Chapter Two    Energy Band Theory

2-1 Electronic Structure of Elements

For multi-electrons atom there are four quantum numbers for each electron in electronic structure of atom:
1- The principal quantum number (n): used to define the size of shell n=1,2,3,…..
2- The orbital angular momentum quantum number (l ): this number indicates the shape of the shell l=0,1,2,…..,n-1
3- The orbital magnetic number (m_l): this number gives the orientation of orbit with respect to applied field m_l=0,±1,±2,……,± l.

As example
a- if l=0 then m_l=0 → single orbit with zero angle as shown in Fig(2-1)a.
b- if l=1 then m_l=0,±1 → three orbit with zero,+45°,-45° angles as shown in Fig(2-1)b.

4- Electronic spin m_s = ±1/2 : this number explain the direction of electron rotation about him self (spin) as shown in Fig.(2-2).
2-2 The Exclusion Principle

In 1925 Pauli stated that: *no two electron in an electron system of atom have the same set of four quantum number n, l, m, and ms.*

2-3 Electronic Shells

All electrons in an atom which have the same value of (n) are said to be the same electron shell. These shells are identified by letter K, L, M, N, …… corresponding to n=1, 2, 3, 4, …… respectively.

A shell is divided into sub-shells corresponding to different value of l and identified as s, p, d, f, …… corresponding to l=0, 1, 2, 3, …… respectively.

Each sub-shell contains ml of orbit, where each orbit has two states corresponding to ms = ±1/2. Tacking account of the exclusion principle, the distribution of electron in an atom among the shells and sub-shells is indicated in table (2-1).
Table (2-1) electrons distribution on shell and sub-shells

<table>
<thead>
<tr>
<th>Shell</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Sub-shell</td>
<td>s</td>
<td>s</td>
<td>p</td>
<td>s</td>
</tr>
<tr>
<td>l</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>m_l</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>†1</td>
<td>†1</td>
<td>†2</td>
<td>†1</td>
</tr>
<tr>
<td>Number of electrons</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>8</td>
<td>18</td>
<td>18</td>
</tr>
</tbody>
</table>

Configuration is 1s², 2s²2p⁶, 3s²3p⁶3d¹⁰, 4s²4p⁶4d¹⁰4f¹⁰, ……

Illustration

>> For K-shell n=1, have one sub-shell (l=0), known 1s, with single orbit (m_l=0). This single orbit has zero angle, R1 radius and contains two electrons (two states \( m_s = \pm \frac{1}{2} \)) as shown in Fig.(2-3), therefore K-shell contain 2 electron only.
For L-shell n=2 have two sub-shells \((l=0,1)\) First sub-shell \((l=0)\), 2s, exactly same as \((1s)\) except its radius is \(R_{21}>R_{1a}\) as shown in Fig(3-4)a. Second sub-shell \((2p)\) has three orbital \(m_l=0,\pm1\) with zero, \(+45^0, -45^0\) angles, \(R_{22}\) radius and each orbital contain two electrons. Therefore 2p sub-shell contain 6 electron and L-shell contain \(6+2=8\) electron as shown in Fig.(2-4)b.

Fig.(2-4) L-shell
Example 2-1

Write the electronic configuration of Carbon, Silicon and Germanium whose atomic number 6, 14 and 32 respectively.

Solution:

By using table (2-1)

>> For Carbon whose atomic number 6

<table>
<thead>
<tr>
<th>Shell</th>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Sub-shell</td>
<td>s</td>
<td>s</td>
<td>p</td>
</tr>
<tr>
<td>l</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Number of electrons</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

Configuration for Carbon is $1s^2, 2s^2 2p^2$.

>> For Silicon whose atomic number 14

<table>
<thead>
<tr>
<th>Shell</th>
<th>K</th>
<th>L</th>
<th>M</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Sub-shell</td>
<td>s</td>
<td>s</td>
<td>p</td>
</tr>
<tr>
<td>l</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Number of electrons</td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

Configuration for Silicon is $1s^2, 2s^2 2p^6, 3s^2 3p^2$.

>> For Germanium whose atomic number 32 (H.W)
2-4 Energy Band of Crystals

A crystal consists of a space of array of atoms or molecules built up by regular and periodic three dimensional patterns as shown in Fig.(3-5). The atoms are arranged in three-dimensional periodic fashion. The periodic arrangement of atoms in a crystal is called lattice. In a crystal, an atom strays far from a single, fixed position. The thermal vibrations associated with the atom are centered about this position. There is a unit cell that is representative of the entire lattice. By repeating the unit cell throughout the crystal, we can generate the entire lattice.

There are several different types of crystal lattice depending upon the symmetry and internal structure. One of them is the cubic crystal lattice. There are three basic types of unit cells in a cubic crystal lattice. These are simple cubic (SC), base centered cubic (BCC) and face centered cubic (FCC). Fig.(2-5)(a) shows a SC crystal. In this unit cell, each corner of the cubic lattice is occupied by an atom (indicated by a small sphere) that has six equidistant nearest neighboring atoms. The dimension "a" is called the lattice constant. Only podium is crystallized into the simple cubic lattice. Fig.(2-5)(b) shows a BCC unit cell. In this unit cell, each atom has eight nearest neighboring atoms. Crystals exhibiting the BCC lattices include those of sodium and tungsten. Fig.(2-5)(c) shows a FCC unit cell. This unit cell has one atom at each of the six cubic faces in addition to the eight corner atoms. In an FCC lattice, each atom has 12 nearest neighboring atoms. A large number of elements exhibit the FCC lattice form. These include aluminum, copper, gold and platinum.
When N atoms arrange in crystalline form, the energy level of each atom changed to N energies levels called **Energy Band**, since the electron in outer shell are shared by more than one atom in crystal as illustrate by the Fig(2-6).

Figure(2-7) illustrate how the energy level of isolated atom are split into energy band when these atoms are brought into close proximity to form a crystal.
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2-5 Insulator, Semiconductor, and Conductor

(Self study)

Fig.(2-7)

Fig.(2-8)a Energy band structure of insulator
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Fig. (2-8)b Energy band structure of Semiconductor

Fig. (2-8)c Energy band structure of Conductor
2-6 Energy Distribution of Electron in Conductors

Each electron in metal may take one value of a number of closely
spaced values within these permitted bands at a given temperature.

At $0^0K$ all energy levels under Fermi Level ($E_f$) are occupied by one electron, and all
levels above Fermi level are empty.

Fermi level for a metal can be found from its electron
concentration (number of free electrons per cubic meter ,N) where:

$$E_f = \left( \frac{3N}{2\gamma} \right)^{\frac{2}{3}} \text{ in eV}$$

Where $\gamma$ is a constant equal to $6.82 \times 10^{27} \left( \frac{m^3 \times \text{eV}}{2} \right)^{-1}$
and N can found using

$$N = \text{A.V number} \times \frac{\text{specific gravity}}{\text{atomic weight}} \times (\text{number of free electron/atom})$$

A.V number$= 6.02 \times 10^{23}$ atoms/mole (Avogadro's number)
Specific gravity is the density of metal (g/cm)

Example 2-2

The specific gravity of Tungsten is $18.8$ g/cm and atomic weight is
$184$ g and there are two free electrons for each atom. Find Fermi level for
Tungsten.

Solution:
N = \frac{6.02 \times 10^{23} \times 18.8}{184} \times 2 \text{ electron atoms} = 1.23 \times 10^{23} \text{ electron /cm}^3

= 1.23 \times 10^{29} \text{ electron /m}^3

E_f = \left( \frac{3 \times 1.23 \times 10^{29}}{2 \times 6.82 \times 10^{27}} \right)^{\frac{2}{3}} = 9.01 \text{ eV}

When temperature of metal increase some electrons will possess energies greater than Fermi level, where number of electron with energy greater than Fermi level is equal to the number of unoccupied level lower than E_f.

### 2-6-1 The Fermi-Dirac Function

The energy distribution of free electrons in metal is governed by laws of Fermi-Dirac statistics which it is found the probability that a given energy state is occupied by an electron is \( f(E) \):

\[
f(E) = \frac{1}{1 + \exp \left( \frac{E - E_f}{kT} \right)} [0 \rightarrow 1]
\]

Where \( k \): Boltzman constant = \( 1.38 \times 10^{-23} \text{ J/K} \)

\( = 8.62 \times 10^{-5} \text{ eV/K} \)

\( T \): Temperature in Kelvin

\( T(\text{Kelvin}) = T(\text{Celsius}) + 273 \)

Figure (2-9) illustrate the energy distribution portability of free electron in a metal at where:
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1- At $0^0K$ $f(E)|_{0^0K} = \begin{cases} 
E < E_f & \frac{1}{1 + \exp(-\infty)} = 1 \\
E = E_f & \frac{1}{1 + \exp(0)} = 0.5 \\
E > E_f & \frac{1}{1 + \exp(+\infty)} = 0 
\end{cases}$

That mean all electrons in metal will be under Fermi level at $0^0K$.

2- When $T>0^0K$ there is a number of electrons lie above Fermi level that made $f(E)$ increase in the region above $E_f$ and decreases under the $E_f$.

\textbf{Note:} For any temperature $f(E_f)=0.5$.

\textbf{Example 2-3}
Find the probability of electrons lie in the energy state with energy $=0.05\text{eV}$ above Fermi level at $227^0\text{C}$.

\textbf{Solution:}
$T=227+273=500^0\text{K}$ and $E=E_f+0.05\text{eV}$ then the probability will:
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\[ f(E_f+0.05) = \frac{1}{1 + \exp \left( \frac{E_f + 0.05 - E_f}{8.62 \times 10^{-5} \times 500} \right)} = 0.238 \]

*Note:* \( (1-f(E)) \) mean probability that energy state \( E \) is empty.

### 2-6-2 Concentration of Free Electrons in the Conductor

Number of free electrons per cubic meter (concentration) lie in the interval \([E_1 \text{ to } E_2]\) can be found by:

\[
n_{[E_1\text{ to } E_2]} = \int_{E_1}^{E_2} N(E) f(E) \, dE \text{ electrons/ m}^3 \text{ and} \]

Where \( N(E) \) is the state density (number of states per electron volt per cubic meter) in the conduction band of metal.

For any conductor \( N(E) = \gamma \sqrt{E} \)

**Example 2-4**

How many free electron per cubic meter in metallic Tungsten (\( N=1.23 \times 10^{29} \) electrons \(/\text{m}^3\)) that lie in energy band between 8eV to 10eV at

A- \(0^0K\)  
B- \(500^0K\)

**Solution:**

\[
E_f = \left( \frac{3 \times 1.23 \times 10^{29}}{2 \times 6.82 \times 10^{27}} \right)^{\frac{2}{3}} \approx 9 \text{eV} 
\]

A- At \(0^0K\) \( f(E) = \begin{cases} 1 & E < 9 \\ 0 & E > 9 \end{cases} \)

\[
n_{[8\text{ to } 10]} = \int_8^9 \gamma \sqrt{E} \times 1 \, dE + \int_9^{10} \gamma \sqrt{E} \times 0 \, dE
\]

\[
= \frac{2}{3} \gamma E^{1.5} \frac{9}{8} = \frac{2}{3} \times 6.82 \times 10^{27} \times \left(9^{1.5} - (8)^{1.5}\right) = \ldots .
\]
B- at $500^0K$

$$n_{[8-10]} = \int_{\frac{E}{8.62 \times 10^{-5} \times 500}}^{10} \frac{\gamma \sqrt{E}}{1 + \exp\left(\frac{E - 9}{8.62 \times 10^{-5} \times 500}\right)} \, dE = \ldots$$

**Example 2-5**

By using equation of $n_{[E_1-E_2]}$ prove that $E_f = \left(\frac{3N}{2\gamma}\right)^{\frac{2}{3}}$ where $N$ is total number of free electron/m$^3$.

**Solution:**

At $0^0K$ all electrons lie under Fermi level and in this region $f(E)=1$ then

$$N = n_{[0-E_f]}\bigg|_{T=0^0K} = \left. E_f \int N(E)f(E) \right|_{0^0K} \, dE \text{ electrons/ m}^3$$

$$N = \int_{0}^{E_f} \gamma \sqrt{E} \times (1) \, dE$$

$$N = \frac{2}{3} \gamma E_f^{\frac{3}{2}} \bigg|_{0}^{E_f} = \frac{2}{3} \gamma (E_f)^{\frac{3}{2}} \rightarrow E_f = \left(\frac{3N}{2\gamma}\right)^{\frac{2}{3}}$$
Tutorial Question

Q1 For multi-electrons atom describe quantum numbers associated with each electron in electronic structure of atom.

Q2 What are the main differences between spin number and principle quantum number.

Q3 Explain the exclusion principle and how could we use it to find electron distribution in an atom among shells and sub shells.

Q4 By using exclusion principle illustrate why:
   1- Sub-shell (2p) contains 6 electrons only.
   2- M-shell contain 18 electron with plotting each sub-shell.

Q5 Describe quantum numbers associated with each electron in 4p sub shield

Q6 What is the physical meaning of the following terms:
   1- Lattice.  2- Unit cell.  3- Fermi level.  4- Femi Dirac function.

Q7 Illustrate how the energy level of isolated atom are split into energy band when these atoms are brought into close proximity to form a crystal. Then draw energy band diagram for insulator, semiconductor and conductor.

Q8 Calculate the temperature at which the there is a 3 percent probability that energy state 0.3eV below the Fermi level will not contain an electron.

Q9 Prove mathematically:
   1- At 0°K , all electrons lie below Fermi level.
2- At 0\(^0\)K, there is no electron will be above Fermi level.

3- At any temperature, there is 50\% probability that Fermi level occupied by an electron.

**Q10**

If the probability of electrons lie in the energy state with energy = 0.05eV below Fermi level equal to 87.36\%. What is the value of temperature that made probability decreased to 76.13\%.

**Q11**

If there is 60\% probability that energy state 0.55 above Fermi level is empty. Find probability that energy state 0.55 below Fermi level be occupied by an electron

**Q12**

Show that the probability of an energy state being occupied at \(\Delta E\) above the Fermi energy is the same as the probability of a state being empty at \(\Delta E\) below the Fermi level.

**Q13**

A Copper wire has \(10^{18}\) electron/m\(^3\) at energy state 0.01eV above the Fermi level at 27\(^0\)C. How many electron will this wire have at this energy state if temperature increase to 100\(^0\)C.