Quantum Mechanics II

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" I am the one who knocks "

- Heisenberg

Contents

1 Symmetries

1.1 3D Schrodinger equation

- In QM the Hamiltonian is written in terms of operators. Momenta becomes $\mathbf{p} \to -i\hbar\nabla$ and the potential $V \to \hat{V}$ also an operator. So the Hamiltonian becomes:

$$\boxed{\frac{-\hbar^2}{2m}\nabla^2 + \hat{V}} \tag{1.1}$$

- The (time independent) Schrodinger equation is:

$$\boxed{H\psi(x,y,z) = E\psi} \tag{1.2}$$

- If we then have a central potential, that is $V = V(r)$, so rotation symmetry generated by a rotational group, we find it best to change co-ords to spherical co-ords. Here the Laplacian is:

$$\boxed{\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Phi}{\partial\theta}) + \frac{1}{r^2\sin^2(\theta)}\frac{\partial^2\Phi}{\partial\phi^2} = 0} \tag{1.3}$$

We then make the typical assumption of separation of variables, that is:

$$\boxed{\psi = R(r)Y(\theta,\phi)} \tag{1.4}$$

The Schrodinger equation then becomes:

$$\boxed{\begin{aligned}-\frac{\hbar^2}{2m}&\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial Y}{\partial\theta}) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]\\ &+ V(r)R(r)Y(\theta,\phi) = ER(r)Y(\theta,\phi)\end{aligned}} \tag{1.5}$$

Dividing by $R(r)Y(\theta,\phi)$ and multiplying by r^2, we get two terms, one a function of r only and one a function of θ and ϕ, adding to a constant E. This means that both these terms must themselves be constant. This gives us two separate equations.

$$\boxed{\begin{gathered}-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E] = l(l+1)\\ \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial Y}{\partial\theta}) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right] = -l(l+1)\end{gathered}} \tag{1.6}$$

The choice $l(l+1)$ as a constant, may seem strange at first but makes sense later. On the later equation we again perform separation of variables, $Y = \Theta(\theta)\Phi(\phi)$, so we get two more equations:

$$\boxed{\begin{aligned} \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} &= -m^2 \\ \sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left(l(l+1)\sin^2\theta - m^2\right)\Theta &= 0 \end{aligned}} \tag{1.7}$$

The first equation here is solved by the usual:

$$\boxed{\Phi \propto e^{\pm im\phi}} \tag{1.8}$$

And Linear combinations of this. Since we would expect that $\Phi(\phi+2\pi) = \Phi(\phi)$, as ϕ is multi-valued, this sets the restriction on m, that m must be an integer.

The solution to Θ solved by the *associated Legendre functions* P_l^m:

$$\boxed{\begin{aligned} \Theta &\propto P_l^m(\cos\theta) \\ P_l^m(x) =& (1-x^2)^{\frac{|m|}{2}}\left(\frac{d}{dx}\right)^{|m|} P_l(x) \end{aligned}} \tag{1.9}$$

Here $P_l(x)$ are the Legendre polynomials, which can be generated from the Rodrigues' formula:

$$\boxed{P_l(x) = \frac{1}{2^l l!}\frac{d^l}{dx^l}(x^2-1)^l} \tag{1.10}$$

This generates a polynomial of degree l, this means that 1.9 vanishes if $|m| > l$ as the nth derivative of a $(n-1)$th order polynomial is 0. So we have that:

$$\boxed{\begin{aligned} &|m| \leq l \\ \implies &m \in \{-l, ..., 0, ..., l\} \end{aligned}} \tag{1.11}$$

There are $2l+1$ allowed values for m. Because the Radial equation 1.6, does not contain m but does depend on l. We get degenerate solutions as the only restriction is $|m| \leq l$. This leads to degenerate solutions due to symmetry.

1.2 Spherical Harmonics

- With the above equations we can now calculate the form of $Y_l^m(\theta,\phi) = \Theta(\theta)\Phi(\phi)$, these functions are known as the spherical harmonics. The first harmonic Y_0^0 is just a constant, It can be of any form to satisfy the differential equation set for Y, but we usually specify it so that the wavefunction is normalised. This turns out to set:

$$\boxed{Y_0^0 = \sqrt{\frac{1}{4\pi}}} \tag{1.12}$$

There is only one harmonic for $l = 0 \implies m = 0$, but for $l = 1, m \in \{-1, 0, 1\}$, so there are three harmonics:

$$\boxed{Y_1^{-1} = \sqrt{\frac{3}{8\pi}} \sin\theta e^{-i\phi}, \quad Y_1^0 = \sqrt{\frac{3}{4\pi}} \cos\theta, \quad Y_1^1 = \sqrt{\frac{3}{8\pi}} \sin\theta e^{i\phi}} \tag{1.13}$$

- We can realise some cool things if we notice how these relate to the standard conversion from Cartesian to spherical co-ords, given by:

$$\boxed{\begin{aligned} x_1 &= r\sin\theta\cos\theta \\ x_2 &= r\sin\theta\cos\theta \\ x_3 &= r\cos\theta \end{aligned}} \tag{1.14}$$

We can construct three new functions $\tilde{Y}_1^\alpha, \alpha = 1, 2, 3$, where:

$$\boxed{\begin{aligned} \tilde{Y}_1^3 \equiv Y_1^0 &= \sqrt{\frac{3}{4\pi}} \frac{x_3}{r} \\ \tilde{Y}_1^1 = \frac{1}{\sqrt{2}}(Y_1^{-1} - Y_1^1) &= \sqrt{\frac{3}{4\pi}} \frac{x_1}{r} \\ \tilde{Y}_1^2 = \frac{1}{\sqrt{2}}(Y_1^{-1} + Y_1^1) &= \sqrt{\frac{3}{4\pi}} \frac{x_2}{r} \end{aligned}} \tag{1.15}$$

If we rotate around the origin by an angle γ then $\mathbf{x}$ transforms by:

$$\boxed{\mathbf{x}' = \Lambda(\gamma)\mathbf{x}} \tag{1.16}$$

Where Λ is just a rotation matrix. It can then be seen that the by the form of the three Y_1^α, that they transform the same way (as r remains constant). They are like the components of the vector $\tilde{\mathbf{Y}}$, with:

$$\boxed{\tilde{\mathbf{Y}}' = \Lambda(\gamma)\tilde{\mathbf{Y}}} \tag{1.17}$$

These $\tilde{Y}_1^\alpha$ form a representation of the group of rotations. When $l = 2$ this becomes a tensor representation.

- We can combine Y_l^m in combinations to form others. Take for instance Y_2^0 given by:

$$\boxed{Y_2^0 = \sqrt{\frac{5}{16\pi}}(3z\cos^2\theta - 1)} \tag{1.18}$$

From examining the above expressions we can see that this must be related to $(Y_1^0)^2 = \frac{3}{4}\cos^2\theta$. In fact we can write Y_1^0 in terms of Y_2^0, where we can take care of any constant term by writing it in terms of Y_0^0. This takes the form:

$$\boxed{(Y_1^0)^2 = \frac{1}{\sqrt{4\pi}}(Y_0^0 + \frac{2}{\sqrt{5}}Y_2^0)} \tag{1.19}$$

It can be noted that for m's the two sides add, $0+0=0+0$, and l's $1+1=0+2$. This becomes important later on.

1.3 Angular Momentum

- Classically angular momentum is defined as $\mathbf{L} = \mathbf{p} \times \mathbf{x}$. In quantum mechanics $P_k \to -i\hbar\frac{\partial}{\partial x_k}$. So the angular momentum operators are:

$$\boxed{\begin{aligned} \hat{L}_1 &= -i\hbar(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}) \\ \hat{L}_2 &= -i\hbar(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}) \\ \hat{L}_3 &= -i\hbar(x_2\frac{\partial}{\partial x_3} - x_3\frac{\partial}{\partial x_2}) \end{aligned}} \tag{1.20}$$

  These have the useful property that $[\hat{L}_\alpha, L_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}\hat{L}_\gamma$

- We also define the total angular momentum operator as:

$$\boxed{\hat{L}^2 = \hat{L}_1^2 + \hat{L}_2^2 + \hat{L}_3^2} \tag{1.21}$$

  This has the property that, $[\hat{L}^2, \hat{L}_k] = 0$, for all $k = 1, 2, 3$.