ANGULAR MOMENTUM

So far, we have studied simple models in which a particle is subjected to a force in one dimension (particle in a box, harmonic oscillator) or forces in three dimensions (particle in a 3-dimensional box). We were able to write the Laplacian, ∇^2, in terms of Cartesian coordinates, assuming ψ to be a product of 1-dimensional wavefunctions. By separation of variables, we were able to separate the Schrödinger Eq. into three 1-dimensional eqs. & to solve them.

In order to discuss the motion of electrons in atoms, we must deal with a force that is spherically symmetric:

$$V(r) \propto 1/r,$$

where r is the distance from the nucleus. In this case, we can solve the Schrördinger Eq. by working in spherical polar coordinates (r, θ, φ), rather than Cartesian coordinates. This allows us to separate the Schrödinger Eq. into three eqs. each depending on one variable--r, θ, or φ (See Fig. 6.5 for definition of r, θ, and φ).

$\psi = f(x)\, g(y)\, h(z)$ or $\psi = R(r)\, \Theta(\theta)\, \Phi(\phi)$

From Fig. 6.5:

$$r^2 = x^2 + y^2 + z^2$$

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

$$\tan\theta = r/x$$

$$\cos\theta = z/(x^2 + y^2 + z^2)^{1/2}$$

Since $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$, by using the above functional relationships, one can transform ∇^2 into

$$\nabla^2 = \partial^2/\partial r^2 + (2/r)\, \partial/\partial r + 1/(r^2 \underline{h}^2)\, L^2$$

where

$$L^2 = - \underline{h}^2 (\partial^2/\partial\theta^2 + \cot\theta\, \partial/\partial\theta + (1/\sin^2\theta)(\partial^2/\partial\phi^2)$$

L^2 is the orbital angular momentum operator.

Orbital Angular Momentum is the momentum of a particle due to its complex (non-linear) movement in space. This is in contrast to linear momentum, which is movement in a particular direction.

Consider the classical picture of a particle of mass m at distance r from the origin. Let **r** (here bold type indicates a vector) be written as

$$\mathbf{r} = \mathbf{i}\, x + \mathbf{j}\, y + \mathbf{k}\, z$$

where **i**, **j**, & **k** are unit vectors in the x, y, & z-directions, respectively. Then velocity, **v**, is given by

$$\mathbf{v} = d\mathbf{r}/dt = \mathbf{i}\, dx/dt + \mathbf{j}\, dy/dt + \mathbf{k}\, dz/dt$$

$$= \mathbf{i}\, v_x + \mathbf{j}\, v_y + \mathbf{k}\, v_z$$

ans linear momentum, **p**, is given by

$$\mathbf{p} = m\, \mathbf{v} = \mathbf{i}\, mv_x + \mathbf{j}\, mv_y + \mathbf{k}\, mv_z$$

$$= \mathbf{i}\, p_x + \mathbf{j}\, p_y + \mathbf{k}\, p_z$$

Then **L**, the angular momentum of a particle, is given by

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

The definition of a vector cross product is

$$\mathbf{A} \times \mathbf{B} = A\, B \sin\theta,$$

where A is the magnitude of vector **A**, etc. One can determine the value of the cross product from a 3x3 determinant:

$$\mathbf{i} \quad \mathbf{j} \quad \mathbf{k}$$

$$\mathbf{A} \times \mathbf{B} = \begin{vmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{vmatrix}$$

$$\mathbf{A} \times \mathbf{B} = \mathbf{i}\,(-1)^{1+1} \begin{vmatrix} A_y & A_z \\ B_y & B_z \end{vmatrix}$$

$$+ \ \mathbf{j}\,(-1)^{1+2} \begin{vmatrix} A_x & A_z \\ B_x & B_z \end{vmatrix}$$

$$+ \ \mathbf{k}\,(-1)^{1+3} \begin{vmatrix} A_x & A_y \\ B_x & B_y \end{vmatrix}$$

$$= \mathbf{i}\,(A_yB_z - A_zB_y) - \mathbf{j}\,(A_xB_z - A_zB_x) + \mathbf{k}\,(A_xB_y - A_yB_x)$$

So $\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{i}\, L_x + \mathbf{j}\, L_y + \mathbf{k}\, L_z$

with $L_x = y\, p_z - z\, p_y$

$L_y = z\, p_x - x\, p_z$

$L_z = x\, p_y - y\, p_x$

The torque, τ, acting on a particle is

$$\tau = \mathbf{r} \times \mathbf{F} = d\mathbf{L}/dt$$

When $\tau = 0$, the rate of change of the angular momentum with respect to time is equal to zero, & the angular momentum is constant (conserved).

In Quantum Mechanics there are two kinds of angular momentum:

Orbital Angular Momentum - same meaning as in classical mechanics

Spin Angular Momentum - no classical analog; will be covered in a later chapter

One can obtain the quantum mechanical operators by replacing the classical forms by their quantum mechanical analogs:

$$x \rightarrow x,\ p_x \rightarrow -i\underline{h}\ \partial/\partial x, \text{ etc.}$$

So $$L_x = -i\underline{h}\ (y\ \partial/\partial z - z\ \partial/\partial y)$$

$$L_y = -i\underline{h}\ (z\ \partial/\partial x - x\ \partial/\partial z)$$

$$L_z = -i\underline{h}\ (x\ \partial/\partial y - y\ \partial/\partial x)$$

For ∇^2 need $L^2 = \mathbf{L} \cdot \mathbf{L}$

Definition of a dot product:

$$\mathbf{A} \cdot \mathbf{B} = (\mathbf{i}A_x + \mathbf{j}A_y + \mathbf{k}A_z) \cdot (\mathbf{i}B_x + \mathbf{j}B_y + \mathbf{k}B_z)$$

$= AB \cos \theta$

The unit vectors are perpendicular to each other, so $\theta = 90^0$ and $\mathbf{i} \cdot \mathbf{j} = 0 = \mathbf{i} \cdot \mathbf{k}$, etc. For the dot product of a vector with itself, $\theta = 0^0$, so $\mathbf{i} \cdot \mathbf{i} = 1$, etc. Therefore,

$$\mathbf{A} \cdot \mathbf{B} = A_xB_x + A_yB_y + A_zB_z$$

and

$$\mathbf{A} \cdot \mathbf{A} = A_x^2 + A_y^2 + A_z^2 = A^2$$

so that

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

{Note that this is how the expression for the Laplacian is derived, since

$$\nabla = \mathbf{i}\, \partial/\partial x + \mathbf{j}\, \partial/\partial y + \mathbf{k}\, \partial/\partial z.$$

Therefore

$$\nabla^2 = \nabla \cdot \nabla = = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2\}$$

Investigate the commutation relationships between the components of the orbital angular momentum:

$[L_x, L_y] = ?$

$[L_x, L_y] = L_x L_y - L_y L_x$

$$= - i\underline{h}\, (y\, \partial/\partial z - z\, \partial/\partial y)\, (-i\underline{h})\, (z\, \partial/\partial x - x\, \partial/\partial z)$$

$$- (-i\underline{h})\, (z\, \partial/\partial x - x\, \partial/\partial z)\, (- i\underline{h})\, (y\, \partial/\partial z - z\, \partial/\partial y)$$

$$= - \underline{h}^2\, \{y\, \partial/\partial z\, (z\, \partial/\partial x - x\, \partial/\partial z) - z\, \partial/\partial y\, (z\, \partial/\partial x - x\, \partial/\partial z)$$

$$- z\, \partial/\partial x\, (y\, \partial/\partial z - z\, \partial/\partial y) + x\, \partial/\partial z\, (y\, \partial/\partial z - z\, \partial/\partial y)\}$$

$$= - \underline{h}^2\, \{y\, (\partial/\partial x + z\, \partial/\partial z\, \partial/\partial x - x\, \partial^2/\partial z^2)$$

$$- z\, (z\, \partial/\partial y\, \partial/\partial x - x\, \partial/\partial y\, \partial/\partial z)$$

$$- z\, (y\, \partial/\partial x\, \partial/\partial z - z\, \partial/\partial x\, \partial/\partial y)$$

$$+ x\, (y\, \partial^2/\partial z^2 - \partial/\partial y - z\, \partial/\partial z\, \partial/\partial y)\}$$

$$= - \underline{h}^2\, \{ (-yx + xy)\, \partial^2/\partial z^2 + (yz\, \partial/\partial z\, \partial/\partial x - zy\, \partial/\partial x\, \partial/\partial z)$$

$$+ (-z^2\, \partial/\partial y\, \partial/\partial x + z^2\, \partial/\partial x\, \partial/\partial y)$$

$$+ (zx\, \partial/\partial y\, \partial/\partial z - xz\, \partial/\partial z\, \partial/\partial y) + (y\, \partial/\partial x - x\, \partial/\partial y)\}$$

Since the first four terms are zero,

$$[L_x, L_y] = (i\underline{h})^2\, (y\, \partial/\partial x - x\, \partial/\partial y)$$

$$= (i\underline{h})\, \{-ih\, (x\, \partial/\partial y - y\, \partial/\partial x)\}$$

$$= i\underline{h}\, L_z$$

The other expressions can be given by symmetry & cyclic permutation: (x, y, z) $\rightarrow$ (y, z, x) $\rightarrow$ (z, x, y)

$$[L_x, L_y] = i\underline{h}\, L_z \qquad [L_y, L_z] = i\underline{h}\, L_x \qquad [L_z, L_x] = i\underline{h}\, L_y$$

$[L^2, L_x] = ?$

$$[L^2, L_x] = [L_x^2 + L_y^2 + L_z^2, L_x]$$

$$= [L_x^2, L_x] + [L_y^2, L_x] + [L_z^2, L_x]$$

But $[L_x^2, L_x] = L_x^2 L_x - L_x L_x^2 = L_x L_x L_x - L_x L_x L_x = 0$

So $[L^2, L_x] = [L_y^2, L_x] + [L_z^2, L_x]$

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

$$= L_y L_y L_x - L_x L_y L_y + L_z L_z L_x - L_x L_z L_z$$

Lets look at some related forms which can be used to simplify the above expression:

$$[L_y , L_x] L_y + L_y [L_y , L_x]$$

$$= (L_y L_x - L_x L_y) L_y + L_y (L_y L_x - L_x L_y)$$

$$= L_y L_x L_y - L_x L_y L_y + L_y L_y L_x - L_y L_x L_y$$

The first & fourth terms cancel, giving

$$[L_y , L_x] L_y + L_y [L_y , L_x] = L_y L_y L_x - L_x L_y L_y$$

Similarly, $[L_z , L_x] L_z + L_z [L_z , L_x] = L_z L_z L_x - L_x L_z L_z$

So, $[L^2, L_x] = [L_y , L_x] L_y + L_y [L_y , L_x]$

$+ [L_z , L_x] L_z + L_z [L_z , L_x]$

$= - i\underline{h} L_z L_y - i\underline{h} L_y L_z + i\underline{h} L_y L_z + i\underline{h} L_z L_y = 0$

One can also show that

$[L^2, L_y] = 0 = [L^2, L_z]$

What is the Physical Significance of Operators that Commute?

If A & B commute, Ψ can simultaneously be an eigenfunction of both operators. That means that the observables a & b can be measured simultaneously if $A\Psi = a \Psi$ & $B\Psi = b \Psi$.

Example: position & momentum operators. In problem 3.11 we showed that

$[x, p_x] = i\underline{h}$.

That means that position & momentum cannot be measured simultaneously--i.e. can't know definite values for x & p_x.

Example: position & energy. Since

$[x, H] = (i\underline{h}/m) p_x$,

can't assign definite values to position & energy. A stationary state Ψ has a definite energy, so it shows a spead of possible values of x.

Example: Derive the *Heisenber g Uncertainty Principle*-- from the product of the standard deviation of property A & the standard deviation of property B.

$\langle A \rangle$: average value of A

$A_i - \langle A \rangle$: deviation of the i-th measurement from the average value

$\sigma_A = \Delta A$: standard deviation of A; measure of the spread of A or uncertainty in the values of A.

$$\Delta A = \langle (A - \langle A \rangle)^2 \rangle^{1/2}$$

$$= \langle A^2 - 2 A \langle A \rangle + \langle A \rangle^2 \rangle^{1/2}$$

$$= (\langle A^2 \rangle - 2 \langle A \rangle \langle A \rangle + \langle A \rangle^2)^{1/2}$$

$$= (\langle A^2 \rangle - \langle A \rangle^2)^{1/2}$$

One can show that

$$(\Delta A) (\Delta B) \geq (1/2) \left| \int \Psi^* [A,B] \Psi \, d\tau \right|$$

If [A,B] = 0, then can have both $\Delta A = 0$ & $\Delta B = 0$, which means both observables can be known precisely.

For $(\Delta x) (\Delta p_x) \geq (1/2) \left| \int \Psi^* (i\hbar) \Psi \, d\tau \right|$

$$\geq (1/2)\,\underline{h}\; |i|\; \left| \int \Psi^* \Psi \, d\tau \right|$$

For a normalized wavefunction, $\left| \int \Psi^* \Psi \, d\tau \right| = 1$.

$|i| = (-i\, i)^{1/2} = (1)^{1/2} = 1$

So $(\Delta x)\,(\Delta p_x) \geq (1/2)\,\underline{h}$.

Operators that communte have observables that can be measured simultaneously. So the operators have simultaneous eigenfunctions.

To return to Angular Momentum--

Since L^2 & L_z commute, we want to find the simultaneous eigenfunctions. Since L^2 commutes with each of its components (L_x, L_y, L_z) we can assign definite values to pair L^2 with each of the components

L^2, L_x $\qquad$ L^2, L_y $\qquad$ L^2, L_z

But since the components don't commute with each other, we can't specify all the pairs--only 1. Arbitrarily choose (L^2, L_z).

Note that L^2 means the square of the magnitude of the vector L.

One can convert from Cartesian to Spherical Polar coordinates & derive expressions for L_x, L_y, & L_z that depend only on r, θ, & ϕ:

$$L_x = i\underline{h}\,(\sin\phi\, \partial/\partial\theta + \cos\theta \cos\phi\, \partial/\partial\phi)$$

$L_y = - i\underline{h} (\cos\phi\, \partial/\partial\theta - \cot\theta \sin\phi\, \partial/\partial\phi)$

$L_z = - i\underline{h}\, \partial/\partial\phi$

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

$= - \underline{h}^2 (\partial^2/\partial\theta^2 + \cot\theta\, \partial/\partial\theta + (1/\sin^2\theta)\, \partial^2/\partial\phi^2)$

Read through the derivation of the simultaneous eigenfunctions of L^2 and L_z in Chapter 5. It involves techniques that we have used--separtation of variables, recursion formulas, etc. The result--the simultaneous eigenfunctions of L^2 and L_z are the Spherical Harmonics, $Y_l^m(\theta, \phi)$.

$L^2 Y_l^m(\theta, \phi) = l (l + 1) \underline{h}^2 Y_l^m(\theta, \phi)$, $\quad l = 0, 1, 2,...$

l : quantum number for total angular momentum

$L_z Y_l^m(\theta, \phi) = m\, \underline{h}\, Y_l^m(\theta, \phi)$, $m = -l, -l+1,...l-1, l$

m : quantum number for angular momentum in the z-direction

The ranges on the quantum numbers result from forcing finite behavior at infinity on the wavefunction, i.e. the wavefunction must be well-behaved in all regions of space

$$Y_l^m(\theta, \phi) = [(2l+1)/(4\pi)]^{1/2} [(l-|m|)!/(l+|m|)!]^{1/2}$$

$$\times P_l^{|m|} (\cos\theta)\, e^{im\phi}$$

$= (1/2\pi)^{1/2} S_{l,m}(\theta) e^{im\phi}$

Y_l^m are the Spherical Harmonics

$P_l^{|m|}$ are the Associated Legendre Functions

$S_{l,m}(\theta) = [(2l+1)/2]^{1/2} [(l-|m|)!/(l+|m|)!]^{1/2} P_l^{|m|} (\cos\theta)$

Values for $S_{l,m}(\theta)$ are given in Table 5.1:

$l = 0$ $S_{0,0}(\theta) = \sqrt{2}/2$

$l = 1$ $S_{1,0}(\theta) = \sqrt{6}/2 \cos\theta$

$S_{1,\pm1}(\theta) = \sqrt{3}/2 \sin\theta = S_{1,-1}(\theta)$

$l = 2$ $S_{2,0}(\theta) = \sqrt{10}/4 (3\cos^2\theta - 1)$

$S_{2,\pm1}(\theta) = \sqrt{15}/2 \sin\theta\cos\theta = S_{2,-1}(\theta)$

$S_{2,\pm2}(\theta) = \sqrt{15}/4 \sin^2\theta = S_{2,-2}(\theta)$

We will use these functions as the angular part of the wavefunction for the hydrogen atom & the rigid rotor.

Since L_x and L_y cannot be specified, we can only say that the vector **L** can lie anywhere on the surface of a cone defined by the z-axis. See Fig. 5.6

The orientations of **L** with respect to the z-axis are determined by m. See Fig. 5.7

$$|\mathbf{L}^2| = \mathbf{L}\cdot\mathbf{L} = l(l+1)\,\hbar^2$$

$$|\mathbf{L}| = [l(l+1)]^{1/2}\,\hbar$$

$$= \text{length of } \mathbf{L}$$

$$m\,\hbar = \text{projection of } \mathbf{L} \text{ onto z-axis}$$

For each eigenvalue of L^2, there are $(2l+1)$ eigenfunctions of L^2 with the same value of l, but different values of m. Therefore, the degeneracy is $(2l+1)$.

The Spherical Harmonic functions are important in *the central force* problem--in which a particle moves under a force which is due to a potential energy function that is spherically symmetric, i.e. one that depends only on the distance of the particle from the origin. Then the wavefunction can be separated as a product

$$\psi = R(r)\, Y_l^m(\theta, \phi)$$

Spherical Harmonics

give the angular dependence of ψ for the H atom describe the energy levels of the diatomic rigid rotor, a model for rotational motion in diatomic molecules