## 5.3: Solution to the Schrödinger Equation

The time-independent Schrödinger equation can be written as follows.

$$\hat{H}\psi(\theta,\phi) = E\psi(\theta,\phi)$$
$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\psi(\theta,\phi) = E\psi(\theta,\phi)$$

Since the Hamiltonian can be expressed as a sum of operators, one in $\theta$ and the other in $\phi$, it follows that the wavefunction should be able to be expressed as a product of two functions.

$$\psi(\theta,\phi) = \Theta(\theta)\Phi(\phi)$$

Making this substitution, the equation becomes

$$-\frac{\hbar^2}{2\mu r^2}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\Theta(\theta)\Phi(\phi) = E\Theta(\theta)\Phi(\phi)$$

With minimal rearrangement, the following result can be derived

$$\frac{\Phi(\phi)}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta)+\frac{\Theta(\theta)}{\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi) = -\frac{2\mu rE}{\hbar^2}\Theta(\theta)\Phi(\phi)$$

And dividing both sides by $\Theta(\theta)\Phi(\phi)$ produces

$$\left(\frac{1}{\Theta(\theta)\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta)\right)+\left(\frac{1}{\Phi(\phi)\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi)\right) = -\frac{2\mu r^2E}{\hbar^2}$$

This expression suggests that the sum of two functions, one only in $\theta$ and the other only in $\phi$, when added together, yields a constant. As the two variables $\theta$ and $\phi$ are independent of one another, the only way this can be true is if each equation is itself equal to a constant.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta) = -\lambda_1^2\Theta(\theta)$$
$$\frac{1}{\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi) = -\lambda_2^2\Phi(\phi)$$

where $\lambda_1$ and $\lambda_2$ are constants of separation (the form of which is chosen for convenience) which satisfy the following relationship.

$$\begin{aligned}-\lambda_1^2-\lambda_2^2 &= -\lambda^2\\ &= -\frac{2\mu r^2E}{\hbar^2}\end{aligned}$$

### Rotation in the xy plane $(\theta = \pi/2)$

We'll tackle the equation in $\phi$ first. One way to picture this part of the equation is that it describes the rotation of a molecule in the xy plane only (defined by $\theta = \pi/2$.) Given this constraint, it is clear that the $\sin^2(\theta)$ term becomes unity, since $\sin(\pi/2) = 1$. The problem then becomes

$$\frac{d^2}{d\phi^2}\Phi(\phi) = -\frac{2\mu r^2E}{\hbar^2}\Phi(\phi)$$

If a substitution is made for the constants on the right-hand side of the equation,

$$-m_l^2 = -\frac{2\mu r^2E}{\hbar^2}$$

we get

$$\frac{d^2}{d\phi^2}\Phi(\phi) = -m_l^2\Phi(\phi)$$

which should look like a familiar problem. Instead of using sine and cosine functions this time though, we will use an imaginary exponential function instead.

$$\Phi(\phi) = A_{m_l} e^{im_l\phi}$$

The boundary condition for this problem is that the function $\Phi(\phi)$ must be single valued. Therefore

$$\Phi(\phi) = \Phi(\phi + 2\pi)$$

So

$$A_{m_l} e^{im_1\phi} = A_{m_1} e^{im_l(\phi+2\pi)}$$

Dividing both sides by $A_{m_l}$ and expressing the second exponential as a product yields

$$\begin{aligned} e^{im_l\phi} &= e^{im_l\phi} e^{im_l 2\pi} \\ 1 &= e^{im_l 2\pi} \end{aligned}$$

Using the Euler relationship

$$e^{i\alpha} = \cos\alpha + i\sin\alpha$$

we see that

$$1 = \cos(2m_l\pi) + i\sin(2m_l\pi)$$

In order for this to be true, the sine term must vanish and the cosine term must become unity. This is true if $m_l$ is an integer, either positive or negative and including zero.

$$m_l = \ldots, -2, -1, 0, 1, 2, \ldots$$

## Energy Levels

As such, the energy of a rigid rotator limited to rotation in the xy plane is given by

$$E_{m_l} = \frac{m_l^2\hbar^2}{2\mu r^2} \quad m_l = 0, \pm 1, \pm 2, \ldots$$

It is important to note that these functions are doubly degenerate for any non-zero value of $m_l$ as there are always two values of $m_l$ that yield the same energy.

## Normalization

The wavefunctions can be normalized in the usual way.

$$\begin{aligned} \int_0^{2\pi} \left(A_{m_l} e^{im_l\phi}\right)^* \left(A_{m_l} e^{im_l\phi}\right) d\phi = 1 \\ &= A_{m_l}^2 \int_0^{2\pi} e^{-im_l\phi} e^{im_l\phi} d\phi \\ &= A_{m_l}^2 \int_0^{2\pi} d\phi \\ &= A_{m_l}^2 [\phi]_0^{2\pi} \\ &= 2\pi A_{m_l}^2 \\ \sqrt{\frac{1}{2\pi}} &= A_{m_l} \end{aligned}$$

As was the case with the particle in a box problem, the normalization factor does not depend on the quantum number. The wavefunctions can be expressed

$$\Phi(\phi)=\sqrt{\frac{1}{2\pi}}e^{im_l\phi} \quad m_l=0,\pm1,\pm2,\ldots$$

## Rotation in three dimensions

We are now ready to tackle the more complicated problem of rotation in three dimensions. Recall the Schrödinger equation as was previously written.

$$\frac{\Phi(\phi)}{\sin\theta}\frac{d}{d\theta}\sin\theta\frac{d}{d\theta}\Theta(\theta)+\frac{\Theta(\theta)}{\sin^2\theta}\frac{d^2}{d\phi^2}\Phi(\phi)=-\frac{2\mu rE}{\hbar^2}\Theta(\theta)\Phi(\phi)$$

We already know the form of the solutions for the $\Phi(\phi)$ part of the equation. However, due to the $1/\sin^2\theta$ term in the $\Phi$ equation, it is possible that the solution to the $\Theta$ part of the equation will introduce a new constraint on the quantum number $m_i$.

### Energy Levels

The only well-behaved functions (functions that satisfy all of the boundary conditions) have energies given by

$$E_l=\frac{l(l+1)\hbar^2}{2\mu r^2} \quad l=0,1,2,\ldots$$

The quantum number $l$ indicated the angular momentum. $m_l$ is the z-axis component of angular momentum. The z-axis is treated differently than the x - or $y$-axes due to the unique manner in which the z-axis is treated in the choice of the spherical polar coordinate system (since $\theta$ is taken as the angle of the position vector with the positive z-axis.) Also, as will be shown later, the operator $\hat{L}_z$, the z-axis angular momentum component operator, has a special relationship with the Hamiltonian (as does the squared angular momentum operator, $\hat{L}^2$.)

### Degeneracy

The interpretation of the quantum number $m_l$ is that it gives the magnitude of the z-axis component of the angular momentum vector. And since no vector can have a component with a magnitude greater than that of the vector itself, the constraint on $m_l$ that is introduced by this solution is

$$|m_l|\leq l$$

so for a given value of $l$, there are $(2l+1)$ values of $m_l$ that fit the constraint. And since the energy expression does not depend on $m_l$, it is clear that each energy level has a degeneracy that is given by $(2l+1)$. That can be demonstrated as in the diagram below for an angular momentum vector of magnitude $2(l=2)$.

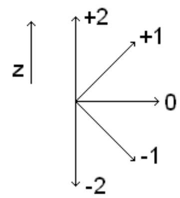


Figure 5.3.1

As can be seen in the diagram, there are five possible values of $m_l$, $+2,+1,0,-1$ and $-2$. These five values correspond to the $(2l+1)$ degeneracy predicted for a state with total angular momentum given by $l=2$ (and therefore $2l+1=5$ ). When we see the wavefunctions in more detail, there will be a new reason for this constraint on the quantum number $m_l$.

### Wavefunctions

For convenience, we'll first look at the solutions where $m_l=0$. The wavefunctions under this constraint have two parts, a normalization constant and a Legendre polynomial in $\cos(\theta)$. The Legendre polynomials are another set of orthogonal polynomials, similar to the Hermite polynomials that occur in the solution to the harmonic oscillator problem. The Legendre polynomials can be generated by the following relationship

$$P_l(x)=\frac{1}{2^l l!}\frac{d'}{dx^l}\left(x^2-1\right)^l$$

The first few Legendre polynomials are given below.

| $\mathbf{l}$ | $\mathbf{P}_l(\mathbf{x})$ | $\mathbf{P}_l(\cos\theta)$ |
|---|---|---|
| 0 | 1 | 1 |
| 1 | $x$ | $\cos(\theta)$ |
| 2 | $\frac{1}{2}(3x^2-1)$ | $\frac{1}{2}\left[3\cos^2(\theta)-1\right]$ |
| 3 | $\frac{1}{2}(5x^3-3x)$ | $\frac{1}{2}\left[5\cos^3(\theta)-3\cos(\theta)\right]$ |

A recursion relation for the Legendre Polynomials is given by

$$(l+1)P_{l+1}(x) = (2l+1)xP_l(x) - lP_{l-1}(x)$$

When $m_l = 0$, the spherical harmonic function $Y_l^m(\theta,\phi) = \Theta(\theta)\Phi(\phi)$ becomes just $\Theta(\theta)$, since the $\phi$ dependence disappears. The $\Theta(\theta)$ part of the wavefunctions are given by

$$\Theta(\theta) = \left[\frac{(2l+1)}{2}\right]^{\frac{1}{2}} P_l(\cos\theta)$$

The functions are slightly different for $m_l \neq 0$. In this case, the functions involve a set of functions that are related to the Legendre Polynomials called the associated Legendre polynomials. These functions are generated from the Legendre polynomials via the following relationship.

$$P_l^{|m_l|}(x) = (-1)^{|m_l|}\left(1-x^2\right)^{\backslash m_l//2} \frac{d^{|m_l|}}{dx^{|m_l|}} P_l(x)$$

Note that for any value of $|m_l| > l$, the derivative of $\mathrm{P}_l(\mathrm{x})$ vanishes.

$$\frac{d^{|m_l|}}{dx^{|m_l|}} P_l(x) = 0 \quad \text{for } |m_l| > l$$

And this is the origin of the constraint on $m_l$.

The associated Legendre polynomials depend on both $l$ and $m_l$. Also, given the $|m_l|$ dependence, the sign of $m_l$ does not matter. (The only place that the sign of $m_l$ matter is in the $\Phi(\phi)$ function.) The first few associated Legendre Polynomials are given in the table below.

| $\boldsymbol{I}$ | $\lvert\boldsymbol{m_l}\rvert$ | $\mathbf{P}^{\lvert m\rvert}(\mathbf{x})$ | $\mathbf{P}^{\lvert m\rvert}(\cos\theta)$ |
|---|---|---|---|
| 0 | 0 | 1 | 1 |
| 1 | 0 | $\mathrm{x}$ | $\cos(\theta)$ |
| | 1 | $(1-\mathrm{x}^2)^{\frac{1}{2}}$ | $\sin(\theta)$ |
| 2 | 0 | $\frac{1}{2}(3\mathrm{x}^2-1)$ | $\frac{1}{2}(3\cos^2(\theta)-1)$ |
| | 1 | $3\mathrm{x}(1-\mathrm{x}^2)^{\frac{1}{2}}$ | $3\cos(\theta)\sin(\theta)$ |
| | 2 | $3(1-\mathrm{x}^2)$ | $3\sin^2(\theta)$ |