CoE 211 ELECTRONIC DEVICE PHYSICS

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Chapter Three

Introduction to Quantum Theory of Solids

This chapter aims to

- quantify the energy levels of electrons in crystal lattices,
- describe the statistical distribution of the very large number of electrons on a crystal.

3.1 Wave Equation for The Hydorgen Atom

- The potential function in hydrogen atom is due to the attraction between the +ve proton and the -ve electron.
  -) The potential function is $V(r) \propto 1/r$.

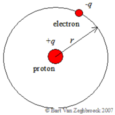


Figure: Potential function $V(r)$ in hydorgen atom.

- In spherical coordinates, the time-independent wave function is denoted by $\Psi(r, \theta, \phi)$.

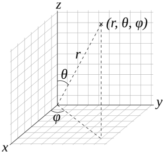


Figure: Spherical coordinates.

- Separable of variables:
  -) Let $\Psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi)$. Obtain three ordinary differential equations and solve for $R(r)$, $\Theta(\theta)$, and $\Phi(\phi)$.
  -) Each differential equation will give a quantized solution and a quantum number.

- There are four quantum numbers:

$$
\begin{aligned}
n &= 1, 2, 3, \cdots ,\\
l &= n-1, n-2, n-3, \cdots ,\\
m &= \pm l, \pm(l-1), \cdots , 0 ,\\
s &= \pm 1/2 .
\end{aligned}
$$

-) s is the intrinsic angular momentum or spin of the electron.
-) The set (n, l, m, s) corresponds to a quantum state which the electron may occupy.

- Pauli exclusion principle: In a given atom, molecule, or crystal, no two electrons may occupy the same quantum state.
- Example: The pdf function for the lowest quantum set $(n = 1, l = 0, m = 0)$ is

$$\Psi(r) = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} exp(-r/a_0) . \qquad (1)$$

-) $a_0 = 0.529$ $\AA$, it is the most probable distance from the nucleus to find the electron.

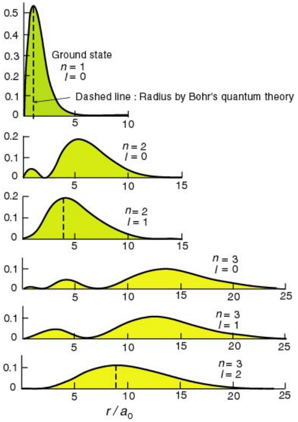


Figure: Pdfs for different quantum sets in the hydrogen atom.

Formation of Energy Bands

- When two hedrogen atoms are in close to each other, their wave functions overlap.
- The discrete quantized energy level with $n = 1$ will split into two discrete energy levels. Each electron has a distinct energy level.

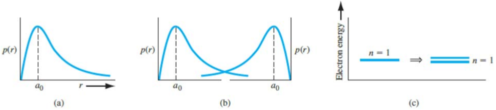


Figure: (a) Pdf for a hedrogen atom. (b) overlapping pdfs for two adjacent hydrogen atoms. (c) The splitting of $n = 1$ state.

- When more than two atoms become in close of each other, the quantized energy level will split into a band of discrete energy levels. Each electron has a distinct energy level.

-) r_0 is the interatomic distance in a crystal at which repulsion and attraction forces between atoms become in equilibrium.

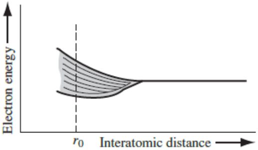


Figure: Splitting of an energy state into a band of allowed energies.

Formation of Energy Bands (cont.)

- Consider now a system of atoms with more than one electrons per atom. Suppose there are $n = 3$ discrete energy levels.
- When atoms are becoming in close of each other, the outermost electrons in the $n = 3$ energy level interact. This energy level will split into a band of allowed energies.
- If the atoms are getting closer, electrons in the $n = 2$ shell will interact and this energy level will split into a band of allowed energies.
- Similarly, the $n = 1$ shell may split if the atoms are getting further close.

- When more than two atoms become in close of each other, there would be *allowed bands of energies and forbidden bands of energies*.
- e.g., Assume a crystal with 10^{19} one-electron atoms. The width of the allowed energy band is 1 eV. The energy level of each electron would be separated by 10^{-19}.

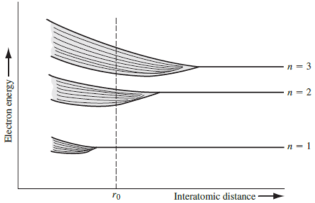
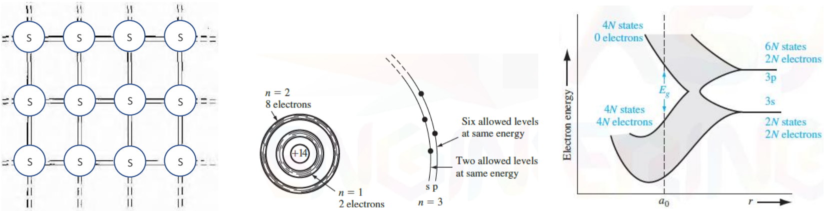


Figure: Splitting of three energy states into allowed bands of energies.

3.3.1 Energy Bands in Semiconductor

- In an isolated Si atom, there are 10 electrons in $n = 1$ and $n = 2$, and they are tightly bound to the nucleus. The other 4 electrons are at 3s and 3p and they are weakly bound.
- Si forms covalent bonding with another 4 Si atoms to have 8 electrons at $n = 3$.
- For N atoms of Si, the 3s and 3p split into three bands: the valence band, conduction band, and forbidden band.
  -) There are 4N quantum (energy) states in the valence band and 4N quantum states in the conduction band. There are no states in the forbidden band.
  -) With $T = 0$ K, the 4N states in the valence band is completely filled with 4N electrons. The 4N states in the conduction band is completely empty.
  -) E_g: is the difference between the lower of conduction band and the upper of valence band.



(a) (b) (c)

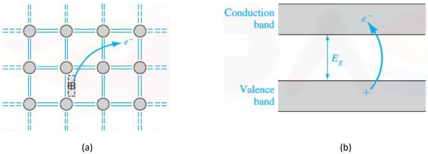
Figure: (a) Covalent bond in Si. (b) Schematic of an isolated Si atom. (c) The splitting of the 3s and 3p energy states of Si into allowed and forbidden energy bands.

3.3.2 Charge Carriers

- For $T > 0$ K, valence electrons may gain enough thermal energy to break the covalent bond and jump to the conduction band. These electrons represent the <u>1st charge carrier</u> in a semiconductor lattice.
- The free valence electron lead to create a +ve charge of an empty state in the valence band to keep the semiconductor neutrally charged.

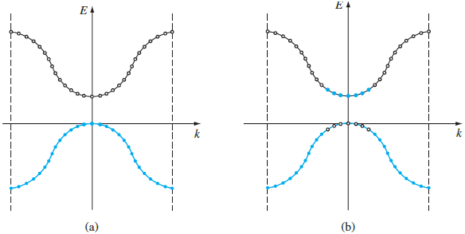
  -) These +ve charge empty state is called holes, and they represent the <u>2nd charge carrier</u> in the semiconductor.

  -) It is common to conceive the holes a subatomic particles that has a charge magnitude equal to the charge magnitude of the electron.



(a) (b)

Figure: (a) Breaking of a covalent bond. (b) Generation of a negative and positive charge when breaking the covalent bond.



(a) (b)

Figure: Energy vs k for the valence and conduction bands (a) $T = 0$ K. (b) $T > 0$.

3.3.3 Electron/Hole Effective Mass

- For a free electron in the space, classical mechanics *match* with quantum mechanics. A force F acting on the free electron would be $F = ma$, m: free electron mass, a: acceleration.
- For an electron moving in a lattice through a periodic potential function, there would an effective mass $m^\star$ that accounts for the particle mass and the effect of the internal forces.
- Recall for a free electron, $E = \frac{p^2}{2m} = \frac{\hbar^2}{2m}k^2$. The second derivative of E with respect to (wrt) k is

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = \frac{1}{m}\,. \tag{2}$$

  Note both d^2E/dK^2 and m are positive and constant.
- Approximate the energy near the bottom of conduction band by a parabola and the top of the valence band by a parabola as well:

$$E - E_c = C_1 k^2\,,$$
$$E - E_v = -C_2 k^2\,.$$

C_1, C_2 are positive quantities.

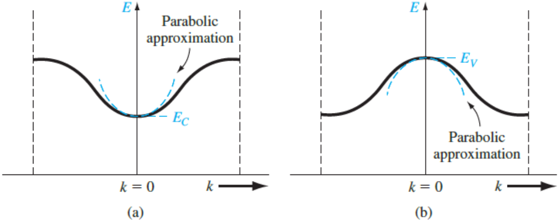


Figure: Parabolic approximation for (a) the conduction band and (b) the valence band.

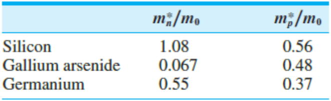
3.3.3 Electron/Hole Effective Mass (cont.)

- The 2nd derivative of E wrt k in the conduction band can be written as

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = 2\frac{C_1}{\hbar^2}\,, \tag{3}$$

and in the valence band as

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = -2\frac{C_2}{\hbar^2}\,. \tag{4}$$



	m_n^*/m_0	m_p^*/m_0
Silicon	1.08	0.56
Gallium arsenide	0.067	0.48
Germanium	0.55	0.37

Figure: Effective electron and hole mass.

- From comparing (2) with (3) and (2) with (4), we conclude

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = \left(2\frac{C_1}{\hbar^2} = \frac{1}{m_n^\star}\right)\,,$$

$$\frac{1}{\hbar^2}\frac{d^2E}{dk^2} = \left(-2\frac{C_2}{\hbar^2} = \frac{1}{m_p^\star}\right)\,.$$

-) $m_n^\star$ is the electron effective mass and $m_p^\star$ is the hole effective mass.

- Valence electrons with -ve charge and +ve mass $m_n^\star$ are the charge carriers in the conduction band,
- Holes with +ve charge and -ve mass $m_p^\star$ are the charge carriers in the valence band.

3.4 Density of Quantum States Function

- Question 1 : What is the total number of allowed quantum states in the conduction and valence bands.
- Consider a free electron with infinite potential function in 3D.

$$V(x,y,z) = \begin{cases} 0\,, & 0 < x < L, 0 < y < L, 0 < z < L \\ \infty\,, & \text{otherwise.} \end{cases}$$

- Similar to the depicted infinite potential well in chapter 2, define the wave numbers k_x, k_y and k_z in the directions x, y and z

$$k_x = \frac{\pi}{L} n_x, k_y = \frac{\pi}{L} n_y, k_z = \frac{\pi}{L} n_z\,.$$

-) n_x, n_y, n_z are integers. Only positive values of these parameters are considered.

-) These wave numbers form the wavevector $\mathbf{k} = (k_x, k_y, k_z)$.

- From the infinite potential well example of chapter 2, we can conclude that

$$\frac{2mE}{\hbar^2} = k^2 = k_x^2 + k_y^2 + k_z^2 = \left(n_x^2 + n_y^2 + n_z^2\right) \frac{\pi^2}{L^2}\,.$$

- The differential density of quantum states, $g_T(k)dk$, in the k-space is

$$g_T(k)dk = 2\left(\frac{1}{8}\right)\frac{4\pi k^2 dk}{\left(\frac{\pi}{L}\right)^3}.$$

-) The factor 2 represents the two spin states of the electron allowed for each quantum state,
-) The factor $1/8$ refers to the quantum states with $+$ve values for k_x, k_y and k_z,
-) The factor $4\pi k^2 dk$ is the differential volume,
-) The factor $(\pi/L)^3$ is the volume of one quantum state.

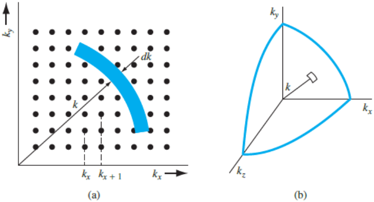


Figure: (a) A 2D array of allowed quantum states in k-space. (b) The positive one-eighth of the spherical k-space.

- Using $\frac{2mE}{\hbar^2} = k^2$ and $dk = \frac{1}{\hbar}\sqrt{\frac{m}{2E}}dE$, then the differential density $g_T(k)dk$ becomes

$$g_T(E)dE = \frac{4\pi L^3}{h^3}(2m)^{3/2}\sqrt{E}dE.$$

- The differential density per unit volume is

$$g_T(E)dE = \frac{4\pi}{h^3}(2m)^{3/2}\sqrt{E}dE.$$

Extension to Semiconductors

- At the bottom of the conduction band, we have

$$E - E_c = \frac{\hbar^2 k^2}{2m_n^\star} \, .$$

-) Thus, $g_T(E)dE$ becomes

$$g_c(E) = \frac{4\pi(2m_n^\star)^{3/2}}{h^3}\sqrt{E - E_c} \, . \qquad (5)$$

- A the top of valence band, we have

$$E_v - E = \frac{\hbar^2 k^2}{2m_p^\star} \, .$$

-) Thus, Thus, $g_T(E)dE$ becomes

$$g_v(E) = \frac{4\pi(2m_p^\star)^{3/2}}{h^3}\sqrt{E_v - E} \, . \qquad (6)$$

- There are no quantum states within the energy band $E_v < E < E_c$.

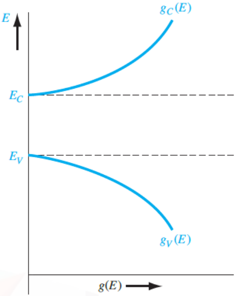


Figure: The density of energy states in the conduction band and in the valence band as a function of energy.

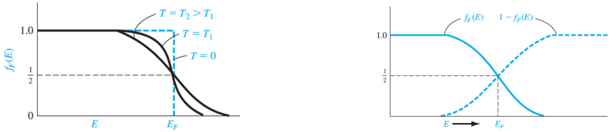
Example 3.1: Determine the total number of energy states in Si at $T = 300$ K
(a) Between E_c and $E_c + k_b T$,
(b) Between E_v and $E_v - k_b T$.
k_b is the Boltzmann constant and it is $k_b = 1.38 \times 10^{-23} \frac{J}{K}$.
The electron effective mass is $m_n^\star = 1.08m$ and the hole effective mass is $m_p^\star = 0.56m$. The free electron mass is $m = 9.11 \times 10^{-31}$ Kg.

3.5 Fermi-Dirac Probability Distribution

- Question 2: How many electrons would existed in the quantum states.
  -) Electrons would fill the allowed energy levels in a random fashion.
- Fermi-Dirac Probability Distribution, $f_F(E)$: This distribution gives the probability of an electron to occupy an energy level E at temperature T:

$$f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_b T}\right)}, \tag{7}$$

  -) E_F is called the Fermi energy ,
- At $T = 0$ K, $f_F(E < E_F) = 1$ and $f_F(E > E_F) = 0$ from (7) . Then, all electrons will occupy energy levels that are below E_F.
- For $T > 0$, the statistical distribution of electrons among the energy levels may change.
  -) There is non-zero probability that some energy states above E_F will be occupied.
  -) Note $f_F(E = E_F) = 0.5$. This means that an electron occupies E_F with probability 0.5.
- The function $(1 - f_F(E))$ represents the probability of an energy state being empty. $1 - f_F(E)$ is symmetric with $f_F(E)$ around E_F.



(a) (b)

Figure: $f_F(E)$ vs energy for different temperatures. (b) The probability functions $f_F(E)$ and $(1 - f_F(E))$.

Example 3.2: Assume the Fermi energy level for a particular material is 0.35 eV above the valence band energy.
(a) Determine the probability of a state being empty of an electron at $E_v - k_b T$ with $T = 300$ K,
(b) Calculate the temperature at which there is a 1% probability that the state $E_v - k_b T$ will not contain an electron.

End of Chapter Three