Quantum Mechanics 2

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Hydrogen Atom

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Schrödinger Equation

The Schrödinger equation of a Hydrogen atom is

$$-\frac{\hbar^2}{2m}\nabla^2 u(r,\theta,\varphi) - \frac{e^2}{4\pi\varepsilon_0 r}u(r,\theta,\varphi) = Eu(r,\theta,\varphi)$$

Since it is a central potential, we separate the wave functions

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

so that the angular part obey [see Central Potential]

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\varphi^2} = -\lambda Y$$

The eigenvalues are [see Angular Momentum]

$$\lambda = l(l+1)\hbar^2$$

and the eigenfunctions are the spherical Harmonics [see Spherical Harmonics 2]

$$Y_{l,m}(\theta,\varphi) = (-1)^m\sqrt{\frac{2l+1}{4\pi}}\sqrt{\frac{(l-m)!}{(l+m)!}}P_{l,m}(\cos\theta)e^{im\varphi}$$

Radial Equation

The radial part on the other hand is [see Central Potential]

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

which can also be written as

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

We will be most interested with the bound states, where $E<0$. We then write $E=-|E|$.

We now pare the equation to its barest form (put all the constants together). The constant term $-2m|E|/\hbar^2$ can be pared down if we can somehow factor it out. We now note that three of the five terms are dimensionally r^{-2}. The factor needed can be attained if we change variable

$$\varrho=\sqrt{\frac{2m|E|}{\hbar^2}}\ r$$

Paring Down the Equation

With the change of variable, we get

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

which reduces to

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

All the constants are now lumped in the fourth term, so we may define

$$\gamma=\sqrt{\frac{2m}{\hbar^2|E|}}\frac{e^2}{4\pi\varepsilon_0}$$

With this,

$$\frac{d^2R}{d\varrho^2}+\frac{2}{\varrho}\frac{dR}{d\varrho}+\left[-1+\frac{\gamma}{\varrho}-\frac{l(l+1)}{\varrho^2}\right]R=0$$

Asymptotic Limits

Wave functions must be square-integrable. Let us then consider the asymptotic limit $\varrho \to \infty$. At this limit, all terms with ϱ in the denominator will be very small compared to the third term. Thus,

$$\frac{d^2 R_\infty}{d\varrho^2} - R_\infty = 0$$

This is an [ODE with constant coefficients], the ansatz

$$R_\infty = e^{\beta\varrho}$$

yields the auxiliary equation

$$\beta^2 = 1$$

Thus,

$$R_\infty = e^{\pm\varrho}$$

As R_∞ must be finite in the asymptotic limit, only

$$R_\infty = e^{-\varrho}$$

is feasible.

Ensuring Square-Integrability

To ensure square-integrability of the radial function, we define

$$R(\varrho) = G(\varrho)e^{-\varrho}$$

With

$$\frac{dR}{d\varrho} = \frac{dG}{d\varrho}e^{-\varrho} - Ge^{-\varrho}$$

$$\frac{d^2R}{d\varrho^2} = \frac{d^2G}{d\varrho^2}e^{-\varrho} - 2\frac{dG}{d\varrho}e^{-\varrho} + Ge^{-\varrho}$$

The radial equation

$$\frac{d^2R}{d\varrho^2} + \frac{2}{\varrho}\frac{dR}{d\varrho} + \left[-1 + \frac{\gamma}{\varrho} - \frac{l(l+1)}{\varrho^2}\right]R = 0$$

becomes

$$\frac{d^2G}{d\varrho^2}e^{-\varrho} - 2\frac{dG}{d\varrho}e^{-\varrho} + Ge^{-\varrho} + \frac{2}{\varrho}\left[\frac{dG}{d\varrho}e^{-\varrho} - Ge^{-\varrho}\right] + \left[-1 + \frac{\gamma}{\varrho} - \frac{l(l+1)}{\varrho^2}\right]Ge^{-\varrho} = 0$$

An Alternative Expression

Factoring out $e^{-\varrho}$, this simplifies to

$$\frac{d^2G}{d\varrho^2} + \left[\frac{2}{\varrho} - 2\right]\frac{dG}{d\varrho} + \left[\frac{\gamma - 2}{\varrho} - \frac{l(l+1)}{\varrho^2}\right]G = 0$$

Note that if we define

$$\rho = 2\varrho = \sqrt{\frac{8m|E|}{\hbar^2}}\ r$$

The last version of the radial equation can be recast as

$$4\frac{d^2G}{d\rho^2} + \left[\frac{8}{\rho} - 4\right]\frac{dG}{d\rho} + \left[\frac{2\gamma - 4}{\rho} - \frac{4l(l+1)}{\rho^2}\right]G = 0$$

or

$$\frac{d^2G}{d\rho^2} + \left[\frac{2}{\rho} - 1\right]\frac{dG}{d\rho} + \left[\frac{\gamma/2 - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right]G = 0$$

An Alternative Expression

Since γ is just a constant, let us also define

$$\alpha = \frac{\gamma}{2} = \sqrt{\frac{m}{2\hbar^2|E|}}\frac{e^2}{4\pi\varepsilon_0}$$

With the second change in variable, we get a “neater” equation in that the minus two of the second and third terms are replaced by minus one.

$$\frac{d^2G}{d\rho^2} + \left[\frac{2}{\rho} - 1\right]\frac{dG}{d\rho} + \left[\frac{\alpha - 1}{\rho} - \frac{l(l+1)}{\rho^2}\right]G = 0$$