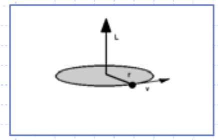
Physical Chemistry

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
    - L ≈ 2.5 x 10^{40} kg m^2 s^{-1}



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

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

$$\mathbf{L} = L_x\mathbf{i} + L_y\mathbf{j} + L_z\mathbf{k}$$
$$L^2 = \mathbf{L}\bullet\mathbf{L} = L_x^2 + L_y^2 + L_z^2$$

- Expression by correspondence

$$\hat{L}_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \quad \hat{L}_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \quad \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$
$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

- Form of operators with a fixed r

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

Quantum angular momentum

- Commutators of operators

$$\left[\hat{L}_x, \hat{L}_y\right] = i\hbar\hat{L}_z \quad \text{and cyclic permutations}$$
$$\left[\hat{L}^2, \hat{L}_i\right] = 0$$

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

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

Operators in spherical co-ordinates

- Natural system for describing angular motion is spherical co-ordinates
- L_z depends only on ϕ
  - Suggests that the wave functions may be written as a product

$$\hat{L}_x = i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} + \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$
$$\hat{L}_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$
$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$
$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

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

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 Θ_{km} ($\equiv$ P(cosθ))
  - Legendre's associated differential equation
  - Depends on a quantum number, ℓ

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

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

where

$$k = \ell(\ell+1) \quad \text{and} \quad \ell = 0, 1, 2, \ldots$$

- Solutions are a complete set called the spherical harmonic functions

Angular-momentum wave functions

- Functions of ϕ are exponentials

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

- Legendre polynomials

ℓ	$\lvert m\rvert$	$P_\ell^{\lvert m\rvert}(\cos\theta)$
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 the hydrogenic wave functions

Quantum rigid rotor

- Hamiltonian

$$\hat{H} = \frac{1}{2mr_0^2}\hat{L}^2$$

- The Hamiltonian commutes with L^2 and L_z
  - The three operators have a complete set of eigenstates in common

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

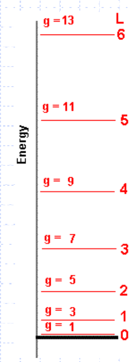
$$\frac{1}{2mr_0^2}\hat{L}^2Y_{\ell m}(\theta,\phi) = \frac{1}{2mr_0^2}\ell(\ell+1)\hbar^2Y_{\ell m}(\theta,\phi)$$

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

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	½
Proton	½
Neutron	½
Deuteron	1
^{12}C	0
^{13}C	½
^{23}Na	½
^{27}Al	5/2
^{63}Cu and ^{65}Cu	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
    - $g_\ell = 2\ell + 1$