Periodic Boundary Conditions

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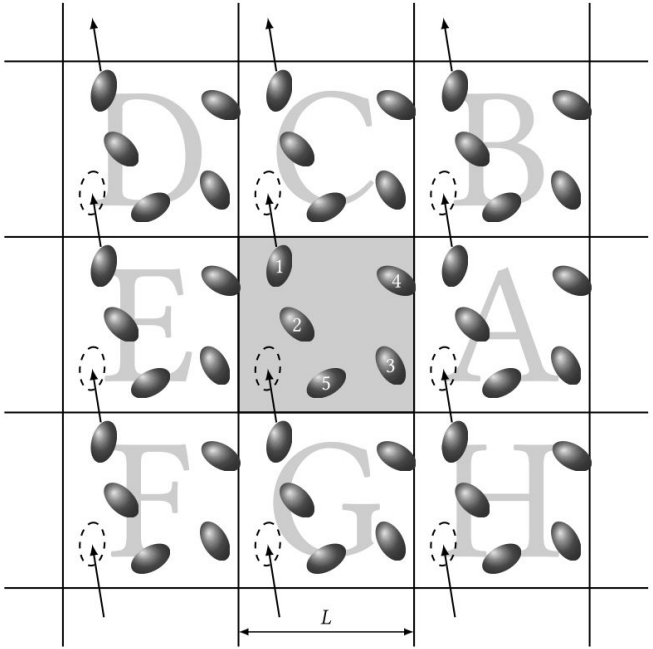
Why PBC?

- System **10 ≤ N ≤ 10000** ; N= total number of particles
- Major part of particles which **lies on the surface** will have experience of acting **force different** than those that are in the **interior part (bulk)** of simulation box.
- For example: in a simple cubic box of 10×10×10 including 1000 particles, 512 molecules are in bulk and the rest 488 are in surface and subsequently we will have inaccurate calculation.
- Even in a very large system, 6% of particles will be in the surface.
- How to overcome this problem: **Periodic Boundary Conditions calculation**

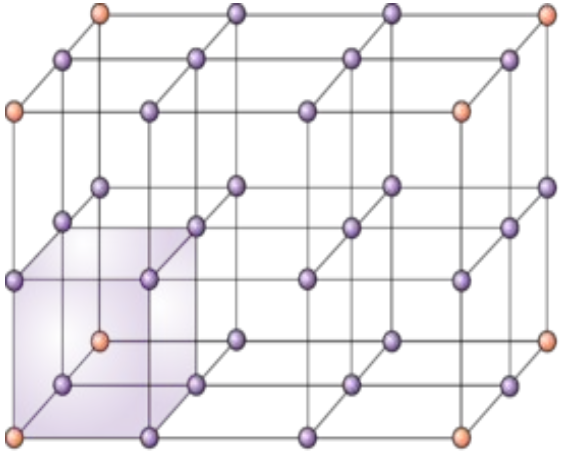
PBC

- **Primitive unit cell** is replicated in three dimensions and there is no wall to make the possibility of locating particles on the surface.
- ***Lines between different boxes:*** arbitrary axes in order to specify the location of each particle at certain point.

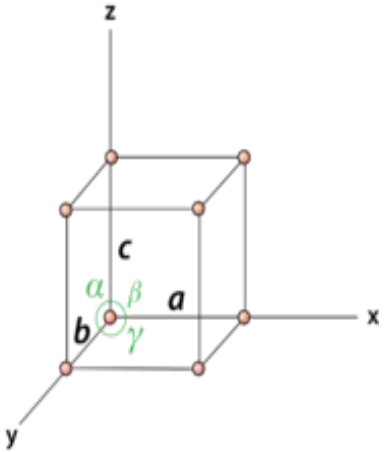


Crystal structure

- Description of particles (atoms, ions, or molecules) which are arranged in a particular order (repeating pattern in 1, 2, or 3D).
- The smallest portion of a crystal lattice is called **unit cell**. Crystal structure is nothing but the replicated unit cell in three dimension.



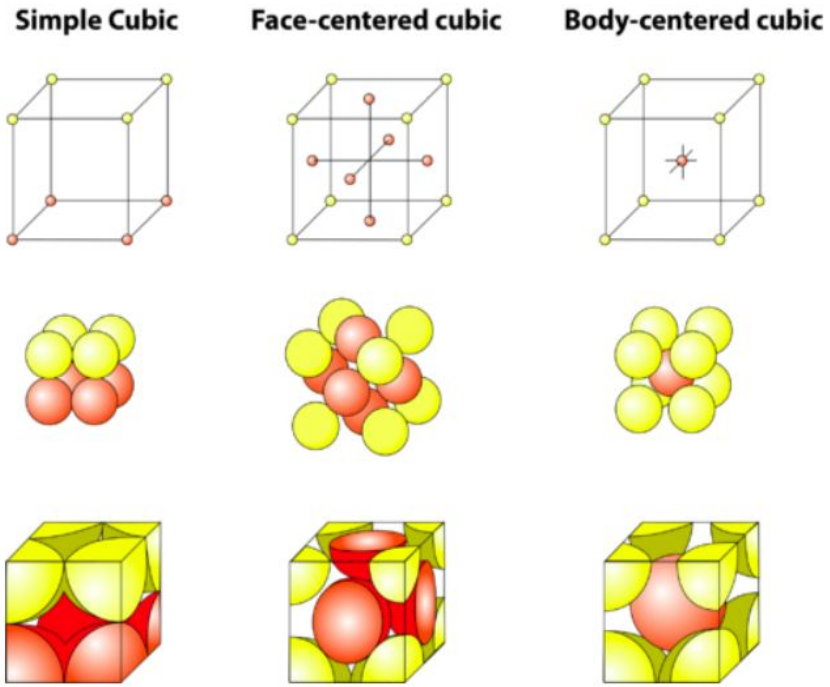
Crystal Lattice



Unit Cell

Different unit cells

- Unit cells occur in many different varieties.
- Example: cubic unit cell
  - **Simple-cubic**
  - **Face-centered cubic**
  - **Body-centered cubic**

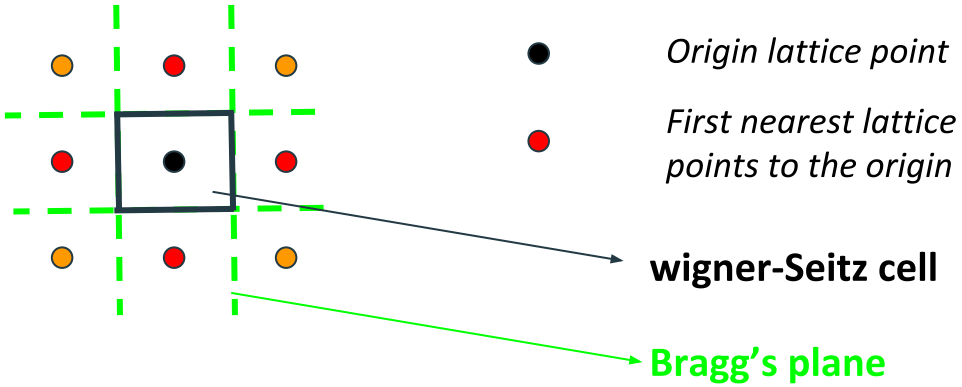


How to define a crystal structure?

- **Real space**: standard x,y,z (cartesian) coordination of a crystal structure
- **Reciprocal space**: inverse of real space
  - For a clear description of band structure
  - Diffraction pattern in material science
- It is a better representation of material structure (using reciprocal space). Nevertheless, there is no difference in the fundamental of material.
- $E = h^2k^2/2m$
  - K: wavevector = $2\pi/\lambda$
  - λ: wavelength
- In real space:
  - We have **a** (lattice vector) while **1/a** in reciprocal space
  - We have $\boldsymbol{\lambda}$ while $\boldsymbol{2\pi/\lambda}$ in reciprocal space

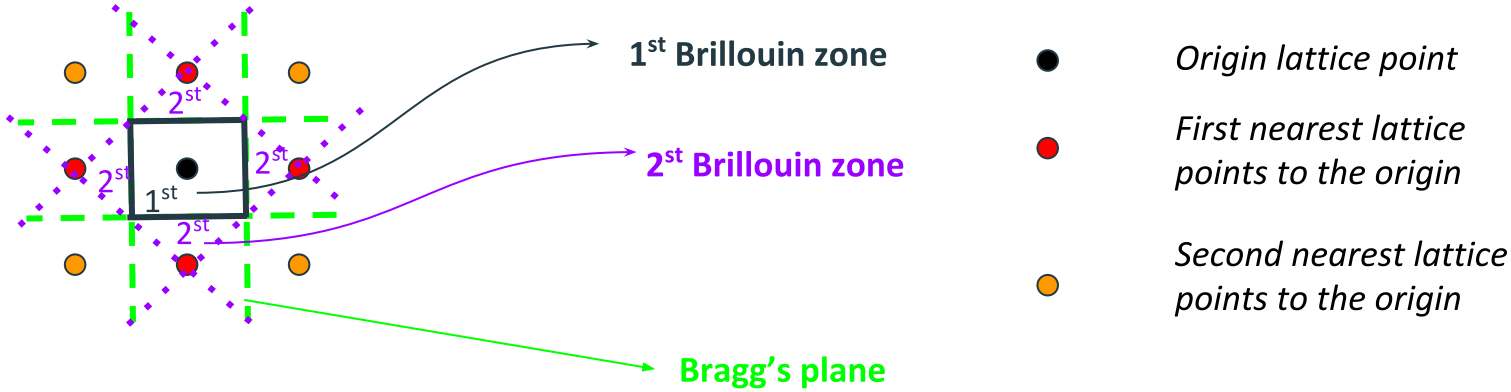
Wigner-Seitz vs Brillouin zone

Wigner-Seitz unit cell: the region in a real space that is closest to a given lattice point than to any other lattice point.



Brillouin Zone (Brillouin zone boundary)

1st Brillouin zone: Wigner-Seitz cell in a reciprocal space



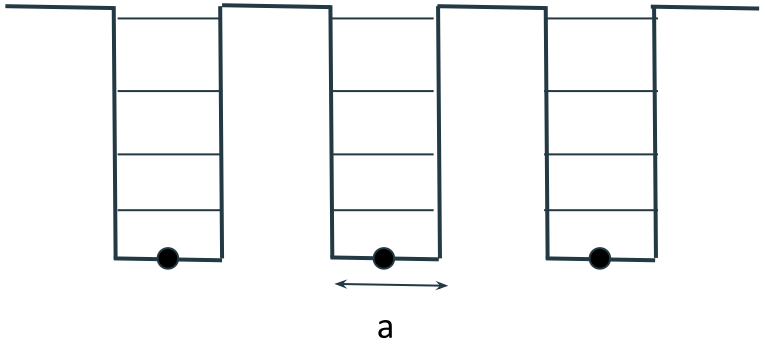
K-space

- Suppose we have a linear lattice in a real space with space **a** and $\boldsymbol{\lambda}$:
- In **reciprocal space** we can represent the mentioned parameters by **1/a** and $\boldsymbol{2\pi/\lambda}$. Therefore, **we just change the scale of this definition** and subsequently we change the **1/a** to $\boldsymbol{2\pi/a}$.
- Then, in **k-space a** and $\boldsymbol{\lambda}$ is defined by $\boldsymbol{2\pi/a}$ and $\boldsymbol{2\pi/\lambda}$, respectively. This representation of parameters in reciprocal space is called k-space.

Bloch theorem for simplified model for a periodic system

Bloch theorem:

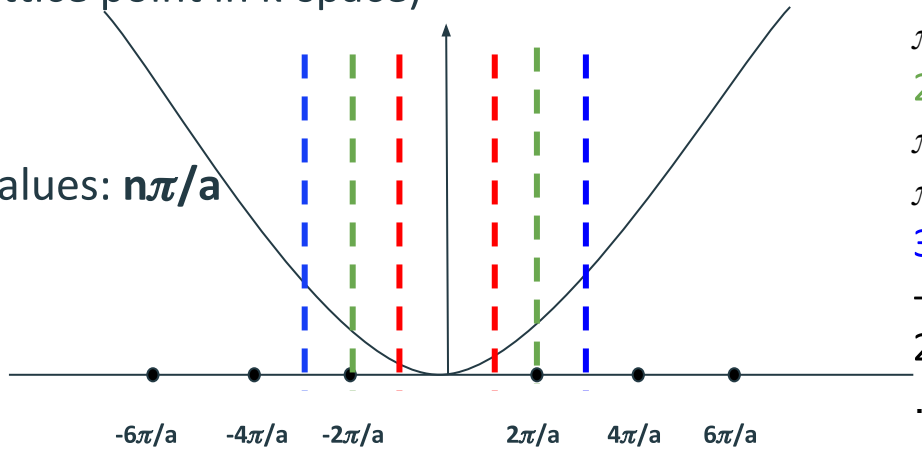
Electrons description in a periodic system



- $\psi(r) = e^{ik.r}\, u(r)$
  - $\psi \rightarrow$ bloch wave
  - $K \rightarrow$ wave vector
  - $r \rightarrow$ position of the electron
  - $u(r) \rightarrow$ periodic function
- Periodicity of the system should be satisfied:
  - $\psi(r) = Ae^{ikr} + Be^{-ikr}$
  - $\psi(r) = A\cos(kr) + B\sin(kr)$
- $\mathbf{E = h^2k^2/2m}$

How to define energy of a crystal structure in k-space?

- a$\rightarrow$**2π/a** (lattice point in k-space)
- **$\lambda\rightarrow 2\pi/\lambda$**
- $E = h^2k^2/2m$
- Allowed k values: **nπ/a**



1st Brillouin zone: -π/a≤k≤π/a

2st Brillouin zone: -2π/a≤k≤-π/a

π/a≤k≤2π/a

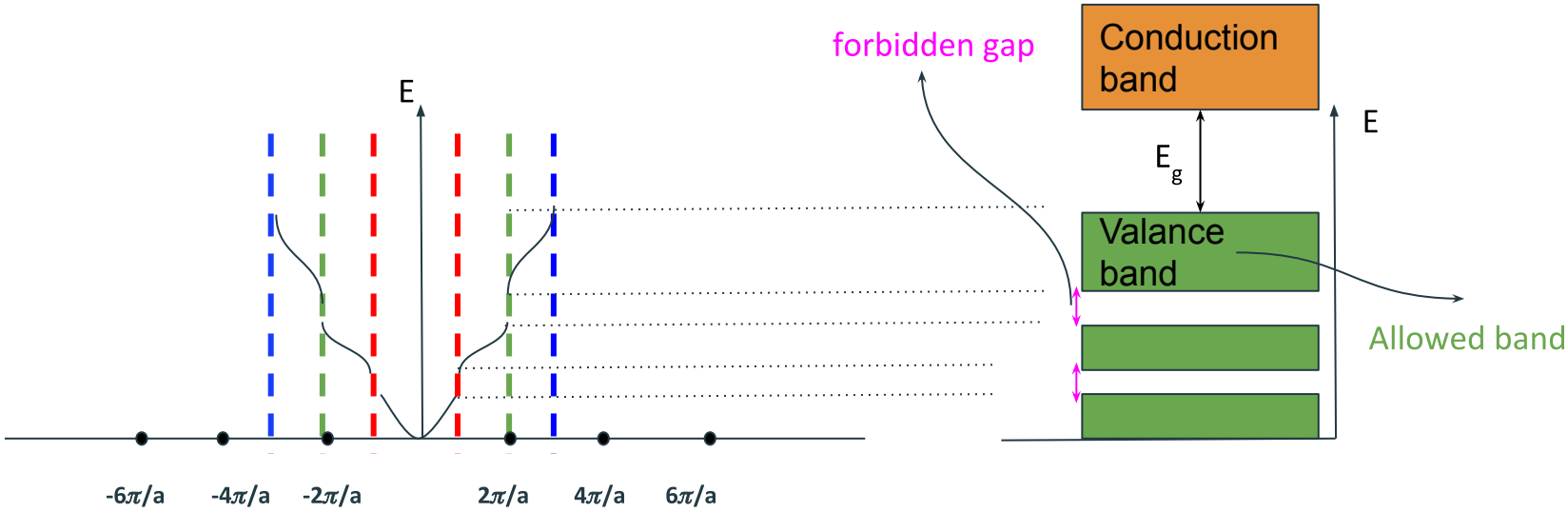
3st Brillouin zone:

-3π/a≤k≤-2π/a

2π/a≤k≤3π/a

….

Band gap

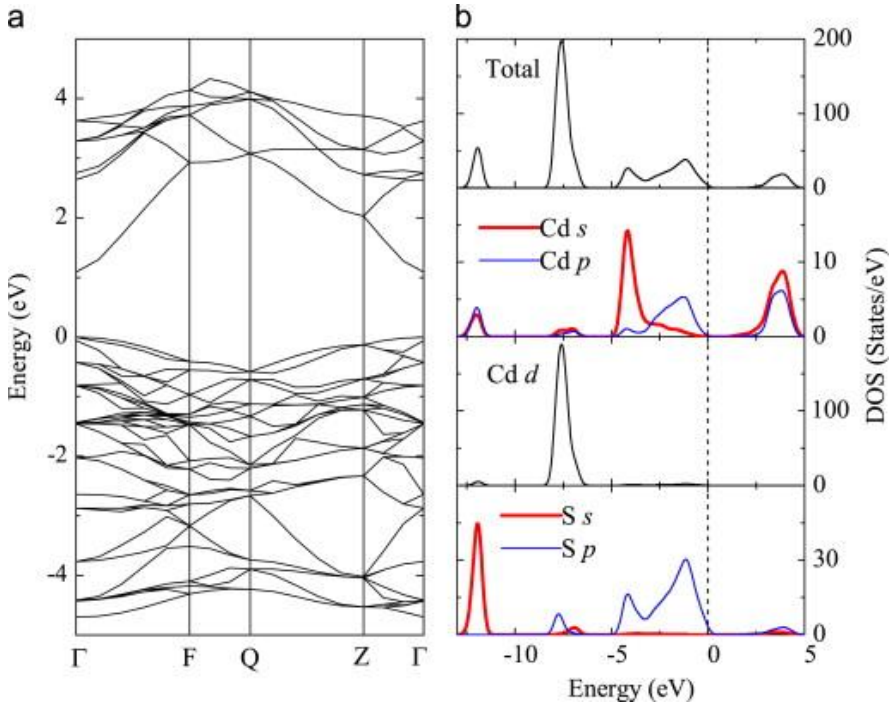

forbidden gap
Conduction band
E
E_g
Valance band
E
Allowed band
-6π/a
-4π/a
-2π/a
2π/a
4π/a
6π/a

Material classification based on the value of E_g

- All electrons are filled in bands and band gaps are defined as forbidden energy values.
- Based on the value of band gap there are three types of materials:
  - **Insulator**: $E_g > 2$ eV
  - **Semiconductor**: $E_g \leq 2$ eV
  - **Metals**: there is no band gap.
- **Fermi level**: the highest occupied energy level in crystal band structure
  - In metal: Fermi is the HOMO as in molecule structure
  - In semiconductor and insulator: Fermi level is somewhere between HOMO and LUMO as in molecule structure

Example of band structure

- CdS lattice: **hexagonal**
- **Greek** and **Roman** letters: for the **high symmetry points for first Brillouin zone** which is indicated the inner and the surface of BZ, respectively.
- **DOS** plot: shows how the electronic levels of a crystal structure are populated.



How to obtain and visualize

How to visualize a crystal structure:

- CrystalMaker
- Mercury
- Gaussview
- **VESTA**: https://jp-minerals.org/vesta/en/download.html

How to obtain a crystal structure:

- CIF: Crystallographic Information Files
- COD database: Crystallography Open Database for organic, inorganic and metal-organics compounds:http://www.crystallography.net/cod/

Packages for QM calculations of solids

- Packages specially designed for QM calculations of Solid:
  - SIESTA
  - VASP
  - CP2K
  - …
- You can find PBC calculations in molecule-based developed packages such as gaussian.
  - There are working based on Gaussian Type basis sets (GTOs) and Slater type basis set (STOs) which is unlikely doing QM calculation for a unit cell including a lot of atoms.

Task (Band gap calculation using Gaussian)

- Go to COD database and download CdS structure.
- Visualize using VESTA and save file as .vasp
- The structure of the system should be like as follows:

Cd	0.000000038	2.396003723	0.000000000
Cd	2.075000048	1.198001742	3.368499994
S	0.000000038	2.396003723	2.526375055
S	2.075000048	1.198001742	5.894875050

- Add TV (translational vectors) to the end of this structure. TV is the same as a unit cell.

Cd	0.000000038	2.396003723	0.000000000
Cd	2.075000048	1.198001742	3.368499994
S	0.000000038	2.396003723	2.526375055
S	2.075000048	1.198001742	5.894875050
TV	***4.1500000954***	***0.000000000***	***0.000000000***
TV	***-2.0750000477***	***3.5940055083***	***0.000000000***
TV	***0.000000000***	***0.0000000000***	***6.7369999886***

- Optimize the system using **HSEh1pbe** function using **def2-svp** basis set.
- If you are using **external basis** set, remember to add **Gen** at root section.
- If you want to do **Band structure** or **PDOS** calculations it is necessary to put **pop=regular** at root section.
- For **band structure and PDOS** calculation one should add the following commands at root section:
  - **IOp(5/181=10) which means that do PDOS calculations**
- In the case of CdS calculation, we know about the space group which is **hexagonal**. It is going to be added as:
  - **IOp(5/184=186)**

- **IOp**: keyword allows the user to set internal options. for detail information,check the link: https://gaussian.com/iop/
- After fulfilling the all conditions, you will find the **band gap** at .log file by searching " **minimum direct gap at k-point**".
- ***The last minimum direct gap is the desire band gap***.
- The value for **HOCO** and **LUCO** are printed in .log file which related to the **H**ighest **O**ccupied **C**rystal **O**rbital and the **L**owest **U**noccupied **C**rystal **O**rbital.

Goodluck!