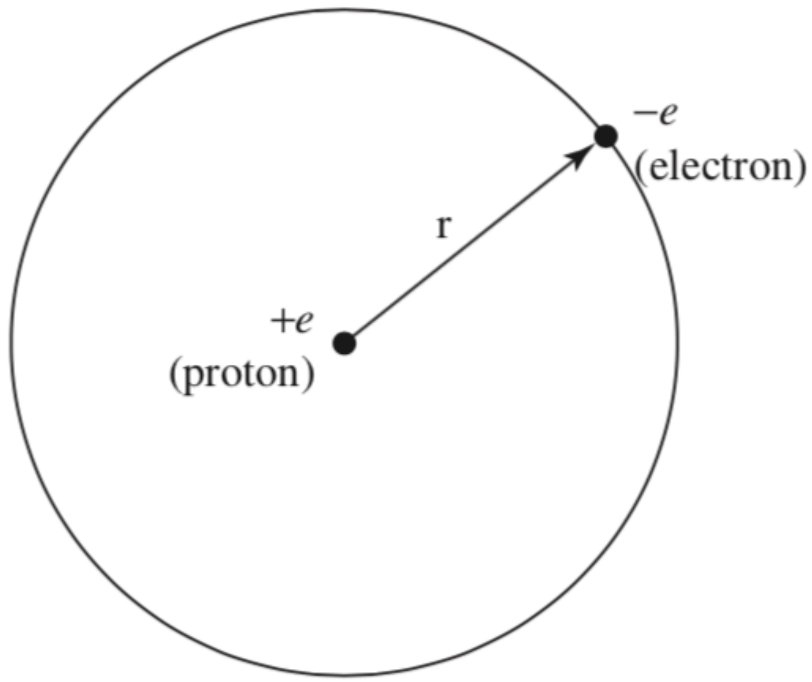
The hydrogen atom



The hydrogen atom consists of proton of charge e, together with a much lighter electron charge –e.

$$m_p = 1.67 \times 10^{-27}\,\text{kg}$$
$$m_e = 9.11 \times 10^{-31}\,\text{kg}$$

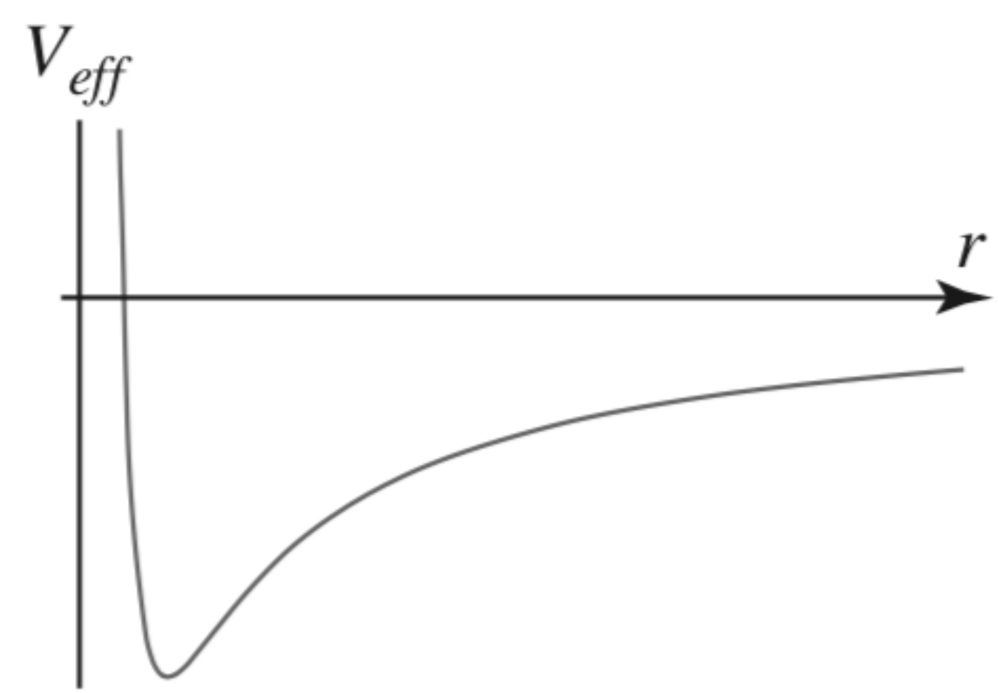
$$e = 1.60 \times 10^{-19}\,\text{c}$$

From Coulomb's law: $F = \dfrac{1}{4\pi\epsilon_0}\dfrac{e^2}{r^2}$ the potential in SI units is: $V(r) = -\dfrac{e^2}{4\pi\epsilon_0}\dfrac{1}{r}$

And the radial equation becomes:

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu$$

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2} + \underbrace{\left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\right]}_{\text{Effective potential } (V_{eff})}u = Eu.$$



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We need to solve this equation for *u*(*r*), and determine the allowed energies.

The Coulomb potential admits:

- Scattering states (E > 0) -> electron-proton scattering
- Bound states (E < 0) -> hydrogen atom

The Radial Wave Function

We are interested in finding bound states (E < 0) of:

$$-\frac{\hbar^2}{2m_e}\frac{d^2u}{dr^2}+\left[-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}+\frac{\hbar^2}{2m_e}\frac{\ell(\ell+1)}{r^2}\right]u=Eu$$

Let's divide this equation by *E* and define: $\kappa \equiv \frac{\sqrt{-2m_eE}}{\hbar}$

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

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The Radial Wave Function

$$\frac{1}{\kappa^2}\frac{d^2u}{dr^2} = \left[1 - \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right]u$$

We introduce:

$$\rho \equiv \kappa r,$$

$$\rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0\hbar^2\kappa},$$

$$\Rightarrow \quad \frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right]u$$

Let's analyse the asymptotic behaviour of this equation.

$$\rho \to \infty \quad \Rightarrow \quad \frac{d^2u}{d\rho^2} = u \quad \Rightarrow \quad u(\rho) = Ae^{-\rho} + \underbrace{\cancel{Be^{\rho}}}_{\text{blows up}} \quad \Rightarrow \quad u(\rho) \sim Ae^{-\rho}$$

(for large ρ)

$$\rho \to 0 \quad \Rightarrow \quad \frac{d^2u}{d\rho^2} = \frac{\ell(\ell+1)}{\rho^2}u \quad \Rightarrow \quad u(\rho) = C\rho^{\ell+1} + \underbrace{\cancel{D\rho^{-\ell}}}_{\text{blows up}} \quad \Rightarrow \quad u(\rho) \sim C\rho^{\ell+1}$$

(for small ρ)

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The Radial Wave Function

We introduce the new function *v(ρ)*:

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

(for large ρ)

$u(\rho) \sim C\rho^{\ell+1}$

(for small ρ)

$$\Rightarrow \quad u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho)$$

$$\frac{du}{d\rho} = \rho^{\ell} e^{-\rho} \left[(\ell + 1 - \rho) v + \rho \frac{dv}{d\rho} \right]$$

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

Therefore:

$$\frac{d^2u}{d\rho^2} = \left[1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2} \right] u \quad \Rightarrow \quad \rho \frac{d^2v}{d\rho^2} + 2(\ell + 1 - \rho) \frac{dv}{d\rho} + [\rho_0 - 2(\ell+1)] v = 0$$

We assume the solution, v(ρ), can be expressed as a power series in ρ:

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

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The Radial Wave Function

$$\rho \frac{d^2 v}{d\rho^2} + 2\left(\ell + 1 - \rho\right)\frac{dv}{d\rho} + \left[\rho_0 - 2\left(\ell + 1\right)\right] v = 0$$

We assume the solution, *v(ρ)*, can be expressed as a power series in ρ, for which we need to determine the coefficients (c_0, c_1, c_2, . . .).

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j$$

$$\frac{dv}{d\rho} = \sum_{j=0}^{\infty} j c_j \rho^{j-1} = \sum_{j=0}^{\infty} (j+1) c_{j+1} \rho^j .$$

$$\frac{d^2 v}{d\rho^2} = \sum_{j=0}^{\infty} j\,(j+1)\, c_{j+1} \rho^{j-1}$$

Replacing into the radial equation above, we get:

$$\sum_{j=0}^{\infty} j\,(j+1)\, c_{j+1} \rho^j + 2\left(\ell + 1\right) \sum_{j=0}^{\infty} (j+1)\, c_{j+1} \rho^j - 2 \sum_{j=0}^{\infty} j c_j \rho^j + \left[\rho_0 - 2\left(\ell + 1\right)\right] \sum_{j=0}^{\infty} c_j \rho^j = 0$$

$$j\,(j+1)\, c_{j+1} + 2\left(\ell + 1\right)(j+1)\, c_{j+1} - 2 j c_j + \left[\rho_0 - 2\left(\ell + 1\right)\right] c_j = 0$$

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The Radial Wave Function

$$\rho \frac{d^2 v}{d\rho^2} + 2(\ell + 1 - \rho)\frac{dv}{d\rho} + [\rho_0 - 2(\ell + 1)]\, v = 0$$

$$\Rightarrow \quad j(j+1)\, c_{j+1} + 2(\ell+1)(j+1)\, c_{j+1} - 2jc_j + [\rho_0 - 2(\ell+1)]\, c_j = 0$$

$$\Rightarrow \quad \boxed{c_{j+1} = \left\{ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right\} c_j}$$

This recursion formula determines the coefficients, and hence the function *v(ρ).*

For large *j* (this corresponds to large *ρ*, where the higher powers dominate):

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j \quad \Rightarrow \quad c_j \approx \frac{2^j}{j!} c_0$$

If this were the *exact* result, it blows up at large ρ (so it is not normalisable):

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho} \quad \Rightarrow \quad u(\rho) = c_0 \rho^{l+1} e^{\rho}$$

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The Radial Wave Function: the Bohr radius

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!}\rho^j = c_0 e^{2\rho} \quad \Rightarrow \quad u(\rho) = c_0 \rho^{l+1} e^{\rho}$$

Thus, the series must terminate: $c_{N-1} \neq 0 \quad \text{but} \quad c_N = 0$

$$c_{j+1} = \left\{ \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)} \right\} c_j \quad \Rightarrow \quad 2(N+\ell) - \rho_0 = 0.$$

which makes *v(ρ)* a polynomial of order *(N – 1)*, with (therefore) *N* – 1 roots, and hence the radial wave function has *N* – 1 nodes.

Let's define: $n \equiv N + \ell \quad \Rightarrow \quad \rho_0 = 2n$

Remember: $$\rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 \kappa},$$

$$\Rightarrow \quad \kappa = \left(\frac{m_e e^2}{4\pi\epsilon_0\hbar^2} \right) \frac{1}{n} = \frac{1}{an} \quad \Rightarrow \quad \boxed{a \equiv \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10}\ \text{m}}$$

This is the so-called **Bohr radius.**

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The Radial Wave Function: the Bohr formula

Remember: $$\rho_0 \equiv \frac{m_e e^2}{2\pi\epsilon_0 \hbar^2 \kappa}, \qquad \kappa \equiv \frac{\sqrt{-2m_e E}}{\hbar}$$

$$E = -\frac{\hbar^2\kappa^2}{2m} = -\frac{m_e e^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}$$

$$\boxed{E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots .}$$

This is the **Bohr formula**

Therefore: $$\rho = \frac{r}{an}$$

The **spatial wave functions** are labeled by three quantum numbers (*n*, *ℓ*, and *m*):

$$\psi_{n\ell m}(r, \theta, \phi) = R_{n\ell}(r)\, Y_\ell^m(\theta, \phi)$$

where: $$R_{n\ell}(r) = \frac{1}{r}\rho^{\ell+1}e^{-\rho}v(\rho)$$

n ≡ principal quantum number
ℓ ≡ azimuthal quantum number
m ≡ magnetic quantum number

and *v(ρ)* is a polynomial of degree *n – ℓ – 1* in *ρ*, whose coefficients are determined (up to an overall normalisation factor) by the recursion formula:

$$c_{j+1} = \frac{2(j + \ell + 1 - n)}{(j+1)(j+2\ell+2)}c_j$$