Energy Band Theory

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Course Structure

- Part A: Introduction to Modelling
- Part B: Monte Carlo Simulations
- **Part C: Density Functional Theory (DFT) Calculations**
  - **Energy Band Theory**
  - Density Functional Theory (2 Parts)
  - Softwares for DFT (2 Parts)
  - Applications of DFT in MSE
- Tutorial 3: Constructing Atomic Models and Visualization
- Introduction to High Performance Computing

Solid State Physics

- This lecture is only a brief introduction to band theory and by no means comprehensive. If you need to understand more on the theories in today's lecture, please refer to the following books:
- C. Kittel, Introduction to Solid State Physics, 8th Edition.
- D. Ashcroft and N. Mermin, Solid State Physics

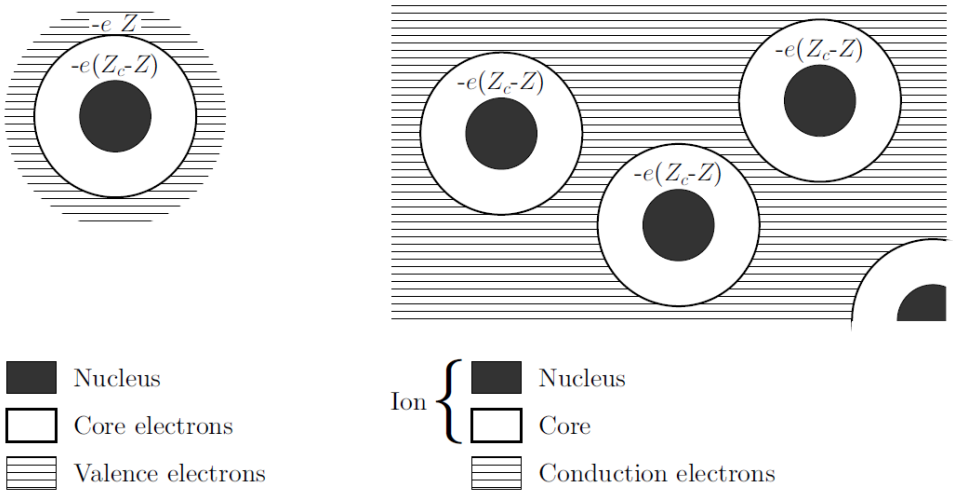
Electrons in Solids

- Let's begin with metals.

  - Metallic state is favored by elements.
  - The bonds that bind the metal together are rather unidirectional. By contrast, ionic and covalent bonds are more directional bonds.
  - There is a lot of "empty space" in metals. The ionic radius of metals is much larger than the ionic radius, leaving a great deal of volume for conduction electrons to move around.

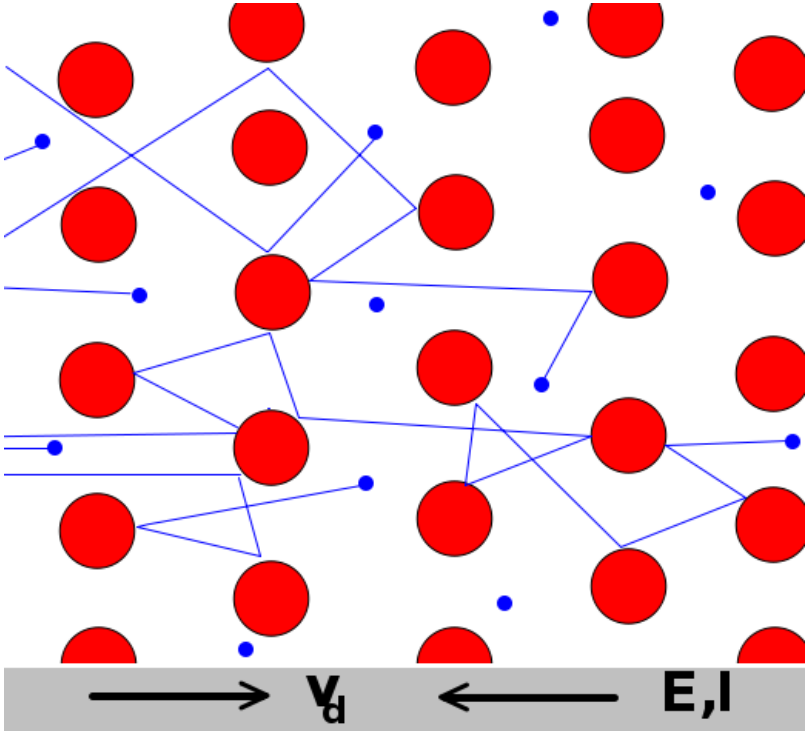
Metals

- An array of widely spaced, small ionic cores, with the mobile valence electrons spread through the volume between.



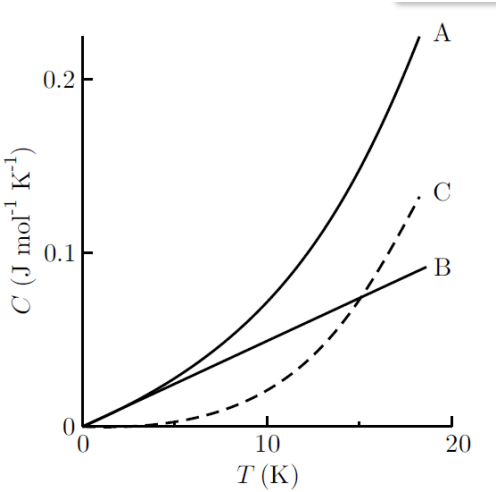
Drude Model

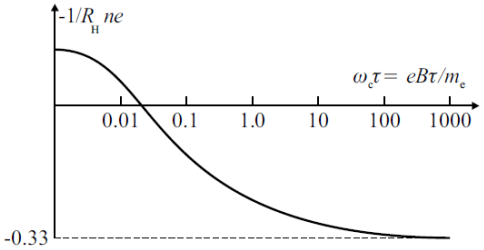
- Proposed in 1900 by *Paul Drude* to explain the transport properties of materials (especially metals).
- Consider metal to be formed of a mass of positively charged ions and a number of “free electrons”.
- A *collision* indicates the scattering of an electron (and only by) and ionic core.
- Between collisions, electron do not interact with each other.
- Electron achieve thermal equilibrium with their surroundings only through *collisions.*)



Failure of Drude Model

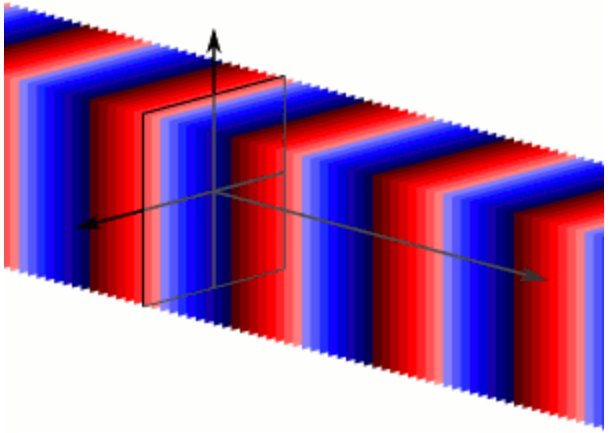
- Attempts to use classical theory to understand electron transport
- Drude model predicts the electronic heat capacity independent of temperature (but experiments show C ~ T)
- Drude model severely underestimate the thermal conductivity.
- Can not explain complex electromagnetic behavior such as Hall effect.
- **We can not treat electrons simply as molecules of a classical gas.**

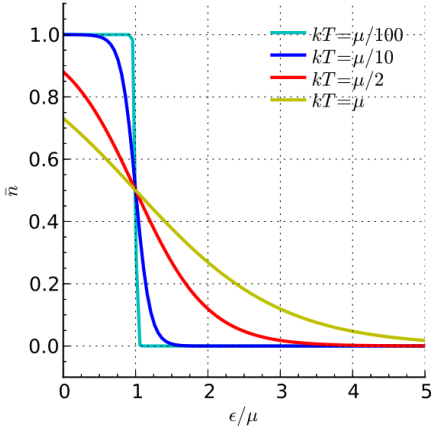




Free Electron Model (Sommerfeld Model)

- Developed by Arnold Sommerfeld and combined classic model (Drude) with quantum mechanical Fermi-Dirac statistics
- Inherit the basic assumptions of Drude model (electron-electron interactions completely neglected)
- Electron motion now described in wave function and solved by Schodinger Equation
- The electron energy statistics described by Fermi-Dirac distribution.

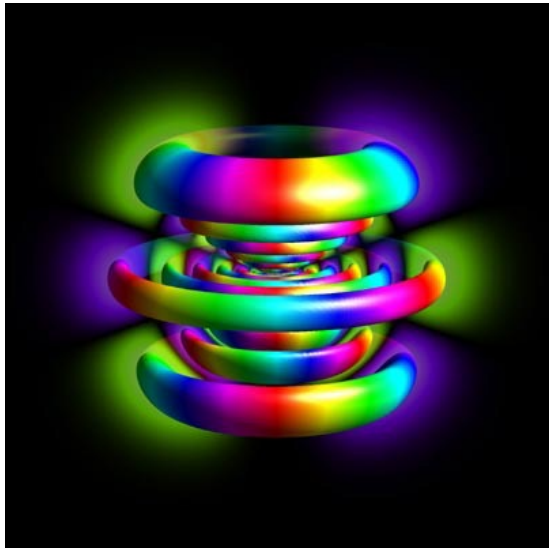


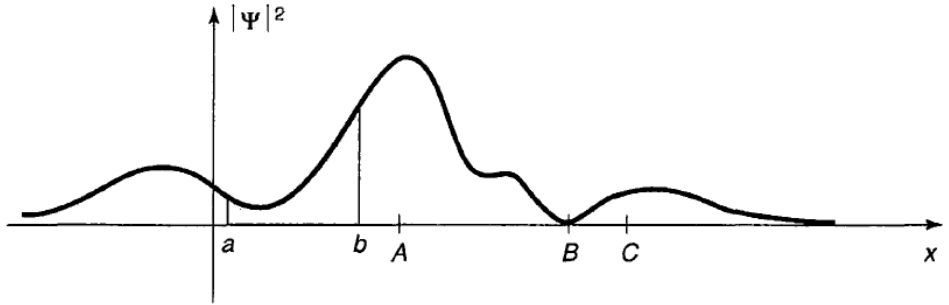


Wavefunction

- The dual behavior of the nuclei and electrons can be described by a function called a wave function $\psi(r)$. This really just describes the electron orbitals.

- The norm of a wavefunction tells us the probability of finding the sub-atomic particle in a given region of space





Failure of Sommerfeld Model

- Although thermal properties now can be appropriately described, electromagnetic behavior still can not be explained.

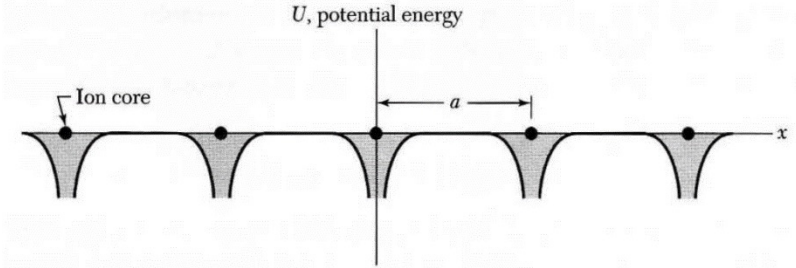
- Most importantly, the model is not applicable to insulators and semiconductors.

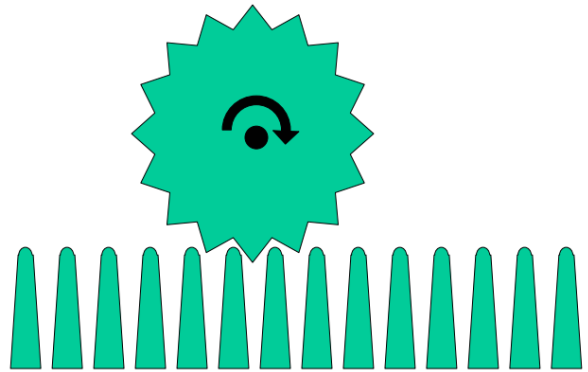
Bloch's Theorem: *Electron Motion in A Periodic Lattice*

- The potential energy of an electron in crystalline solids has a perfect periodicity.
- V(r+T) = V(r)

- Bloch's theorem states that the solution to the Schrodinger equation for electrons within a periodic potential has the form
- ψ (r) = $u(r)\exp(ik \cdot r)$
- u(r) is a function with the periodicity of the real-space Bravis lattice.

- Bloch's theorem is the underlying foundation of solving electronic structure in a crystalline lattice.





Reciprocal Space (k space)

- Fourier transform of real lattice
- Defined by exp(iK*R)=1, where K is the reciprocal lattice vector and R is the real lattice vector.
- Reciprocal lattice lets us conveniently write the wavefunction in the form of a sum of plane waves.
- The points in reciprocal space reflects the periodicity in real space (Recall Bragg's Law, and the relationship $d(hkl)=2\pi/|G|$.

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

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

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

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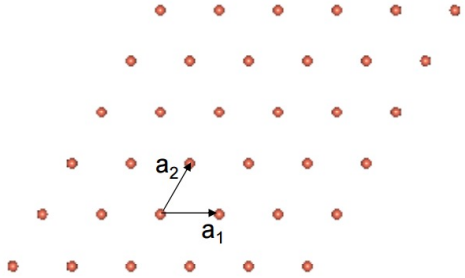
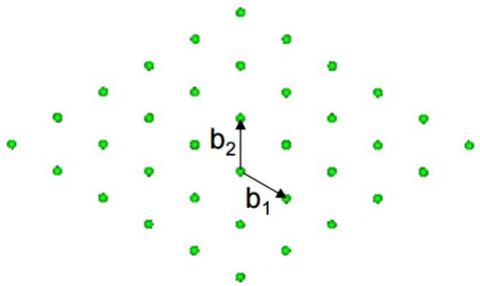
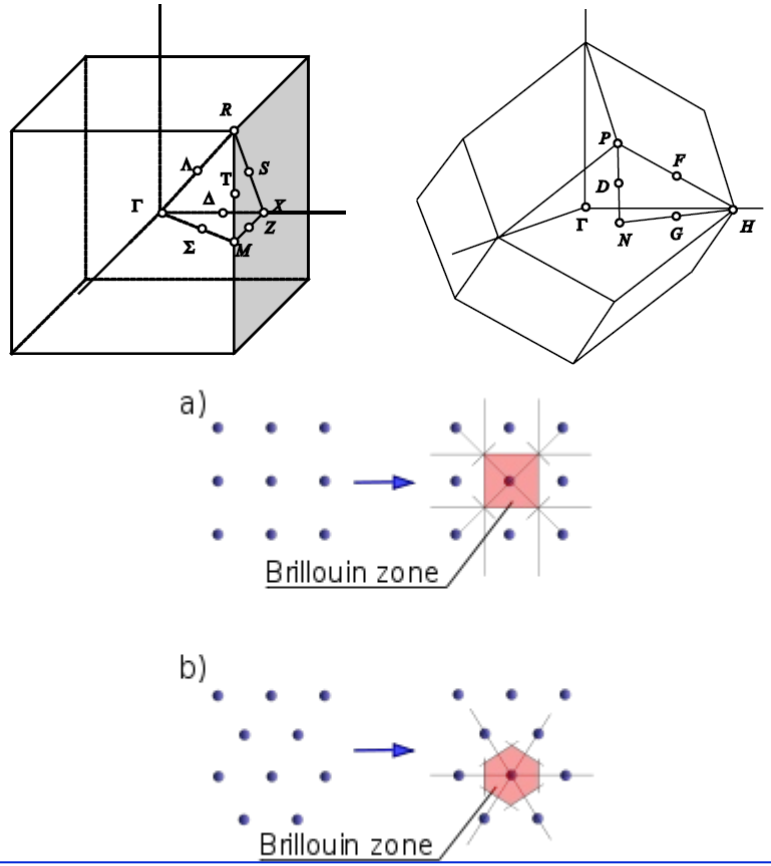




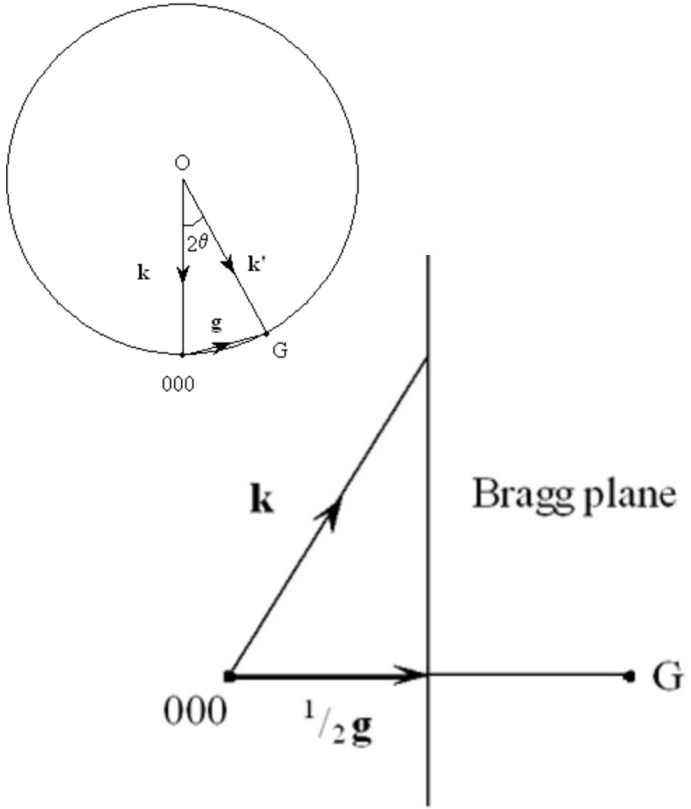
First Brillouin Zone

- Wigner-Seitz Cell of the reciprocal lattice (also primitive cell in the reciprocal lattice)
- Contains a set of points that can be reached from origin without crossing any Bragg plane.



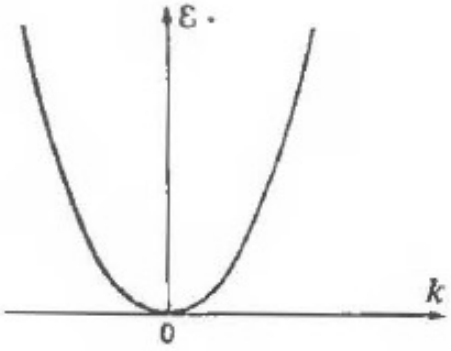
First Brillouin Zone

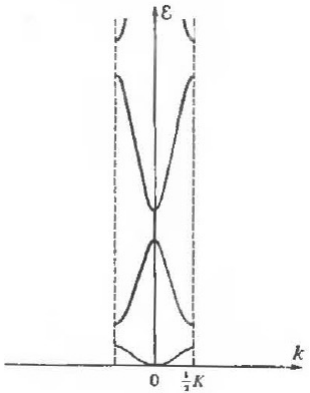
- The Bragg's law can be written in terms of primitive reciprocal lattice vector by k'-k=g
- Further transform to $k \cdot 1/2g = 1/2g \cdot 1/2g$
- Any wavevector drawn from origin to the Bragg plane satisfies Bragg's law.
- These Bragg's planes defines the boundary of 1st Brillouin zone
- 1st Brillouine zone therefore contains all symmetry of a crystalline lattice
- Later, we'll see electronic structure of a periodic lattice is contained in 1st Brillouin zone.

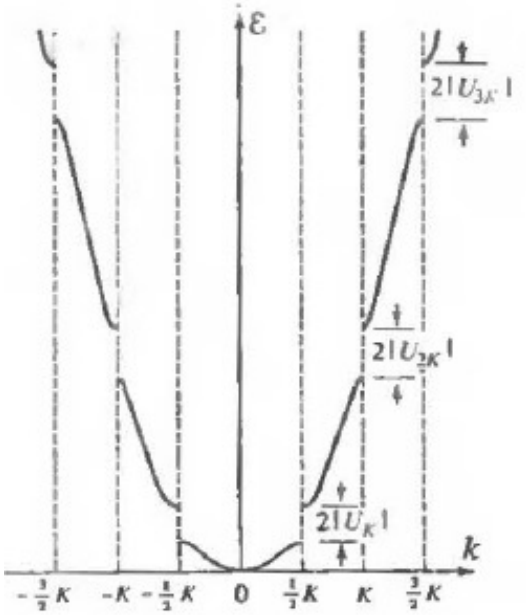


Near Free Electron Model

- Constructed to respond to “how electron moves in a periodic structure”
- Electron still “free” within each order of Bragg planes.
- Energy discontinuity rises at the Bragg planes (boundary of Brillouin zones) due to electron diffraction.
- This discontinuity creates “energy band” and “band gap”.

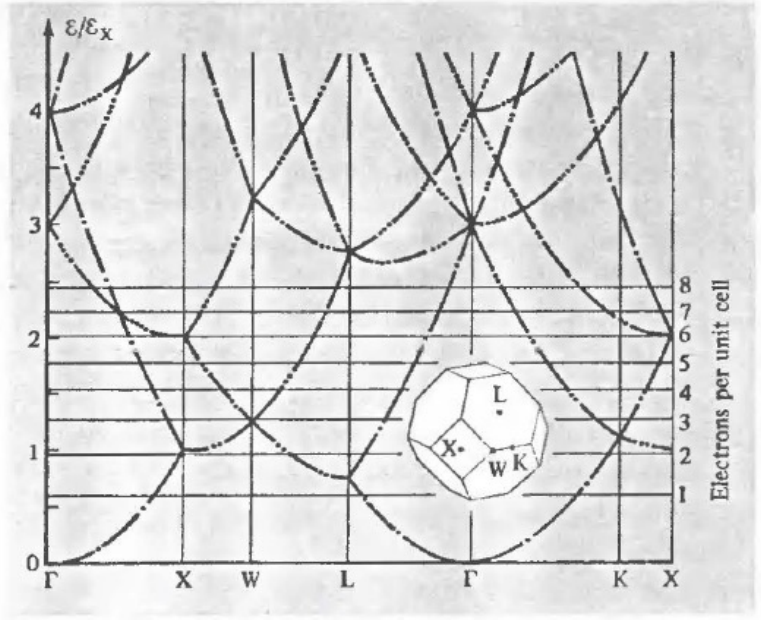




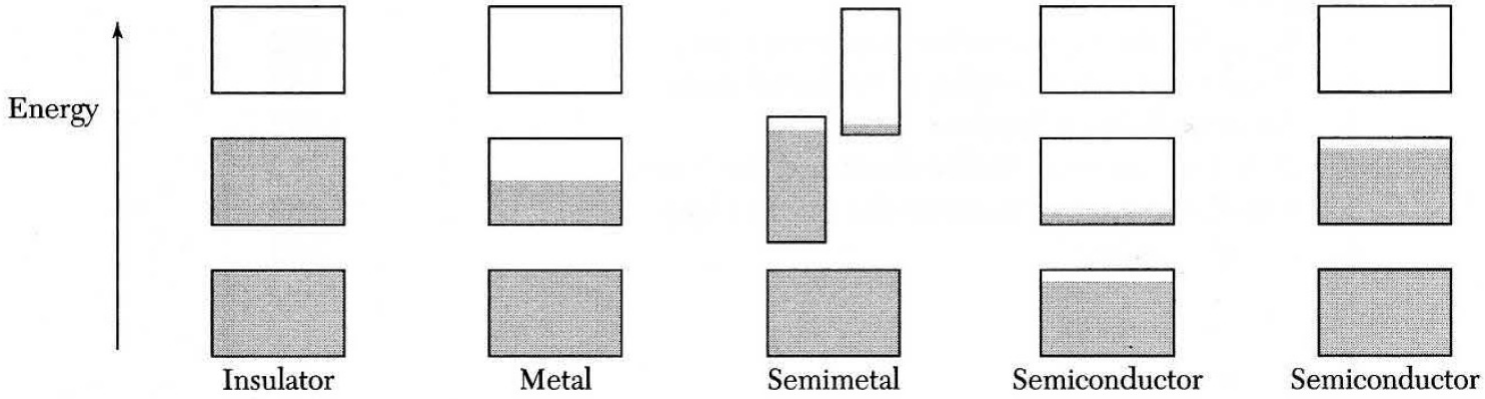


Band Structure in Three Dimensions

- Band structure: electron energy dispersion in k-space
- Normally we plot along the boundary of 1st Brillouin Zone to reflect crystalline periodicity.
- Electronic structure at higher Brillouin zone is folded back to 1st by symmetry.
- Band structure serves as a **key link between its crystal structure and physical properties.**



Band Structure of Different Materials



- Depend on how electrons occupy these energy levels

Coming up: DFT

- How do we use computational modelling to obtain electronic structures?

Summary

- Models to describe electron motion in solids: Drude, Sommerfeld, NFE
- Reciprocal lattice and Brillouin zone
- Bloch theorem
- Band structure diagrams