

Quantum Mechanics 2

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Hydrogen Atom



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Schrödinger Equation

The Schrödinger equation of a Hydrogen atom is

$$-\frac{\hbar^2}{2m} \nabla^2 u(r, \theta, \varphi) - \frac{e^2}{4\pi\epsilon_0 r} u(r, \theta, \varphi) = E u(r, \theta, \varphi)$$

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 [\[see Central Potential\]](#)

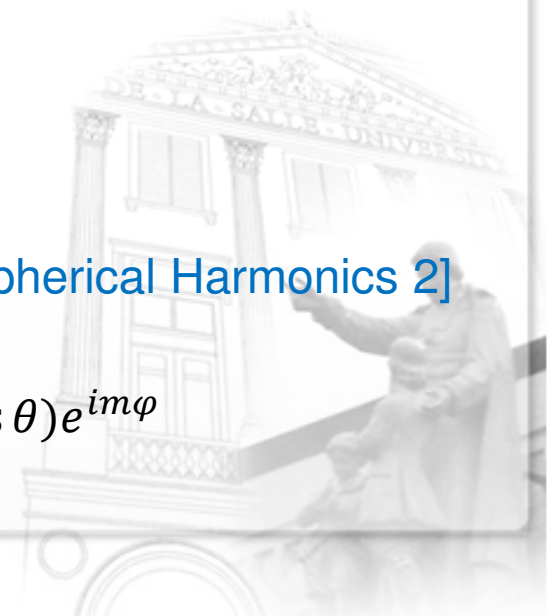
$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \varphi^2} = -\lambda Y$$

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 [\[see Central Potential\]](#)

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2m}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right] r^2 R = 0$$

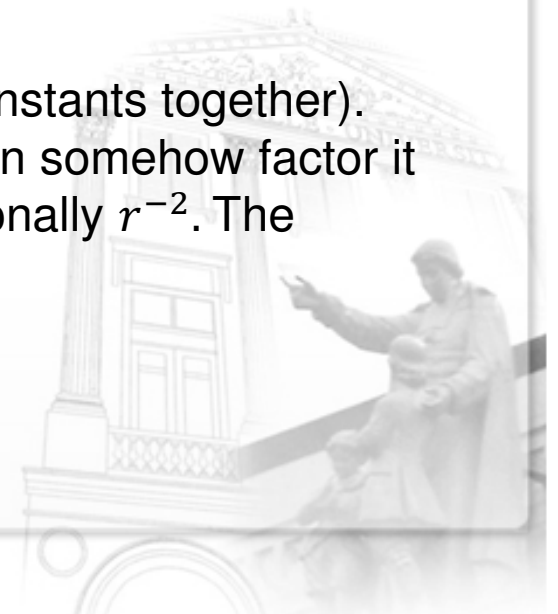
which can also be written as

$$\frac{d^2 R}{dr^2} + \frac{2}{r} \frac{dR}{dr} + \frac{2m}{\hbar^2} \left[E + \frac{e^2}{4\pi\epsilon_0 r} - \frac{l(l+1)\hbar^2}{2mr^2} \right] R = 0$$

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

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



Paring Down the Equation

With the change of variable, we get

$$\frac{2m|E|}{\hbar^2} \left(\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} \right) + \frac{2m|E|}{\hbar^2} \left[-1 + \frac{1}{|E|} \sqrt{\frac{2m|E|}{\hbar^2} \frac{e^2}{4\pi\epsilon_0\rho}} - \frac{2m|E| l(l+1)\hbar^2}{\hbar^2 2m|E|\rho^2} \right] R = 0$$

which reduces to

$$\frac{d^2 R}{d\rho^2} + \frac{2}{\rho} \frac{dR}{d\rho} + \left[-1 + \sqrt{\frac{2m}{\hbar^2|E|} \frac{e^2}{4\pi\epsilon_0\rho}} - \frac{l(l+1)}{\rho^2} \right] R = 0$$

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

$$\gamma = \sqrt{\frac{2m}{\hbar^2|E|} \frac{e^2}{4\pi\epsilon_0}}$$

With this,

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



Asymptotic Limits

Wave functions must be square-integrable. Let us then consider the asymptotic limit $\varrho \rightarrow \infty$. 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

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

With

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

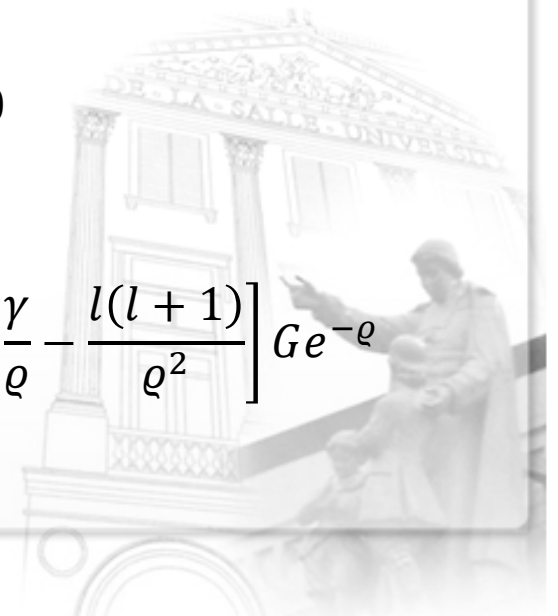
$$\frac{d^2R}{d\rho^2} = \frac{d^2G}{d\rho^2}e^{-\rho} - 2\frac{dG}{d\rho}e^{-\rho} + Ge^{-\rho}$$

The radial equation

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

becomes

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



An Alternative Expression

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

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

Note that if we define

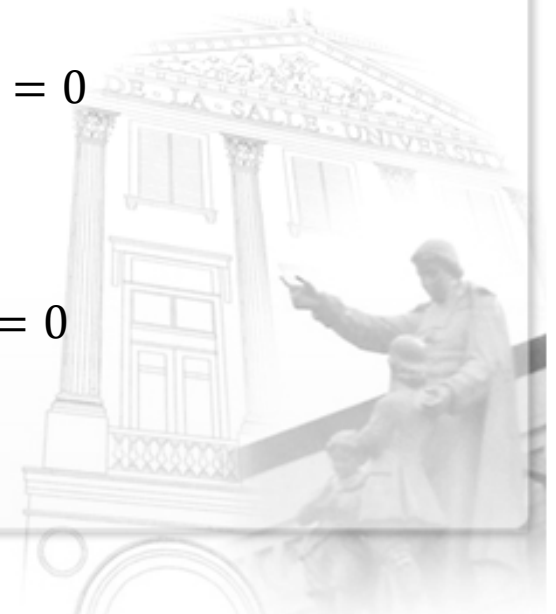
$$\rho = 2\varrho = \sqrt{\frac{8m|E|}{\hbar^2}} r$$

The last version of the radial equation can be recast as

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

or

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



An Alternative Expression

Since γ is just a constant, let us also define

$$\alpha = \frac{\gamma}{2} = \sqrt{\frac{m}{2\hbar^2|E|} \frac{e^2}{4\pi\epsilon_0}}$$

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.

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

