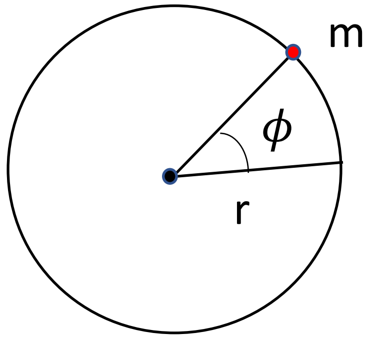
CHEM 3541

Physical Chemistry

Week 11

2-D rotational motion

- A particle of mass m moving in a ring of radius r in the xy-plane with zero potential: $\widehat{H} = -\frac{\hbar^2}{2m}\nabla^2$
  - Cylindrical coordinate: $\nabla^2 = \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}$
    - Since r, z are fixed, $\nabla^2 = \frac{1}{r^2}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}$
  - S.E. $-\frac{\hbar^2}{2mr^2}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}\psi = E\psi$
    - Denote $I = mr^2$ as moment of inertia, $-\frac{\hbar^2}{2I}\frac{\mathrm{d}^2}{\mathrm{d}\phi^2}\psi(\phi) = E\psi(\phi)$
    - Denote $\epsilon = \frac{2IE}{\hbar^2}$, $\psi = Ne^{\pm i\sqrt{\epsilon}\phi}$



Boundary condition

- Cyclic boundary condition: $\psi(0) = \psi(2\pi)$, i.e. $N = Ne^{\pm i2\pi\sqrt{\epsilon}}$
  - $\because e^{\pm i2\pi\sqrt{\epsilon}} = 1, \therefore \sqrt{\epsilon} = 0,1,2, \ldots$
  - $\psi = Ne^{im\phi}, m = 0, \pm 1, \pm 2, \ldots$
- Normalisation: $1 = \int_0^{2\pi} |\psi|^2 \mathrm{d}\phi = 2\pi N^2, N = \frac{1}{\sqrt{2\pi}}$
- $\psi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}, m = 0, \pm 1, \pm 2, \ldots$

Physical Observables

- Energy:
  - $\hat{H}\psi_m = \frac{\hbar^2}{2I} m^2 \psi_m, E_m = \frac{m^2\hbar^2}{2I}, m = 0, \pm 1, \pm 2, \dots$
  - Ground state energy is zero
  - First excited states are degenerated $E_{\pm 1} = \frac{\hbar^2}{2I}$ with degeneracy 2

Continued

- Linear momentum:

$$\hat{p} = \frac{\hbar}{i}\nabla = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}(r\phi)} = \frac{\hbar}{ir}\frac{\mathrm{d}}{\mathrm{d}\phi}$$

  - $\hat{p}\psi_m = \frac{m\hbar}{r}\psi_m$, $p_m = \frac{m\hbar}{r}$, i.e. ψ_m are also eigenfunctions of $\hat{p}$

- Angular momentum:
  - Classically, $\vec{l} = \vec{r}\times\vec{p}$
  - In quantum mechanics, for a particle in a circle $\hat{l} = \hat{r}\hat{p} = \frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}\phi}$
  - $\hat{l}\psi_m = m\hbar\psi_m$, $l_m = m\hbar$, i.e. ψ_m are also eigenfunctions of $\hat{l}$

The compatibility theorem

- Giving two Hermitian operators $\hat{A}$ and $\hat{B}$, if $\hat{A}$ and $\hat{B}$ are commuting, viz $\left[\hat{A}, \hat{B}\right] = 0$, we can conclude that $\hat{A}$ and $\hat{B}$ have a common eigen basis, i.e. we can find a set of ψ_i satisfying $\hat{A}\psi_i = a_i\psi_i$ and $\hat{B}\psi_i = b_i\psi_i$
- Examples: $\left[\hat{H}, \hat{p}\right] = \left[\hat{H}, \hat{l}\right] = \left[\hat{l}, \hat{p}\right] = 0$, so $\psi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi}$ are their common eigenfunctions

3-D rotational motion

- A particle of mass m moving on the surface of a sphere of radius r with zero potential: $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2$
  - Spherical coordinate: $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\Lambda^2}{r^2}$ where

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)$$

    - Since r is fixed, $\nabla^2 = \frac{\Lambda^2}{r^2}$
- S.E. $\hat{H}Y(\theta,\phi) = EY(\theta,\phi)$, i.e. $\Lambda^2 Y = -\epsilon Y$

Separation of variables

Let $Y(\theta, \phi) = \Theta(\theta)\Phi(\phi)$, then we have

$$\frac{\Theta}{\sin^2\theta}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\Phi}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) = -\epsilon\Theta\Phi$$

Dividing two sides by $\Theta\Phi$ and rearranging the eq. we have

$$\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} + \frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \epsilon\sin^2\theta = 0$$

Thus, $\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -\beta$ and $\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \epsilon\sin^2\theta = \beta$ should hold

Continued

- For $\frac{1}{\Phi}\frac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -\beta$, the solution is $\Phi_{m_l} = \frac{1}{\sqrt{2\pi}}e^{im_l\phi}$, $m_l = 0, \pm 1, \pm 2, \ldots$
- For $\frac{\sin\theta}{\Theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right) + \epsilon\sin^2\theta = m_l^2$, let $u = \cos\theta$, this eq. can be rewritten as associated Legendre equation

$$(1-u^2)\frac{\mathrm{d}^2\Theta}{\mathrm{d}u^2} - 2u\frac{\mathrm{d}\Theta}{\mathrm{d}u} + \left(\epsilon - \frac{m_l^2}{1-u^2}\right)\Theta = 0$$

  - Solutions $\Theta_{lm_l}(\theta)$ are called associated Legendre functions where $l = 0,1,2, \ldots$ and $m_l = 1, \pm 1, \pm 2, \ldots, \pm l$

Continued

- The overall solutions $Y_{lm_l}(\theta, \phi) = \Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$ are called spherical harmonics
- First few spherical harmonics

l \ m_l	0	± 1	± 2
0	$\sqrt{1/4\pi}$		
1	$\sqrt{3/4\pi}\cos\theta$	$\mp\sqrt{3/8\pi}\sin\theta\, e^{\pm i\phi}$	
2	$\sqrt{5/16\pi}(3\cos^2\theta - 1)$	$\mp\sqrt{15/8\pi}\cos\theta\sin\theta\, e^{\pm i\phi}$	$\sqrt{15/32\pi}\sin^2\theta\, e^{\pm 2i\phi}$

Assignment 3 (Deadline 26 Nov, 2018)

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- Discussion questions
  - 8B.2 8B.3 8C.1 8C.3
- Exercises
  - 8B.2(a) 8B.3(a) 8B.5(a) 8B.6(a) 8B.8(a) 8C.1(a) 8C.3(a) 8C.4(a) 8C.6(a) 8C.8(a)
- Problems
  - 8B.1 8B.5 8B.11 8C.1 8C.3 8C.5 8C.7 8C.8 8C.9