Lecture 7

Monday, October 2, 2023 15:43

CHEM*3860 Midterm Exam

October 18, MacKinnon 310

16:00 – 17:15

bring a non-graphing calculator

Exam booklet and equation sheet will be provided

No class on Thanksgiving (Oct. 9)

cutoff: October 11 lecture (including)

Monday October 16: review

Linear momentum operators

$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \quad \hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \quad \hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$$

$$\hat{p}_x = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 = \frac{\hbar}{i}\frac{\partial}{\partial x}\frac{\hbar}{i}\frac{\partial}{\partial x} = -\hbar^2\frac{\partial^2}{\partial x^2}$$

$$\hat{A}^n = \hat{A}\cdot\hat{A}\cdot\hat{A}\ \ldots \ n \text{ times}$$

$$\frac{d}{dx}\, x\, f(x) = \frac{d}{dx}\left[x\, f(x)\right]$$

$$E = \underset{\underset{\dfrac{p^2}{2m}}{\uparrow}}{T} + V$$

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\psi_i = E_i\psi_i$$

particle in a box wavefunctions

$$\psi = \left(\frac{2}{\ell}\right)^{1/2} \sin\left(\frac{n\pi x}{\ell}\right)$$

Are these wavefunctions eigenfunctions of $\hat{p}_x$?

equivalently

Does the particle have a definite value of p_x?

$$\hat{p}_x \Psi = \frac{\hbar}{i}\frac{d}{dx}\left(\frac{2}{\ell}\right)^{1/2}\sin\left(\frac{n\pi x}{\ell}\right)$$

$$\hat{p}_x \Psi = \frac{n\pi\hbar}{i\ell}\left(\frac{2}{\ell}\right)^{1/2}\cos\left(\frac{n\pi x}{\ell}\right)$$

$\therefore$ Ψ is not an eigenfunction of $\hat{p}_x$.

(But we still must get eigenvalues of $\hat{p}_x$ when the momentum is measured.)

Apply $\hat{p}_x^{\,2}$ to Ψ:

$$\hat{p}_x^{\,2}\Psi = -\hbar^2\frac{d^2}{dx^2}\left(\frac{2}{\ell}\right)^{1/2}\sin\left(\frac{n\pi x}{\ell}\right)$$

$$\hat{p}_x^{\,2}\Psi = \frac{\hbar^2 n^2\pi^2}{\ell^2}\underbrace{\left(\frac{2}{\ell}\right)^{1/2}\sin\left(\frac{n\pi x}{\ell}\right)}_{\Psi}$$

$$\hat{p}_x^{\,2}\Psi = \frac{h^2 n^2}{4\ell^2}\Psi \qquad \hbar = \frac{h}{2\pi}$$

$\therefore$ Ψ is an eigenfunction of $\hat{p}_x^{\,2}$.

Will always obtain $\frac{h^2n^2}{4\ell^2}$ when a measurement is made.

$$\hat{H} = \hat{T} + \underset{\substack{\uparrow \\ 0 \text{ inside the box}}}{\hat{V}} = \hat{T} = \frac{p_x}{2m}$$

$$\hat{H}\psi = E\psi = \frac{\hat{p}_x^2}{2m}\psi$$

$$\hat{p}_x^2\psi = 2mE\psi = 2m\frac{n^2h^2}{8ml^2}\psi$$

$$= \frac{n^2h^2}{4l^2}\psi$$

$$\boxed{\therefore p_x^2 = \frac{n^2h^2}{4l^2}}$$

- A measurement of property B must give a result that is one of the eigenvalues of the operator $\hat{B}$.
- If ψ is an eigenfunction of $\hat{B}$ with eigenvalue b, then a measurement will be certain to yield b.

– If Ψ is not an eigenfunction of $\hat{B}$, we will still get an eigenvalue of $\hat{B}$, but we cannot predict which eigenvalue will be obtained. (Probabilistic; discussed later)

3.4 The Three-Dimensional, Many-Particle Schrödinger Equation

1 particle in 3 dimensions:

$$H = T + V = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) + V(x,y,z)$$

classical Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\underbrace{\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)} + V(x,y,z)$$

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^3} + \frac{\partial^2}{\partial z^2}$$

Laplacian

$$-\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi = E\Psi$$

Extend to n particles:

$$T = \frac{1}{2m_1}\left(p_{x_1}^2 + p_{y_1}^2 + p_{z_1}^2\right)$$

$$+ \frac{1}{2m_2}\left(p_{x_2}^2 + p_{y_2}^2 + p_{z_2}^2\right)$$

$$+ \cdots + \frac{1}{2m_n}\left(p_{x_n}^2 + p_{y_n}^2 + p_{z_n}^2\right)$$

$$\hat{T} = -\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}\right)$$

$$- \cdots - \frac{\hbar^2}{2m_n}\left(\frac{\partial^2}{\partial x_n^2} + \frac{\partial^2}{\partial y_n^2} + \frac{\partial^2}{\partial z_n^2}\right)$$

$$\hat{T} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_i} \nabla_i^2$$

$$\nabla_i^2 \equiv \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$$

restrict to cases where

$$V = V(x_1, y_1, z_1, \ldots, x_n, y_n, z_n)$$

$$\boxed{\hat{H} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_i} \nabla_i^2 + V(x_1, \ldots, z_n)}$$

$$\left[-\sum_{i=1}^{n}\frac{\hbar^2}{2m_i}\nabla_i^{2}+V(x_1,\ldots,z_n)\right]\psi=E\psi$$

$$\psi=\psi(x_1,y_1,z_1,\ldots,x_n,y_n,z_n)$$

Example: consider a system of two particles interacting so that the potential energy is inversely proportional to the distance between them, with c being the proportionality constant.

distance between two particles:

$$\left[(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2\right]^{1/2}$$

$$V=\frac{c}{\left[(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2\right]^{1/2}}$$

The Hamiltonian is:

$$-\frac{\hbar^2}{2m_1}\left(\frac{\partial^2}{\partial x_1^{2}}+\frac{\partial^2}{\partial y_1^{2}}+\frac{\partial^2}{\partial z_1^{2}}\right)$$

$$-\frac{\hbar^2}{2m_2}\left(\frac{\partial^2}{\partial x_2^2}+\frac{\partial^2}{\partial y_2^2}+\frac{\partial^2}{\partial z_2^2}\right)$$

$$+\frac{c}{\left[(x_2-x_1)^2+(y_2-y_1)^2+(z_2-z_1)^2\right]^{1/2}}$$

$$\psi=\psi(x_1,y_1,z_1,x_2,y_2,z_2)$$

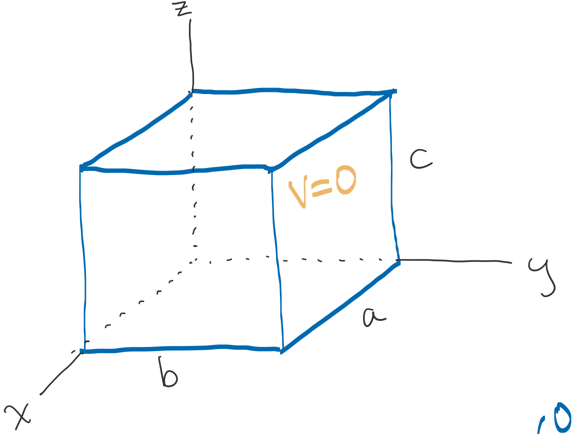
Moving on to $|\psi|^2$ for an n-particle system:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}|\psi|^2\,dx_1\,dy_1\,dz_1\cdots dx_n\,dy_n\,dz_n=1$$

$$\boxed{\int|\psi|^2\,d\tau=1}$$

although we do not specify limits, this is a definite integral

3.5 The Particle in a Three-Dimensional Box



$$V(x,y,z)=0 \text{ in the region } \begin{cases} 0<x<a \\ 0<y<b \\ 0<z<c \end{cases}$$

$V=\infty$ elsewhere

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)=E\psi$$

Assume that

$$\psi(x,y,z)=f(x)g(y)h(z)$$

(can be proven) separation of variables

$$\frac{\partial^2\psi}{\partial x^2} = f''(x)\,g(y)\,h(z)$$

$$\frac{\partial^2\psi}{\partial y^2} = f(x)\,g''(y)\,h(z)$$

$$\frac{\partial^2\psi}{\partial z^2} = f(x)\,g(y)\,h''(z)$$

$$-\frac{\hbar^2}{2m}f''gh - \frac{\hbar^2}{2m}fg''h - \frac{\hbar^2}{2m}fgh'' = Efgh$$

$$-\frac{\hbar^2}{2m}f''gh - \frac{\hbar^2}{2m}fg''h - \frac{\hbar^2}{2m}fgh'' - Efgh = 0$$

divide by fgh

$$-\frac{\hbar^2 f''}{2mf} - \frac{\hbar^2 g''}{2mg} - \frac{\hbar^2 h''}{2mh} - E = 0$$

$$-\frac{\hbar^2 f''(x)}{2mf(x)} = \frac{\hbar^2 g''(y)}{2mg(y)} + \frac{\hbar^2 h''(z)}{2mh(z)} + E$$

$$E_x \equiv -\frac{\hbar^2 f''(x)}{2mf(x)}$$ ← E_x is independent of y and z

$$E_x = \frac{\hbar^2 g''(y)}{2m\, g(y)} + \frac{\hbar^2 h''(z)}{2m\, h(z)} + E$$

$\uparrow$ E_x is independent of x

$\therefore$ E_x is a constant

$$E_y = -\frac{\hbar^2 g''(y)}{2m g(y)}, \quad E_z = -\frac{\hbar^2 h''(z)}{2m\, h(z)}$$

$$E = E_x + E_y + E_z$$

$$\frac{d^2 f(x)}{dx^2} + \frac{2m}{\hbar^2} E_x f(x) = 0$$

$$\frac{d^2 g(y)}{dy^2} + \frac{2m}{\hbar^2} E_y\, g(y) = 0$$

$$\frac{d^2 h(z)}{dz^2} + \frac{2m}{\hbar^2} E_z\, h(z) = 0$$

$$f(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n_x \pi x}{a}\right)$$

$$E_x = \frac{n_x^2 h^2}{8ma^2}, \quad n_x = 1, 2, 3, \ldots$$

$$g(y) = \left(\frac{2}{b}\right)^{1/2} \sin\left(\frac{n_y \pi y}{b}\right)$$

$$E_y = \frac{n_y^2 h^2}{8mb^2}, \quad n_y = 1, 2, 3, \ldots$$

$$h(z) = \left(\frac{2}{c}\right)^{1/2} \sin\left(\frac{n_z \pi z}{c}\right)$$

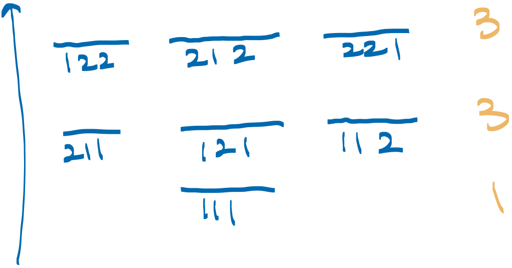
$$E_z = \frac{n_z^2 h^2}{8mc^2}, \quad n_z = 1, 2, 3, \ldots$$

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

$$\boxed{\psi(x,y,z) = \left(\frac{8}{abc}\right)^{\frac{1}{2}} \sin\left(\frac{n_x \pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right) \sin\left(\frac{n_z \pi z}{c}\right)}$$

suppose we have a cubic box:

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

degeneracy: the number of states with the same energy