Physics 371 Lecture 27

The Schrödinger equation in 3D

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V\,\Psi(x,y,z,t)$$

$$\rightarrow \quad E\,\psi(x,y,z) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(x,y,z)\right]\psi(x,y,z)$$

(time-indep. form)

$$\vec{p} = \frac{\hbar}{i}\nabla \quad \text{momentum opertor}$$

$$\nabla \equiv \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$$

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

i) <u>Free particle</u> ($V=0$)

$$\psi_{\vec{k}}(x,y,z) = e^{i\vec{k}\cdot\vec{r}}$$

$$\vec{r} = (x, y, z), \quad \vec{k} = (k_x, k_y, k_z)$$

$$\hat{H}\,\psi_{\vec{k}}(\vec{r}) = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right)\psi_{\vec{k}}(\vec{r})$$

$$= \frac{\hbar^2 \vec{k}^2}{2m}\,\psi_{\vec{k}}(\vec{r})$$

$$\Longrightarrow \quad E_{\vec{k}} = \frac{\hbar^2 \vec{k}^2}{2m}$$

ii) Particle in a box

$$0 < x < L_1$$
$$0 < y < L_2$$
$$0 < z < L_3$$

Separation of variables:

let $\psi(x, y, z) = \psi_1(x)\,\psi_2(y)\,\psi_3(z)$

$$-\frac{2mE}{\hbar^2} = \frac{1}{\psi_1}\frac{d^2\psi_1}{dx^2} + \frac{1}{\psi_2}\frac{d^2\psi_2}{dy^2} + \frac{1}{\psi_3}\frac{d^2\psi_3}{dz^2}$$

$$\frac{1}{\psi_1}\frac{d^2\psi_1}{dx^2} = \text{const.} \equiv -\frac{2mE_1}{\hbar^2}$$

B.C.s: $\psi_1(0) = 0 = \psi_1(L_1)$

$$\Rightarrow \psi_1(x) = A \sin\left(\frac{n_1 \pi x}{L_1}\right),$$

$$E_1 = \frac{\hbar^2 \pi^2 n_1^2}{2m L_1^2}, \quad n_1 = 1, 2, 3, \ldots, \infty$$

similarly, $\psi_2(y) = B \sin\left(\frac{n_2 \pi y}{L_2}\right)$,

$$E_2 = \frac{\hbar^2 \pi^2 n_2^2}{2m L_2^2}, \quad n_2 = 1, 2, 3, \ldots, \infty;$$

$$\psi_3(z) = C \sin\left(\frac{n_3 \pi z}{L_3}\right),$$

$$E_3 = \frac{\hbar^2 \pi^2 n_3^2}{2m L_3^2}, \quad n_3 = 1, 2, 3, \ldots, \infty$$

$$\Rightarrow \psi(x, y, z) = D \sin\left(\frac{n_1 \pi x}{L_1}\right) \sin\left(\frac{n_2 \pi y}{L_2}\right) \sin\left(\frac{n_3 \pi z}{L_3}\right)$$

$$E = E_1 + E_2 + E_3 = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)$$

$0 < n_1, n_2, n_3 \in \mathbb{Z}$ $\quad (D = ABC)$

normalization

$$1 = \int_0^{L_1} dx \int_0^{L_2} dy \int_0^{L_3} dz \, |\psi(x,y,z)|^2$$

$$= |D|^2 \int_0^{L_1} dx \, \sin^2\left(\frac{n_1 \pi x}{L_1}\right) \int_0^{L_2} dy \, \sin^2\left(\frac{n_2 \pi y}{L_2}\right)$$

$$\times \int_0^{L_3} dz \, \sin^2\left(\frac{n_3 \pi z}{L_3}\right)$$

$$= |D|^2 \frac{L_1}{2} \frac{L_2}{2} \frac{L_3}{2} = |D|^2 \frac{V_{box}}{8}$$

$$\Rightarrow D = \sqrt{\frac{8}{V_{box}}}$$

iii) Special case: Cube, $L_i = L$

$$E = \frac{\hbar^2 \pi^2}{2 m L^2} \left(n_1^2 + n_2^2 + n_3^2\right)$$

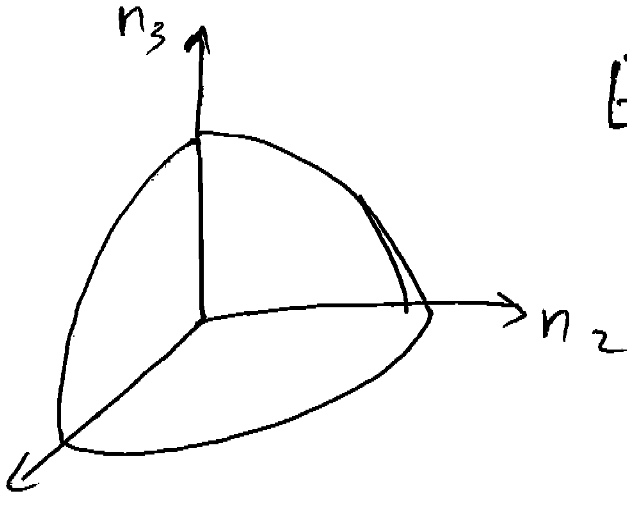
$$= \frac{\hbar^2 \pi^2 \vec{n}^2}{2 m L^2}$$

$\frac{2mL^2}{\hbar^2\pi^2} E$	n_1	n_2	n_3	
3	1	1	1	
6	2	1	1	
6	1	2	1	$d=3$
6	1	1	2	
9	2	2	1	
9	2	1	2	$d=3$
9	1	2	2	

etc.

Counting states

$$N(\varepsilon < E) \cong \frac{1}{8}\frac{4\pi}{3} n(E)^3 = \frac{\pi}{6} n(E)^3$$



$$E = \frac{\pi^2 \hbar^2 \vec{n}^2}{2m L^2} \equiv \frac{\pi^2 \hbar^2}{2m L^2} n(E)^2$$

$$n(E) = \sqrt{\frac{2mL^2 E}{\pi^2 \hbar^2}}$$

$$n(E)^3 = \left(\frac{2mE}{\pi^2 \hbar^2}\right)^{3/2} V$$

$$\frac{N(E)}{V} = \frac{1}{6\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2} = \frac{k^3}{6\pi^2}$$

where $$E \equiv \frac{\hbar^2 k^2}{2m} = \frac{p^2}{2m}$$

$$\frac{N(E)}{V} = \frac{p^3}{6\pi^2\hbar^3} = \frac{4\pi}{3}\frac{p^3}{h^3}$$

$$N(E) = \int d^3x \; \frac{4\pi}{3}\frac{p^3}{h^3}$$

$$N(E) = \frac{1}{h^3}\int d^3x \int d^3p$$

$$= \frac{\text{volume in phase space}}{h^3}$$

$\Longrightarrow$ statistical mechanics