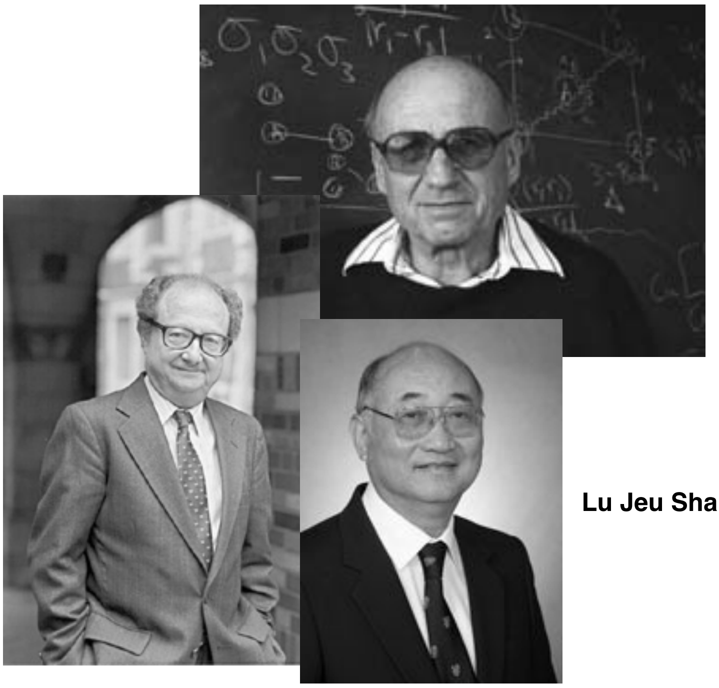
MSE 468 Lectures 6-7

FROM HF TO DFT - PART II

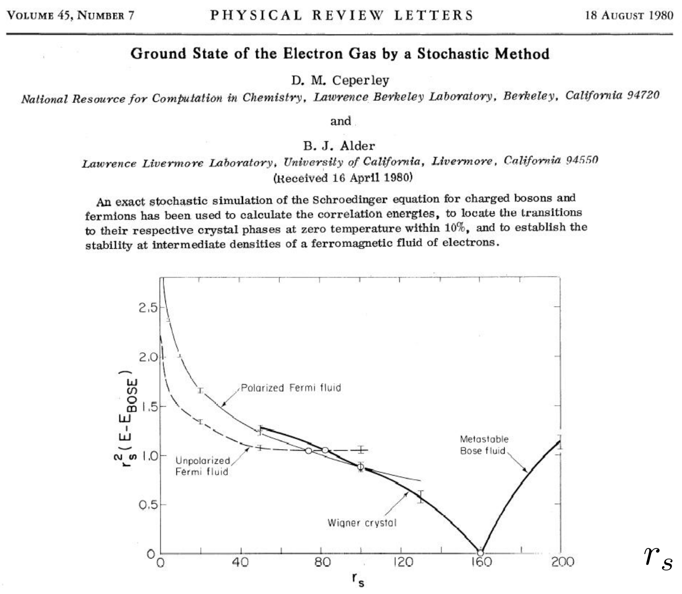


EPFL “Indicative Student Feedback on Teaching”

- https://www.epfl.ch/education/teaching/teaching-support/resources-for-students/#indicativefeedback
- **Please fill in the *single* question by this Sunday (23rd March)!**
  - “The running of the course enables my learning and an appropriate class climate”
  - Longer constructive comments are welcome (yes/no have very limited value)

What about E_{xc}? LDA!

Quantum Monte Carlo accurate calculation of the total energy of a homogeneous electron gas



VOLUME 45, NUMBER 7 PHYSICAL REVIEW LETTERS 18 AUGUST 1980

Ground State of the Electron Gas by a Stochastic Method

D. M. Ceperley
National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, Berkeley, California 94720

and

B. J. Alder
Lawrence Livermore Laboratory, University of California, Livermore, California 94550
(Received 16 April 1980)

An exact stochastic simulation of the Schroedinger equation for charged bosons and fermions has been used to calculate the correlation energies, to locate the transitions to their respective crystal phases at zero temperature within 10%, and to establish the stability at intermediate densities of a ferromagnetic fluid of electrons.

$$r_s = (3/4\pi n)^{\frac{1}{3}}$$

Fitting with an analytical formula: Perdew-Zunger

$$\begin{aligned} E_{XC}[n(\mathbf{r})] &= \int d\mathbf{r}\; e_{XC}[n(\mathbf{r})]\, n(\mathbf{r}) \\ &\approx \int d\mathbf{r}\; [e_X^{hom}(n(\mathbf{r})) + e_C^{hom}(n(\mathbf{r}))]\, n(\mathbf{r}) \end{aligned}$$

$$E_X = C\int n(\vec{r})^{4/3} d\vec{r}$$

$$e_X^{hom}(n) = -(81/64\pi)^{1/3} n^{1/3}(\mathbf{r})$$

$$e_C^{hom}(n) = \begin{cases} -0.1423(1+1.0529\sqrt{r_s}+0.3334 r_s)^{-1} & \text{if} \quad r_s \geq 1, \\ -0.0480 + 0.0311\ln r_s - 0.0116 r_s + 0.002 & r_s \quad \ln r_s \\ & \text{if} \quad r_s < 1. \end{cases}$$

$r_s := (4\pi n(\mathbf{r})/\mathbf{3})^{-1/3}$ Wigner-Seitz radius

[see, e.g. Perdew & Zunger, PRB **23** 5048 (1981)]

- We are approximating the exact (non-local) XC functional by a local one, obtained from a (numerical solution of the) homogeneous **interacting** electron gas
  (note: Thomas-Fermi was for non-interacting electrons)

It works!

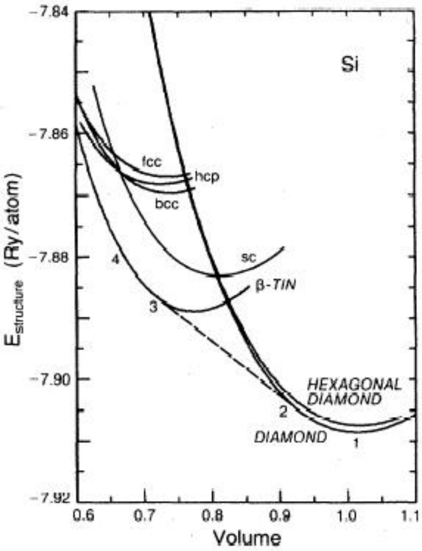


FIG. 5. Total-energy curves of the seven phases of Si as a function of the atomic volume normalized to Ω_{expt} (Ref. 31). Dashed line is the common tangent of the energy curves for the diamond phase and the β-tin phase ($c/a=0.552$).

Yin and Cohen, PRL 1980 and PRB 1982

LDA across materials space

Material	Expt	Theory	Delta	Type
LaBi	6.57	6.648	1.2%	alloy
CaF_2	5.4626	5.496	0.6%	halide
Ag	4.086	4.112	0.6%	metal
V	3.028	3.019	-0.3%	metal
ZrN	4.62	4.634	0.3%	misc
NbO	4.2103	4.2344	0.6%	oxide
GaAs	5.653	5.663	0.2%	semiconductor
$CoSi_2$	5.36	5.3	-1.1%	silicide

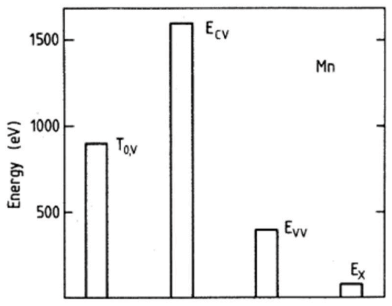
…

Milman et al., Int. J. Quantum Chem. 77, 895–910 (2000)

LDA

- Works typically quite well for lattice constants, bulk moduli, vibrational spectra, ...
- It works because it approximates only a very small part of the energy

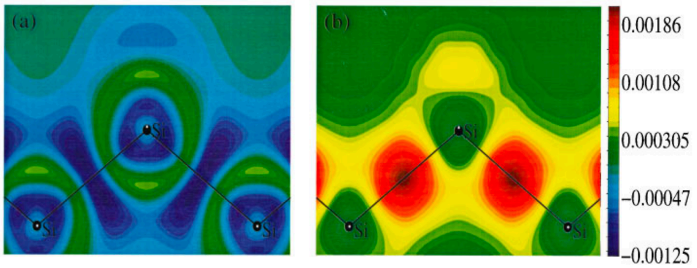
Kinetic Electrostatic Exchange



and correlation energy $E_c \sim 0.1\ E_x$

- It works also because there is *cancellation of errors*: E_x too large, E_c too small

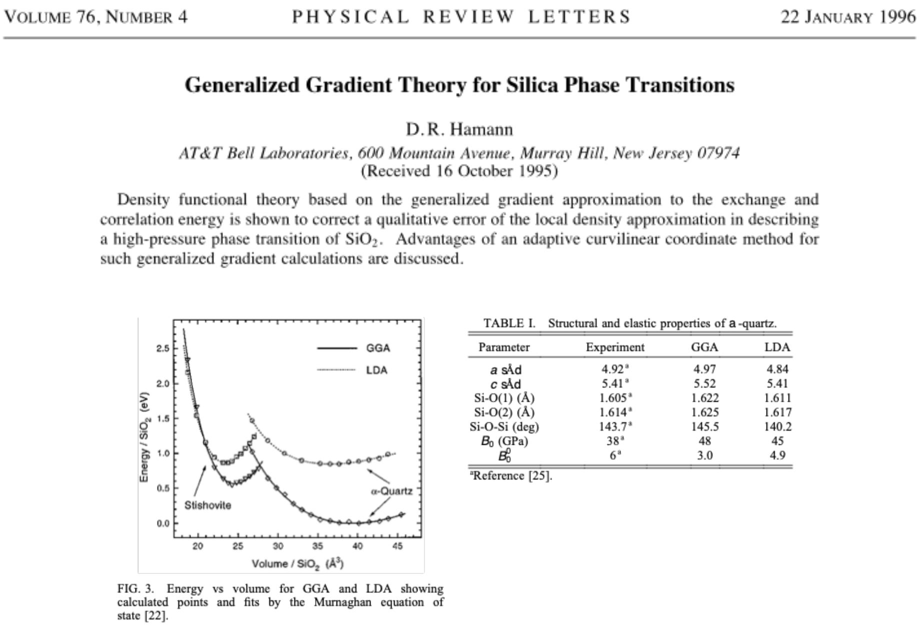
Error on E_x Error on E_c



From Hood et al., PRB 57 8972 (1998)

Well, it does not always work…

SiO$_2$ relative phase stability incorrect with LDA



VOLUME 76, NUMBER 4 PHYSICAL REVIEW LETTERS 22 JANUARY 1996

Generalized Gradient Theory for Silica Phase Transitions

D. R. Hamann
AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974
(Received 16 October 1995)

Density functional theory based on the generalized gradient approximation to the exchange and correlation energy is shown to correct a qualitative error of the local density approximation in describing a high-pressure phase transition of SiO$_2$. Advantages of an adaptive curvilinear coordinate method for such generalized gradient calculations are discussed.

FIG. 3. Energy vs volume for GGA and LDA showing calculated points and fits by the Murnaghan equation of state [22].

TABLE I. Structural and elastic properties of a -quartz.

Parameter	Experiment	GGA	LDA
a sÅd	4.92[a]	4.97	4.84
c sÅd	5.41[a]	5.52	5.41
Si-O(1) (Å)	1.605[a]	1.622	1.611
Si-O(2) (Å)	1.614[a]	1.625	1.617
Si-O-Si (deg)	143.7[a]	145.5	140.2
B_0 (GPa)	38[a]	48	45
B_0^0	6[a]	3.0	4.9

[a]Reference [25].

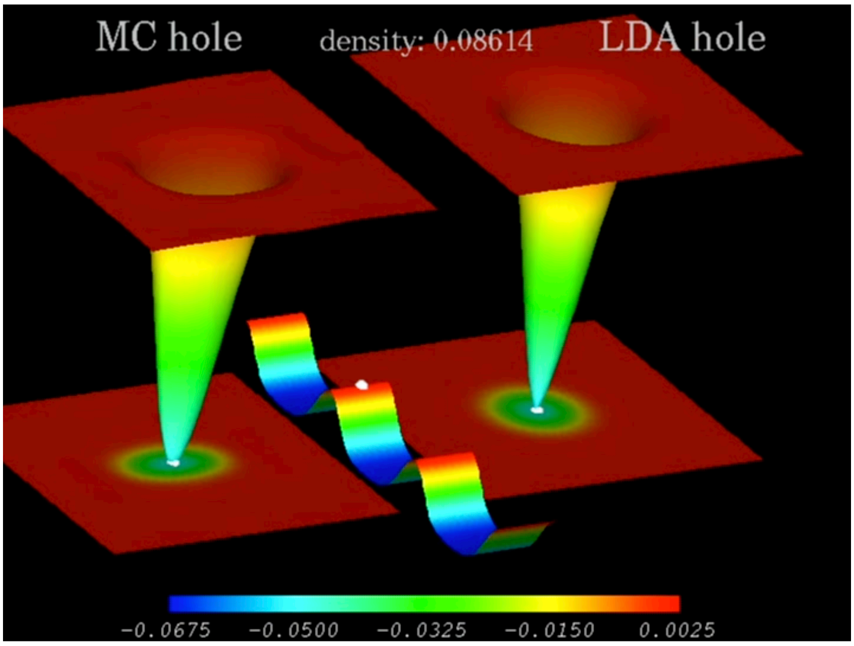
GGA: Generalised Gradient Approximation

- In molecules: electron density can vary rapidly, so uniform electron gas is not the best model
- Next improvement: use a **non-local** functional
- Simplest thing to do: use also the first derivative

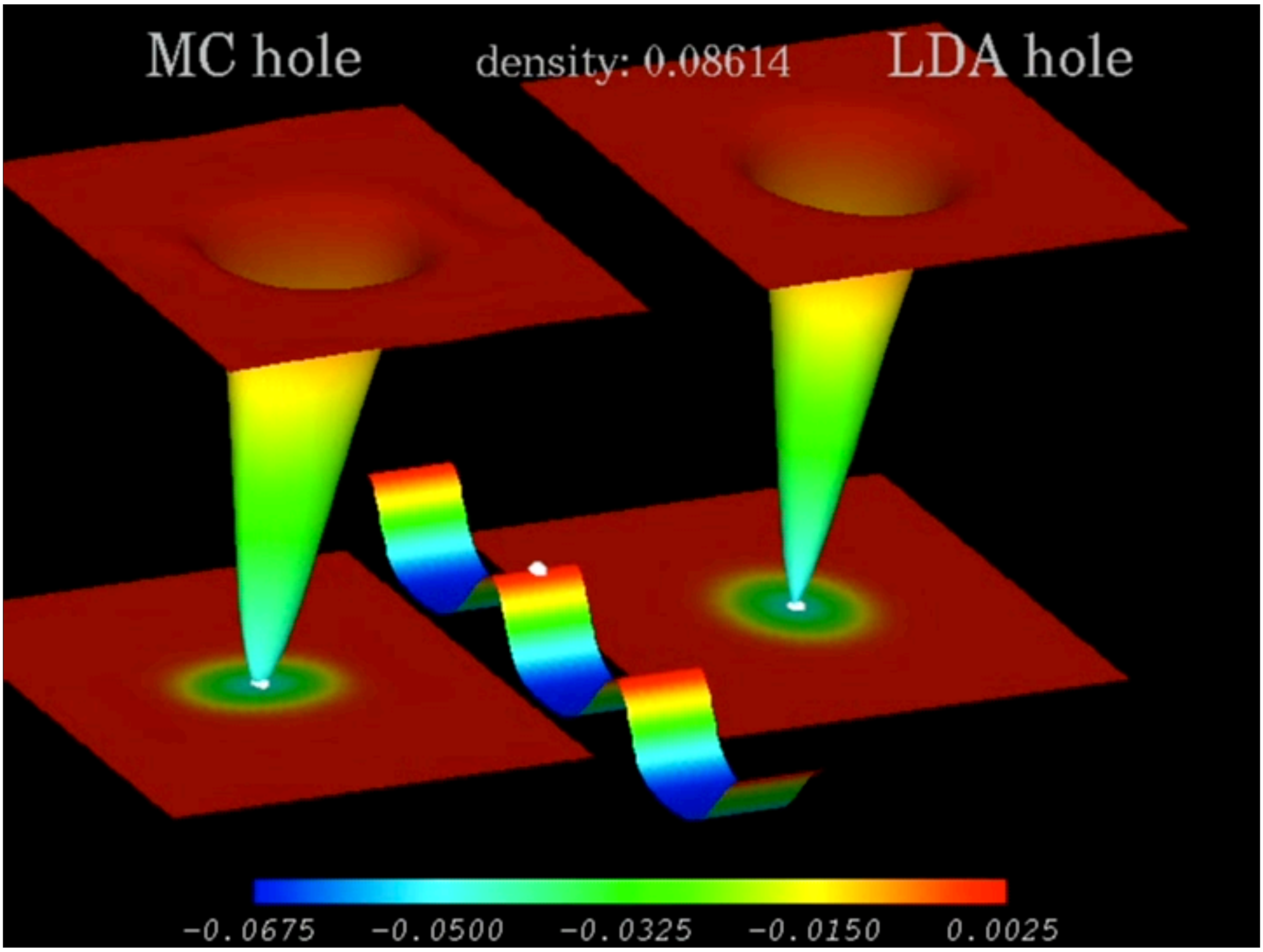
$$E_{XC}^{GGA}[n] = \int n(\vec{r})\varepsilon_{XC}^{GGA}\big(n(\vec{r}), \vec{\nabla}n(\vec{r})\big)d\vec{r}$$

- It took quite some time to figure out the correct conditions for a good GGA functional that weren't worsening the results from LDA

XC hole in a model insulator



Nekovee, Foulkes, Needs, PRL 87, 036401 (2001)



Spherical average (Si atom)

The XC hole only appears in the expression of the total energy via its spherical average

The spherical average of the LDA excludes exactly 1 electron, as it should

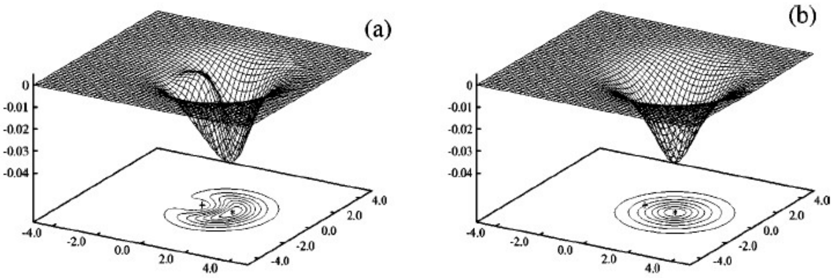


FIG. 3. (a) The Monte Carlo exchange-correlation hole with the fixed electron set at the charge density maximum (0,1.36), marked by a star, and the ion set at the origin, marked by a cross. All quantities are in atomic units. (b) The same quantity spherically averaged. Each contour line represents a change of 0.005 starting at -0.035 and going to -0.005. Each graph shows one plane in position space.

From Puzder et al., PRA 64, 022501 (2001)

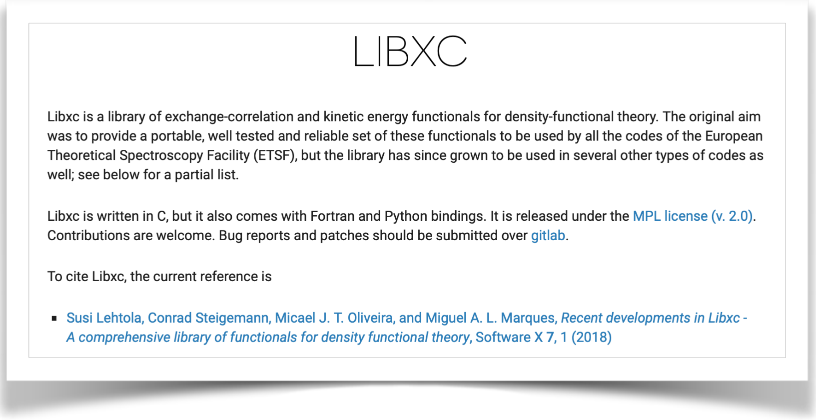
Summary on XC

- **LDA** (local density approximation)
- GGA (generalized gradient approximation): BP88, PW91, **PBE, PBEsol**, BLYP, …
- WDA (weighted density approximation – not much used)
- **Meta-GGA**: Laplacian (second derivative): R2SCAN, ...
- **Hybrids** (B3LYP, PBE0PBE, HSE): part of Fock exchange

- **Unpleasant part of DFT: there is no systematic way to improve the accuracy of the functionals**

LibXC

https://libxc.gitlab.io/



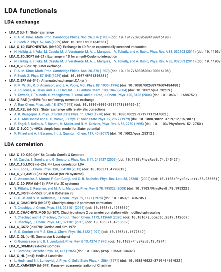
LIBXC

Libxc is a library of exchange-correlation and kinetic energy functionals for density-functional theory. The original aim was to provide a portable, well tested and reliable set of these functionals to be used by all the codes of the European Theoretical Spectroscopy Facility (ETSF), but the library has since grown to be used in several other types of codes as well; see below for a partial list.

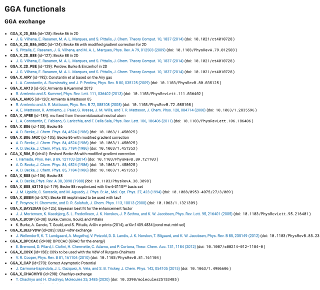
Libxc is written in C, but it also comes with Fortran and Python bindings. It is released under the MPL license (v. 2.0). Contributions are welcome. Bug reports and patches should be submitted over gitlab.

To cite Libxc, the current reference is

- Susi Lehtola, Conrad Steigemann, Micael J. T. Oliveira, and Miguel A. L. Marques, *Recent developments in Libxc - A comprehensive library of functionals for density functional theory*, Software X 7, 1 (2018)



LDA functionals



GGA functionals

meta-GGA functionals

…

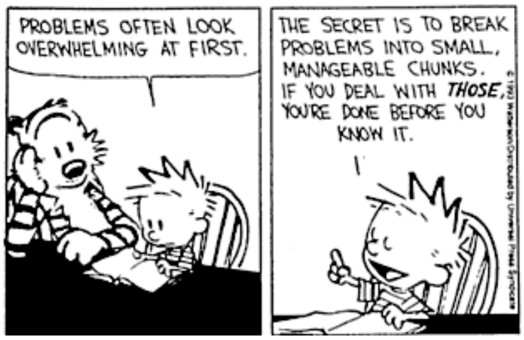
LDA vs GGA vs hybrids

- LDA good for metals, under predicts bond lengths and lattice parameters
- GGA better for molecules and solids (use PBEsol rather than PBE in this case), but often over predicts bond lengths and lattice parameters
- GGA reduces by 3-5x errors on atomisation energies
- Meta-GGA (R2SCAN) starts to emerge as a more accurate alternative (but pseudos not readily available)
- Hybrids (with HF mixed in) typically better for energies and band gaps, but up to 100x more expensive!

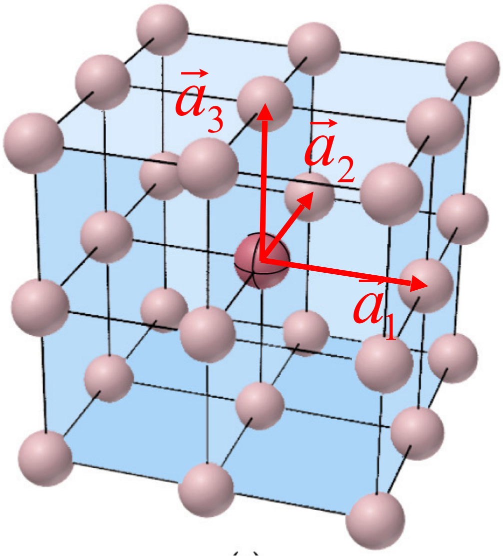
What can I do with it?

- Which properties are “ground state” properties?
- How accurate are we?
- What is the microscopic origin of the observed behavior?
- How can we be realistic?
    - Introduce the effects of temperature, pressure, composition
    - Study non-periodic systems such as liquids
    - go from a few atoms to many

Density-functional Practice



Bravais Lattices



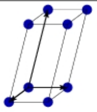
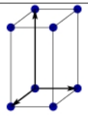
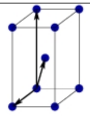
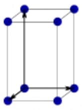
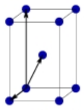
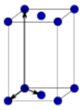
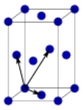
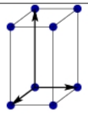
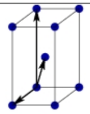
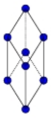
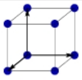
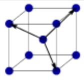
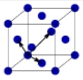
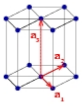
- Infinite array of points with an arrangement and orientation that appears exactly the same regardless of the point from which the array is viewed.
- 14 Bravais lattices exist in 3 dimensions (~1850)

$\vec{R} = l\vec{a}_1 + m\vec{a}_2 + n\vec{a}_3$ l,m and n integers

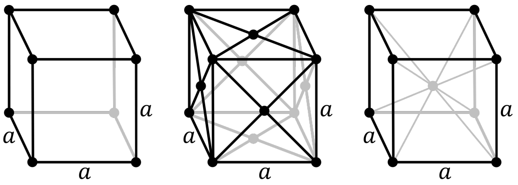
$\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ primitive lattice vectors

4 Lattice types

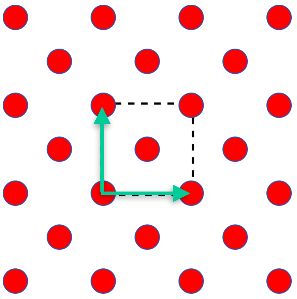
7 Crystal classes

14 Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

2d: are the "simple square" and "face-centred square lattices" different?



- **In 3D**: simple cubic, face-centered cubic, and body-centered cubic are different lattices



- **In 2D**: simple square and face-centered square are the same!

- For the same reason, in 3D a face-centered tetragonal can always be reinterpreted as a body-centered tetragonal (think about it!)

Bloch Theorem

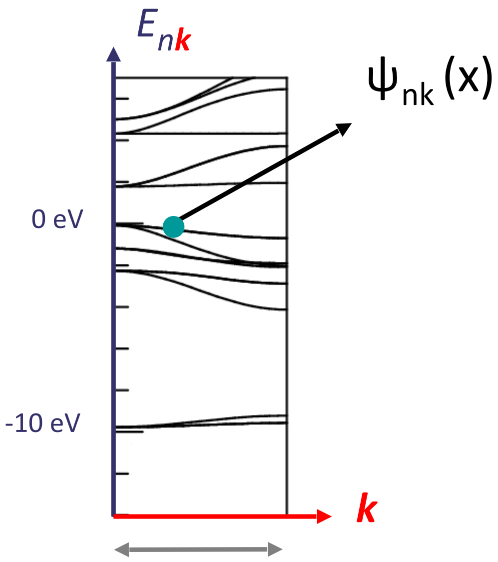
- For periodic systems, the Hamiltonian is periodic, and Bloch theorem gives us the general form (and quantum numbers *n*, **k**) for a wave function:

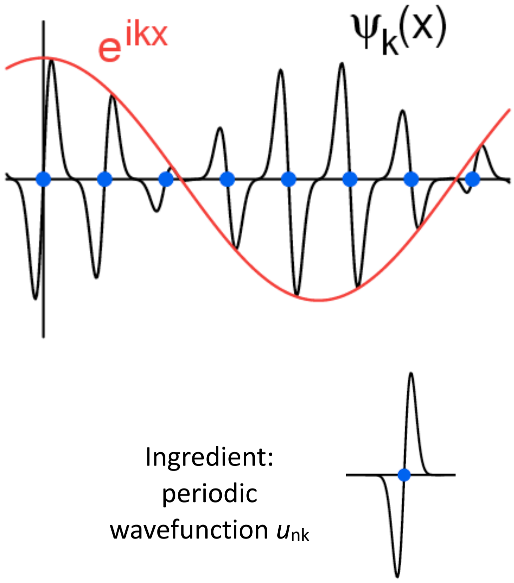
$$[\,\hat{H},\,\hat{T}_{\mathbf{R}}\,] = 0 \;\;\Rightarrow\;\; \Psi_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r})\,e^{i\mathbf{k}\cdot\mathbf{r}}$$

- *n, **k*** are the quantum numbers (band index *n* and crystal momentum ***k***)
- *u* is periodic (same periodicity as Hamiltonian)

Bands and Bloch Theorem

Bloch wavefunction

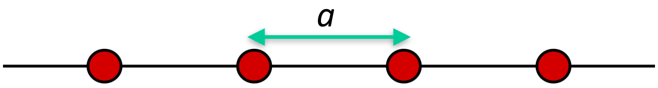




Ingredient:
periodic
wavefunction u_{nk}

Reciprocal lattice (1D)

- What are the wavevectors *G* for which our plane wave has the same amplitude at all lattice points?



Bloch theorem: $\Psi_{nk}(x) = u_{nk}(x)e^{ikx}$

- Alternative form of Bloch theorem (amplitude of the wave function in neighbouring cells):

$$\Psi_{nk}(x+a) = u_{nk}(x+a)e^{ik(x+a)} = u_{nk}(x)e^{ik(x+a)} = \Psi_{nk}(x)e^{ika}$$

- Adding to *k* any *G*=*G*$_n$ doesn't change the wavefunction:

$$e^{ika} = e^{i(k+G)a} \quad \Rightarrow \quad e^{iGa} = 1 \quad \Rightarrow \quad G_n = \frac{2\pi n}{a}$$

Reciprocal lattice

- In 3D: what are the wavevectors *G* for which our plane wave has the same amplitude at all lattice points ?

$$\vec{a}_1, \vec{a}_2, \vec{a}_3 \text{ : real-space lattice vectors}$$

$$e^{i\vec{G}\cdot\vec{r}} = e^{i\vec{G}\cdot(\vec{r}+\vec{R})}$$

$$e^{i\vec{G}\cdot\vec{R}} = 1$$

$$e^{i\vec{G}\cdot(l\vec{a}_1+m\vec{a}_2+n\vec{a}_3)} = 1$$

$$\vec{G}_i \cdot \vec{a}_j = 2\pi n\delta_{ij}, \quad n \in \mathbb{Z}$$

$$\vec{G}_1, \vec{G}_2, \vec{G}_3 \text{ : reciprocal-space lattice vectors}$$

Reciprocal lattice

Reciprocal-lattice vectors *G*$_i$ defined by all vectors

$$\vec{G}_i \cdot \vec{a}_j = 2\pi n \delta_{ij}, \quad n \in \mathbb{Z}$$

G vectors can be written on a **basis set** of 3 reciprocal lattice vectors b_i (h_i integers: the "scaled" reciprocal coordinates):

$$\vec{G}_i = h_1 \vec{b}_1 + h_2 \vec{b}_2 + h_3 \vec{b}_3$$

The b_i vectors are thus defined by (matrix inversion!):

$$\vec{b}_i \cdot \vec{a}_j = 2\pi \delta_{ij}$$

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}, \quad \vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

Examples of reciprocal lattices

Direct lattice	Reciprocal lattice
Simple cubic	Simple cubic
FCC	BCC
BCC	FCC
Orthorhombic	Orthorhombic

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

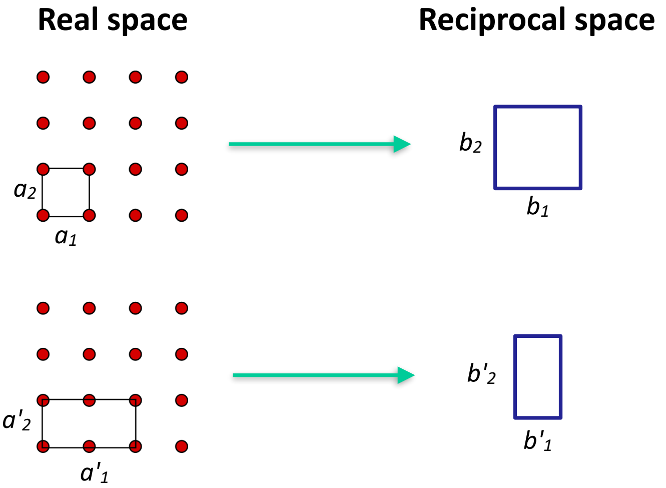
Supercells (case of orthorhombic cells)

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

For orthorhombic cells:

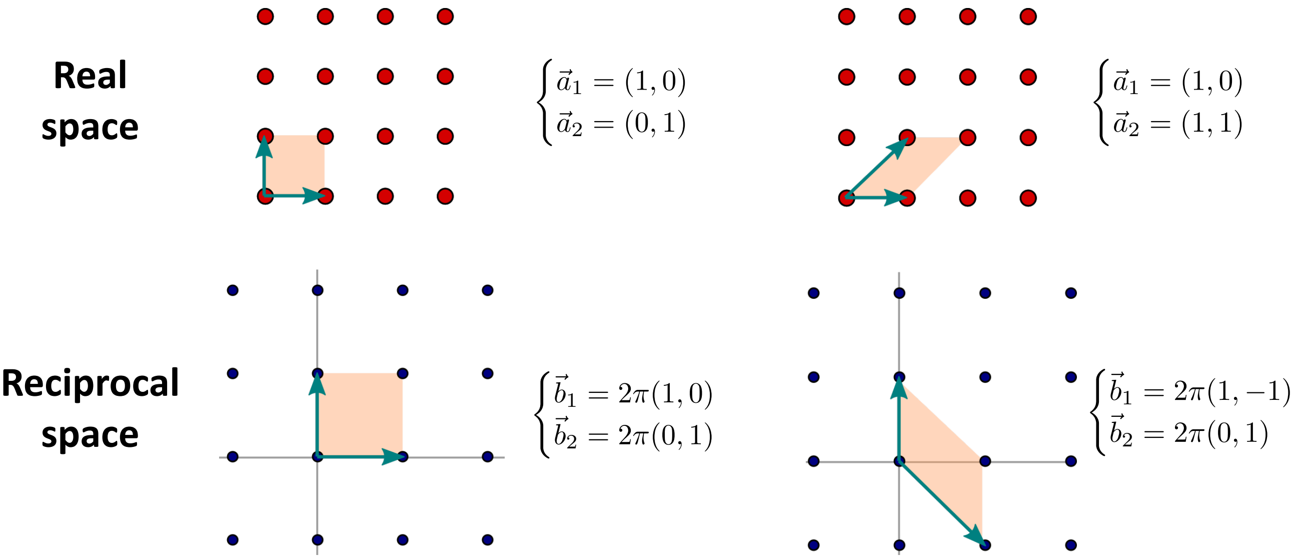
$$\vec{b}_1 \mathbin{/\!/} \vec{a}_1, \quad \vec{b}_2 \mathbin{/\!/} \vec{a}_2, \quad \vec{b}_3 \mathbin{/\!/} \vec{a}_3$$

$$\left|\vec{b}_1\right| = \frac{2\pi}{a_1}, \quad \left|\vec{b}_2\right| = \frac{2\pi}{a_2}, \quad \left|\vec{b}_3\right| = \frac{2\pi}{a_3}$$



The first Brillouin Zone (2D)

Same real-space lattice, different choice of Bravais lattice vectors => different choice of reciprocal vectors, but **same reciprocal lattice**



$$\begin{cases} \vec{a}_1 = (1,0) \\ \vec{a}_2 = (0,1) \end{cases} \qquad \begin{cases} \vec{a}_1 = (1,0) \\ \vec{a}_2 = (1,1) \end{cases}$$

$$\begin{cases} \vec{b}_1 = 2\pi(1,0) \\ \vec{b}_2 = 2\pi(0,1) \end{cases} \qquad \begin{cases} \vec{b}_1 = 2\pi(1,-1) \\ \vec{b}_2 = 2\pi(0,1) \end{cases}$$

The first Brillouin Zone (2D)

S s

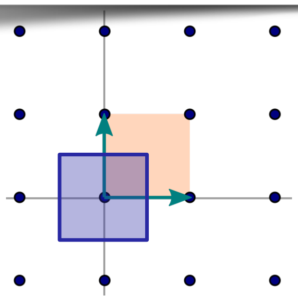
=> ce

Re $(1,0)$

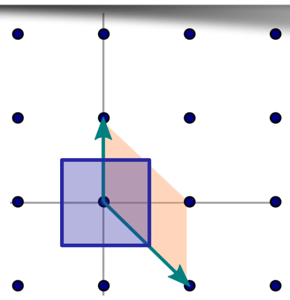
sp $(1,1)$

First Brillouin Zone (BZ):
region of points in reciprocal space that is closer to the origin ***b***=(0,0) than to any other point

Reciprocal space



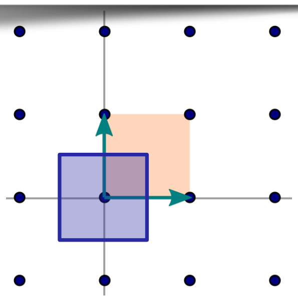
$$\begin{cases} \vec{b}_1 = 2\pi(1,0) \\ \vec{b}_2 = 2\pi(0,1) \end{cases}$$



$$\begin{cases} \vec{b}_1 = 2\pi(1,-1) \\ \vec{b}_2 = 2\pi(0,1) \end{cases}$$

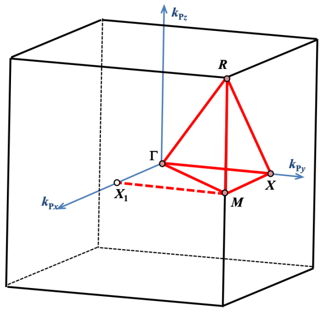
The first Brillouin Zone (2D)

First Brillouin Zone (BZ):
region of points in reciprocal space that is closer to the origin ***b***=(0,0) than to any other point



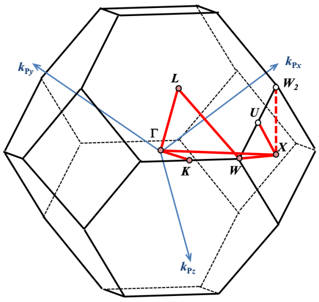
- Any integral over the whole reciprocal space: equivalent to integrating just in the BZ (blue) or in the primitive reciprocal cell (orange) because of PBC
- Primitive reciprocal cell easier numerically
- BZ is instead better to "understand", as it "preserves" the system symmetries

The first Brillouin Zone (3D)



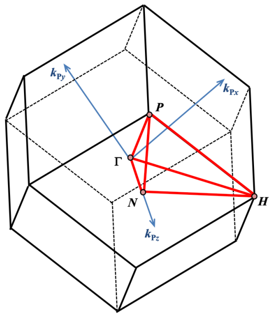
cP:
Γ–X–M–Γ–R–X | R–M (–X_1)

Simple cubic



cF:
Γ–X–U | K–Γ–L–W–X (–W_2)

FCC



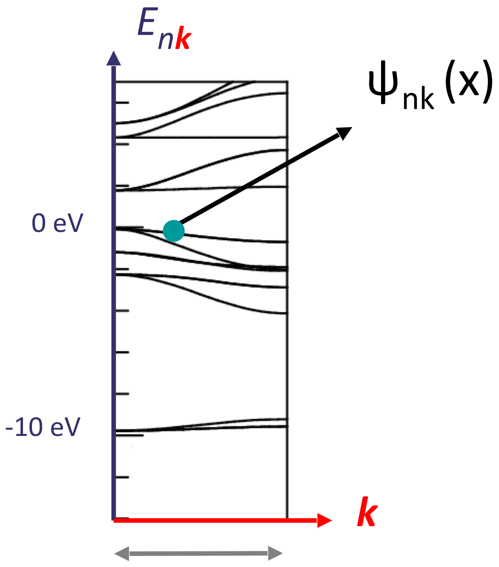
cI:
Γ–H–N–Γ–P–H | P–N

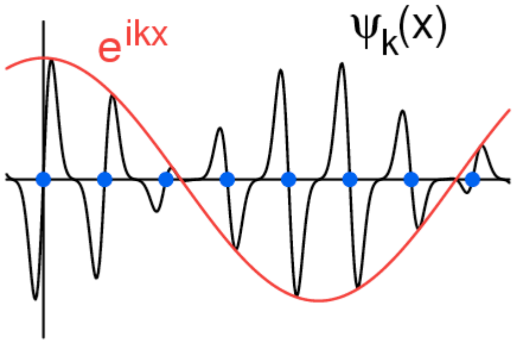
BCC

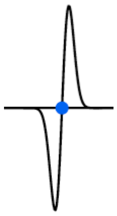
…

Band structures

- Plot of energy bands as a function of *k* in reciprocal space
- k is a 3D variable! How can we get a 4D plot? **Band paths through high symmetry points**

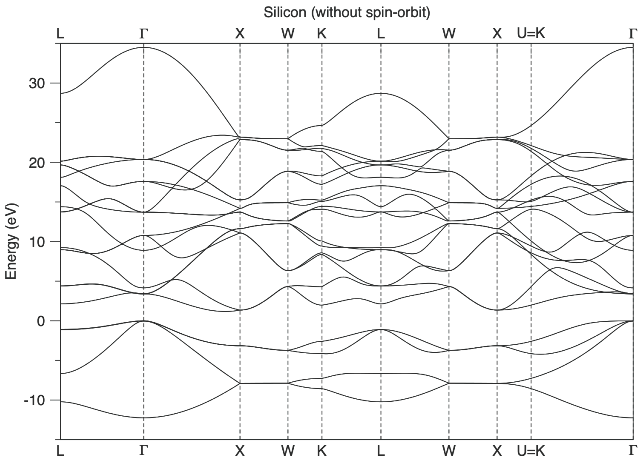


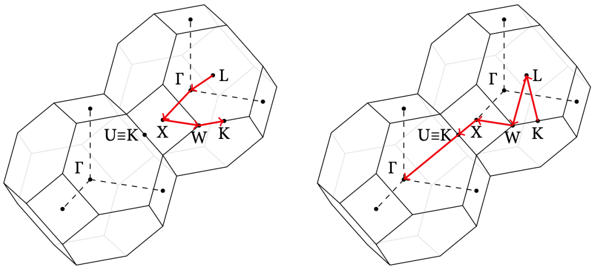




Ingredient:
periodic
wavefunction u_{nk}

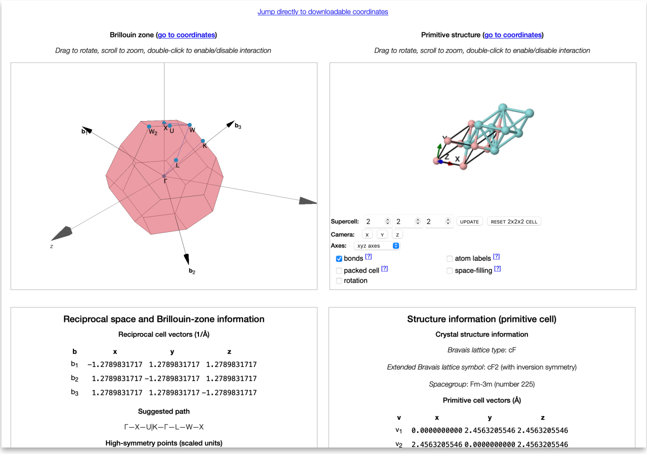
Silicon bands





Seekpath

https://www.materialscloud.org/seekpath



Jump directly to downloadable coordinates

Brillouin zone (go to coordinates)

Drag to rotate, scroll to zoom, double-click to enable/disable interaction

Primitive structure (go to coordinates)

Drag to rotate, scroll to zoom, double-click to enable/disable interaction

Supercell: 2 2 2 UPDATE RESET 2x2x2 CELL

Camera: X Y Z

Axes: xyz axes

☑ bonds [?]

☐ atom labels [?]

☐ packed cell [?]

☐ space-filling [?]

☐ rotation

Reciprocal space and Brillouin-zone information

Reciprocal cell vectors (1/Å)

b	x	y	z
b_1	−1.2789831717	1.2789831717	1.2789831717
b_2	1.2789831717	−1.2789831717	1.2789831717
b_3	1.2789831717	1.2789831717	−1.2789831717

Suggested path

Γ—X—U|K—Γ—L—W—X

High-symmetry points (scaled units)

Structure information (primitive cell)

Crystal structure information

Bravais lattice type: cF

Extended Bravais lattice symbol: cF2 (with inversion symmetry)

Spacegroup: Fm-3m (number 225)

Primitive cell vectors (Å)

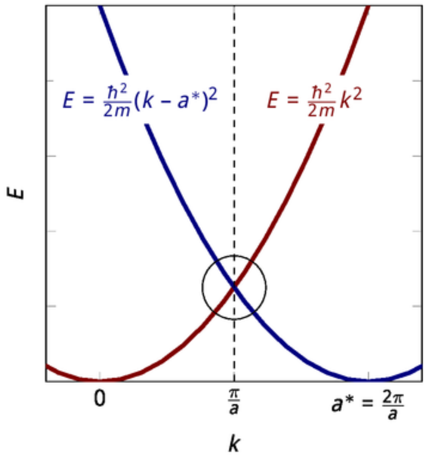
v	x	y	z
v_1	0.0000000000	2.4563205546	2.4563205546
v_2	2.4563205546	0.0000000000	2.4563205546

- **All possible BZs**
- Can **parse an input structure** and provide the corresponding BZ
- Provides the **coordinates** of the high-symmetry points
- Provides a suggested **band path**
- Provides **input templates** for various codes (including Quantum ESPRESSO)

Band Structure of the Free Electron Gas

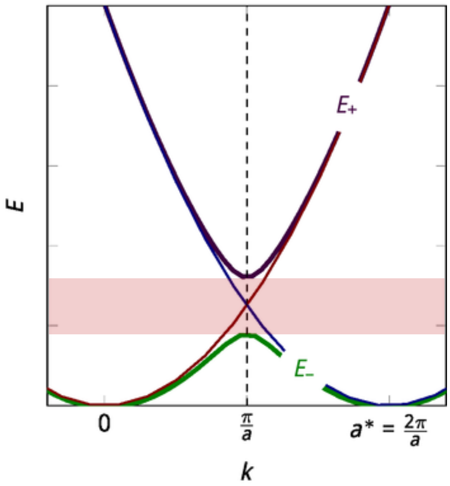
$$E = \frac{\hbar^2 k^2}{2m}$$

- An equivalent solution found by shifting by a *G* vector
- Bands "fold": several bands in the BZ equivalent to single parabola without PBC
- Zone folding depends on unit cell (arbitrary for free electron gas, given by system in actual crystal)



Adding a periodic potential

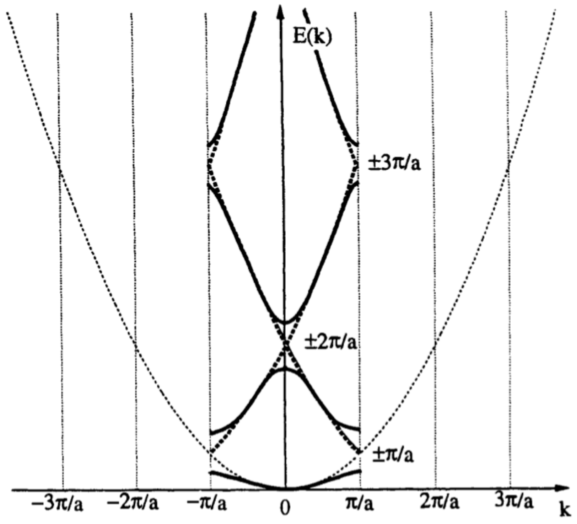
- Weak periodic potential (from atoms) opens up gaps at BZ edge
- Certain energies become forbidden (no electron, independent of *n* and **k**, can have those energies): **band gap**



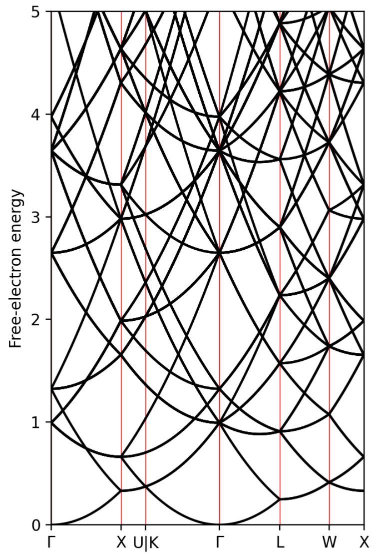
Free electron bands and folding

OSSCAR

https://osscar-quantum-mechanics.materialscloud.io/voila/render/band-theory/free_electron.ipynb

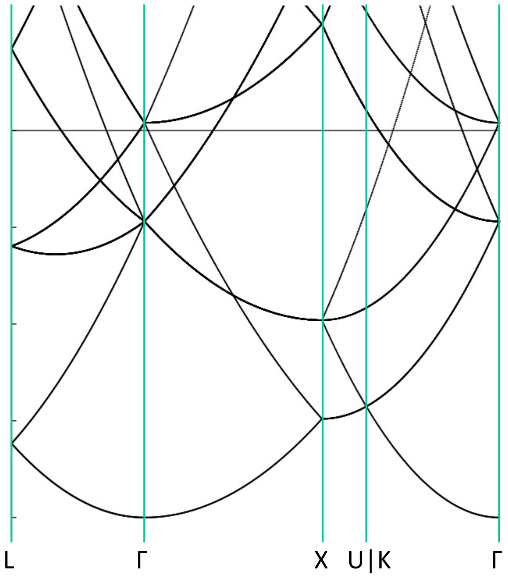


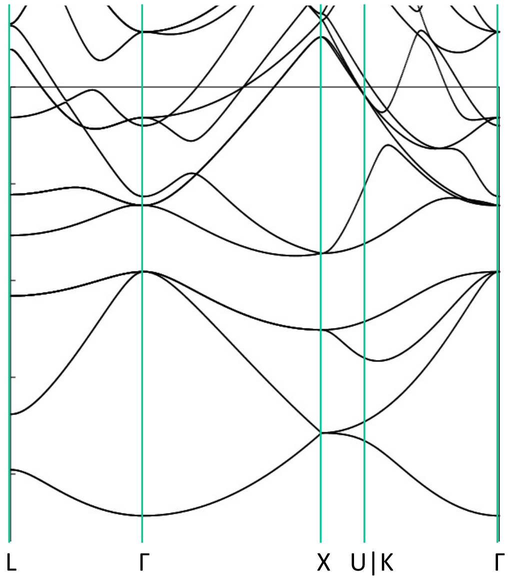
1D



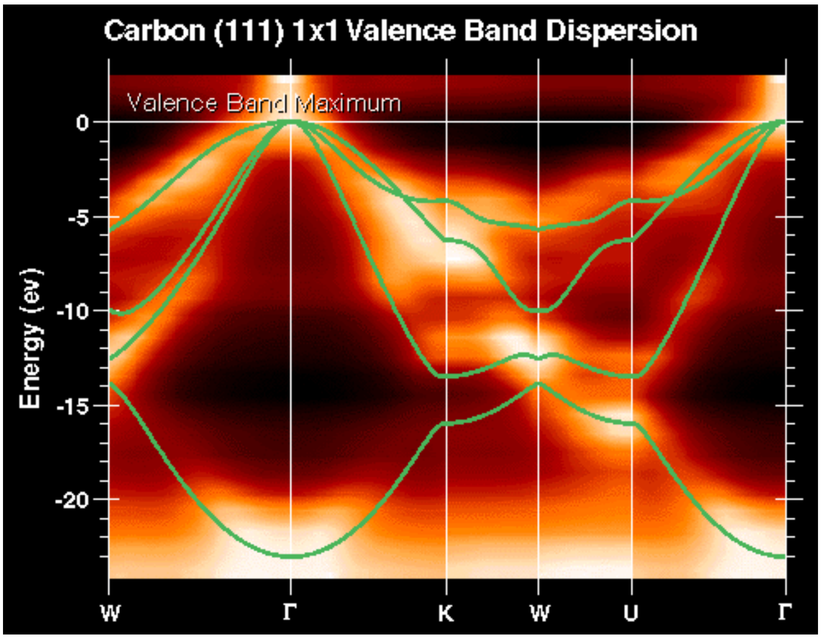
3D
(FCC lattice)

Free Electron Gas vs. Silicon

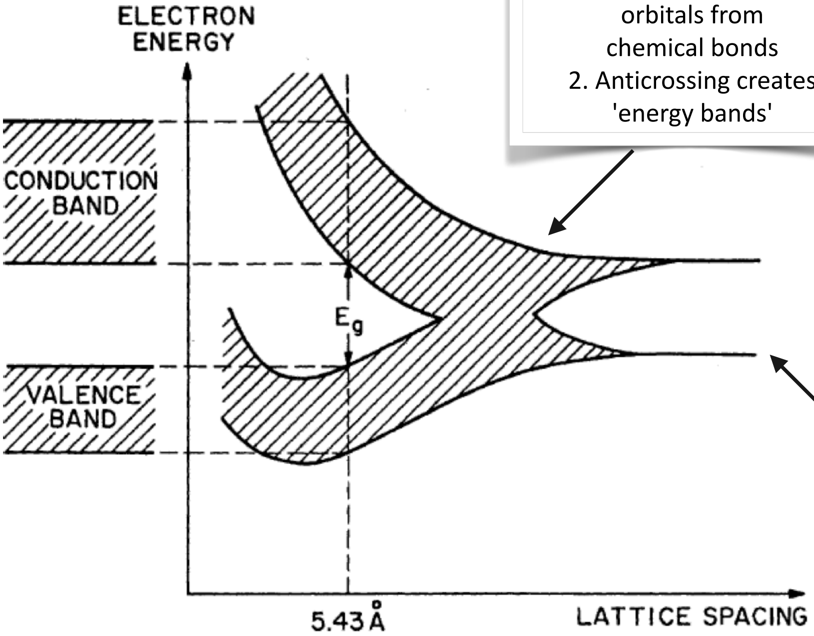




Band Structure of Diamond (ARPES measurement)



From atoms to solids



Atoms get closer and interact
1. Bonding/antibonding orbitals from chemical bonds
2. Anticrossing creates 'energy bands'

Atoms far away
Atomic levels
are all degenerate

Differential eqs. as a linear algebra problem

$$\hat{H}|\psi\rangle = E|\psi\rangle$$

$$|\psi\rangle = \sum_{n=1,k} c_n |\varphi_n\rangle \qquad \{|\varphi_n\rangle\} \text{ orthogonal}$$

$$\langle\varphi_m|\hat{H}|\psi\rangle = E\langle\varphi_m|\psi\rangle$$

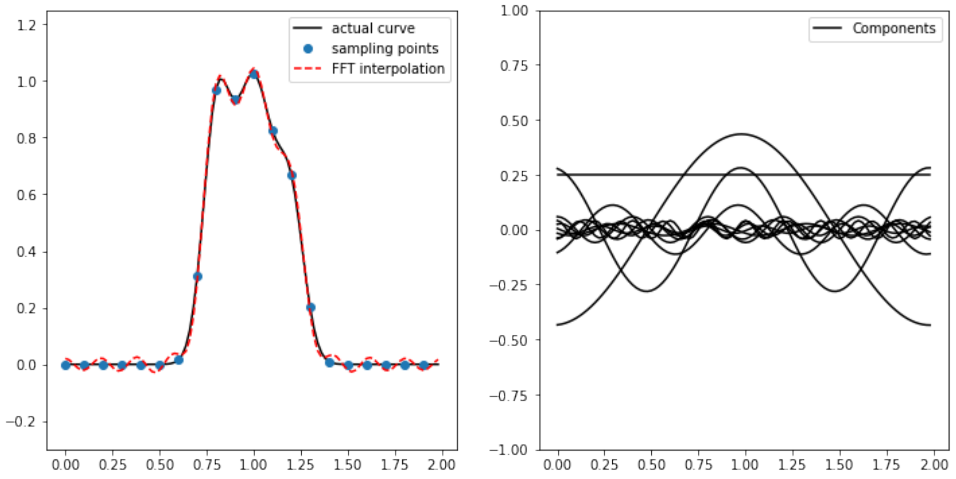
$$\sum_{n=1,k} c_n \langle\varphi_m|\hat{H}|\varphi_n\rangle = Ec_m$$

What choice for a basis ?

- For molecules: often atomic orbitals, or localized functions as Gaussians
- For solids, periodic functions such as sines and cosines (plane waves)

Expansion in a basis

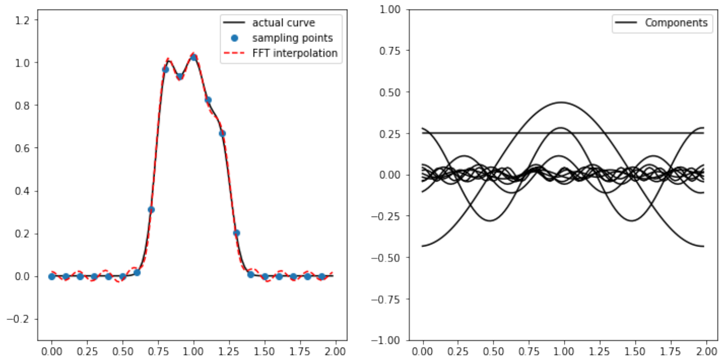
$$\psi(\vec{r})=\sum_{n=1,k} c_n\varphi_n\left(\vec{r}\right)$$



Plane wave expansion

$$\psi_{n\vec{k}}(\vec{r})=u_{n\vec{k}}(\vec{r})\exp\left(i\vec{k}\cdot\vec{r}\right)$$

$$u_{n\vec{k}}(\vec{r})=\sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}}\exp(i\vec{G}\cdot\vec{r})$$

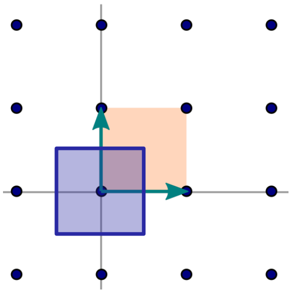


- It is a 3D **Fourier transform**!
- In 1D: expansion of wave functions as a function of e^{iGr} plane waves (i.e.: sines and cosines)

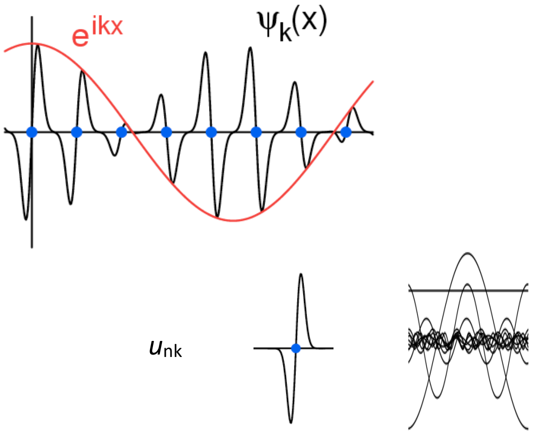
Plane wave expansion

$$\psi_{n\vec{k}}(\vec{r}) = u_{n\vec{k}}(\vec{r})\exp\left(i\vec{k}\cdot\vec{r}\right)$$

$$u_{n\vec{k}}(\vec{r}) = \sum_{\vec{G}} c_{n\vec{k}}^{\vec{G}} \exp(i\vec{G}\cdot\vec{r})$$



- **Important!**
  - **"*k points*"**: in the first BZ, give long-range modulation of wavefunction
  - **"G vectors"**: reciprocal lattice vectors (discrete lattice): high-frequency oscillations to approximate the periodic part u_{nk}

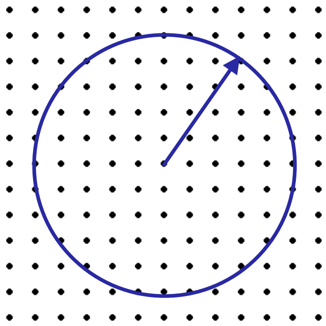


3D: the cutoff sphere

- Size of plane-wave basis set ("resolution") can be defined by the number of vectors (but depends on lattice parameter, since spacing of *G* vectors ~1/*a*) or more "transferably" by **kinetic-energy cut-off**

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$\sum_{\mathbf{G}}\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 c_{\mathbf{k}+\mathbf{G}}e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$



- Only include those **G** that satisfy

$$\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 < E_{\mathrm{cutoff}}$$

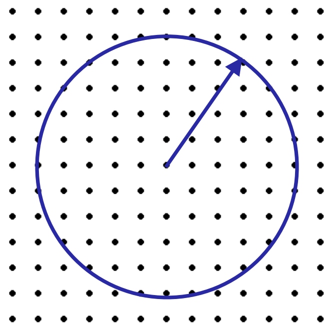
3D: the cutoff sphere

- Size of plane-wave basis set ("resolution") can be defined by lattice par more "transferably" by kinetic energy cut-off

NOTE: kinetic operator (second derivative) is simply a multiplication in reciprocal space!

$$-\frac{\hbar^2}{2m}\nabla^2\psi_k(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2\sum_{\mathbf{G}} c_{\mathbf{k}+\mathbf{G}}\, e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$

$$\sum_{\mathbf{G}}\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 c_{\mathbf{k}+\mathbf{G}}\, e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$$



- Only include those **G** that satisfy

$$\frac{\hbar^2}{2m}|\mathbf{k}+\mathbf{G}|^2 < E_{\mathrm{cutoff}}$$

Brillouin zone integrations

- Integrals over all space (or, in practice, over the BZ) needed to get densities and energies

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

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

Sum over all possible quantum states that are occupied by electrons

$$\rho(\mathbf{r}) = \frac{1}{N_k}\sum_{n\mathbf{k}}|\psi_{n\mathbf{k}}(\mathbf{r})|^2$$

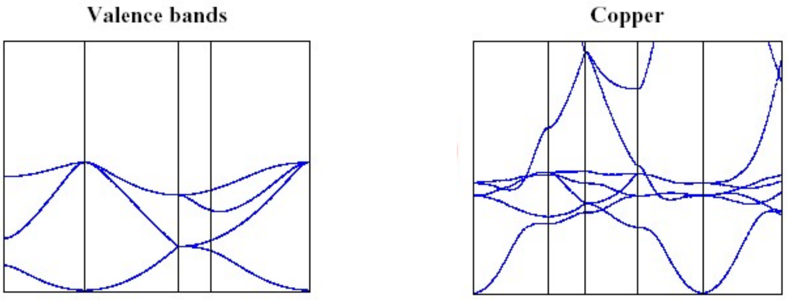
In particular:

sum (actually, average) over reciprocal space

NOTE: sum is ONLY over occupied states

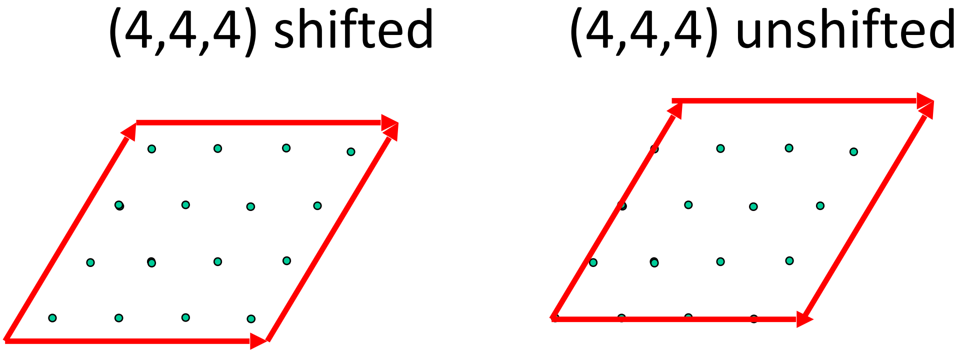
Brillouin Zone integrations

1. Sampling at one point (the best – Baldereschi point, or the simplest – Gamma point)
2. Sampling at regular meshes (Monkhorst-Pack grids)
3. For metallic systems, integration of the discontinuity is improved introducing a fictitious electronic temperature (see later)



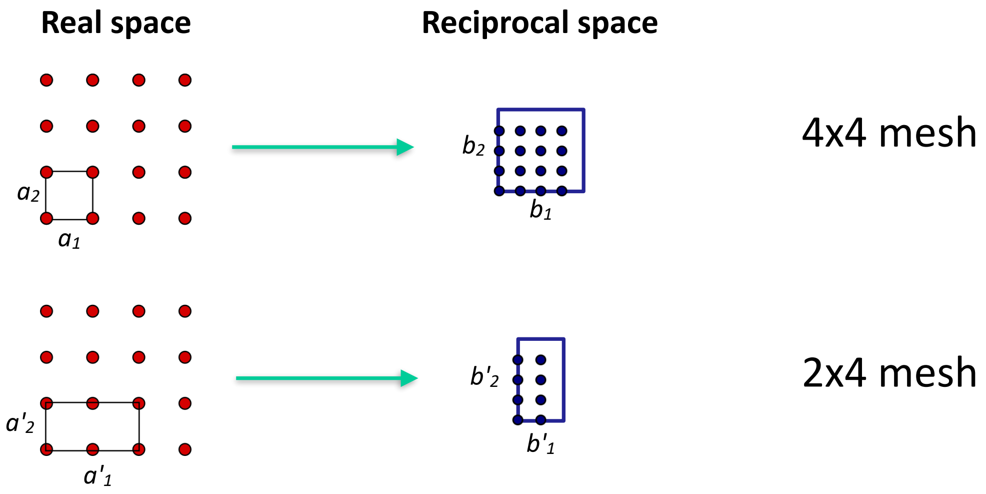
Monkhorst-Pack meshes

- Regular, equispaced meshes in the Brillouin Zone (can be generated automatically by Quantum ESPRESSO – “automatic” keyword)



Supercells and k-points sampling

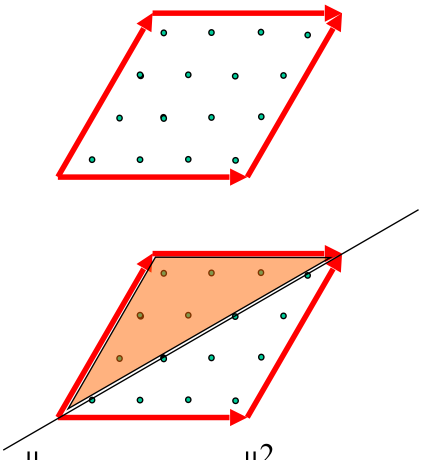
- You never have a "converged" k-points mesh
- If you make a supercell, to get the same exact total energy you need to adapt the k-points accordingly



Symmetry

- **Symmetry operations**: actions that transform an object into a new but undistinguishable configuration
- **Symmetry elements**: geometric entities (axes, planes, points…) around which we carry out the symmetry operations

Exploiting symmetry



$$\rho(\vec{r})=\sum_{n,\vec{k}}\left\|\Psi_{n,\vec{k}}\left(\vec{r}\right)\right\|^{2}$$

$$\Psi_{n,\vec{k}}\left(S^{-1}\vec{r}\right)=\Psi_{n,S\vec{k}}\left(\vec{r}\right)$$

$$\rho(\vec{r})=\sum_{n,\vec{k}}\left\|\Psi_{n,\vec{k}}\left(\vec{r}\right)\right\|^{2}=\sum_{n,S,\vec{k}_{irr}}\left\|\Psi_{n,S\vec{k}_{irr}}\left(\vec{r}\right)\right\|^{2}=$$

$$=\sum_{n,S,\vec{k}_{irr}}\left\|\Psi_{n,\vec{k}_{irr}}\left(S^{-1}\vec{r}\right)\right\|^{2}$$

Time-reversal symmetry

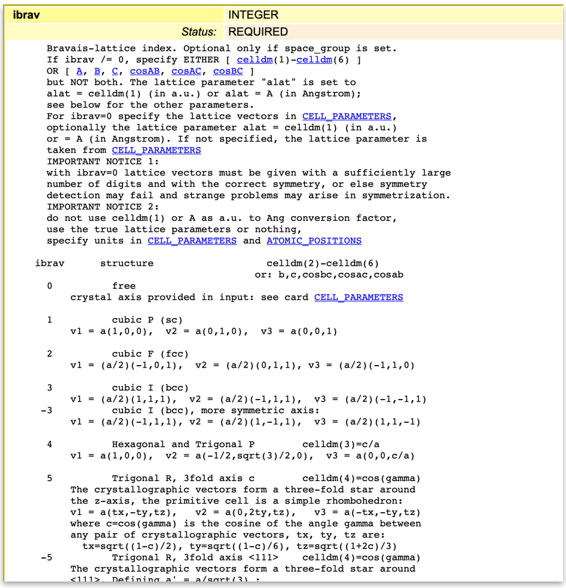
Periodic Hamiltonian for u_{nk}
(apply Bloch form $u_{nk}\, e^{ikr}$ to H)

$$\left[\frac{1}{2}\left(\frac{1}{i}\nabla+\mathbf{k}\right)^{2}+V(\mathbf{r})\right]u_{n\mathbf{k}}=\epsilon_{n\mathbf{k}}u_{n\mathbf{k}}$$

$$u_{nk}\left(\vec{r}\right)=u^{*}_{n\,-k}\left(\vec{r}\right)$$

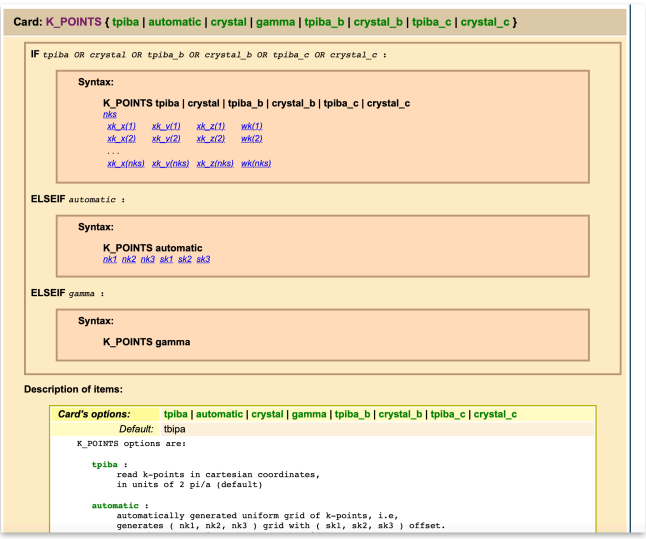
Bravais Lattices and k-points in INPUT_PW (Quantum ESPRESSO pw.x)

https://www.quantum-espresso.org/Doc/INPUT_PW.html



ibrav	INTEGER
Status:	REQUIRED

```
Bravais-lattice index. Optional only if space_group is set.
If ibrav /= 0, specify EITHER [ celldm(1)-celldm(6) ]
OR [ A, B, C, cosAB, cosAC, cosBC ]
but NOT both. The lattice parameter "alat" is set to
alat = celldm(1) (in a.u.) or alat = A (in Angstrom);
see below for the other parameters.
For ibrav=0 specify the lattice vectors in CELL_PARAMETERS,
optionally the lattice parameter alat = celldm(1) (in a.u.)
or = A (in Angstrom). If not specified, the lattice parameter is
taken from CELL_PARAMETERS
IMPORTANT NOTICE 1:
with ibrav=0 lattice vectors must be given with a sufficiently large
number of digits and with the correct symmetry, or else symmetry
detection may fail and strange problems may arise in symmetrization.
IMPORTANT NOTICE 2:
do not use celldm(1) or A as a.u. to Ang conversion factor,
use the true lattice parameters or nothing,
specify units in CELL_PARAMETERS and ATOMIC_POSITIONS

ibrav      structure                   celldm(2)-celldm(6)
                                     or: b,c,cosbc,cosac,cosab
  0          free
    crystal axis provided in input: see card CELL_PARAMETERS

  1          cubic P (sc)
    v1 = a(1,0,0),  v2 = a(0,1,0),  v3 = a(0,0,1)

  2          cubic F (fcc)
    v1 = (a/2)(-1,0,1),  v2 = (a/2)(0,1,1), v3 = (a/2)(-1,1,0)

  3          cubic I (bcc)
    v1 = (a/2)(1,1,1),  v2 = (a/2)(-1,1,1),  v3 = (a/2)(-1,-1,1)
 -3          cubic I (bcc), more symmetric axis:
    v1 = (a/2)(-1,1,1), v2 = (a/2)(1,-1,1),  v3 = (a/2)(1,1,-1)

  4          Hexagonal and Trigonal P        celldm(3)=c/a
    v1 = a(1,0,0),  v2 = a(-1/2,sqrt(3)/2,0),  v3 = a(0,0,c/a)

  5          Trigonal R, 3fold axis c        celldm(4)=cos(gamma)
    The crystallographic vectors form a three-fold star around
    the z-axis, the primitive cell is a simple rhombohedron:
    v1 = a(tx,-ty,tz),   v2 = a(0,2ty,tz),   v3 = a(-tx,-ty,tz)
    where c=cos(gamma) is the cosine of the angle gamma between
    any pair of crystallographic vectors, tx, ty, tz are:
      tx=sqrt((1-c)/2), ty=sqrt((1-c)/6), tz=sqrt((1+2c)/3)
 -5          Trigonal R, 3fold axis <111>    celldm(4)=cos(gamma)
    The crystallographic vectors form a three-fold star around
    <111>. Defining a' = a/sqrt(3) :
```



Card: K_POINTS { tpiba | automatic | crystal | gamma | tpiba_b | crystal_b | tpiba_c | crystal_c }

IF *tpiba OR crystal OR tpiba_b OR crystal_b OR tpiba_c OR crystal_c :*

Syntax:

K_POINTS tpiba | crystal | tpiba_b | crystal_b | tpiba_c | crystal_c

nks

xk_x(1) *xk_y(1)* *xk_z(1)* *wk(1)*

xk_x(2) *xk_y(2)* *xk_z(2)* *wk(2)*

. . .

xk_x(nks) *xk_y(nks)* *xk_z(nks)* *wk(nks)*

ELSEIF *automatic :*

Syntax:

K_POINTS automatic

nk1 *nk2* *nk3* *sk1* *sk2* *sk3*

ELSEIF *gamma :*

Syntax:

K_POINTS gamma

Description of items:

Card's options:	tpiba | automatic | crystal | gamma | tpiba_b | crystal_b | tpiba_c | crystal_c
Default:	tbipa

```
K_POINTS options are:

   tpiba :
        read k-points in cartesian coordinates,
        in units of 2 pi/a (default)

   automatic :
        automatically generated uniform grid of k-points, i.e,
        generates ( nk1, nk2, nk3 ) grid with ( sk1, sk2, sk3 ) offset.
```

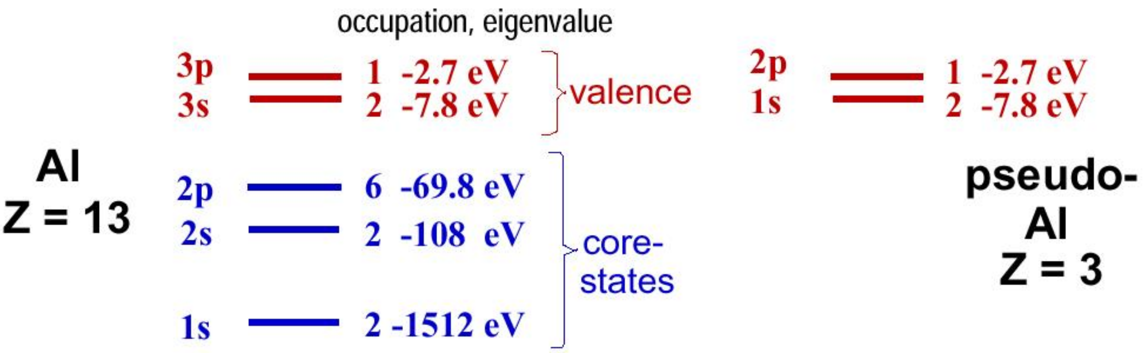
The plane-wave basis set: summary

- **Systematic improvement of completeness/resolution**
- Huge number of basis elements – only possible because of pseudopotentials (we will discuss later)
- Allows for easy evaluation of gradients and Laplacian
- Kinetic energy in reciprocal space, potential in real space (FFT - Fast Fourier Transforms - performed to move between reciprocal and real space)
- Basis set does not depend on atomic positions: there are no Pulay terms *in the forces*

Other possibilities - many

- Gaussian basis sets (Hartree-Fock codes)
- Real space representations
- LCAO
- LMTO, LAPW
- Wavelets
- …

Pseudopotentials

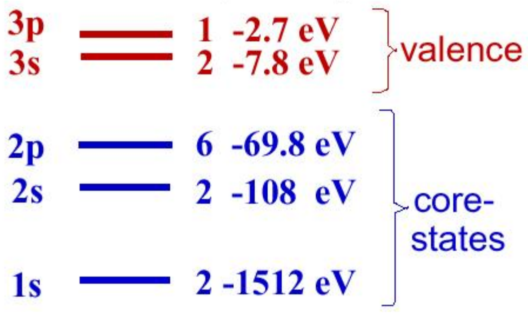


$$(-\frac{1}{2}\nabla^2 + v_{\text{eff}})\psi_j = \varepsilon_j \psi_j$$

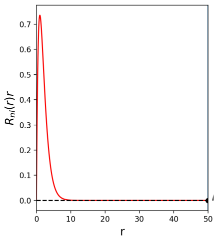
$$(-\frac{1}{2}\nabla^2 + v_{\text{eff}}^{(\text{ps})})\psi_j^{(\text{ps})} = \varepsilon_j \psi_j^{(\text{ps})}$$

From Eckhard Pehlke lecture notes – Fritz-Haber Institut
http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2001/pehlke1.pdf

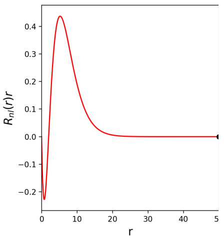
Pseudopotentials



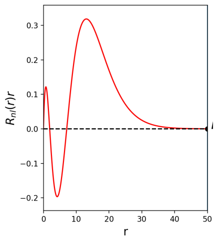
- Core states:
  - **Chemically inert**, I care only of valence states for chemical bonding (flat bands)
  - **Very large (in abs value) energy** => small % error gives large errors on the total energy of the system
  - **Very localised** => require a lot of plane waves to be represented



1s



2s

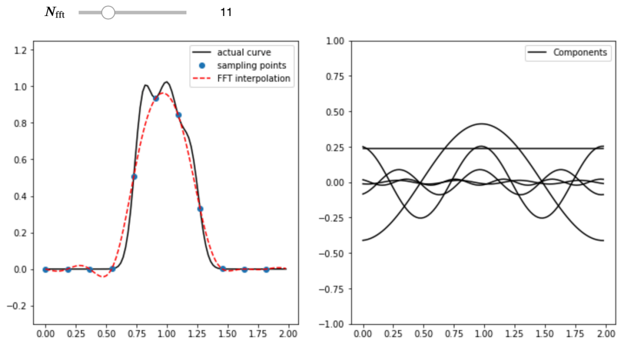


3s

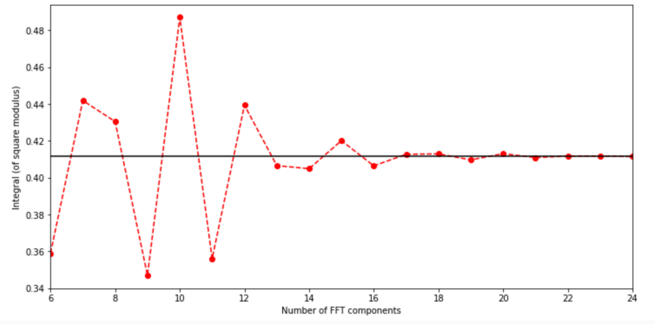
- Valence states:
  - need also large oscillations close the nucleus in order to be orthogonal to the core states

---

Convergence as a function of the number of G vectors (1D example)



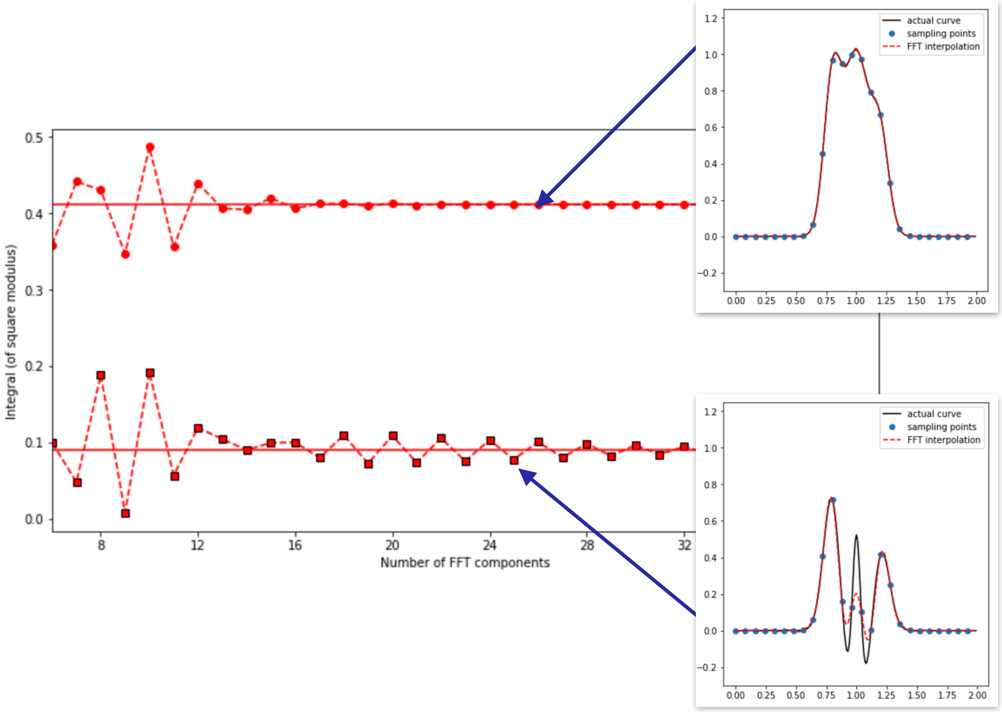
See OSSCAR notebook:
https://osscar-quantum-mechanics.materialscloud.io/voila/render/band-theory/FFT_and_planewaves.ipynb



Convergence of the norm of of the function vs. the number of plane waves (i.e., of G vectors) in the expansion

Convergence vs number of G vectors

(and computational cost)



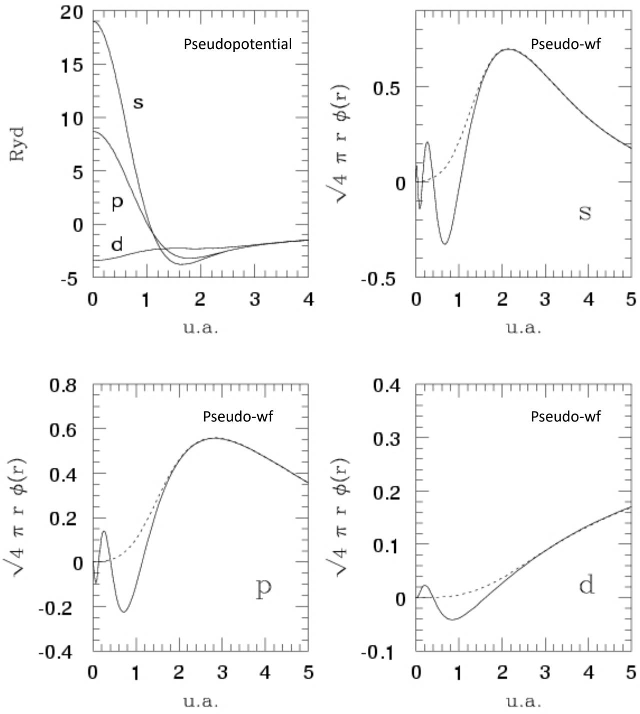
Norm-conserving pseudopotentials

- Real and pseudo valence **eigenvalues** agree for a chosen atomic configuration
- Real and pseudo **wavefunctions** agree beyond a core radius
- The **integral** of real and pseudo charge from 0 to a distance greater than core radius agree
- The **logarithmic derivatives** of the real and pseudo wavefunctions, and their first energy derivatives, agree for distances greater than the core radius
  - It means that the atom and the pseudo-atom have the same scattering properties (how they scatter plane waves into spherical waves)

Non-local, norm conserving

Different **angular momenta** scatter differently from the core (*states that have shells below them, with same angular momentum, are repelled more*)

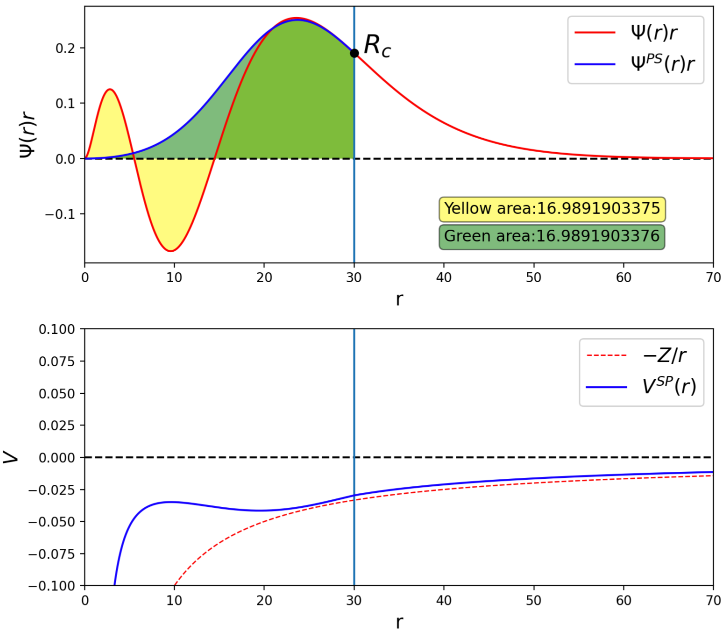
Non-local pseudopotential



Pseudopotentials

OSSCAR

https://osscar-quantum-mechanics.materialscloud.io/voila/render/index.ipynb



Wavefunction and charge density cutoffs

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

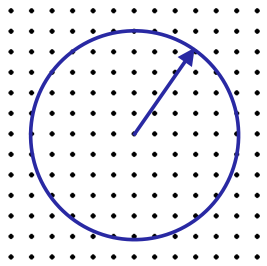
$$|\psi_{n\mathbf{k}}(\mathbf{r})|^2 = |u_{n\mathbf{k}}(\mathbf{r})|^2 = \sum_{\mathbf{G},\mathbf{G}'} c_{n\mathbf{k}}^{\mathbf{G}} c_{n\mathbf{k}}^{\mathbf{G}'} e^{i(\mathbf{G}+\mathbf{G}')\cdot\mathbf{r}}$$

Sphere for charge density: **twice the radius** of the sphere of the wavefunctions

$$E = \frac{\hbar G^2}{2m} \rightarrow$$

Double radius implies 4x energy cutoff

Given an energy cutoff for the wavefuntions (*ecutwfc*), you need 4x that cutoff for the charge density (*ecutrho*)

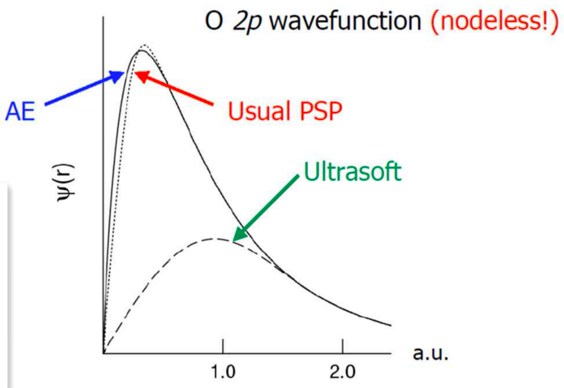


Note on ultrasoft pseudopotentials (USPP)

- Release norm conservation, to obtain **smoother pseudo wave functions**
- Split pseudo wave functions into two parts:
  (1) Ultrasoft valence wave function (not norm conserving) +
  (2) a core "augmentation charge"
- USPP are norm-conserving in a generalised sense:

$$\langle \psi_\alpha^{\mathrm{ps}} | 1 + \hat{N}_{nl}^{\mathrm{ps}} | \psi_\alpha^{\mathrm{ps}} \rangle = \langle \psi_\alpha^{\mathrm{ae}} | \psi_\alpha^{\mathrm{ae}} \rangle$$

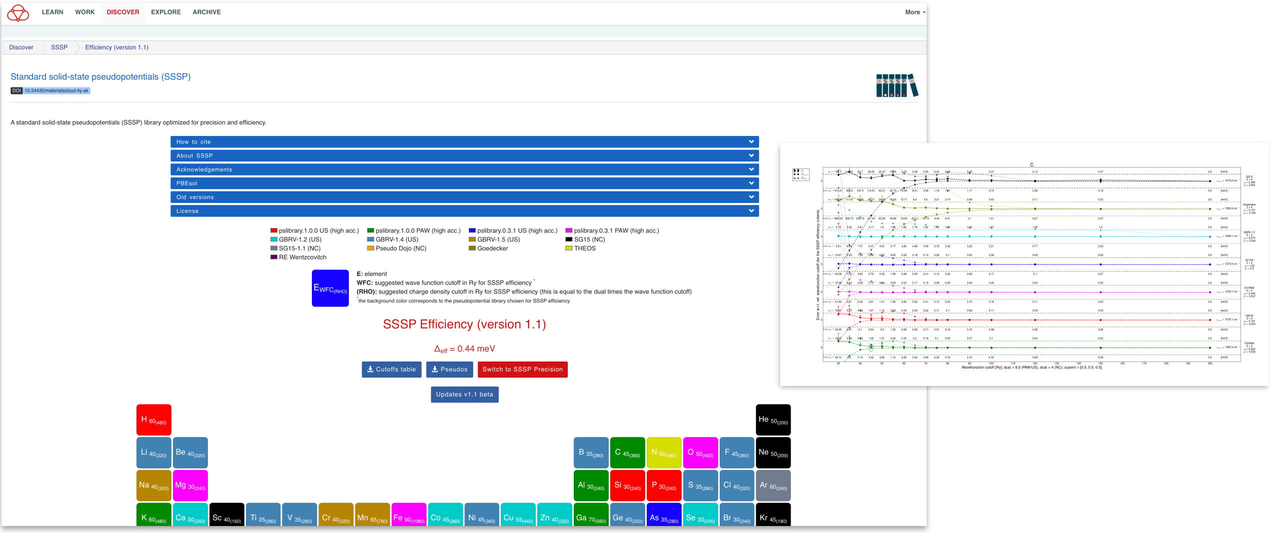
Note: the charge density is physical => its cutoff cannot be reduced; but we can reduce the cutoff for the wave functions



D. Vanderbilt, Phys. Rev. B 41, 7892 (1990)
www.physics.rutgers.edu/~dhv/talks/bangalore-july06.pdf

SSSP: a library of pseudopotentials with convergence tests (for the cutoffs)

https://www.materialscloud.org/sssp/



Standard solid-state pseudopotentials (SSSP)

DOI 10.24435/materialscloud:4y-ak

A standard solid-state pseudopotentials (SSSP) library optimized for precision and efficiency.

🟥 pslibrary.1.0.0 US (high acc.)	🟩 pslibrary.1.0.0 PAW (high acc.)	🟦 pslibrary.0.3.1 US (high acc.)	🟪 pslibrary.0.3.1 PAW (high acc.)
■ GBRV-1.2 (US)	■ GBRV-1.4 (US)	■ GBRV-1.5 (US)	■ SG15 (NC)
■ SG15-1.1 (NC)	🟧 Pseudo Dojo (NC)	■ Goedecker	🟨 THEOS
■ RE Wentzcovitch			

$E_{WFC(RHO)}$

E: element
WFC: suggested wave function cutoff in Ry for SSSP efficiency *
(RHO): suggested charge density cutoff in Ry for SSSP efficiency (this is equal to the dual times the wave function cutoff)
*the background color corresponds to the pseudopotential library chosen for SSSP efficiency

SSSP Efficiency (version 1.1)

Δ_{eff} = 0.44 meV

H $60_{(480)}$ | He $50_{(200)}$
Li $40_{(320)}$ | Be $40_{(320)}$ | B $35_{(280)}$ | C $45_{(360)}$ | N $60_{(480)}$ | O $50_{(400)}$ | F $45_{(360)}$ | Ne $50_{(200)}$
Na $40_{(320)}$ | Mg $30_{(240)}$ | Al $30_{(240)}$ | Si $30_{(240)}$ | P $30_{(240)}$ | S $35_{(280)}$ | Cl $40_{(320)}$ | Ar $60_{(240)}$
K $60_{(480)}$ | Ca $30_{(240)}$ | Sc $40_{(160)}$ | Ti $35_{(280)}$ | V $35_{(280)}$ | Cr $40_{(320)}$ | Mn $65_{(780)}$ | Fe $90_{(1080)}$ | Co $45_{(360)}$ | Ni $45_{(360)}$ | Cu $55_{(440)}$ | Zn $40_{(320)}$ | Ga $70_{(560)}$ | Ge $40_{(320)}$ | As $35_{(280)}$ | Se $30_{(240)}$ | Br $30_{(240)}$ | Kr $45_{(180)}$