CHEM 3541

Physical Chemistry

Week 5 & 6

Uncertainty principle for energy and time

- From time-dependent S.E. $i\hbar\frac{\partial}{\partial t}\psi = \hat{H}\psi$, we define $\hat{H} = i\hbar\frac{\partial}{\partial t}$

$\because \left[\hat{H}, t\right]\phi = \hat{H}(t\phi) - t\left(\hat{H}\phi\right) = i\hbar\phi$

$\therefore \left[\hat{H}, t\right] = i\hbar$

So that $\Delta E \cdot \Delta t \geq \hbar/2$

- If a quantum state has definite energy, i.e. $\Delta E = 0$, then the life time of this state will be $\Delta t \rightarrow \infty$
- In reality, energy level is broadened, and $\Delta t \sim \hbar/\Delta E$ is regarded as life time of the energy level

Translation motion – 1D particle-in-a-box model

One particle with mass m confined in a box $[0, L]$

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$$

where

$$V(x) = \begin{cases} 0, \ 0 < x < L \\ +\infty, \ x \leq 0 \ or \ x \geq L \end{cases}$$

Within $(0, L)$, the S.E. has solution

$$\psi = Ae^{ikx} + Be^{-ikx}, k = \sqrt{2mE}/\hbar$$

Outside $(0, L)$, $\psi = 0$

Continued

Since wave function should be continuous, we impose boundary conditions $\psi(0) = \psi(L) = 0$

$\psi(0) = A + B = 0 \rightarrow A = -B$

$\psi(L) = -Be^{ikL} + Be^{-ikL} = -2iB \sin kL = 0 \rightarrow kL = n\pi, n = 1,2, \ldots$

So that within $(0, L)$, $\psi(x) = -2iB \sin\left(\frac{n\pi}{L}x\right)$

After normalization, $\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right), n = 1,2, \ldots$

Energy $E_n = \frac{\hbar^2 k^2}{2m} = \frac{n^2\pi^2\hbar^2}{2mL^2}, n = 1,2, \ldots$

Orthogonality

For $n \neq m$, the following integral should be zero

$$
\begin{aligned}
\int_0^L \mathrm{d}x \psi_n^* \psi_m &= \frac{2}{L} \int_0^L \mathrm{d}x \sin\frac{n\pi x}{L} \sin\frac{m\pi x}{L} \\
&= -\frac{1}{L} \int_0^L \mathrm{d}x \left[\cos\frac{(n+m)\pi x}{L} - \cos\frac{(n-m)\pi x}{L}\right] \\
&= -\frac{1}{L} \left[\frac{L}{(n+m)\pi} \cdot \sin\frac{(n+m)\pi x}{L}\Bigg|_0^L - \frac{L}{(n-m)\pi} \cdot \sin\frac{(n-m)\pi x}{L}\Bigg|_0^L\right] \\
&= 0
\end{aligned}
$$

Check uncertainty principle for ground state

We define uncertainty of an operator $\hat{A}$ as

$$\Delta A = \sqrt{\langle \left(\hat{A} - \langle \hat{A} \rangle\right)^2 \rangle}$$

$$= \sqrt{\langle \hat{A}^2 - 2\hat{A}\langle \hat{A} \rangle + \langle \hat{A} \rangle^2 \rangle}$$

$$= \sqrt{\langle \hat{A}^2 \rangle - 2\langle \hat{A} \rangle\langle \hat{A} \rangle + \langle \hat{A} \rangle^2}$$

$$= \sqrt{\langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2}$$

Continued

$$\begin{aligned}\langle\hat{x}\rangle &= \frac{2}{L}\int_0^L x\sin^2\frac{\pi x}{L}\,\mathrm{d}x\\ &= \frac{1}{L}\int_0^L x\left(1-\cos\frac{2\pi x}{L}\right)\mathrm{d}x\\ &= \frac{L}{2}-\frac{1}{L}\int_0^L x\cos\frac{2\pi x}{L}\,\mathrm{d}x\\ &= \frac{L}{2}\end{aligned}$$

Continued

$$\begin{aligned}
\langle \hat{x}^2 \rangle &= \frac{2}{L}\int_0^L x^2 \sin^2\frac{\pi x}{L}\,\mathrm{d}x \\
&= \frac{1}{L}\int_0^L x^2\left(1 - \cos\frac{2\pi x}{L}\right)\mathrm{d}x \\
&= \frac{L^2}{3} - \frac{1}{L}\int_0^L x^2 \cos\frac{2\pi x}{L}\,\mathrm{d}x \\
&= \frac{L^2}{3} - \frac{L^2}{2\pi^2}
\end{aligned}$$

Continued

$$\langle \hat{p} \rangle = \frac{2\hbar}{iL} \cdot \frac{\pi}{L} \int_0^L \sin \frac{\pi x}{L} \cos \frac{\pi x}{L} \, \mathrm{d}x$$

$$= \frac{\hbar \pi}{iL^2} \int_0^L \sin \frac{2\pi x}{L} \, \mathrm{d}x$$

$$= 0$$

Continued

$$\begin{aligned}\langle \hat{p}^2 \rangle &= \frac{2\hbar^2}{L} \cdot \frac{\pi^2}{L^2} \int_0^L \sin^2 \frac{\pi x}{L} \, \mathrm{d}x \\ &= \frac{\pi^2 \hbar^2}{L^3} \int_0^L \left(1 - \cos \frac{2\pi x}{L} \right) \mathrm{d}x \\ &= \frac{\pi^2 \hbar^2}{L^2}\end{aligned}$$

Continued

$$\Delta x = \sqrt{\left(\frac{L^2}{3} - \frac{L^2}{2\pi^2}\right) - \left(\frac{L}{2}\right)^2}$$

$$= \frac{L}{2\pi}\sqrt{\frac{\pi^2}{3} - 2}$$

$$\Delta p = \frac{\pi\hbar}{L}$$

So

$$\Delta x \cdot \Delta p = \frac{\hbar}{2} \cdot \sqrt{\frac{\pi^2}{3} - 2} \approx 1.136 \cdot \frac{\hbar}{2} > \frac{\hbar}{2}$$

Appendix

Let $\alpha(k) = \int_0^L \sin kx \, \mathrm{d}x = \frac{1-\cos kL}{k}$

$$\frac{\mathrm{d}\alpha(k)}{\mathrm{d}k} = \int_0^L x \cos kx \, \mathrm{d}x$$

$$= \frac{L \sin kL}{k} + \frac{\cos kL - 1}{k^2}$$

So

$$\int_0^L x \cos \frac{2\pi x}{L} \mathrm{d}x = \left. \frac{\mathrm{d}\alpha(k)}{\mathrm{d}k} \right|_{k=2\pi/L} = 0$$

Continued

Let $\beta(k) = \int_0^L \cos kx \, \mathrm{d}x = \frac{\sin kL}{k}$

$$\frac{\mathrm{d}^2\beta(k)}{\mathrm{d}k^2} = -\int_0^L x^2 \cos kx \, \mathrm{d}x$$

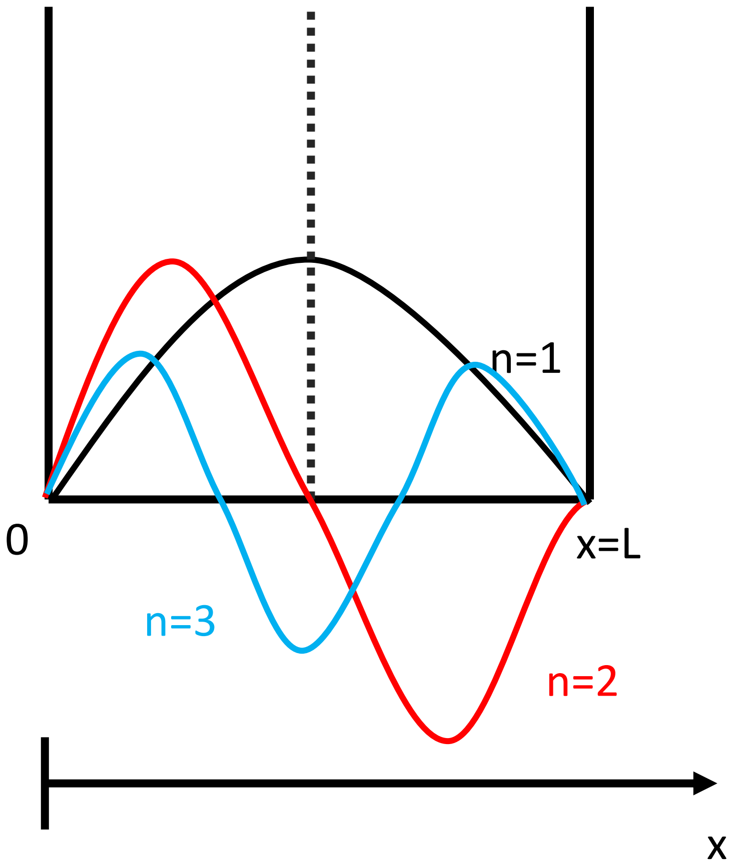
$$= -\frac{L^2 \sin kL}{k} - \frac{2L \cos kL}{k^2} + \frac{2 \sin kL}{k^3}$$

So

$$\int_0^L x^2 \cos \frac{2\pi x}{L} \mathrm{d}x = -\left.\frac{\mathrm{d}^2\beta(k)}{\mathrm{d}k^2}\right|_{k=2\pi/L} = \frac{L^3}{2\pi^2}$$

Review

- One particle in a 1D box



Wave Function:

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \qquad n = 1,2,3, \ldots$$

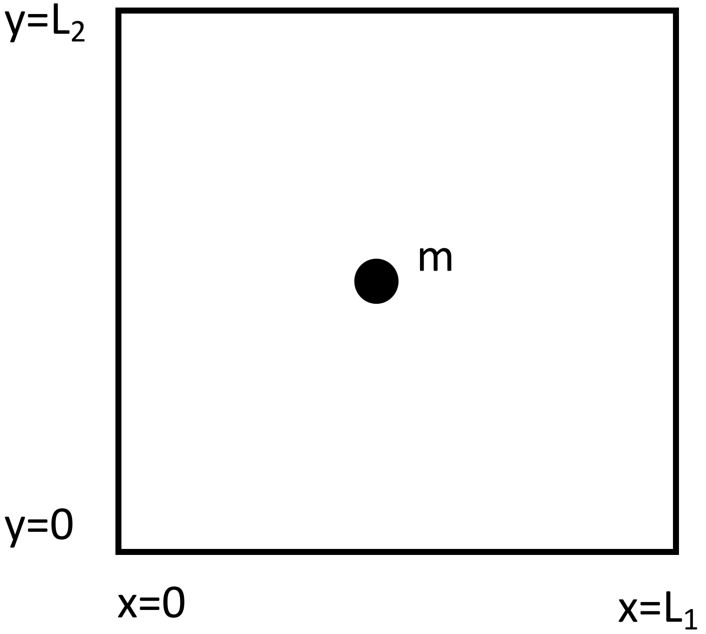
Energy Levels:

$n = 3 \qquad E_3 = \frac{9\pi^2\hbar^2}{2mL^2}$

$n = 2 \qquad E_2 = \frac{2\pi^2\hbar^2}{mL^2}$

$n = 1 \qquad E_1 = \frac{\pi^2\hbar^2}{2mL^2}$ Ground State

One particle in a 2D box



Hamiltonian operator:

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

$$V(x, y) = \begin{cases} 0, & 0 < x < L_1 \ and \ 0 < y < L_2 \\ +\infty, & otherwise \end{cases}$$

Schrödinger Equation

$$\hat{H}\psi(x,y) = E\psi(x,y)$$

Within $0 < x < L_1$ and $0 < y < L_2$,

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

Boundary conditions

$$\psi(0,y) = \psi(L_1,y) = \psi(x,0) = \psi(x,L_2) = 0$$

Separation of variables

Let $\psi(x, y) = X(x)Y(y)$ and plug this equation into S.E., we get

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2 X}{\mathrm{d}x^2}Y + X\frac{\mathrm{d}^2 Y}{\mathrm{d}y^2}\right) = EXY$$

Divide both sides by XY

$$-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\mathrm{d}^2 X}{\mathrm{d}x^2} + \frac{1}{Y}\frac{\mathrm{d}^2 Y}{\mathrm{d}y^2}\right) = E$$

Continued

To ensure $-\frac{\hbar^2}{2m}\left(\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}+\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}\right)=E$, each term in the LHS should be some constant, viz.

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{\mathrm{d}^2X}{\mathrm{d}x^2}=E_1$$

$$-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2}=E_2$$

And $E_1+E_2=E$

Continued

The 2D S.E. of $\psi(x, y)$ has been decomposed into two 1D S.E.

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2X}{\mathrm{d}x^2} = E_1X$$

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2Y}{\mathrm{d}y^2} = E_2Y$$

With solution where $n_1, n_2 = 1,2,3, \ldots$

$$\psi_{n_1,n_2} = \begin{cases} \frac{2}{\sqrt{L_1L_2}}\sin\frac{n_1\pi x}{L_1}\sin\frac{n_2\pi y}{L_2}, within\ 2D\ box \\ 0, outside\ box \end{cases}$$

$$E_{n_1,n_2} = \frac{n_1^2\pi^2\hbar^2}{2mL_1^2} + \frac{n_2^2\pi^2\hbar^2}{2mL_2^2}$$

Mid-term summary

① Schrödinger Equation

$$\hat{H}\Psi = E\Psi$$

- $\hat{H} = \hat{K} + \hat{V}$ Hamiltonian/Energy operator = Kinetic energy operator + potential energy operator
- For one-particle system: 3D $\hat{T} = -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z)$, where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is a Laplacian operator; 1D $\hat{T} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$

Continued

② Probability density - $|\Psi(x)|^2$

- The probability to find the particle between x and $x + \mathrm{d}x$ is $|\Psi(x)|^2 \mathrm{d}x$
- The probability to find the particle in whole space should be 1

③ Normalization of wave function $\Psi / \sqrt{\int \mathrm{d}\tau \, |\Psi|^2}$

④ Hermitian operator $\int \mathrm{d}\tau \phi^* \hat{\Omega} \psi = \left(\int \mathrm{d}\tau \psi^* \hat{\Omega} \phi \right)^*$

- e.g. $\hat{p} = \frac{\hbar}{i} \nabla, \hat{p}_x = \frac{\hbar}{i} \frac{\mathrm{d}}{\mathrm{d}x}$

Continued

⑤ Eigen value and eigen function

- $\hat{H}\psi_i = E_i\psi_i$
- $\int \mathrm{d}\tau \psi_i^* \psi_j = 0$ if $E_i \neq E_j$

⑥ Uncertainty principle

- $[\hat{x}, \hat{p}_x] = i\hbar$, $\Delta x \cdot \Delta p_x \geq \hbar/2$
- $\Delta E \cdot \Delta t \geq \hbar/2$

⑦ $-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi$, $E > V$

- $\psi = Ne^{\pm ikx}$, $k = \sqrt{2m(E-V)}/\hbar$, N is normalization factor