2. Quantum Mechanics of Particles in a Box

M. App: B1 and B2; B&S Chapter 7.1 – 7.3, K&K p72

Imagine a cubic box of side L.

2.1 Single Particle Energy Eigenvalues

$$-\frac{\hbar^2}{2M}\nabla^2 \psi + V\psi = E\psi$$

V = 0 inside the box. V = ∞ outside the box.
⇒ ψ = 0 on the walls.
For a 1D well of width L;
 $\sqrt{2}$

$$\Psi = \sqrt{\frac{L}{L}} \sin kx$$

where $k = \frac{\ell \pi}{L}$, $\ell = 1, 2, 3, ...$
 $E = \frac{\hbar^2 k^2}{2M}$



 ψ has an integral number of half-wavelengths in the box.

For 3D "cubic" well;

$$\Psi(x, y, z) = \left(\sqrt{\frac{2}{L}}\right)^3 \sin k_x x \sin k_y y \sin k_z z$$
$$k_x = \frac{\ell \pi}{L}, \ k_y = \frac{m \pi}{L}, \ k_z = \frac{n \pi}{L}$$

 ℓ, m, n are positive integers.

NB: integer values are forced by the boundary condition $\psi(x=0,y,z) = (x=L,y,z) = 0$.

$$E = \frac{\hbar^2 k^2}{2M}$$
 where $k^2 = k_x^2 + k_y^2 + k_z^2$ (confirm this - + or x?)
 $\ell = 0 \rightarrow \psi = 0$ so zero is not allowed.

Negative integers $\rightarrow [\psi \rightarrow -\psi] \rightarrow$ this is not a distinct state.

2.2 The concept of Reciprocal Space (also called momentum space or k-space)

Very important concept. Used in particle, nuclear, atomic and solid state physics. It allows the plotting of the eigenstates.

The <u>k</u>-vector has components $(k_x, k_y, k_z) = \frac{\pi}{L}(\ell, m, n)$.



(supposed to be a 3D box with a vector pointing to the point...)

The point represents the state ℓ, m, n with energy $\frac{\hbar^2 k^2}{2M}$ and distance squared from the origin in k space

origin in k-space.

The states of the particle in the box are referred to as k-states.

Why reciprocal space? Because k has dimensions of $\frac{1}{length}$.

Why k-space? k is universally used for wave numbers.

Why momentum space? Because $\hbar k$ has dimensions of momentum.

 $\ell \rightarrow \ell + 1$ would be equivalent to a displacement $\frac{\pi}{L}$ along k_x .

 $m \rightarrow m+1$ would be equivalent to a displacement $\frac{\pi}{L}$ along k_y .

 $n \rightarrow n+1$ would be equilavent to a displacement $\frac{\pi}{L}$ along k_z .

The totality of states corresponds to all positive values of ℓ, n, m .

The points representing these states map out a simple cubic lattice in k space of side π

$$\overline{L}$$

2.3 The density of states

(This will definitely be on the exam.)

Say we have a $1cm^3$ box of Helium atoms at T = 300k.

The energy
$$k_0 T = \frac{\hbar^2 \pi^2}{2 M L^2} (\ell^2 + m^2 + n^2).$$

 $\ell^2 + m^2 + n^2 \approx 5 \times 10^{16}.$

We are usually interested in states far from the origin i.e. large ℓ, m, n (except for the important case of Bose-Einstein condensation).

One state occupies a volume $\left(\frac{\pi}{L}\right)^3$ of k-space. Therefore the density of states

$$=\left(\frac{L}{\pi}\right)^3 = \frac{V}{\pi^2}$$
 states per unit volume of k-space.

How many states in a spherical shell of k-space?

Shell between k and k + dk. Assume $dk >> \frac{\pi}{2}$.



3D case:

The number of states in the shell is:

$$\frac{1}{8}4\pi k^2 dk \times \frac{V}{\pi^3}$$

where $\frac{1}{8}$ is the positive octant $k_x, k_y, k_z > 0$ only, the second part is the spherical shell volume, and the last part is the density of state.

$$=\frac{Vk^2}{2\pi^2}dx=\rho(k)dk$$

where $\rho(k) = \frac{Vk^2}{2\pi^2}$. This is also called the density of states. It is the rate at which the number of states increases per unit increases in the magnitude of k

number of states increases per unit increase in the magnitude of k.

 $\rho(k)dx$ is the number of states between k and k + dk.

Let $g(\varepsilon)d\varepsilon$ equal the number of stases whose energies lie between ε and $\varepsilon + d\varepsilon$. $g(\varepsilon)d\varepsilon = \rho(k)dk$.

$$\varepsilon = \frac{\hbar \hat{k}}{2M} \text{ for non-relativistic particles.}$$

For photons:
 $\varepsilon = pc = \hbar ck$
Now:
 $g(\varepsilon) = \rho(k) \frac{dk}{d\varepsilon}$
For non-relativistic particles
 $\frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{M}$
Therefore:
 $g(\varepsilon) = \frac{Vk^2}{2\pi^2} \frac{M}{\hbar^2 k} = \frac{VMk}{2\pi^2 \hbar^2}$
 $k = \left(\frac{2M\varepsilon}{\hbar^2}\right)^{\frac{1}{2}}$
So:
 $g(\varepsilon) = \frac{V}{4\pi^2} \left(\frac{2M}{\hbar^2}\right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}}$
For photons $\varepsilon = \hbar ck$:
 $\frac{d\varepsilon}{dk} = \hbar c$
 $g(\varepsilon) = \rho(k) \frac{dk}{d\varepsilon} = \frac{Vk^2}{2\pi^2} \frac{1}{\hbar c} = \frac{V}{2\pi^2 \hbar c} k^2 = \frac{V}{2\pi^2} \left(\frac{\varepsilon}{\hbar c}\right)^2$
 $9^{(\varepsilon)}$
 $= photons$
Allow for spin degeneracy:
 $g(\varepsilon) = (2s+1) \frac{V}{4\pi^2} \left(\frac{2M}{\hbar^2}\right)^{\frac{3}{2}} \varepsilon^{\frac{1}{2}}$

might be occupied (say for electrons) by \uparrow - 1) is the spin degeneracy (23)or \downarrow electron.

2.4 Two dimensional density of state Density of states:

$$k(x) = \frac{m\pi}{L} \quad k_y = \frac{n\pi}{L} \quad (m, n \text{ are positive integers})$$
Area of one box = $\left(\frac{\pi}{L}\right)^2 = \frac{\pi^2}{A}$
 $L^2 = A$ the area of the box.
Density of states = $\frac{1}{\left(\frac{\pi}{L}\right)^2} = \frac{A}{\pi^2}$
No. of states between k and $k + dk$ (k , $dk \gg \frac{\pi}{2}$) = $\frac{1}{4}2\pi k dk \frac{A}{\pi^2}$

Where $\frac{1}{4}2\pi kdk$ is the area between the curved lines, and $\frac{A}{\pi^2}$ the density of states in two dimensions.

$$\frac{A}{2\pi}k = \rho(k)$$

$$g(\varepsilon)d\varepsilon = \rho(k)dk$$

$$g(\varepsilon) = \rho(k)\frac{dk}{d\varepsilon}$$

$$\varepsilon = \frac{\hbar^2 k^2}{2M}$$

$$\frac{d\varepsilon}{dk} = \frac{\hbar^2 k}{M}$$

$$g(\varepsilon) = \frac{A}{2\pi}k\frac{M}{\hbar^2 k} = \frac{A}{2\pi}\frac{M}{\hbar^2}$$

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