

Fig. 5.4. First four wave functions (solid lines) and the corresponding energy levels (broken lines) of an electron in a one-dimensional crystal.

10.3 THREE DIMENSIONAL POTENTIAL WELL

For simplicity, let us now consider a situation when the electrons are moving inside a three dimensional potential box of side “a” as shown in Fig. 10.6. Like one dimensional case, the potential energy inside the cube is taken as zero and very high (tending to infinity) outside it. Under this assumption, the Schrodinger wave equation becomes

$$\frac{d^2\psi(x, y, z)}{dx^2} + \frac{d^2\psi(x, y, z)}{dy^2} + \frac{d^2\psi(x, y, z)}{dz^2} + \frac{8\pi^2m}{h^2} E\psi(x, y, z) = 0 \quad (9)$$

for which straightforward solution of the standing wave type may be assumed, i.e.

$$\psi(x, y, z) = A_x \sin(k_x x) A_y \sin(k_y y) A_z \sin(k_z z) \quad (10)$$

where

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

Like one dimensional case, the value of the constants A_x , A_y and A_z can be determined by

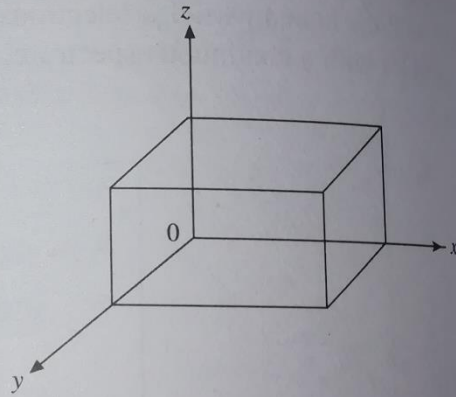


Fig. 10.6 A three dimensional potential box

Refer Solid State Physics S.O. Pillai for full derivation-similar to the topic discussed “electron moving in one dimensional potential box

applying the suitable boundary conditions, i.e. $x = 0$ and $x = a$, $y = 0$ and $y = a$ and $z = 0$ and $z = a$, we have

$$A_x = \left(\frac{2}{a}\right)^{1/2}, A_y = \left(\frac{2}{a}\right)^{1/2} \text{ and } A_z = \left(\frac{2}{a}\right)^{1/2}$$

Therefore, the normalized wave function for a cubical box becomes

$$\psi_n = \left(\frac{2}{a}\right)^{3/2} \sin \frac{n_x \pi x}{a} \cdot \sin \frac{n_y \pi y}{a} \cdot \sin \frac{n_z \pi z}{a} \quad (11)$$

The corresponding form of energy is given by

$$E_n = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad (12)$$

or

$$E_n = \frac{h^2 n^2}{8ma^2}, \text{ where } n^2 = n_x^2 + n_y^2 + n_z^2 \quad (13)$$

Thus, in three-dimensions, we have three quantum numbers n_x , n_y and n_z which can take only positive integer values.

Example: Find the lowest energy of an electron confined to move in a three dimensional potential box of length 0.5 \AA

Solution: Given: $a = 0.5 \text{ \AA} = 0.5 \times 10^{-10} \text{ m}$, E (lowest) = ?

The possible energies of a particle in a cubical box of side a are given by

$$E_n = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

For lowest energy $n_x = n_y = n_z = 1$. Therefore

$$\begin{aligned} E_{111} &= \frac{3h^2}{8ma^2} = \frac{3 \times (6.626 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (0.5 \times 10^{-10})^2} \\ &= 7.24 \times 10^{-17} \text{ J} = \frac{7.24 \times 10^{-17}}{1.6 \times 10^{-19}} = 452 \text{ eV} \end{aligned}$$

in the energy state immediately above the lowest energy state at which the average energy is in the upper level

XV. DENSITY OF ENERGY STATES AND FERMI ENERGY

The Fermi function does not, by itself, give us the number of electrons which have a certain energy; it gives us only the probability of occupation of an energy state by a single electron. Since even at the highest energy, the difference between neighbouring energy levels is as small as 10^{-6} eV, we can say that in a macroscopically small energy interval dE there are still many discrete energy levels. So we can introduce the concept of density of energy states which will simplify our calculation considerably. To know the actual number of electrons with a given energy, one must know the number of states in the system which have the energy under consideration. Then by multiplying the number of states by the probability occupation we get the actual number of electrons. If $N(E)$ is the number of electrons in a system that have energy E , and $Z(E)$ is the number of states at that energy, then

$$N(E) dE = Z(E) dE F(E)$$

(6.104)

We know that, the number of energy states, with a particular value of E , depends on how many combinations of the quantum numbers result in the same value of n . Since we are dealing with

almost a continuum of energy levels, we may construct a space of points represented by the values of n_x , n_y and n_z and let each point with integer values of the coordinates represent an energy state.

A radius vector n from the origin may be drawn to a point n_x, n_y, n_z in this space, and all points on the surface of a sphere of radius n will have the same energy. Thus n represents a vector to a point n_x, n_y, n_z ($n^2 = n_x^2 + n_y^2 + n_z^2$) in three-dimensional space. In this space every integer specifies a state; that is, a unit cube contains exactly one state. Hence the number of states in any volume is just equal to the numerical value of the volume expressed in units of cubes of lattice parameters.

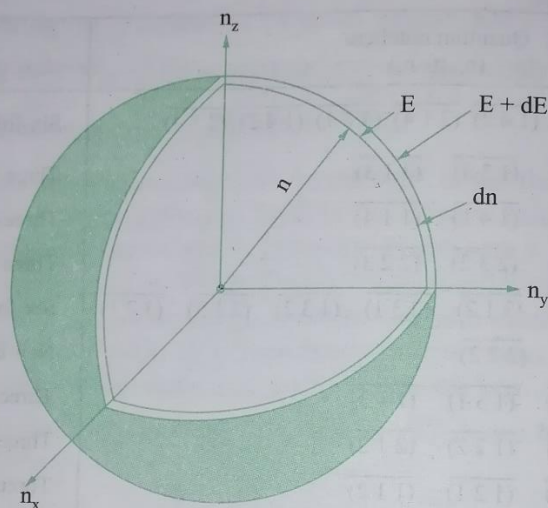


Fig. 6.17 Density of energy states calculation

Therefore, the number of available states within a sphere of radius n is given by $\frac{1}{8} \left(\frac{4\pi}{3} \pi n^3 \right)$. The factor $\frac{1}{8}$ accounts for the fact that only positive integers are allowable and thus only one octant of the sphere alone be considered. Again the number of states within a sphere of radius $(n + dn)$ is, therefore, $\frac{1}{8} \left(\frac{4\pi}{3} \right) (n + dn)^3$. Thus the number of energy states having energy values lying between E and $E + dE$ (i.e., in the energy interval dE) is given by

$$Z(E) dE = \frac{1}{8} \left(\frac{4\pi}{3} \right) (n + dn)^3 - \frac{1}{8} \left(\frac{4\pi}{3} \right) n^3$$

$$Z(E) dE = \frac{\pi}{6} [(n + dn)^3 - n^3] = \frac{\pi}{6} [n^3 + dn^3 + 3n^2 dn + 3dn^2 n - n^3]$$

$$\cong \frac{\pi}{6} (3n^2 dn) = \frac{\pi}{2} n^2 dn$$

(6.105)

From equation (6.99)

$$E = \frac{h^2 n^2}{8ma^2}$$

$$n^2 = \frac{8ma^2 E}{h^2} \text{ and } n = \left[\frac{8ma^2}{h^2} \right]^{1/2} E^{1/2}$$

i.e.,

$$2n \, dn = \left[\frac{8ma^2}{h^2} \right] dE$$

and

$$dn = \left(\frac{1}{2n} \right) \left[\frac{8ma^2}{h^2} \right] dE$$

or

Substituting these values in equation (6.105), we get

$$Z(E) \, dE = \left(\frac{\pi}{2} \right) n (n \, dn)$$

i.e.,

$$Z(E) \, dE = \frac{\pi}{2} \left[\frac{8ma^2}{h^2} \right]^{1/2} E^{1/2} \left[n \frac{1}{2n} \left(\frac{8ma^2}{h^2} \right) dE \right]$$

$$Z(E) \, dE = \frac{\pi}{4} \left[\frac{8ma^2}{h^2} \right]^{3/2} E^{1/2} \, dE$$

It should be now remembered that the Pauli's exclusion principle permits two electrons in each state, so that the number of energy levels actually available are

$$Z(E) \, dE = 2 \frac{\pi}{4} \left[\frac{8ma^2}{h^2} \right]^{3/2} E^{1/2} \, dE$$

$$Z(E) \, dE = \frac{\pi}{2} \left[\frac{8ma^2}{h^2} \right]^{3/2} E^{1/2} \, dE \quad (6.106)$$

The simple parabolic function is illustrated in Fig. 6.18.

Hence the number of energy states present in unit volume having energy values lying between E and $E + dE$ (called *density of energy states*) is given by

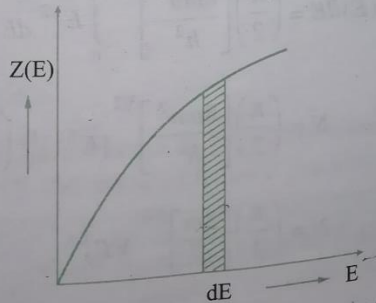


Fig. 6.18 Density of energy states for a free electron gas

$$Z'(E) dE = \frac{\pi}{2} \left[\frac{8m}{h^2} \right]^{3/2} E^{1/2} dE$$

The actual number of electrons $N(E) dE$ in a given energy interval dE will now be obtained by multiplying the number of energy states in the interval by the Fermi distribution function.

$$N(E) dE = Z(E) dE F(E)$$

$$N(E) dE = \left(\frac{\pi}{2} \right) \left[\frac{8m}{h^2} \right]^{3/2} V E^{1/2} \frac{dE}{1 + \exp[(E - E_F)/k_B T]}$$

This distribution is shown in Fig. 6.19.

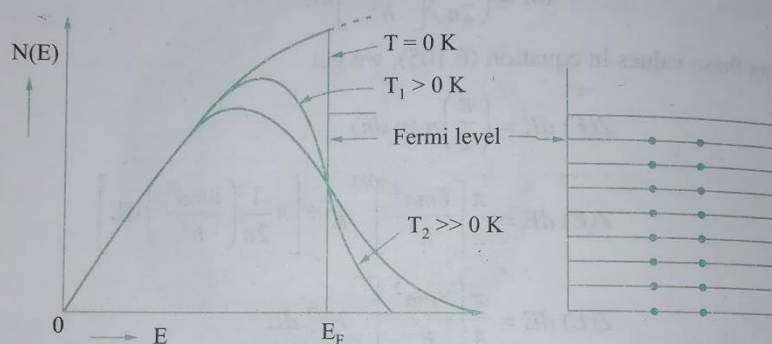


Fig. 6.19 The population density of a free electron gas

At absolute zero, the distribution problem is simple, all states up to Fermi level are filled and those above E_F are empty. At higher temperature the typical tailing appears, the extent of this tailing being, of course, very small compared with the scale of the distribution until very high temperatures are reached. The relation for the Fermi level in a metal is possible at any temperature, but is simple at zero degree absolute. The general expression for $N(E) dE$ is

$$\frac{\pi}{2} \left[\frac{8ma^2}{h^2} \right]^{3/2} E^{1/2} dE F(E)$$

When

$T = 0 \text{ K}$, $F(E) = 1$ since $E < E_F$

Thus,

$$\int N(E) dE = \left(\frac{\pi}{2} \right) \left[\frac{8ma^2}{h^2} \right]^{3/2} \int_0^{E_F} E^{1/2} dE$$

$$N = \left(\frac{\pi}{2} \right) \left[\frac{8ma^2}{h^2} \right]^{3/2} [E^{3/2}]_0^{E_F} \left(\frac{2}{3} \right)$$

$$N = \left(\frac{\pi}{3} \right) \left[\frac{8m}{h^2} \right]^{3/2} V E_F^{3/2}$$

(6.1)

Therefore, the number of electrons per unit volume (called density of electrons) is

$$n = \frac{N}{V} = \frac{\pi}{3} \left[\frac{8m}{h^2} \right]^{3/2} E_F^{3/2} \quad (6.109)$$

$$E_F^{3/2} = \left(\frac{3n}{\pi} \right) \left[\frac{h^2}{8m} \right]^{3/2}$$

$$E_F = \left(\frac{h^2}{8m} \right) \left[\frac{3n}{\pi} \right]^{2/3}$$

$$E_F = \left(\frac{h^2}{2m} \right) \left[\frac{3n}{8\pi} \right]^{2/3} = 0.58 \times 10^{-37} n^{2/3} \text{ joule} \quad (6.110)$$

$$E_F = 3.65 \times 10^{-19} n^{2/3} \text{ (in electron volt)}$$

This expression for Fermi energy is a very useful quantity, because whenever we use the free electron model, which is quite often, the value of E_F gives the top most energy level at absolute zero. The Fermi energy values of some selected metals are given in Table 6.1.

XVIII. MEAN ENERGY OF ELECTRON GAS AT ABSOLUTE ZERO

The Fermi energy at absolute zero is given by equation (6.110), i.e.,

$$E_F = \left(\frac{h^2}{2m} \right) \left[\frac{3n}{8\pi} \right]^{2/3}$$

It is now possible to estimate the average electron energy at 0 K. To do this, first obtain the total energy U_0 at 0 K, which is given by the following equation:

$$U_0 = \int_0^{E_F} Z(E) dE \quad \text{with } F(E) = 1 \quad (6.110b)$$

From equation (6.106)

$$U_0 = \left(\frac{\pi}{2} \right) \left[\frac{8ma^2}{h^2} \right]^{3/2} \int_0^{E_F} E^{3/2} dE = \frac{\pi}{5} \left[\frac{8ma^2}{h^2} \right]^{3/2} [E_F]^{5/2}$$

Thus, the mean energy of the electron at 0 K is

$$\bar{E}_0 = \frac{U_0}{N}$$

Substituting the value of N from equation (6.108), we get

$$\bar{E}_0 = \frac{\pi \left[\frac{8ma^2}{h^2} \right]^{3/2} (E_F)^{5/2}}{\frac{\pi}{3} \left[\frac{8ma^2}{h^2} \right]^{3/2} E_F^{3/2}}$$

(6.111)

$$\bar{E}_0 = \frac{3}{5} E_F$$

insulate. When we considered the solid as a collection of free electrons in a box, we imposed the condition that the wave function vanishes at the walls of the box—that is, on the surface of the sample, allowing the conduction electrons to move in a region of constant potential. Obviously this approximation of the potential inside the crystal is too drastic.

It is now suggested to disregard the surface and to treat the crystal as an infinite array of lattice points. To do this, slightly different forms of boundary conditions, called cyclic or periodic boundary conditions, have been developed. Inside a real crystal, there is a periodic arrangement of positively charged ions through which the electrons move. The motion of a representative electron is shown in Fig. 6.42 (a). The potential of the electron at the positive ion site is zero and is maximum in between. So in Fig. 6.42 (b). We find that the potential varies periodically, with the same period as the lattice. We have now to study the motion of the electron in such a lattice and energy states it can occupy. The appropriate Schrödinger equation for the motion of the electron is given by

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)]\psi = 0$$

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m}{h^2} [E - V(x)]\psi = 0 \quad (6.170)$$

where, the potential function $V(x)$ has the periodicity of the lattice given by

$$V(x) = V(x + a) \quad (6.171)$$

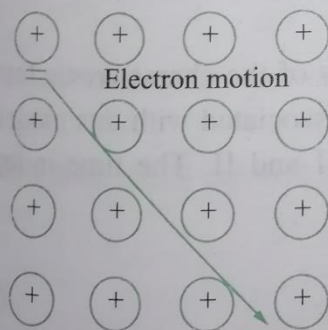
with a as the periodicity of the lattice.

Bloch has shown that an equation of the type (6.170) has a solution of the form

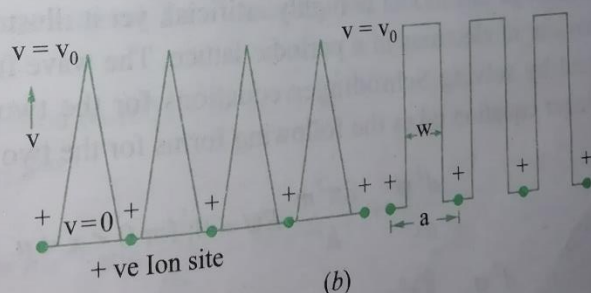
$$\psi(x) = u_K(x)e^{iKx} \quad (6.172)$$

where, $u_K(x)$ has the periodicity of the lattice given by

$$u_K(x) = u_K(x + a) \quad (6.173)$$



(a)



(b)

Fig. 6.42 One-dimensional periodic potential distribution for a crystal