The Hydrogen Atom

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Radial Wave Function

Radial Wave Function in General

- separation of variables rewrites the stationary states of the wave function as $\psi(\mathbf{r}) = R(r)\, Y(\theta, \phi)$
- for the sake of simplification, a new variable u is defined, such that $u(r) = rR(r)$
- the time-independent "radial equation" is thus given by

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

- this is identical to the one-dimensional Schrödinger equation, except the effective potential contains an additional component

$$V_{\text{eff}} = V + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2}$$

Wave Function of Hydrogen

- the hydrogen atom is comprised by a proton of charge e, and an electron of charge $-e$
- the proton may be thought to be motionless and centered at the origin
- by Coulomb's law, we may express the potential energy as

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r}$$

- we substitute this into the radial equation

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \left[-\frac{e^2}{4\pi\varepsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u = Eu.$$

Wave Function of Hydrogen

- the Coulomb potential admits both
  - continuum states ($E > 0$), describing electron-proton stattering
  - discrete bound states ($E < 0$), describing the hydrogen atom
- we simplify the notation by introducing κ, defined by

$$\kappa = \frac{\sqrt{-2mE}}{\hbar}$$

- we are only interested in bound states, so E is negative, so κ is real

Wave Function of Hydrogen

- dividing the wave equation by E, in terms of m and κ, we obtain

$$\frac{1}{\kappa^2}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} = \left[1 - \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa}\frac{1}{(\kappa r)} + \frac{\ell(\ell+1)}{(\kappa r)^2}\right]u$$

- let $\rho = \kappa r$ and $\rho_0 = me^2/(2\pi\varepsilon_0\hbar^2\kappa)$

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

Wave Function of Hydrogen

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

- as $\rho \to \infty$, the equation simplifies to

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = u$$

- which has general solution

$$u(\rho) = A \exp(-\rho) + B \exp(\rho)$$

- since $\exp(\rho) \to \infty$ as $\rho \to \infty$, $B = 0$ for large ρ

$$u(\rho) \sim A \exp(-\rho)$$

Wave Function of Hydrogen

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

- as $\rho \to 0$, the equation simplifies to

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u$$

- which has general solution

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}$$

- as $\rho \to 0$, $\rho^{-\ell} \to \infty$, so $D = 0$

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

Wave Function of Hydrogen

- we introduce a new function, $v(\rho)$, defined implicitly by

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

- it is simply $u(\rho)$ stripped of its asymptotic behaviour
- we compute $\frac{\mathrm{d}u}{\mathrm{d}\rho}$ and $\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2}$, and substitute into the radial equation, giving:

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

- the solution to $v(\rho)$ can be given by the power series

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

Wave Function of Hydrogen

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

- to find the coefficients, c_0, c_1, $\ldots$, we first find the derivatives

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

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

Wave Function of Hydrogen

- recall the wave equation was given by

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

- substituting $v(\rho)$, $\frac{\mathrm{d} v}{\mathrm{d}\rho}$, and $\frac{\mathrm{d}^2 v}{\mathrm{d}\rho^2}$ we obtain

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

Wave Function of Hydrogen

- dividing through by ρ^j gives us

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

- solving for c_{j+1} gives us the recursive definition

$$c_{j+1} = \frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}\,c_j$$

- for large values of j, we have

$$c_{j+1} \approx \frac{2j}{j(j+1)}\,c_j = \frac{2}{j+1}\,c_j$$

Wave Function of Hydrogen

$$c_{j+1} \approx \frac{2j}{j(j+1)} c_j = \frac{2}{j+1} c_j$$

- if this approximation were exact, then we would have

$$c_j = \frac{2^j}{j!} c_0$$

- implying

$$v(\rho) = c_0 \sum_{j=0}^{\infty} \frac{2^j}{j!} \rho^j = c_0 e^{2\rho}$$

- so $u(\rho)$ displays asymptotic behaviour, which we tried to get rid of

Wave Function of Hydrogen

- it seems that there is only one way to deal with the issue of asymptotic behaviour: the series must be finite
- there must exist a maximum j, such that

$$c_{j_{\text{max}}+1} = 0$$

- implying

$$2(j_{\text{max}} + \ell + 1) = \rho_0$$

- we now define the **principal quantum number** to be

$$n \equiv j_{\text{max}} + \ell + 1$$

- meaning

$$2n = \rho_0$$

Results

Spectrum of Hydrogen

- energy depends on ρ_0

$$E = -\frac{\hbar^2 \kappa^2}{2m} = -\frac{m e^4}{8\pi^2 \varepsilon_0^2 \hbar^2 \rho_0^2}$$

- the allowed energies are thus given by

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2}$$

where $n \in \mathbb{Z}^+$

Bohr Radius

- recall

$$\rho_0 \equiv \frac{me^2}{2\pi\varepsilon_0\hbar^2\kappa} = 2n$$

- solving for κ gives

$$\kappa = \left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an}$$

- where a is the Bohr Radius

$$a = \frac{4\pi\varepsilon_0\hbar^2}{me^2} \approx 5.29 \times 10^{-11}\,\mathrm{m}$$

- from the definition of ρ we see

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

Quantum Numbers

- we have thus far seen three quantum numbers, n, ℓ, and m
- the spatial wave functions for hydrogen are separated as

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

- from Section 4.1 we have

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

- the ground state occurs when $n = 1$, so the binding energy is given by

$$E_1 = -\left[\frac{m}{2\hbar}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\right] = -13.6\,\mathrm{eV}$$

Ground State

- consider $\psi_{100}(r,\theta,\phi) = R_{10}(r)\,Y_0^0(\theta,\phi)$

$$R_{10}(r) = \frac{c_0}{a}\exp(-r/a)$$

- normalizing gives c_0

$$\int_0^\infty |R_{10}|^2 r^2\,\mathrm{d}r = \frac{|c_0|^2}{a^2}\int_0^\infty \exp(-2r/a)\,r^2\,\mathrm{d}r = |c_0|^2\frac{a}{4} = 1$$

$$c_0 = \frac{2}{\sqrt{a}}$$

$$Y_0^0 = \frac{1}{\sqrt{4\pi}}$$

- the ground state of Hydrogen is given by

$$\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}}\exp(-r/a)$$

Thank You