QNO1:

Define Seperation of variables, Seperate the variables in sehordingers wave equation for hydrogen atom?

In methematics seperation of variables is any of several methods for Solving ordinary and partial differential equations in which algebra allows one to re-write an equation So that each of two variables occur on different side of equation.

Sehordingers wave equation for Hydrogen atom:

For hydrogen atom one proton, one electron and the electrostatic potential that holds them together The potential energy in this case is:

$$V = \frac{e^2}{4\pi\varepsilon_0 r}$$

Which is the attractive potential between charges of +e and -e seperated by a distance r.

Now this potential looks Quite simple. But notice that it is a function of a ·r, not X or (xyz).

On approch would be to expsess V in terms of (xyz), where

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

In some cases you might be able to go get away with that but here you would make the Problem quite difficult (the square rod of sum of squares is a pain to deal with

The appropriate approch is to let the symmetric potential tells us to use spherical polar coordinates

In spherical polar coordinates r, is length of radius vector from the origin to a point (xyz)

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

Scanned with CamScanner

Another coordinate is θ, the angle between the radius vector and +z axis

$$\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$$

The third coordinate (because we are in three dimensions, we need three coordinates) is φ the angle between Projection of the radius vector into the xy plane and the +x axis.

$$\varphi = \tan^{-1}\left[\frac{y}{x}\right]$$

Note that we have three coordinates $(r\theta\varphi)$ which we have relate to (xyz) above. we can also express (xyz) in terms of $(r\theta\varphi)$:

$x = r\sin\cos\varphi \quad y = r\sin\theta\sin\varphi \quad z = r\cos\theta$

Now, we can rewrite schrodingers equation

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{h^2}(E-V)\psi = 0$$

In spherical polar coordinate as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin\theta}\frac{\partial^2\psi}{\partial\varphi^2}$$

$$+\frac{2m}{h^2}(E-V) = 0.$$

if we plug in our potential V and multiply both sides by $r^2\sin^2\theta$, we get

$$\sin^2\theta\frac{\partial}{\partial r}\left[r^2\frac{\partial\psi}{\partial r}\right] + \sin\theta\frac{\partial}{\partial\theta}\left[\sin\theta\frac{\partial\psi}{\partial\theta}\right] + \frac{\partial^2\psi}{\partial\varphi^2} + \frac{2mr^2\sin^2\theta}{h^2}$$

$$\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right] = 0$$

let's talk about this equation it looks nasty, but we will see that its not quite bad as it looks

This equation gives us the wave function ψ for electron in hydrogen atom. if we can solve for ψ in principal we know every thing that is to know about the hydrogen atom. When we solved equation in one dimensions we found that one Quantum number was necessary to describe our systems For example, in bohr atom, the electron moves in an orbit but we need only one quantum number Here in three dimensions and with three boundary conditions we will find that we need three quantum numbers to describe our electron
Beiser at the end of this Section tells what Quantum number for hydrogen atom are and give their possible values, but untill we see where they come from and what they mean and they are not of much use to us

Another comment: we are really solving Schrogdiness equation for electron in a hydrogen atom aren't we. Nevertheless we talk about doing the "hydrogen atom" because our solution will provide us with much of what we need to know about Hydrogen.

Seperation of Variables:

We now discuss the technique for solving our equation for the electron in hydrogen atom

Here are some things we like in decreasing order of liking

- Linear algebric equations
- Coupled algebric equations (i.e xy multiplied together)
- Linear differential equations
- Coupled differential equations

When we have the equation like one above, we like to see if we can "seperate" the variables "split" the equations into different parts

with only one variable in each part
Our problem will then be much simplified if we can write

$$\psi(r, \theta, \varphi) = R(r)\,\Theta(\theta)\,\Phi(\varphi) = R\Theta\Phi$$

Let assume we can write ψ like that and see where it leads us if our assumption works, in the orderly work of methamatics we know it must have been right.

Here, How we take the partial derivatives in Schrodinger's equation:

$$\frac{\partial \psi}{\partial r} = \Theta\Phi\frac{\partial R}{\partial r} = \Theta\Phi\frac{dR}{dr}$$

$$\frac{\partial \psi}{\partial \theta} = R\Phi\frac{\partial \Theta}{\partial \theta} = R\Phi\frac{d\Theta}{d\theta}$$

$$\frac{\partial^2 \psi}{\partial \varphi^2} = R\Theta\frac{\partial^2 \Phi}{\partial \varphi^2} = R\Theta\frac{d^2\Phi}{d\varphi^2}$$

Where the partial derivatives become full derivatives because R, Θ and Φ depends on r, θ and φ only.

Scanned with CamScanner

To seperate the variables, plug $\psi = R \Theta \Phi$ into Schrodiger's equation and divide by $R \Theta \Phi$ The result is

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} +$$

$$\frac{2mr^2\sin^2\theta}{h^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) = 0$$

Now we have seperated out the φ variable, the term

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2}$$

is a function of φ only. Let us put it over on the right hand side of equation. This gives us.

$$\frac{\sin^2\theta}{R}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) +$$

$$\frac{2mr^2\sin^2\theta}{h^2}\left[\frac{e^2}{4\pi\varepsilon_0 r} + E\right] = \frac{-1}{\Phi}\frac{d^2\Phi}{d\varphi^2}$$

Notice the form of equation it is in the form $f(r, \theta) = g(\varphi)$.

Where f is function of r and θ only and g is function of φ only

Under what condition this can be possible?

If an r or θ shows up on the LHS, it can't be satisfied because r and θ never show up on the RHS.

Similarly, if a φ shows up on RHS the equation cannot be satisfied because φ never shows up on the LHS. The only way for the equation to be satisfied is for

$f(r,\theta)$ = a constant, independent of r, θ

and $\phi = g(\varphi)$

Notice what we have done,

We have taken the one nasty equation for r, θ and ϕ, and separated into two equations one is r and θ and other one in φ only.

At this point, we will begin quoting some results from differential equations

As we have seen several times before in this course some differential equations can be solved only if certian conditions are satisfied. These conditions have led to quantum numbers. They will do so in this case also

Let me follow Beisers developement and anticipate some of requirements.

It turns out that the constant in the last equation on Previous page is square of an integer. Thus we can write the RHS of Beiser's eq as

$$-\frac{1}{\Phi}\frac{d^2\Phi}{d\varphi^2} = m_l^2$$

We will hear more about this m_l later.

If we set LHS equal to m_l^2, divide by $\sin^2\theta$ and rearrange, we get.

$$r\frac{1}{R}\frac{d}{dr}\left[r^2\frac{dR}{dr}\right] + \frac{2mr^2}{\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) = \frac{m_l^2}{\sin^2\theta} - \frac{1}{\Theta\sin\theta}\frac{d}{d\theta}\left[\sin\theta\frac{d\Theta}{d\theta}\right]$$

Scanned with CamScanner

Once again we have seperated variables The LHS is the function of r only and the RHS is a function of θ only

Again the only way to satisfy this equation is for LHS = a Constant = RHS.

Conditions on the constant will arrive from the solution of differential equations. In this case, we call the constant $l(l+1)$

We conclude this section by taking our three differential equations for r, θ and φ rearranging them slightly and writting them in the form

$$\frac{d^2\Phi}{d\varphi^2} + m_l^2\Phi = 0$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) + \left[l(l+1) - \frac{m_l^2}{\sin^2\theta}\right]\Theta = 0$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{2m}{h^2}\left(\frac{e^2}{4\pi\varepsilon_0 r} + E\right) - \frac{l(l+1)}{r^2}\right]R = 0$$

All of above seems like alot of work but we have seperated our big partial differential equation into three simple ones each of which is a function of a single variable and each of which is much easier to handle.