CHEM 3541

Physical Chemistry

Week1

- Textbook:
  - Atkins' Physical Chemistry, 7th ed., pp. 304-316
  - Atkins' Physical Chemistry, 10th ed., pp. 290, 292-305

Schrödinger Equation (S.E.)

- $\hat{H}\Psi = E\Psi$
  - $\hat{H}$: Hamiltonian operator
  - Ψ: Wave function, $\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n)$
  - $\hat{H} = \hat{K} + \hat{V}$: Kinetic energy operator and potential energy operator

1-D system with one particle

- $\hat{H} = -\frac{\hbar^2}{2m} \cdot \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$, $\hbar = \frac{h}{2\pi}$, h is Planck constant
- In many situations, $\hat{V}(x)$ operator is simply a function
- S.E. $\left[-\frac{\hbar^2}{2m} \cdot \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)\right]\Psi(x) = E\Psi(x)$

Probability density

- $|\Psi(x)|^2$ is called probability density
- The probability to find the particle between x and $x + \mathrm{d}x$ is $|\Psi(x)|^2 \mathrm{d}x$
- Normalization
  - Total probability to find the particle between $-\infty$ and $+\infty$ should be 1
  - If $\int_{-\infty}^{+\infty} |\Psi(x)|^2 \mathrm{d}x = 1$, then $\Psi(x)$ is normalized
  - Normalization of $\Psi'(x)$: $\Psi(x) = \frac{\Psi'(x)}{\sqrt{\int_{-\infty}^{+\infty} |\Psi'(x)|^2 \mathrm{d}x}}$

Example: constant potential

- For $V(x) = \text{const.}$, S.E. $\frac{\mathrm{d}^2\Psi}{\mathrm{d}x^2} = -\frac{2m}{\hbar^2}(E - V)\Psi$
- For $E > V$, the general solution is $\Psi(x) = Ae^{ikx} + Be^{-ikx}, A, B \in \mathbb{C}$, where $k = \sqrt{2m(E - V)}/\hbar$ is the wave vector
- Kinetic energy $= E - V = \frac{\hbar^2 k^2}{2m}$
- Momentum $p = \hbar k = \frac{h}{\lambda}$, λ is de Broglie wavelength
    - To see the meaning of λ, let $\widetilde{\Psi} = e^{ikx} + e^{-ikx} = 2\cos kx$, then the period of $\widetilde{\Psi}$ is $\frac{2\pi}{k} = \frac{h}{p} = \lambda$

Eigenvalue problem

- Two wave functions with different energy
  - $\Psi_1 = e^{ik_1 x}, k_1 = \frac{\sqrt{2m(E_1 - V)}}{\hbar}$
  - $\Psi_2 = e^{ik_2 x}, k_2 = \frac{\sqrt{2m(E_2 - V)}}{\hbar}$
- Generally $\Psi' = Ae^{ik_1 x} + B^{ik_2 x}, (A, B \neq 0)$ is **NOT** a solution of S.E. $\hat{H}\Psi' = E\Psi'$
  - $\hat{H}\Psi' = AE_1\Psi_1 + BE_2\Psi_2 =^{?} E\Psi'$
  - Only when $E_1 = E_2 = E, AE_1\Psi_1 + BE_2\Psi_2 = E(A\Psi_1 + B\Psi_2) = E\Psi'$

A particle with mass m in 3-D space(x, y, z)

- Wave function is $\Psi(x, y, z)$
- The probability to find the particle in $[x, x + \mathrm{d}x]\&[y, y + \mathrm{d}y]\&[z, z + \mathrm{d}z]$ is $|\Psi(x, y, z)|^2\mathrm{d}x\mathrm{d}y\mathrm{d}z = |\Psi|^2\mathrm{d}\tau$
- $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(x, y, z)$,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
- S.E. $\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V\right]\Psi = E\Psi$