HYDROGEN ATOM - RADIAL EQUATION

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We've seen that we can solve the three-dimensional Schrödinger equation by separation of variables, provided that the potential is a function of r only. In that case, the angular parts of the equation can be solved in general in terms of spherical harmonics, so the wave function has the form $\psi(r,\theta,\phi)=R(r)Y(\theta,\phi)$, where the Y functions are the spherical harmonics, and $R(r)$ is the, as yet unsolved, radial function, which satisfies the differential equation

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}(V(r)-E)R=l(l+1)R \tag{1}$$

By making the further substitution

$$u(r)\equiv rR \tag{2}$$

we can convert the above equation into a differential equation for $u(r)$:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left(V+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)u=Eu \tag{3}$$

This equation has the same form as the original Schrödinger equation except that the potential has picked up an extra so-called centrifugal term. We must now solve this equation when $V(r)$ is the potential found in the hydrogen atom.

The hydrogen atom consists of a proton and an electron. The proton is, in the first approximation, taken to be fixed, since its mass is more than a thousand times that of the electron. The force between the two particles can be taken as solely electric, since the gravitational force is many orders of magnitude smaller and will have essentially no effect. In this case, the potential is

$$V(r)=-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} \tag{4}$$

where e is the elementary charge and $1/4\pi\epsilon_0$ is the Coulomb constant. The equation to be solved is thus:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2}+\left(-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)u=Eu \tag{5}$$

The solution of this equation follows a similar method as was used in solving the harmonic oscillator. We first investigate the asymptotic behaviour of the equation for large and small r, factor out this behaviour and then use a series to try to find the solution of what's left.

First, we can introduce a couple of symbol changes. If we define

$$\kappa \equiv \frac{\sqrt{-2mE}}{\hbar} \tag{6}$$

(note that since $E<0$ for bound states, κ is real), then we can rewrite 5 as

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2}=\left[1-\frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{\kappa r}+\frac{l(l+1)}{(\kappa r)^2}\right]u \tag{7}$$

Since r occurs always multiplied by κ, we can try using a new variable

$$\rho \equiv \kappa r \tag{8}$$

and this results in

$$\frac{d^2u}{d\rho^2}=\left[1-\frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{\rho}+\frac{l(l+1)}{\rho^2}\right]u \tag{9}$$

We can simplify the notation a bit more by defining a constant

$$\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \tag{10}$$

giving us the equation

$$\frac{d^2u}{d\rho^2}=\left[1-\frac{\rho_0}{\rho}+\frac{l(l+1)}{\rho^2}\right]u \tag{11}$$

Now we can investigate the asymptotic behaviour. First, for large ρ, the two terms in the brackets that depend inversely on ρ become negligible, so we get in this limit:

$$\frac{d^2u}{d\rho^2}=u \tag{12}$$

This has the general solution

$$u=Ae^{-\rho}+Be^{\rho} \tag{13}$$

and only the first term is acceptable, since the term Be^{ρ} becomes infinite for large ρ. So for large ρ, we must have

$$u(\rho) \sim Ae^{-\rho} \tag{14}$$

At the other end, when ρ is very small, the term in ρ^{-2} becomes the largest, so the approximate equation to solve is

$$\frac{d^2u}{d\rho^2} = \frac{l(l+1)}{\rho^2}u \tag{15}$$

[This argument fails if $l = 0$, but all we're after here is looking at asymptotic behaviour in an attempt to factor this behaviour out of the overall solution. As we'll see when we finally get the solution, it is valid for $l = 0$ as well.]

In this case, the general solution is

$$u(\rho) = C\rho^{l+1} + D\rho^{-l} \tag{16}$$

This can be verified by direct substitution:

$$\frac{d^2u}{d\rho^2} = Cl(l+1)\rho^{l-1} + D(-l)(-l-1)\rho^{-l-2} \tag{17}$$

$$= \frac{l(l+1)}{\rho^2}u \tag{18}$$

In this case, the term $D\rho^{-l}$ becomes infinite as $\rho \to 0$, so $D = 0$ and

$$u(\rho) \sim C\rho^{l+1} \tag{19}$$

So now we know the behaviours at the two extremes, and we can factor both of these out, hoping to solve for what is left over. That is, we can write

$$u(\rho) = \rho^{l+1}e^{-\rho}v(\rho) \tag{20}$$

where $v(\rho)$ is what we must find. Note that we have absorbed the two constants A and C into $v(\rho)$.

The idea is to plug 20 back into 11 and see what sort of equation we get for $v(\rho)$ as a result. We need the second derivative of u in terms of v. We need to use the product rule a few times to get it.

$$\frac{du}{d\rho} = (l+1)\rho^l e^{-\rho} v - \rho^{l+1} e^{-\rho} v + \rho^{l+1} e^{-\rho} \frac{dv}{d\rho} \tag{21}$$

$$= \rho^l e^{-\rho}\left((l+1-\rho)v + \rho\frac{dv}{d\rho}\right) \tag{22}$$

$$\frac{d^2u}{d\rho^2} = l\rho^{l-1}e^{-\rho}\left((l+1-\rho)v + \rho\frac{dv}{d\rho}\right) - \rho^l e^{-\rho}\left((l+1-\rho)v + \rho\frac{dv}{d\rho}\right) + \tag{23}$$

$$\rho^l e^{-\rho}\left(-v + (l+1-\rho)\frac{dv}{d\rho} + \frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right) \tag{24}$$

$$= \rho^l e^{-\rho}\left[\left(\frac{l(l+1)}{\rho} + \rho - 2l - 2\right)v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right] \tag{25}$$

Plugging this back into 11 and collecting terms we get

$$\rho^l e^{-\rho}\left[\left(\frac{l(l+1)}{\rho} + \rho - 2l - 2\right)v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right] = \left[1 - \frac{\rho_0}{\rho} + \frac{l(l+1)}{\rho^2}\right]\rho^{l+1}e^{-\rho}v \tag{26}$$

$$\rho^l e^{-\rho}\left[\left(\frac{l(l+1)}{\rho} + \rho - 2l - 2\right)v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right] = \left[\rho - \rho_0 + \frac{l(l+1)}{\rho}\right]\rho^l e^{-\rho}v \tag{27}$$

$$\left[\left(\frac{l(l+1)}{\rho} + \rho - 2l - 2\right)v + 2(l+1-\rho)\frac{dv}{d\rho} + \rho\frac{d^2v}{d\rho^2}\right] = \left[\rho - \rho_0 + \frac{l(l+1)}{\rho}\right]v \tag{28}$$

$$\rho\frac{d^2v}{d\rho^2} + 2(l+1-\rho)\frac{dv}{d\rho} + (\rho_0 - 2l - 2)v = 0 \tag{29}$$

This version of the differential equation may not look any friendlier than the original, but we can now try to solve it by expressing $v(\rho)$ as a series in ρ, which we will do in the next post.

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