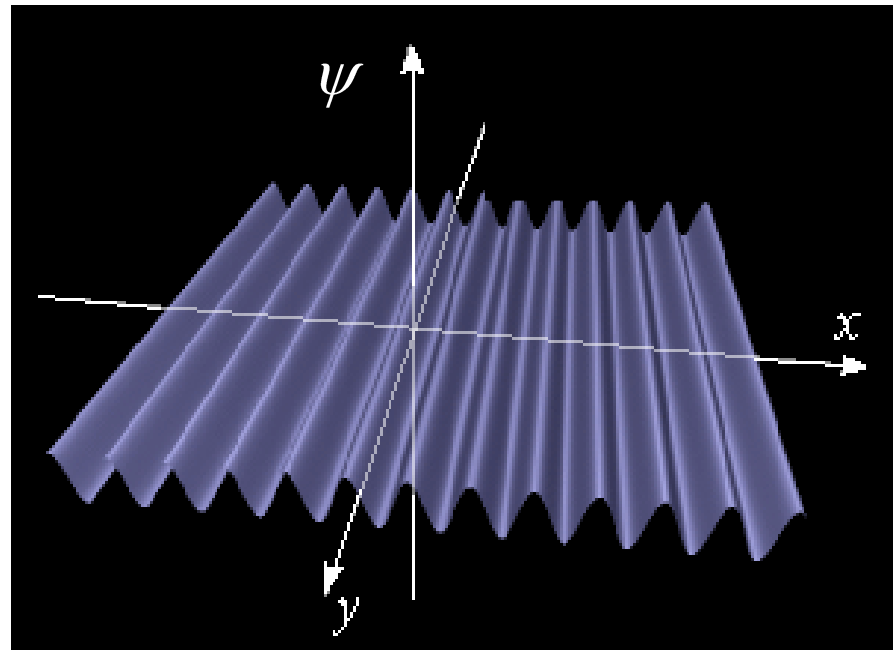$$E = \frac{\hbar^2 |\mathbf{k}|^2}{2m} = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m}$$

k_y

k_x

3-D

$$E = \frac{\hbar^2 |\mathbf{k}|^2}{2m}$$

$$= \frac{\hbar^2 (k_x^2 + k_y^2 + k_z^2)}{2m}$$

Note:
- Energies depend on **k**.
- All energies allowed.

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Free Electrons: Wavefunctions

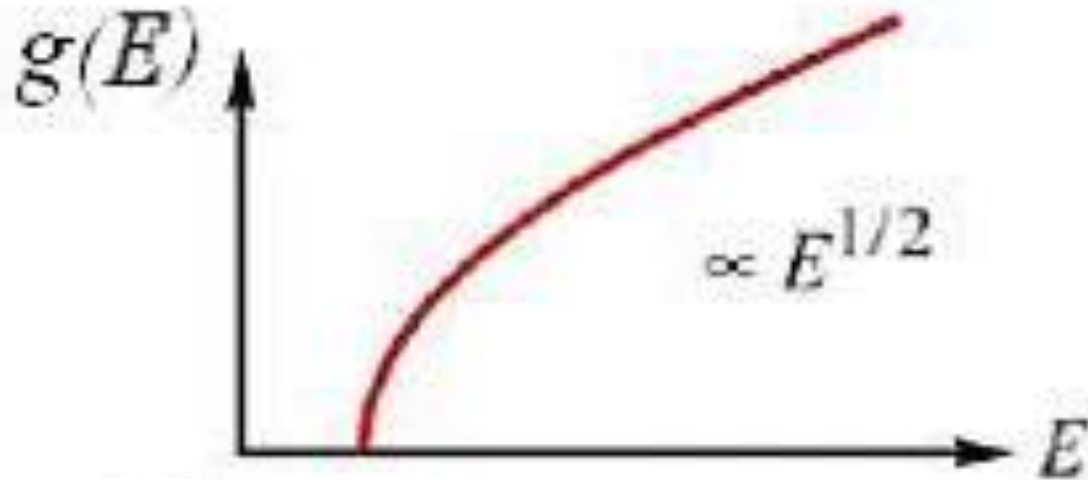The wavefunctions of free electrons are plane waves:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\bullet\mathbf{r}}$$

www.rpi.edu/dept/phys/ScIT/InformationTransfer

Free Electrons: Density of States

Tells how the available states are distributed in energy. e.g., in 3-D:

$$g(E) \propto E^{1/2}$$

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II. Electrons In A Periodic Potential

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Bloch's Theorem

- Consider electrons in a periodic potential $V(\mathbf{r})$, s.t. $V(\mathbf{r}+\mathbf{R})=V(\mathbf{r})$

- The wavefunction of the system will then have the form:

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

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

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

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Fourier Expansion

- 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

- Reciprocal lattice vectors defined by

$$\mathbf{G}\bullet\mathbf{R} = 2\pi n,$$ where $n \in Z,$ or $$e^{i\mathbf{G}\bullet\mathbf{R}} = 1$$
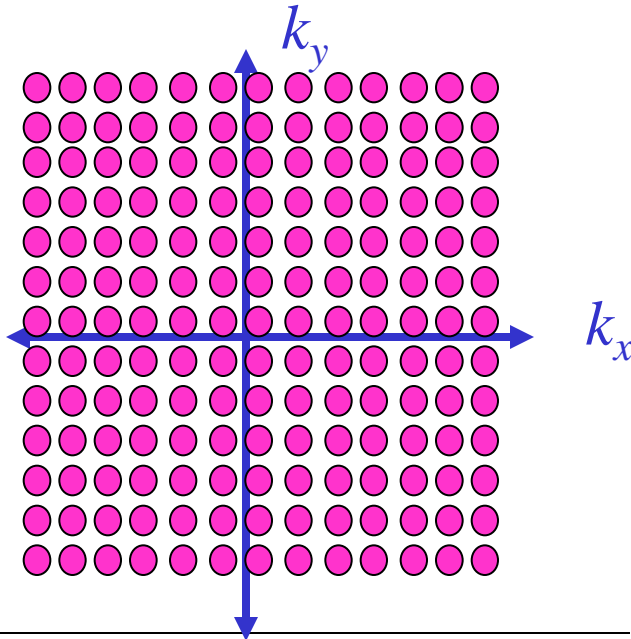
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Plane Wave Expansion of Wavefunction

- 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 $\mathbf{G}$ = 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.

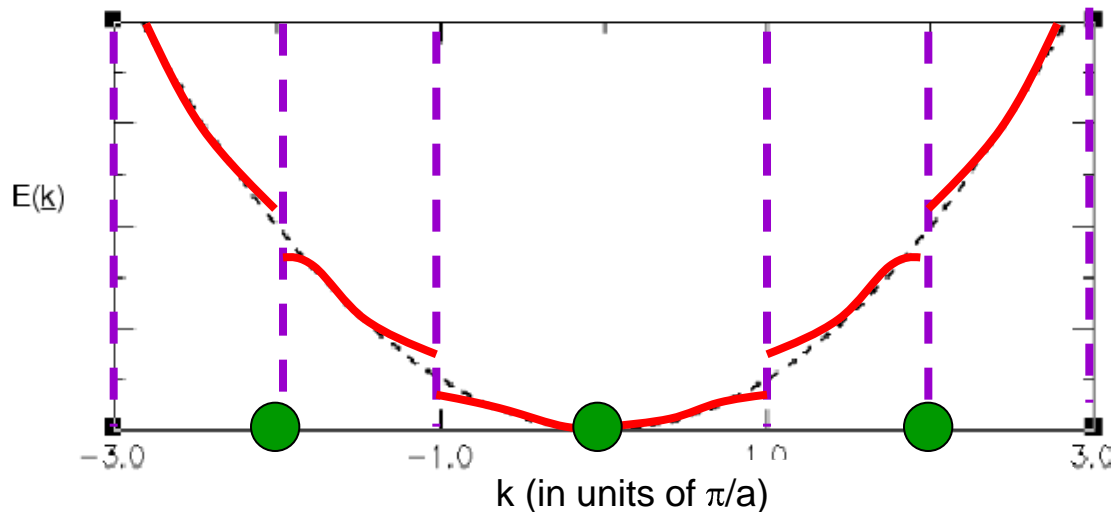- In principle, still need infinite number of plane waves.

Periodic Potentials and Gaps

- The effect of a periodic potential is to open up gaps at Bragg planes (1/2 **G**).

- e.g., in 1-D:

Free electron band

k (in units of π/a)

Periodic Potentials and Gaps

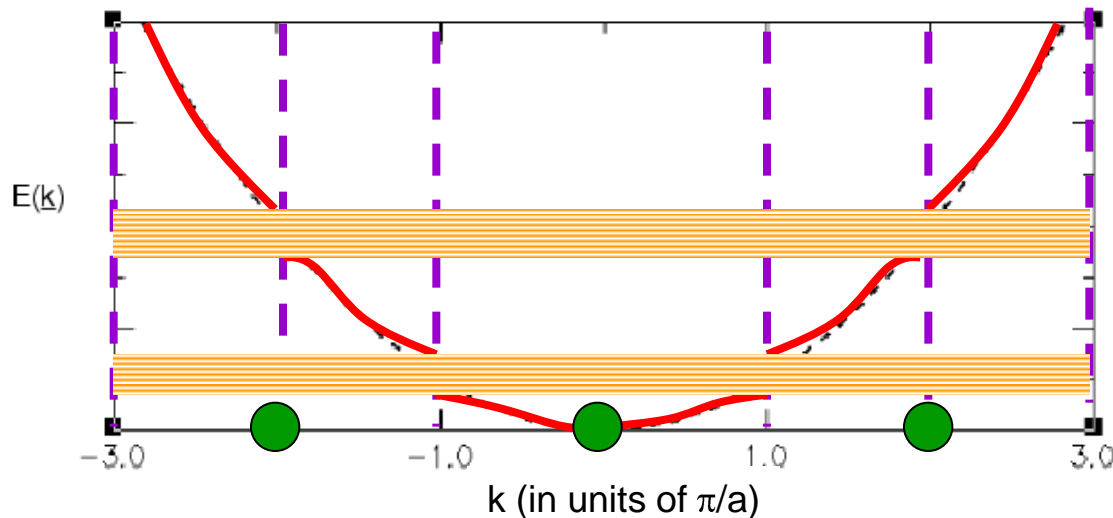- The effect of a periodic potential is to open up gaps at Bragg planes (1/2 **G**).

- e.g., in 1-D:

(Extended zone scheme)

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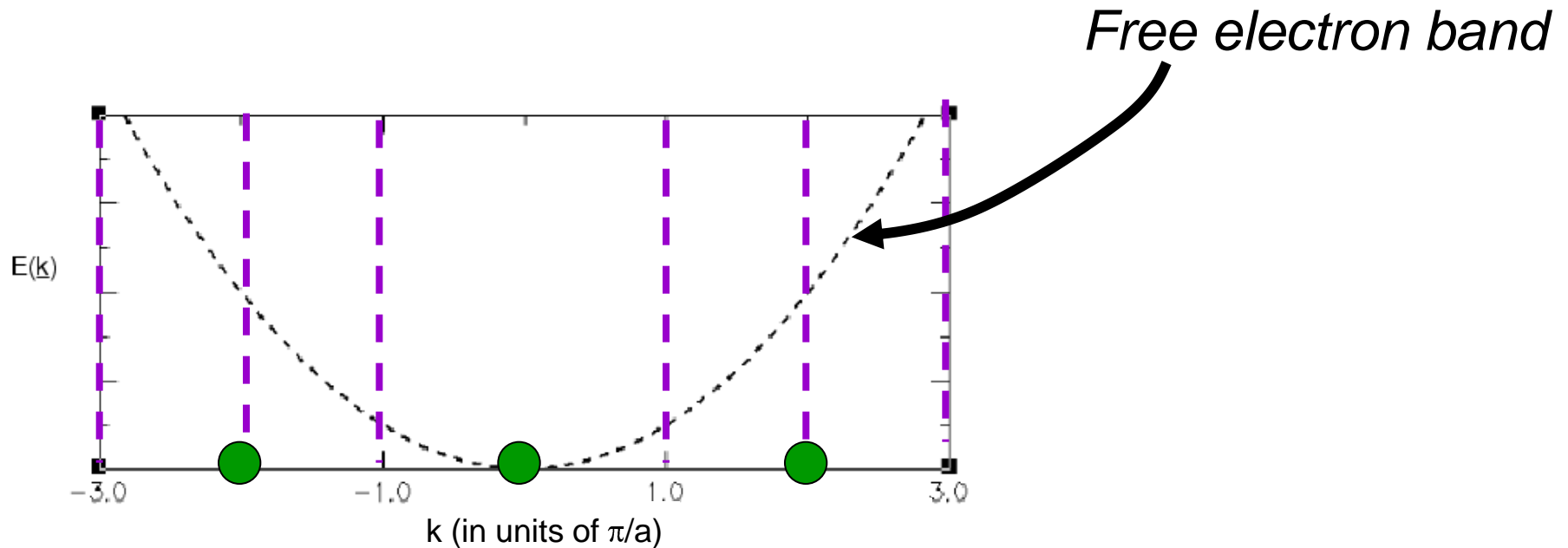
Periodic Potentials and Gaps

- The effect of a periodic potential is to open up gaps at Bragg planes (1/2 **G**).

- e.g., in 1-D:

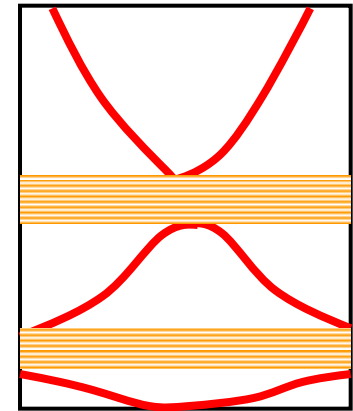*(Extended zone scheme)*

(Reduced or folded zone scheme)

Density of States in a Periodic Potential

$g(E)$

$g(E)$

E

E
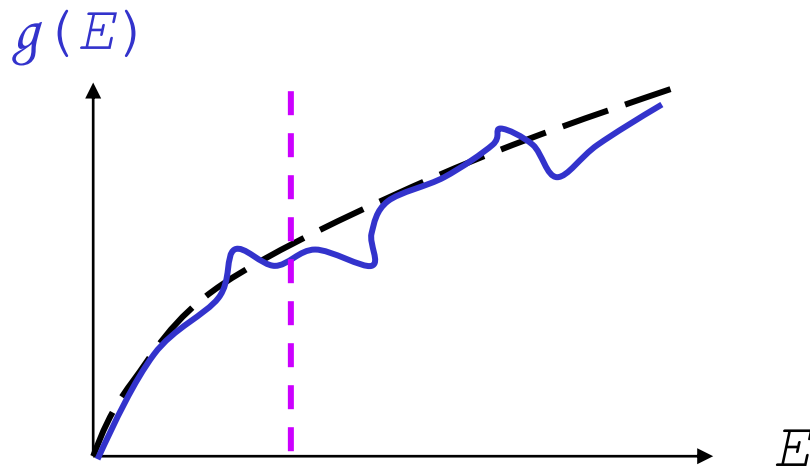
In a weak potential
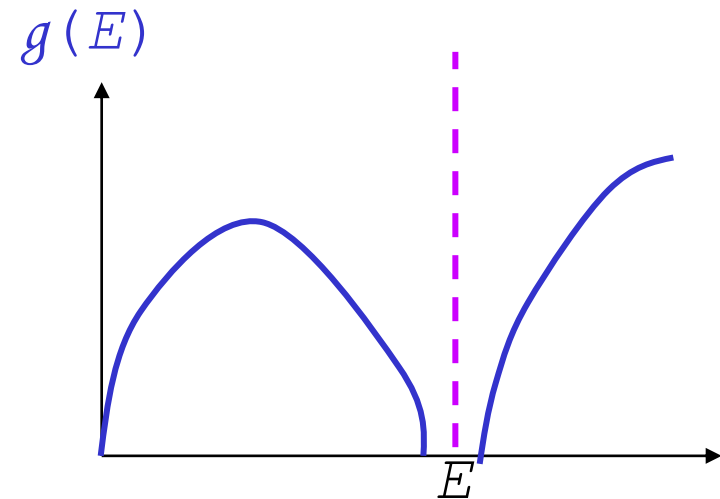
In a strong potential

Filling Up Bands: Fermi-Dirac Distribution

$$f(E_i) = \frac{1}{e^{(E_i - \mu)/k_B T} + 1}$$

$f(E)$

At $T = 0$

1

0

$\mu = E_F$

E
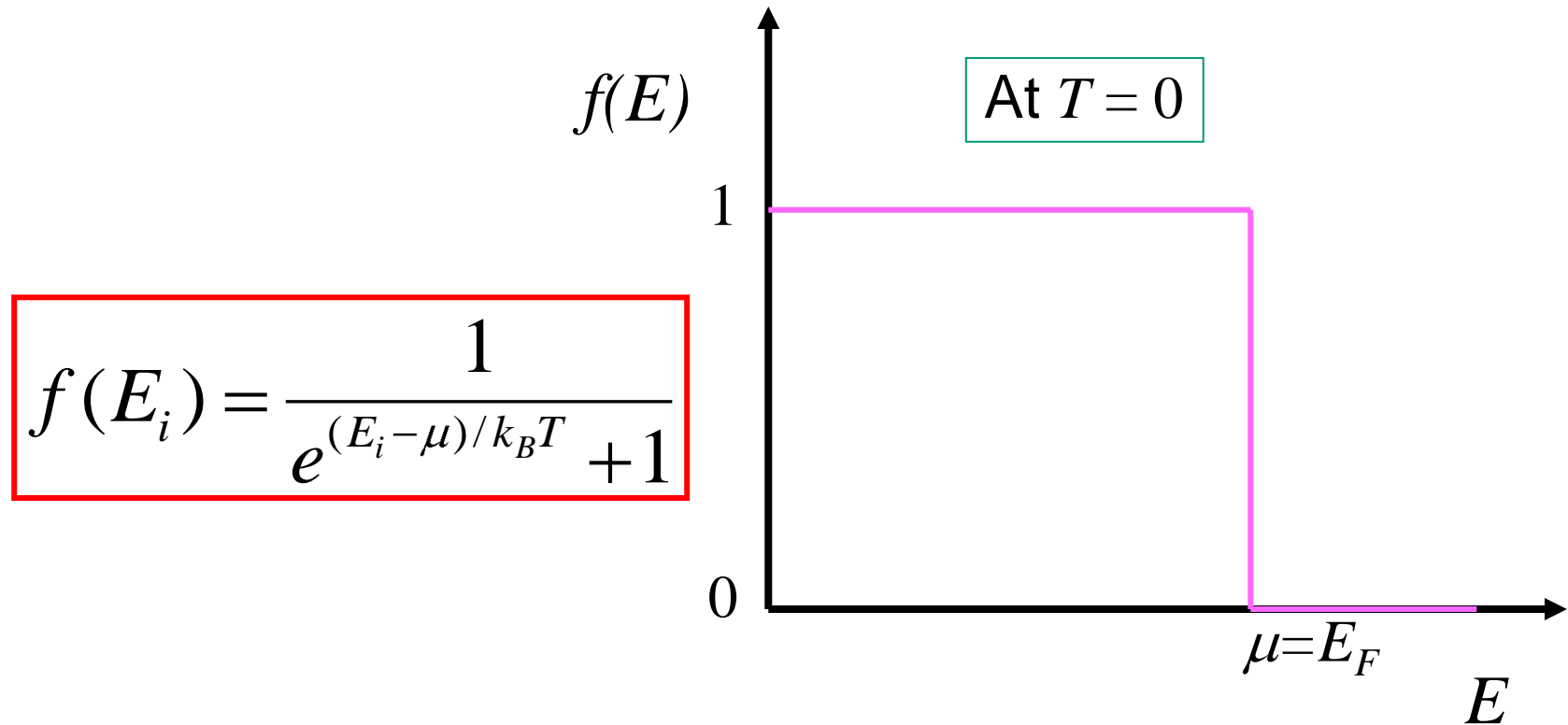
Metals & Insulators

Metal

$g(E)$

E_F

Partially filled band

Insulator

$g(E)$

E_F

Wholly filled band
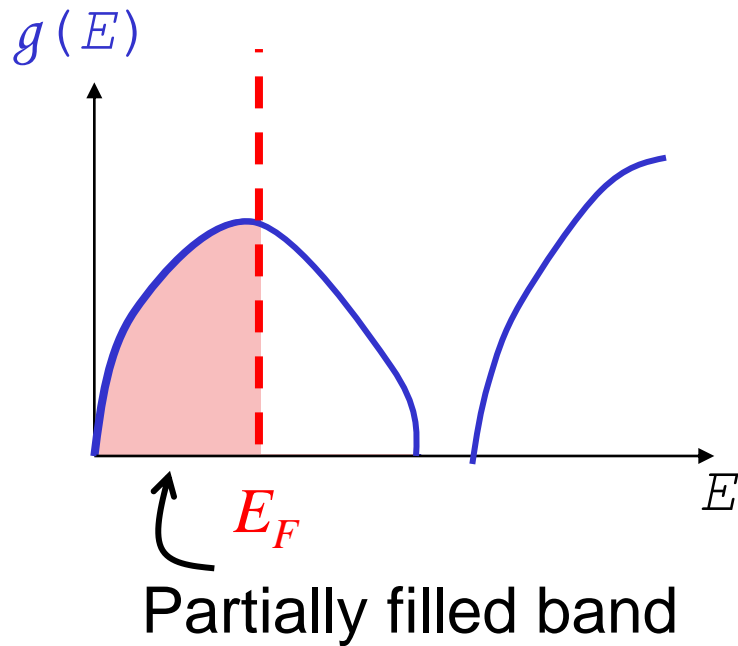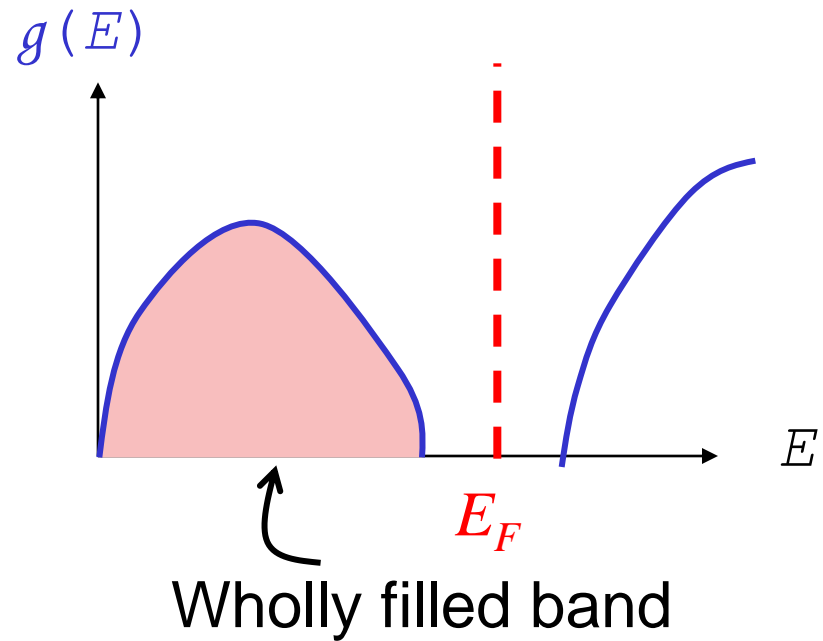
Here we will do Worksheet 4 on Bandstructures & DOS

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Density of States

- For Al:
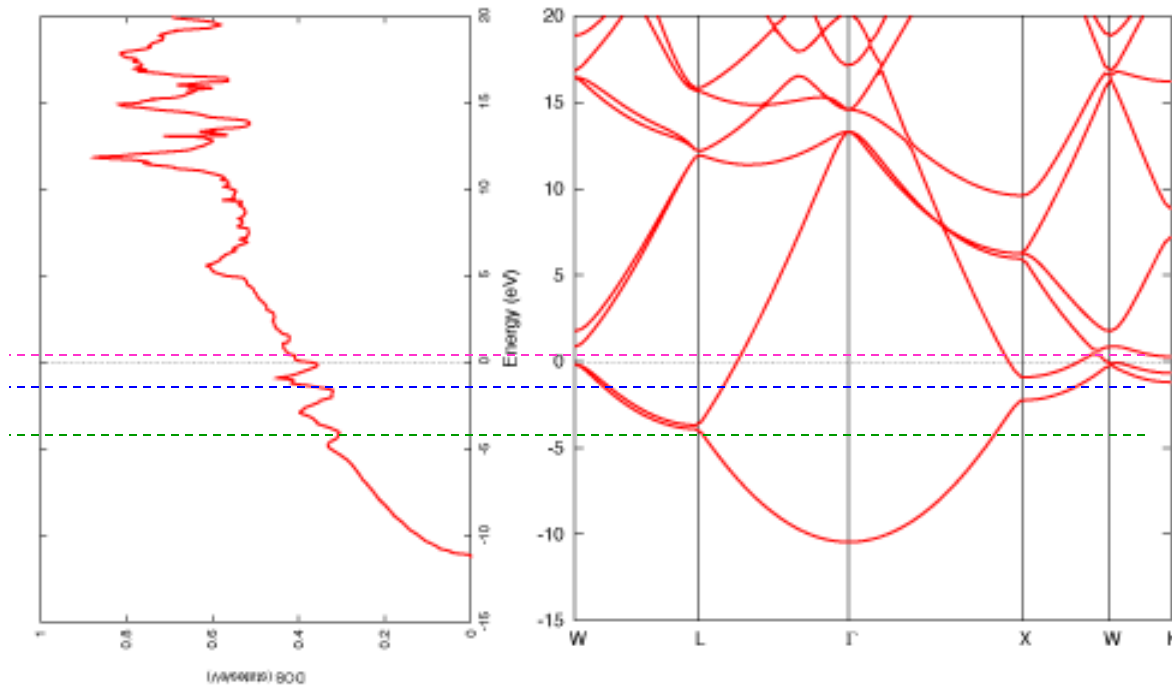
www.fsis.iis.u-tokyo.ac.jp

Density of States

- For Pb:

E_F
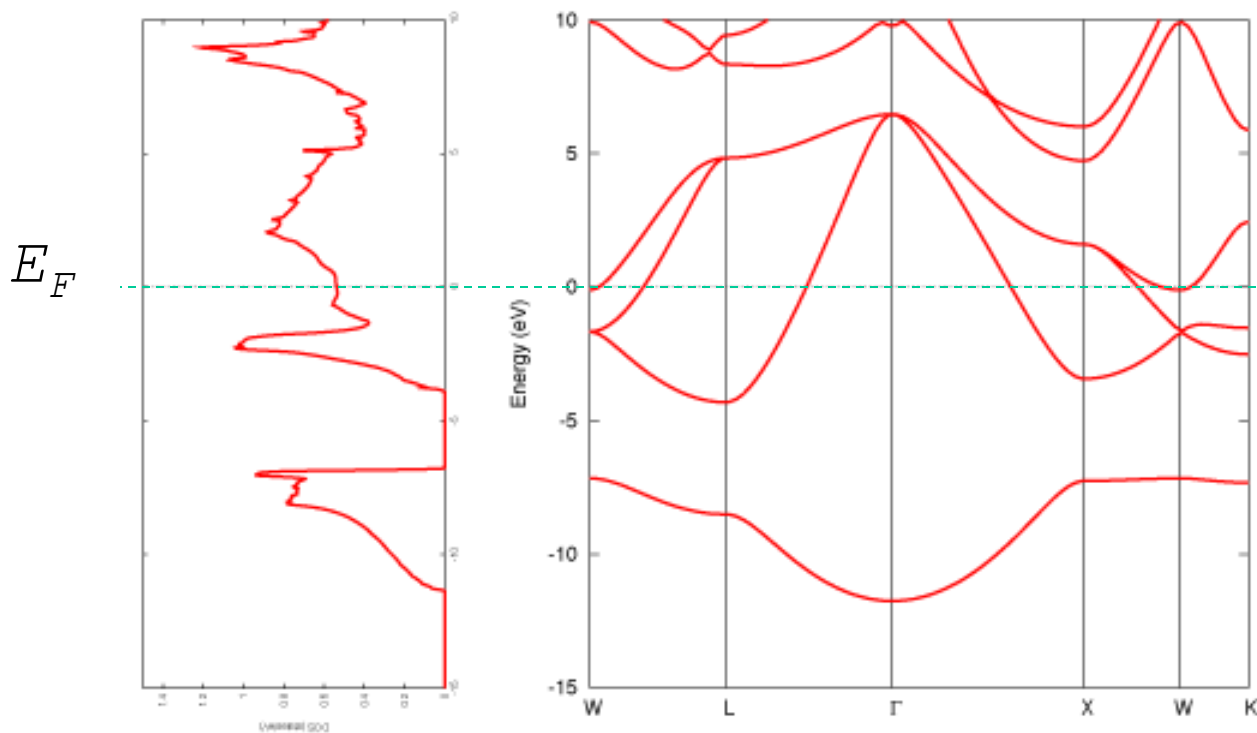
www.fsis.iis.u-tokyo.ac.jp

Density of States

- For C (diamond structure):
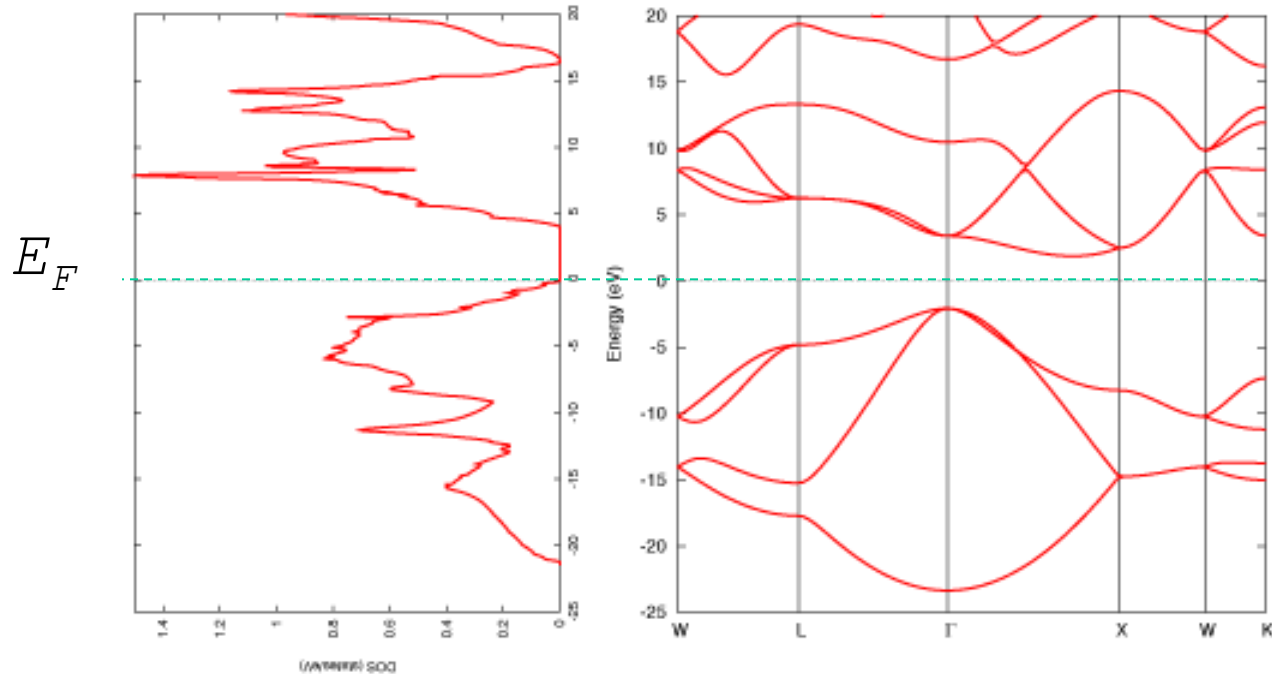
www.fsis.iis.u-tokyo.ac.jp

Density of States

- For Si:

E_F

www.fsis.iis.u-tokyo.ac.jp

20
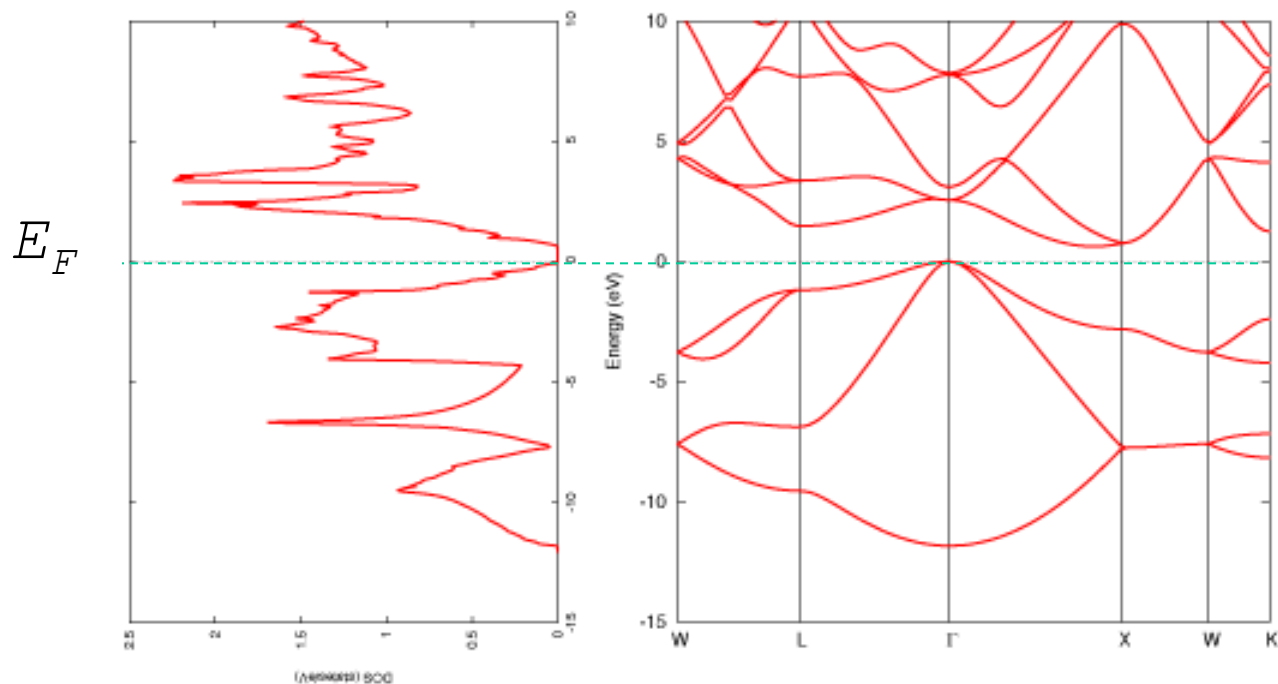
III. Solving the Kohn-Sham Equations Using the pwscf code of Quantum ESPRESSO

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Quantum ESPRESSO

- www.quantum-espresso.org

Quantum ESPRESSO

4 important things about Quantum ESPRESSO:

- It uses a plane wave basis.
- It uses pseudopotentials.
- It is open source.
- It is free!

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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

V_{nuc} known/constructed

↓

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

↓

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

↓

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

↓

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

↓

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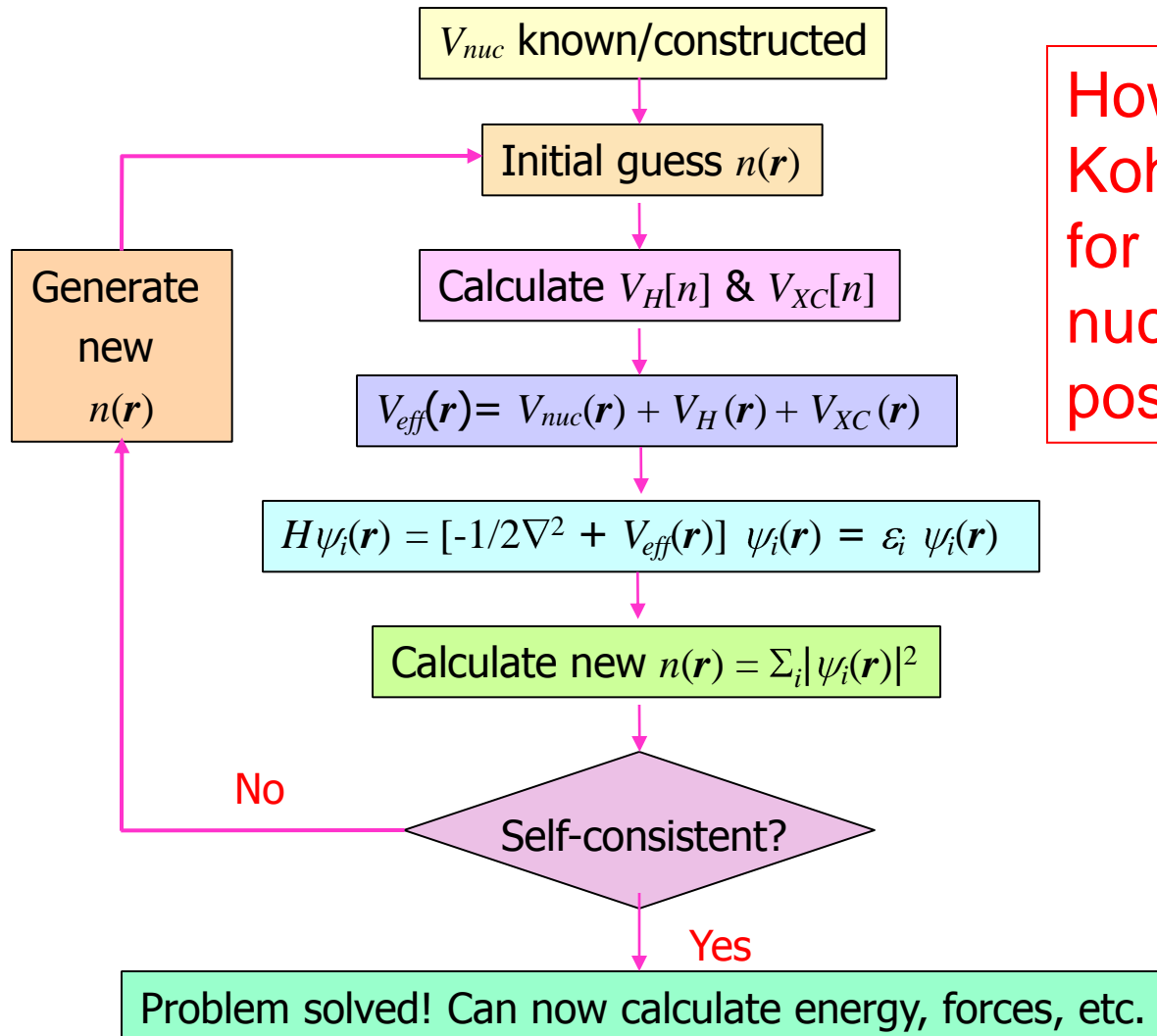
How to solve the Kohn-Sham eqns. for a set of fixed nuclear (ionic) positions.

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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:

$$\sum_\beta H_{\alpha\beta}\, c_{i\beta} = \varepsilon_i\, c_{i\alpha}$$

Matrix element   *Eigenvalue*   *Eigenvector*

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

Size of basis

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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:

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

   (Will discuss…solution = introduction of pseudopotentials.)

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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**

$$E = E_{cut}$$

k_y

k_x

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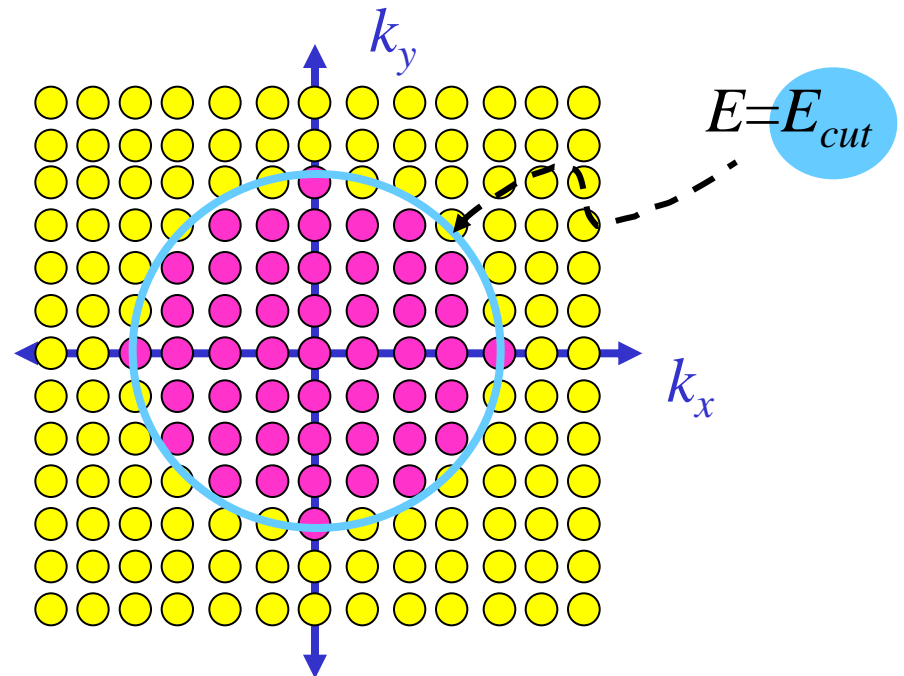
Checking Convergence wrt ecutwfc

- Must always check.
- Monotonic (variational).

Silicon: Convergence wrt plane wave cutoff
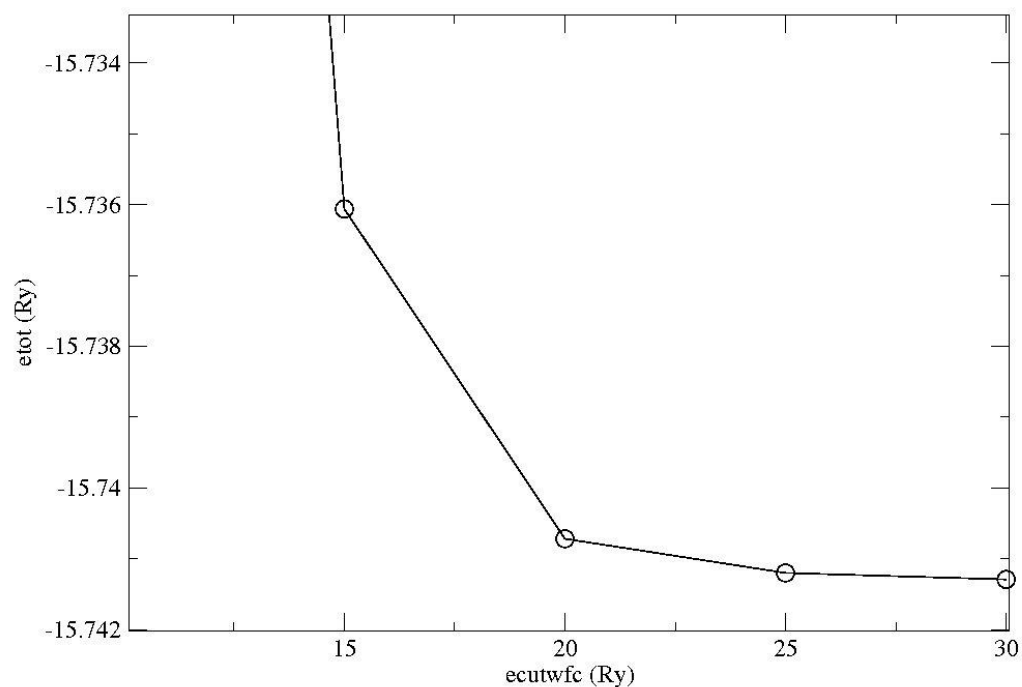
What if the system is not periodic?

- <u>Example 1</u>: Want to study properties of a system with a surface.

- Presence of surface $\Rightarrow$ No periodicity along z.

Surface atom

Bulk atom

z

x
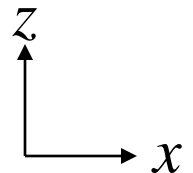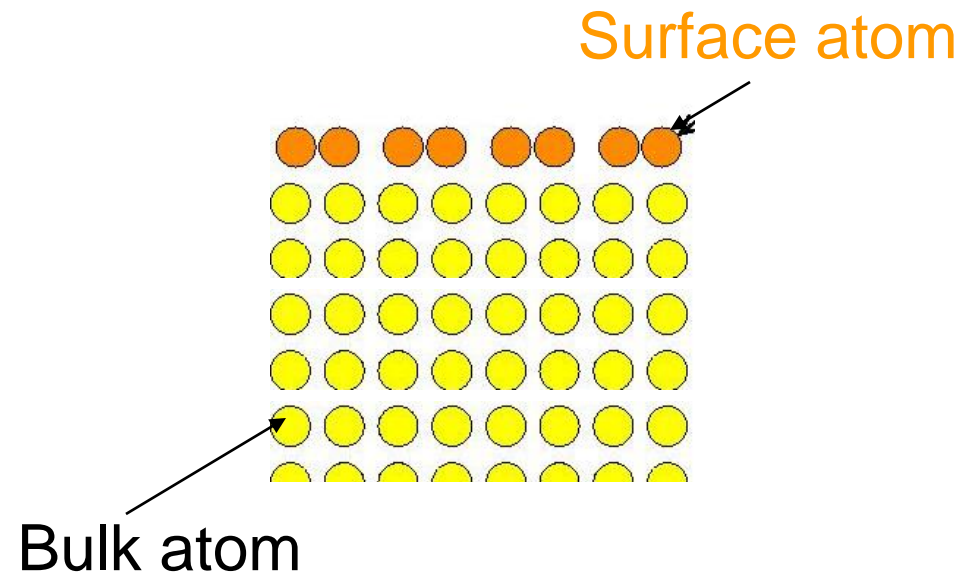
What if the system is not periodic?

- <u>Example 1</u>: 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.
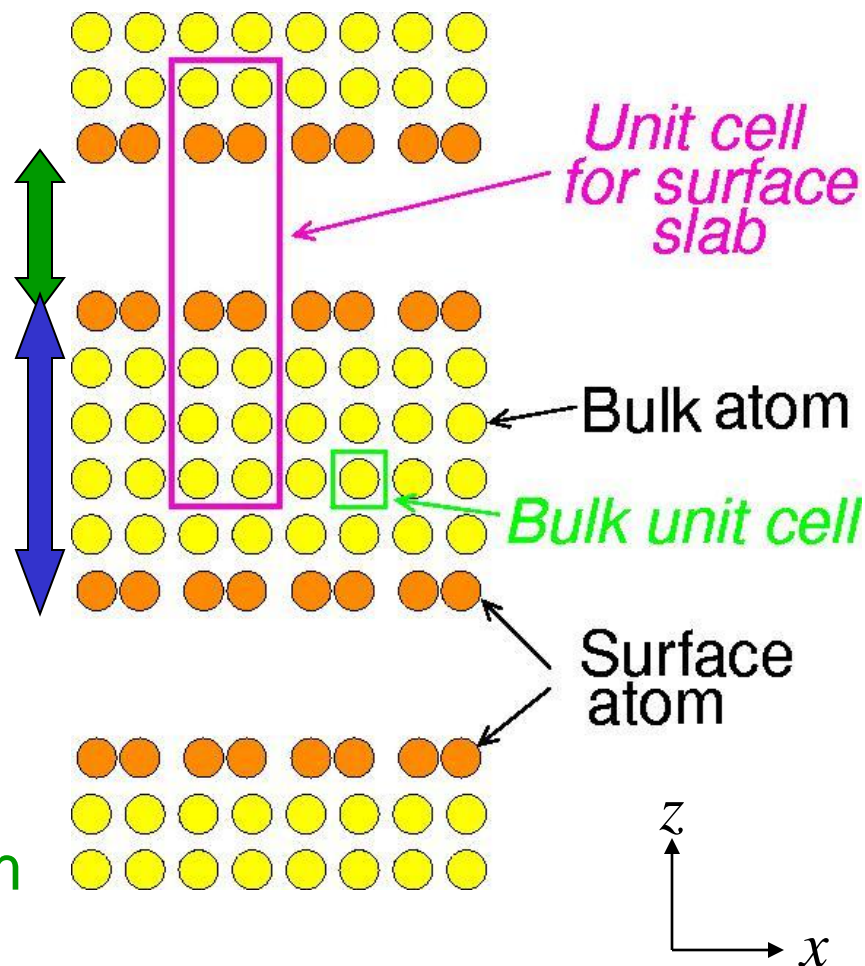
Unit cell for surface slab

Bulk atom

Bulk unit cell

Surface atom

z

x

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What if the system is not periodic?

- <u>Example 2</u>: Want to study properties of a nanowire.

z

y

- <u>Example 3</u>: Want to study properties of a cluster
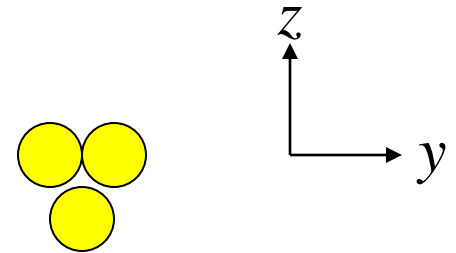
What if the system is not periodic?

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

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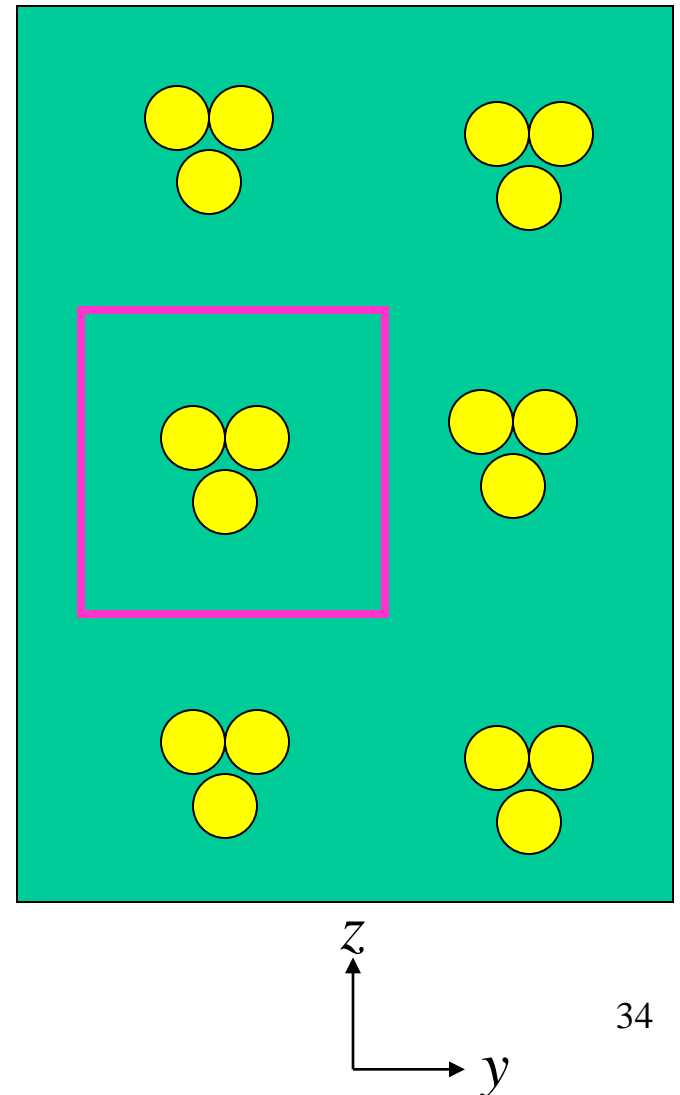
z

y
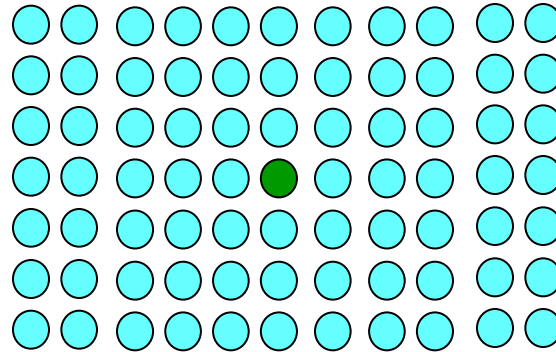
What if the system is not periodic?

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

What if the system is not periodic?

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

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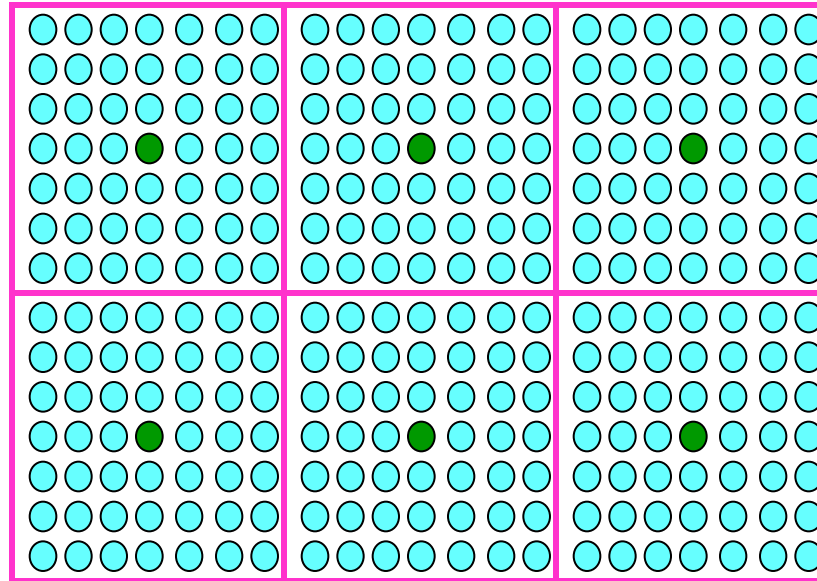
What if the system is not periodic?

- <u>Example 5</u>: Want to study an amorphous or quasicrystalline system.
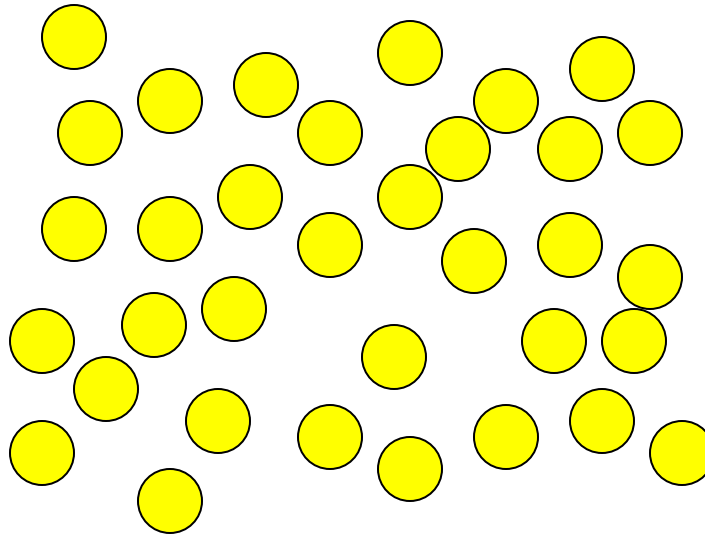
What if the system is not periodic?

- <u>Example 5</u>: Want to study an amorphous or quasicrystalline system: approximate by a periodic system (with large unit cell).
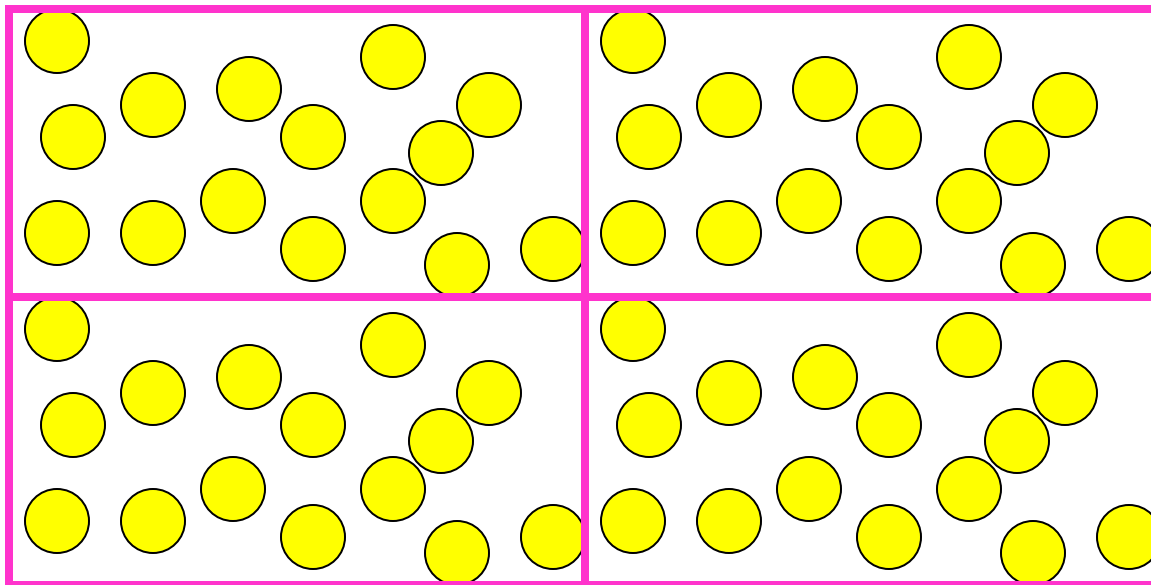
Artificially Periodic Systems $\Rightarrow$ Large Unit Cells

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

$$\Downarrow$$

- Long $\mathbf{a}$, $\mathbf{a}_2$, $\mathbf{a}_3$ (primitive lattice vectors) (or *a,b,c*)

$$\Downarrow$$

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

$$\Downarrow$$

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

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Using Supercells Increases Computation Time

Calculation takes longer when unit cell size increased:

REAL SPACE

RECIPROCAL SPACE

k_y

$E=E_{cut}$

k_x

k_y

$E=E_{cut}$

k_x
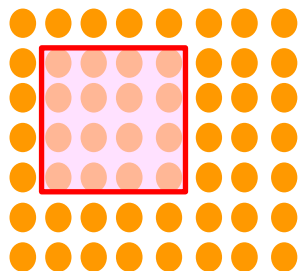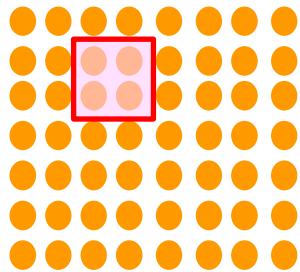
Unit cell expands

1st Brillouin zone

shrinks

Step 1: Obtaining V_{nuc}

V_{nuc} known/constructed

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

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

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

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

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

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

Self-consistent?

No

Yes

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

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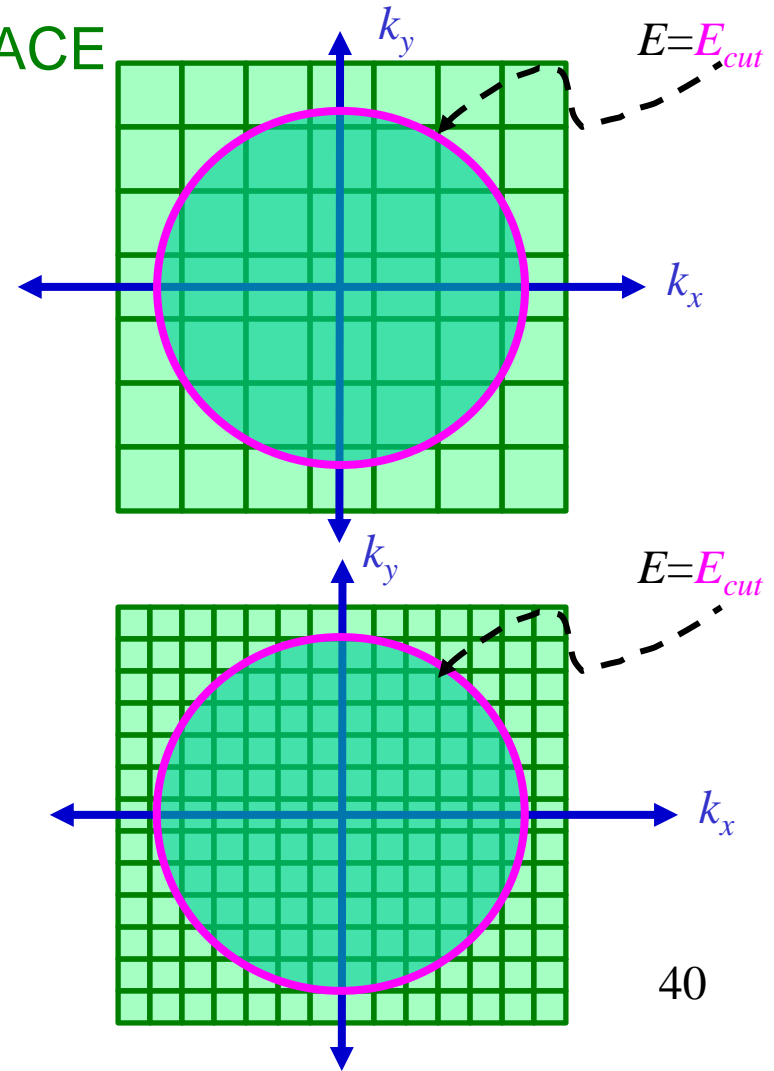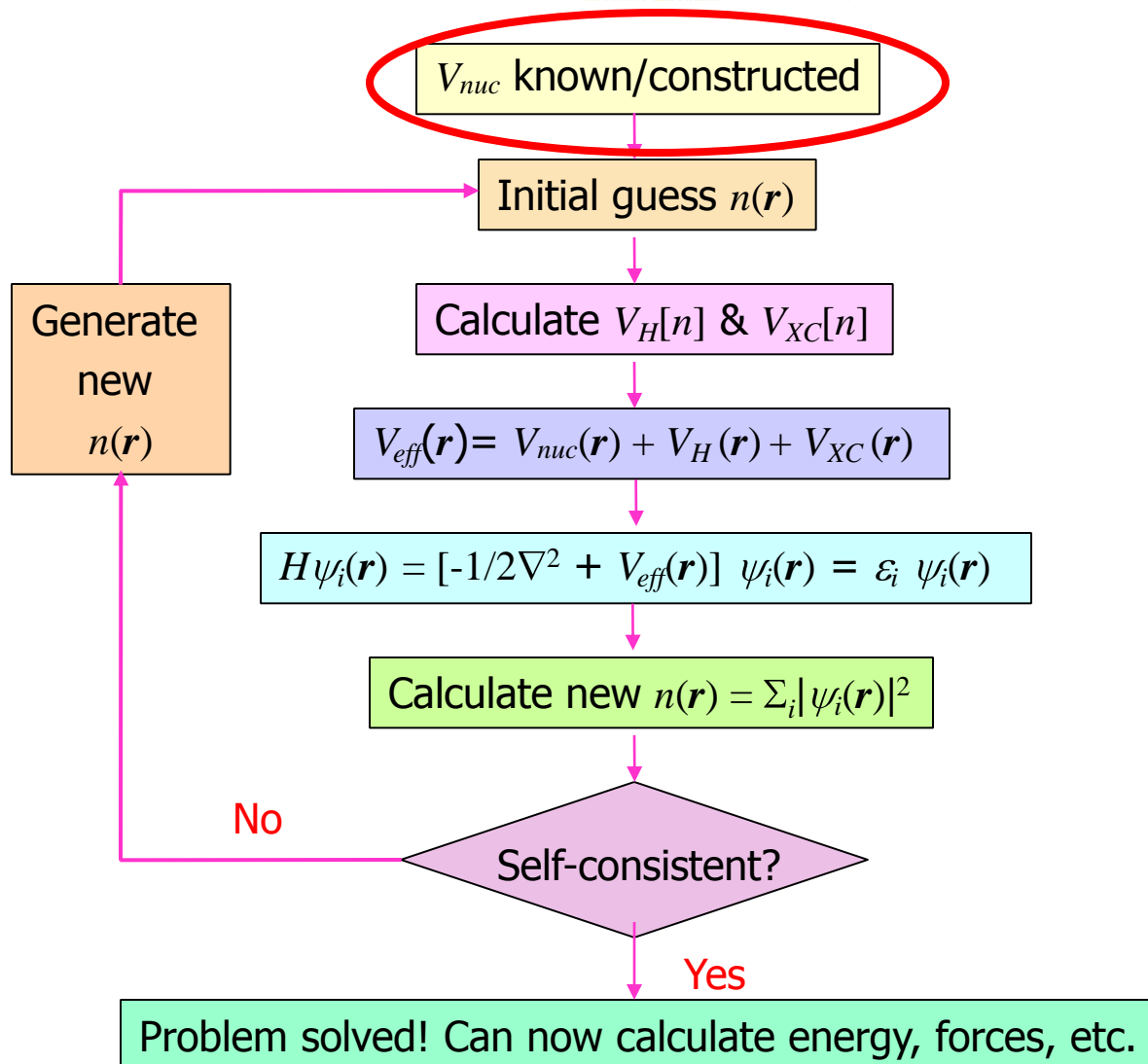
Nuclear Potential

- 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.

An analogy!

- "Dummy cops" used by many law-enforcement agencies!

Stick a mannequin in uniform by the highway … if it looks like a cop, it works like a cop!

Don't care about internal structure as long as it works right!
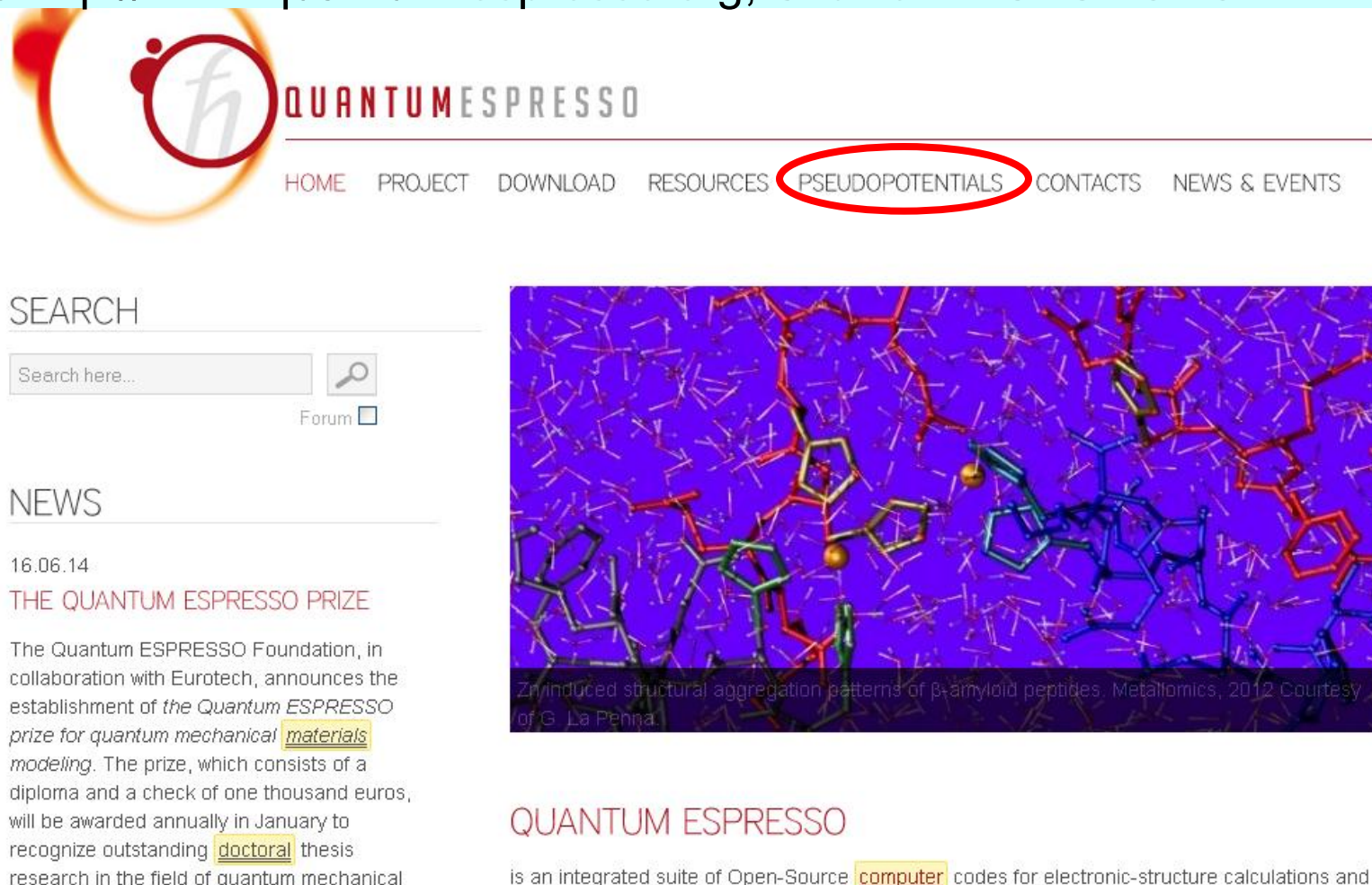
But cheaper!!

Obviously it can't reproduce all the functions of a real cop, but should be convincing enough to produce desired results….

Pseudopotentials for Quantum Espresso - 1

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

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- Click on element for which pseudopotential wanted.

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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 (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-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.:

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

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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

XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
    from readpp : error #         2
    inconsistent DFT read
XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

stopping ..
```

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

V_{ion} known/constructed

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

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

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

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

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

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

Self-consistent?

No

Yes

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

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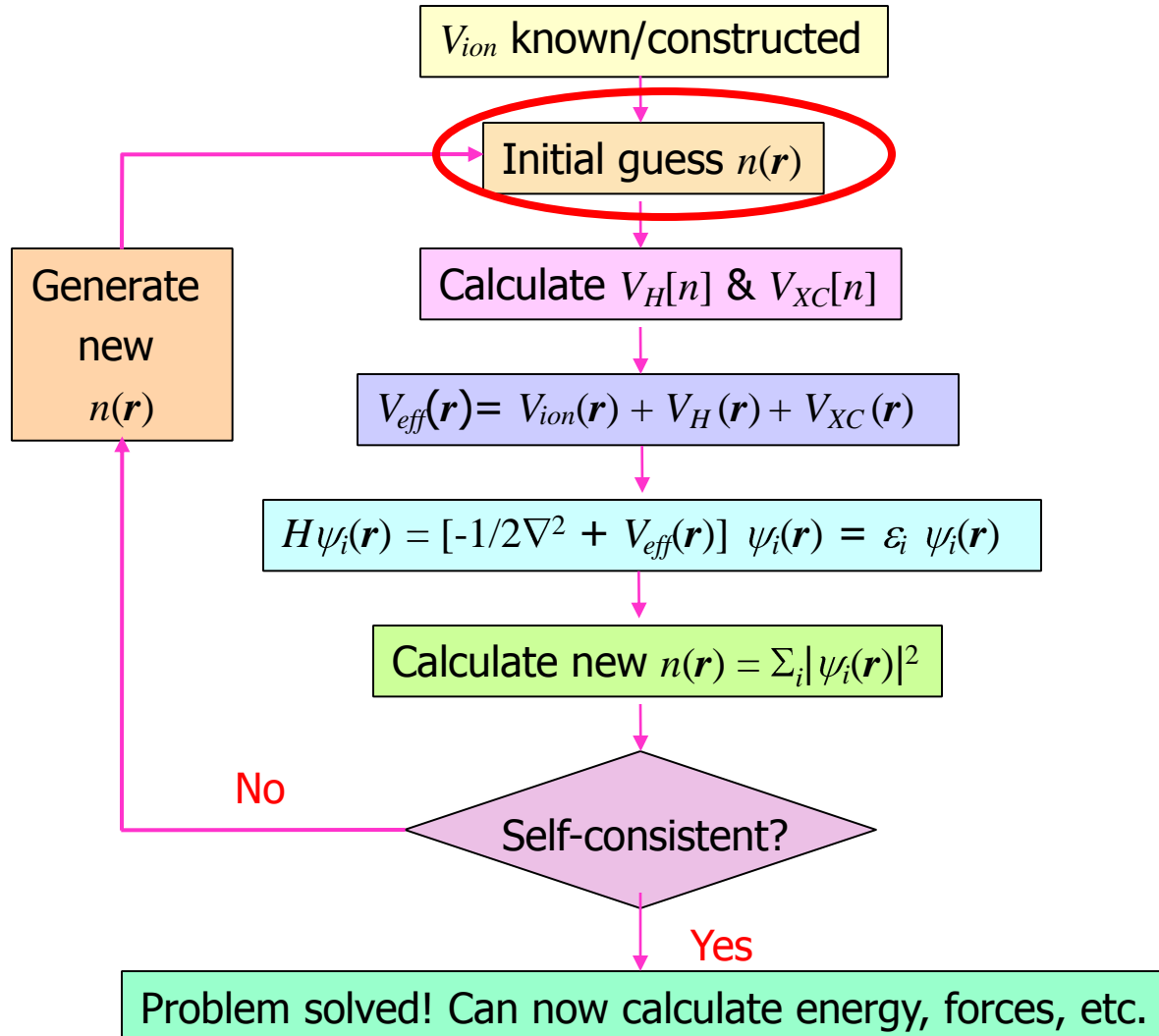
Starting Wavefunctions

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 $\psi_i(\mathbf{r})$

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

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

Yes

Problem solved! Can now calculate energy, forces, etc.
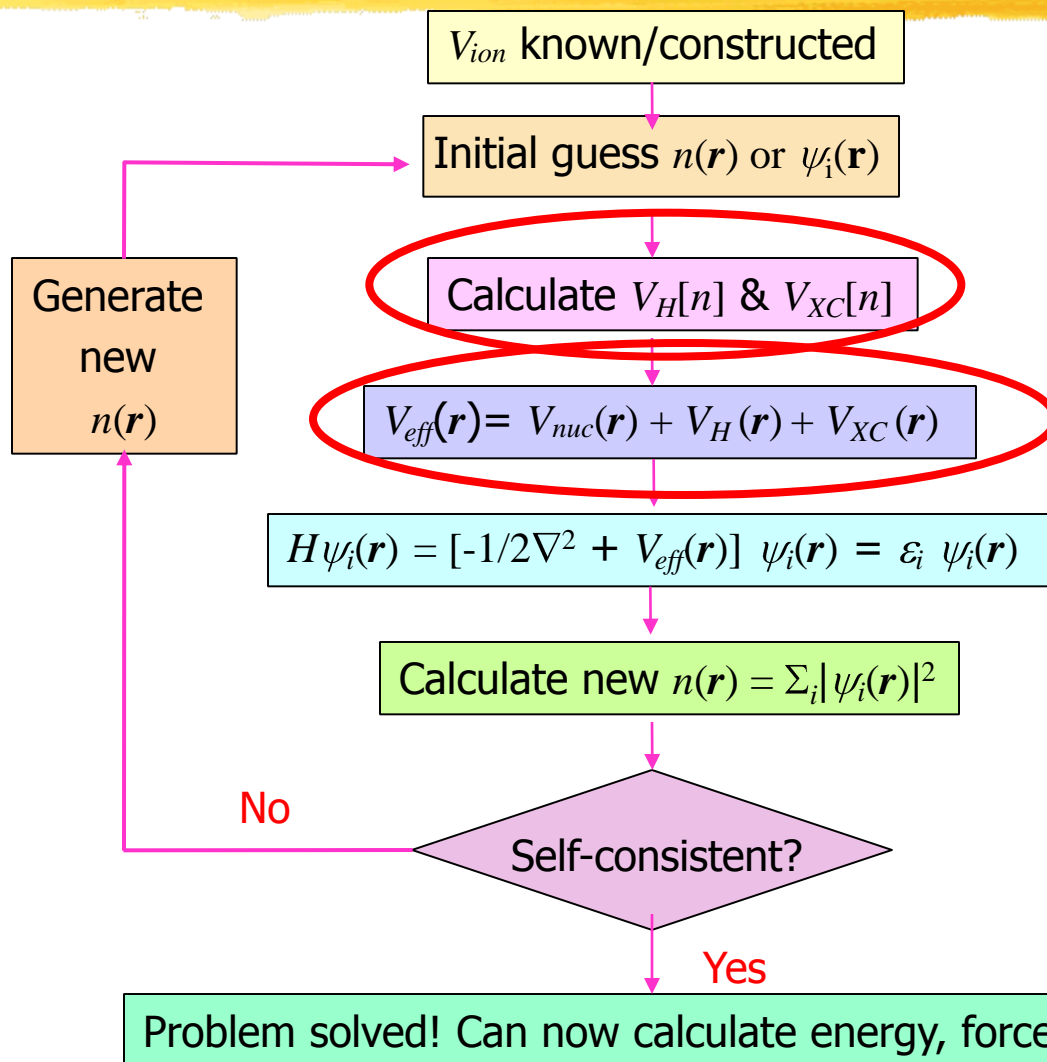
Note that type of exchange-correlation chosen while specifying pseudopotential

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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)

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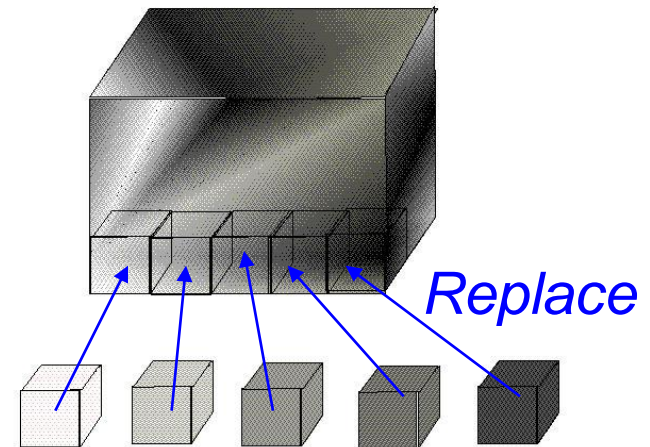
- Generalized Gradient Approximation(s): Include terms involving gradients of $n(\mathbf{r})$

  pw91, pbe (in name of pseudopotential)

55

Step 5: Diagonalization

V_{ion} known/constructed

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

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

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

Expensive! ☹

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

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.

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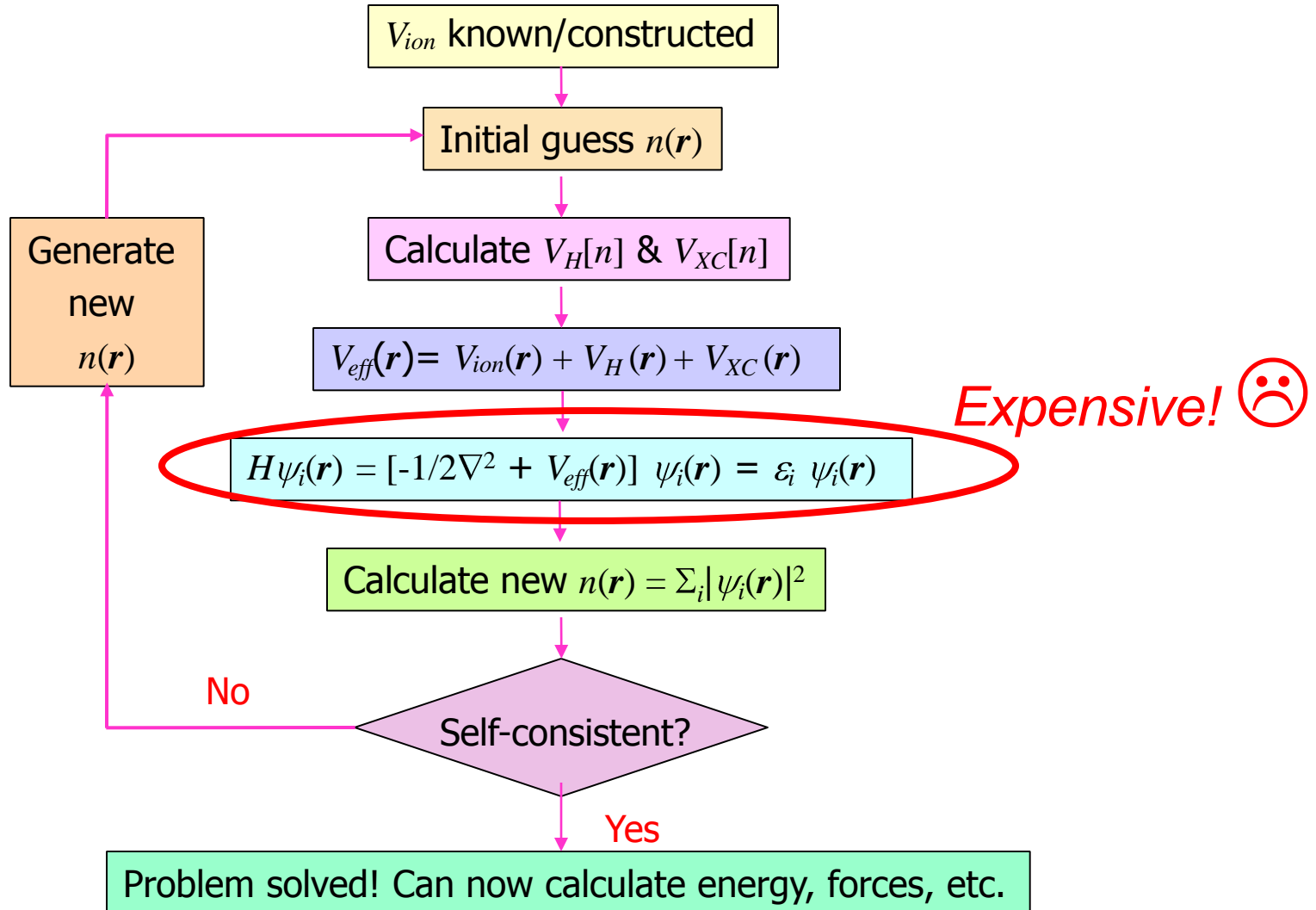
Diagonalization

- 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`

V_{ion} known/constructed

↓

Initial guess $n(r)$

↓

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

↓

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

↓

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

↓

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

↓

Self-consistent?

No → Generate new $n(r)$

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

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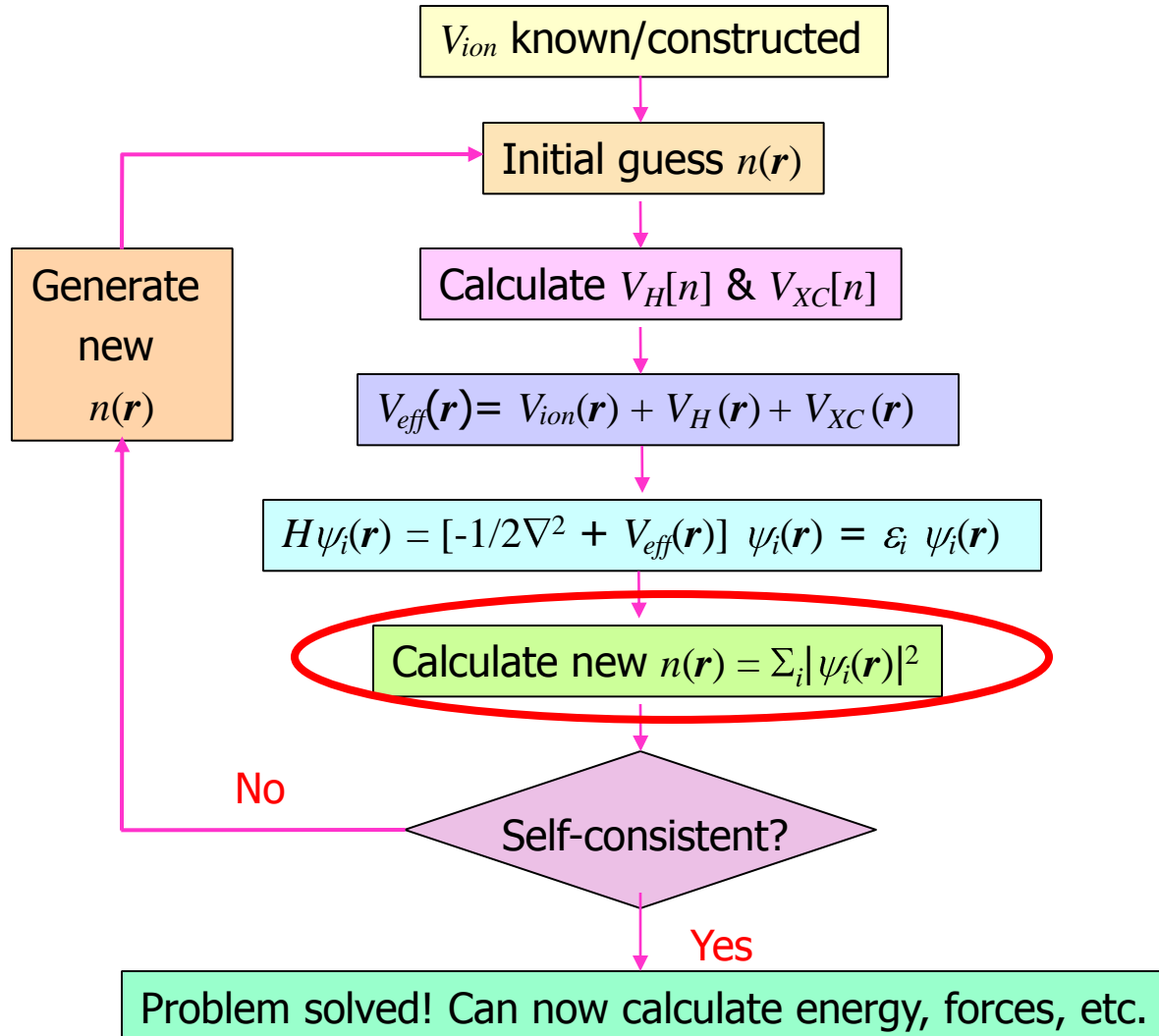
First Brillouin Zone

- Wigner-Seitz cell (primitive unit cell) in reciprocal space.
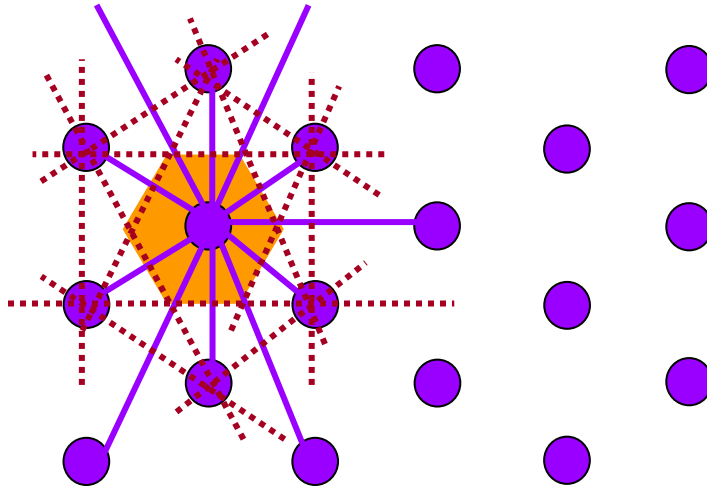
(Or could choose to use parallelepiped defined by $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$)

e.g., 1st BZ for FCC lattice →

(www.iue.tuwien.ac.at)

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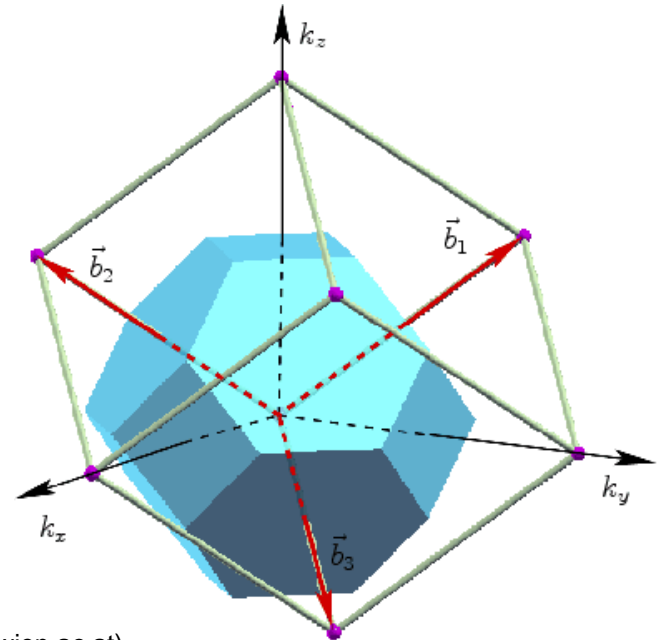
Irreducible Brillouin Zone

- Smallest wedge of the 1st BZ such that any wave-vector **k** in the 1st BZ can be obtained from a wave-vector **k** in the IBZ by performing symmetry operations of the crystal structure.

This wedge is the Irreducible Brillouin zone.

e.g., for FCC lattice
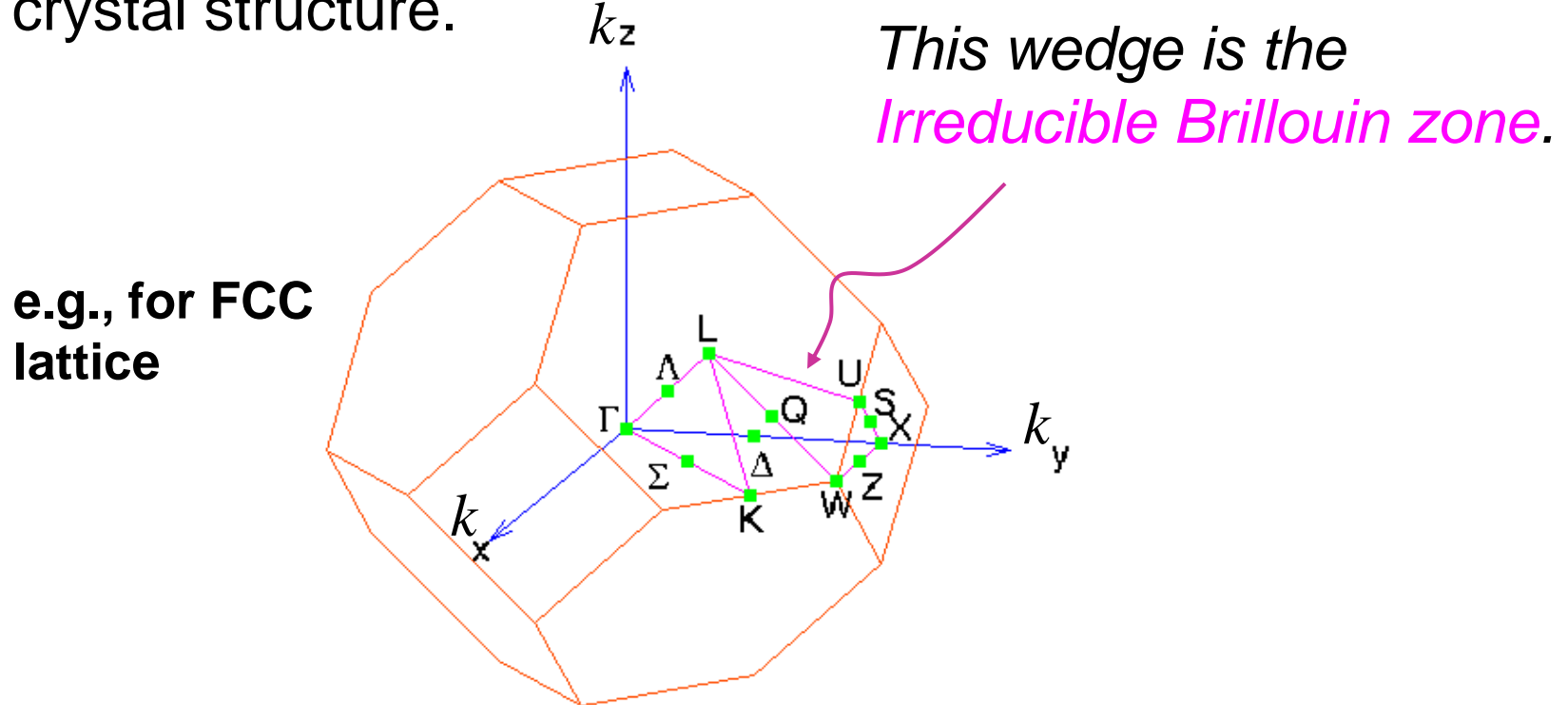
cst-www.nrl.navy.mil

Brillouin Zone Sums

- Many quantities (e.g., density, total energy) involve integrals over $\mathbf{k}$:

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

- $\mathbf{k}$ (wave-vector) is in the first Brillouin zone,

- n (band index) runs over occupied manifold.

- In principle, need infinite number of $\mathbf{k}$'s.

- In practice, sum over a finite number: BZ "Sampling".

Brillouin Zone Sums

- In practice, sum over a finite number: BZ "Sampling".

$$\langle P \rangle = \frac{1}{N_{\mathbf{k}}} \sum_{\substack{\mathbf{k} \in BZ \\ n\ occ}} P_n(\mathbf{k})$$

- For computational reasons, want # $\mathbf{k}$'s to be small.
- Number needed depends on band structure.
- Need to test convergence w.r.t. k-point sampling.

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Analogy: Numerical Integration of Gaussian

Let us approximately integrate $\int_{-xcut}^{xcut} e^{-x^2} dx$

by dividing the range from -5 to 5 into $ndiv$ divisions:
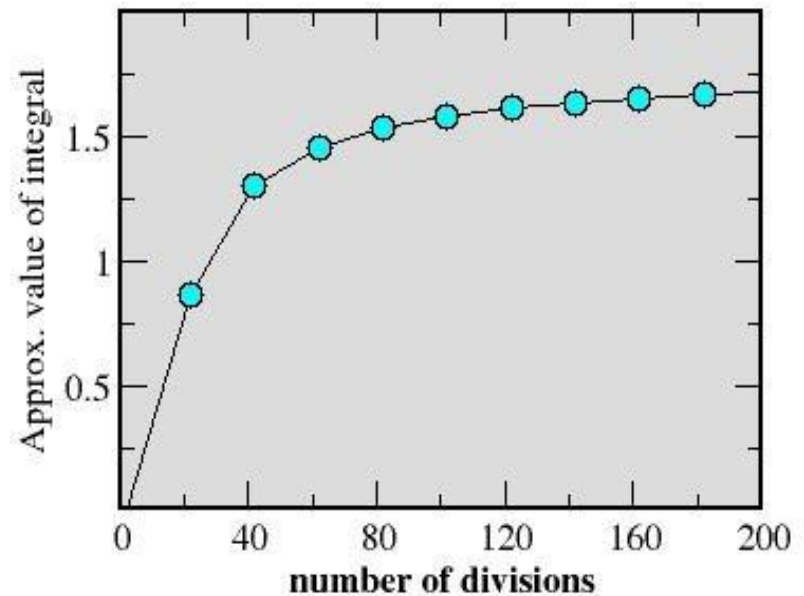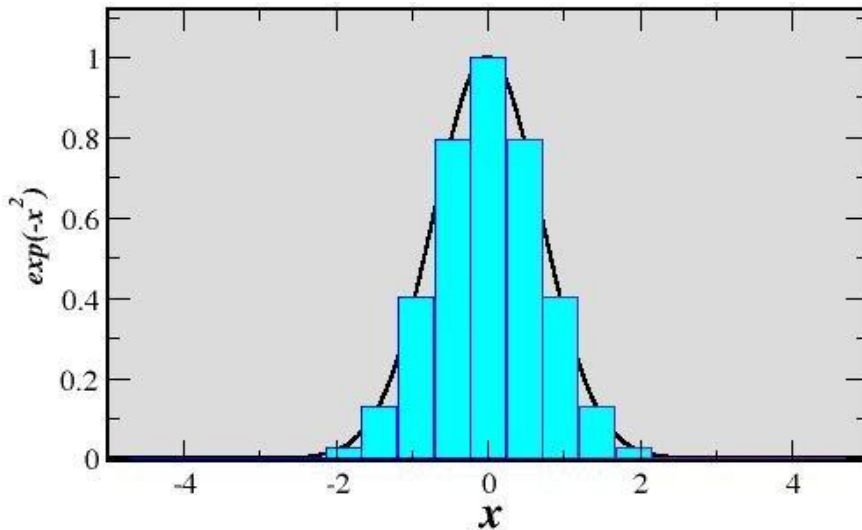
- Larger $ndiv$: more accurate answer but longer cpu time.

- Sharper the features in fn.: larger $ndiv$ needed for accuracy.

Using the Irreducible BZ; Weights

- Need not sum over **k**'s in entire BZ; can restrict to Irreducible BZ, with appropriate weights.

e.g., for FCC:

k_z

Count this 8 x ½ = 4 times.

Count this only once.

L
Λ
U
S
Q
X
Σ
Δ
Z
K
W

k_y

k_x

$$\langle P \rangle = \sum_{\substack{\mathbf{k} \in IBZ \\ n\ occ}} P_n(\mathbf{k})w(\mathbf{k})$$

Count this 48 times.
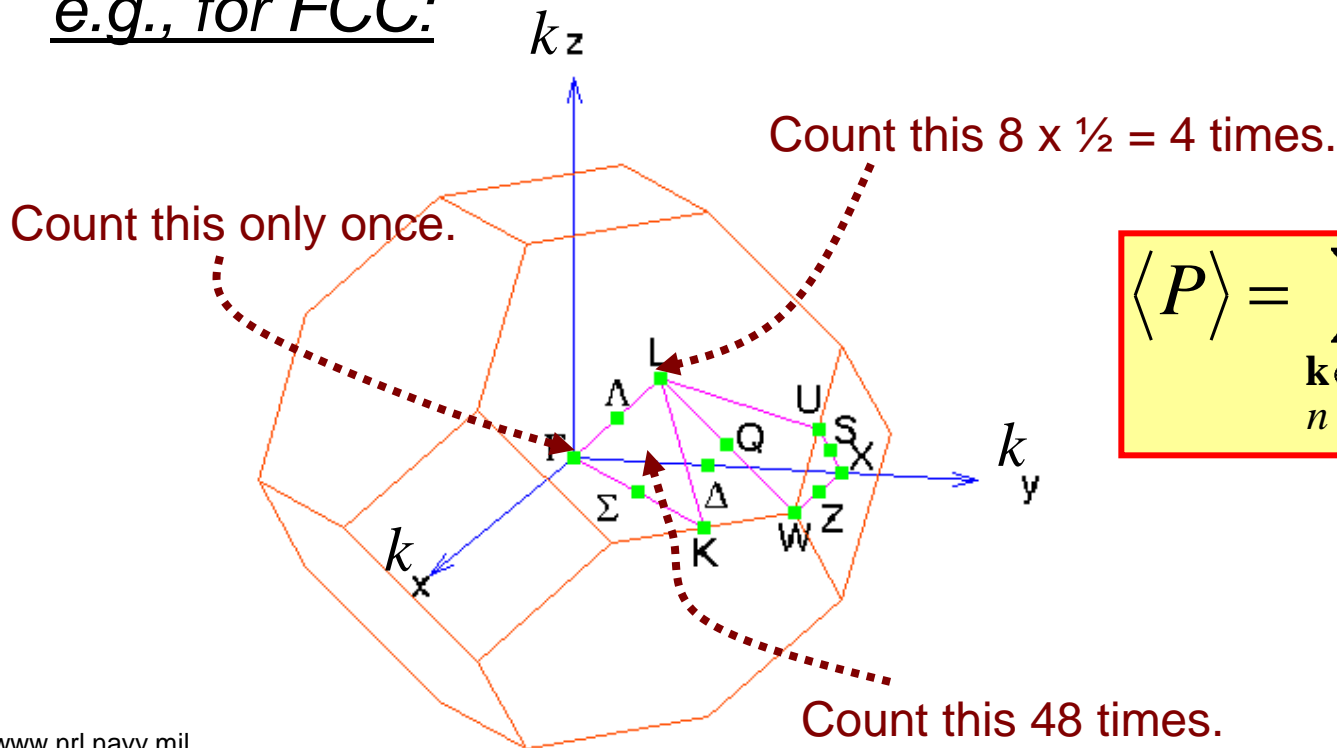
Types of k-point meshes

- **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']

$\mathbf{b}_2$ K_POINTS { tpiba | automatic | crystal | gamma }

1st BZ

If 'automatic', use M-P mesh:

nk1, nk2, nk3, k1, k2, k3

shift

$\mathbf{b}_1$

nk1=nk2=4

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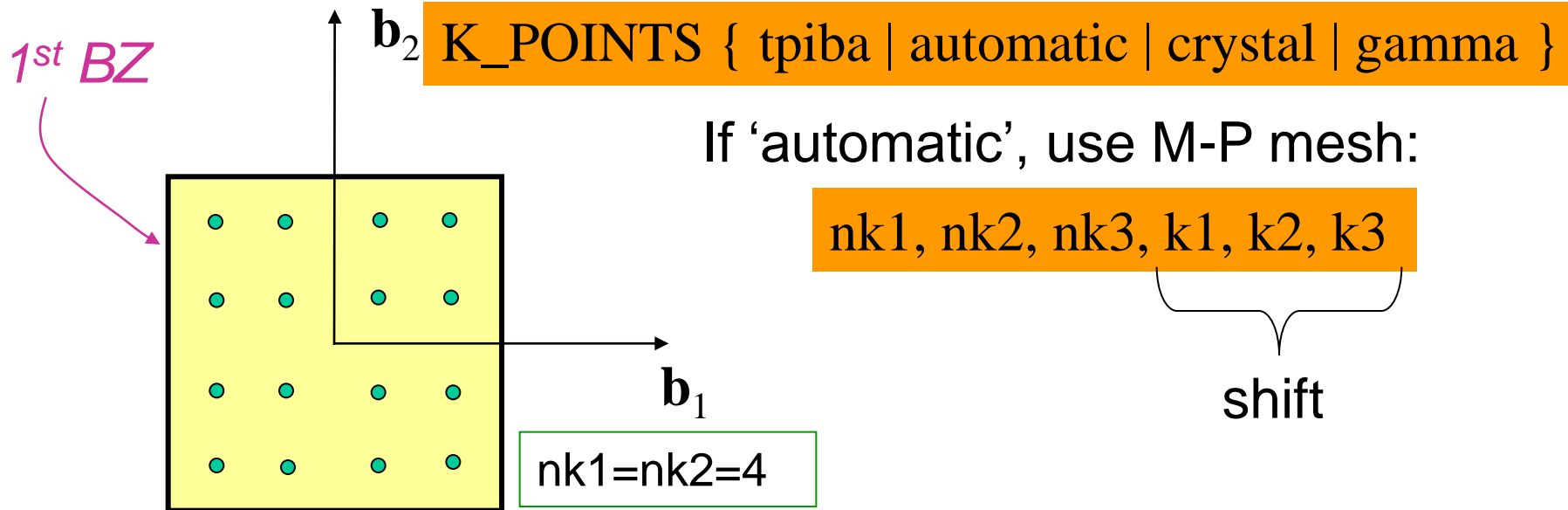
Why it might be better to use a shifted grid
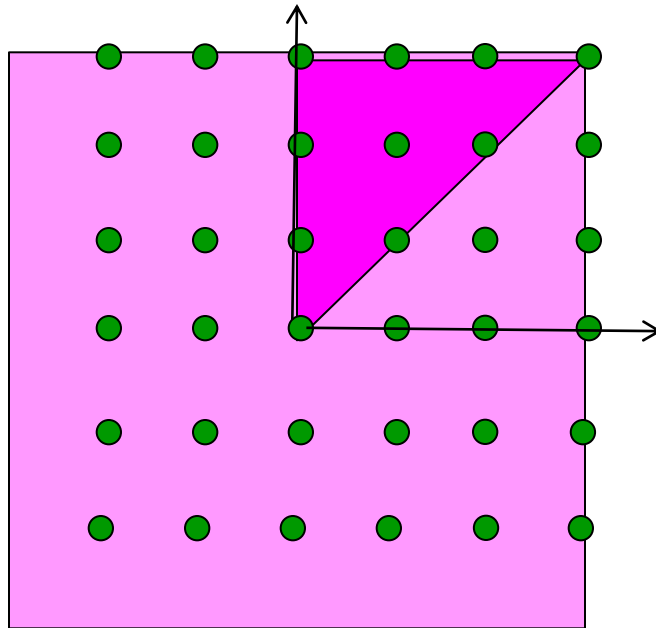
Unshifted

10 pts in IBZ
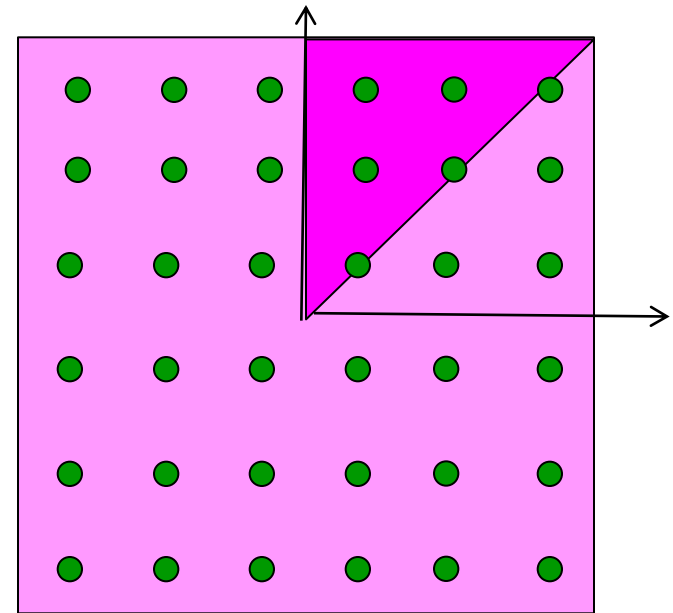
Shifted

6 pts in IBZ

Choosing Grid Divisions

- Space grid in a way (approximately) commensurate with length of primitive reciprocal lattice vectors **b**'s.

- Remember that dimensions in reciprocal space are the inverse of the dimensions in real space!
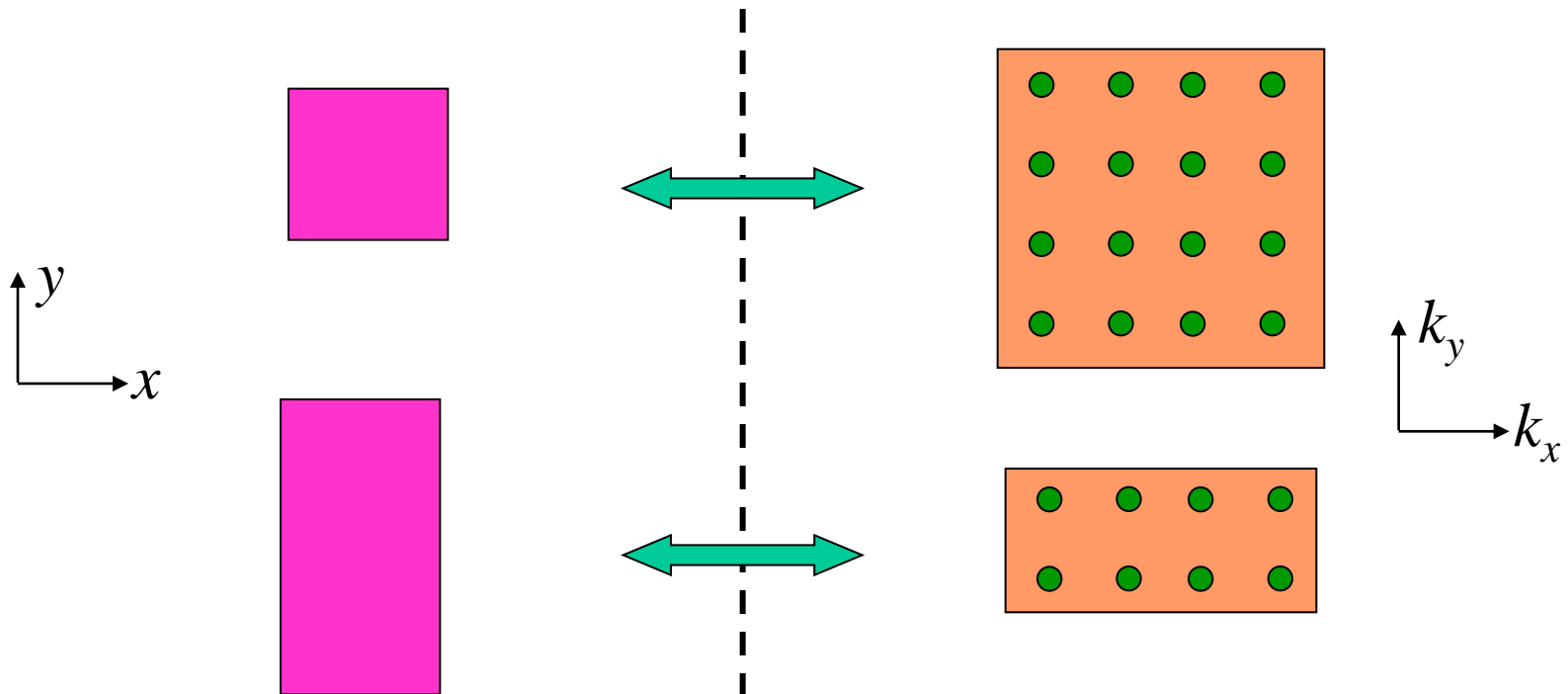
Convergence wrt BZ sampling

Carbon in diamond structure
Lat. Const. = 3.57Å
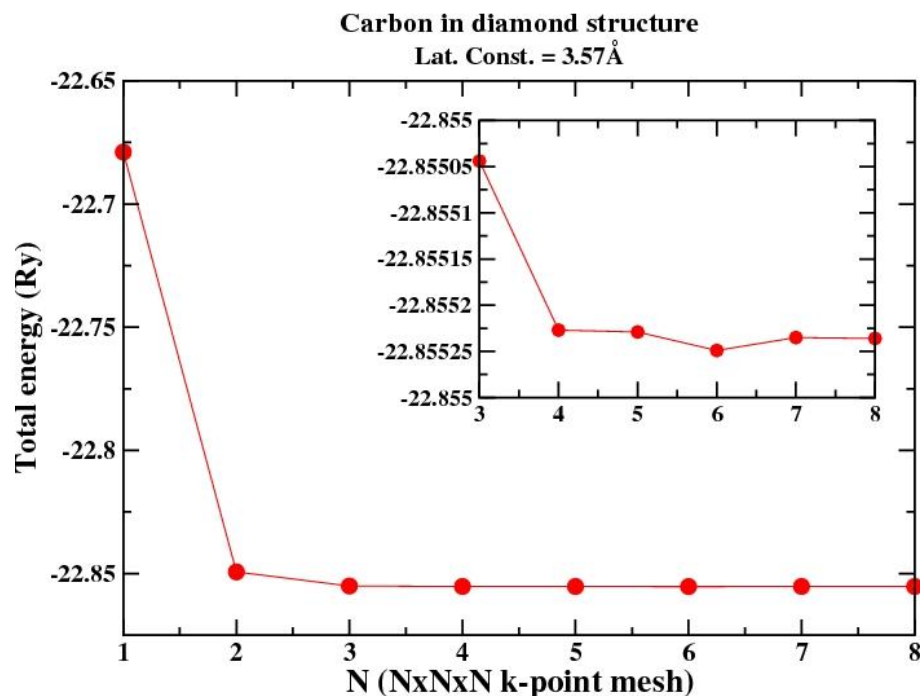
Madhura Marathe

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

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Problems with Metals

- Recall:

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

- 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 <u>many</u> k-points to reproduce this accurately.

- Also can lead to scf convergence problems because of band-crossings above/below Fermi level.

Cu
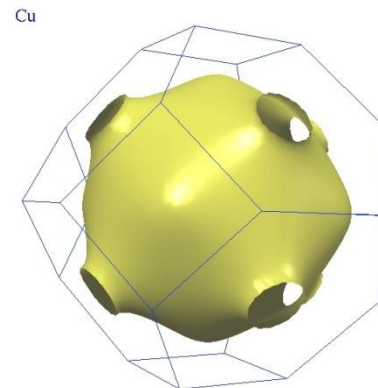
Fermi Surface of Cu
iramis.cea.fr

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Problems with Metals

The basic problem is that anything with sharp edges or features can't be reproduced well if it is sampled coarsely…

…So smear out the quantity we are sampling into something that <u>can </u>be sampled coarsely…but of course…the procedure of smearing out may lead to errors…

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.

- (Not discussing details due to lack of time!)

PhD Comics

Step 7: Check if Convergence Achieved

V_{ion} known/constructed

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

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

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

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

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

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

Self-consistent?

No

Yes

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

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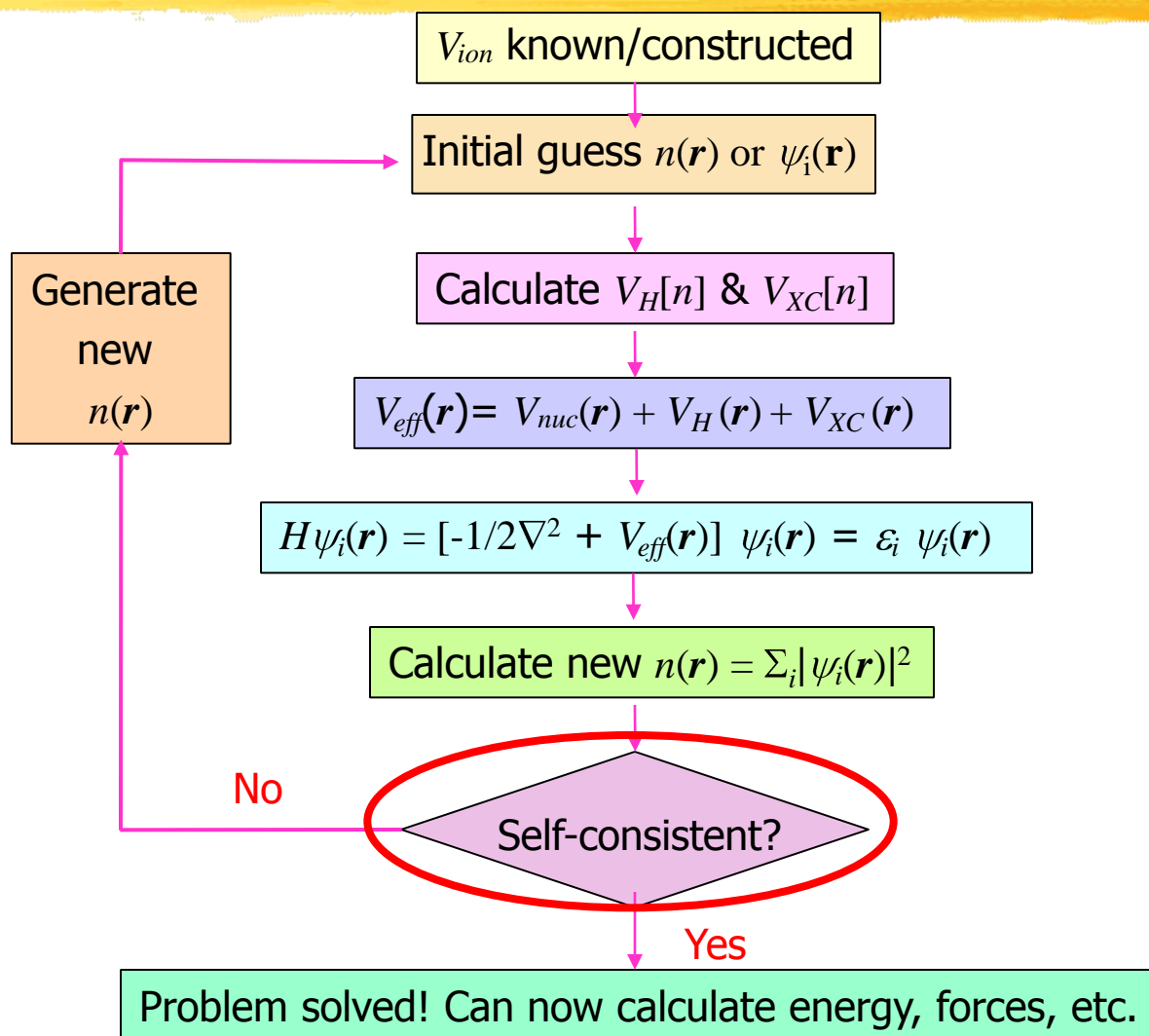
Testing for scf convergence

- 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`

73

Step 8: Mixing

Can take a long time to reach self-consistency!

☹

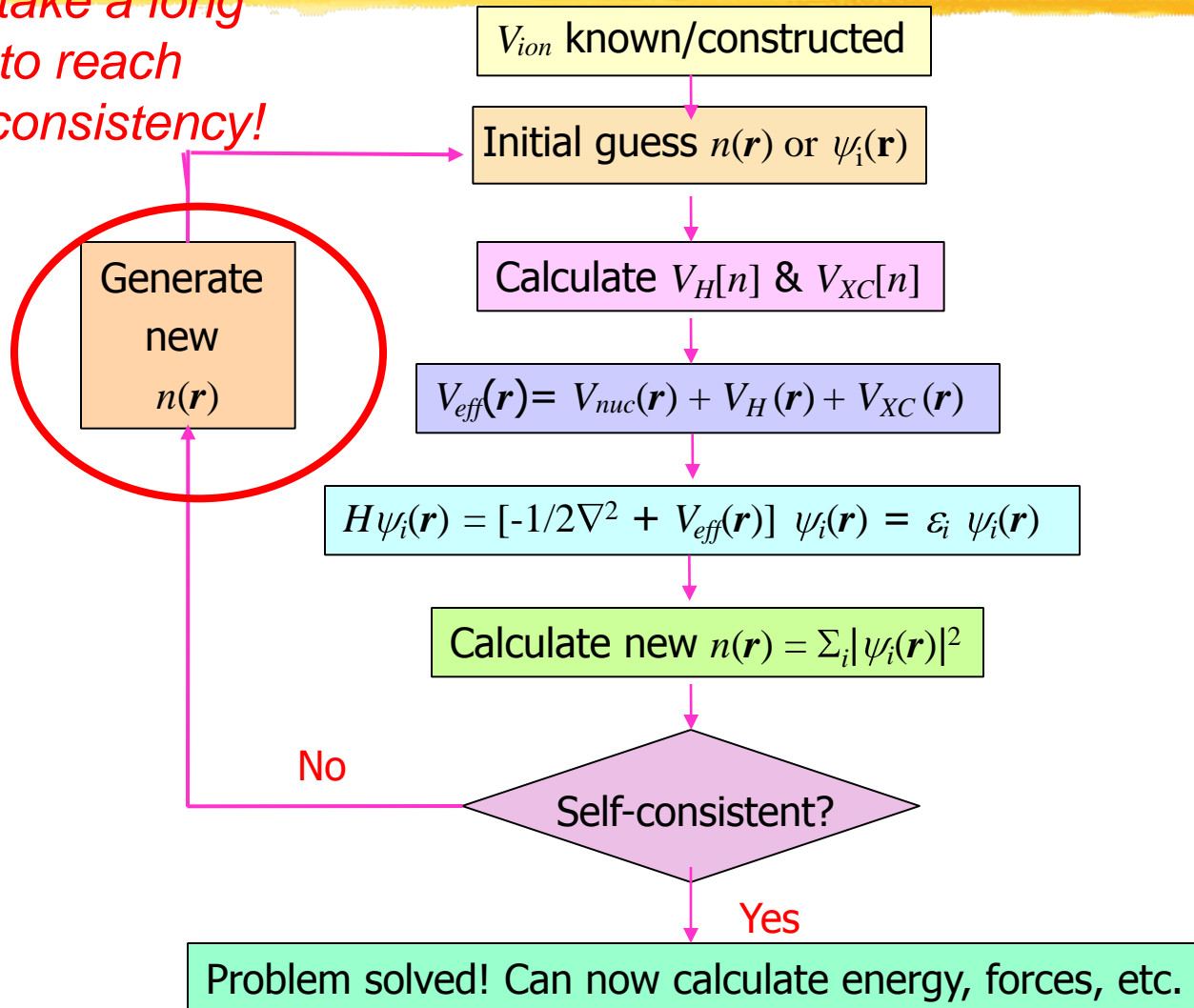V_{ion} known/constructed

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?

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

No

Yes

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

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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.

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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

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 !

Shobhana Narasimhan, JNCASR

The End!

Have fun with Quantum-ESPRESSO!

Shobhana Narasimhan, JNCASR