Quantum Solutions For A Harmonic Oscillator

Particle in a Box Analogy:

\[ V(x) = \frac{k x^2}{2} \]

Quantization -

Zero Point Energy -

Nodes -

Symmetry of \( \psi \) -

The Schrödinger equation for a particle of mass \( \mu \) is

\[ -\frac{\hbar^2}{2\mu} \frac{d^2 \psi(x)}{dx^2} + \frac{kx^2}{2} \psi(x) = E \psi(x) , \]

which looks a lot like the first homework eigenvalue problem
ACTUALLY,
\[ E_n = \hbar (k/m)^{1/2} (n + \frac{1}{2}) \quad n = 0, 1, 2, 3, \ldots \]

\[ \Psi_n(x) = N_n H_n(\beta x) e^{-\frac{\beta x^2}{2}} \]

where \( \beta^2 = \mu k/\hbar^2 \), and the \( H_n \) are Hermite polynomials. (See text)

- \( H_0 = 1 \) even
- \( H_1 = 2 \beta x \) odd
- \( H_2 = 4(\beta x)^2 - 2 \) even
- \( H_3 = 8(\beta x)^3 - 12\beta x \) odd

What do the solutions look like?

Again, to get a sense of the wavefunctions and the time dependence, look at the falstad website [http://www.falstad.com/qm1d/](http://www.falstad.com/qm1d/) and select “Setup: Harmonic Oscillator” from the drop down menu.
What about various integrals of the harmonic oscillator functions?

\[ \langle \psi_i | \psi_j \rangle = \delta_{ij} \]  

(WHY??)

where \( \delta_{ij} = 1 \) for \( i = j \)  
\( 0 \) for \( i \neq j \)  
the Kronecker delta

what about \( \langle x | x | \rangle \)  
(WHY??)

Note that both the particle in a box and the harmonic oscillator eigenfunctions have a definite parity and that it alternates with the quantum number. This result has to do with the symmetry of \( V(x) \).

We can generalize this result with operators. Let the parity operator \( \hat{A} \) be such that  
\( \hat{A} f(x) = f(-x) \)

Then \( \hat{A}^2 f(x) = \hat{A} \hat{A} f(x) = \hat{A} f(-x) = f(x) = 1 \ f(x) \)

Since any function \( f(x) \) is an eigenfunction of \( \hat{A}^2 \) with eigenvalue 1, the only possible eigenvalues of \( \hat{A} \) are \( \pm 1 \).

Suppose \( f(x) \) is odd about \( x = 0 \). Then \( \hat{A} f(x) = (-1) \ f(x) \)

Suppose \( g(x) \) is even about \( x = 0 \). Then \( \hat{A} g(x) = (1) \ g(x) \)

What is \( \langle f | g \rangle \)?  
(WHY??)
Three Dimensional Harmonic Oscillator

Now let's quickly add dimensions to the problem. Consider a three dimensional harmonic oscillator for a particle of mass m with different force constants $k_x$, $k_y$, and $k_z$ in the x, y and z directions. The potential energy is $V(x, y, z) = \frac{k_x x^2}{2} + \frac{k_y y^2}{2} + \frac{k_z z^2}{2}$ and the Hamiltonian is given by

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \frac{k_x x^2}{2} + \frac{k_y y^2}{2} + \frac{k_z z^2}{2}.$$

This Hamiltonian is clearly separable into x-, y- and z- equations, each of which looks just like the one we have already solved. Thus the solutions are

$$E_{n_x, n_y, n_z} = \hbar \sqrt{\frac{k_x}{m} \left(n_x + \frac{1}{2}\right)} + \hbar \sqrt{\frac{k_y}{m} \left(n_y + \frac{1}{2}\right)} + \hbar \sqrt{\frac{k_z}{m} \left(n_z + \frac{1}{2}\right)}$$

with $n_x = 0, 1, 2, \ldots$, $n_y = 0, 1, 2, \ldots$, $n_z = 0, 1, 2, \ldots$

and $\psi_{n_x, n_y, n_z}(x, y, z) = N_{n_x} H_{n_x}(x) e^{i\beta x} N_{n_y} H_{n_y}(y) e^{i\beta y} N_{n_z} H_{n_z}(z) e^{i\beta z}$

It's really that simple! Now consider the isotropic 3-D oscillator with all three force constants equal. Then $k_x = k_y = k_z = k$ and we have $V(x, y, z) = \frac{k}{2} \left(x^2 + y^2 + z^2\right) = \frac{k}{2} r^2$. Here

$$r = \sqrt{x^2 + y^2 + z^2},$$

the distance from the origin. The result is

$$E_{n_x, n_y, n_z} = \hbar \sqrt{\frac{k}{m} \left(n_x + n_y + n_z + \frac{3}{2}\right)} = \hbar \nu_{\text{class}} \left(n_x + n_y + n_z + \frac{3}{2}\right)$$

with $n_x = 0, 1, 2, \ldots$, $n_y = 0, 1, 2, \ldots$, $n_z = 0, 1, 2, \ldots$

Now we see new energy degeneracies since the problem has high symmetry. Consider the level $E = (9/2) \hbar \nu_{\text{class}}$. Then $(n_x + n_y + n_z + 3/2) = 9/2$

or $n_x + n_y + n_z = 3$. The possibilities are as follows:
The level is 10 fold degenerate!

The potential $V(r)$ is a very special potential, acting in three-dimensional space in a direction along the line from $r$ to the origin. If we imagine placing a proton at the origin, and allow an electron to move around it, then we have the Coulomb potential we have seen earlier, $V(r) = -\frac{e^2}{r}$. This is a special case because the proton is so heavy that the center of mass is essentially located on the proton, at the origin. We will quickly wave our hands through a generalization to obtain center of mass coordinates.

Potentials of the form $V(r)$ are called Central Potentials, and are of great importance in quantum mechanics. We will solve all central potential problems as a simple equivalent one-dimensional problem and in the process learn about angular momentum.

First, we deal with the separation of center-of-mass motion from internal motion.

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Consider as a concrete example an ideal spring with masses $m_1$ and $m_2$ at the ends of the spring, and constrained to move only in the $z$-direction. Let $\ell_0$ be the unstretched (equilibrium) length of the spring. We have the following picture.

The potential energy of the spring can be written in terms of $z_1$ and $z_2$ as

$$V(z_1, z_2) = \frac{1}{2}k[(z_2 - z_1) - \ell_0]^2$$

and the Hamiltonian is given by

$$\hat{H} = \frac{p_{z_1}^2}{2m_1} + \frac{p_{z_2}^2}{2m_2} + \frac{1}{2}k[(z_2 - z_1) - \ell_0]^2$$

This Hamiltonian is certainly not separable in $z_1$ and $z_2$ coordinates. However, there is a change of variables to $z$ and $Z$, one that makes the expression separable. The quantity $z$ is an internal distance $(z_2-z_1)$ while $Z$ is the location of the center of mass of the system,

$$Z = \frac{m_1 z_1 + m_2 z_2}{m_1 + m_2}$$

After a little algebra, we can show that
\( \mathcal{H}(Z, z) = \mathcal{H}(z, Z) = \frac{p_z^2}{2\mu} + \frac{k}{2}(z - \ell_0)^2 + \frac{p_z^2}{2(m_1 + m_2)} \)

where \( \mu = \frac{m_1 m_2}{m_1 + m_2} \) the REDUCED MASS

so the Hamiltonian is separable into motion of the center of mass (COM) and internal motion. i.e.

\[ \dot{\mathcal{H}} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dz^2} + \frac{k(z - \ell_0)^2}{2} - \frac{\hbar^2}{2(m_1 + m_2)} \frac{d^2}{dZ^2} \]

and the wave function \( \psi(z, Z) \) can be written in product form,

\[ \psi(z, Z) = \phi(z) f_{cm}(Z) \]

where \( f(Z) \) describes the free (unquantized) motion of the center of mass in \( Z \) and \( \phi(z) \) is the solution to the other part. Now \( E = E_Z + E_z \).

In effect, the one problem separates into two independent problems:

1. The motion of a fictitious particle of mass \( (m_1 + m_2) \) positioned at the center of mass, and subject only to the external forces acting on the system.
2. The motion of a fictitious particle of reduced mass \( \mu \), subject only to the internal forces. The center of mass of this system does not move.

Note that if we put this system in a box, then the \( Z \) motion would be quantized. This should answer your worry about where the second quantum number went, since there are two particles in one dimension.

So the harmonic oscillator problem becomes what we have seen before,

\[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dz^2} \phi(z) + \frac{k(z - \ell_0)^2}{2} \phi(z) = E \phi(z) \]

with the known solutions, now simply centered about \( \ell_0 \) rather than zero. This same procedure will always work in 3 dimensions, and the motion of the center of mass reduces by three the number of internal quantum numbers. These center of mass motions when the "particle" is confined to a box give rise to the translational heat capacity expression we will derive in the statistical mechanic portion of the course.

**We will always implicitly separate out the center of mass motion in the future.**

Soon we will see that when the 3 dimensional potential \( V(x,y,z) \) depends only on the distance from the origin, i.e. \( V(x,y,z) = V(r) \), a central potential, then the Hamiltonian will be separable in spherical polar coordinates, \((r, \theta, \phi)\). The \( \theta \) and \( \phi \) parts of the solution will be the same for any radial potential: coulomb, harmonic, rigid rotor or whatever!!

The \( \theta \) and \( \phi \) parts will refer to the angular momentum properties of the system, no matter what system \( V(r) \) describes. For example, if \( V(r) \) is the \( 1/r \) Coulomb potential (H atom), then the quantum numbers arising from the \( \theta \) and \( \phi \) parts give rise to the \( \ell \) and \( m_\ell \) quantum numbers we know well.

Before that time, however we make a short foray into commutation relations and the basics of angular momentum.
Commutation Relationships

We have seen something of commutation relations. We need to say a little more about why they are important.

First remember that if a state function is an eigenfunction of operator $\hat{A}$, then every measurement of the A property gives the eigenvalue $a_i$. This means that the property A is an exact description of that aspect of the system. (energy, angular momentum, whatever) We wish to find as many sharp properties of the system as possible.

In our 3D harmonic oscillator we saw that the function
$$\Psi_{nx,ny,nz}(x,y,z) = N_n H_n(\beta x)e^{-\beta x^2/2} H_n(\beta y)e^{-\beta y^2/2} H_n(\beta z)e^{-\beta z^2/2}$$
is simultaneously an eigenfunction of $[KE_x + V(x)]$, $[KE_y + V(y)]$ and $[KE_z + V(z)]$. The harmonic oscillator Hamiltonian commutes with all of these operators. The properties are all "sharp", i.e., characterized by zero standard deviation in a measurement. **We will always want to utilize such sharp such properties to characterize a system.**

For an H atom, they might be total energy, total angular momentum and one component of angular momentum. How do we identify such properties?

**Theorem 1:** If $\hat{A}$ commutes with $\hat{O}$ (i.e., $[\hat{O}, \hat{A}] = 0$), then there exists a complete set of functions which are simultaneously eigenfunctions of $\hat{O}$ and $\hat{A}$.

**Theorem 2:** If two operators $\hat{O}$ and $\hat{A}$ have a common, complete set of eigenfunctions, then they commute, i.e. $[\hat{O}, \hat{A}] = 0$.

The proof follows from the fact that any function can be expanded in the common, complete set of eigenfunctions.

**Theorem 3:** If Hermitian operator $\hat{A}$ commutes with $\hat{O}$, and if $\phi_1$ and $\phi_2$ are eigenfunctions of $\hat{A}$ with eigenvalues $a_1$ and $a_2$, then the **MATRIX ELEMENT** $O_{1,2}$ vanishes unless $a_1 = a_2$.

Here $O_{1,2} = \langle \phi_1 | \hat{O} | \phi_2 \rangle$, the definition of a matrix element.

**Proof:**
First $\hat{A}\phi_1 = a_1\phi_1$ and $\hat{A}\phi_2 = a_2\phi_2$
Now $\langle \phi_1 | \hat{O} \hat{A} | \phi_2 \rangle = a_2 \langle \phi_1 | \hat{O} | \phi_2 \rangle$.
Also $\langle \phi_1 | \hat{O} \hat{A} | \phi_2 \rangle = \langle \phi_1 | \hat{A} \hat{O} | \phi_2 \rangle$ since they commute
$\langle \phi_1 | \hat{A} \hat{O} | \phi_2 \rangle = \langle \hat{A}\phi_1 | \hat{O} | \phi_2 \rangle = a_1 \langle \phi_1 | \hat{O} | \phi_2 \rangle$
Thus $a_2 \langle \phi_1 | \hat{O} | \phi_2 \rangle = a_1 \langle \phi_1 | \hat{O} | \phi_2 \rangle$
or $(a_2 - a_1) \langle \phi_1 | \hat{O} | \phi_2 \rangle = 0$. 

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Since \( a_1 \neq a_2 \), the matrix element must vanish. This theorem will be extremely useful in applying symmetry to assist in obtaining wavefunctions. It also begins to show the importance of matrix elements in quantum mechanics.

As a follow up, consider the harmonic oscillator problem

\[
\hat{\mathcal{H}} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{kx^2}{2}
\]

with state functions \( \psi_n(x) \) as we know.

Now \( \mathcal{H}_{ij} \equiv \langle \psi_i | \hat{\mathcal{H}} | \psi_j \rangle \)

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**Central Field Potential**

Consider the case where there are two particles of mass \( m_1 \) and \( m_2 \) interacting via a potential \( V(r) \), which depends only on the distance between the particles. **(a central field)** The Hamiltonian operator is given by

\[
\widehat{\mathcal{H}}_{\text{cent}} = -\frac{\hbar^2}{2\mu} \nabla^2 + V(r)
\]

If we start with rectangular \( (x,y,z) \) coordinates, we must transform this expression to spherical polar coordinates, \( r, \theta, \phi \) where \( 0 \leq r < \infty \), \( 0 \leq \theta \leq \pi \) and \( 0 \leq \phi \leq 2\pi \). This is easily done as shown:

\[
x = r \sin \theta \cos \phi \\
y = r \sin \theta \sin \phi \\
z = r \cos \theta
\]

We can transform the \( x, y \) and \( z \) derivatives into \( r, \theta, \) and \( \phi \) terms. After much manipulation, sweat, blood and tears, we would obtain the time independent Schrödinger
equation for a central field. Alternatively, we look up the form of $V^2$ in spherical polar coordinates.

In either case, we finally obtain the time independent Schrödinger equation for a central field:

$$\frac{-\hbar^2}{2\mu} \left[ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) \right] \psi(r, \theta, \phi)$$

$$+ \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \psi(r, \theta, \phi) + V(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

Various forms of $V(r)$ give us important problems:

<table>
<thead>
<tr>
<th>$V(r)$</th>
<th>Problem</th>
</tr>
</thead>
<tbody>
<tr>
<td>$kr^2/2$</td>
<td>3D Isotropic Harmonic oscillator</td>
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<tr>
<td>$0$ for $r = R$</td>
<td>Rigid Rotor</td>
</tr>
<tr>
<td>$\infty$</td>
<td>otherwise</td>
</tr>
<tr>
<td>$-ze^2/r$</td>
<td>Hydrogen-like atom</td>
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</tbody>
</table>

What do we do now?

What we will find out is that all of the angular part of the Schrödinger equation above is really the square of the angular momentum operator, $\hat{L}$. The Schrödinger equation will in this case simplify to

$$\frac{-\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \psi(r, \theta, \phi) + \frac{\hat{L}^2}{2\mu r^2} \psi(r, \theta, \phi) + V(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)$$

When we learn more about angular momentum, we will see that this equation (which has all the $\theta$ and $\phi$ mess hidden in the $\hat{L}$ part) is an enormous simplification.
Angular Momentum

Classically the angular momentum \( \mathbf{\tilde{L}} \) of a particle of mass \( m \) is given by \( \mathbf{\tilde{L}} = \mathbf{r} \times \mathbf{p} \), a vector quantity which can be expressed as a determinant,

\[
\mathbf{\tilde{L}} = \begin{vmatrix}
\mathbf{i} & \mathbf{j} & \mathbf{k} \\
x & y & z \\
p_x & p_y & p_z
\end{vmatrix}
\]

\[
= \mathbf{i}(yp_z - zp_y) + \mathbf{j}(zp_x - xp_z) + \mathbf{k}(xp_y - yp_x)
\]

We of course know that an isolated system has a constant angular momentum vector. We also remember that the angular momentum version of \( \mathbf{\tilde{F}} = m \mathbf{a} = \frac{dp}{dt} \) involves \textbf{torque} \( \mathbf{\tau} \) and is written

\[
\mathbf{\tau} = \frac{d\mathbf{\tilde{L}}}{dt}.
\]

If \( \mathbf{\tau} = 0 \), then \( \frac{d\mathbf{\tilde{L}}}{dt} = 0 \) \( \Rightarrow \frac{dL_x}{dt} = \frac{dL_y}{dt} = \frac{dL_z}{dt} = 0 \)

Thus \( \mathbf{\tilde{L}}, L_x, L_y, \) and \( L_z \) are \textbf{constant} in this case. They are "Constants of the Motion" Think about tops or gyroscopes!

We shall see that quantum mechanically only the square of the total angular momentum and one component can be constants of the motion. That is to say, they have \textbf{commuting operators}. Thus we will look at the QM operators, their commutation relations and their representation in spherical polar coordinates.

Looking at the quantum mechanical operator,

\[
\hat{\mathbf{L}}_{op} = \begin{vmatrix}
\mathbf{i} & \mathbf{j} & \mathbf{k} \\
x & y & z \\
p_x & p_y & p_z
\end{vmatrix}
= \hat{L}_x \mathbf{i} + \hat{L}_y \mathbf{j} + \hat{L}_z \mathbf{k}
\]

where

\[
\hat{L}_x = -i \hbar \begin{pmatrix}
\frac{\partial}{\partial z} & -z \frac{\partial}{\partial y} \\
\end{pmatrix}
\]

\[
\hat{L}_y = -i \hbar \begin{pmatrix}
z \frac{\partial}{\partial x} & -x \frac{\partial}{\partial z} \\
\end{pmatrix}
\]

\[
\hat{L}_z = -i \hbar \begin{pmatrix}
x \frac{\partial}{\partial y} & -y \frac{\partial}{\partial x} \\
\end{pmatrix}
\]

Also,

\[
\hat{\mathbf{L}}^2 = \hat{\mathbf{L}} \cdot \hat{\mathbf{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2
\]

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Let us look at commutation relations, e.g., $[\hat{L}_x, \hat{L}_y]$

First $\hat{L}_x \hat{L}_y f = \hat{L}_x \left(-i\hbar \left[ \frac{\partial f}{\partial x} - \frac{x \partial f}{\partial z} \right] \right)$

Then evaluate $\hat{L}_y \hat{L}_x f$ and subtract. After a bunch of algebra, we obtain the commutator

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$

By cyclic permutation of variables ($x \rightarrow y$, $y \rightarrow z$, $z \rightarrow x$), we also get

$$[\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z$$
$$[\hat{L}_y, \hat{L}_z] = i\hbar \hat{L}_x$$
$$[\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y$$

Since none of these commutators are zero, we have that

**No two components of angular momentum commute.**

Thus we cannot specify two components of angular momentum at the same time!

We also find that $[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$

So we can find functions that are simultaneously eigenfunctions of $\hat{L}^2$ and **any one component of the angular momentum**.

We switch to spherical polar coordinates ($r, \theta, \phi$) and find that we can write the operators $\hat{L}^2$ and $\hat{L}_z$ in the following form:

$$\hat{L} \cdot \hat{L} \equiv \hat{L}^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

$$\hat{L}_z = -i \hbar \frac{\partial}{\partial \phi}$$

$\hat{L}_x$ and $\hat{L}_y$ are given in the text, and are more complex.
So finally we obtain
\[
[\hat{L}^2, \hat{L}_x] = 0 \quad [\hat{\mathcal{H}}_{\text{cent}}, \hat{L}_y] = 0 \quad [\hat{L}_x, \hat{L}_y] = i\hbar \hat{L}_z
\]
\[
[\hat{L}^2, \hat{L}_y] = 0 \quad [\hat{\mathcal{H}}_{\text{cent}}, \hat{L}_x] = 0 \quad [\hat{L}_y, \hat{L}_x] = i\hbar \hat{L}_z
\]
\[
[\hat{L}^2, \hat{L}_z] = 0 \quad [\hat{\mathcal{H}}_{\text{cent}}, \hat{L}_x] = 0 \quad [\hat{L}_z, \hat{L}_x] = i\hbar \hat{L}_y
\]
\[
[\hat{\mathcal{H}}_{\text{cent}}, \hat{L}^2] = 0
\]

So we can find eigenfunctions of the central field Hamiltonian, \(\hat{\mathcal{H}}_{\text{cent}}\), that are simultaneously eigenfunctions of \(\hat{\mathcal{H}}_{\text{cent}}, \hat{L}^2\) and one component of the total angular momentum. Conventionally, and for mathematical simplicity this is taken to be the unique axis (z). Thus we add \(\hat{L}_z\) to our list of eigenfunctions. Since there are only three possible quantum numbers for this system (WHY??), our list is complete. We now go on our way about solving the three eigenvalue equations for \(\hat{L}_z, \hat{L}^2\) and \(\hat{\mathcal{H}}_{\text{cent}}\).

**Note that our solutions for the first two must be valid for any central field problem.**

I. Z - Component

We can readily solve the \(\hat{L}_z\) eigenvalue equation,
\[
\hat{L}_z \Phi(\phi) = -i \hbar \frac{\partial \Phi}{\partial \phi} = C \Phi(\phi),
\]

to obtain \(\Phi(\phi) = e^{im\phi}\) for \(0 \leq \phi \leq 2\pi\) with the eigenvalues \(C\) being \(m\hbar\).

In order for \(\Phi(\phi)\) to be single valued, we must satisfy the boundary condition \(\Phi(0) = \Phi(2\pi)\). This restriction requires that \(m = 0, \pm 1, \pm 2, \ldots\). Thus the z-component of total angular momentum is quantized. This quantum number will turn out to be the \(m\) quantum number we have seen before in the hydrogen atom.

Show that the corresponding eigenvalues are \(m\hbar\). Note that this must mean that \(\hbar\) has units of angular momentum.
II. Square of Total Angular Momentum

The solution to the $\hat{L}^2$ eigenvalue equation is not so straightforward, and we will not go through it. However, the solution is a standard function of mathematical physics called the spherical harmonics, $Y_{\ell,m}(\theta,\phi)$. These are tabulated in the text (and in any standard quantum mechanics text). The key properties of these functions are summarized by their eigenvalues:

$$\hat{L}^2 \ Y_{\ell,m}(\theta,\phi) = (\ell)(\ell+1) \hbar^2 \ Y_{\ell,m}(\theta,\phi) \quad \ell = 0, 1, 2, \ldots$$

and

$$\hat{L}_z \ Y_{\ell,m}(\theta,\phi) = m \hbar \ Y_{\ell,m}(\theta,\phi) \quad m = -\ell, -\ell+1, \ldots, 0, \ldots, \ell$$

What is the physical significance of this result? Now $\hat{L}^2$ and $\hat{L}_z$ must both be sharp quantities. That obviously means that $|L|$ must also be exact. With a little more thought, we see that $|L|$ must be precessing about $L_z$ and the m-quantum number represents a spatial quantization.

As an example, consider $\ell = 1$. Then $|L| = \sqrt{2}\hbar$ and there are three possible m-values,

\[ m = 1 \quad m = 0 \quad m = -1 \]
Some of the spherical harmonics are listed below:

\[
Y_{0,0}(\theta, \phi) = \sqrt{\frac{2}{4\sqrt{2\pi}}} \\
Y_{1,0}(\theta, \phi) = \sqrt{\frac{3}{2}} \cos \theta \frac{1}{\sqrt{2\pi}} \\
Y_{1,\pm 1}(\theta, \phi) = \sqrt{\frac{3}{4}} \sin \theta \frac{1}{\sqrt{2\pi}} e^{\pm i\phi} \\
Y_{2,0}(\theta, \phi) = \sqrt{\frac{5}{8}} (3\cos^2 \theta - 1) \frac{1}{\sqrt{2\pi}} \\
Y_{2,\pm 1}(\theta, \phi) = \sqrt{\frac{15}{4}} \sin \theta \cos \theta \frac{1}{\sqrt{2\pi}} e^{\pm i\phi} \\
Y_{2,\pm 2}(\theta, \phi) = \sqrt{\frac{15}{16}} \sin^2 \theta \frac{1}{\sqrt{2\pi}} e^{\pm 2i\phi}
\]

What about nodes in these functions?

**III. Radial Part**

Now back to the central potential problem. We had previously obtained the Schrödinger equation for a central force as

\[
-\frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \psi(r, \theta, \phi) \right) + \frac{\hbar^2}{2\mu r^2} \psi(r, \theta, \phi) + V(r) \psi(r, \theta, \phi) = E \psi(r, \theta, \phi)
\]

Let a solution be of the form \( \psi_{n,\ell,m}(r, \theta, \phi) = R_{n,\ell}(r)Y_{\ell,m}(\theta, \phi) \).

When we make this substitution, we can explicitly carry out the angular momentum operation, and bring the \( Y_{\ell,m}(\theta, \phi) \) terms through the \( r \) - derivatives and the \( V(r) \) \( R_{n,\ell}(r) \) term through the angular momentum operator. We then divide through by \( Y_{\ell,m}(\theta, \phi) \).

The \( R_{n,\ell}(r) \) must satisfy the following ordinary differential equation:

\[
-\frac{\hbar^2}{2\mu r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} R_{n,\ell} \right) + \left[ V(r) + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} \right] R_{n,\ell} = E R_{n,\ell}(r)
\]

expanding this expression,

\[
-\frac{\hbar^2}{2\mu} \left( \frac{2}{r} \frac{d}{dr} R_{n,\ell} \right) + \frac{d^2}{dr^2} R_{n,\ell} \left[ V(r) + \frac{\hbar^2 \ell(\ell + 1)}{2\mu r^2} \right] R_{n,\ell}(r) = E R_{n,\ell}(r)
\]

As this is a one-dimensional equation, we can readily obtain a numerical solution. Thus the central field problem is a numerically solvable system.

If we consider the nucleus of an atom to be infinitely heavy, and neglect the electron-electron repulsion, we shall see that the \( n \)-electron atom problem separates and becomes \( n \) - one
electron atom problems. This is the starting point for ANY system, and is the reason that the solutions of the hydrogen atom problem play such a key role in our understanding of atomic and molecular structure!

**Rigid Rotor Energies and Wavefunctions**

The rigid rotor consists of a pair of particles of masses \( M_1 \) and \( M_2 \) (reduced mass \( \mu \)) separated by a **fixed** distance \( R_o \). With this model, we can set the central potential to be \( V(r) = 0 \) for \( R = R_o \), and infinite otherwise. The \( R(r) \) derivatives in the preceding equation can be shown to be zero, basically for the same reasons as for the infinite square well solved earlier. Thus at \( r = R_o \), the radial Schrödinger equation becomes

\[
\frac{\hbar^2}{2\mu} \left( \frac{\ell(\ell + 1)}{R_o^2} \right) Y_{\ell,m}(\theta, \phi) = E Y_{\ell,m}(\theta, \phi)
\]

By convention, the \( \ell \) quantum number in the rotor problem is replaced by \( j \). Thus the allowed energies are given by

\[
E_{j,m} = \frac{\hbar^2}{2\mu R_o^2} j(j+1) = \frac{\hbar^2}{2I} j(j+1) = B j(j+1)
\]

with \( j = 0,1,2,... \) and \( m = -j,-j+1,...,-1,0,1...j \)

where \( \psi(r, \theta, \phi) = Y_{j,m}(\theta, \phi) \)

The quantity \( I \) is the classical moment of inertia, \( I = \mu R_o^2 \).

The quantity \( B \) is known as the rotational constant.

Clearly, if we can measure the positions of the rotational energy levels, we can then derive the length of a bond. This is the essence of rotational spectroscopy.

Notice that \( \langle Y_{j,m} | Y_{j',m'} \rangle = \delta_{j,j'} \delta_{m,m'} \).

Note the \( 2j + 1 \) energy degeneracy of level \( E_j \).

What is the significance of the \( m \) quantum number and what is the nature of the degeneracy associated with it?