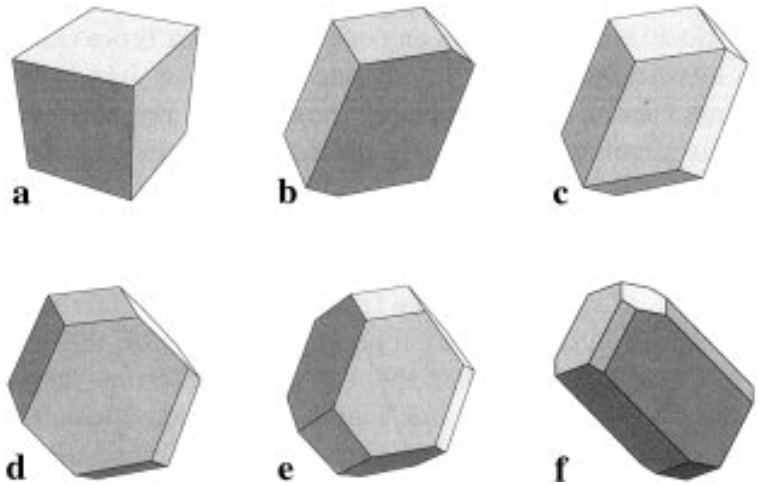
Introduction to Computational Quantum Chemistry

Lesson 12: Periodic calculations

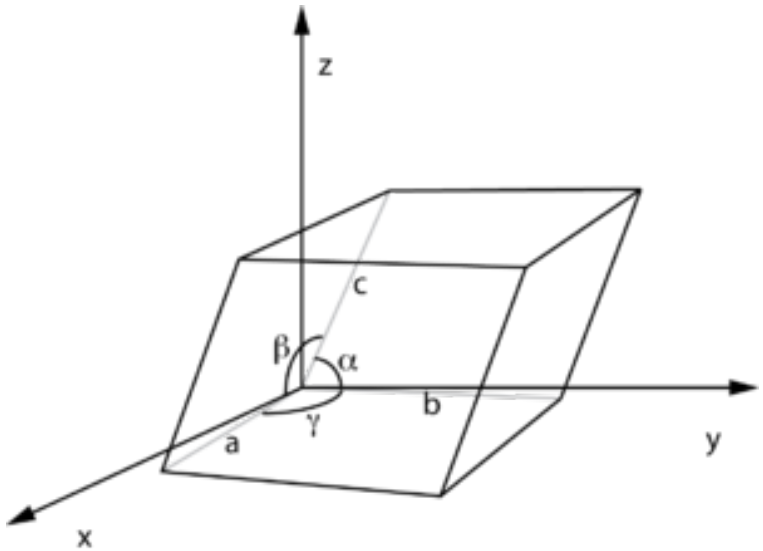
Periodic systems

- “1D”-3D objects
- Closely connected to crystals
- Periodic systems (explicit-solvent MD)
- Boundary conditions:
  - System is enclosed in an object which upon replication fills the whole space
  - Commonly used space-filling objects:



Input structure

- Structure of the molecule
- Information about the periodic box
- In crystallography usually you get:
  - 3 crystallographic axes: a, b, c
  - 3 principal angles: α, β, γ
- These define the translational operations in three directions
- For planar or chain systems you do not need 3 vectors



Wigner-Seitz cell and Brillouin zone

- W-S cell is a real-world object which contains unique information about the system
- Brillouin zone has the same property, however it is defined in a reciprocal space
- Wigner-Seitz cell has dimension units in Å, Brillouin zone in $Å^{-1}$

Plane wave basis functions

- The periodicity of the system must be satisfied
- Either we can replicate STOs/GTOs
- Define a new type of basis functions: Plane waves

$$\phi(x) = Ae^{ikx} + Be^{-ikx} \tag{1}$$

$$\phi(x) = Acos(kx) + Bsin(kx) \tag{2}$$

$$E = \frac{1}{2}k^2 \tag{3}$$

Plane wave basis functions II

$$\chi_k(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \tag{4}$$

- where **k** is similar to the exponent of the GTO
- **k** values must satisfy:

$$\mathbf{k} \cdot \mathbf{t} = 2\pi m \tag{5}$$

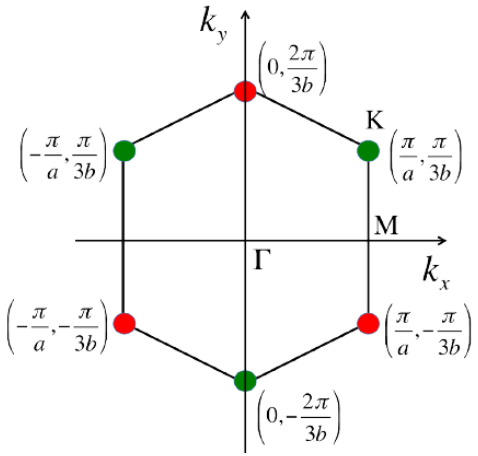
- **t** is the translational vector of the system
- m is a positive integer
- Typical spacing between **k** vectors is 0.01 eV
- Size of basis set is defined with a threshold (200 eV)
- Use of pseudopotentials for core regions is mandatory

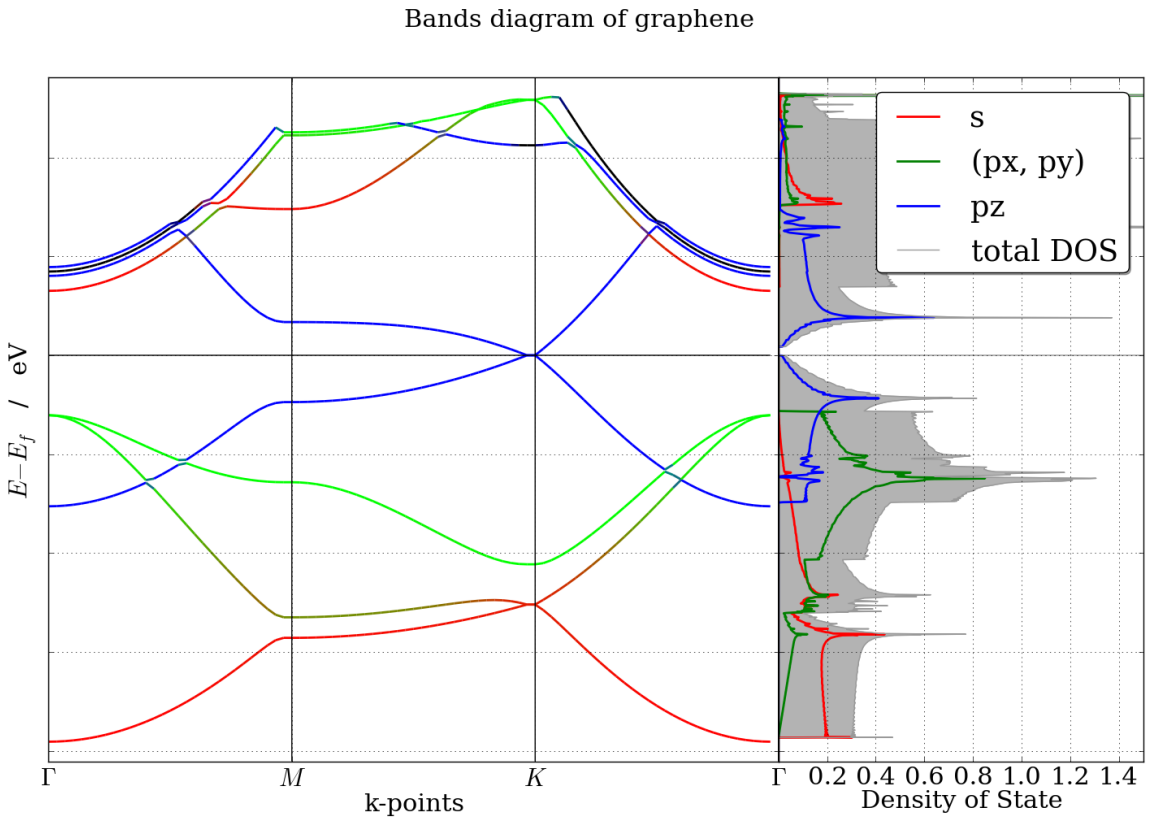
Bands

- As in molecules, the electrons are filled into the bands
- Each band is represented by a function in k-space
- HOMO is called the Fermi level
- 3 different states occur:
  - Insulator: large band gap
  - Semimetal: small band gap
  - Metal: no band gap
- Insulators and semimetals can be viewed as closed-shell systems
- Metals as open-shell (fractional occupations of bands)

Band Diagram and Density Of States

- Band diagram shows the evolution of bands along key-symmetry paths
- DOS shows how are the levels in the crystal populated





Visualization of crystallographic data

- CIF files - Crystallographic Information Files
- Contain the structure in a unit cell along with the unit cell
- Detailed description of the structure
- Mercury - Free visualization software
- Gaussview - can read and prepare input for gaussian

How to obtain structure

- From a crystallographer
- From a database:
  - PDB - biological structures (proteins, NA)
  - CSD - organic crystals
  - COD - inorganic crystals

QM packages

- Most of the commercially available packages have some implementation of PBC
  - Gaussian, Turbomole, ADF...
  - Still work with GTOs or STOs
- Packages developed specially for solids:
  - VASP
  - SIESTA
  - CP2K
  - ONESTEP
  - GPAW
- Unfortunately we don't have a licences for native solid-state QM :(

Task

- Calculate the band gap for:
  - Lithium fluoride
  - Silicon
  - Aluminium
- Use PBC implemented in Gaussian09 and Turbomole
- Use Gaussview for generation of the structure (reuse in TM)
- PBEPBE/STO-3G; PBE/def2-SV(P) method
- Increase the memory to max. of your machine

Solution

- Go to COD and download appropriate structures
- Prepare standard G09 job and include the translational vectors (Symbol TV)
- Converge the SCF and look on the bottom of the output for the band gaps
- Silicon and Lithium fluoride should be treated as singlet states
- Aluminium (metal) should be treated as open shell system
- Increase the multiplicity to get minimum energy
- Gap should increase Al < Si < LiF