

Physical Chemistry

Lecture 15

Angular Momentum and the Rigid Rotor

Angular momentum

- ◆ Vector property that describes circular motion of a particle or a system of particles
- ◆ Rigid rotor model: A particle of mass m fixed to a massless rod



- ◆ Examples
 - Swinging a bucket of water
 - Movement of the Earth around the Sun

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}$$

Classical constant-angular-momentum problem

- ◆ Solve for trajectories for constant angular momentum
- ◆ Frequency, ω , must be constant
- ◆ r must be constant
- ◆ Constant L is provided by the fact that r and ω are constant

$$\mathbf{L} = \text{constant} = mr^2\omega \mathbf{k}$$

$$\mathbf{r}(t) = r(\mathbf{i}\cos\omega t + \mathbf{j}\sin\omega t)$$

$$\mathbf{p}(t) = mr\omega(\mathbf{i}\sin\omega t - \mathbf{j}\cos\omega t)$$

Quantum angular-momentum operators

- ◆ Vector definitions

$$\mathbf{L} = L_x \mathbf{i} + L_y \mathbf{j} + L_z \mathbf{k}$$

$$L^2 = \mathbf{L} \cdot \mathbf{L} = L_x^2 + L_y^2 + L_z^2$$

- ◆ Expression by correspondence

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$

$$L^2 = L_x^2 + L_y^2 + L_z^2$$

- ◆ Form of operators with a fixed r

$$\mathbf{L} = -i\hbar \mathbf{r} \times \nabla$$

$$L^2 = -\hbar^2 (\mathbf{r} \times \nabla) \cdot (\mathbf{r} \times \nabla)$$

Quantum angular momentum

- ◆ Commutators of operators

$$[L_x, L_y] = i\hbar L_z \quad \text{and cyclic permutations}$$

$$[L^2, L_i] = 0$$

- ◆ Can have common set of eigenstates of L^2 and **any one** component

$$L^2 \Psi_{km} = k\hbar^2 \Psi_{km}$$

$$L_z \Psi_{km} = m\hbar \Psi_{km}$$

Operators in spherical coordinates

- ◆ Natural system for describing angular motion is spherical coordinates

$$L_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

- ◆ L_z depends only on ϕ

- Suggests that the wave functions may be written as a product

$$L^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$\Psi_{km}(\theta, \phi) = \Theta_{km}(\theta)\Phi_m(\phi)$$

Differential equations for angular-momentum eigenstates

- ◆ The z component yields a simple differential equation for Φ_m

$$-i\hbar \frac{\partial \Phi_m}{\partial \phi} = m\hbar \Phi_m$$

- ◆ The square of the angular momentum yields an equation for $\Theta_{k,m}$ ($\equiv P(\cos\theta)$)

$$-\left(\frac{\partial^2 \Theta_{k,m}}{\partial \theta^2} + \cot\theta \frac{\partial \Theta_{k,m}}{\partial \theta} - \frac{m^2}{\sin^2 \theta} \Theta_{k,m}\right) = k\Theta_{k,m}$$

- ◆ Legendre's associated differential equation
- ◆ Depend on a quantum number, ℓ

$$Y_{\ell m}(\theta, \phi) = A_{\ell m} P_{\ell}^{m}(\cos\theta) \Phi_m(\phi)$$

where

- ◆ Solutions are a complete set called the **spherical harmonic functions**
- $k = \ell(\ell+1)$ and $\ell = 0, 1, 2, \dots$

Angular-momentum wave functions

- ◆ Functions of ϕ are exponentials

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi)$$

- ◆ Legendre polynomials

ℓ	$ m $	$P_{\ell}^{ m }$
0	0	1
1	0	$\cos\theta$
1	1	$\sin\theta$
2	0	$3\cos^2\theta - 1$
2	1	$\sin\theta \cos\theta$
2	2	$\sin^2\theta$

- ◆ Should look familiar, as these are the angular parts of hydrogenic wave functions

Quantum rigid rotor

- ◆ Hamiltonian $H = \frac{1}{2mr_0^2} L^2$

- ◆ The Hamiltonian commutes with L^2 and L_z

- ◆ The three operators have a complete set of eigenstates in common

$$HY_{\ell m}(\theta, \phi) = E_{\ell m} Y_{\ell m}(\theta, \phi)$$

$$\frac{1}{2mr_0^2} L^2 Y_{\ell m}(\theta, \phi) = \frac{1}{2mr_0^2} \ell(\ell+1) \hbar^2 Y_{\ell m}(\theta, \phi)$$

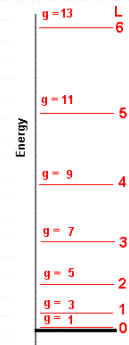
$$E_{\ell m} = \frac{\hbar^2}{2mr_0^2} \ell(\ell+1)$$

Grotrian diagram for the rigid rotor

- ◆ Rigid rotor's energies determined by the quantum number, ℓ

- ◆ Each energy level is degenerate
 - ◆ States with different values of m have the same energy

$$g_{\ell} = 2\ell + 1$$



Spin

- ◆ **Goudschmidt** and **Uehlenbeck** proposed electronic "intrinsic angular momentum" to explain spectroscopic anomalies

- ◆ Fundamental property of particle called **spin**

- ◆ Often labeled **I** or **S**
- ◆ Acts like other quantum angular momenta
- ◆ Integer or half-integer values

- ◆ **Dirac** theory of an electron

- ◆ Consequence of relativistic motion of electron

PRINCIPAL SPIN QUANTUM NUMBERS OF PARTICLES	
Electron	$\frac{1}{2}$
Proton	$\frac{1}{2}$
Neutron	$\frac{1}{2}$
Deuteron	1
^{12}C	0
^{13}C	$\frac{1}{2}$
^{23}Na	$\frac{1}{2}$
^{27}Al	$\frac{5}{2}$
^{63}Cu and ^{65}Cu	$\frac{3}{2}$

Summary

- ◆ Angular momentum is quantized

- ◆ Combination of
 - ◆ Rotation equation
 - ◆ Legendre's differential equation

- ◆ Restricted values of ℓ and m
 - ◆ ℓ must be a positive integer
 - ◆ $|m|$ must be less than or equal to ℓ
 - ◆ m must be an integer

- ◆ Rigid rotor

- ◆ Hamiltonian is directly proportional to L^2
- ◆ Same set of eigenstates
- ◆ Degenerate levels
 - ◆ $g_{\ell} = 2\ell + 1$