CHEM 3541

Physical Chemistry

Week 3

Review

- Hermitian operator $\widehat{\Omega}$
  - Definition: $\int \mathrm{d}\tau \psi_j^* \widehat{\Omega} \psi_i = \left(\int \mathrm{d}\tau \psi_i^* \widehat{\Omega} \psi_j \right)^*$
  - All operators corresponding to physical observables (properties that can be measured) are Hermitian operators
    - e.g. momentum operator $\hat{p} = \frac{\hbar}{i} \nabla = \frac{\hbar}{i} \left(\vec{e}_x \frac{\partial}{\partial x} + \vec{e}_y \frac{\partial}{\partial y} + \vec{e}_z \frac{\partial}{\partial z} \right)$ is Hermitian since every components of it are Hermitian
  - For $\widehat{\Omega} \psi_i = \omega_i \psi_i$
    - ω_i is real number
    - $\int \mathrm{d}\tau \psi_j^* \psi_i = 0$ if $\omega_i \neq \omega_j$

Continued

- Average value/ expectation value
  - Energy: $\hat{H}\psi_i = E_i\psi_i$, constructing $\psi = c_1\psi_1 + c_2\psi_2$, the expectation value of energy for a quantum state ψ is $\langle \hat{H} \rangle = \int \mathrm{d}\tau \psi^* \hat{H} \psi = |c_1|^2 E_1 + |c_2|^2 E_2$
  - For any operator $\hat{\Omega}$ in a quantum state ψ, its expectation value is

$$\langle \hat{\Omega} \rangle = \int \mathrm{d}\tau \, \psi^* \hat{\Omega} \psi$$

Heisenberg’s uncertainty principle

Measuring position x and momentum p_x N times ($N \gg 1$), define uncertainty of x and $\hat{p}_x$ as

$$\Delta x = \sqrt{\frac{\sum_{i=1}^{N}(x_i - \bar{x})^2}{N}}, \Delta p = \sqrt{\frac{\sum_{i=1}^{N}\left(p_{x\,i} - \bar{p}_x\right)^2}{N}}$$

then

$$\Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$

Continued

- e.g.
  - $\psi_k = e^{ikx}$ has definite momentum $p_x = \hbar k$, so that $\Delta p_x = 0$. Δx must be $+\infty$, which means the particle is diffused in the whole x space
  - If $\Delta x = 0$, we have $\Delta p_x \to +\infty$, thus $\langle \hat{H} \rangle = \langle \frac{\hat{p}_x^2}{2m} + V \rangle = \frac{\langle \hat{p}_x^2 \rangle}{2m} + \langle V \rangle \to +\infty$. This means we need infinity energy to constrain one quantal particle to a certain position

Continued

- Given an arbitrary wave function $\phi(x)$

$$\hat{p}_x\hat{x}\phi = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}(x\phi) = \frac{\hbar}{i}\phi + x\frac{\hbar}{i}\frac{\mathrm{d}\phi}{\mathrm{d}x} = \frac{\hbar}{i}\phi + \hat{x}\hat{p}_x\phi$$

$$\Rightarrow (\hat{x}\hat{p}_x - \hat{p}_x\hat{x})\phi = i\hbar\phi \Rightarrow \hat{x}\hat{p}_x - \hat{p}_x\hat{x} = i\hbar$$

- Denote commutator of $\hat{A}$ and $\hat{B}$ as $\left[\hat{A}, \hat{B}\right] = \hat{A}\hat{B} - \hat{B}\hat{A}$
  - $[\hat{x}, \hat{p}_x] = i\hbar$
  - Set $\hbar \to 0$, quantum mechanics will degenerate to classical mechanics

Proof of uncertainty principle

Given two operators $\hat{A}$ and $\hat{B}$ and an arbitrary wave function ϕ, constructing a non-negative integral with real variable ξ

$$I(\xi) = \int \mathrm{d}\tau \left| \xi \hat{A}\phi + i\hat{B}\phi \right|^2$$

Noted that for a complex number c, $|c|^2 = c^* c$. Expanding above integral, we have

$$I(\xi) = \xi^2 \int \mathrm{d}\tau \left| \hat{A}\phi \right|^2 + \int \mathrm{d}\tau \left| \hat{B}\phi \right|^2$$

$$+ i\xi \int \mathrm{d}\tau \left(\hat{A}\phi \right)^* \left(\hat{B}\phi \right) - i\xi \int \mathrm{d}\tau \left(\hat{B}\phi \right)^* \left(\hat{A}\phi \right)$$

Continued

$$I(\xi) = \xi^2 \int \mathrm{d}\tau \phi^* \hat{A}^2 \phi + \int \mathrm{d}\tau \phi^* \hat{B}^2 \phi + i\xi \int \mathrm{d}\tau \phi^* \left[\hat{A}, \hat{B}\right] \phi \geq 0$$

Denoted $\left[\hat{A}, \hat{B}\right] = i\hat{C}$, we have

$$4\langle \hat{A}^2 \rangle \langle \hat{B}^2 \rangle - \langle \hat{C} \rangle^2 \geq 0$$

$$\sqrt{\langle \hat{A}^2 \rangle \langle \hat{B}^2 \rangle} \geq \frac{1}{2} \left| \langle \hat{C} \rangle \right|$$

Continued

Define $\Delta\hat{A} = \hat{A} - \langle\hat{A}\rangle$, $\Delta\hat{B} = \hat{B} - \langle\hat{B}\rangle$.

Apparently,

$$\begin{aligned}[\Delta\hat{A}, \Delta\hat{B}] &= (\hat{A} - \langle\hat{A}\rangle)\hat{B} - (\hat{A} - \langle\hat{A}\rangle)\langle\hat{B}\rangle - \hat{B}(\hat{A} - \langle\hat{A}\rangle) + \langle\hat{B}\rangle(\hat{A} - \langle\hat{A}\rangle) \\ &= \hat{A}\hat{B} - \langle\hat{A}\rangle\hat{B} - \hat{B}\hat{A} + \hat{B}\langle\hat{A}\rangle \\ &= \hat{A}\hat{B} - \hat{B}\hat{A} \\ &= [\hat{A}, \hat{B}]\end{aligned}$$

Thus

$$[\Delta\hat{A}, \Delta\hat{B}] = i\hat{C}$$

Continued

Substitute $\hat{A}$, $\hat{B}$ with $\Delta\hat{A}$ and $\Delta\hat{B}$ respectively in $\sqrt{\langle\hat{A}^2\rangle\langle\hat{B}^2\rangle} \geq \frac{1}{2}\left|\langle\hat{C}\rangle\right|$,

$$\sqrt{\langle\left(\Delta\hat{A}\right)^2\rangle\langle\left(\Delta\hat{B}\right)^2\rangle} \geq \frac{1}{2}\left|\langle\hat{C}\rangle\right|$$

Noted that $\Delta A = \sqrt{\langle\left(\Delta\hat{A}\right)^2\rangle}$ and $\Delta B = \sqrt{\langle\left(\Delta\hat{B}\right)^2\rangle}$, we have

$$\Delta A \cdot \Delta B \geq \frac{1}{2}\left|\langle\hat{C}\rangle\right|$$

Example of uncertainty principle

- $\hat{A} = \hat{x}$, $\hat{B} = \hat{p}_x$. $[\hat{x}, \hat{p}_x] = i\hbar$, $\hat{C} = \hbar$. $\Delta x \cdot \Delta p_x \geq \hbar/2$
- If two operators commute, i.e. $\hat{A}\hat{B} = \hat{B}\hat{A}$, $\hat{C} = 0$, we have $\Delta A \cdot \Delta B \geq 0$. So $\hat{A}$ and $\hat{B}$ can be measured precisely at the same time.
  - e.g. $[\hat{x}, \hat{p}_y] = 0$
- A particle with mass m moves along x direction subjected to a potential $V(x)$. Find whether $\hat{H}$ and $\hat{p}_x$ commute.
  - $\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$, $\hat{p}_x = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}$
  - $[\hat{H}, \hat{p}_x]\psi(x) = i\hbar\psi(x)\frac{\mathrm{d}V(x)}{\mathrm{d}x}$, thus $[\hat{H}, \hat{p}_x] = i\hbar\frac{\mathrm{d}V(x)}{\mathrm{d}x}$. If and only if $V(x)$ is equal to some constant will $\hat{H}$ and $\hat{p}_x$ commute. (ref. week 1 slides pp. 6)

Assignment 1

Atkins' Physical Chemistry, 10th ed., pp. 311 – 313

Exercises: 7B.3(a)(b)

Problems: 7B.4 7B.5 7B.6

Exercises: 7C.2(a)(b) 7C.3(a) 7C.4(a) 7C.5(b) 7C.6(a) 7C.8(a) 7C.9(a)(b)

Problems: 7C.1 7C.3 7C.4 7C.6 7C.7 7C.10 7C.12 7C.13 7C.16

Due: 28th Sept. 2018