The Figures are mostly from Prof. Kasap’s book but they have been modified and I have added my additional notes as well. I have added my additional notes as well.
1. **Hydrogen Molecule – Molecular Orbitals Theory of Bonding**
2. **Scattering Electrons in an Atom - Sec. 4.1**
3. **Band Theory of Solids …Energy Band Formation - Sec. 4.2**
4. **Semiconductors – Section 4.3**
5. **Electrons Effective Mass – sec. 4.4**
6. **Density of States in An Energy band – Sec. 4.5**
7. **Statistics: Collection of Particles – Boltzman’s Statistics- sec. 4.6**
8. **Quantum Theory of Metals – sec. 4.7**
9. **Fermi Energy Significance – sec. 4.8**
10. **Thermionic Emission- sec. 4.9**
11. **Phonons –Sec. 4.10**
12. **Brillouin Zones – Band Theory of Metals – section 4-11**
Molecular Orbitals - Hydrogen Atoms

1. Atomic State
2. Bonding
3. Antibonding

**Bond Formation Between Two Hydrogen Atoms**

*may be explained by the Behavior of Electrons within the molecules*

1. **We can use** Molecular Orbital, $\psi$ as a function of separation Distance “$r$”

2. **In a molecule Pauli’s Exclusion Principle** is obeyed, so opposite spins within the molecule. 
   (cannot have individual 1s states from each hyd. atom)

3. **The atomic $\psi_{1s}$ orbitals overlap**

4. **Also Two Atomic wave Functions are generated with different Energies and Quantum Numbers.**

5. **For the two Hydrogen atoms**

   \[ \psi_{\sigma} = \psi_{1s}(r_A) + \psi_{1s}(r_B) \]
   \[ \psi_{\sigma^*} = \psi_{1s}(r_A) - \psi_{1s}(r_B) \]

6. **These are Obtained by Linear combination of two identical orbitals $\psi_{1s}$** … This can achieved by “LCAO” = Linear Combination of Atomic Orbitals Method.
Hydrogen Molecule

Bonding and Anti-bonding Probabilities

(a) Electron probability distributions for bonding and antibonding orbitals, \( \psi_\sigma \) and \( \psi_{\sigma^*} \). (b) Lines represent contours of constant probability (darker lines represent greater relative probability).

Electron Density Map

JUPITER

He+H (Liq. Metallic)

Bond Formation Between Two Hydrogen Atom may be explained by the behavior of electrons within the molecules.

- The \( \psi_\sigma \) is symmetric function and has high magnitude.
- The \( \psi_{\sigma^*} \) is antisymmetric function and has low magnitude.
- Resulting electron probability distribution is:
  \[
  |\psi_\sigma|^2 \quad \text{and} \quad |\psi_{\sigma^*}|^2
  \]
  - are shown in Fig. Above (Right) has a node between atom. i.e. bond does not exist.
  \[
  |\psi_\sigma|^2 \quad \text{and} \quad |\psi_{\sigma^*}|^2
  \]
- The electrostatic Potential Energy “PE” energy \( \psi_\sigma \) and the thus total energy will be lower than \( \psi_{\sigma^*} \), as well than for individual Atoms.

Fig. 4.14: The interior of Jupiter is believed to contain liquid hydrogen which is metallic (drawing adapted from T. Hey and P. Walters, *The Quantum Universe*, Cambridge University Press, 1988; Fig. 7.1, p. 96)

MSE 433 Chapter 4. Chandra
True Wave Functions in $H_2$ molecules may be determined by Schrödinger equation:

1. We use $\psi_\sigma$ and $\psi_\sigma^*$ in terms of Potential Energy function ($V$) in H-H system
2. Electron – Electron and Proton – Proton Repulsion $\rightarrow$ PE as + Positive Contribution

REPULSIVE PART OF $H_2$

BONDING ENERGY DIAGRAM

Multi-atoms Band Formation

Single Atom Discrete levels

Interatomic Separation [R]
Continuing with the Schrödinger equation:

1. We now have attractive forces (PE Diagram) $\psi_\sigma$ in terms of Potential Energy function ($V$) in H-H system.

2. Electron – Electron and Proton – Proton Attraction $\rightarrow$ PE as – Negative Bonding Contribution
Notes:

- Energy vs Interatomic distance - Equilibrium
- Splitting of States to form a molecule as they approach each other. One can have Molecular Hydrogen

Energies for Hydrogen Atom Pl.
see Fig. 3.23 (Chap. 3 for details. Bond energy is negative (eV).
Fig. 4.3: Electron energy in the system comprising two hydrogen atoms. (a) Energy of $\psi_\sigma$ and $\psi_{\sigma^*}$ vs. the interatomic separation, $R$. (b) Schematic diagram showing the changes in the electron energy as two isolated H atoms, far left and far right, come to form a hydrogen molecule.
• **Splitting of one Atom Energy level to form a Molecule is equivalent to Splitting of Resonant Frequency RLC in an inductive coupling**

• **When 2 RLC are coupled (driven by Ac Voltage) then the resonant Frequency: \( \omega \rightarrow \omega_1 + \omega_2 \)**

• **Due to mutual Inductance that couples the 2 circuits.**

• **This can viewed as Analogy for splitting of levels ; one above and one below to that of the single atoms**

**Resonant Frequency Analogy of Splitting of Energy Levels**

Fig. 4.4: (a) There is one resonant frequency, \( \omega_0 \), in an isolated LCR circuit. (b) There are two resonant frequencies in two coupled LCR circuits. One below and the other above \( \omega_0 \).

Why is “Helium” gas not in a molecular Form??

1. Because “He” has 2 electron in 1s shell.
2. When these atoms combine the 4 electrons distribute themselves in Bonding and Antibonding states→ System Energy is not Decreased

He atom has 2 el/atom. Quantum mechanical calculations show that Antibonding $E_{\sigma^*}$ shifts higher than $E_{\sigma}$, so no molecular He.

Fig. 4.3: Electron energy in the system comprising two hydrogen atoms. (a) Energy of $\psi_{\sigma}$ and $\psi_{\sigma^*}$ vs. the interatomic separation, $R$.
(b) Schematic diagram showing the changes in the electron energy as two isolated H atoms, far left and far right, come to form a hydrogen molecule.

03/23/2006

**H-F bond**

**H atom (1) -1/2 Empty $\psi_{1s}$ orbital (only one electron)**

**F atom (9) – 1s 2s are full, 2p shell is partially full: $1/2 p_x$ empty, but full $p_y$ and $p_z$.**

Fig. 4.6: H has one half empty $\psi_{1s}$ orbital. F has one half empty $p_x$ orbital but full $p_y$ and $p_z$ orbitals. The overlap between $\psi_{1s}$ and $p_x$ produces a bonding orbital and an antibonding orbital. The two electrons fill the bonding orbital and thereby form a covalent bond between H and F.

Band Theory of Solids

3 Molecular Orbital Configuration - Simplified

Energy Bond Formation

1. We bring 3 Hydrogen together and see if this is a stable or unstable situation?

2. We generate 3 separate Molecular Orbital Functions from $\psi_{1s}$ State:

   $\psi_a = \psi_{1s}(A) + \psi_{1s}(B) + \psi_{1s}(C)$

   $\psi_b = \psi_{1s}(A) - \psi_{1s}(C)$

   $\psi_c = \psi_{1s}(A) - \psi_{1s}(B) + \psi_{1s}(C)$

   where $\psi_{1s}(A), \psi_{1s}(B), \psi_{1s}(C)$ are atomic wave functions centred around atoms A, B, and C.

Fig. 4.7: (a) Three molecular orbitals from three $\psi_{1s}$ atomic orbitals overlapping in three different ways. (b) The energies of the three molecular orbitals labeled as $a$, $b$ and $c$ in a system with 3 H atoms (highly simplified).

Band Theory of Solids (Cont’d)

\[ H_3 \text{ has one extra electron and raises the energy level as compared to 2 electrons...thus } H_2 \text{ is more stable than } H_3 \]

Fig. 4.7: (a) Three molecular orbitals from three \( \psi_{1s} \) atomic orbitals overlapping in three different ways. (b) The energies of the three molecular orbitals labeled as \( a \), \( b \) and \( c \) in a system with 3 H atoms (highly simplified).


Three Hydrogen Atoms

Two Hydrogen Atoms
Energy Bands in Solids - Example Li (At. No. 3)

Band Overlaps in Metals

Fig. 4.8: The formation of a 2s-energy band from the 2s-orbitals when \( N \) Li atoms come together to form the Li solid. The are \( N \) 2s-electrons but \( 2N \) states in the band. The 2s-band therefore is only half full. The atomic 1s orbital is close to the Li nucleus and remains undisturbed in the solid. Thus each Li atom has a closed K-shell (full 1s orbital).

1. 2s electrons in Li involved in Bonding
2. Assume Avo. No. of Atoms \((N \sim 10^{23})\)
3. The single 2s energy Level split into \( 10^{23} \) finely separated energy levels
4. \( \frac{1}{2} \) the levels are full due to Pauli’s Exclusion Principle \((N/2)..<\)these levels are so fine one assume them be in continuum!!
Energy Bands in Solids - with more Electrons

Band Overlaps in Metals

Band Overlap representations – Note the formation of multi-atom solid

1. The 2p levels, as well as the higher levels 3s, and others may provide “Extended bands”

2. The top of the 2s Band is filled and overlaps with 2p and 3s... Thus it extends to the to about work function of the material (\(\phi\))

3. The 3s band is unusually higher than the Vacuum level thus the electron leaves the solid in vacuum before it reach the top of the 3s band!!!

**Band Overlap representations**

**Fermi Level and $\phi$**

---

**Important Reference Energy Considerations to Estimate Fermi Levels and Work Function**

Concept $\Phi$ – For removal of electron in free space or vacuum

1. **At $T= 0K$ electrons do not have sufficient thermal energy to excite to the higher levels**

2. **So all the electrons pair (Pauli’s exclusion Principle)**

3. **To fill levels up to $E_{FO}$ @ $T= 0K$.

---

**Fig. 4.11: Typical electron energy band diagram for a metal**

All the valence electrons are in an energy band which they only partially fill. The top of the band is the vacuum level where the electron is free from the solid ($PE = 0$).

---


Table 4.1 The Fermi energy and work function of selected metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ag</th>
<th>Al</th>
<th>Au</th>
<th>Cs</th>
<th>Cu</th>
<th>Li</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Φ (eV)</td>
<td>4.26</td>
<td>4.28</td>
<td>5.1</td>
<td>2.14</td>
<td>4.65</td>
<td>2.3</td>
<td>3.7</td>
<td>2.75</td>
</tr>
<tr>
<td>$E_{F_0}$ (eV)</td>
<td>5.5</td>
<td>11.7</td>
<td>5.5</td>
<td>1.58</td>
<td>7.0</td>
<td>4.7</td>
<td>7.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

**Summary Slide**

Fig. 4.8: The formation of a 2s-energy band from the 2s-orbitals when \( N \) Li atoms come together to form the Li solid. The 2s-electrons but 2\( N \) states in the band. The 2s-band therefore is only half full. The atomic 1s orbital is close to the Li nucleus and remains undisturbed in the solid. Thus each Li atom has a closed K-shell (full 1s orbital).

**Energy Bands in Solids - with more Band Overlaps in Metals**

Fig. 4.9: As solid atoms are brought together from infinity, the atomic orbitals overlap and give rise to bands. Outer orbitals overlap first. The 3s orbitals give rise to the 3s band, 2p orbitals to the 2p band and so on. The various bands overlap to produce a single band in which the energy is nearly continuous.

**Band Overlap representations – Note the formation of muti-atom solid**

Fig. 4.10: In a metal the various energy bands overlap to give a single band of energies that is only partially full of electrons. There are states with energies up to the vacuum level where the electron is free.

**Work Function Concept \( \Phi \) – For removal of electron in free space or vacuum**

Fig. 4.11: Typical electron energy band diagram for a metal. All the valence electrons are in an energy band which they only partially fill. The top of the band is the vacuum level where the electron is free from the solid (\( PE = 0 \)).
Fermi level Concepts for Movement of Electron to Produce Current Flow

$E_B = 0 \text{ ev}$

$E_{F0} (\text{Li}) = 4.7 \text{ eV}$

**With No Potential**

(a)

(b)

(c)

**With Applied Potential x-direction**

Electrons have Momentum but there are collisions with lattice atoms

Energy band Tilt with an Applied Potential

Fig. 4.12 (a) Energy band diagram of a metal. (b) In the absence of a field, there are as many electrons moving right as there are moving left. The motions of two electrons at each energy can cancel each other as for $a$ and $b$.

(c) In the presence of a field in the $-x$ direction, the electron $a$ accelerates and gains energy to $a'$ where it is scattered to an empty state near $E_{F0}$ but moving in the $-x$ direction. The average of all momentum values is along the $+x$ direction and results in a net electrical current.

1. **Without Potential** Electrons in the metal in $+x$ and $-x$ direction and motion of electron cancel out at each energy level for $a$ and $b$.

2. **In presence of the Field** in the $-x$ direction: The average momentum value is in the $+$ leading to net conduction or electrical current flow in the $+x$-direction.

3. **Finally**, Energy of the electron increases as: $E = \frac{p^2}{2m_e}$

4. **Typically lattice vibration** have small energies but high momentum.
5. The momentum of the electron at level a’ is flipped -x direction and motion of electron moves back towards the level b’

6. Thus a current flow in the -x direction, along the electric field.

7. Under steady State the electron from a’ replenishes the electron at b’ level

8. Finally electron Above “b’” level are moving to the right and their momentum is not cancelled out…so net motion to the right.

9. So electron motion occurs near the Fermi level between a’-b’ with energies =10^{-6} eV.

10. Compare this with Fermi level, typically 2-10 eV.. very large!!

11. So, for practical purposes the levels a’ and b’ are Fermi level.
Table 4.2  The effective mass $m_e^*$ of electrons in some metals.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ag</th>
<th>Au</th>
<th>Bi</th>
<th>Cu</th>
<th>K</th>
<th>Li</th>
<th>Na</th>
<th>Ni</th>
<th>Pt</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>$m_e^*/m_e$</td>
<td>0.99</td>
<td>1.10</td>
<td>0.047</td>
<td>1.01</td>
<td>1.12</td>
<td>1.28</td>
<td>1.2</td>
<td>28</td>
<td>13</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 4.5  Debye temperatures ($T_D$), heat capacities and thermal conductivities of selected elements. $C_m$, $c_s$ and $\kappa$ are at 25 °C. $T_D$ is obtained by fitting the Debye curve to the experimental molar heat capacity data at the point $C_m = 1/2(3R)$.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Ag</th>
<th>Be</th>
<th>Cu</th>
<th>Diamond</th>
<th>Ge</th>
<th>Hg</th>
<th>Si</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_D$ (K)</td>
<td>215</td>
<td>1000</td>
<td>315</td>
<td>1860</td>
<td>360</td>
<td>100</td>
<td>625</td>
<td>310</td>
</tr>
<tr>
<td>$C_m$ (J K$^{-1}$ mol$^{-1}$)</td>
<td>25.6</td>
<td>16.46</td>
<td>24.5</td>
<td>6.48</td>
<td>23.38</td>
<td>27.68</td>
<td>19.74</td>
<td>24.45</td>
</tr>
<tr>
<td>$c_s$ (J K$^{-1}$ g$^{-1}$)</td>
<td>0.237</td>
<td>1.825</td>
<td>0.385</td>
<td>0.540</td>
<td>0.322</td>
<td>0.138</td>
<td>0.703</td>
<td>0.133</td>
</tr>
<tr>
<td>$\kappa$ (W m$^{-1}$ K$^{-1}$)</td>
<td>429</td>
<td>183</td>
<td>385</td>
<td>1000</td>
<td>60</td>
<td>8.65</td>
<td>148</td>
<td>173</td>
</tr>
</tbody>
</table>


Fig. 4.13 Conduction in a metal is due to the drift of electrons around the Fermi level. When a voltage is applied, the energy band is bent to be lower at the positive terminal so that the electron's potential energy decreases as it moves towards the positive terminal. ($E_x$ is the electric field.)

Another way to Conceptualize the Movement of Electron for Current Flow – Fermi Sphere Concept (velocities $v_x$, $v_y$)

$\sigma = \frac{N e^2 l_F}{m^* v_F}$

Where, $N =$ No. of Conduction electrons

$l_F =$ Mean free path

$v_F =$ Velocity of electron at F. Surface.

Displacement of Fermi Sphere with Electric Field showing the shift of the velocity sphere, and the (low) number of states or Conduction Electrons in this Yellow Region. Majority Cancel…. Only the electron near Fermi Energy Conduct in the Crescent.
Fig. 4.12 (a) Energy band diagram of a metal. (b) In the absence of a field, there are as many electrons moving right as there are moving left. The motions of two electrons at each energy can cancel each other as for \( a \) and \( b \). (c) In the presence of a field in the \(-x\) direction, the electron \( a \) accelerates and gains energy to \( a' \) where it is scattered to an empty state near \( E_{\text{FO}} \) but moving in the \(-x\) direction. The average of all momenta values is along the \(+x\) direction and results in a net electrical current.

**SUMMARY PAGE**

Another way to Conceptualize the Movement of Electron for Current Flow –Fermi Sphere Concept (velocities \( v_x, v_y \))

\[
\sigma = Ne^2l_F/m*v_F
\]

Where, \( N \) = No. of Conduction electrons
\( l_F \) = Mean free path
\( v_F \) = Velocity of electron at F. Surface.

Ref: Solid State Physics by Omar

Fig. 4.13 Conduction in a metal is due to the drift of electrons around the Fermi level. When a voltage is applied, the energy band is bent to be lower at the positive terminal so that the electron's potential energy decreases as it moves towards the positive terminal. \((E_x\) is the electric field.)


Effective Mass in Vacuum and Crystal

When an Electric Field (Ex) is Applied

- An electron near the Fermi level can gain energy from this applied electric field and move into higher energy levels.
- The mass of an electron may be defined as “me” if electron travels in vacuum.
- If the electron travels in a crystal the mass of the electron is defined as \( m_e^* \) due to periodic potential resulting from collisions with the ion cores.
- \( F = m_e a \) (acceleration is not strictly valid in a crystal, but OK in vacuum).
- When an external electric field in vacuum is applied the electron will accelerate by an amount:

\[
a_{\text{vac}} = \frac{F_{\text{ext}}}{m_e}.
\]

- When the same electric field is applied inside a crystal (\( F_{\text{int}} \) = Internal Forces). The acceleration, \( a_{\text{cryst}} \)

\[
a_{\text{cryst}} = \frac{F_{\text{ext}} + F_{\text{int}}}{m_e}.
\]

\[
a_{\text{cryst}} = \frac{F_{\text{ext}}}{m_e^*}.
\]

\[
F_{\text{ext}} = eE_x \text{ in } x-\text{direction}
\]

\[
a_{\text{vac}} = \frac{F_{\text{ext}}}{m_e}
\]

\[
a_{\text{cryst}} = \frac{F_{\text{ext}}}{m_e^*}
\]

Fig. 4.19: (a) An external force \( F_{\text{ext}} \) applied to an electron in vacuum results in an acceleration \( a_{\text{vac}} = F_{\text{ext}} / m_e \). (b) An external force \( F_{\text{ext}} \) applied to an electron in a crystal results in an acceleration \( a_{\text{cryst}} = F_{\text{ext}} / m_e^* \). (\( E_x \) is the electric field.)


All the internal forces are Incorporated in the effective mass.
Table 4.2  The effective mass $m_e^*$ of electrons in some metals.

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<td>1.2</td>
<td>28</td>
<td>13</td>
<td>0.85</td>
</tr>
</tbody>
</table>

- Effective Mass in metals with Not full valence Bands may still be “$m_e$” but we still use $m_e^*$ for the crystal
- Semiconductors the effective mass is negative - that means the electrons decelerate under an applied electric field …which can be explained by the formation of holes (by the displacement of electron) traveling in the opposite direction. More details later.
- $m_e^* = \hbar^2/2\pi [d^2E/dk^2]$ where magnitude of $k$ vector is $k = 2\pi/l$ or $k = 2\pi/n$, where $a$ is d-spacing (related lattice parameter), and $n=1,2,3,$ quantum numbers. (see page 399 Prof. Kasap’s book)….very important as the crystal plane is now involved!!! Pl. see the next page.
- We can write a relationship $k= np/d$ related to the crystal

- The $m_e^*$ is obtained from Schrödinger Equation …it is complex!!
- In metals $m_e^*$ is nearly equal $m_e$  Ex: Cu the $m_e^*=m_e$
- But for Li: $m_e^*= 1.28 \ m_e$ (positive)
**Velocity and Acceleration of Bloch electron in a crystal**

*Velocity* of an Electron in Vacuum and Crystal

Consider a Free Electron: \( p = \text{Momentum} \)

Velocity, \( v = \frac{\hbar \cdot k}{m_o} = \frac{p}{m_o} \)

Thus velocity \( \propto \) wave vector, \( |k| = \frac{2\pi}{\lambda} \)

- **Free Electron:** velocity is parallel to vector \( k = \frac{2\pi}{\lambda} \)
- **Block Electron:** velocity is not necessary to follow parallel is not vector \( k \)

**Fermi Velocity Spheres**

- **Free Electron**
- **Bloch Electron**
Consider an Elecron Bound in a metallic crystal →

The velocity is also a function of \( k \) but the functional relationship is different: 
The derivation involves group velocities etc.
angular velocites, too detailed refer to a Solid State Physics text
Consider an Electron Bound in the a metallic crystal

The velocity is also a function of \( \vec{k} \)
but the functional relationship is different:
The derivation involves group velocities etc.,
angular velocities, too detailed refer to
Omar's Solid State Physics text

In One dimensional Case: Velocity, \( v = \frac{1}{\hbar} \left( \frac{\partial E}{\partial k} \right) \) ...Eq.1

**Acceleration is same as derivative of velocity:**

Thus \( a = \frac{dv}{dt} \)

Now we bring in wave vector:

\[ a = \frac{dv}{dt} \cdot \frac{dk}{dt} \]

......but if we substitute Eq.No.1 (above),

\[ a = \frac{dv}{\hbar} \cdot \frac{d^2 E}{dk^2} \cdot F \]

also, \( \hbar \cdot \frac{dk}{dt} = eE = F \) (Electric Force)

**known as acceleration Theorem**
This is the same form as the Newtons second Law: and we define this as dynamical effective Mass:

\[ m^* = e_m^* = \frac{\hbar^2}{\left( \frac{d^2 E}{dk^2} \right)} \]

\( \frac{d^2 E}{dk^2} \Rightarrow \text{LARGE} \)

Small Mass

Large Mass

\( \frac{d^2 E}{dk^2} \Rightarrow \text{SMALL} \)

-k [-1-10]

+k [110]
$kc = \text{Inflection Point}$

**Effective Mass of Electron $m^*$ vs $k$**

- $k_c$ (Inflection Point)
- $\pm \pi/a$
- $m^*$
- $+k [110]$
- $-k [-1-10]$
1. Hydrogen Molecule – Molecular Orbitals Theory of Bonding
2. Scattering Electrons in an Atom - Sec. 4.1
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4. Semiconductors – Section 4.3
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9. Fermi Energy Significance – sec. 4.8
10. Thermionic Emission- sec. 4.9
11. Phonons –Sec. 4.10
Energy Levels for 1,2,3 and 4 Valence Elements

Top Bands are called Conduction Bands and they are empty (i.e. no electrons reside in case metals)

**METALS**

- **Na⁺¹**
  - At. No. 11
- **Mg⁺²**
  - At. No. 12
- **Al⁺³**
  - At. No. 13

Forbidden Gaps ...means electrons do not have Speeds in that regions

**SEMICONDUCTORS**

- **Si⁺⁴**
  - At. No. 14

Conduction Band

Valence Band

VALENCE BAND IS COMPLETELY FULL OF ELECTRONS

CONDUCTION BAND IS EMPTY(@ 0°K)

Top Bands are called Conduction Bands and they are empty (i.e. no electrons reside in case metals)
Energy Levels for 1, 2, 3 and 4 Valence Elements

Top Bands are called Conduction Bands and they are empty (i.e. no electrons reside in case metals)

**METALS**

**SEMICONDUCTORS**

CONDUCTION BAND IS EMPTY (@ 0°K)

VALENCE BAND IS COMPLETELY FULL OF ELECTRONS

Forbidden Gaps ...means electrons do not have speeds in that regions
Si (14 electrons –sp³ hybrid)

Sp³ Hybrid in Diamond Structure Si. Also Applies to C Diamond structure.

Hypothetical (but Incorrect) Electronic structure of Si (Diamond)

BONDING IN SILICON CRYSTAL STRUCTURE
Fig. 4.15: Hypothetical (but Incorrect) Electronic structure of Si (Diamond)

Fig. 4.16: Sp^3 Hybrid in Diamond Structure Si. Also Applies to C Diamond structure.

Fig. 4.17: (a) Formation of energy bands in the Si crystal first involves hybridization of 3s and 3p orbitals to four identical ψ_{hyb} orbitals which make 109.5° with each other as shown in (b). (c) ψ_{hyb} orbitals on two neighboring Si atoms can overlap to form ψ_B or ψ_A. The first is a bonding orbital (full) and the second is an antibonding orbital (empty). In the crystal ψ_B overlap to give the valence band (full) and ψ_A overlap to give the conduction band (empty).
**Density of States in An Energy band and Thermal Excitation at Room Temperature**

**Completely Filled Valence Bands for Si^{+4}**

**Fig. 4.18:** Energy band diagram of a semiconductor. CB is the conduction band and VB is the valence band. At 0 K, the VB is full with all the valence electrons.

Fig. 4.20: (a) This arbitrary atom in a single plane has 4 nearest neighbors. Isolated from others, this system of 5 interacting atoms would have 5 split energy levels with the widest energy separation; the interaction is between nearest neighbors. (b) There are eight 4th-neighbors on this plane. In isolation from the rest, this 9-atom system would have 9 split energy levels which are narrowly separated as the atoms are further isolated. (c) In the crystal there are hundreds and thousands of distant neighbors so the number of energy levels, which are narrowly split in energy, will be correspondingly very large. Note: This is only an intuitive picture. (d) The density of states, $g(E)$ across an energy band.

Density of States in An Energy band (cont’d)

Density of States \( g(E) \)

and \( g(E) \, dE \Rightarrow \text{No. of States (wavefunctions)} \) in the interval \((E + dE)/\text{unit volume of the sample}\)

No. of States / unit volume = \( S_v \)

and, \( S_v(E') = \int_{E=0}^{E=E'} g(E) \, dE \ldots \) these are states below \( E' \)

\( E' \) is some arbitrary energy level.

Now Recall:

The energy of an electron in a Cubic PE well is given by:

\[
E = \frac{\hbar^2}{8m_e L^2} \left( n_x^2 + n_y^2 + n_z^2 \right)
\]

• Energy Levels are so close ~10^{-12} eV
• Can be considered as Quasi Continuous
Fig. 4.21: Each state, electron wavefunction in the crystal, can be represented by a box at $n_1,n_2$.

Electron Wave Function Representation for many atoms - 3D Model

3D Quantum States for Many Many Electrons – Volume of an Octant as measure of number of Quantum States with an energy of ~Emax.

In here $n_1^2 + n_2^2 + n_3^2 \leq n'^2$

Vol. \(\frac{1}{8}(\frac{4}{3} \pi n'^3)\)

Fig. 4.22: In three dimensions, the volume defined by a sphere of radius $n'$ and the positive axes $n_1$, $n_2$ and $n_3$, is all the possible combinations of positive $n_1$, $n_2$ and $n_3$, values which satisfy $n_1^2 + n_2^2 + n_3^2 \leq n'^2$.

No. of Quantum States / unit Volume of the Crystal:

\[ g(E) = N(E) = \frac{\pi}{4} \left( \frac{8m_e}{\hbar^2} \right)^{\frac{3}{2}} \cdot E^{\frac{1}{2}} \]

There is a detailed derivation in the book that you can look up.
Fermi-Dirac Distribution of Electrons

The Fermi-Dirac function, \( f(E) \), describes the statistics of electrons in a solid. The electrons interact with each other and the environment so that they obey the Pauli Exclusion Principle.


**Effect of Temperature**

**Fermi – Dirac Statistics :**

\[
f(E) = P(E) = \frac{1}{1 + \exp \left( \frac{E - E_F}{kT} \right)} \quad \text{.........Fermi Function}
\]

*At a few kT above \( E_F \) or \( E - E_F >> kT \)*

\[
f(E) = P(E) = \exp \left( \frac{E - E_F}{kT} \right) \quad \text{........Behaves like Boltzman Function}
\]

**Electron Distribution Functions**

\[
\eta = \frac{\pi}{6} \left( \frac{8m}{\hbar^2} \right)^{3/2} E^{3/2}
\]

\[
N(E) = \frac{d\eta}{dE} = \frac{\pi}{6} \left( \frac{8m}{\hbar^2} \right)^{3/2} E^{1/2}
\]

\[
N(E) = \frac{d\eta}{dE} = \frac{\pi}{6} \left( \frac{8m}{\hbar^2} \right)^{3/2} E^{1/2} \quad \text{(if \( L^3=1 \) or per unit volume)}
\]

\[
P(E) = \frac{d\eta}{dE} = \frac{1}{\exp \left[ (E-E_F)/kT \right]+1}
\]

\[
F(E) = N(E) \cdot P(E)
\]

Fig. 4.26: The Fermi-Dirac function, \( f(E) \), describes the statistics of electrons in a solid. The electrons interact with each other and the environment so that they obey the Pauli Exclusion Principle.
Fig. 4.27: (a) Above 0 K, due to thermal excitation, some of the electrons are at energies above $E_F$. (b) The density of states, $g(E)$ vs $E$ in the band. (c) The probability of occupancy of a state at an energy $E$ is $f(E)$. The product $g(E)f(E)$ is the number of electrons per unit energy per unit volume or electron concentration per unit energy. The area under the curve with the energy axis is the concentration of electrons in the band.
Fermi Energy

**Number of Valence Electrons/unit volume**

\[
n = \frac{8\pi \cdot 2^{1/2} \cdot m_e^{3/2}}{h^3} \int_0^\infty \frac{\sqrt{E} \cdot dE}{1 + \left(\frac{E - E_F}{k.T}\right)}
\]

\[E_F = E_{F0} \text{ @ } T = 0K\]

**Temp. Independent**

\[E_{F0} = \frac{\hbar^2}{8m_e} \left(\frac{3n}{\pi}\right)^{2/3}\]

\[\text{@ } T = 0K\]

**Temp. Dependent**

\[E_F(T) = E_{F0} \left[1 - \frac{\pi^2}{12} \left(\frac{k.T}{E_{F0}}\right)^2\right]\]

And the Average KE of an Electron in a Metal:

\[
\frac{1}{2} m_e \cdot v_e^2 = E_{av.} \approx \frac{3}{5} E_{F0}
\]
• This ends part 4A of this Chapter.
• Next Section will be on Conduction In metals
ELECTRONIC MATERIALS
CHAPTER 4     Part 4B                #2 Handout
Modern Theory of Solids

MSE 433 Class Presentation
Spring Semester, 2006

Prof. Dhanesh Chandra
College of Engineering
Metallurgical and Materials Engineering
University of Nevada, Reno
Reno, NV 89557
775-784-4960

The Figures are mostly from Prof. Kasap’s book but they have been modified and I have added my additional notes as well. I have added my additional notes as well.
1. Hydrogen Molecule – Molecular Orbitals Theory of Bonding
2. Scattering Electrons in an Atom - Sec. 4.1
3. Band Theory of Solids …Energy Band Formation - Sec. 4.2
4. Semiconductors – Section 4.3
5. Electrons Effective Mass – sec. 4.4
6. Density of States in An Energy band – Sec. 4.5
7. Statistics: Collection of Particles – Boltzmann’s Statistics- sec. 4.6
8. Quantum Theory of Metals – sec. 4.7
9. Fermi Energy Significance – sec. 4.8
10. Thermionic Emission- sec. 4.9
12. Phonons –Sec. 4.10
Boltzmann and Fermi-Dirac Statistics of Energy Distribution

No. of Electrons in the Band

- Equation used to find the number of electrons (n) in the band is:
  \[ n = \int f(E) \cdot G(E) \, dE = \int f(E) \cdot N(E) \]
- \( G(E) \) or \( N(E) \) = Density of States
- \( f(E) = \text{Probability that a state with an energy (E) is occupied. (E= Electron Energy) or Fermi Function.} \)
- Note: Nix uses the equation **Electron distribution function** \( F(E) : \)
  \[ F(E) = 2 \cdot f(E) \cdot N(E) \]

Interaction of Electrons and Change in wave function \( \psi \); for ex: from \( \psi_1 \) to \( \psi_3 \)

Statistical Events and Low interaction when the number of electrons are few compared to the states

\[ \propto \exp(-E/kT) \]

![Graph](image)

Fig. 4.24: Two electrons initially with wavefunctions \( \psi_1 \) and \( \psi_2 \) at \( E_1 \) and \( E_2 \), interact and end up at different energies at \( E_3 \) and \( E_4 \). Their corresponding wavefunctions are \( \psi_3 \) and \( \psi_4 \).

Boltzmann Probability Function:

Suppose We have \( N_1 \) Particles at Energy Level \( E_1 \), and \( N_2 \) Particles at Energy Level \( E_2 \), then Boltzmann Statistics says:

\[
\frac{N_2}{N_1} = \exp\left( - \frac{(E_2 - E_1)}{kT} \right)
\]

As the Temp. increases the ratio \((N_2/N_1)\) increases, i.e. populates more higher level states.
4.7.2 CONDUCTION IN MATERIALS

- Quasi-continuous energy levels (discrete levels) and electron not full valence band for +1, +2, and +3 valence metals

• Electron a moves to a’ (higher energy level)

• Then it scatters from an ion core to an empty space > b’

• In steady State the electron are moving to the right and cannot be cancelled by moving them to the left; so there is current flow

• The external electric field or force = eE = \Delta p_x/\Delta t

• Where \Delta p_x = Momentum

\[ \Delta t = \text{Time interval electron travel w/o collision or scattering time (\tau)} \]

\[ \Delta p_x = \tau \cdot e \cdot E_x \]
4.7.2 CONDUCTION IN MATERIALS

Energy \((E)\) of Electron “a”: is \(E = \frac{p_x}{2m_e^*}\) where \(m_e^*\) is effective mass

Differentiating the above w.r.t. \(m_e\)

\[
\frac{\Delta E}{\Delta p_x} = \frac{p_x}{m_e^*}
\]

Substituting we have:

\[
\Delta E = \Delta p_x (\tau. eE_x) = (m_e^*/m_e^*). v_F. (\tau. eE_x) = e.v_F.\tau. E_x
\]

The current density \((J_x)\) due to all electrons in the energy range \(DE\) moving towards the right is:

\[
J_x = e.n_F.v_F = e^2.v_F^2\tau. g(E_F) E_x
\]

\[
\sigma = e^2.v_F^2\tau. g(E_F)
\]

for one dimensional so you multiply this by 3.
CONDUCTIVITY OF FERMI ELECTRONS
\[ \sigma = \left( \frac{1}{3} \right) e^2 \cdot v_F^2 \cdot \tau \cdot g(E_F) \] in 3 dimensional crystal

Drude Model (Eq. 4.22 ) relates the total number of conduction electrons (n) to the E_F

\[ \sigma = \frac{e^2}{m_e} \cdot n \cdot \tau \]

Eq. 4-27

Eq. 4-28
Energy Levels for 1,2,3 and 4 Valence Elements

Top Bands are called Conduction Bands and they are empty (i.e., no electrons reside in case metals)

1. Conductivity Expression (last page) is in Sharp Contrast with the Classical Expression in which all the electrons conduct.

2. According to the Eq.

\[ \sigma = \frac{1}{3} e^2 \nu_F \tau \cdot g(E_F) \]

Only electrons that are important are at the Fermi Level.. i.e. \( g(E_F) \)

3. Classically, \( \text{Cu}^{+1} \) ....and \( \text{Mg}^{+2} \)

4. One can expect more conduction in Mg!

5. But the BOTTOM TAIL of the 3p band has low density of States

6. Cu on the other hand has the density of States in the middle of the Band...so has better conduction.
Concept of Contact Potential and Significance of Fermi Energy

Fig. 4.28: When two metals are brought together, there is a contact potential, $\Delta V$. (a) Electrons are more energetic in Mo so they tunnel to the surface of Pt. (b) Equilibrium is reached when the Fermi levels are lined up.

- Consider two metals: Pt and Mo
- The work function ($\phi$) of Mo is low and $E_F$ is high so the electrons flow into Pt when in Contact
- The $E_F$ becomes equal in contact and there is a contact voltage developed (1.16 eV)
- Pt becomes: -ve
- Mo becomes: +ve
- System reaches Equilibrium

1. It is apparent that there is no Flow of Current (I=0) under equilibrium and cannot drive an external circuit!

2. We Define For a Metal: $E_F$ as the FREE ENERGY/ELECTRON which is called "ELECTROCHEMICAL POTENTIAL" $\mu$.

3. Fermi Level w.r.t. Vacuum is different.

4. This means difference in $\Delta \mu$

5. But there is no current Flow. So, $\Delta \mu=0$

6. We need an external source for current source
SEEBECK EFFECT: Temperature Gradient Along a Conductor Leads to a Potential difference

Fig. 4.30: The Seebeck effect: A temperature gradient along a conductor gives rise to a potential difference.

**SEEBECK EFFECT: Temperature Gradient Along a Conductor Leads to a Potential difference**

1. The voltage developed between Hot and Cold side, with the hot end Positive.

2. The Potential difference $\Delta V$ due to $\Delta T$ is called “Seebeck Effect”

We define:

Thermoelectric Power ($S$) or Seebeck Coefficient ($S$):

$$ S = \frac{dV}{dT} $$
### Table 4.3  Seebeck coefficients of selected metals (from various sources)

<table>
<thead>
<tr>
<th></th>
<th>$S$ at 0 °C</th>
<th>$S$ at 27 °C</th>
<th>$E_F$</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>($\mu$V K$^{-1}$)</td>
<td>($\mu$V K$^{-1}$)</td>
<td>(eV)</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>−1.6</td>
<td>−1.8</td>
<td>11.6</td>
<td>2.78</td>
</tr>
<tr>
<td>Au</td>
<td>+1.79</td>
<td>+1.94</td>
<td>5.5</td>
<td>−1.48</td>
</tr>
<tr>
<td>Cu</td>
<td>+1.70</td>
<td>+1.84</td>
<td>7.0</td>
<td>−1.79</td>
</tr>
<tr>
<td>K</td>
<td>-12.5</td>
<td>2.0</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>+14</td>
<td>4.7</td>
<td>−9.7</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>−1.3</td>
<td>7.1</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>−5</td>
<td>3.1</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>−9.00</td>
<td>−9.99</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>−4.45</td>
<td>−5.28</td>
<td></td>
<td></td>
</tr>
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Table 4.3  Seebeck coefficients of selected metals (from various sources)

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<td>−1.48</td>
</tr>
</tbody>
</table>

Reason why Al has −ve $S$. Coeff.:

• By Convention the sign of the “$S$” represents the potential on the cold side.

• If electrons diffuse from hot end to cold end then the Cold side is −ve. w.r.t the hot side.

• So the $S = -ve$ for Al

• Opposite effects in Au
Reason why Al has –ve S. Coeff. :

• By Convention the sign of the “S” represents the potential on the cold side.

• If electrons diffuse from hot end to cold end then the Cold side is -ve. w.r.t the hot side.

• So the S = -ve for Al

• Opposite effects in Au:

• The mean free path changes in hot and cold sides in Au or Cu. Please see the next Page.
Fig. 4.31: Consider two neighboring regions H (hot) and C (cold) with widths corresponding to the mean free paths \( l \) and \( l' \) in H and C. Half the electrons in H would be moving in +\( x \) direction and the other half in -\( x \) direction. Half of the electrons in H therefore cross into C, and half in C cross into H.

In Al (MP=680\(^o\)C) :
Electron H side are more energetic.
- Have longer mean free path (\( l \)). So \( l > l' \)...
  means net migration from hot to cold side.
  And \( S = -ve \)

In Cu (Electron on C have a longer mean free path (\( l' \))
- Have longer mean free path (\( l \)). So \( l ' > l \)...
  means net migration from cold to hot side.
- So \( S = +ve \)
Outline

1. Fermi Energy Significance –
2. 4.8- Contact Potential
3. Thermionic Emission- sec. 4.9
4. Phonons –Sec. 4.10
5. Brillouin Zones – Band Theory of Metals – section 4-11
Seebeck Voltage Generated is 0 if the wires are same
Different metal wires generate voltage so we have thermocouples.

Mott and Jones Eq. for Seebeck Co.efft:
\[ S \approx \frac{\pi^2 \cdot k^2 \cdot T}{3 \cdot e \cdot E_{F0}} \cdot x \]
x= Numerical constants for different metals which takes into account various charge transport parameters such as “l”.

Fig.4.32: (a) If same metal wires are used to measure the Seebeck voltage across the metal rod, then the net emf is zero. (b) The thermocouple from two different metals, type A and B. The cold end is maintained at 0 °C which is the reference temperature. The other junction is used to sense the temperature. In this example it is heated to 100 °C.
THERMOCOUPLE EMF Generation Equations

Available EMF From the Two Metals

Al (A)  \( E_{F_{0A}} = 11.6 \text{ eV} \)  and Cu (B)  \( E_{F_{0B}} = 7 \text{ eV} \)

\[
\Delta V_{AB} = \Delta V_A - \Delta V_B = \int_{T_o}^T (S_A - S_B) \, dT = \int_{T_o}^T S_{AB} \, dT \\
= -\frac{\pi^2 k^2}{6e} \left[ \frac{x_A}{E_{F_{AO}}} - \frac{x_B}{E_{F_{BO}}} \right] (T^2 - T_o^2) \\
= C(T^2 - T_o^2)
\]

S = Seebeck Coefficient
x = Numerical Constant from Mott and Jones equations

Thermocouple EMF Calculations.

A reference is usually Pt ref. at 0°C

for example Pt-Cu, Pt-Al emf's are given in Table 4.4

\( V_{Al-Pt} = 0.42 \text{ mV} \), and
\( V_{Cu-Pt} = 0.76 \text{ mV at 100°C} \)

\[
V_{Al-Cu} = V_{Al-Pt} - V_{Cu-Pt} = 0.42 \text{ mV} - 0.76 \text{ mV} = -0.34 \text{ mV}
\]

There is a reasonable agreement with the calculation using the Mott and Jones equation.
Fig. 4.33: Output emf vs temperature (°C) for various thermocouples between 0 to 1000°C.


### Table 4.4 Thermoelectric emf for metals at 100 and 200 °C with respect to Pt and the reference junction at 0 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>emf, mV At 100 °C</th>
<th>emf, mV At 200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper, Cu</td>
<td>0.76</td>
<td>1.83</td>
</tr>
<tr>
<td>Aluminum, Al</td>
<td>0.42</td>
<td>1.06</td>
</tr>
<tr>
<td>Nickel, Ni</td>
<td>–1.48</td>
<td>–3.10</td>
</tr>
<tr>
<td>Palladium, Pd</td>
<td>–0.57</td>
<td>–1.23</td>
</tr>
<tr>
<td>Platinum, Pt</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Silver, Ag</td>
<td>0.74</td>
<td>1.77</td>
</tr>
<tr>
<td>Alumel</td>
<td>–1.29</td>
<td>–2.17</td>
</tr>
<tr>
<td>Chromel</td>
<td>2.81</td>
<td>5.96</td>
</tr>
<tr>
<td>Constantan</td>
<td>–3.51</td>
<td>–7.45</td>
</tr>
<tr>
<td>Iron, Fe</td>
<td>1.89</td>
<td>3.54</td>
</tr>
<tr>
<td>90%Pt-10%Rh (Platinum-Rhodium)</td>
<td>0.643</td>
<td>1.44</td>
</tr>
</tbody>
</table>

*K-type: (90%Ni – 10%Cr)*

*J-type: (60%Ni – 40%Cr)*

*Alumel: (94%Ni – 2%Al – 3%Mn – 1%Si)*
The Seebeck effect: A temperature gradient along a conductor gives rise to a potential difference.

\[ \text{Seebeck Coefficient or sometime called Thermoelectric Power } = \frac{dV}{dT}, \]

But it is actually voltage difference.

**Mott and Jones Eq. for Seebeck Co. eff:**

\[ S \approx \left[ \frac{\pi^2 kT}{3eE_F_0} \right] x \]

\( x \) = Numerical constants for different metals which takes into account various charge transport parameters such as “\( l \)”.

---

**Fig. 4.30:** The Seebeck effect: A temperature gradient along a conductor gives rise to a potential difference.

**Fig. 4.31:** Consider two neighboring regions H (hot) and C (cold) with widths corresponding to the mean free paths \( \ell \) and \( \ell' \) in H and C. Half the electrons in H would be moving in +x direction and the other half in -x direction. Half of the electrons in H therefore cross into C, and half in C cross into H.

**Fig. 4.32:** (a) If same metal wires are used to measure the Seebeck voltage across the metal rod, then the net emf is zero. (b) The thermocouple from two different metals, type A and B. The cold end is maintained at 0°C which is the reference temperature. The hot end is heated to 100°C.

**Fig. 4.33:** Output emf vs temperature (°C) for various thermocouples between 0 to 1000°C.
Richardson Dushman Equation:

\[ J = B_0 T^2 e^{\frac{\phi}{kT}} \]

where,

\[ B_0 = \frac{4\pi e m_e k^2}{h^3} \]

\[ B_0 = 1.2 \times 10^6 \text{ A.m}^{-2}.\text{K}^{-2} \]

Fig. 4.34: (a) Thermionic electron emission in a vacuum tube. (b) Current-voltage characteristics of a vacuum diode.
Richardson Dushman Equation:

Relates to Current Density

\[ J = B_o T^2 e^{\frac{\phi}{kT}} \]

\[ B_o = 1.2 \times 10^6 \text{ A.m}^{-2}.\text{K}^{-2} \]

where,

\[ B_o = \frac{4\pi e m_e k^2}{h^3} \]  
Richard Dushman Constant

\[ J \propto e^\phi \]

\[ J = B_e T^2 e^{-\frac{\phi}{kT}} \]

Where: Emission Constant:

\[ B_e = (1-R)B_o \]

\[ R = \text{Reflection Coefficient} \]

For Most Metals \( B_e \sim 1/2 B_o \). can be as low as \( 1 \times 10^2 \)
Fig. 4.35: Fermi Dirac function, $f(E)$ and the energy density of electrons, $n(E)$, (electrons per unit energy and per unit volume) at three different temperatures. The electron concentration extends more and more to higher energies as the temperature increases. Electrons with energies in excess of $E_F + \Phi$ can leave the metal (thermionic emission).
1. When an electrical potential is applied w.r.t. to Cathode. This lowers the potential barrier or work function ($\phi$), and helps Thermionic Emission. This is called “Schottky Effect”
In a simple capacitor:

Two parallel plates a distance "x".

Charge \( q \) \( \propto \) Voltage \( V \)

or \( q = C \cdot V \)

\[
C = \frac{q}{V} = \text{Capacitance}
\]

1 Farad = \( \frac{1 \text{ Coulomb}}{\text{Volt}} \)

\[
C = \varepsilon_o \cdot \frac{A}{d}
\]

where, \( A = \text{Area of plate} \) and \( d = \text{distance between plates} \)

Permittivity: \( \varepsilon_o = 8.854 \times 10^{-12} \text{ F/m} \)

When a material is placed in between (rather than free space)

Then

\[
C = \frac{\kappa \cdot \varepsilon_o \cdot A}{d}
\]

where \( \kappa = \text{capacitance factor} \) of the capacitor that is increased by a factor \( \kappa \)
Dielectric Constant

In a simple capacitor:
Two parallel plates a distance "x"
Charge (q) $\propto$ Voltage (V)
or $q = C \cdot V$

$C = \frac{q}{V} = \text{Capacitance}$

1 Farad = \frac{1 \text{ Coulomb}}{\text{Volt}}

$C = \varepsilon_0 \cdot \frac{A}{d}$

where, $A = \text{Area of plate}$
and $d = \text{distance between plates}$

Permitivity: $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$

When a material is placed in between (rather than free space)

Then $C = \frac{\kappa \cdot \varepsilon_0 \cdot A}{d}$

where, $\kappa = \text{capacitance of the capacitor that is increased by a factor } \kappa$
SCHOTTKY EFFECT AND FIELD EMMISSION

The electron at a distance from the surface of the conductor has a Potential Energy (PE)

Theorem of Image Charges

The electron at a distance from the surface of the conductor has a Potential Energy (PE)

Electron @ distance “x”

Image PE

$E + \phi$

$PE_{image} (x) = -\frac{e^2}{16 \pi \varepsilon_0 x}$

$x \gg \text{atomic separation} "a"

Reference of Zero potential @ $x = \infty$

But we defined $PE = 0$ inside the metal

$\varepsilon_0 = \text{Absolute Permittivity}$

Electron @ distance “x” from the surface

03/23/2006 (a)
SCHOTTKY EFFECT  
AND FIELD EMMISION

**But** we defined $PE = 0$ inside the metal.  
We can artificially bring this down to $PE$ from $x$ to zero @ $x = 0$

$$PE_{image} (x) = (E_F + \phi) - \frac{e^2}{16 \pi \varepsilon_o x}$$

**Range** $PE = 0$ to $(E_F + \phi)$

Electron Still over comes the $\phi$ ...so Ok

Fig. 4.36:  (a) $PE$ of the electron near the surface of a conductor; (b) 
Electron $PE$ due to an applied field e.g. between cathode and anode
(c) The overall $PE$ is the sum

http://Materials.usask.ca
When a Voltage Difference Applied between the Anode and Cathode There is a Potential gradient just outside the surface given by \( eV(x) \):

\[
P_E_{applied}(x) = -e\cdot x \cdot E
\]

Th is filed is given by Figure b

Fig. 4.36: (a) \( P_E \) of the electron near the surface of a conductor, (b) Electron \( P_E \) due to an applied field e.g. between cathode and anode (c) The overall \( P_E \) is the sum

The Net Potential Energy, \( PE(x) \)

\[
PE(x) = PE_{\text{image}}(x) + PE_{\text{Applied}}(x)
\]

\[
PE(x) = (E_F + \phi) - \left( \frac{e^2}{16\pi\varepsilon_0 x} \right) - e \cdot x \cdot E
\]

As “E” increases the term \( E_F + \phi_{\text{eff}} \) decreases, as depicted by the black and red line. So one can actually apply a high potential \( E \), and release electrons without heating the metal!!

Fig. 4.36: (a) \( PE \) of the electron near the surface of a conductor, (b) Electron \( PE \) due to an applied field e.g. between cathode and anode (c) The overall \( PE \) is the sum.


Effective Work “$\phi_{\text{eff}}$” with an Applied Potential

Effective Work Function Under an external potential:

$$\phi_{\text{eff}} = \phi - \left( \frac{e^3}{4\pi \varepsilon_o} \cdot E \right)^{1/2}$$

Thus the Work Function is lowered by applying a potential across the conductor!!

This is called Schottky Effect
Field Assisted Thermionic Emission (J)

When an Positive Voltage is applied to the ANODE w.r.t Cathode, the electric field at Cathode help the Thermionic process.

\[
J = B_e T^2 e^{-\frac{(\phi - \beta_s E^{1/2})}{k.T}}
\]

Where:

\[
\beta_s = \frac{e^3}{4\pi\varepsilon_0} \approx 3.79 \times 10^{-5}
\]

Field Emission: Tunneling of electron through a Narrow Potential energy Barrier PE induced by large applied Fields
\[ P \approx e^{-\frac{2(m_e \phi_{\text{eff.}})^{1/2}(x_F)}{\hbar}} \]

If the field is strong then the \( n \) we can go back to the original equation:

**The Net Potential Energy, \( PE(x) \)**

\[ PE(x) = PE_{\text{image}}(x) + PE_{\text{Applied}}(x) \]

\[ PE(x) = (E_F + \phi) - \left[ \frac{e^2}{16\pi \varepsilon_0 x} \right] - e.x.E \]

and substitute then around \( x \approx x_F \) and \( PE(x_F) = E_F \)

*In the above eq. this gives:*

\[ \phi = e.E_{x_F} \]

\[ P \approx e^{-\frac{2(m_e \phi_{\text{eff.}})^{1/2} \cdot \phi}{e\hbar E}} \]
Summary of Field Emission Process

For Example: FESEM that we have purchased uses Field Emission

Tunneling of electron through a Narrow Potential energy Barrier PE induced by large applied Fields

Tunneling Probability (P) of an Electron is depends on $\phi_{\text{eff}}$ and $x_F$ (tunneling distance)

$$P \approx e^{- \frac{2(m_e \phi_{\text{eff}})^{1/2}(x_F)}{\hbar}}$$

$$P \approx e^{\frac{-2(m_e \phi_{\text{eff}})^{1/2} \phi}{e \cdot \hbar \cdot E}}$$

Fig. 4.37 (a) Field emission is the tunneling of an electron at an energy $E_F$ through the narrow PE barrier induced by a large applied field. (b) For simplicity we take the barrier to be rectangular. (c) A sharp point cathode has the maximum field at the tip where the field emission of electrons occurs.
Zone Theory Concepts

- So far we have covered the theory of Quantized states of Electrons but not discuss the interaction of Atom or ion cores with delocalized electron inside a metal.

- This gives rise to Bands and discontinuities in and develops “so called” forbidden zones or Band gaps in every material……. But this band gap occurs for one particular direction only.

- However, if you now consider all possible directions that the electrons move in a crystal, then we have a situation where there may be an:
  1. Overlap of Bands such that electrons remain delocalized.
  2. If there may be Band gap between the valence and Conduction Bands …i.e. there is virtually no transport of electrons inside the solid without an external energy source.
Zone Theory Concepts

• This gives rise to Semiconducting properties; i.e. temporary conduction.

• For example in Si we have hybridized structure of Diamond; i.e. 4 atoms of Si surrounding one Si atom.

• When an external energy is radiated on the Si single crystal then if the energy is high it may jump an electron from valence band into conduction band.
Interaction of Electrons with the atoms in the Crystal Lattice

1. Bragg's Law:
   \[ n\lambda = 2d \sin \theta \]
   But:
   \[ k = \frac{2\pi}{\lambda} \quad \text{or} \quad \lambda = \frac{2\pi}{k} \]
   \[ \therefore n \cdot \frac{2\pi}{k} = 2d \sin \theta \]
   or
   \[ k \approx \frac{2\pi}{d \sin \theta} \]

No, we make \( \theta = 90^\circ \) and \( d = a \)

Then:
\[ k = \frac{n\pi}{a} \]
\( n = 1, 2, 3, \ldots \text{ or } \) can be positive or negative directions
Fig. 4.51: Diffraction of the electron in a two dimensional cubic crystal. Diffraction occurs whenever \( k \) has a component satisfying 
\[ k_1 = \pm n\pi / a, \quad k_2 = \pm n\pi / a \text{ or } \quad k_3 = \pm n\pi \sqrt{2}/a. \]
In general terms, when 
\[ ks\sin\theta = n\pi / a. \]
Classical Model - With No Energy Gaps

Electrons are free to move about in the crystal

Zone Theory showing energy Gaps

½ Zone Shown in the <100>

½ Zone Shown in the <110>

Band Gap or Forbidden Zone
All bands are overlapped
And no Band Gap—leads to free conduction in metals

\[ E = h \nu = \frac{h.c}{\lambda} \]
Depiction of Brillouin Zones in lattice to Show Movement of Electron a Crystal Lattice. Atoms are not shown in the Cubic Cell for Clarity

Electron
Comparison of Band Structures of Metals and Semiconductors
(only Half Band is shown on the right hand side Diagrams)

Full band Diagram

Energy (E)

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E

$\frac{\pi}{a}$

$\frac{2\pi}{a}$

$\frac{\sqrt{2}\pi}{a}$

$\frac{2\sqrt{2}\pi}{a}$

$\langle 100 \rangle$

$\langle 110 \rangle$
BAND OVERLAP LEADING TO DIFFERENT PROPERTIES IN A CRYSTAL

Brillouin Zones and movement of Electrons in the crystal

Example of 3D model showing Brillouin Zones with Band Gaps in different directions

And

Movement of Electrons within a crystal
Fig. 4.50: The energy of the electron as a function of its wavevector $k$ inside a one-dimensional crystal. There are discontinuities in the energy at $k = \pm n\pi/a$ values where the waves suffer Bragg reflections in the crystal. There are energy gaps at these $k$ values. For example, there can be no energy value for the electron between $E_c$ and $E_s$. $E_s - E_c$ is therefore an energy gap at $k = \pm \pi/a$. Away from the critical $k$ values, the $E-k$ behavior is like that of a "free" electron, $E$ increasing with $k$ as $E = (\hbar k)^2/2m_e$. These energies fall within an energy band inside a solid.
More details of Band Structure related to crystal directions

Fig. 4.52: The $E$-$k$ behavior for the electron along different directions in the two dimensional crystal. The energy gap along $[10]$ is at $\pi/a$ whereas it is at $\pi\sqrt{2}/a$ along $[11]$.

**Conclusion From This Slide:**

In different crystal directions we have different Brillouin Zone Boundaries. ($\pi/a$ or $\sqrt{2}\pi/a$ etc.)
Fig. 4.50: The energy of the electron as a function of its wavevector $k$ inside a one-dimensional crystal. There are discontinuities in the energy at $k = \pm n \pi / a$ values where the waves suffer Bragg reflections in the crystal. There are energy gaps at these $k$ values. For example, there can be no energy value for the electron between $E_c$ and $E_s$. $E_c - E_s$ is therefore an energy gap at $k = \pm \pi / a$. Away from the critical $k$ values, the $E-k$ behavior is like that of a "free" electron, $E$ increasing with $k$ as $E = (h \bar{k})^2 / 2m_e$. These energies fall within an energy band inside a solid.


Fig. 4.51: Diffraction of the electron in a two dimensional cubic crystal. Diffraction occurs whenever $k$ has a component satisfying $k_1 = \pm n \pi / a$, $k_2 = \pm n \pi / a$ or $k_3 = \pm n \pi \sqrt{2} / a$. In general terms, when $k \sin \theta = n \pi / a$.


Fig. 4.52: The $E-k$ behavior for the electron along different directions in the two dimensional crystal. The energy gap along [10] is at $\pi / a$ whereas it is at $\pi \sqrt{2} / a$ along [11].


Fig. 4.53: (a) Metal: For the electron in a metal there is no apparent energy gap because the 2nd BZ (Brillouin Zone) along [10] overlaps the 1st BZ along [11]. Bands overlap the energy gaps. Thus the electron can always find any energy by changing its direction. (b) Semiconductor or insulator: For the electron in a semiconductor there is an energy gap arising from the overlap of the energy gaps along [10] and [11] directions. The electron can never have an energy within this energy gap, $E_g$.

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Density of States representation of Differences between Metal, Semiconductor and Insulator Band Structure

**Metals**

Very large band gap and it is difficult for electrons to jump the band gap under reasonable conditions so they are electrically non-conductive.

**Insulators**

**Semiconductors**

Very large band gap and it is difficult for electrons to jump the band gap under reasonable conditions so they are electrically non-conductive.
2-D Brillouin Representation for a particular System
**BRILLOUIN ZONES AND BAND GAPS**

*Connection between E vs k diagram (Below) and BZ crystal diagram (right)*

Fig. 4.54: The Brillouin zones in two dimensions for the cubic lattice. The Brillouin zones identify the boundaries where there are discontinuities in the energy, where there are energy gaps.

Energy Contours in eV in BZ Zones – 2 Dimensional – Metals Overlapping Bands

First BZ

Second BZ

Energy contour for $E = 3 \text{ eV}$ in the first BZ

E=1 eV

E=2 eV

E=3 eV

E=4 eV

E=7 eV

E=9 eV

E=11 eV

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Energy Contours in eV in BZ Zones – 2 Dimensional – Semiconductors with band gap

This slide tells us: Energy Gap between the highest Energy Contour (6 eV) in the 1st. BZ, and the lowest energy Contour (10 eV) in the 2nd. BZ

Fig. 4.55: Energy contours in k space (space defined by $k_x$, $k_y$). Each contour represents the same energy value. Any point $P$ on the contour gives the values of $k_x$ and $k_y$ for that energy in that direct
Fig. 4.55: Energy contours in $k$ space (space defined by $k_x$, $k_y$). Each contour represents the same energy value. Any point $P$ on the contour gives the values of $k_x$ and $k_y$ for that energy in that direction from O. For the point $P$, $E = 3$ eV and $OP$ is $k$ along [11]. (a) In a metal the lowest energy in the second zone (5 eV) is lower than the highest energy (6 eV) in the first zone. There is an overlap of energies between the Brillouin zones. (b) In a semiconductor or an insulator, there is an energy gap between the highest energy contour (6 eV) in the first zone and the lowest energy contour (10 eV) in the second zone.

Fermi Surface in 2 Dimensions for various materials

Example Reactive Metals:
Na, Li, K
have one 3 s electron/atom
Electron fill up to Fermi Energy Level \( E_F \).
Behavior: Like Free electron
Follow: \[ E = \frac{(\hbar k)^2}{2m_e} \]
We can assume there is no effective mass change.

Example Transition Metals:
Cu, Ag, Au
have one 3 s electron/atom
Electron fill up to Fermi Energy Level \( E_F \).
Behavior: NOT Like Free electron
Different Behavior as compared to Na near BZ
But they do follow this Eq. inside the Fermi Sphere
\[ E = \frac{(\hbar k)^2}{2m_e} \]
We can assume there is no effective mass change.

\[ R_H = \frac{1}{e.n} \]
For Na:
\[ R_H = -2.5 \times 10^{-10} \text{ m}^3 \text{ C}^{-1} \]
(Measured)
Calculating ns for \( R_H \)
\[ \rho = 0.97 \text{ g/cc} \]
Atomic Mass = 23
1 valence Electron / atom
\[ n = 2.54 \times 10^{28} \text{ atoms/cc} \]
\[ R_H = -2.46 \times 10^{-10} \text{ m}^3 \text{ C}^{-1} \]
(Calculated)
**Example Metals**

**Such as:**

**Be, Mg, Ca are divalent metals**

- have closed outer sub - should have full s - band
- There is overlap of the s and p bands forming one partially filled continuous band
- i.e Second Zone overlapping with the First Zone
- Electron fill up to Fermi Energy Level ($E_F$).

**Behavior:** **Like Free electron** inside the Fermi Sphere

**At Fermi surface they do not follow**

**this Eq.:**

$$E = \frac{(\hbar \cdot k)^2}{2m_e}$$

*We can assume effective mass change*
Semiconductor Brillouin Zones

1st BZ Boundary

2nd BZ Boundary

Semiconductor
Lattice Vibrations Represented by Phonons

And Effects on Electrical Conduction in Metals and Semiconductors
Fig. 4.38: (a) Harmonic vibrations of an atom about its equilibrium position assuming its neighbors are fixed. (b) The PE curve $V(x)$ vs. displacement from equilibrium, $x$. (c) The energy is quantized.

Fig. 4.40: (a) Frequency $\omega$ vs. wavevector $K$ relationship for lattice waves. (b) Group velocity $v_g$ vs. wavevector $K$. 
Longitudinal and Transverse Waves

Fig. 4.39: (a) A chain of $N$ atoms through a crystal in the absence of vibrations. (b) Coupled atomic vibrations generate a traveling longitudinal (L) wave along $x$. Atomic displacements ($u_r$) are parallel to $x$. (c) A transverse (T) wave traveling along $x$. Atomic displacements ($u_r$) are perpendicular to the $x$-axis. b and c are snapshots at one instant.

**Transverse Waves**

![Diagram of Standing Waves](image)

**Fig. 4.41:** Four examples of standing waves in a linear crystal corresponding to $q = 1$, 2 and 4. $q$ is maximum when alternating atoms are vibrating in opposite directions. A portion from a very long is crystal shown.

---

Transverse Waves
Fig. 4.42: Density of states for phonons in copper. The solid curve is deduced from experiments on neutron scattering. The broken curve is the three-dimensional Debye approximation, scaled so that the areas under the two curves are the same. This requires that \( \omega_{\text{max}} = 4.5 \times 10^{13} \text{ radians s}^{-1} \), or a Debye characteristic temperature \( T_D = 344 \text{ K} \).
**Fig. 4.44:** Atoms executing longitudinal vibrations parallel to \( x \).

Heat Capacity Curve
**Fig. 4.43:** Debye constant-volume molar heat capacity curve. The dependence of the molar heat capacity $C_m$ on temperature with respect to the Debye temperature: $C_m$ vs. $T/T_D$. For Si, $T_D = 625$ K so that at room temperature (300 K), $T/T_D = 0.48$ and $C_m$ is only $0.81(3R)$. 

Fig. 4.45: Phonons generated in the hot region travel towards the cold region and thereby transport heat energy. Phonon-phonon unharmonic interaction generates a new phonon whose momentum is towards the hot region.
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Fig. 4.44: Atoms executing longitudinal vibrations parallel to $x$.


Fig. 4.45: Phonons generated in the hot region travel towards the cold region and thereby transport heat energy. Phonon-phonon unharmonic interaction generates a new phonon whose momentum is towards the hot region.

**Fig. 4.46:** Thermal conductivity of Sapphire and MgO as a function of temperature


**Fig. 4.47:** Low angle scaterring of a conduction electron by a phonon. (E is the electric field.)


**Fig. 4.48:** An electron wave propagation through a linear lattice. For certain $k$ values the reflected waves at successive atomic planes reinforce each other to give rise to a reflected wave travelling in the backward direction. The electron then cannot propagate through the crystal.


**Fig. 4.49:** Forward and backward waves in the crystal with $k = \pm \pi / a$ give rise to two possible standing waves, $\psi_c$ and $\psi_s$. Their probability density distributions, $|\psi_c|^2$ and $|\psi_s|^2$, have maxima either at the ions or between the ions.

WE will end this chapter here