Engineering Physics (2025)
Course code 25PY101
Module 2 Unit 1: Quantum theories of solids

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November 27, 2025

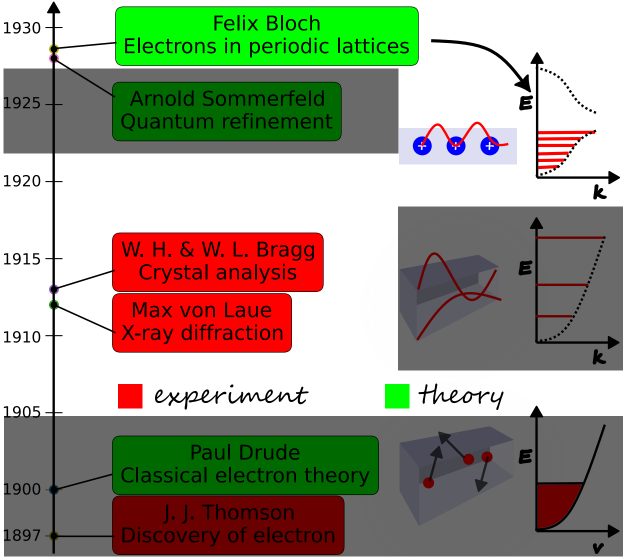
Unit 2 Plan

1. Quantum Free Electron Theory
2. Fermi-Dirac distribution
3. Electronic specific heat of solids
4. Density of states (qualitative)
5. Success and Failures of quantum free electron theory of solids
6. E-k diagram
7. Classification of materials based on bands in solids

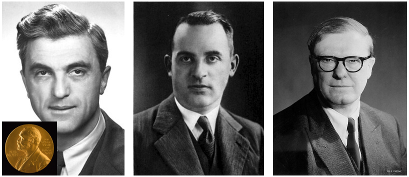
Unit 2 Plan

Electron theories of metals

1. Classical free electron theory
2. Quantum free electron theory
3. Quantum band theory (QBT)



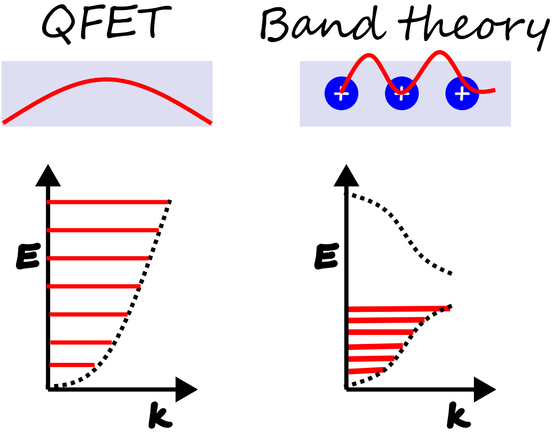
Quantum band theory (QBT)



F. Bloch, R. Kronig, W. Penney

- Proposed by Felix Bloch, Ralph Kronig, William Penney and co-workers in 1928 by extending QFET.
- Assumed "electron gas" is **not free** and is under the influence of lattice – **periodic potential approximation**.

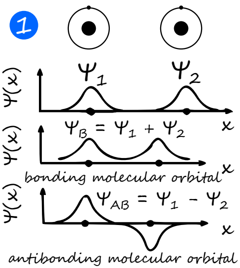
$V(x)$: QFET vs QBT

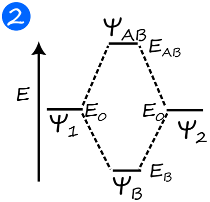


Key Insight

In Quantum band theory, the electron is **not** free!

Splitting of energy levels – Formation of H_2 molecule



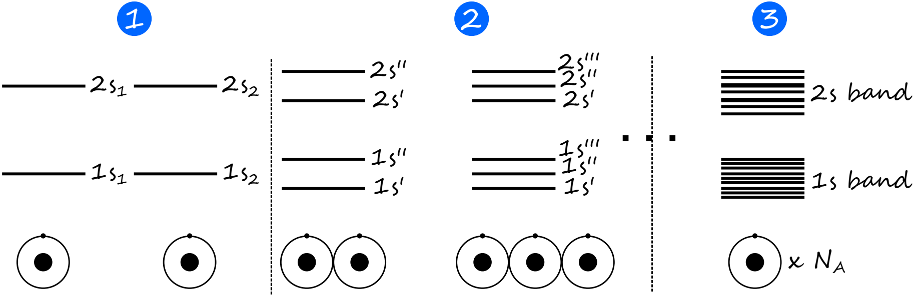


1. At large inter atomic distance, the wavefunction of electron in each H atom is 1 s. As the separation decreases, due to Pauli exclusion principle, the wavefunctions **hybridize** to form **bonding** and **anti-bonding** molecular orbitals.
2. The energy levels of individual H atoms **split** into bonding molecular orbital with lower energy and anti-bonding molecular orbital with higher energy.

Key Insight

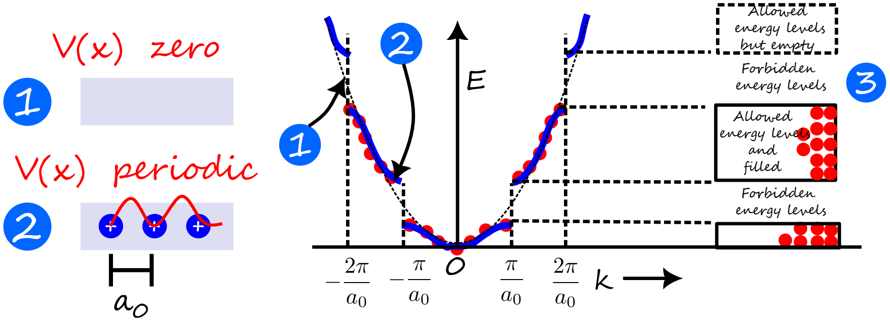
Splitting of energy levels is due to Pauli exclusion principle.

Band formation – discrete to continuous



1. At large interatomic separation, the energy levels of two H atom system match the energy levels of isolated H atom.
2. At the equilibrium separation, as the number of H atoms increase, there is splitting of energy levels.
3. For an Avagadro number of H atoms, the **discrete** energy levels group into a "band" of continuous energy levels.
   - The width of the band is called **energy bandwidth**.
   - The bandwidth is of the order of 1 eV.

Mapping of dispersion relation to band structure



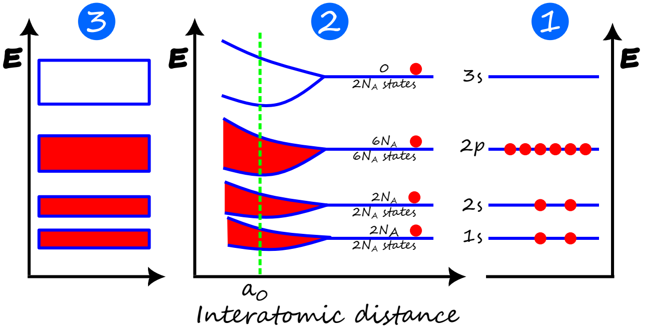
1. For a free electron, potential is zero and the dispersion relation E vs k has parabolic form.
2. For an electron in crystalline solid with lattice constant a_0, the potential is periodic and the E vs k **opens up** at specific values of $k = \pm\frac{\pi}{a_0}, \pm\frac{2\pi}{a_0}, \ldots$.
3. The mapping of energy levels leads to collection of **allowed** and **forbidden** bands.

Quantum Band theory – Postulates

Postulates

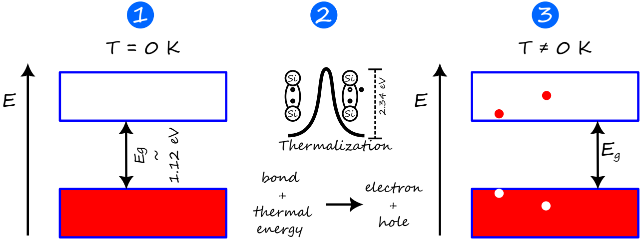
1. **Waves:** Electrons are quantum waves with wavevector k, angular frequency ω.
2. **Fermion:** Electron is a spin $\frac{1}{2}$ particle and obeys Pauli's exclusion principle.
3. **Independent electron approximation:** Electrons are independent and mutual repulsion between them is ignored.
4. **Periodic potential approximation:** Electrons move in a periodic potential.
5. **Quantum Thermodynamics:** The thermalization is governed by Fermi-Dirac statistics.

Energy band structure of Ne – gas to solid



1. Consider Avagadro number of Ne atoms at infinity – Ne gas. The energy levels are given by atomic energy levels
2. As the interatomic separation **decreases**, due to Pauli exclusion principle, band formation happens and bandwidths **increase**.
3. At equilibrium lattice constant a_0 – Ne solid, there are allowed and forbidden bands.

Energy band diagram



1. At $T = 0\,\mathrm{K}$,
   - The topmost occupied band is called **valence band**.
   - The lower most unoccupied is called **conduction band**.
   - These two bands are separated by a forbidden gap called the **energy band gap**.
2. When temperature is increased, the covalent bond is broken due to thermalization. This results in the formation of **electron-hole pair** [1].
3. At $T \neq 0\,\mathrm{K}$, the electron occupies energy level in the conduction band whereas the hole occupies energy level in the valence band.

[1] Hole is the absence of electron in the valence band.

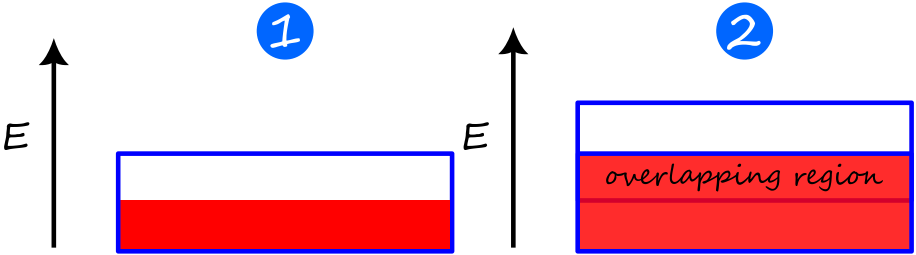
Classification of solids

- According to band theory, conductivity of solid is determined by the band gap separating the conduction band and valence band.
- Based on the band gap, the solids are classified into
  1. metals or conductors
  2. semiconductors
  3. insulators

Key Insight

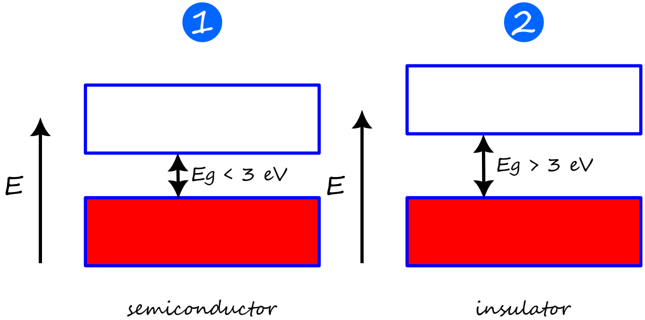
The classification of solids is based on energy band gap.

Energy band diagram – Conductor



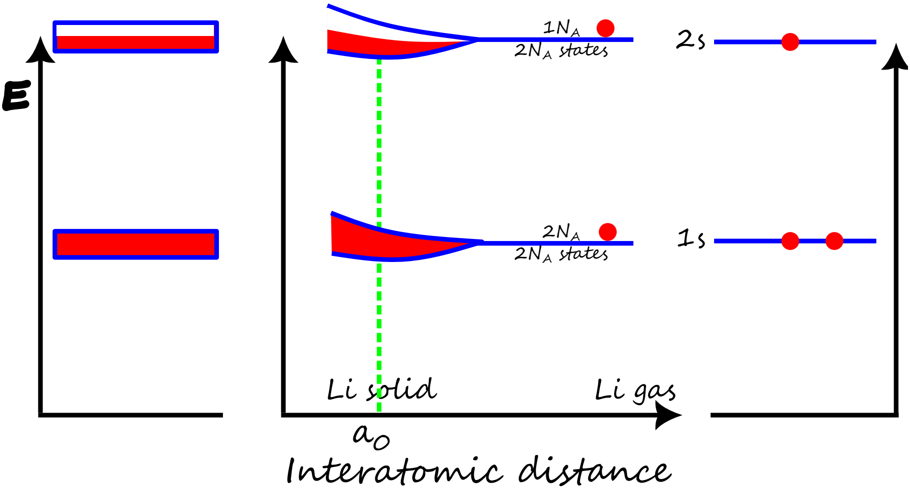
- In conductors, there are two cases
  1. the conduction band is half filled.
  2. the conduction band overlaps with empty upper band.
- In both cases, there is no band gap so that empty states are available for conduction.
- Since there is no band gap, there is no absence of electron at $T \neq 0$. Therefore, there are no holes in conductors.

Energy band diagram – Semiconductor



- In either semiconductor or insulator, there is a band gap so that empty states are not available for conduction.
  1. The energy band gap is less than 3 eV for semiconductor.
  2. The energy band gap is greater than 3 eV for insulator

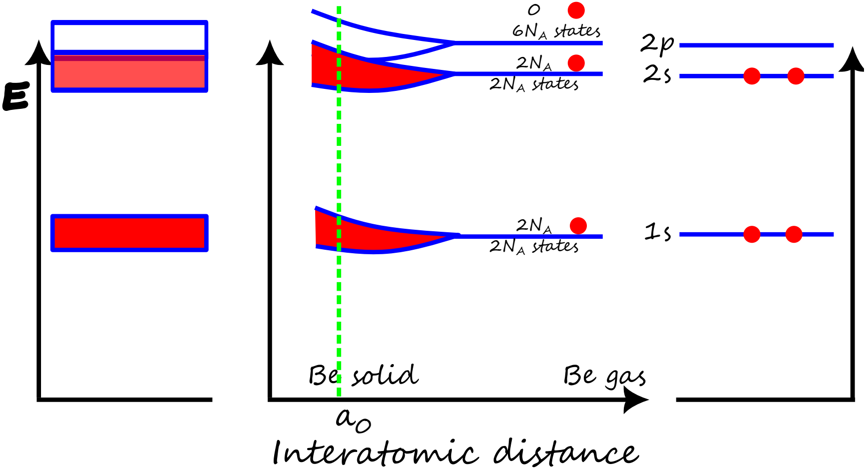
Energy band diagram of Li – half filled conduction band



Key Insight

The conduction band is only half filled for lithium.

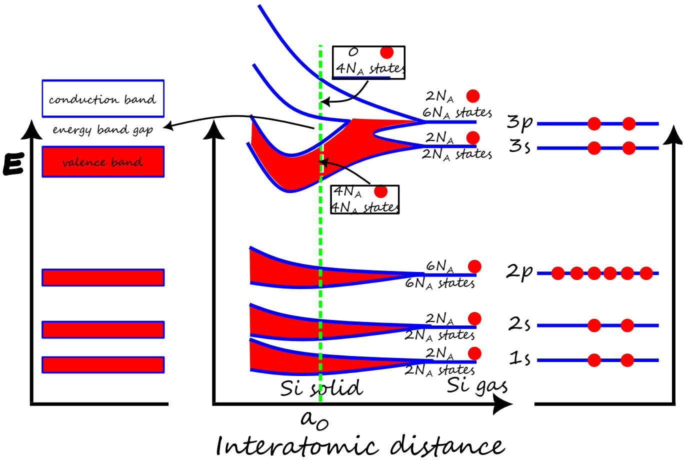
Energy band diagram of Be – overlapping conduction bands



Key Insight

The conduction band overlaps with next empty band for beryllium.

Energy band diagram – Si



Key Insight

The valence band is completely filled and the conduction band is completely empty at $T = 0\,\mathrm{K}$.