Introduction to density functional theory

Mini course on DFT for PhD
February-March 2026

LECTURE 2

(many slides are adapted by M. Peressi from S. Baroni, P. Giannozzi)

I part theory

- **periodic systems**
- **reciprocal space and wavevectors**
- **plane-wave basis set**

(and related convergence tests for the kinetic energy cutoff)

- **k-point sampling**

(and related convergence tests for the k-point mesh)

For some slides - credits also to: Shobhana Narasimhan, Arkady Krasheninnikov

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Crystal Structures

- Crystals possess a structure that is built up out of translationally repeating units (unit cells).
- Every crystal structure consists of:

  (i) a Bravais Lattice (shape of unit cell & how it repeats).

  Specified by primitive lattice vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$.

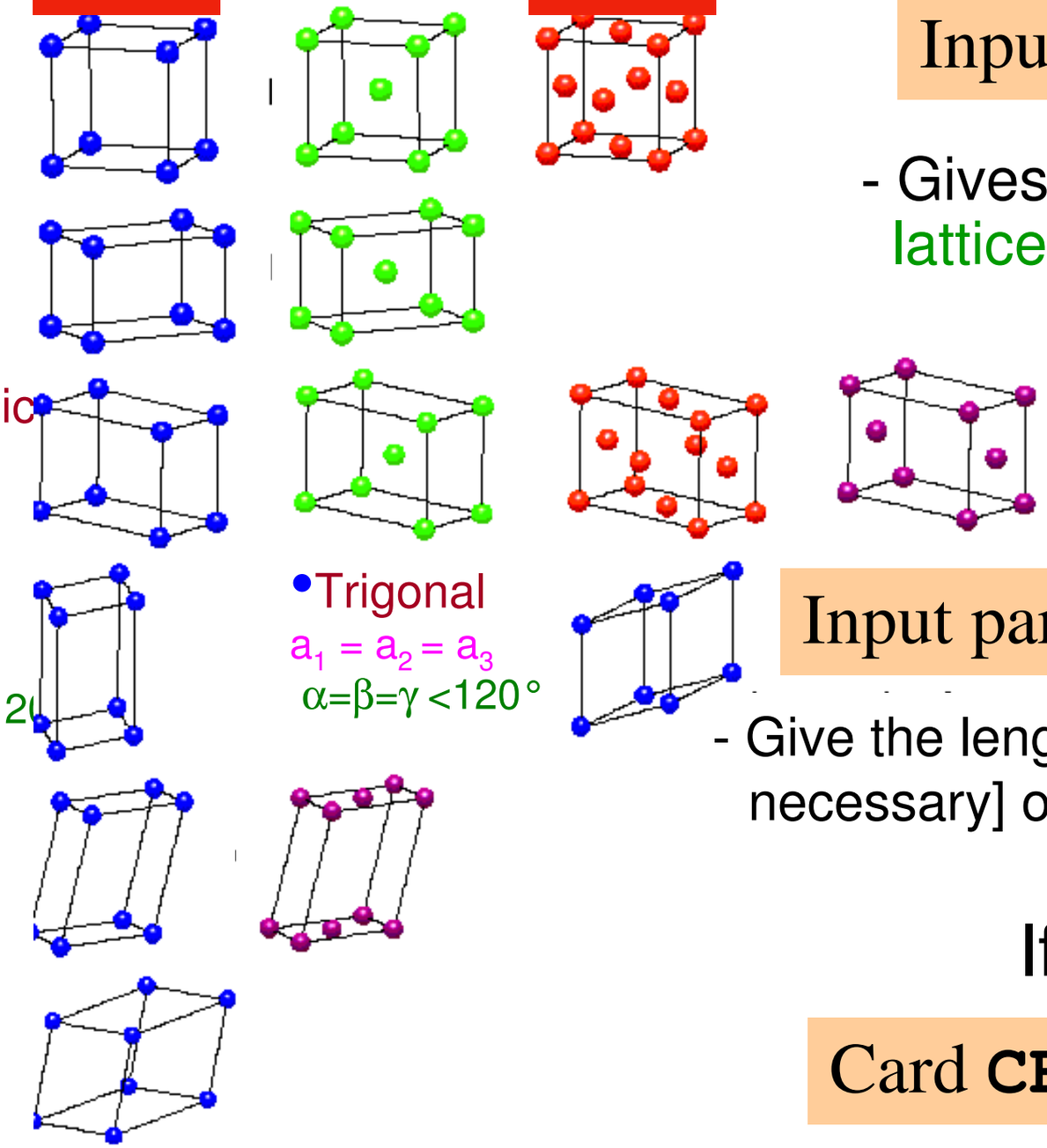
  $\underline{R} = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$, where n_1, n_2, n_3 are integers.

Each vector (or point, or site) of the Bravais lattice is described by this linear combination of primitive lattice vectors

Bravais Lattices & Crystal Systems in 3-D

- Cubic
  $a_1 = a_2 = a_3$,
  $\alpha=\beta=\gamma = 90°$
- Tetragonal
  $a_1 = a_2 \neq a_3$
  $\alpha=\beta=\gamma = 90°$
- Orthorhombic
  $a_1 \neq a_2 \neq a_3$
  $\alpha=\beta=\gamma = 90°$
- Hexagonal
  $a_1 = a_2 \neq a_3$
  $\alpha=\beta=90°\ \gamma = 120°$
- Monoclinic
  $a_1 \neq a_2 \neq a_3$,
  $\alpha=\beta=90° \neq \gamma$
- Triclinic
  $a_1 \neq a_2 \neq a_3$,
  $\alpha\neq\beta\neq\gamma$
- Trigonal
  $a_1 = a_2 = a_3$
  $\alpha=\beta=\gamma < 120°$

ibrav=1 ibrav=2



Input parameter **ibrav**

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

+

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

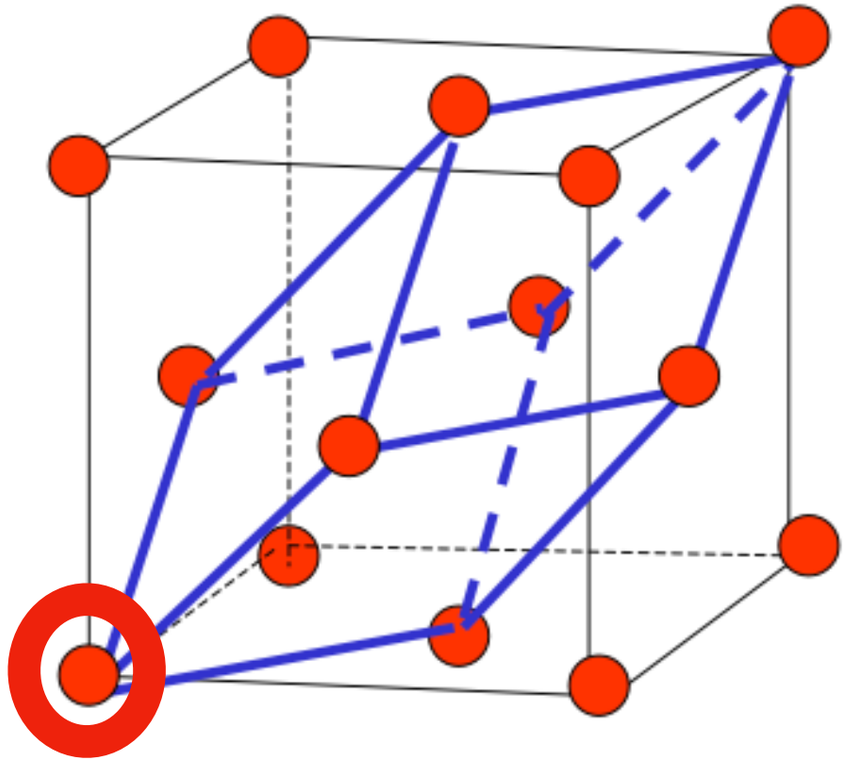
- Give the lengths [& directions, if necessary] of the lattice vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$

If **ibrav = 0**

Card **CELL_PARAMETERS**

e.g., Choices of Unit Cell for FCC Lattice

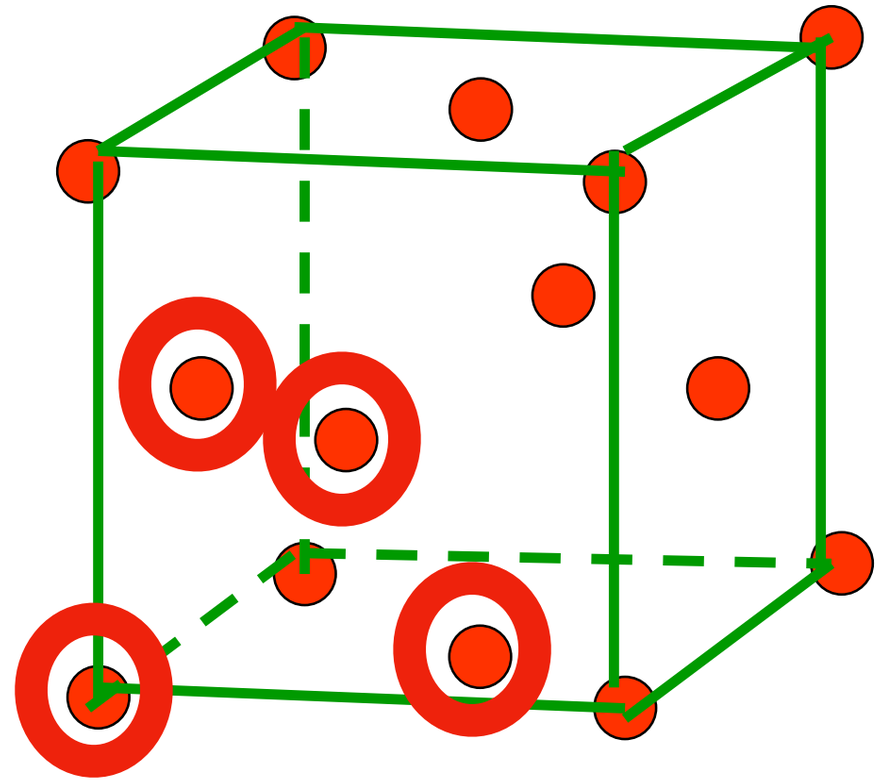
(it can be seen as a pure mathematical object)



Primitive Unit Cell

1 lattice point/cell

i.e., the **minimal cell**



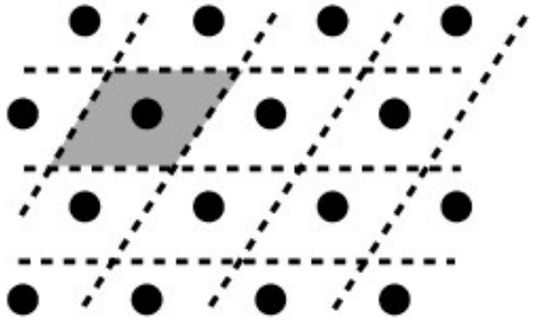
Conventional Cubic Unit Cell

4 lattice points/cell

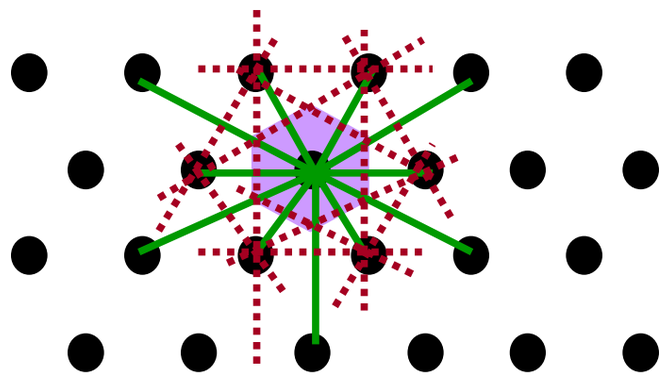
Unit Cells for Bravais Lattices

Primitive (non-primitive) unit cells contain 1 (>1) lattice pt. and generate the whole lattice by translation, without overlapping and without space missing.

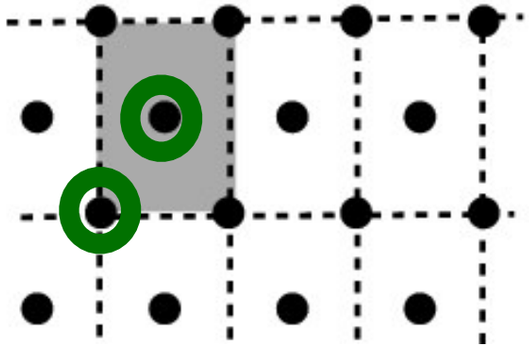
e.g., consider the 2-D Hexagonal Lattice:



A Primitive Unit Cell



Wigner-Seitz (Primitive) Unit Cell



Non-primitive Unit Cell

Crystal Structures

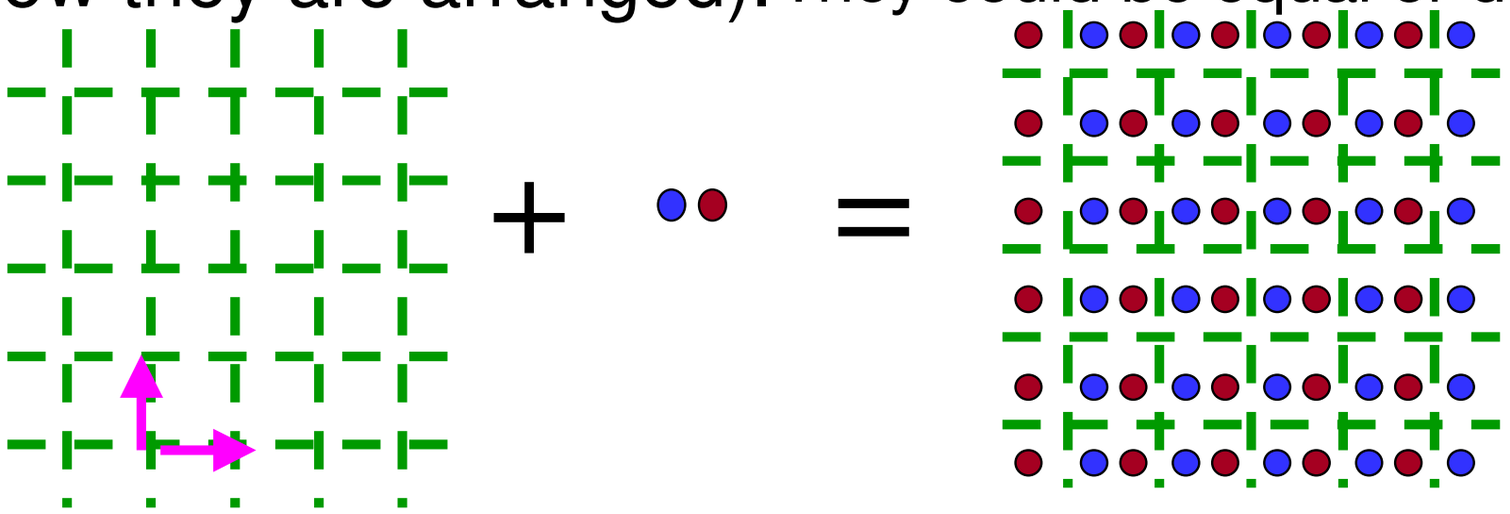
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- Every crystal structure consists of:

  (i) a Bravais Lattice (shape of unit cell & how it repeats).

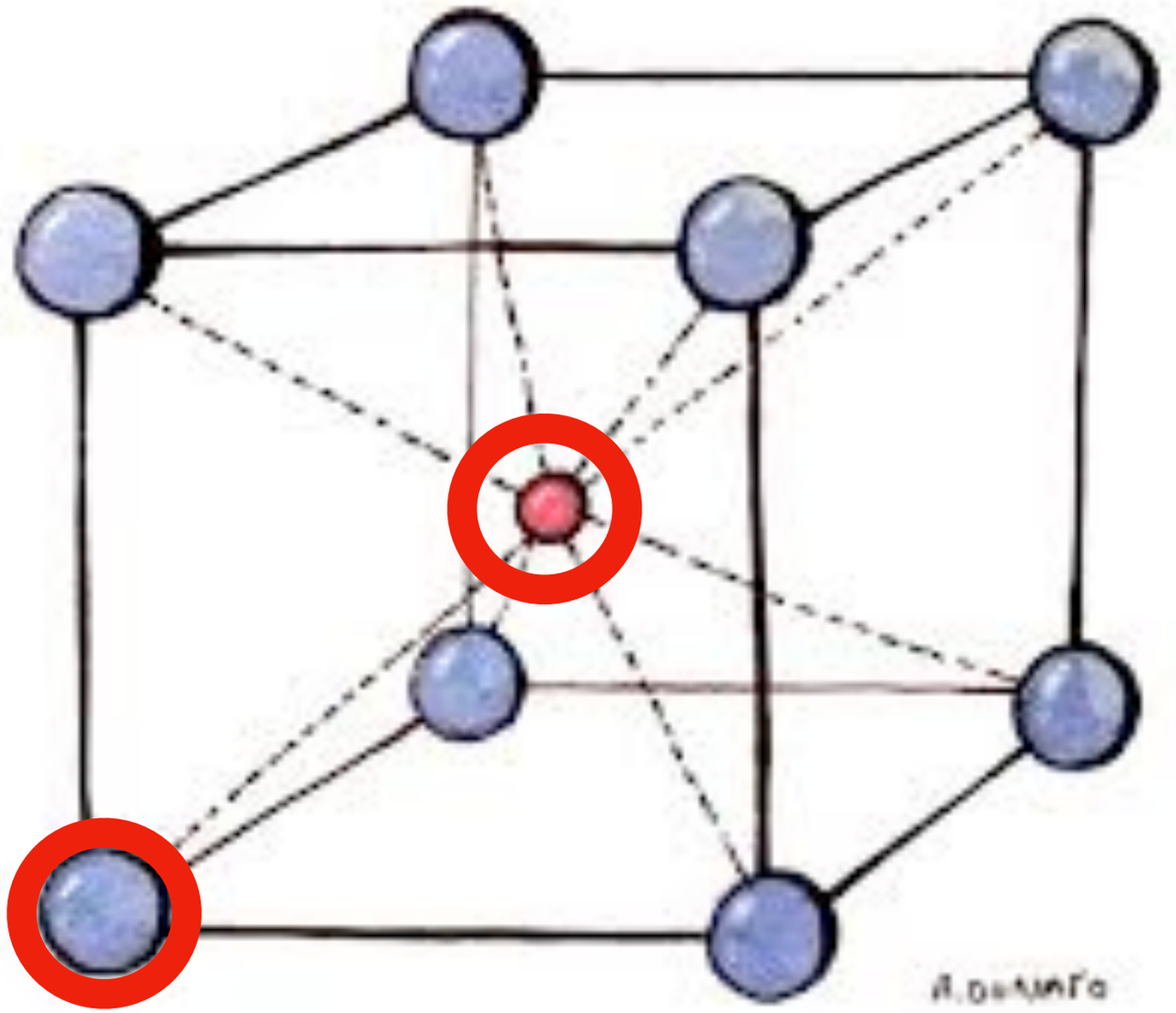
  Specified by primitive lattice vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$.

  $\underline{R} = n_1\underline{a}_1 + n_2\underline{a}_2 + n_3\underline{a}_3$, where n_1, n_2, n_3 are integers.

  (ii) an Atomic Basis (how many atoms are in the unit cell, and how they are arranged). They could be equal or different



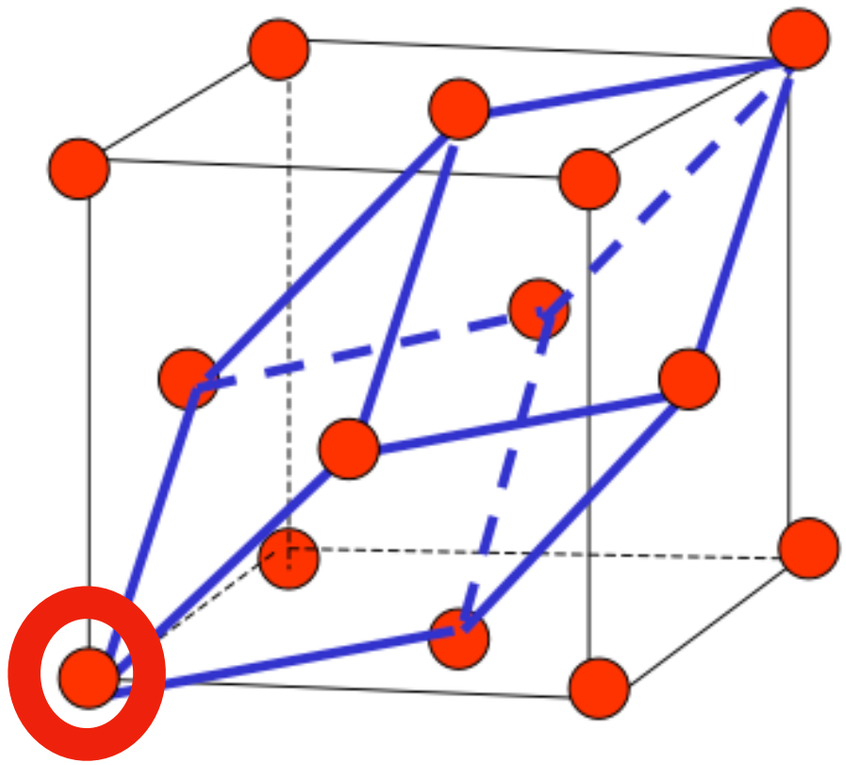
real systems
e.g. Choice of Unit Cell for CsCl



the unit cell contains 2 atoms

real systems
e.g. Choice of Unit Cell for Aluminum & Silicon

for Aluminum (Al):

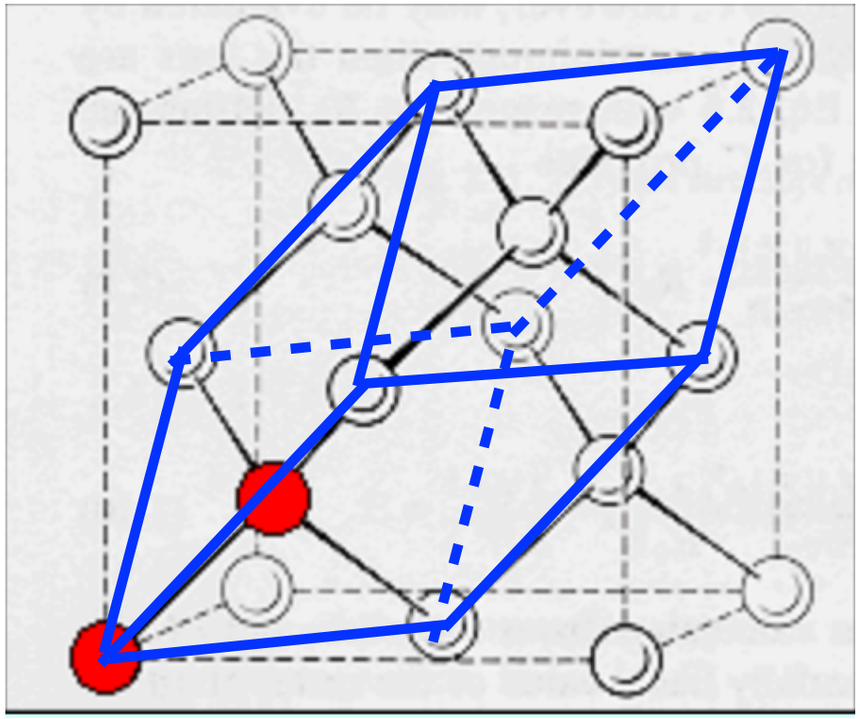


Primitive Unit Cell
1 lattice point/cell

which corresponds also to
1 atom

for Silicon (Si):

diamond structure



Primitive Unit Cell
1 lattice point/cell
BUT
2 atoms

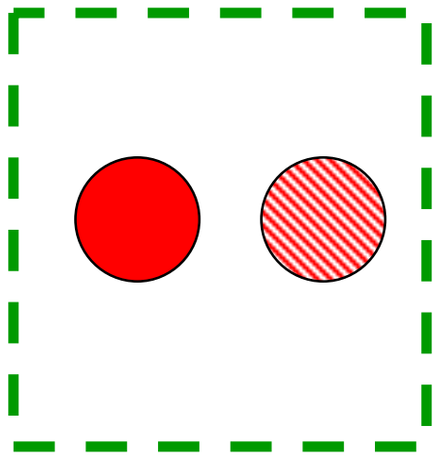
same Unit Cell
but different internal basis

Describe the system:

1) Specify the Bravais lattice

2) Positions of Atoms Within Unit Cell

- "Decorate" each unit cell with atomic basis.



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`**")

(* for cubic crystals, usually specify in units of side of "conventional cubic cell", even if it's not the primitive unit cell.)

I part theory

- periodic systems
- **reciprocal space and wavevectors**
- plane-wave basis set

(and related convergence tests for the kinetic energy cutoff)

- **k-point sampling**

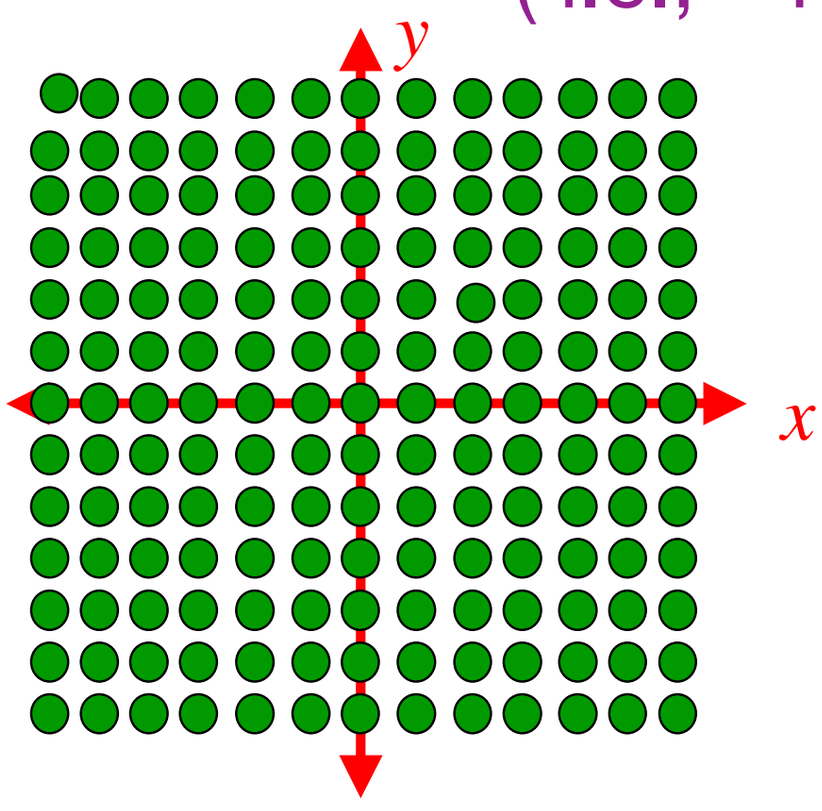
(and related convergence tests for the k-point mesh)

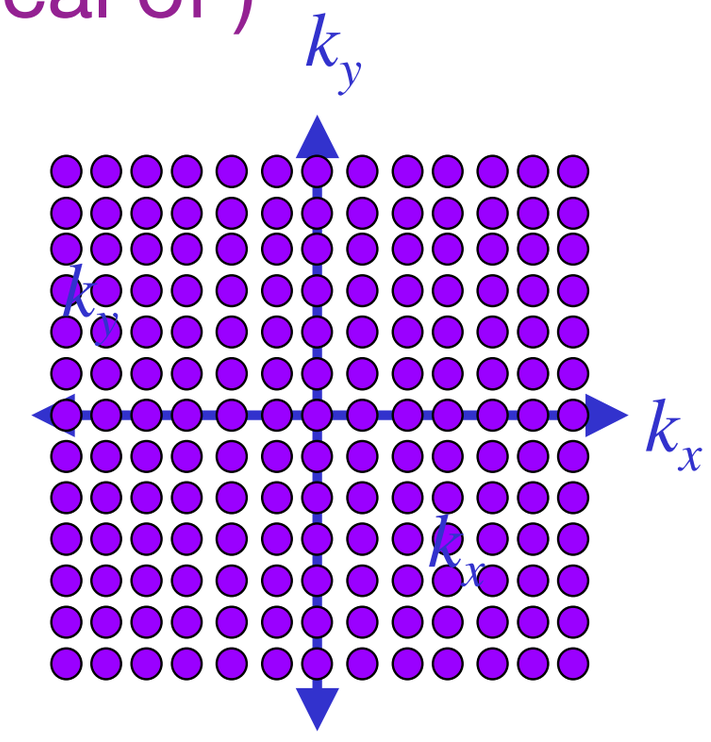
For some slides - credits also to: Shobhana Narasimhan, Arkady Krasheninnikov

Reciprocal Lattice

- Every Bravais lattice (in real space) has a corresponding Reciprocal lattice (in "k-space" or "reciprocal space").
- The Reciprocal lattice: {**G**} s.t. $\mathbf{G}\bullet\mathbf{R} = 2\pi n, \quad n \in Z$
- Spacing of **R**'s inversely proportional to spacing of **G**'s

(i.e., reciprocal of)





Reciprocal lattice

all the vectors of the **reciprocal lattice** can be written as (*n*: **integer coefficients**):

$$\mathbf{G} = \sum_{i=1}^{3} n_i \mathbf{b}_i$$

where $\{\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3\}$ are the **primitive reciprocal** lattice vectors defined as:

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{|\mathbf{a}_i \cdot \mathbf{a}_j \times \mathbf{a}_k|}$$

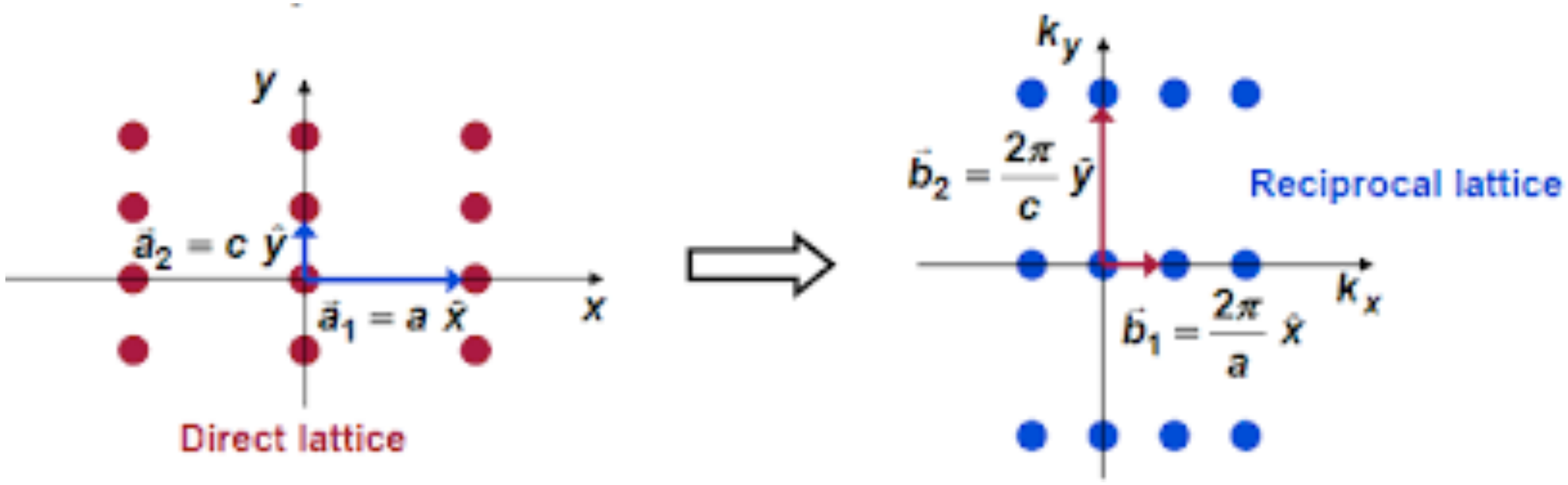
A linear combination of the {**b**}s with **real** coefficients x_i

gives a vector $\mathbf{k} = \sum_{i=1}^{3} x_i \mathbf{b}_i$ lying in the **reciprocal space**

The {**b**}s, {**G**}s, {**k**}s have the dimension of a reciprocal of a length => they are **wavevectors**

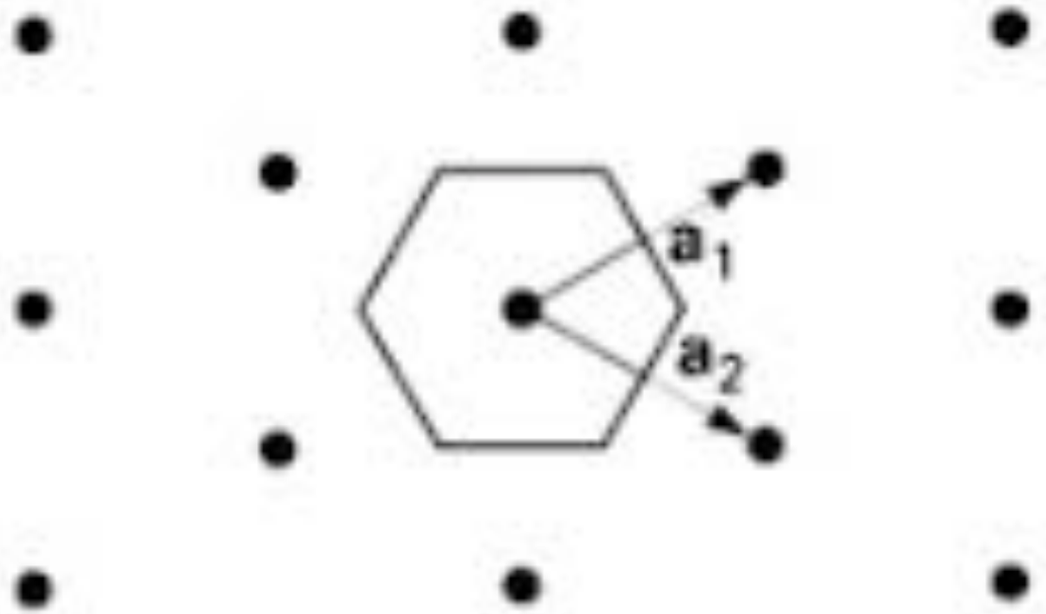
Reciprocal lattice
Example of rectangular lattice

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{|\,\mathbf{a}_i \cdot \mathbf{a}_j \times \mathbf{a}_k\,|}$$

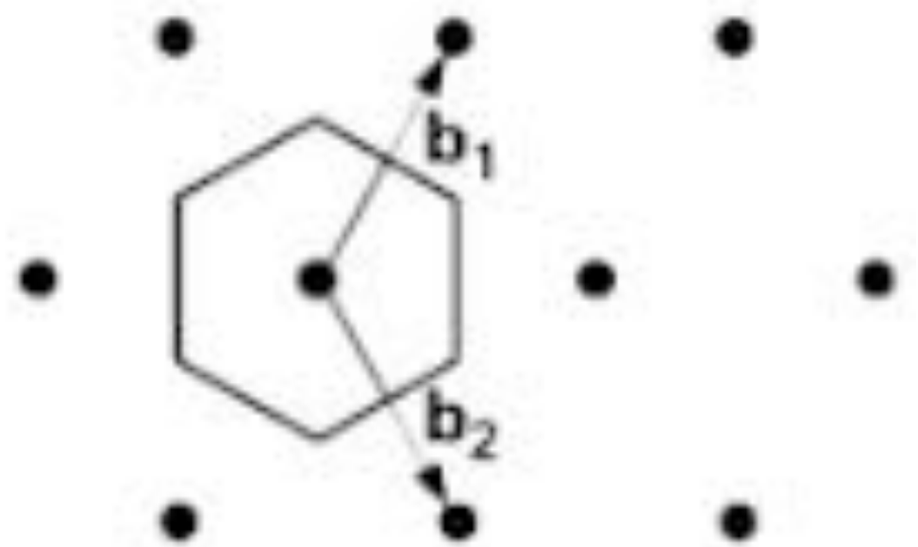


Reciprocal lattice
Example of hexagonal lattice

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{|\,\mathbf{a}_i \cdot \mathbf{a}_j \times \mathbf{a}_k\,|}$$



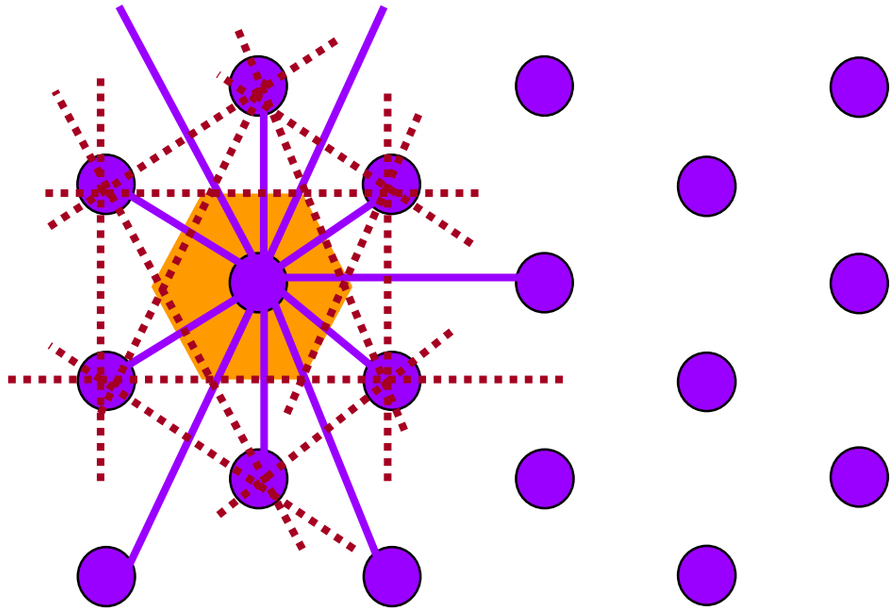
Direct lattice



Reciprocal lattice

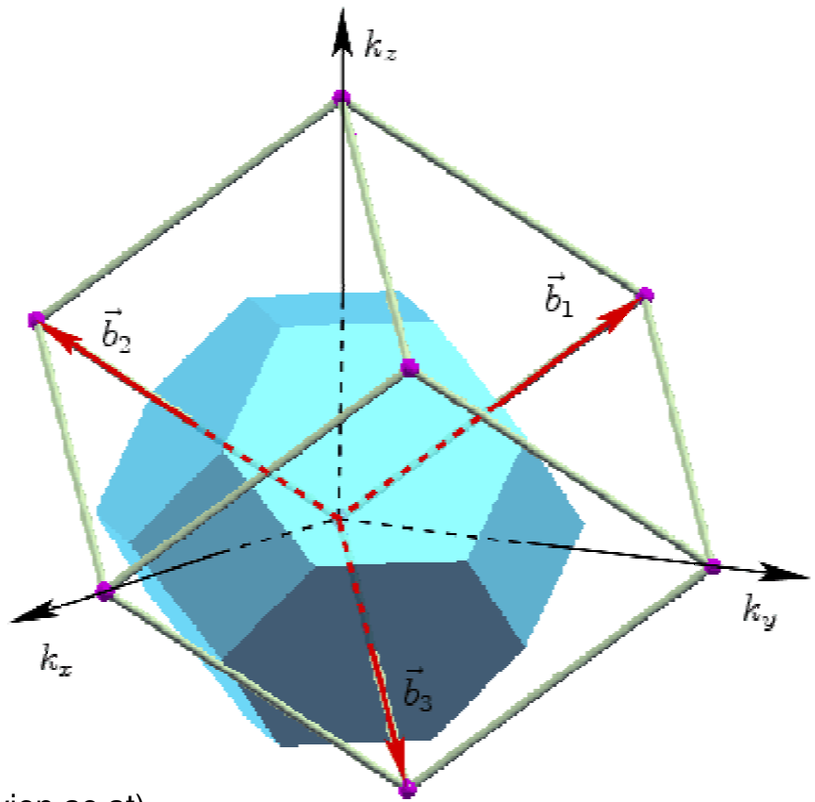
First Brillouin Zone

- Wigner-Seitz 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 →



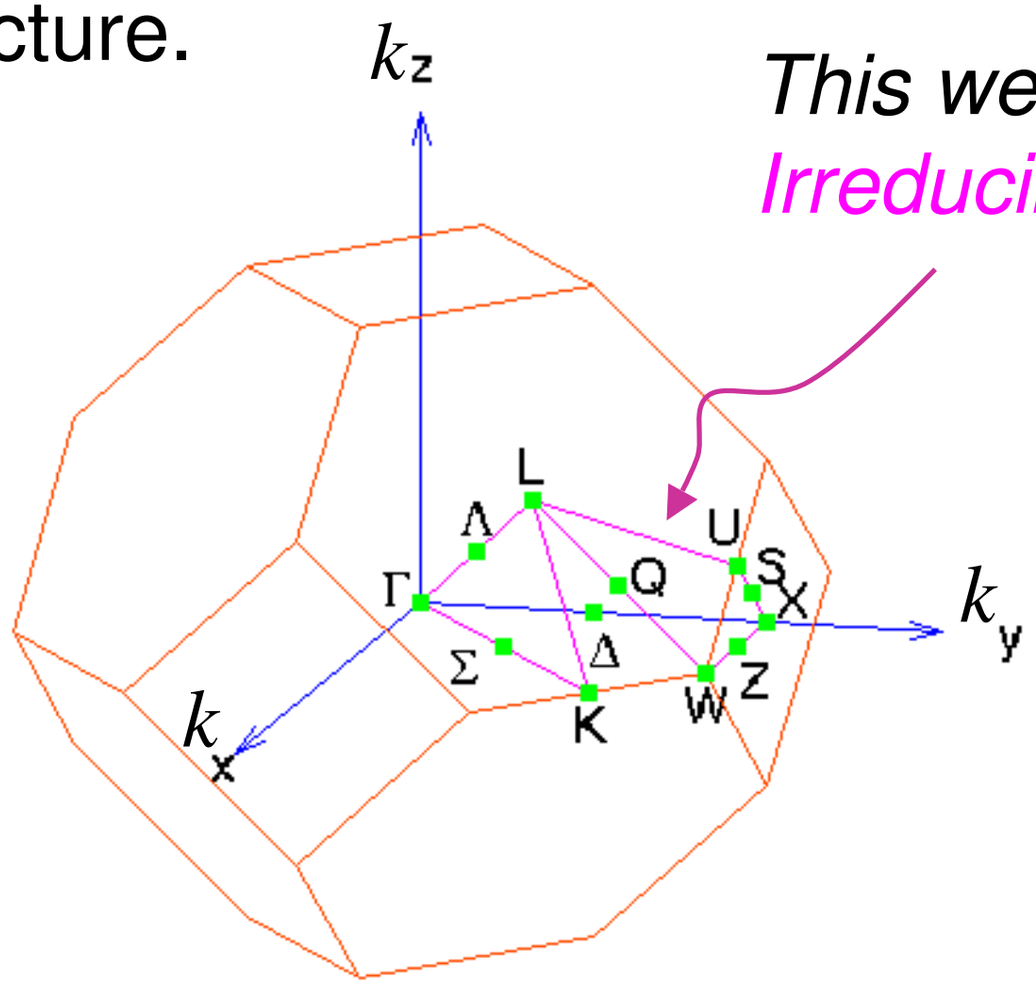
(www.iue.tuwien.ac.at)

Irreducible Brillouin Zone

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

This wedge is the Irreducible Brillouin zone.

e.g., for FCC lattice



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- **plane-wave basis set**

(and related convergence tests for the kinetic energy cutoff)

- **k-point sampling**

(and related convergence tests for the k-point mesh)

For some slides - credits also to: Shobhana Narasimhan, Arkady Krasheninnikov

Plane-wave basis set - o

wavevectors (both **k** and **G**) are important for periodic systems because:

Consider the Scroedinger equation $\mathscr{H}\psi(\mathbf{r}) = E\psi(\mathbf{r})$ where $\mathscr{H}$ contains a periodic potential $V(\mathbf{r})$ such that $V(\mathbf{r}+\mathbf{R}) = V(\mathbf{r})$

=> the solution ψ can be labelled by a wavevector $\mathbf{k}$ (and hence also E is E($\mathbf{k}$)) and can be written as:

$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$ where $u_{\mathbf{k}}$ has the same periodicity of V

or (equivalent formulation)

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

(BLOCH THEOREM)

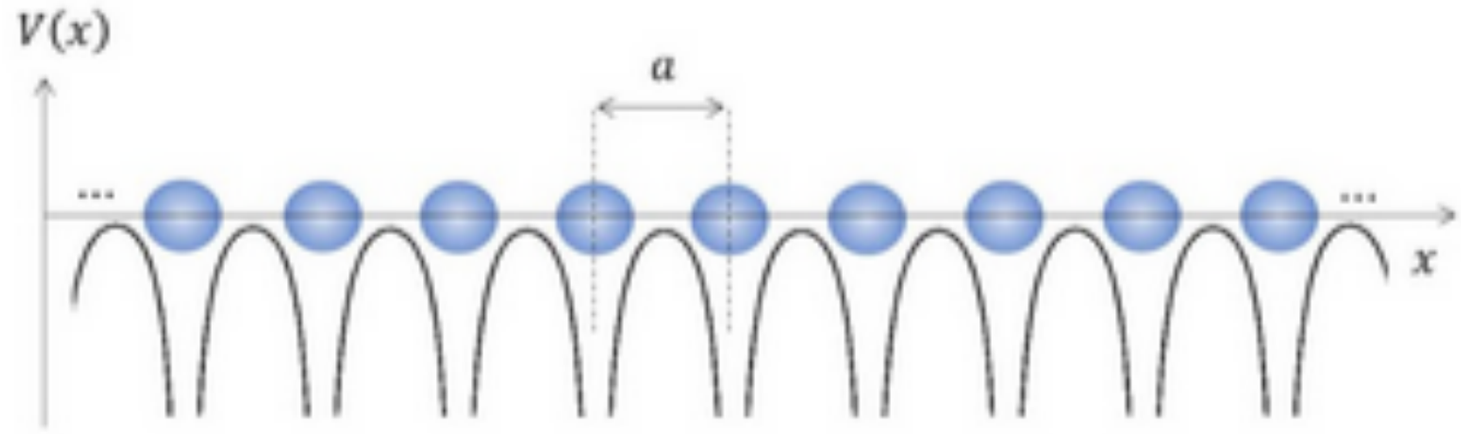
and typically the longer is the PW series, the more precise is the description of ψ

Electrons in a periodic potential

Time-independent Schrodinger equation with periodic potential

Periodic potential

$$V(x) = V(x + a)$$



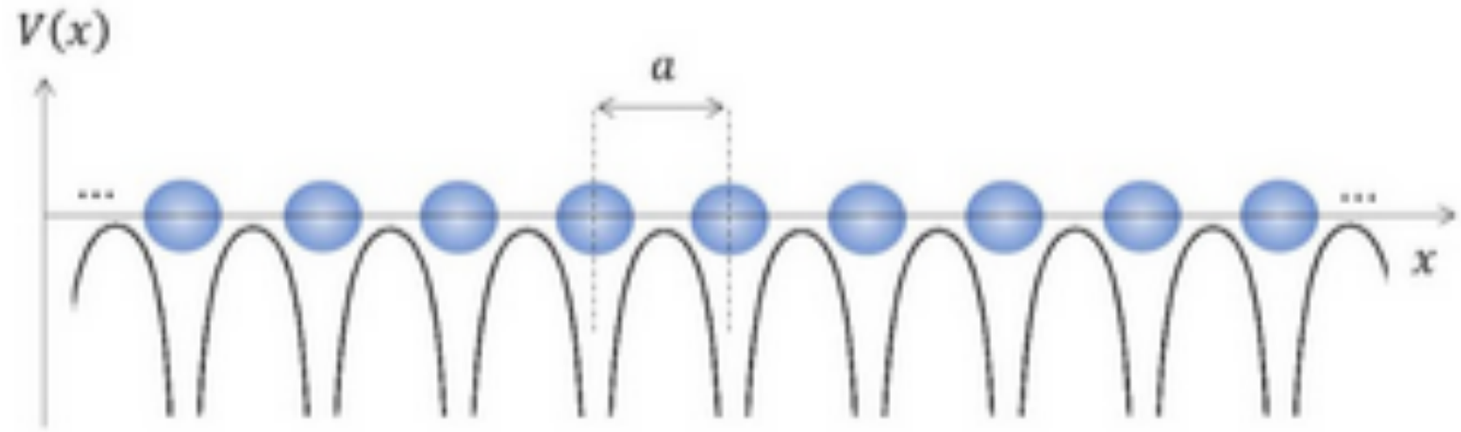
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

Electrons in a periodic potential

Time-independent Schrodinger equation with periodic potential

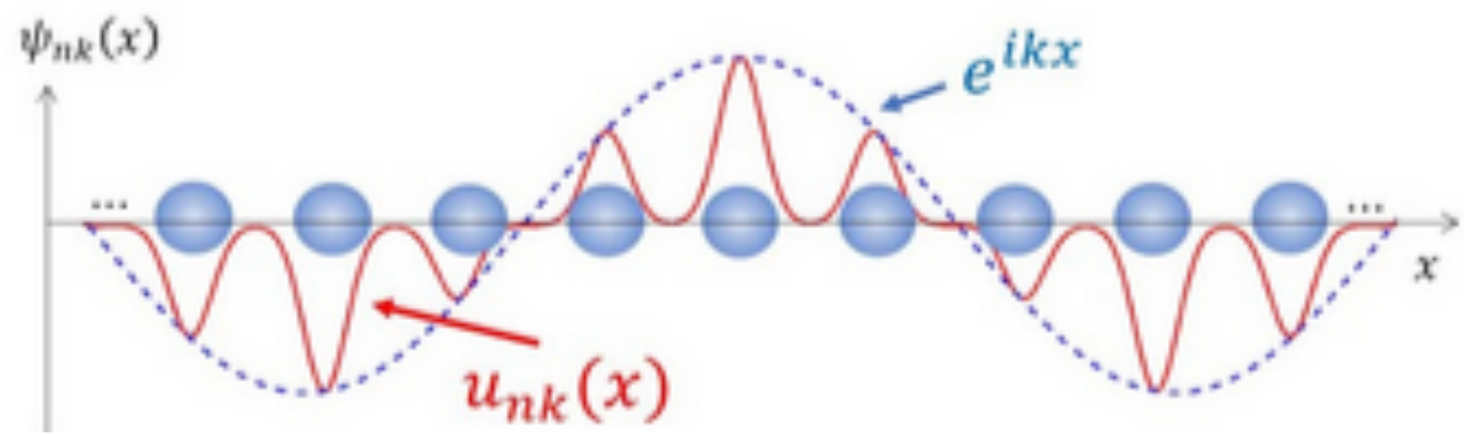
Periodic potential

$$V(x) = V(x + a)$$



Bloch's theorem

$$\psi_{nk}(x) = u_{nk}(x)e^{ikx}$$



NOTE: the periodicity of V(x) leads to the introduction of a wavevector **k** as a **parameter** in the Schroedinger equation and hence in the wavefunction

(it has the dimensions of a wavevector, but it is NOT an eigenvalue of the momentum operator)

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.,

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

- Note: This implies that $\mathbf{k}$ is a good quantum number.

Note that on this slide n represents the band index!

(progressive label of eigenvalues & eigenfunct. for a given k)



Plane-wave basis set - o

wavevectors (both **k** and **G**) are important for periodic systems because:

the solution ψ can be written as:

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

or (equivalent formulation)

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

and typically **the longer is the PW series, the more precise is the description of** ψ

Plane-wave basis set - 1

the higher the kinetic energy, the more precise is the description of ψ => **do convergence test!**

A PW basis set for states of wave vector $\mathbf{k}$ is defined as

$$\phi_{\mathbf{k+G}}(\mathbf{r}) = \langle \mathbf{r}|\mathbf{k}+\mathbf{G}\rangle = \frac{1}{\sqrt{\mathcal{N}\Omega}} e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}, \quad \frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 \leq E_{cut}$$

$\Omega =$ unit cell volume, $\mathcal{N}\Omega =$ crystal volume, $E_{cut} =$ cutoff on the kinetic energy of PWs (in order to have a finite number of PWs!). The PW basis set is *complete* for $E_{cut} \to \infty$ and *orthonormal*: $\langle \mathbf{k}+\mathbf{G}|\mathbf{k}+\mathbf{G}'\rangle = \delta_{\mathbf{G}\mathbf{G}'}$

In a PW basis set one works with *Fourier components* ($c_{i,\mathbf{k+G}}$ below):

$$|\psi_i\rangle = \sum_{\mathbf{G}} c_{i,\mathbf{k+G}} |\mathbf{k}+\mathbf{G}\rangle$$

$$c_{i,\mathbf{k+G}} = \langle \mathbf{k}+\mathbf{G}|\psi_i\rangle = \frac{1}{\sqrt{\mathcal{N}\Omega}} \int \psi_i(\mathbf{r}) e^{-i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}} d\mathbf{r} = \widetilde{\psi}_i(\mathbf{k}+\mathbf{G}).$$

Real-space quantities can be obtained on a grid using Fast Fourier Transform.

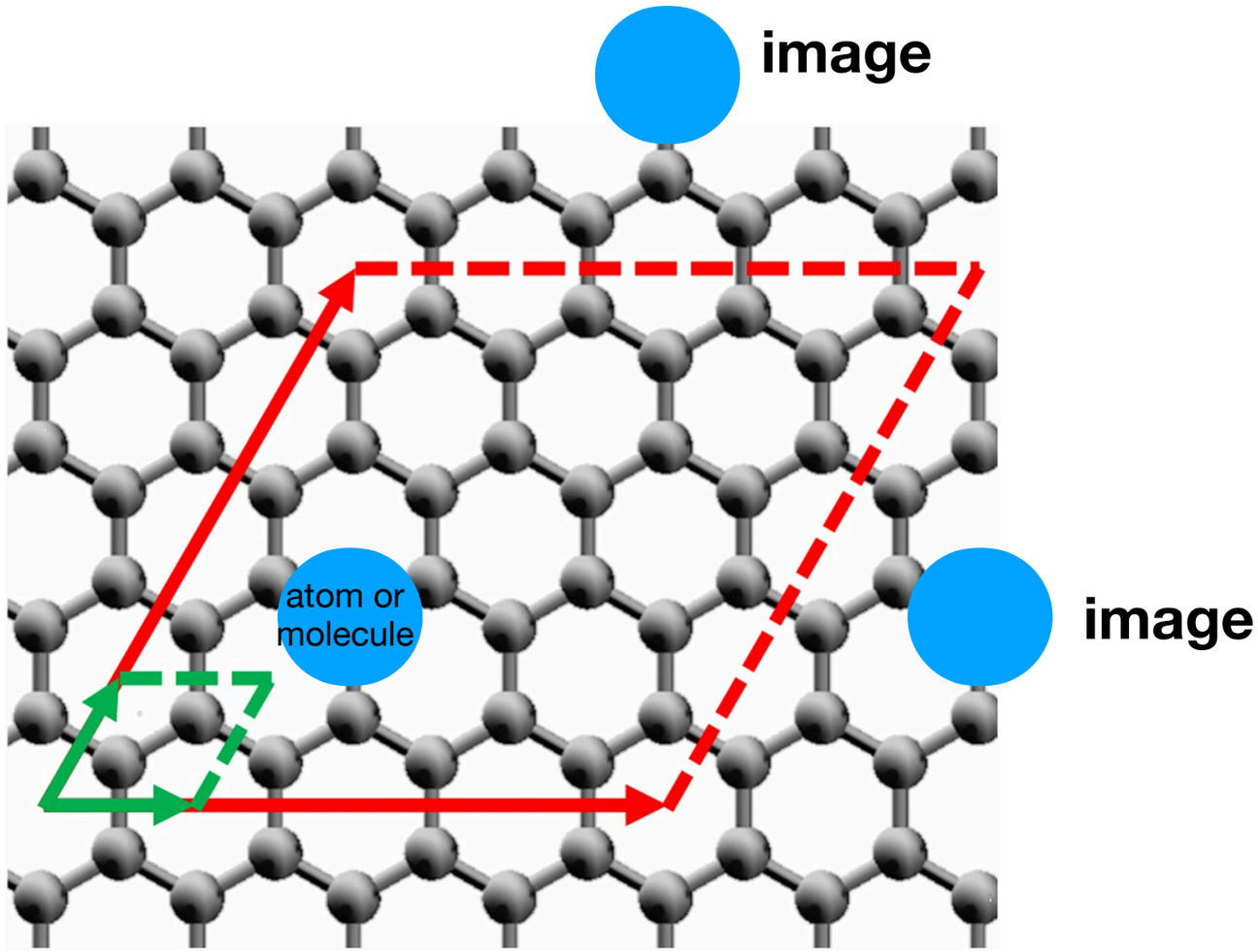
Plane-wave basis set - 2

- Plane Waves:
  - slow convergence with respect to basis set size (many more PWs than localized functions needed)
  - require periodicity: in finite systems, *supercells* must be introduced
  + easy to evaluate convergence quality (just increase a single parameter, the *cutoff*)
  + easy to use (Fourier transform)

Periodicity needed !

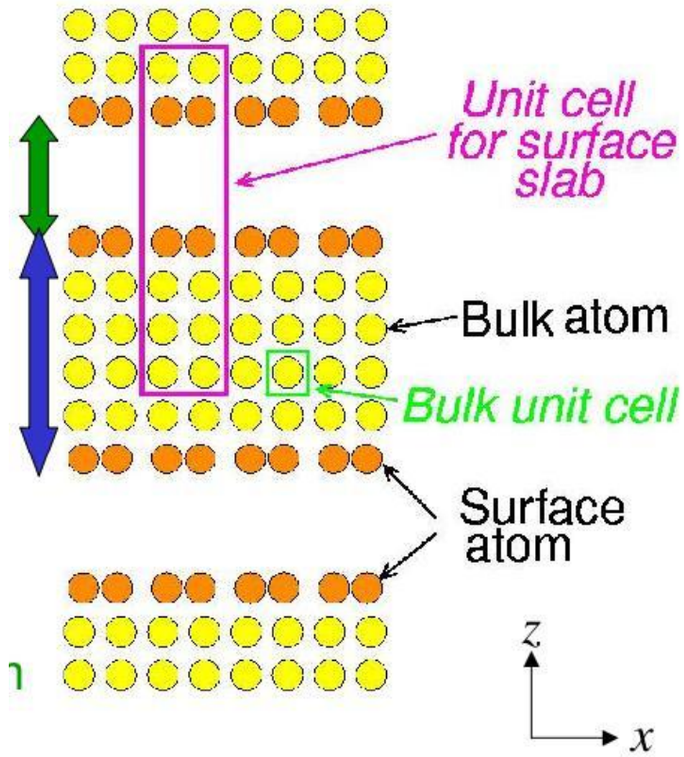
Non-periodic systems: supercells - 1

Imposing Periodic Boundary Conditions (which allows for a Fourier transform treatment)
=> **Artificial repetition** of a “building block”
but “supercells” (cells larger than the normal size of bulk periodic systems) allows to reasonably describe even **non periodic systems provided that images from adjacent cells are separated enough not to interact each other**

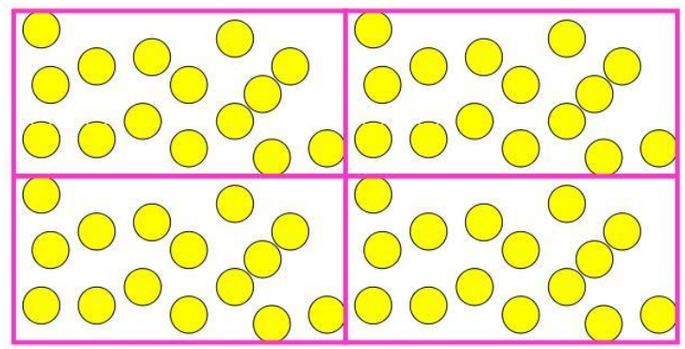


Non-periodic systems: supercells - 2

- Surfaces:
  slab geometry. The number of layers of the materials must be "big enough" to have "bulk behaviour" in the furthest layer from the surface. The number of empty layers must be "big enough" to have minimal interactions between layers in different regions.



- Alloys, amorphous materials, liquids:
- the supercell must be "big enough" to give a reasonable description of physical properties.



I part theory

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(and related convergence tests for the kinetic energy cutoff)

- **k-point sampling**

(and related convergence tests for the k-point mesh)

Brillouin zone sampling

We wrote:

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

but actually we have to calculate:

$$n(\mathbf{r}) = \sum_{\mathbf{k}} \sum_i |\psi_{\mathbf{k},i}(\mathbf{r})|^2$$

where the $\{\mathbf{k}\}$s are inside the first Brillouin zone; the finer is the $\mathbf{k}$-mesh, the more precise is the description of ψ => **do convergence test!**

Numerical approximations

- finiteness of: basis set (kinetic energy cutoff)
- Integration in reciprocal space ("special" k-point)
- {discretized meshes for differentiation (FFT grid) : somehow automatically set}
- ...

we need to study convergence !!!

the exercises of today!

Recommendations:
- change 1 parameter at a time

we need to study convergence !!!

ok, but “what”, which quantity has to converge?

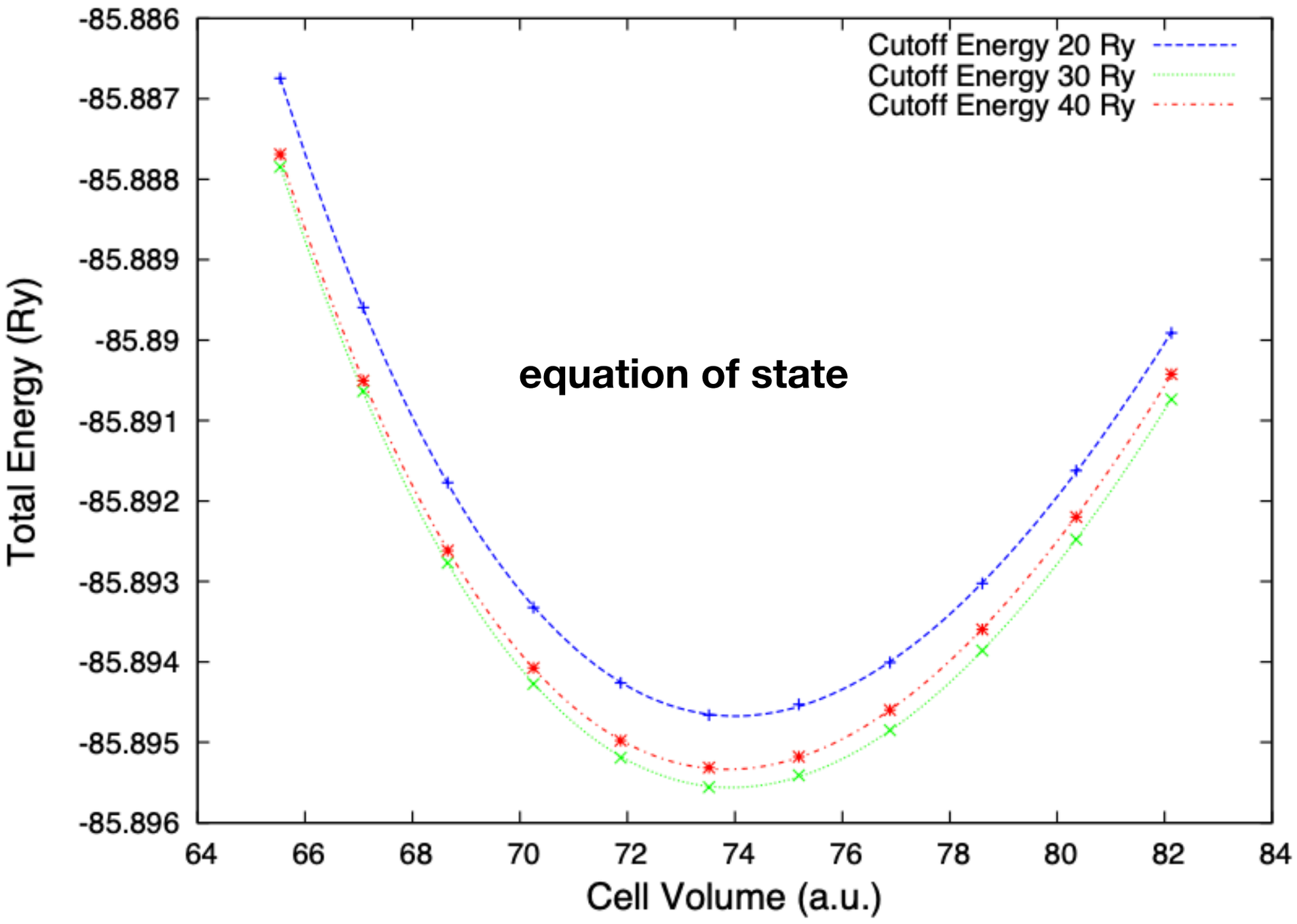
=> **total energy** as a function of k-point mesh: OK

BUT

=> total energy as a function of Ecut would continue to decrease as Ecut increases (for progressive improvement towards completeness of the pw basis set)

=> look at a meaningfully physical quantity such as **the equilibrium lattice parameter** as a function of Ecut

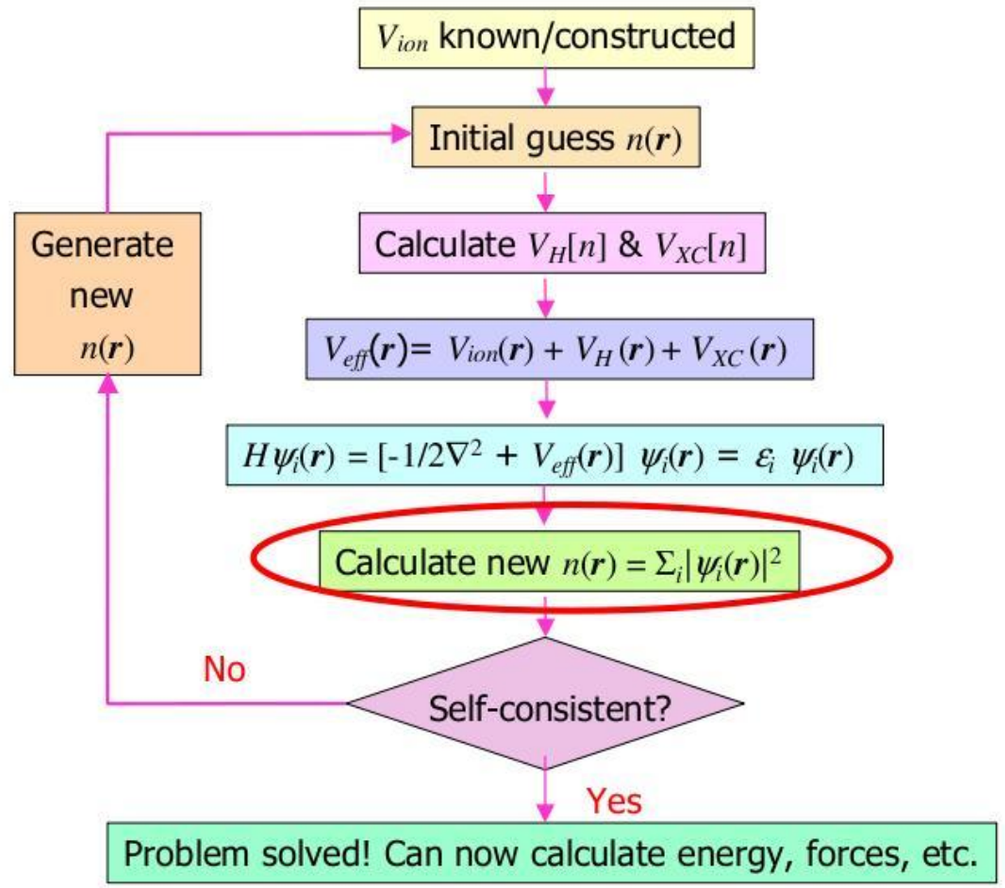
Equilibrium lattice parameter as a function of Ecut



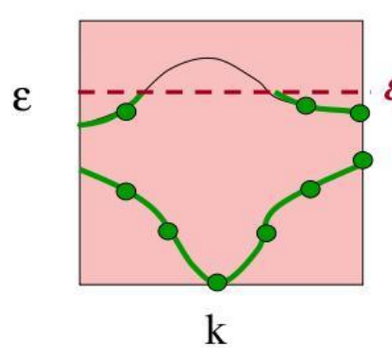
More on k points and Brillouin zone sampling

$$n(\mathbf{r}) = \sum_{\mathbf{k}} \sum_{i} |\psi_{\mathbf{k},i}(\mathbf{r})|^2$$

- The calculation of the charge density (and of many other quantities) requires sums over all **k**-points in the Brillouin Zone (BZ); in practice, some form of *BZ sampling* is needed. Convergence wrt **k**-point sampling *must be tested*!



- For insulators in large supercells, amorphous systems, liquids, molecules, sampling with Γ ($\mathbf{k} = 0$) only is fine. For other insulators, a small number of **k**-points is usually sufficient.



next lecture

- For metals, a very fine sampling of the *Fermi surface*, together with some *broadening*, or *smearing*, technique, is needed. One could in principle use Fermi-Dirac occupations at finite T, but this would require either very high T or too fine sampling

More on k points and Brillouin zone sampling

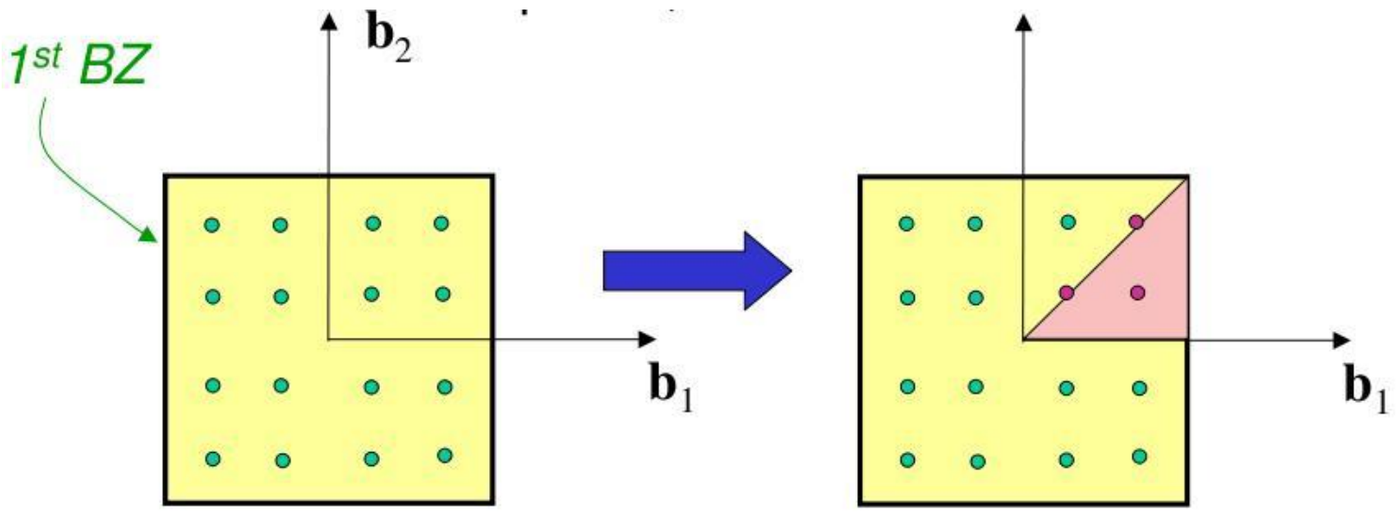
Typical ways of sampling the Brillouin Zone (BZ):

- **Special Points** (e.g. Baldereschi, Chadi and Cohen)
  Points designed to give quick convergence for particular crystal structures.

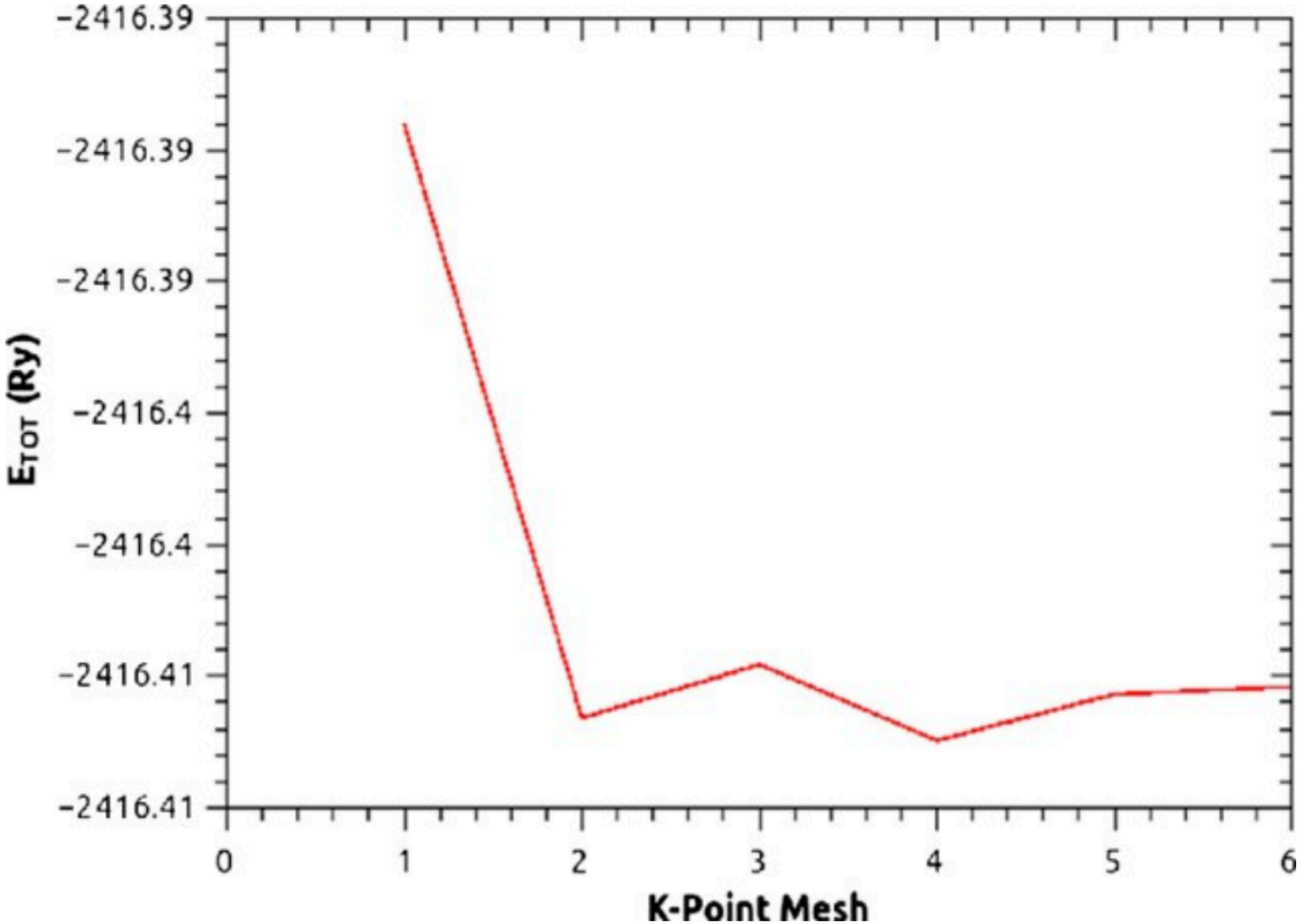
- **Uniform Grids** (e.g. Monkhorst-Pack)
  Equally spaced in reciprocal space. May be centred on origin ("non-shifted") or not ("shifted").

In presence of *symmetry*, only **k**-points in the *Irreducible* BZ, or IBZ, need to be computed: the charge density is reconstructed using symmetry. Appropriate *weights* for **k**-points must be specified (or can be calculated).

$$\frac{1}{L}\sum_{\mathbf{k}} f_{\mathbf{k}}(\mathbf{r}) \longrightarrow \sum_{i} w_i f_{\mathbf{k}_i}(\mathbf{r})$$



total energy as a function of k-point mesh: OK



Bibliography (k points)

Special points for the Bz integration

A. Baldereschi,
Mean-Value Point in the Brillouin Zone,
Phys. Rev. B **7**, 5212 (1973).

D. J. Chadi and M. L. Cohen,
Special Points in the Brillouin Zone,
Phys. Rev. B **8**, 5747 (1973)

H. J. Monkhorst and J. D. Pack,
Special points for Brillouin-zone integrations,
Phys. Rev. B **13**, 5188 (1976).

END of the I part theory

II part theory

We are doing **ground-state** calculations

output of the self-consistent cycle are:

- total energies
- Kohn-Sham orbitals (eigenvalues and eigenfunctions)
- …

We are doing **ground-state** calculations

output of the self-consistent cycle are:

- total energies **structural properties**
- Kohn-Sham orbitals (eigenvalues and eigenfunctions) **electronic properties**
- …

We are doing **ground-state** calculations

output of the self-consistent cycle are:

- total energies
- Kohn-Sham orbitals (eigenvalues and eigenfunctions)
- …





Kohn-Sham eigenvalues

(T=0k! For molecules or insulators or semiconductors, where we can distinguish between filled and empty states => occupancy 0 or 1

Hands-on session: Review the output of

1) CO (HOMO-LUMO gap? ok, easy because we only used one **k** point (Γ=(000)) => identify the energy of the HOMO and of LUMO

2) CsCl (valence-conduction gap? : answer not immediate…, since we use more **k** points... let's estimate, **k** point by **k** point, the maximum occupied and minimum unoccupied energy eigenvalues, but which is the right one? Since minima and maxima change at the various **k** points, what do we do? May be, intuitively, looking at the "simplest" point, Γ=(000), a first estimate of the gap is possible? Let's try…)

Kohn-Sham eigenvalues

2) CsCl - electronic properties can we do something better?

Post-processing!

Once we get the self-consistent potential, we “freeze” it and we can calculate many electronic properties
by even more accurate accurately sampling of the Brillouin zone

Electronic structure

- Individual Khon-Sham orbitals done
- Band gap done
- Band dispersion E(**k**) ← let’s give a look
- Charge densities (and charge transfer, magnetisation, …)
- Density of states and projection on atoms or orbitals
- k-resolved projection on atoms or orbitals

Electronic structure

(band structure)

- bands E(k)

*1) SCF calculation (**pw.x**) => calculate the crystalline potential V in $\mathcal{H}$*

*2) <u>BANDS</u> calculations (**pw.x**) => reads/uses the ground state electron density, Hartree, exchange and correlation potentials obtained in the SCF cycle to calculate E(k) on a <u>list</u> of k points.*

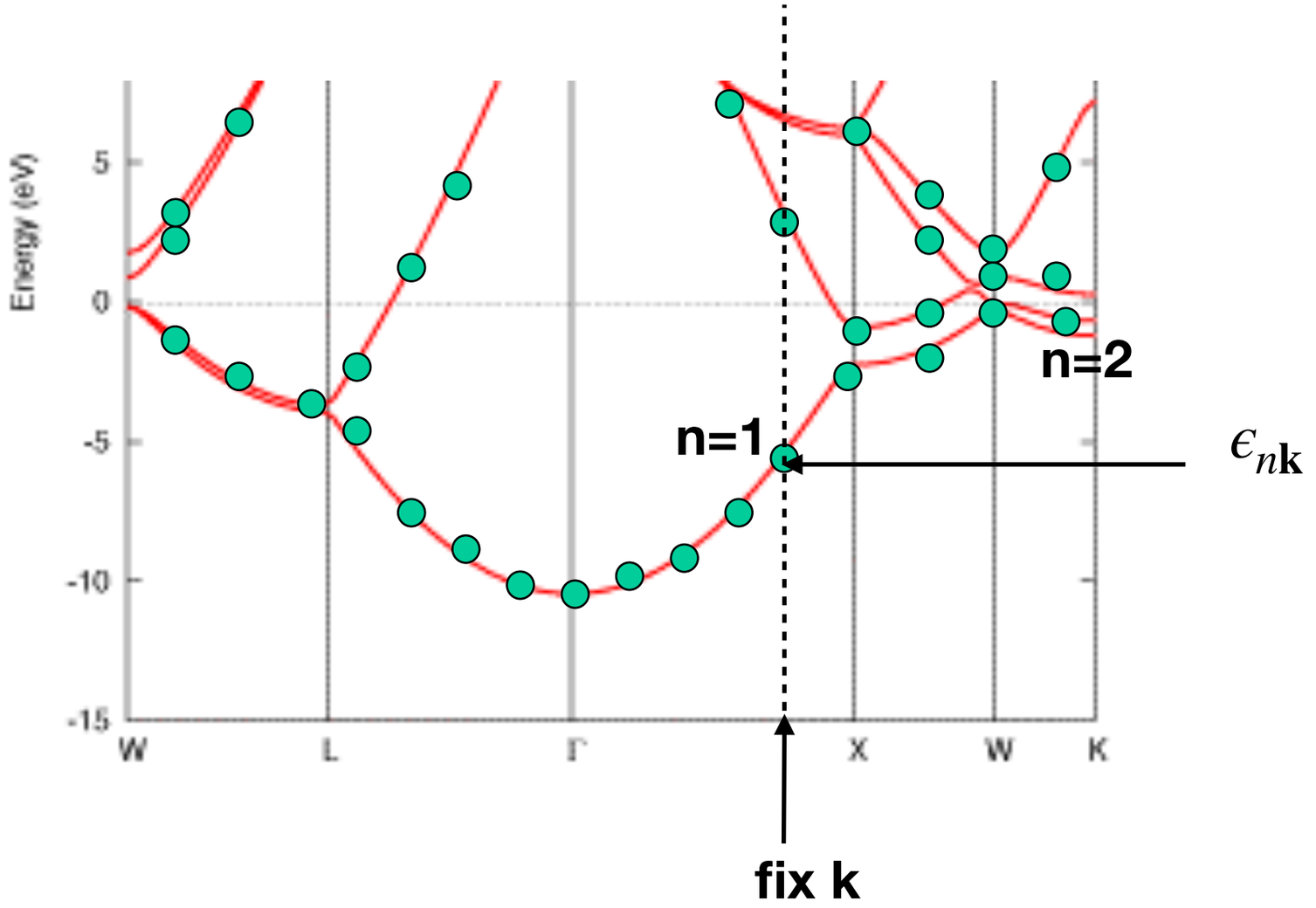
The list of k points is given in input, with arbitrary weights (not used).

*3) run **bands.x** from the postprocessing (PP) module*

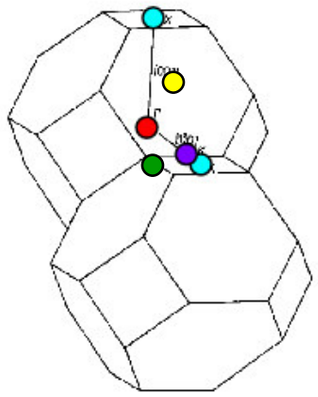
*4) PLOT E(k) along the list of k points (**plotband.x**) to visualize the band structure*

Calculating the Band Structure in Practice

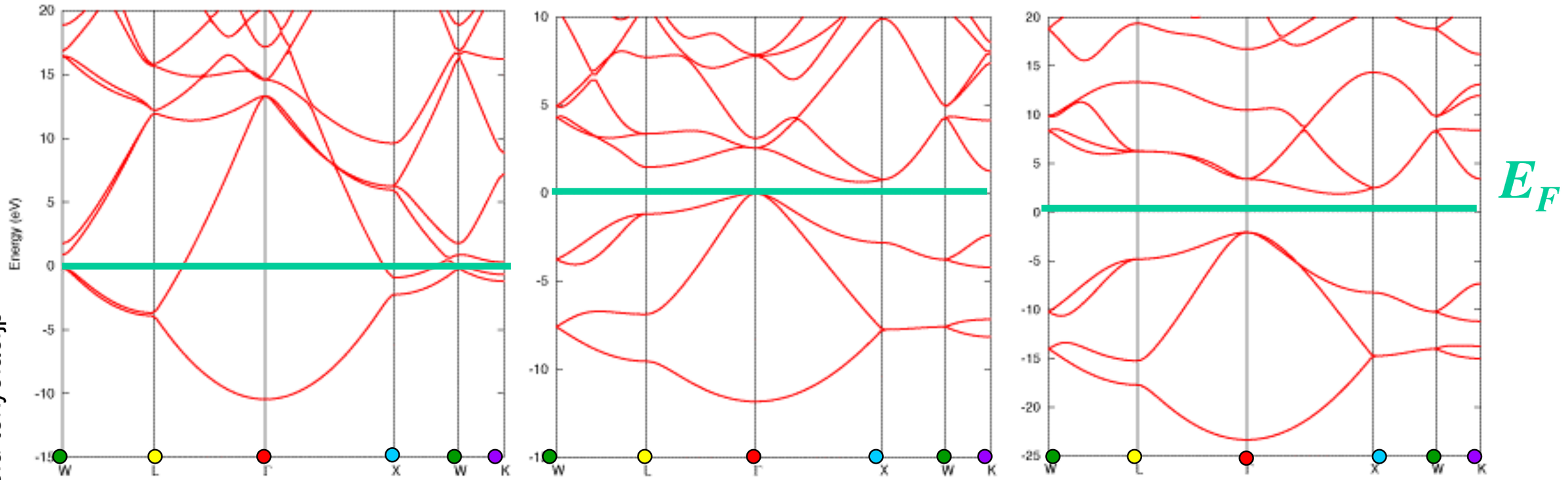
- Except for some simple models where an analytical solution is possible, one calculates the band structure numerically at certain values of wave-vector **k.**



Band Structure



- "Band structure" (graph of ε_n vs. $\mathbf{k}$):
  what states are available for electrons.
- At T=0, all states that lie below/above Fermi level are occupied/empty.



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Al
(metal)

Si
(semiconductor)

C (diamond)
(insulator)

END of the II part theory

III part theory

Other issues…

- from interacting many-body Schr. eq. =>

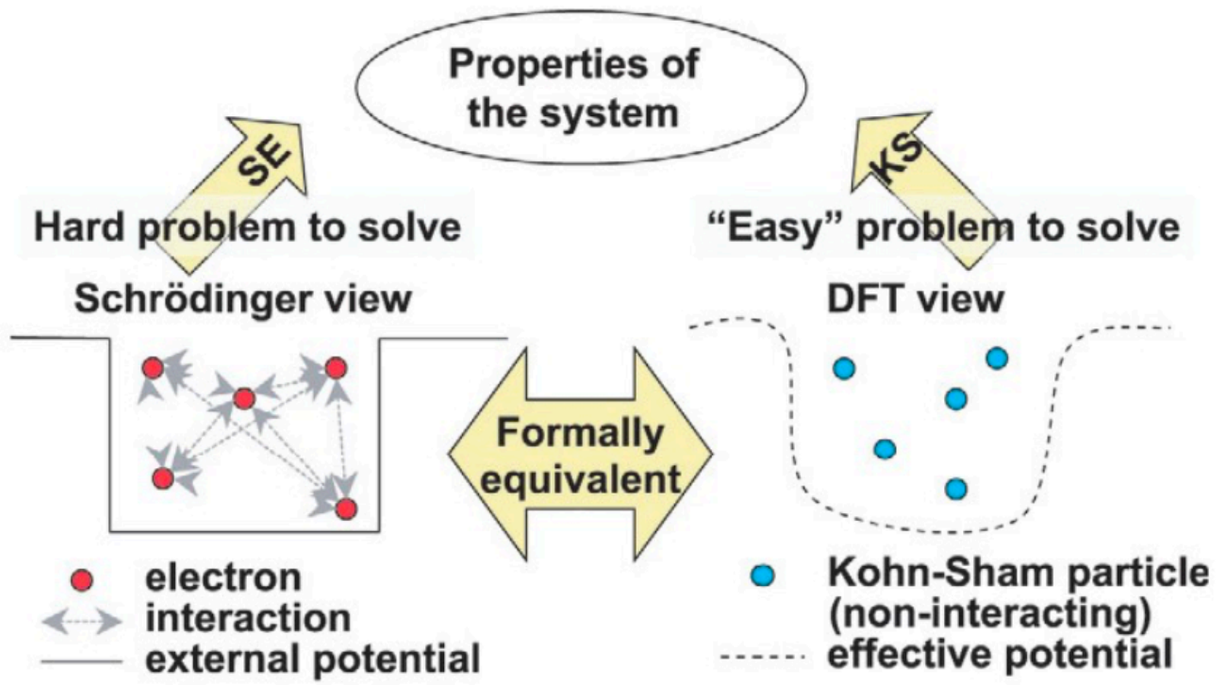
non interacting many body Schr. eq. =>
one electron (Kohn-Sham) Schr. eq.

- functionals: different approximations

Interacting => non interacting system

if n(r) is the only relevant variable
we can map the interacting system into a non-interacting one with the same density

- interacting system → non interacting system
- $n(r) \leftrightarrow V_{ext}(r)$
- $$\begin{cases} \left(-\frac{1}{2m_e}\nabla^2 + V_{eff}(\boldsymbol{r}, n(\boldsymbol{r}))\right)\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r}) \\ n(\boldsymbol{r}) = \sum_i |\psi_i(\boldsymbol{r})|^2 \end{cases}$$



We introduce V_{eff} in the functional

HK theorem and functionals

Consequence of the HK theorem:

E is a functional $E[n(\mathbf{r})]$ of $n(\mathbf{r})$

interacting el. potential ↓ U ; external potential ↓ V

$$E[n(\mathbf{r})] = \langle\Psi|T+U+V|\Psi\rangle = \langle\Psi|T+U|\Psi\rangle + \langle\Psi|V|\Psi\rangle$$
$$= F[n(\mathbf{r})] + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

$F[n(\mathbf{r})]$ is a universal functional of $n(\mathbf{r})$ (and not of $V(\mathbf{r})$)
(unknown!)

Problem: determine $n(\mathbf{r})$ which minimizes $E[n(\mathbf{r})]$

Kohn-Sham equations (II)

recover the expression for the energy:

$$E[n(\mathbf{r})] = F[n(\mathbf{r})] + \int n(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

From the mapping on to a non-interacting system:

$$F[n(\mathbf{r})] = T_s[n(\mathbf{r})] + E_H[n(\mathbf{r})] + E_{xc}[n(\mathbf{r})]$$

with:

$T_s[n(\mathbf{r})] = -\frac{\hbar^2}{2m}\sum_i \int \Psi_i^*(\mathbf{r})\nabla^2\Psi_i(\mathbf{r})d\mathbf{r}$ kinetic energy of non-interacting electrons

$E_H[n(\mathbf{r})] = \frac{e^2}{2}\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}'$ Hartree energy:
electrostatic energy of non-interacting electrons

$E_{xc}[n(\mathbf{r})]$ exchange-correlation energy:

contains all the remaining terms!!! (unknown)

Kohn-Sham equations

=> The system of interacting electrons is mapped onto a non-interacting electrons having the same density $n(\mathbf{r})$.
For non-interacting electrons:

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

(for all the fully occupied orbitals;
otherwise, insert an occupation factor)

link between *n(**r**)* and single-electron wavefunctions

with $\psi_i(\mathbf{r})$ one-electron orthonormal orbitals (Kohn-Sham orbitals) satisfying:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \underbrace{V(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})]}_{= V_{KS}[n(\mathbf{r})]} \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r})$$

in practice, this is V_{nucl}

How to solve the <u>one-electron</u> Schr. eq.? (Kohn-Sham)

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + V_H[n(\mathbf{r})] + V_{xc}[n(\mathbf{r})]\right)\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

where

- $n(\mathbf{r}) = \sum_i f_i|\psi_i(\mathbf{r})|^2$ is the charge density, f_i are occupation numbers
- V is the nuclear (pseudo-)potential acting on electrons (may be nonlocal)
- $V_H[n]$ is the Hartree potential, $V_H(\mathbf{r}) = e^2\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$
- $V_{xc}[n]$ is the exchange-correlation potential.

contains all the remaining terms (UNKNOWN!!!)

How to solve the one-electron Schr. eq.?

The formal derivation of the KS equations is exact, but approximations are necessary for the practical implementation of the theory:

- how to describe ψ ? use of **plane-waves** for wavefunction expansion (and **periodic boundary conditions**)
- how to describe V_{nucl} ? use of **pseudopotentials**
- how to perform the integrations? use of **k-point** discrete meshes for numerical integration in k-space
- how to describe V_{xc} ? choice of **approximate exchange-correlation (*xc*) functionals**



The exchange-correlation (xc) functional

Local density approximation

for the exchange-correlation energy and potential

Kohn-Sham approximate the functional with a function of the density:

$$E_{xc}[n(\mathbf{r})] = \int \epsilon(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}$$

and analogously for the potential:

$$V_{xc}[n] = \mu_{xc}(n(\mathbf{r}))$$

But $\epsilon(n(\mathbf{r}))$ and $\mu_{xc}(n(\mathbf{r}))$ are **unknown** even in case of homogeneous electron gas! Use approximate forms

Local density approximation: successes and failures

- simpler than other approaches (e.g. Hartree-Fock)
- several results of good quality (e.g. structural properties)
- good even in highly inhomogeneous systems such as atoms and molecules

- self-interaction not exactly cancelled
- overbinding (overestimate of cohesive energies ~20% and more; VdW interactions: absent by construction (due to charge fluctuations, not to overlap!) but part of the attractive effect recovered by wrong overestimate of the overlap)
- underestimate of band gap in insulators (up to 50%!)

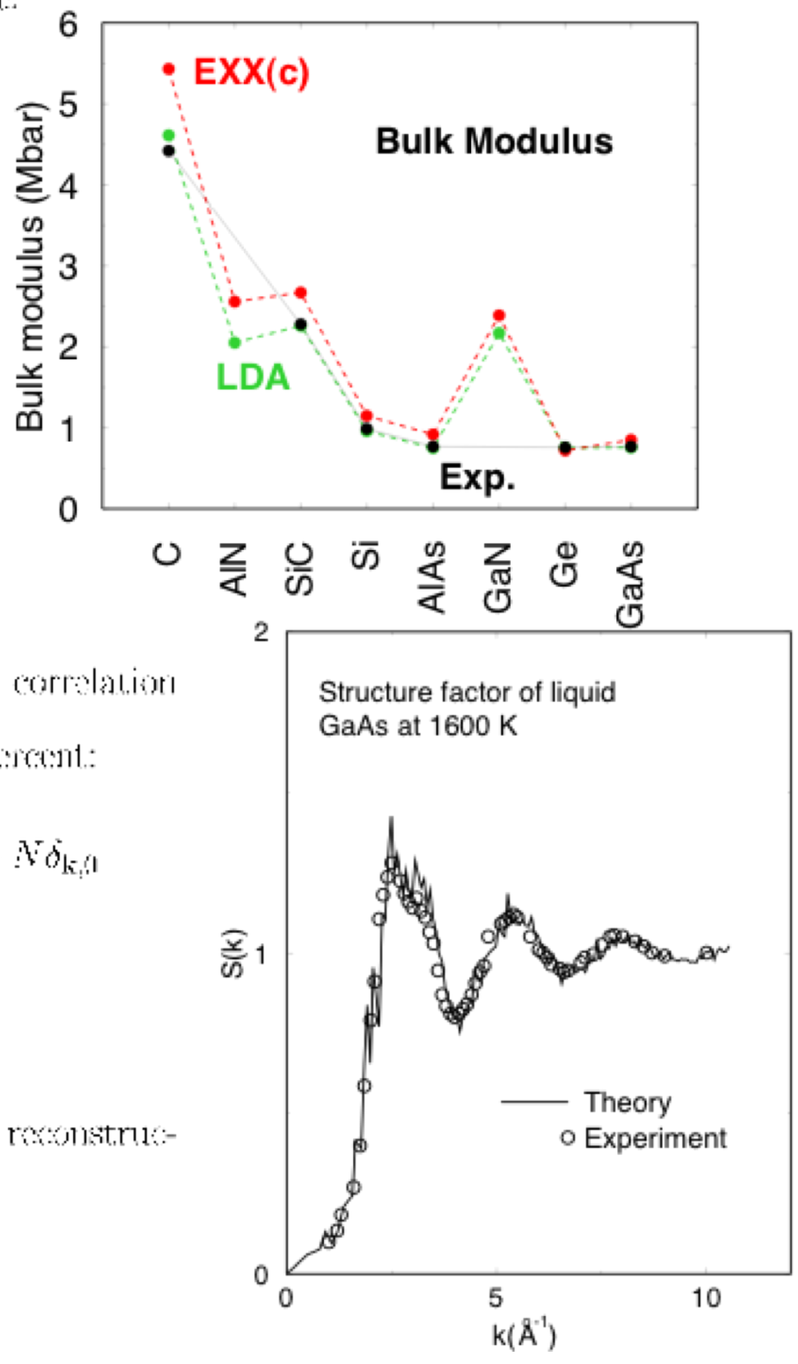
• several results of good quality (e.g. structural properties)

• Bulk moduli B to within $\perp 10\%$.

$$B = -V \left.\frac{\partial P}{\partial V}\right|_{V_0} = -V \left.\frac{\partial^2 E}{\partial V^2}\right|_{V_0}$$

V = crystal volume,

$P = \partial E/\partial V$ = pressure.



• Structure factor ($\Rightarrow$ pair correlation function) to within a few percent:

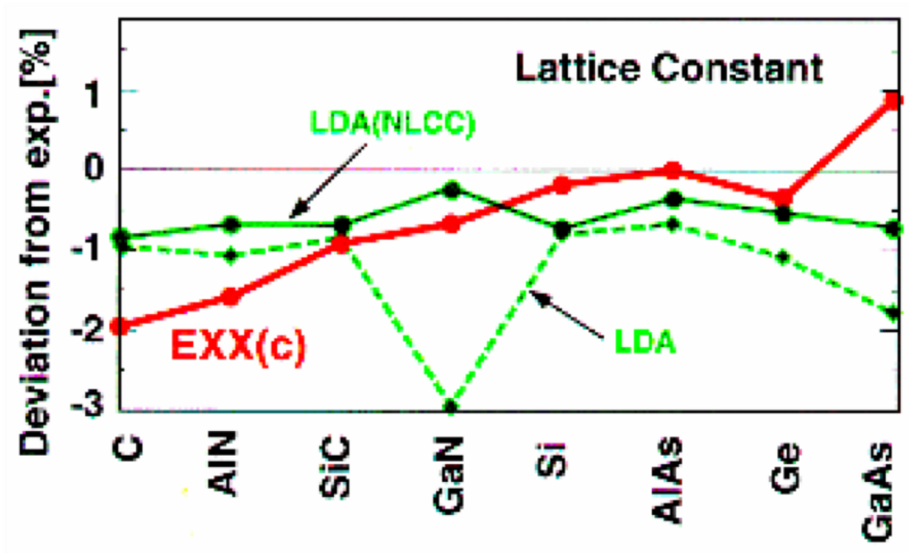
$$S(\mathrm{k}) = \frac{1}{N}\langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle - N\delta_{\mathbf{k},0}$$

$$\rho(\mathbf{k}) = \sum_{\alpha} e^{-i\mathbf{k}\cdot\mathbf{R}_\alpha}$$

$\mathbf{R}_\alpha$ = atomic position.

• Phonon frequencies, surface reconstructions, catalysis, ...

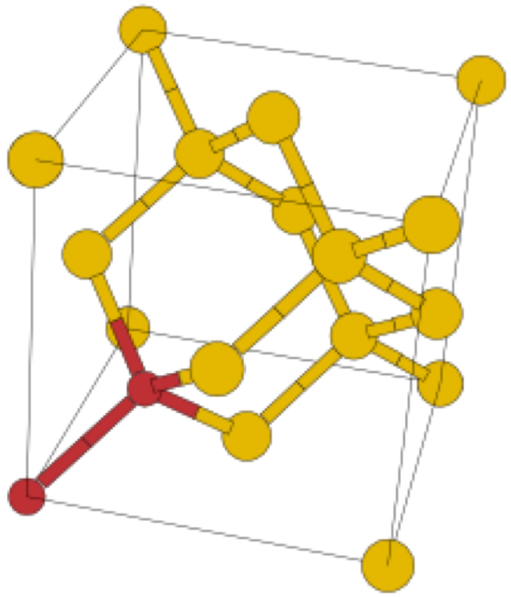
• Lattice constants to within -1%.

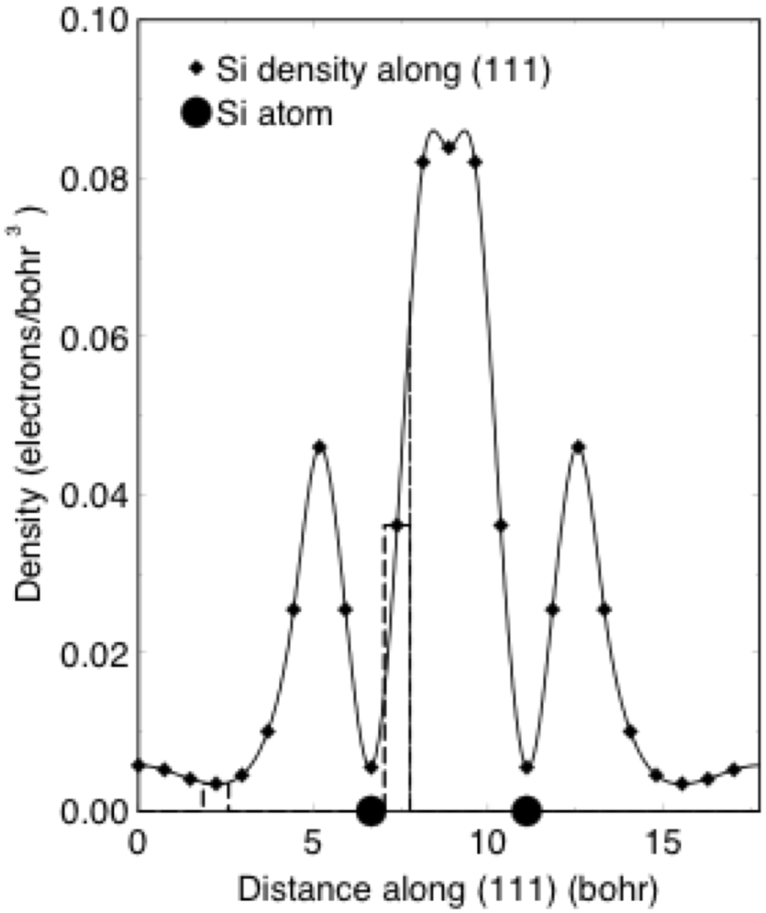


LDA(NLCC) = approximate treatment of core electrons.

LDA = core electrons not treated.

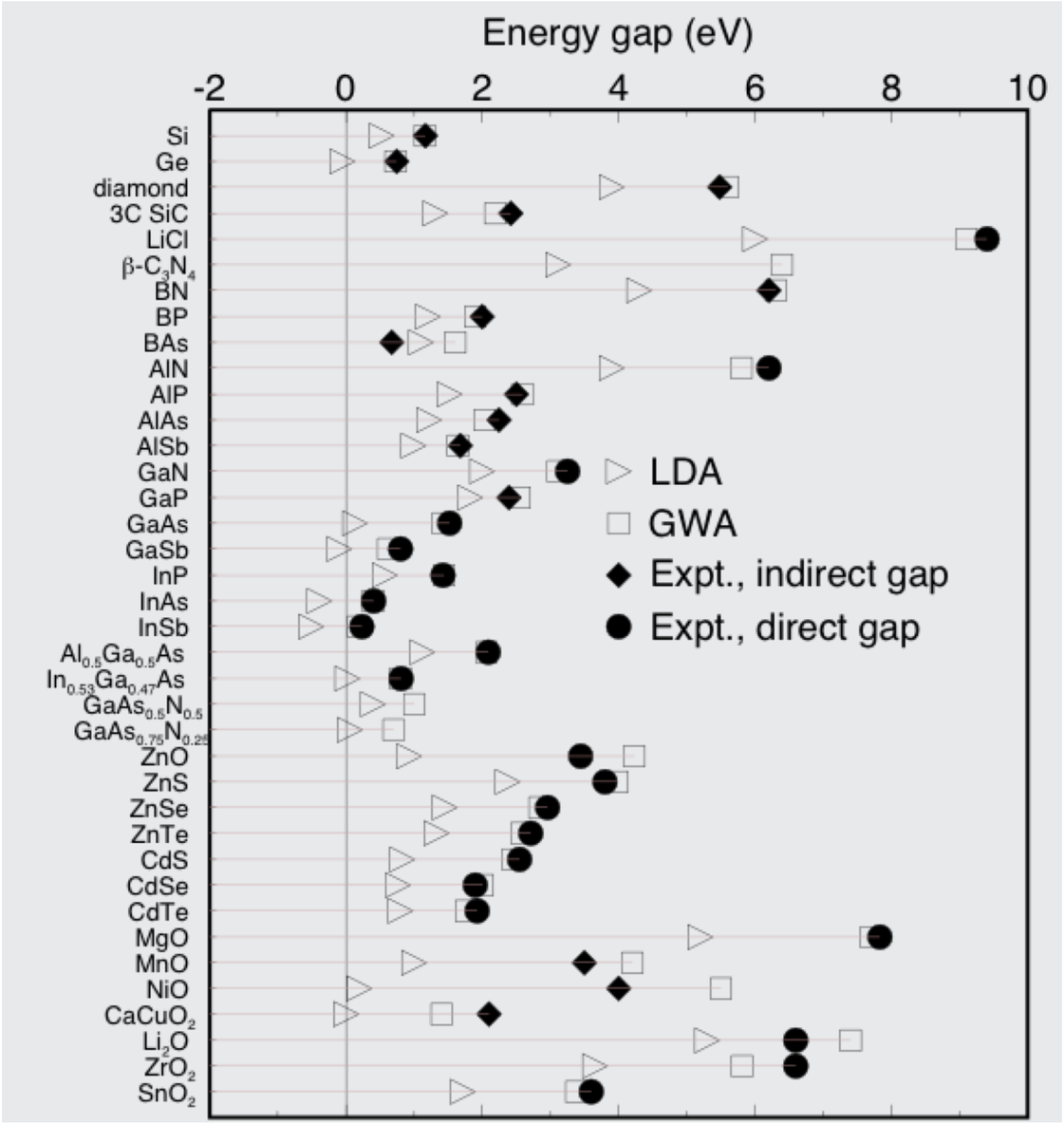
- good even in highly inhomogeneous systems such as atoms, molecules, non metallic solids...





correct description of not-so-slowly varying density along the chemical bonds

- **underestimate of band gap in insulators (up to 50%!)**



Other approximations

generalized gradient approximations (GGA)

$$E_{\mathrm{XC}}^{\mathrm{GGA}}[n_\uparrow, n_\downarrow] = \int \varepsilon_{\mathrm{XC}}(n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow) n(\mathbf{r})\, \mathrm{d}^3\mathbf{r}.$$

Other approximations

- **LDA (Local Density Approximation):** Relies only on the local electron density at a specific point.
- **GGA (Generalized Gradient Approximation):** Considers the local density and its gradient (density change). Common examples include PBE, BLYP.
- **Meta-GGA:** Includes the Laplacian of the density or the kinetic energy density. Examples: SCAN, TPSS.
- **Hybrid Functionals:** Mixes a portion of exact exchange from Hartree-Fock theory with DFT exchange-correlation.
- …

Common Functional GGA Types

- **B3LYP:** One of the most popular functionals in chemistry for molecules.
- **PBE:** Standard for solid-state physics calculations.

THE END