Chapter 3
Introduction to Quantum Theory of Solids

Outline

- Allowed and forbidden energy bands
- Electrical conduction in solid
- Extension to three dimension
- Density of state
- Statistical mechanics
3.1 Allowed and forbidden energy bands

- **In one-electron atom**
  - Only **discrete values of energy** are allowed
  - The probability function shows that the electron is **not** localized at a **given radius**
  - We can extrapolate these single-atoms results to a crystal and quantitatively derive the concepts of **allowed and forbidden energy bands**

\[ E_n = \frac{-m_e e^4}{(4\pi\varepsilon_0)^2 2\hbar^2 n^2} \]

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3.1.1 Formation of energy bands

- Fig. (a) shows the **radial probability density function** for the lowest electron energy state of the single, non-interacting hydrogen atom Fig. (b) shows the **radial probability** curves for two atoms that are in close proximity to each other
- Due to **Pauli exclusion principle**, no two electrons may occupy the same quantum state, the interaction of two electrons give each discrete quantized energy level splitting into two discrete energy levels
By pushing the numbers of hydrogen type atoms together with a regular periodic arrangement, the initial quantized energy level will split into a band of discrete energy levels.

The Pauli exclusion principle states that the joining of atoms to form a system (crystal) does not alter the total number of quantum states.

The discrete energy must split into a band of energies in order that each electron can occupy a distinct quantum state.

For a system with $10^{19}$ one-electron atoms with a width of allowed energy band of 1 eV, if the discrete energy states are equidistant, then the energy levels are separated by $10^{-19}$ eV, which is extremely small.

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**Example 3.1 Small change of kinetic energy**

Consider an electron traveling at a velocity of $10^7$ cm/s. Assume the velocity increases by a value of 1 cm/s. Find the increase in kinetic energy.

\[
E = \frac{1}{2} m \nu^2 = \frac{1}{2} (9.11 \times 10^{-31}) (10^5)^2 = 4.56 \times 10^{-21} \text{ J} = \frac{4.56 \times 10^{-21}}{1.6 \times 10^{-19}} = 2.85 \times 10^{-2} \text{ eV}
\]

\[
\Delta E = \frac{1}{2} m \nu_2^2 - \frac{1}{2} m \nu_1^2
\]

Let $\nu_2 = \nu_1 + \Delta \nu$

\[
\Rightarrow \nu_2^2 = (\nu_1 + \Delta \nu)^2 = \nu_1^2 + 2\nu_1 \Delta \nu + (\Delta \nu)^2
\]

\[
\Rightarrow \Delta E \approx \frac{1}{2} m (2\nu_1 \Delta \nu) = m \nu_1 \Delta \nu
\]

\[
\Delta E \approx m \nu_1 \Delta \nu = (9.11 \times 10^{-31}) (10^5) (0.01) = 9.11 \times 10^{-28} \text{ J}
\]

\[
\Delta E = \frac{9.11 \times 10^{-28}}{1.6 \times 10^{-19}} = 5.7 \times 10^{-9} \text{ eV}
\]
### Discrete energy levels for a hydrogen atom

\[ E_n = \frac{-m_e e^4}{(4\pi \varepsilon_0)^2 2\hbar^2 n^2} \]

\[ E_1 = -13.6 \text{ eV} \]
\[ E_2 = \frac{E_1}{2^2} = -3.4 \text{ eV} \]
\[ E_3 = \frac{E_1}{3^2} = -1.51 \text{ eV} \]
\[ E_4 = \frac{E_1}{4^2} = -0.85 \text{ eV} \]

\[ \Delta E = 0.66 \text{ eV} \]
\[ \Delta E = 1.89 \text{ eV} \]
\[ \Delta E = 10.2 \text{ eV} \]

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- For a atom contains electrons up through the \( n=3 \) energy level, when we bought these atoms close together from initially far apart
  - The \( n=3 \) energy shell will begin to interact initially, followed by \( n=2 \) energy shell interaction and finally the innermost \( n=1 \) shell interaction

- If \( r_o \) is the equilibrium interatomic distance, then at this distance we have
  - **Bands of allowed energies** (electrons may occupy)
  - **Bands of forbidden energies**

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**Figure 3.3** Schematic showing the splitting of three energy states into allowed bands of energies.
For silicon atoms, having 14 electrons,
- 2 electrons occupy \( n=1 \) energy level
- 8 electrons occupy \( n=2 \) energy level
- 4 remaining valence electrons occupying \( n=3 \) energy level are involved in chemical reactions

Isolated silicon atom (a)

- For silicon crystal
  - 3s states corresponds to \( n=3 \) and \( l=0 \) (containing 2 quantum states)
    \( n=3, l=0, s=-1/2, +1/2 \)
  - 3p states corresponds to \( n=3 \) and \( l=1 \) (containing 6 quantum states)
    \( n=3, l=+1, m=1, s=-1/2, +1/2 \)
    \( n=3, l=0, m=0, s=-1/2, +1/2 \)
    \( n=3, l=-1, m=-1, s=-1/2, +1/2 \)

As the interatomic distance decreases, the 3s and 3p states and gradually merge together to form broad band

At the equilibrium interatomic distance, the broad band has again split with 4 quantum states per atom in the lower band and 4 quantum states per atom in the upper band

The upper band is assigned as conduction band
the lower band is called valence band

Since each Si atom has only 4 valence electrons
- At 0 K, electrons are in the lowest energy states
  all states in the valence band will be full, and all states in the conduction band will be empty
3.1.2 The Kronig-Penney Model

- Fig. (a) shows potential function of a single, noninteracting, one-electron atom
- Fig. (b) shows potential function for the case when several atoms are in close proximity arranged, one-dimensional array
- Fig. (c) is the net potential function in Fig. (b)
- One-dimensional square periodic potential function is used in K.P model

\[
V(x) = \begin{cases} 
0 & 0 < x < a \\
V_o & -b < x < 0 
\end{cases}
\]

- Block Theorem
- The theorem states that all one-electron wave functions involving periodically varying potential energy functions must be of the form

\[u(x) : \text{periodic function with period}(a + b)\]

\[e^{ikx} \quad \text{traveling wave}\]

The general time-independent wave function

\[\Psi(x,t) = \psi(x)\phi(t) = u(x)e^{ikx}e^{-j\omega t} \quad \omega = \frac{E}{\hbar} \quad (E = \hbar \omega)\]
Time-independent Schrodinger wave equation

\[
\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0 \quad \iff \quad \psi(x) = u(x)e^{jkx}
\]

Region I:
\[
\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2mE}{\hbar^2}\psi(x) = 0 \quad (0 \leq x \leq a)
\]

Region II:
\[
\frac{\partial^2 \psi(x)}{\partial x^2} + \frac{2m(E - V_o)}{\hbar^2}\psi(x) = 0 \quad (-b \leq x \leq 0)
\]

Region I:
\[
\frac{d^2 u_1(x)}{dx^2} + 2jk\frac{du_1(x)}{dx} - (k^2 - \alpha^2)u_1(x) = 0 \quad \iff \quad \alpha^2 = \frac{2mE}{\hbar^2}
\]

\(u_1(x)\): the amplitude of the wave function in region I

Region II:
\[
\frac{d^2 u_2(x)}{dx^2} + 2jk\frac{du_2(x)}{dx} - (k^2 - \beta^2)u_2(x) = 0
\]

if \(V_o > E\)
\[
\beta = \sqrt{\frac{2m(E - V_o)}{\hbar^2}} = j\gamma
\]

\(u_2(x)\): the amplitude of the wave function in region II

\[
u_1(x) = Ae^{j(\alpha-k)x} + Be^{-j(\alpha+k)x} \quad \text{for} \quad 0 < x < a
\]

\[
u_2(x) = Ce^{j(\beta-k)x} + Be^{-j(\beta+k)x} \quad \text{for} \quad -b < x < 0
\]

if \(E > V_o\)
\[
\beta^2 = \alpha^2 - \frac{2mV_o}{\hbar^2}
\]
\( u_1(x) = Ae^{j(\alpha-k)x} + Be^{-j(\alpha+k)x} \quad \text{for } 0 < x < a \)

\( u_2(x) = Ce^{j(\beta-k)x} + Be^{-j(\beta+k)x} \quad \text{for } -b < x < 0 \)

4 unknowns, 4 BCs

The wave function \( \psi(x) \) and its derivative \( \partial \psi / \partial x \) must be continuous

\[ \Rightarrow u(x) \text{ and its derivative } \frac{\partial u}{\partial x} \text{ must be continuous} \]

\[ \psi(x^-) = \psi(x^+) \quad \Rightarrow \quad u(x^-)e^{j\kappa x^-} = u(x^+)e^{j\kappa x^+} \quad \Rightarrow \quad u(x^-) = u(x^-) \]

\[ \frac{\partial \psi(x)}{\partial x} \bigg|_{x^-} = \frac{\partial \psi(x)}{\partial x} \bigg|_{x^+} \]

\[ \Rightarrow \frac{\partial u(x)}{\partial x} \bigg|_{x^-} e^{j\kappa x^-} + j\kappa u(x^-)e^{j\kappa x^-} = \frac{\partial u(x)}{\partial x} \bigg|_{x^+} e^{j\kappa x^+} + j\kappa u(x^+)e^{j\kappa x^+} \]

\[ \Rightarrow \frac{\partial u(x)}{\partial x} \bigg|_{x^-} = \frac{\partial u(x)}{\partial x} \bigg|_{x^+} \]

\[ \psi(x) = u(x)e^{j\kappa x} \]

\[ \frac{\partial \psi(x)}{\partial x} = \frac{\partial u(x)}{\partial x} e^{j\kappa x} + j\kappa u(x)e^{j\kappa x} \]

\[ B.C.1: \quad u_2(0^-) = u_1(0^+) \quad \Rightarrow \quad A + B = C + D \]

\[ B.C.2: \quad \frac{\partial u_2}{\partial x} \bigg|_0 = \frac{\partial u_2}{\partial x} \bigg|_{0^+} \quad \Rightarrow \quad (\alpha - k)A - (\alpha + k)B - (\beta - k)C + (\beta + k)D = 0 \]

\[ B.C.3: \quad u_1(a) = u_2(-b) \quad \Rightarrow \quad Ae^{j(\alpha-k)a} + Be^{-j(\alpha+k)a} = Ce^{-j(\beta-k)b} + Be^{j(\beta+k)b} \]

\[ B.C.4: \quad \frac{\partial u_1}{\partial x} \bigg|_{x=a} = \frac{\partial u_2}{\partial x} \bigg|_{x=-b} \quad \Rightarrow \quad (\alpha - k)e^{j(\alpha-k)a} + (\alpha + k)e^{-j(\alpha+k)a} \]

\[ = (\beta - k)e^{-j(\beta-k)b} - (\beta + k)e^{j(\beta+k)b} \]
From the above 4 eq, derived from 4 BCs, we obtain the parameter k in relation of the total energy E (through the parameter $\alpha$) and the potential function $V_0$ (through the parameter $\beta$)

Kronig-Penny Model

$$\frac{-(\alpha^2 + \beta^2)}{2\alpha \beta} (\sin \alpha x)(\sin \beta b) + (\cos \alpha a)(\cos \beta b) = \cos k(a + b)$$

$$V(x) = \begin{cases} 
0 & 0 < x < a \\
V_0 & -b < x < 0 
\end{cases}$$

3.1.3 The k-space diagram

$$\alpha = \sqrt{\frac{2mE}{\hbar^2}}, \quad \beta = j\gamma = j\sqrt{\frac{2m(V_0 - E)}{\hbar^2}}, \quad \gamma > 0$$

Case 1: Free particle:
- $bV_0$ is finite value, and $b=0$
- $V_0=0$

$$\beta = \alpha = \sqrt{\frac{2mE}{\hbar^2}}$$
\[-\frac{(\alpha^2 + \alpha^2)}{2\alpha^2}(\sin \alpha \sin \alpha) + (\cos \alpha \cos \alpha) = \cos k(a + b)\]

\[
\cos \alpha \alpha = \cos k \alpha \quad \text{(free particle)} \quad \Rightarrow \quad \alpha = k
\]

\[
\alpha = \frac{2mE}{h^2} = \frac{2m(\frac{1}{2}mv^2)}{h^2} = \frac{mv}{h} = p = k \quad \Rightarrow \quad \sqrt{\frac{2mE}{h^2}} = k
\]

\[
\Rightarrow \begin{cases} 
  p = \hbar k \\
  E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}
\end{cases}
\]

\[p: \text{ particle momentum} \quad k: \text{ wave number}\]

For the case of free particle, \textbf{parabolic relation} is valid between energy \(E\) and momentum \(p\).

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**Case 2: bound electrons in crystal:**

- \(bV_o\) is finite value, but \(b \rightarrow 0\)
- \(V_o \rightarrow \infty \Rightarrow E << V_o\)

Periodic \(\delta\) function potential barrier

\[V(x)\]

Periodic \(\delta\) function potential barrier

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\[p: \text{ momentum of wave motion}\]

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\[
\frac{-(\alpha^2 + \beta^2)}{2\alpha\beta} (\sin \alpha a)(\sin \beta b) + (\cos \alpha a)(\cos \beta b) = \cos k(a + b)
\]

\[
\alpha = \sqrt{\frac{2mE}{h^2}} \quad \Downarrow \quad E << V_o \Rightarrow \beta = j\gamma = j\sqrt{\frac{2m(V_o - E)}{h^2}}, \quad \gamma > 0
\]
decaying wave at barrier region

\[
\frac{\gamma^2 - \alpha^2}{2\alpha\gamma} (\sin \alpha a)(\sinh \gamma b) + (\cos \alpha a)(\cosh \gamma b) = \cos k(a + b)
\]

\[
b \to 0 \Rightarrow \sinh \gamma b \approx \gamma b \quad \& \quad \cosh \gamma b \to 1 \quad \Downarrow \quad \therefore \sin \theta = \frac{1}{2j} [e^{i\theta} - e^{-j\theta}] \quad \cos \theta = \frac{1}{2} [e^{i\theta} + e^{-j\theta}]
\]

\[
\frac{mV_o ba}{h^2} \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a) = \cos ka
\]

\[
P^* \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a) = \cos ka
\]

\[
E - k \text{ equation} \quad \alpha = \sqrt{\frac{2mE}{h^2}}
\]

The above eq does not lend itself to an analytical solution, but must be solved using numerical or graphical techniques to obtain the relation between \(k\), \(E\) and \(V_o\).

\[
\sinh x = \frac{e^x - e^{-x}}{2} \quad \cosh x = \frac{e^x + e^{-x}}{2}
\]

\[
\cosh x = \frac{e^x + e^{-x}}{2}
\]

\[
\sinh x = \frac{e^x - e^{-x}}{2}
\]
The parameter $\alpha$ is related to the total energy $E$ of the particle \[ \alpha = \frac{\sqrt{2mE}}{\hbar} \]
The right figure shows the energy $E$ as a function of the wave number $k$.

The plot shows the concept of allowed energy bands for particle propagating in the crystal lattice.

Since the energy $E$ is discontinuities, we also have the concept of forbidden energy for particles in the crystal.

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**Example 3.2 bandwidth**

Coefficient $P'=10$, potential width $a=5\text{Å}$

\[ f(\alpha a) = P \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a) = \cos \alpha a \]

**Solution**

The lowest allowed band occurs as $\alpha a$ changes from 0 to $\pi$.

For $\alpha a = 0$

\[ P \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a) = +1 \]

Using numerical technique (trial and error), we find $\alpha a = 2.628$

\[ \alpha = \sqrt{\frac{2mE}{\hbar^2}} \Rightarrow \alpha a = \sqrt{\frac{2mE_{\text{upper}}}{\hbar^2}} a = 2.628 \]

\[ E_{\text{lower}} = \frac{(2.628)^2 \hbar^2}{2ma^2} = \frac{(2.628)^2 (1.054 \times 10^{-34})^2}{2(9.11 \times 10^{-31})(5 \times 10^{-10})^2} = 1.68 \times 10^{-19} \text{ J} = 1.053 \text{ eV} \]
For $ka = \pi$, as seen from the figure it happens $\alpha a = \pi$

\[
\alpha a = \sqrt{\frac{2mE_{\text{upper}}}{h^2}} a = \pi
\]

\[
E_{\text{upper}} = \frac{\pi^2 h^2}{2ma^2} = \frac{\pi^2 (1.054 \times 10^{-34})^2}{2(9.11 \times 10^{-31})(5 \times 10^{-10})^2} = 2.407 \times 10^{-19} \text{ J} = 1.50 \text{ eV}
\]

\[
\Delta E = E_{\text{upper}} - E_{\text{lower}} = 1.50 - 1.053 = 0.447 \text{ eV}
\]

\[
P_a \frac{\sin \alpha a}{\alpha a} + (\cos \alpha a) = \cos ka
\]

\[
\cos ka = \cos(ka + 2n\pi) = \cos(ka - 2n\pi)
\]

Displacement of portions of the curve in left figure by $2\pi$ still satisfy the $E-k$ equation
The entire $E$ versus $k$ plot is contained within $-\pi/a < k < \pi/a$.

For free electron, the particle momentum and the wave number $k$ are related by

\[
\text{momentum } p = \hbar k \quad \text{(free electron)}
\]

Given the similarity between the free electron solution and the results of the single crystal, the parameter $\hbar k$ in a single crystal is referred to as the **crystal momentum**, which is not the actual momentum of the electron in the crystal, but is a constant of motion that includes the crystal interaction.

\[
\text{crystal momentum: } \hbar k
\]

### 3.2 Electrical conduction in solids

- For covalent bonding of silicon crystal, each silicon atom is surrounded by 8 valence electrons, 4 from itself, 4 from the 4 nearest Si neighbor.
- For $N$ silicon atoms in the crystal, there are $4N$ energy states in lower valence band and $4N$ energy states in higher conduction band. Each energy state allow only one electron to reside.
- At $T=0K$, all valence electrons are lying in their lowest energy states, valence band, i.e. the valence band is fully occupied and the conduction band is completely empty.
Covalent bond breaking

- At \( T>0K \), a few valence band (VB) electrons may gain enough thermal energy to break the covalent band and jump into conduction band (CB)
  - VB: covalent bonding position
  - CB: elsewhere
- Since the pure semiconductor is neutrally charged, as the negatively charged electron breaks away from its covalent bonding position, a positively charged “empty state” is created in the original covalent bonding position in the VB.

\[ \text{Covalent bond breaking} \]

\[ \text{At } T=0K, \text{ the energy states in the VB in E-k diagram are completely full, and the states in CB are empty (Fig. (a))} \]

\[ \text{At } T>0K, \text{ a few valence band (VB) electrons may gain enough thermal energy to break the covalent band and jump into CB (Fig (b))} \]
### 3.2.3 Drift current

- **N**: total number of flow charge
- **n**: volume density of flow charge
- **A**: cross-sectional area
- **v**: average drift velocity
- **ℓ**: traveling length of carrier per Δt

Flux \( \Phi = \frac{N}{\Delta t} = \frac{nA\ell}{\Delta t} = \frac{nA(v\Delta t)}{\Delta t} = nA v \) \( \text{(#/sec)} \)

Flux density \( \phi = \frac{\Phi}{A} = n v \) \( \text{(#/sec \cdot cm}^2) \)

**Drift current density** \( J = q\phi = qnv_d \) \( \text{(A/cm}^2) \)

\[
J = q\sum_{i=1}^{n} v_i
\]

\( v_i \): the velocity of the \( i \)th charged carrier

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### E-k diagram under external bias

- **Under no external force**, the electron distribution in CB is an even function of \( k \), since the net momentum is zero under thermal equilibrium.

- Under applied force, electrons in CB can gain energy and a net momentum

\[
dE = Fdx = Fvdt
\]

**Figure 3.15** | The asymmetric distribution of electrons in the \( E \) versus \( k \) diagram when an external force is applied.
3.2.3 Electron effective mass

The movement of an electron in a lattice is different from that of an electron in free space.

\[ F_{\text{total}} = F_{\text{ext}} + F_{\text{int}} = ma \]

\( F_{\text{int}} \): due to the interaction between the moving electron and other charged particles, such as ions, protons and else electrons in the lattice.

\[ F_{\text{ext}} = m^* a \]

\( m^* \): effective mass

Which takes into account of the particle mass and the effects of internal forces.

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E-k diagram and particle mass in free space

\[ E = \frac{1}{2} m_o \nu^2 = \frac{p^2}{2m_o} = \frac{(\hbar k)^2}{2m_o} \quad \text{(parabolic curve)} \]

\( p = \hbar k \)

\[ \frac{\partial E}{\partial k} = \frac{2\hbar^2 k}{2m_o} = \frac{\hbar p}{m_o} = \frac{\hbar m_o \nu}{m_o} \]

\( \Rightarrow \) velocity: \( \nu = \frac{1}{\hbar} \frac{\partial E}{\partial k} \) (free electron)

\[ \frac{\partial^2 E}{\partial k^2} = \frac{\partial}{\partial k} \left( \frac{\hbar^2 k}{2m_o} \right) = \frac{\hbar^2}{m_o} \]

\( \Rightarrow \) mass: \( \frac{1}{m_o} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \)

- The first derivative of \( E \) with \( k \) is related to the velocity of free particle.
- The second derivative of \( E \) versus \( k \) is inversely proportional to the mass of free particle.

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Figure 3.7 | The parabolic \( E \) versus \( k \) curve for the free electron.
Electron effective mass & E-k diagram in crystal

**Conduction band**
The energy near the bottom of CB may be approximated by a parabola, just as that of free particle

\[ E - E_c = C_1 k^2, \quad C_1 > 0 \]

**mass:** \[ \frac{1}{m_o} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \]

(free electron)

**effective mass:** \[ \frac{1}{m_n^*} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k^2} \]

(Block electron)

\[ E_c \]

\[ k = 0 \]

\[ k \]

Thus acceleration of Block electron with external force is

\[ F_{ext} = m_n^* a \]

If we apply an electric field, the acceleration is

\[ a = \frac{F_{ext}}{m_n^*} = -\frac{eE}{m_n^*} \]

**Effective mass parameter** is used to relate quantum mechanics and classical mechanics

- The larger the bowing of E-k diagram, the small the effective mass is
3.2.4 Concept of hole

- The empty state is created when a covalent bond is broken.
- The movement of a valence electron into the empty state is equivalent to the movement of a positively charged empty state itself.
- The above positive charge carrier is called “hole.”
- The crystal now has a second equally important charge carrier, hole, that can give rise to a current.

![Diagrams showing the concept of hole]

The drift current in VB

Under external biased voltage, it is the electrons that moving in the VB, not the positively charged ions.

The drift current due to electrons in VB:

\[
J = (-e) \sum_{i \text{ (filled)}} v_i
\]

\[
J = (-e) \sum_{i \text{ (full)}} v_i + (e) \sum_{i \text{ (empty)}} v_i
\]

\[
\therefore J = q \sum_{i=1}^{n} v_i, \quad q = -e \text{ for electron}
\]

\[
q = +e \text{ for + ion}
\]

![Graphs showing the drift current in VB]
\((-e) \sum_{i(full)} v_i = \) (full valence band)

The velocity of individual electron is given

\[ v_e(E) = \frac{1}{\hbar} \frac{\partial E}{\partial k} \]

- The valence band is symmetric in \( k \) and every state in VB is occupied so that every electron with a velocity \( |v| \), there is a corresponding electron with a velocity \(-|v|\)

- Since the valence band is full, the distribution of electrons with respect to \( k \) has no chance to be changed by an external applied. The net drift current density generated from a completely full band electrons, then, is zero

\[ (-e) \sum_{i(full)} v_i = 0 \]

The net drift current density due to electrons in VB

\[ J = (-e) \sum_{i(full)} v_i + (+e) \sum_{i(\text{empty})} v_i = (+e) \sum_{i(\text{empty})} v_i \]

- The net drift current due to electrons in VB is entirely equivalent to placing a positively charged particle in the empty state (assigned as hole) and assuming all other states in the band are neutrally charged

- The associated hole velocity is exactly the velocity of the electron who occupy the empty state
Valence band

The energy near the bottom of VB may be approximated by a parabola, just as that of free particle

\[ E_{v} - E = C_{2}k^{2} \]

\[ \frac{\partial E}{\partial k} = -2C_{2}k \quad (C_{2} > 0), \quad \frac{\partial^{2} E}{\partial k^{2}} = -2C_{2} \]

\[ \Rightarrow \quad \frac{1}{m^{*}_{e}} = \frac{1}{\hbar^{2}} \frac{\partial^{2} E}{\partial k^{2}} = -\frac{2C_{2}}{\hbar^{2}} < 0 \]

An electron moving near the top of valence band behaves as if it has a negative mass

Thus acceleration of Block electron near the top of VB with external force is

\[ F_{ext} = m^{*}_{e}a = (-e)E \quad m_{e}^{*}: \text{negative quantity} \]

We may rewrite

\[ a = \frac{F_{ext}}{m_{e}^{*}} = \frac{F_{ext}}{m_{e}^{*}} > 0 \]

\[ = -\frac{eE}{m_{e}^{*}} + \frac{eE}{m_{p}^{*}} \]

\[ m_{p}^{*} = -m_{e}^{*} \]

\[ \frac{1}{m_{p}^{*}} = \frac{1}{m_{e}^{*}} = -\frac{1}{\hbar^{2}} \frac{\partial^{2} E}{\partial k^{2}} \]

\[ \nu_{h}(E) = -\nu_{e}(E) = -\frac{1}{\hbar} \frac{\partial E}{\partial k} \]
Now we can model VB as having particles with a positive electronic charge and a **positive effective mass**, so it will move in the **same direction** as the direction of **applied field**.

- The new particle is the **hole**.
- The density of hole is the same as the density of empty states in VB.

### 3.2.5 Metals, insulators and semiconductors

- **Insulator**:
  - The allowed bands are either **completely empty** or **completely full**.
  - Since empty band and full band contribute no current at all, the resistivity of an insulator is very large.
  - The bandgap of insulator is usually on the order of 3.5 to 6 eV or larger.

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![Diagram of bands in insulators and semiconductors](image-url)
**Semiconductor:**
- The allowed bands are at conditions either **almost empty** or **almost full**
- Both the electrons in CB and holes in VB can contribute the current
- The bandgap of semiconductor is on the order of 1 eV
- The resistivity of semiconductor can be controlled and varied over many orders of magnitude

**Metal:**
- The band diagram for a metal may be in one of two forms
  - partially full band
  - overlapped conduction and valence bands
- In the case of partially full band, many electrons are available for conduction, so that the material can exhibit a large electrical conductivity
- For overlapped conduction and valence bands, there are large numbers of electrons as well as large numbers of holes can move, so this material can also exhibit a very high electrical conductivity

**Figure 3.21** | Two possible energy bands of a metal showing (a) a partially filled band and (b) overlapping allowed energy bands.
3.3 Extension to three dimensions

- The basic concept of allowed and forbidden energy bands comes from the electrons moving in periodic potential arrangement in crystal lattice.
- For three dimensional crystal, the distance between atoms varies as the direction through the crystal changes.

![Diagram](image)

*Figure 3.22: The (100) plane of a face-centered cubic crystal showing the [100] and [110] directions.*

- The E-k diagram is symmetric in k so that no new information is obtained by displaying the negative axis.
- In following plot of E-k diagrams, E-k diagrams at two directions are plotted. [100] portion of the diagram with +k to the right and [111] portion of the diagram with +k to the left are plotted.
- **Direct bandgap**
  the minimum conduction band is at $k=0$ so that the transitions for electron between CB & VB can take place with no change in crystal momentum

- **Indirect bandgap**
  the minimum conduction band occurs not at $k=0$ so that the transitions for electron between CB & VB includes an interaction with the crystal

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**Effective mass concept in 3-dim crystal**
3.4.1 Density of states for free electron

- To determine the density of allowed quantum states as a function of energy, we need to consider an appropriate mathematical model.
- Consider a free electron confined to a three-dimensional cubic with length $a$ with infinite potential well:

$$V(x, y, z) = 0 \quad \text{for } 0 < x < a$$
$$\quad \text{for } 0 < y < a$$
$$\quad \text{for } 0 < z < a$$
$$V(x, y, z) = \infty \quad \text{elsewhere}$$

Using the separation of variables technique in 3 dimensional Schrodinger’s wave equation, we can have:

$$\frac{2mE}{\hbar^2} = k^2 = k_x^2 + k_y^2 + k_z^2$$

Two-dimensional plot of allowed quantum states in k space

$$k_x = n_x \frac{\pi}{a}, \quad k_y = n_y \frac{\pi}{a}, \quad k_z = n_z \frac{\pi}{a}$$

$n_x, n_y, n_z$: positive integers

Positive and negative values of $k_x, k_y$ or $k_z$ have the same energy and represent the same quantum state.

The volume $V_k$ of a single quantum state in k-space is:

$$V_k = \left(\frac{\pi}{a}\right)^3$$
The density of quantum state in k-space for whole cubic box is

\[ g_T(k) dk = 2\left(\frac{1}{8}\right) \frac{4\pi k^2 dk}{V_k} \]

2: due to two spin states allowed for each quantum state
1/8: due to the positive values of \( k_x, k_y, \) and \( k_z \)

\[ g_T(k) dk = \frac{k^2 dk}{\pi^2} \cdot a^3 \]

\[ g_k(k) dk = \frac{k^2 dk}{\pi^2} \cdot a^3 \Rightarrow g(E)dE = \frac{4\pi(2m)^{3/2}}{h^3} \sqrt{E}dE \]

\[ \therefore k^2 = \frac{2mE}{\hbar^2}, \quad k = \frac{1}{\hbar} \sqrt{2mE} \]

\[ dk = \frac{1}{\hbar} \sqrt{2m} \cdot \frac{1}{2} \cdot \frac{1}{\sqrt{E}} dE = \frac{1}{\hbar} \sqrt{\frac{m}{2E}} dE \]

The number of energy states for whole cubic box between \( E \) and \( E + dE \), i.e., between \( k \) and \( k + dk \) is given by

\[ g_k(k) dk = \frac{k^2 dk}{\pi^2} \cdot a^3 = g(E)dE \]

\[ g(E)dE = \frac{2mE}{\hbar^2} \cdot \frac{1}{\pi^2} \cdot \frac{1}{\hbar} \sqrt{\frac{m}{2E}} dE \cdot a^3 = \frac{4\pi a^3}{h^3} \cdot (2m)^{3/2} \cdot \sqrt{E}dE \]
The density of quantum states per unit energy per unit volume of the crystal is given by

\[ g(E)dE = \frac{g_1(E)dE}{V} = \frac{g_1(E)dE}{a^3} \]

where \( g_1(E) \) is the density of states per volume and \( V \) is the volume. The density of states is given by

\[ g(E)dE = \frac{4\pi(2m)^{3/2}}{h^3} \sqrt{E}dE \]

- The density of states is proportional to the energy \( E \). As the energy of the free particle becomes large, the number of available quantum states increases.
- The density of states is dependent on the mass of the free particle.

---

**Example 3.3 Density of states**

Calculate the total density of states for free electron per unit volume with energies between 0 and 1 eV.

\[ N = \int_0^{1\text{eV}} g(E)dE = \left. \frac{4\pi(2m)^{3/2}}{h^3} \sqrt{E} \right|_0^{1\text{eV}} \]

\[ N = \frac{4\pi(2m)^{3/2}}{h^3} \cdot \frac{2}{3} \cdot E^{3/2} \]

\[ N = \frac{4\pi[2 \cdot (9.11 \times 10^{-31})]}{(6.625 \times 10^{-34})^3} \cdot \frac{2}{3} \cdot (1.6 \times 10^{-19})^{3/2} = 4.5 \times 10^{27} \text{ m}^{-3} \]

\[ N = 4.5 \times 10^{21} \text{ states/cm}^{-3} \]

- The density of states is typically a large number ranging from \( 10^{18} \) to \( 10^{22} \) cm\(^{-3}\).
- The density of quantum states in semiconductor is usually less than the density of atoms in semiconductor crystal.
3.4.2 Density of states for semiconductor

The parabolic relationship between energy and momentum of a free electron is

\[ E = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \]

The E-k curve near k=0 at conduction band can be approximated as a parabola, so we have

\[ E - E_c = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \]

The density of states in CB is

\[ g_c(E) dE = \frac{4\pi(2m_n^*)^{3/2}}{\hbar^3} \sqrt{E - E_c} \ dE \]

Similarly, the E-k parabolic relationship for a free hole in VB

\[ E_V - E = \frac{p^2}{2m_p^*} = \frac{\hbar^2 k^2}{2m_p^*} \]

The density of states for holes (electrons) in VB is

\[ g_v(E) dE = \frac{4\pi(2m_p^*)^{3/2}}{\hbar^3} \sqrt{E_V - E} dE \]
3.5 Statistical mechanics

- In dealing with large numbers of particles, we are interested only in the statistical behavior of the group as a whole rather than in the behavior of each individual particle.
- There are three distribution laws determining the distribution of particles among available energy states.

- **Maxwell-Boltzmann distribution**
  - Particles are distinguishable
  - No limit to the number of particles allowed in each energy state
  - The exemplary case is low-pressure gas molecules in a container

- **Bose-Einstein distribution**
  - Particles are indistinguishable
  - No limit to the number of particles allowed in each energy state
  - The exemplary case is photon

- **Fermi-Dirac distribution**
  - Particles are indistinguishable
  - Only one particle is permitted in each energy state
  - The exemplary case is electrons in crystal
3.5.2 The Fermi-Dirac Probability Function

For $i$th energy level with $g_i$ quantum states, only one particle is allowed in each state.

First particle: $g_i$ ways of choosing to place the particle.

Second particle: $(g_i - 1)$ ways of choosing to place the particle.

$N_i$ particle: $[g_i - (N_i - 1)]$ ways of choosing to place the particle.

Then the total number of ways of arranging $N_i$ particles in the $i$th energy level is

$$(g_i)(g_i - 1) \cdots (g_i - (N_i - 1)) = \frac{g_i!}{(g_i - N_i)!}$$

Since the particles are indistinguishable, the interchange of any two electrons does not produce a new arrangement.

The actual number of independent ways to distribute the $N_i$ particles in the $i$th level is

$$W_i = \frac{g_i!}{N_i!(g_i - N_i)!}$$
\[
\frac{N(E)dE}{g(E)dE} = f_E(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)} \quad (N(E) < g(E))
\]

\(N(E)dE\) (number density): Number of particles per unit volume per unit energy \((E \text{ to } E+dE)\)

\(g(E)dE\): number of quantum states per unit volume per unit energy

Meaning of Fermi energy

At \(T=0K\),

- The probability of a quantum state being occupied is unity for \(E<E_f\)
- The probability of a quantum state being occupied is zero for \(E>E_f\)

\[
f_E(E) = \begin{cases} 
1 & \text{for } E < E_f \\
0 & \text{for } E > E_f 
\end{cases}
\]

\(f_E(E) = 0 \quad \text{for } E > E_f\)
\(f_E(E) = 1 \quad \text{for } E < E_f\)
3.5.3 Features of Fermi-Dirac Function

- For $T>0K$
  - The probability of a state being occupied at $E=E_f$ is always $\frac{1}{2}$

\[
f_E(E) = \frac{1}{1 + \exp(0)} = \frac{1}{2}
\]

\[f(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)} \approx \frac{1}{1 + \exp\left(\frac{3kT}{kT}\right)} = \frac{1}{1 + 20.09} = 0.0474\%
\]

At energy above $E_f$, the probability of a state being occupied by an electron becomes significantly less than unity.

---

**Example 3.6 3kT above the Fermi-energy**

\[f(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)} \approx \frac{1}{1 + \exp\left(\frac{3kT}{kT}\right)} = \frac{1}{1 + 20.09} = 0.0474\%
\]

At energy above $E_f$, the probability of a state being occupied by an electron becomes significantly less than unity.
**Example 3.7  99% probability**

Assume Fermi energy is 6.25 eV, Calculate the temperature at which there is 1% probability that a state 0.30 below the Fermi energy level will not contain an electron

\[
1 - f_E(E) = 1 - \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)}
\]

\[
0.01 = 1 - \frac{1}{1 + \exp\left(-\frac{0.30}{kT}\right)}
\]

\[
\Rightarrow kT = 0.06529\text{eV} \Rightarrow T = 756\text{K}
\]

\[
k = 1.38 \times 10^{-23} \text{J/K} = 8.62 \times 10^{-5} \text{eV/K}
\]

---

**Maxwell-Boltzmann Approximation**

\[
f_E(E) = \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)}
\]

When \(E - E_f > kT\), the exponential term in the denominator is much greater than the unity

\[
f_E(E) \approx \exp\left(\frac{E - E_f}{kT}\right) \quad \text{for} \quad E - E_f > 3kT
\]

\[
kT = 0.026 \text{eV at } T = 300\text{K}
\]

- The Fermi-Dirac probability for \(E - E_f > 3kT\) can be approximated by Boltzmann distribution
- For \(E - E_f > 3kT\), the Boltzmann approximation is slightly larger than the Fermi-Dirac curve with inaccuracy less than 5%
Example 3.8 3kT

Calculate the energy at which the difference between Boltzmann approximation and the Fermi-Dirac function is 5%

\[
\exp\left(-\frac{E - E_f}{kT}\right) - \frac{1}{1 + \exp\left(\frac{E - E_f}{kT}\right)} = 0.05
\]

\[
1 \approx \exp\left(\frac{E - E_f}{kT}\right) \cdot \left\{1 + \exp\left(\frac{E - E_f}{kT}\right)\right\} - 1 = 0.05
\]

\[
\exp\left(-\frac{E - E_f}{kT}\right) = 0.05 \quad \Rightarrow \quad E - E_f = kT \ln\left(\frac{1}{0.05}\right) \approx 3kT
\]