Physics 323
October 27, 2016

Quantum Mechanics in 3D – A change to polar coordinates

We can write Schrodinger's equation in the stationary form if we solve the following equation.

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\varphi_E(\vec{r}) + V(\vec{r})\varphi_E(\vec{r}) = E\varphi_E(\vec{r}) \quad where \quad \vec{\nabla}^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$$

The full, time-dependent version then has the solution

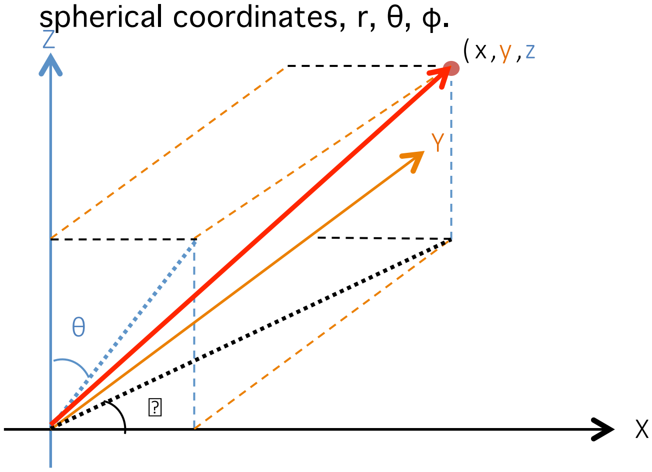
$$\varphi_E(\vec{r},t) = \varphi_E(\vec{r})e^{-\frac{i}{\hbar}Et}$$

However, many times in nature the potential does not depend individually on x, y, and z. Instead, it depends only on the distance from some fixed point. That is, it's spherically symmetric. One such example is electric potential energy, given by

$$V(\vec{r_q}) = \frac{Qq}{4\pi\varepsilon_0}\frac{1}{|\vec{r}|}$$

The more general form of the potential is $V\left(\overrightarrow{|r|}\right);\ |\vec{r}| = \sqrt{x^2 + y^2 + z^2}$

The problem that arises here is that this gives us an equation in terms of a combination of x, y, and z. A more appropriate approach would be to convert these equations to spherical coordinates, r, θ, ϕ.



A line from an origin to a point in three dimensional space forms a vector, r. The projection of this vector onto the x,y plane has an angle φ with respect to the x axis. Likewise, the has an angle θ with the z axis. With a little trigonometric intuition, it is easy enough to see in the picture that the coordinates (x,y,z) of the point can individually be represented with sine and cosine, where:

$$x = rsin\theta cos\varphi \quad y = rsin\theta sin\varphi \quad z = rcos\theta$$

Intuitively, this tells us to look for a solution where the eigenstate is represented in terms of r, θ, ϕ. The only thing left to do is to represent the gradient squared operator in terms of our newfound equations for x,y, and z.

$$\vec{\nabla}^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} = \frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2sin^2\theta}\frac{\partial^2}{\partial\varphi^2}$$

Substituting this back into the original equation and expanding the coefficient of the gradient squared operator leaves us with:

$$\left\{-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}-\frac{\hbar^2}{2mr^2}\frac{1}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}-\frac{\hbar^2}{2mr^2}\frac{1}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}\varphi_E(r,\theta,\varphi)+V(r)\varphi_E(r,\theta,\varphi)=E\varphi_E(r,\theta,\varphi)$$

What a mess! We need to find a way to clean this up a bit. The RHS is a constant and the left hand side is split into two parts: one part depending on r and its derivatives and one part depending on theta and its derivatives. This would lead us to look for a function for the eigenstate to be expressed as a product of two separate functions: one function is expressed solely in terms of r and the second function is expressed in terms of theta and phi:

$$\varphi_E(r,\theta,\varphi)=R(r)Y(\theta,\varphi)$$

We can perform a separation of variables on the equation and introduce these two new functions, and divide through by ϕ_E.

$$\frac{1}{R(r)}\left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r}\right)R(r)+\frac{1}{Y(\theta,\varphi)}\left(-\frac{1}{2mr^2}\left[\frac{\hbar^2}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}+\frac{\hbar^2}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi)\right)=E-V(r)$$

Since the first term on the lhs and the rhs are both functions of *r* only, the part of the lhs dependent on theta and phi (inside the square brackets) must be actually independent of theta and phi and is therefore a constant. This leads us to find a solution such that,

$$[\quad]Y(\theta,\varphi)=constant\ Y(\theta,\varphi)$$

To solve this equation would require weeks of higher level math, so we take a simple case where θ = 90°. This removes theta from the equation because the sine of 90° is 1, and since theta is constant its derivative is zero. We're left with:

$$-\hbar^2\frac{\partial^2}{\partial\varphi^2}F(\varphi)=constant\ F(\varphi)$$

So we're looking for a function whose second derivative multiplied by $-\hbar^2$ yields a constant multiplied by that same function. A possible solution is the natural exponential function,

$$F(\varphi)=e^{i\alpha\varphi}$$

This means that the constant on the RHS is $(-\alpha^2)(-\hbar^2)$. However, we're not done. This equation introduces to us yet another problem. The variable phi goes from 0 to 2π, which are the same point (meaning ϕ + 2π = ϕ). We must require that

$$e^{i\alpha(\varphi+2\pi)}=e^{i\alpha\varphi}$$

For this to be true, α has to be some integer, m, where m = 0, ±1, ±2, ±..., ±∞. This requirement tells us that the solution we found is quantized. It can only exist in multiples of $\hbar$, similar to the square well.

The next part requires a gigantic leap of faith as it's the very, very heavy math intensive portion. It all leads to finding the angular momentum operator(s).

Angular Momentum Operator(s)

If we look at the differential operator above, it turns out to be the angular momentum operator component along the z axis.

$$\frac{\hbar}{i}\frac{\partial}{\partial\varphi} = L_z, \qquad L_z = (\vec{r}_z \; x \; \vec{p}_z) \;\; cross\ product$$

This is plausible by analogy to the momentum operator in *x*-direction (containing the derivative with respect to *x*) which describes motion in *x*, while the angular momentum operator (containing a derivative with respect to φ) describes motion in the φ-direction. (Also, the units of $\hbar$ are indeed those of angular momentum - kg m^2/s). We find that the solution F(ϕ) follows:

$$L_z F(\varphi) = m\hbar F(\varphi)$$

Bringing the three equations together, we can more easily see the relationship:

$$\frac{\hbar}{i}\frac{\partial}{\partial\varphi} = L_z \;\; ; \quad -\hbar^2\frac{\partial^2}{\partial\varphi^2}F(\varphi) = (-\alpha^2)(-\hbar^2)F(\varphi) \;\; ; \quad L_z F(\varphi) = m\hbar F(\varphi)$$

$$\left(\frac{\hbar}{i}\frac{\partial}{\partial\varphi}\right)^2 = (L_z)^2 \quad => \quad -\hbar^2\frac{\partial^2}{\partial\varphi^2} = {L_z}^2$$

$${L_z}^2 F(\varphi) = m^2\hbar^2 F(\varphi)$$

$$L_z F(\varphi) = m\hbar F(\varphi)$$

These particular functions are eigenfunctions of the z component of the angular momentum. This means that they have a well-defined value of that angular momentum with zero uncertainty, which is $m\hbar$**.** True to quantum mechanics, this means that angular momentum is quantized and can only exist in integer multiples of $\hbar$.

<u>Example</u>: A dancer (or ice skater) spinning on his or her toes.

> If we could measure accurately enough, we would find that the angular momentum of the spinning dancer or skater would not decrease continuously, rather it would decrease discretely only in integer multiples of $\hbar$. Of course, we have no way to measure such minute changes ($\hbar$ is on the order of 10^{-34}) in the angular momentum of a (relatively) macroscopic object. This phenomenon can, however, be measured for microscopic objects such as atoms, molecules, quarks, etc.

Now back to the original solution,

$$[\quad]Y(\theta,\varphi) = constant\; Y(\theta,\varphi)$$

What does [ ] represent? What belongs in these brackets? Well, if F(ϕ) represents the angular momentum about the z-axis and F(ϕ) is special case (a case that eliminated θ, which would correlate to momentum about the y-axis) of Y(θ,ϕ) then we can safely assume that the total angular momentum belongs inside the brackets!

$$\vec{L}^2 Y(\theta,\varphi) = constant\, Y(\theta,\varphi)$$

If we look back at the equation,

$$\frac{1}{Y(\theta,\varphi)}\left(-\frac{1}{2mr^2}\left[\frac{\hbar^2}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}-\frac{\hbar^2}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi)\right)$$

We can see that L_z^2 is on the right side inside the brackets. The portion inside the brackets corresponds to the total angular momentum operator, and the part,

$$-\frac{\hbar^2}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}$$

represents the x AND y components of the angular momentum. We cannot find eigenstates to the individual three components individually. The different components of the angular momentum fulfill a similar equation (follow a similar requirement) as Heisenberg's Uncertainty Principle. Namely, the product of the uncertainty is always greater than zero. Quantum Mechanics says that you can have simultaneous eigenstates to the total squared momentum and ONLY one component. Now we just need to find these simultaneous eigenstates!

It pays to find as many operators as possible where we can have simultaneous eigenvalues. We are always going to look for simultaneous eigenstates to as many operators as we can.

**Note: Simultaneous in this sense does not imply relativistic operations. All of the QM covered in this course is non-relativistic.

So, we must find an eigenvalue that works for both the L^2 operator and the L_z operator simultaneously. We require that:

$$\vec{L}^2 Y(\theta,\varphi) = constant\, Y(\theta,\varphi) \quad ALSO \quad L_z = Y(\theta,\varphi) = m\hbar Y(\theta,\varphi)$$

We recall from earlier that m is an integer such that m = 0, ±1, ±2, ±..., ±∞. The answer to this is the eigenvalue to the total angular momentum squared operator is,

$$\vec{L}^2 Y(\theta,\varphi) = \hbar^2 l(l+1) Y(\theta,\varphi)$$

Where l is also an integer, such that l = 0, 1, 2,... We must introduce a restriction on the integer m. The highest value that m can have is ±l. The integers l and m are quantum numbers: numbers used to label a state.

Example 1

If l=0, then m=0. We must come up with a function that when applied to both operators gives us zero. Looking at the whole complicated operator,

$$-\frac{1}{2mr^2}\left[\frac{\hbar^2}{sin\theta}\frac{\partial}{\partial\theta}sin\theta\frac{\partial}{\partial\theta}-\frac{\hbar^2}{sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]Y(\theta,\varphi)$$

we see that each term contains a differential operator. For a derivative to be zero, then it must act on a function that does not depend on a variable: a constant function. Thus,

$$Y_{00}(\theta,\varphi) = constant = \frac{1}{\sqrt{4\pi}}$$

The value of the constant was found by normalizing the state.

$$\int_0^{2\pi}\int_0^{\pi} sin\theta d\theta = 4\pi$$

$$|Y_{00}|^2 = \frac{1}{4\pi};\ Y_{00} = \frac{1}{\sqrt{4\pi}}$$

Example 2

If we claim that l=1, m=1;

$$Y_{11} = -\sqrt{\frac{3}{8\pi}}sin\theta e^{i\varphi}$$

$$L_z Y_{11} = 1\hbar$$

$$\vec{L}^2 Y_{11} = 2\hbar^2$$

A visual representation of different values of l and m can be seen at:

http://ww2.odu.edu/~skuhn/PHYS621/SphericalHarmonics+Bessel/QM_Special_Functions.html