

CHEM 3541

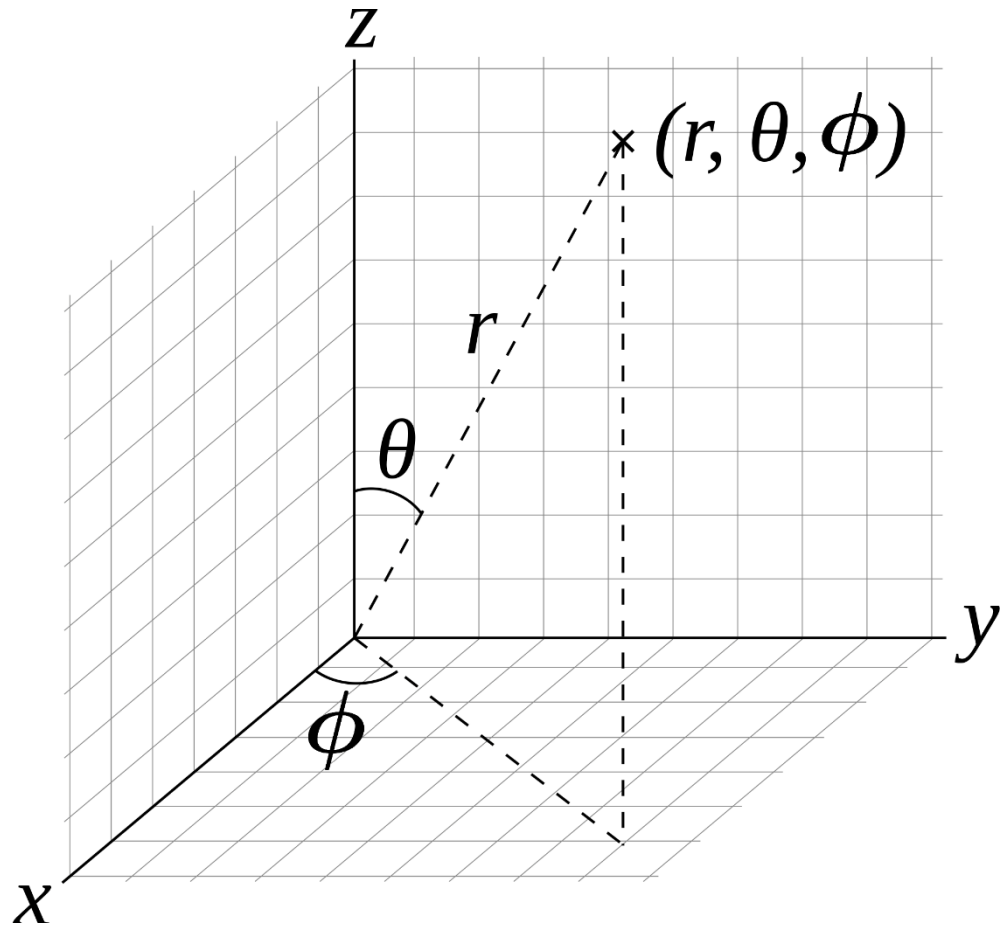
Physical Chemistry

Week 2

3-D system with a particle of mass m

- S.E. $\left[-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z) \right] \Psi(x, y, z) = E\Psi(x, y, z)$
 - Wave function, energy are unknown variables
 - Laplacian ∇^2 has different expressions under Cartesian and spherical polar coordinates:
 - Cartesian $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$
 - Spherical polar $\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{\Lambda^2}{r^2}$, where $\Lambda^2 = \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \csc^2 \theta \frac{\partial^2}{\partial \phi^2}$

Spherical polar coordinates



Relationship to Cartesian coordinates

$$\begin{cases} x = r \sin \theta \cos \phi \\ y = r \sin \theta \sin \phi \\ z = r \cos \theta \end{cases}$$

r : radial distance

θ : polar angle

ϕ : azimuth angle

Time-dependent Schrödinger Equation

- If potential V and thus wave function depend on time explicitly, we have following time-dependent S.E.

$$i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \hat{H} \Psi(\mathbf{r}, t)$$

Exercise

- Q. Given a wave function $\psi(\mathbf{r}) \propto e^{-r/a_0}$ where a_0 is a given constant, try to normalize it. Note that r in the exponent is radial distance but not position vector.
- A.

$$\int (e^{-r/a_0})^2 d\mathbf{r} = 4\pi \int_0^\infty r^2 e^{-2r/a_0} dr$$
$$= 4\pi I(k)$$

Where $k = 2/a_0$.

Continued

$$\begin{aligned} I(k) &= \int_0^{\infty} r^2 e^{-kr} \, dr \\ &= \frac{d^2}{dk^2} \int_0^{\infty} e^{-kr} \, dr \\ &= \frac{d^2}{dk^2} \left(\frac{1}{k} \right) \\ &= \frac{2}{k^3} \end{aligned}$$

Finally, we have

$$\psi(\mathbf{r}) = (\pi a_0^3)^{-1/2} e^{-r/a_0}$$

Eigen value equation

- The solution of S.E. $\hat{H}\Psi = E\Psi$ is a set of eigen energy/value E_i and eigen function $\Psi_i, i = 1, 2, \dots, \infty$
- For any operator $\hat{\Omega}$, if there exists some values satisfy $\hat{\Omega}\psi = \Omega\psi$, ψ is called eigen function of operator $\hat{\Omega}$
 - e.g. $\hat{\Omega} = \frac{d}{dx}$, $\psi = e^{-\alpha x}$. Since $\hat{\Omega}\psi = -\alpha\psi$, ψ is an eigen function of $\hat{\Omega}$ with corresponding eigen value $-\alpha$
 - $\psi = e^{-\alpha x^2}$ is not an eigen function of $\hat{\Omega}$

Hermitian operator

- Definition

$$\int d\tau \psi_j^* \hat{\Omega} \psi_i = \left(\int d\tau \psi_i^* \hat{\Omega} \psi_j \right)^*$$

- E.g. $\frac{d}{dx}$ is not a Hermitian operator since

$$\begin{aligned} \int_{-\infty}^{+\infty} dx \psi_j^* \frac{d\psi_i}{dx} &= \psi_j^* \psi_i \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} dx \psi_i \frac{d\psi_j^*}{dx} \\ &= - \left(\int_{-\infty}^{+\infty} dx \psi_i^* \frac{d\psi_j}{dx} \right)^* \\ &\neq \left(\int_{-\infty}^{+\infty} dx \psi_i^* \frac{d\psi_j}{dx} \right)^* \end{aligned}$$

Continued

- $\frac{1}{i} \frac{d}{dx}$ is a Hermitian operator

$$\begin{aligned} \int_{-\infty}^{+\infty} dx \psi_j^* \frac{1}{i} \frac{d\psi_i}{dx} &= -\frac{1}{i} \left(\int_{-\infty}^{+\infty} dx \psi_i^* \frac{d\psi_j}{dx} \right)^* \\ &= \left(\int_{-\infty}^{+\infty} dx \psi_i^* \frac{1}{i} \frac{d\psi_j}{dx} \right)^* \end{aligned}$$

Momentum operator

- For particle in constant potential (ref. to first week's slides pp. 6)
 - Wave function $\psi_k = e^{ikx}$
 - $\frac{\hbar}{i} \frac{d}{dx} \psi_k = \hbar k \psi_k = p \psi_k$
 - Thus $\hat{p}_x = \frac{\hbar}{i} \frac{d}{dx}$ is the momentum operator for x direction

Eigen value of Hermitian operators

- Any eigen value of Hermitian operator is a real number
- Proof: For a Hermitian operator $\hat{\Omega}$ with eigen value function $\hat{\Omega}\psi_i = \omega_i\psi_i$, where ψ_i are normalized. With the definition of Hermitian operator, we have

$$\begin{aligned}\omega_i &= \int d\tau \psi_i^* \hat{\Omega} \psi_i \\ &= \left(\int d\tau \psi_i^* \hat{\Omega} \psi_i \right)^* \\ &= \omega_i^*\end{aligned}$$

Thus ω_i must be real.

Eigen function of Hermitian operators

- For two eigen functions ψ_i, ψ_j with different eigen value $\omega_i \neq \omega_j$, $\int d\tau \psi_i^* \psi_j = 0$, i.e. ψ_i and ψ_j are orthogonal
- Proof: Using the definition of Hermitian operator, we have

$$\begin{aligned} \int d\tau \psi_i^* \hat{\Omega} \psi_j &= \left(\int d\tau \psi_j^* \hat{\Omega} \psi_i \right)^* \\ &= \left(\omega_i \int d\tau \psi_j^* \psi_i \right)^* \\ &= \omega_i \int d\tau \psi_j \psi_i^* \quad (1) \end{aligned}$$

Continued

Also, we can calculate the Left-hand side (LHS) of Eq. (1) as

$$\int d\tau \psi_i^* \hat{\Omega} \psi_j = \omega_j \int d\tau \psi_i^* \psi_j \quad (2)$$

Subtracting Eq. (1) from Eq. (2) gives

$$0 = (\omega_j - \omega_i) \int d\tau \psi_i^* \psi_j$$

Since $\omega_j \neq \omega_i$, we conclude that

$$\int d\tau \psi_i^* \psi_j = 0$$

Expectation value

- For Hamiltonian with normalized wave function $\hat{H}\psi_i = E_i\psi_i, i = 1, 2, \dots$, we construct a wave function $\psi = c_1\psi_1 + c_2\psi_2$ where $c_1 = 0.316, c_2 = 0.949$ and $E_1 \neq E_2$.
 - The average value of energy

$$\begin{aligned}\bar{E} &= \int d\tau \psi^* \hat{H} \psi \\ &= \int d\tau (c_1^* \psi_1^* + c_2^* \psi_2^*) (c_1 E_1 \psi_1 + c_2 E_2 \psi_2) \\ &= |c_1|^2 E_1 \int d\tau \psi_1^* \psi_1 + c_1^* c_2 E_2 \int d\tau \psi_1^* \psi_2 + \\ &\quad c_2^* c_1 E_1 \int d\tau \psi_2^* \psi_1 + |c_2|^2 E_2 \int d\tau \psi_2^* \psi_2\end{aligned}$$

Continued

$$\begin{aligned}\bar{E} &= |c_1|^2 E_1 + |c_2|^2 E_2 \\ &= 0.1E_1 + 0.9E_2\end{aligned}$$

- The expectation value of $\hat{\Omega}$ is

$$\bar{\Omega} = \int d\tau \psi^* \hat{\Omega} \psi$$