

First principles calculations within DFT

some practical concerns

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Nov 16, 2022



Outline

- 1 k -sampling
- 2 Plane wave cutoff
- 3 Pseudo-potential
- 4 Born-von Karman PBC: look back
- 5 Summary: PP+PW within DFT
- 6 Further readings

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 \hbar and m)

$$\begin{bmatrix} \frac{1}{2} (\mathbf{k})^2 & V_{\text{eff}}(\mathbf{G}_1) & V_{\text{eff}}(\mathbf{G}_2) & V_{\text{eff}}(\mathbf{G}_3) & \dots \\ V_{\text{eff}}(\mathbf{G}_1) & \frac{1}{2} (\mathbf{k} + \mathbf{G}_1)^2 & V_{\text{eff}}(\mathbf{G}_2 - \mathbf{G}_1) & V_{\text{eff}}(\mathbf{G}_3 - \mathbf{G}_2) & \dots \\ V_{\text{eff}}(\mathbf{G}_2) & V_{\text{eff}}(\mathbf{G}_2 - \mathbf{G}_1) & \frac{1}{2} (\mathbf{k} + \mathbf{G}_2)^2 & V_{\text{eff}}(\mathbf{G}_3 - \mathbf{G}_2) & \dots \\ V_{\text{eff}}(\mathbf{G}_3) & V_{\text{eff}}(\mathbf{G}_3 - \mathbf{G}_1) & V_{\text{eff}}(\mathbf{G}_3 - \mathbf{G}_2) & \frac{1}{2} (\mathbf{k} + \mathbf{G}_3)^2 & \dots \\ \dots & \dots & \dots & \dots & \dots \end{bmatrix} \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \\ \dots \end{bmatrix} = \epsilon \begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ C_3 \\ \dots \end{bmatrix}$$

Brillouin zone integration

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

Electron density

$$\begin{aligned}n(\mathbf{r}) &= \frac{1}{\Omega_{FBZ}} \sum_i^{\text{occ.}} \int_{FBZ} n_{i,\mathbf{k}}(\mathbf{r}) d\mathbf{k}, & n_{i,\mathbf{k}}(\mathbf{r}) &= |\psi_{i,\mathbf{k}}(\mathbf{r})|^2 \\&= \frac{1}{\Omega_{FBZ}} \sum_i \int_{FBZ} f_{i,\mathbf{k}} \cdot n_{i,\mathbf{k}}(\mathbf{r}) d\mathbf{k} \\&= \frac{1}{N_k} \sum_{\mathbf{k}} \sum_i f_{i,\mathbf{k}} \cdot n_{i,\mathbf{k}}(\mathbf{r})\end{aligned}$$

k-point sampling: uniform vs non-uniform

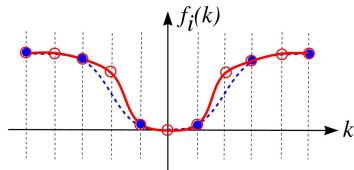
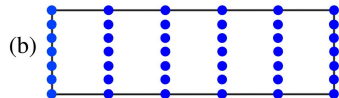
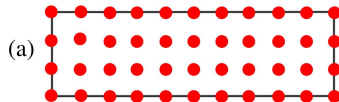
Moreno and Soler (Phys. Rev. B **45**(24):13891, 1992):

A mesh with **uniformly** distributed k-points is **preferred**.

Example: A rectangular lattice

(a) isotropic sampling

(b) finer sampling vertically
poor sampling horizontally



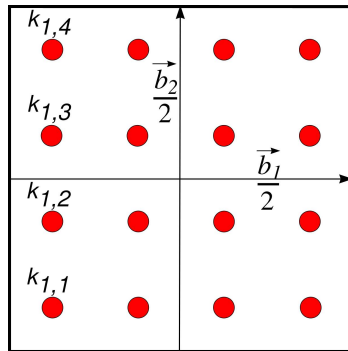
Monkhorst-Pack scheme

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

$$\mathbf{k} = \sum_{i=1}^3 \frac{2n_i - N_i + 1}{2N_i} \mathbf{b}_i, \quad n_i = 1, \dots, N_i$$

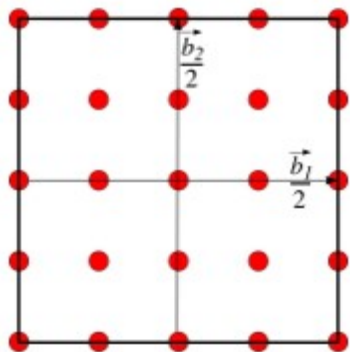
Example: $4 \times 4 \times 1$ MP mesh for 2D square lattice

$$\begin{aligned} k_{1,1} &= \left(-\frac{3}{8}, -\frac{3}{8}\right) & k_{1,3} &= \left(-\frac{3}{8}, \frac{1}{8}\right) \\ k_{1,2} &= \left(-\frac{3}{8}, -\frac{1}{8}\right) & k_{1,4} &= \left(-\frac{3}{8}, \frac{3}{8}\right) \end{aligned}$$



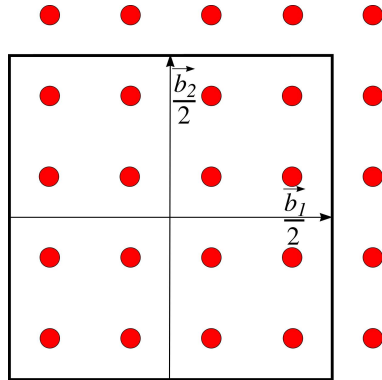
Shifted Monkhorst-Pack mesh

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 \mathbf{k} in the first Brillouin zone

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

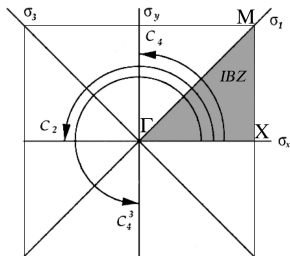
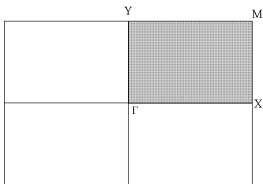
$$\begin{aligned} \left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} &= \epsilon u_{\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\mathbf{r}} \\ \left[-\frac{\hbar^2}{2m_e} \nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] u_{\mathbf{k}}^*(\mathbf{r})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

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

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

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

Symmetry on \mathbf{k} in the first Brillouin zone



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

$$\begin{aligned}\hat{S}\psi_{i\mathbf{k}}(\mathbf{r}) &= \psi_{i\mathbf{k}}(\hat{S}\mathbf{r}) \\ &= u_{i\mathbf{k}}(\hat{S}\mathbf{r})e^{i\check{\mathbf{S}}\mathbf{k}\cdot\hat{S}\mathbf{r}} \\ &= u_{i\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}'\cdot\mathbf{r}}\end{aligned}$$

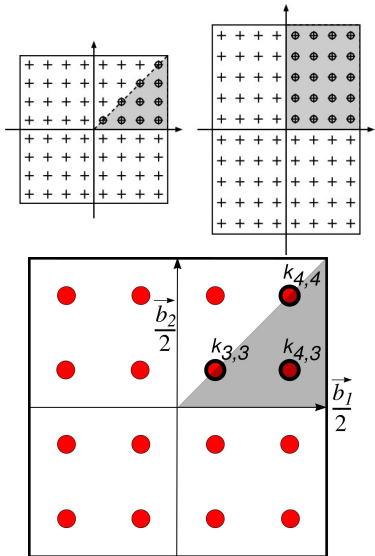
$\psi_{i\mathbf{k}}(\mathbf{r})$ is a solution at $\mathbf{k} \implies \psi_{i\hat{S}\mathbf{k}}(\mathbf{r})$ is a solution at $\hat{S}\mathbf{k}$, with same energy/density.

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

$\mathbf{k} \in$ irreducible Brillouin zone

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

Irreducible Brillouin zone



Example:

MP-mesh for 2D square lattice

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

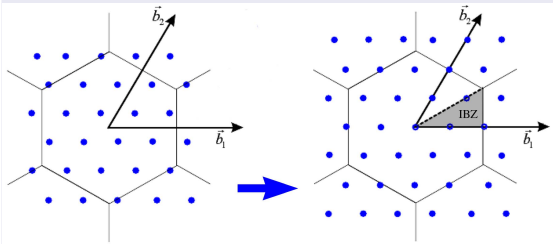
- 4 equivalent $k_{4,4} = (\frac{3}{8}, \frac{3}{8}) \Rightarrow w_1 = 0.25$
- 4 equivalent $k_{3,3} = (\frac{1}{8}, \frac{3}{8}) \Rightarrow w_2 = 0.25$
- 8 equivalent $k_{4,3} = (\frac{3}{8}, \frac{1}{8}) \Rightarrow w_3 = 0.50$

Brillouin zone integration

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

Irreducible Brillouin zone

Symmetry break: Hexagonal cell



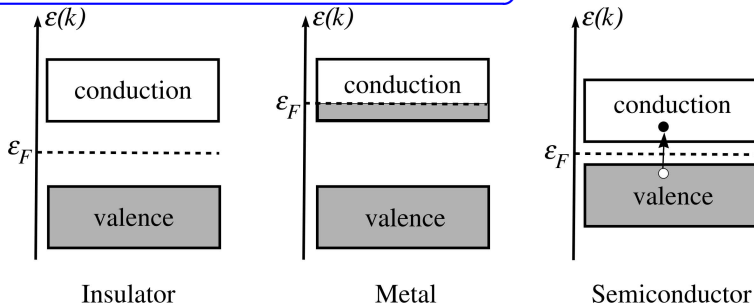
Even meshes break the symmetry, while meshes centered on Γ preserves it. Shift the k -point mesh to preserve hexagonal symmetry!

k -sampling: rules of thumb

- Keep density of k constant in each direction: $\frac{b_i}{N_i} = \text{const.}$
- 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.



IBZ integration over the filled states: Occupation number

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

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.

Smearing method: fractional occupation numbers

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

- Fermi-Dirac smearing

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

- Gaussian smearing

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

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

- Methfessel-Paxton smearing

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

Cutoff: finite basis set

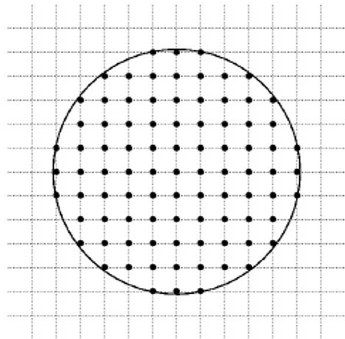
Computationally, a complete expansion in terms of infinitely many plane waves is not possible.

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,

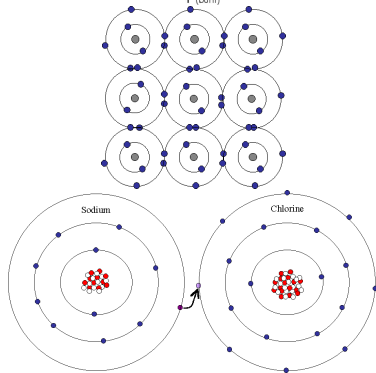
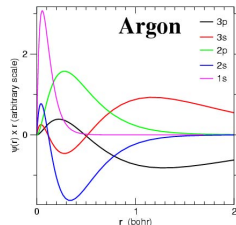
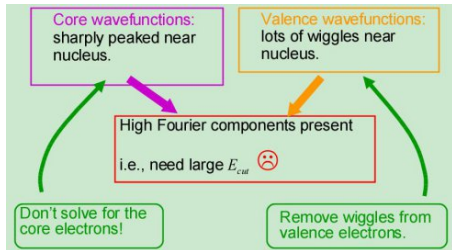
$$\frac{\hbar^2 |\mathbf{k} + \mathbf{G}_m|^2}{2m} < E_{\text{cut}}$$

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?

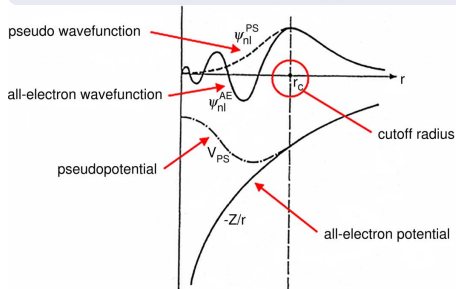
- Reduction of basis set size
effective speedup of calculation
- Reduction of number of electrons
reduces the number of *d.o.f.*
- Unnecessary
Why bother? They are inert anyway...
- Inclusion of relativistic effects
relativistic effects can be included partially



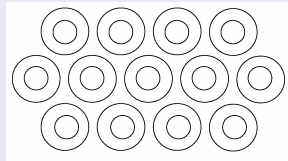
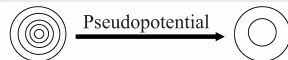
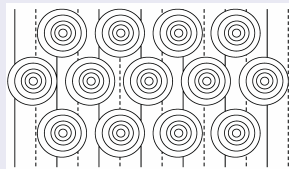
Pseudopotential: how?

Pseudopotential (PP)

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

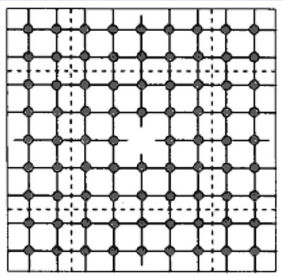


- Norm conserving PP;
- Ultrasoft PP;
- Projector Augmented Wave PP;
- ...

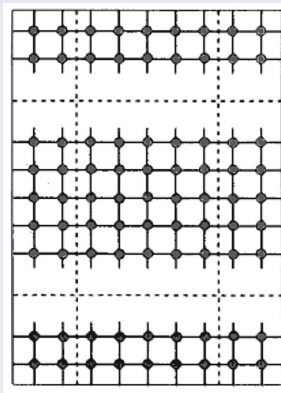


Born-von Karman PBC: always a necessity?

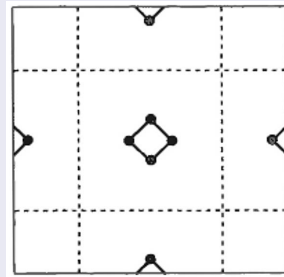
Supercell approach



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

- Total energy
- Forces
- Lattice constants
- Bond lengths
- Vibrational frequencies
- Phonon frequencies
- Electron density
- Static dielectric response

DFT cannot predict

- Excited state energies
- Band gap
- Band structures
- Wave functions
- Fermi surface
- Superconductivity
- Excitons
- Electronic transport

Accuracy

Accuracies can be expected

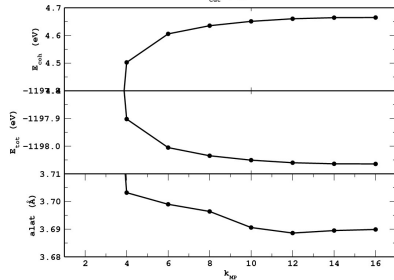
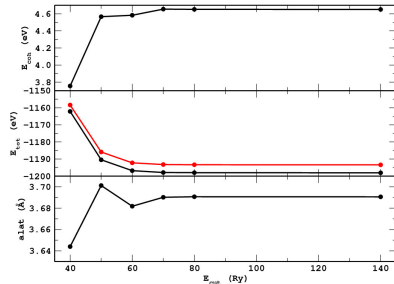
bond length	$\sim 3\%$ too small
bulk modulus	$\sim 10\%$ too high
phonon frequency	$\sim 10\%$ too high
energy difference	> 1 mHartree
cohesive energy	very poor (much too high)

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
- ...



References and further readings

- ① <http://www.fhi-berlin.mpg.de/th/Meetings/FHlmd2001/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.
- ⑤ <http://cms.mpi.univie.ac.at/vasp/>
- ⑥ <http://www.quantum-espresso.org/>
- ⑦ <http://www.abinit.org/>
- ⑧ <http://www.cpmd.org/>
- ⑨ <http://www.icmab.es/siesta/>
- ⑩ <http://abacus.ustc.edu.cn/index.html>