First principles calculations within DFT
some practical concerns

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Outline

Kohn-Sham Equation for crystals

Schrödinger Equation $\Rightarrow$ Eigen problem

$$\sum_m \left[\frac{\hbar^2 |\mathbf{k} + \mathbf{G}_m|^2}{2m_e} \delta_{m,m'} + v_{m-m'} \right] c_{i,m} = \epsilon_i c_{i,m'}$$

Matrix equation
(here we have omitted the constants h and m)

$$
\begin{bmatrix}
\frac{1}{2}(k)^2 & V_{eff}(G_1) & V_{eff}(G_2) & V_{eff}(G_3) & \dots \\
V_{eff}(G_1) & \frac{1}{2}(k+G_1)^2 & V_{eff}(G_2-G_1) & V_{eff}(G_3-G_2) & \dots \\
V_{eff}(G_2) & V_{eff}(G_2-G_1) & \frac{1}{2}(k+G_2)^2 & V_{eff}(G_3-G_2) & \dots \\
V_{eff}(G_3) & V_{eff}(G_3-G_1) & V_{eff}(G_3-G_2) & \frac{1}{2}(k+G_3)^2 & \dots \\
\dots & \dots & \dots & \dots &
\end{bmatrix}
\begin{bmatrix}
C_0 \\ C_1 \\ C_2 \\ C_3 \\ \\
\end{bmatrix}
= \mathcal{E}
\begin{bmatrix}
C_0 \\ C_1 \\ C_2 \\ C_3 \\ \\
\end{bmatrix}
$$

Brillouin zone integration

Properties like the electron density, total energy, etc., can be evaluated by integration over the first Brillouin zone.

Electron density

$$n(\mathbf{r}) = \frac{1}{\Omega_{FBZ}} \sum_i^{occ.} \int_{FBZ} n_{i,\mathbf{k}}(\mathbf{r}) d\mathbf{k}, \qquad n_{i,\mathbf{k}}(\mathbf{r}) = |\psi_{i,\mathbf{k}}(\mathbf{r})|^2$$

$$= \frac{1}{\Omega_{FBZ}} \sum_i \int_{FBZ} f_{i,\mathbf{k}} \cdot n_{i,\mathbf{k}}(\mathbf{r}) d\mathbf{k}$$

$$= \frac{1}{N_k} \sum_\mathbf{k} \sum_i f_{i,\mathbf{k}} \cdot n_{i,\mathbf{k}}(\mathbf{r})$$
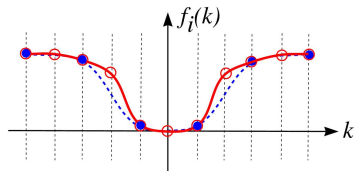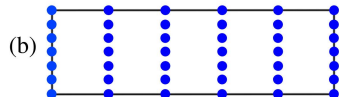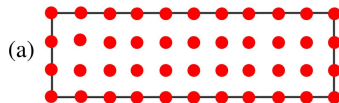
k-point sampling: uniform vs non-uniform

Moreno and Soler (Phys. Rev. B **45**(24):13891, 1992):
A mesh with uniformly distributed k-points is preferred.

(a)

Example: A rectangular lattice
 (a) isotropic sampling
 (b) finer sampling vertically
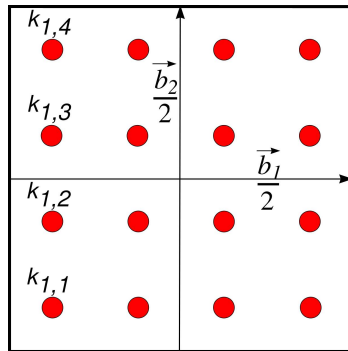   poor sampling horizontally

(b)

Monkhorst-Pack scheme

Monkhorst & Pack (Phys. Rev. B **13**:5188, 1976.):

$$\mathbf{k} = \sum_{i=1}^{3} \frac{2n_i - N_i - 1}{2N_i} \mathbf{b}_i, \quad n_i = 1, \cdots, N_i$$
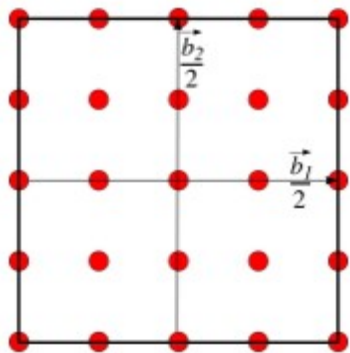
Example: $4 \times 4 \times 1$ MP mesh for 2D square lattice

$$k_{1,1} = \left(-\frac{3}{8}, -\frac{3}{8}\right) \qquad k_{1,3} = \left(-\frac{3}{8}, \frac{1}{8}\right)$$

$$k_{1,2} = \left(-\frac{3}{8}, -\frac{1}{8}\right) \qquad k_{1,4} = \left(-\frac{3}{8}, \frac{3}{8}\right)$$
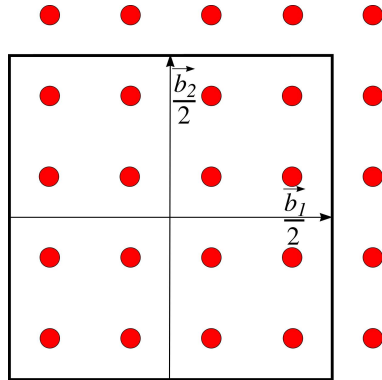
Shifted Monkhorst-Pack mesh

Centered on Γ

25 *k*-points

Centered around Γ

Shifted by $(1/8, 1/8, 0)$
16 *k*-points

Yet the same *k*-point density.

Symmetry on **k** in the first Brillouin zone

$$\psi_{\mathbf{k+G}} = \psi_{\mathbf{k}} \Rightarrow \text{Limit } \mathbf{k} \text{ in FBZ.}$$

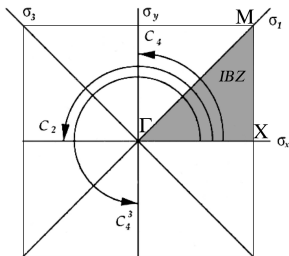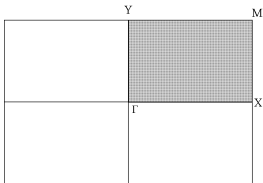$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{kr}} = \epsilon u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{kr}}$$

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) \right] u_{\mathbf{k}}^*(\mathbf{r}) e^{-i\mathbf{kr}} = \epsilon u_{\mathbf{k}}^*(\mathbf{r}) e^{-i\mathbf{kr}} \qquad \text{Congugate}$$

$$\left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) \right] u_{-\mathbf{k}}^*(\mathbf{r}) e^{i\mathbf{kr}} = \epsilon u_{-\mathbf{k}}^*(\mathbf{r}) e^{i\mathbf{kr}} \qquad \text{replace } \mathbf{k} \text{ by } \mathbf{-k}$$

$$u_{-\mathbf{k}}^* = u_{\mathbf{k}} \Rightarrow u_{-\mathbf{k}} = u_{\mathbf{k}}^*$$

$$\psi_{-\mathbf{k}} = u_{-\mathbf{k}} e^{-i\mathbf{kr}} = \left(u_{\mathbf{k}} e^{i\mathbf{kr}} \right)^* = \psi_{\mathbf{k}}^*$$

$$\epsilon_{-\mathbf{k}} = \epsilon_{\mathbf{k}}$$

$$\hat{S}\psi_{i\mathbf{k}}(\mathbf{r}) = \psi_{i\mathbf{k}}(\hat{S}\mathbf{r})$$

$$= u_{i\mathbf{k}}(\hat{S}\mathbf{r})e^{i\check{S}\mathbf{k}\cdot\hat{S}\mathbf{r}}$$

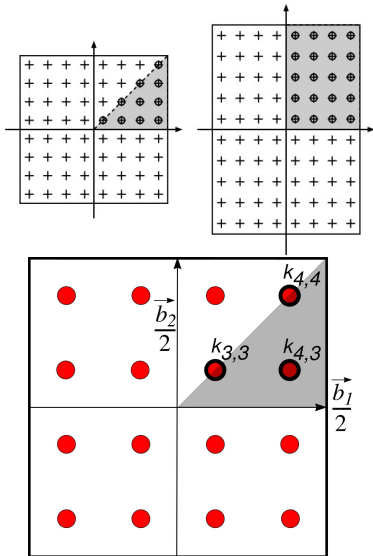$$= u_{i\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}'\mathbf{r}}$$

$\psi_k(r)$ is a solution at $k \Longrightarrow \psi(\hat{S}r)$ is a solution at $\check{S}k$, with same energy/density.

$$n(\mathbf{r}) = \sum_{\mathbf{k}} \omega_{\mathbf{k}} \sum_i f_{i,\mathbf{k}} \cdot n_{i,\mathbf{k}}(\mathbf{r})$$

$k \in$ irreducible Brillouin zone

$$\omega_k = \frac{\text{\# of sym. connected } k}{\text{total \# of } k \text{ in FBZ}}$$

$$\hat{S}\psi_{i\mathbf{k}}(\mathbf{r}) = \psi_{i\mathbf{k}}(\hat{S}\mathbf{r})$$

Irreducible Brillouin zone

Example:

MP-mesh for 2D square lattice

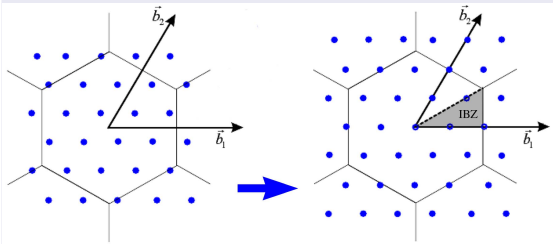$4 \times 4 \times 1$ MP mesh = 16 k-points in the FBZ.

- 4 equivalent $k_{4,4} = \left(\frac{3}{8}, \frac{3}{8}\right) \Rightarrow w_1 = 0.25$
- 4 equivalent $k_{3,3} = \left(\frac{1}{8}, \frac{3}{8}\right) \Rightarrow w_2 = 0.25$
- 8 equivalent $k_{4,3} = \left(\frac{3}{8}, \frac{1}{8}\right) \Rightarrow w_3 = 0.50$

Brillouin zone integration

$$n(r) = \frac{1}{4} \sum_{i}^{occ.} n_{i,k_{4,4}} + \frac{1}{4} \sum_{i}^{occ.} n_{i,k_{3,3}} + \frac{1}{2} \sum_{i}^{occ.} n_{i,k_{4,3}}$$

Irreducible Brillouin zone

Symmetry break: Hexagonal cell

Even meshes break the symmetry, while meshes centered on Γ preserves it. Shift the k-point mesh to preserve hexagonal symmetry!

k-sampling: rules of thumb

- Keep density of k constant in each direction: $\frac{\mathbf{b}_i}{N_i} = const.$
- Denser $k \Rightarrow$ more precise results.
- N_k^{IBZ} does not necessarily scale with N. Symmetry matters
- No k sampling needed for atoms or molecules!
- Generally need to do convergence test!

Smearing method: fractional occupation numbers

Fermi level ϵ_F: the energy of the highest occupied band.

Insulator   Metal   Semiconductor
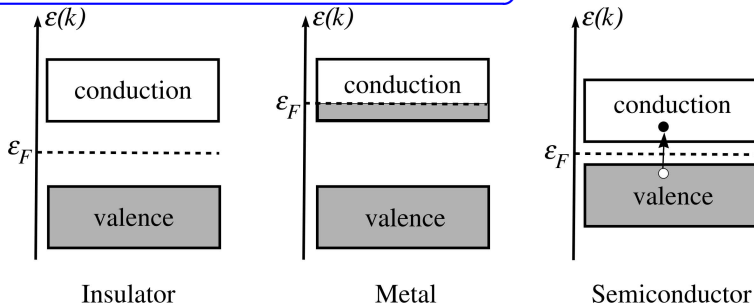
IBZ integration over the filled states: Occupation number

$$f_{i,\mathbf{k}} = \Theta(\epsilon_{i\mathbf{k}} - \epsilon_F), \qquad \Theta(x) = \begin{cases} 1 & x \leq 0 \\ 0 & x > 0 \end{cases}$$

For insulators and semiconductors, DOS goes to zero smoothly at the gap.
For metals, the resolution of the step function at ϵ_F is very sensitive.

Trick is to replace sharp step function with a smoother function allowing partial occupancies at the Fermi level.

- Fermi-Dirac smearing

$$f_{i\mathbf{k}} = \frac{1}{1 + \exp(x)}, \qquad x = \frac{\epsilon_{i\mathbf{k}} - \epsilon_F}{\sigma}, \qquad \sigma = k_B T$$

- Gaussian smearing

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \mathrm{d}t$$

$$f_{i\mathbf{k}} = \frac{1}{2}[1 - \mathrm{erf}(x)], \qquad \sigma \text{ has no physical meaning.}$$

- Methfessel-Paxton smearing

$$\delta(x) \simeq D_N(x) = \sum_n^N A_n H_{2n} e^{-x^2}; \qquad f_{i\mathbf{k}} \simeq S_N = 1 - \int_{-\infty}^x D_N(\tau) d\tau$$

Cutoff: finite basis set

Computationally, a complete expansion in terms of infinitely many plane waves is not possible. The coefficients, $c_{i,m}(\mathbf{k})$ decrease rapidly with increasing PW kinetic energy $\frac{\hbar^2|\mathbf{k}+\mathbf{G}_m|^2}{2m}$.

A cutoff energy value, E_{cut}, determines the number of PWs (N_{pw}) in the expansion, satisfying,
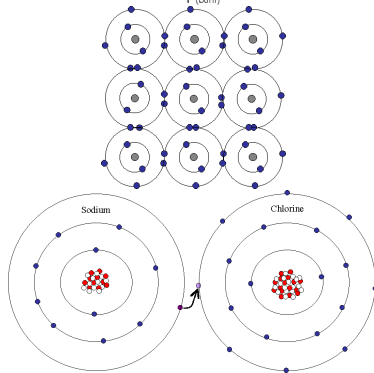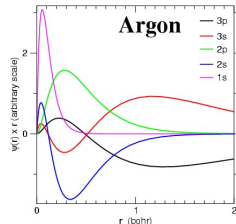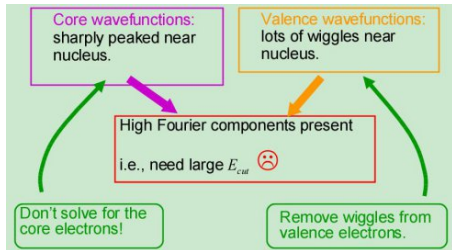
$$\frac{\hbar^2|\mathbf{k}+\mathbf{G}_m|^2}{2m} < E_{\text{cut}}$$

N_{pw} is a discontinuous function of the PW kinetic energy cutoff, while depends only on the computational cell size and the cutoff energy value.
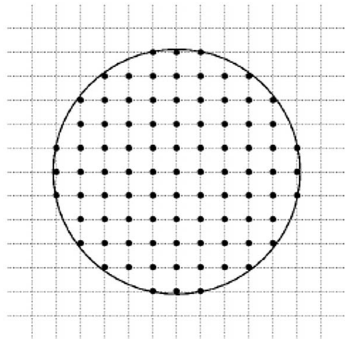
Pseudopotential: why?

- Reduction of basis set size
  effective speedup of calculation
- Reduction of number of electrons
  reduces the number of *d.o.f.*
- Unnecessary
  Why bother? They are inert anyway···
- Inclusion of relativistic effects
 relativistic effects can be included partially


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.

Pseudopotential (PP)

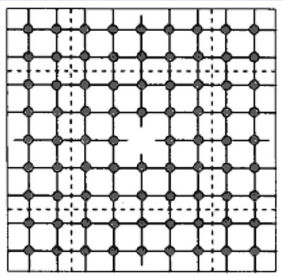A smooth effective potential that reproduces the effect of the nucleus plus core electrons on valence electrons.

Pseudopotential
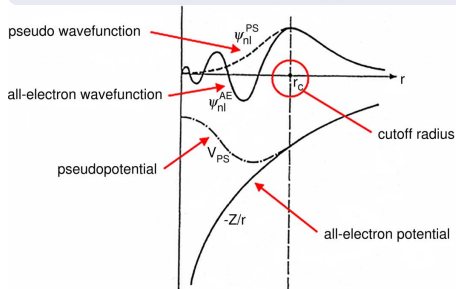
- Norm conserving PP;
- Ultrasoft PP;
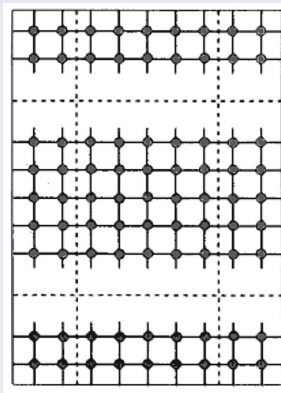- Projector Augmented Wave PP;
- · · ·
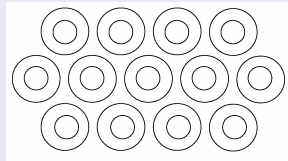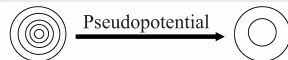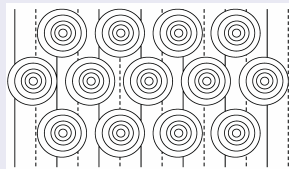
Born-von Karman PBC: always a necessity?
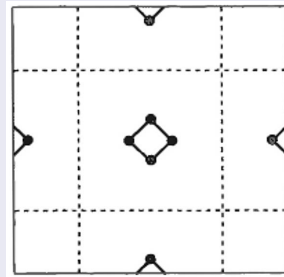
Supercell approach

point defect   free surface   single molecule

Supercell must be sufficiently large to maintain isolation.

DFT: Ability and disability

Fundamentally, DFT can only predict the ground state electronic density and the ground state total energy of a set of electrons under an external potential.

DFT can predict	DFT cannot predict
• Total energy	• Excited state energies
• Forces	• Band gap
• Lattice constants	• Band structures
• Bond lengths	• Wave functions
• Vibrational frequencies	• Fermi surface
• Phonon frequencies	• Superconductivity
• Electron density	• Excitons
• Static dielectric response	• Electronic transport

Accuracy

## Accuracies can be expected

bond length	$\sim 3\%$ too small
bulk modulus	$\sim 10\%$ too high
phonon frequency	$\sim 10\%$ too high
energy difference	> 1 mHartree
cohesive energy	very poor (much too high)

Accuracies for properties that DFT technically does not predict

band gap	50% too small
band structure	qualitatively reasonable
fermi surface	qualitatively reasonable

Influencing factors

- Born-Oppenheimer approximation;
- Density functional theory
  - LDA, GGA
  - LSDA
- Pseudopotential
- Kinetic energy cutoff
- k-sampling
- convergence criterion
- $\cdots$
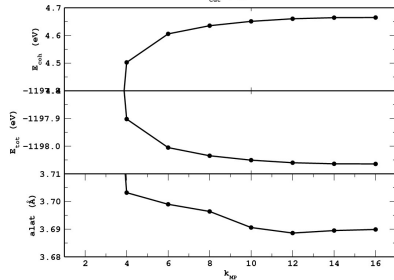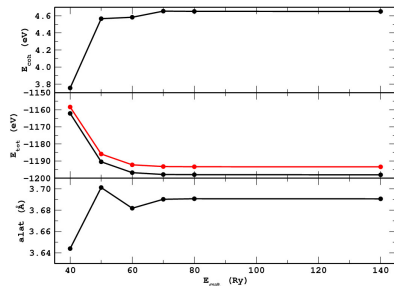
References and further readings

1. http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2001/pehlke1.pdf
2. http://itp.tugraz.at/LV/ewald/TFKP/Literatur_Pseudopotentiale/Roundy_05_DFT+PPsumm.pdf
3. http://www.phys.sinica.edu.tw/TIGP-NANO/Course/2007_Spring/Class%20Notes/CMS.20070531.pseudo.pdf
4. J. Singleton, *Band theory and electronic properties of solids*, Oxford University press.
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