FAQs & their solutions for Module 4:
Particle in a three-dimensional box

Question1: For a free particle inside a cube, the potential energy variation of the form

$$\begin{aligned} V(x,y,z) &= \quad \text{for} \quad 0<x<L \;;\; 0<y<L\;;\; 0<z<L \\ &= \qquad\quad \infty \;\; \text{everywhere else} \end{aligned} \tag{1}$$

Solve the Schrödinger equation and obtain the energy eigenvalues and eigenfunctions.

Solution1: For a free particle inside the box, the Schrödinger equation is given by

$$\nabla^2\psi + \frac{2\mu E}{\hbar^2}\psi = 0 \quad \begin{cases} 0<x<L \\ 0<y<L \\ 0<z<L \end{cases} \tag{2}$$

The boundary condition is that ψ should vanish everywhere on the surface of the cube. We use the method of separation of variables and write $\psi = X(x)\, Y(y)\, Z(z)$ to obtain

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2\mu E}{\hbar^2} \tag{3}$$

The first term is a function of x alone, the second term of y alone, etc., so that each term has to be set equal to a constant. We write

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2 \tag{4}$$

and similar equations for $Y(y)$ and $Z(z)$ with

$$k_x^2 + k_y^2 + k_z^2 = \frac{2\mu E}{\hbar^2} \tag{5}$$

We have set each term equal to a negative constant; otherwise the boundary conditions cannot be satisfied. The solution of Eq. (3) is

$$X(x) = A\sin k_x x + B\cos k_x x$$

and since ψ has to vanish on all points on the surface $x = 0$ we must have $B = 0$. Further, for ψ to vanish on all points on the surface $x = L$, we must have

$$\sin k_x L = 0$$

or

$$k_x = \frac{n\pi}{L} \quad \text{with} \quad n_x = 1, 2, \ldots \tag{6}$$

Similarly for k_y and k_z. Using Eq.(5) we get the following expression for energy eigenvalues

$$E = \frac{\pi^2\hbar^2}{2\mu L^2}(n_x^2 + n_y^2 + n_z^2) \;;\; n_x, n_y, n_z = 1,2,3,.. \tag{7}$$

The corresponding normalized wave functions are

$$\psi(x,y,z)=\left(\frac{8}{L^3}\right)^{1/2}\ \sin\frac{n_x\pi}{L}x\ \sin\frac{n_y\pi}{L}y\ \sin\frac{n_z\pi}{L}z \tag{8}$$

<u>Question2:</u> For a free particle inside the box, the energy eigenvalues are given by

$$E=\frac{\pi^2\hbar^2}{2\mu L^2}(n_x^2+n_y^2+n_z^2)\ ;\ n_x,n_y,n_z=1,2,3,.. \tag{9}$$

Calculate the density of states $g\ E$ where $g\ E\ dE$ represents the number of states whose energy lies between E and $E+dE$

<u>Solution2:</u> Let $g\ E\ dE$ represents the number of states whose energy lies between E and $E+dE$. If $N\ E$ represents the total number of states whose energies are less than E, then

$$N(E)=\int_0^E g(E)\ dE \tag{10}$$

and therefore

$$g(E)=\frac{dN(E)}{dE} \tag{11}$$

Now,

$$n_x^2+n_y^2+n_z^2=\frac{2\mu L^2 E}{\pi^2\hbar^2}=R^2\quad\text{(say)} \tag{12}$$

Thus $N\ E$ will be the number of sets of integers whose sum of square is less than R^2. In the n_x, n_y, n_z space each point corresponds to a unit volume and if we draw a sphere of radius R then the volume of the positive octant will approximately represent[1] $N\ E$; we have to take the positive octant because n_x, n_y and n_z take positive values. Thus

$$N(E)=2\times\frac{1}{8}\times\frac{4\pi}{3}R^3=\frac{(2\mu)^{3/2}L^3}{3\pi^2\hbar^3}\ E^{3/2} \tag{13}$$

where an additional factor of 2 has been introduced as a state can be occupied by two electrons (corresponding to the two spin states). Using Eq. (9) we get

$$g(E)=\frac{(2\mu)^{3/2}V}{2\pi^2\hbar^3}\ E^{1/2} \tag{14}$$

where $V(=L^3)$ represents the volume of the box.

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[1] If the reader finds it difficult to understand he may first try to make the corresponding two-dimensional calculations in which one is interested in finding the number of sets of integers such that $n_x^2+n_y^2<R^2$. If one takes a graph paper then each corner corresponds to a set of integers and each point can be associated with a unit area. Thus the number of sets of integers would be $\pi R^2/4$ where the factor ¼ is because of the fact that we are interested only in the positive quadrant.

Question3: In a metal (like Na, Cu etc.) electrons are assumed to be free and at absolute zero (i.e., at $T = 0$) all states below a certain level E_{F_0} are assumed to be occupied; the energy E_{F_0} is referred to as the Fermi energy at absolute zero. Using the results of the previous problem, derive an expression for E_{F_0}.

Solution3: In a metal like Na, electrons are assumed to be free and at absolute zero (i.e., at $T = 0$) all states below a certain level E_{F_0} are assumed to be occupied. Thus

$$
\begin{aligned}
N &= \int_0^{E_{F_0}} g \quad E \quad dE \\
&= (2\mu)^{3/2} \frac{V}{2\pi^2\hbar^3} \int_0^{E_{F_0}} E^{1/2} \, dE \qquad (15) \\
&= (2\mu)^{3/2} \frac{V}{3\pi^2\hbar^3} E_{F_0}{}^{3/2}
\end{aligned}
$$

Simple manipulations give us

$$E_{F_0} = \frac{\hbar^2}{2\mu}(3\pi^2 n)^{2/3} \qquad (16)$$

where $n(= N/V)$ represents the number of free electrons per unit volume.

Substituting the numerical values of various constants

$$m_e = 9.1093897 \times 10^{-31} \text{ kg} \quad \text{and} \quad \hbar = \frac{h}{2\pi} = 1.05457266 \times 10^{-34} \text{ Js}$$

we get

$$
\begin{aligned}
E_{F_0} &\approx 5.84 \times 10^{-27} \, n^{2/3} \text{ erg} \\
&\approx 3.65 \times 10^{-15} \, n^{2/3} \text{ eV}
\end{aligned} \qquad (17)
$$

where n is measured in cm^{-3}. For sodium with one free electron per atom and having a density of 0.97 g/cm^3 we get

$$n \approx \frac{6.023 \times 10^{23} \times 0.97}{23} = 2.54 \times 10^{22} \text{ electrons/cm}^3$$

Thus

$$E_{F_0} \approx 3.2 \text{ eV}$$

Now at $T \approx 300^\circ$ K, $kT \approx 0.025$ eV. Thus $E_{F_0} \gg kT$

Question4: For sodium with one free electron per atom and having a density of 0.97 g/cm^3 calculate the value of E_{F_0} and show that at room temperatures ($T \approx 300^o$ K), the electron gas is almost completely degenerate i.e., $E_{F_0} \gg kT$.

Solution4: For copper we assume one free electron per atom. Its density is about 8.94 g/cm^3 and its atomic mass is 63.5. Thus

$$n \approx \frac{6.023\times 10^{23}\times 8.94}{63.5} = 8.48\times 10^{22} \text{ electrons/cm}^3$$

Using the formula derived above we get $E_{F_0} \approx 7.0$ eV