The Hydrogen Atom

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March 26, 2015

- Consider a hydrogen atom - a proton, an electron and a radius between them
- We would like to figure out which energies it is possible for the electron to have by solving for $u(r)$. To do so, we begin with the radial equation:

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

- Substituting Coulomb's Law in for V we have

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

- Now we divide both sides by E. At this point we will define $\kappa \equiv \frac{\sqrt{-2mE}}{\hbar}$. Note that $E < 0$ for bound states, so κ is real.

$$\begin{aligned} u &= -\frac{\hbar^2}{2mE}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \left[-\frac{e^2}{4\pi E r \epsilon_0} + \frac{\hbar^2}{2mE}\frac{l(l+1)}{r^2}\right] u \\ &= \frac{1}{\kappa}\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \left[\frac{me^2}{2\pi\epsilon_0\hbar^2\kappa^2 r} - \frac{l(l+1)}{\kappa^2 r^2}\right] u \\ &= \frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} + \left[\frac{\rho_0}{\rho} - \frac{l(l+1)}{\rho^2}\right] u \end{aligned}$$

- Here we have defined $\rho \equiv \kappa r$ and $\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa}$

- Rearranging the equation we have

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

- If we consider the equation as $\rho \to \infty$ (the asymptotic form of the solutions), then we have

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

- This ordinary differential equation has general solution

$$u(\rho) = Ae^{-\rho} + Be^{\rho}$$

- Since $e^{\rho} \to \infty$ as $\rho \to \infty$ we know $B = 0$ so when ρ is very large the general solution can be approximated by

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

- Now let us consider when $\rho \to 0$. So long as $l \neq 0$ the centrifugal term will rise far greater than the other terms, so our equation becomes

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

- This is also a differential equation, and its general solution is given by

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

- Snce $\rho^{-l} \to \infty$ as $\rho \to 0$ we know $D = 0$ so when ρ is very small the general solution can be approximated by

$$u(\rho) \approx C\rho^{l+1}$$

- We can now synthesize our results in an attempt to get rid of asymptotic behavior

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

- We are now including a new function $v(\rho)$. By computing $\frac{\mathrm{d}u}{\mathrm{d}\rho}$ and $\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2}$ and plugging into the radial equation we have

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

Also, we know from Numerical Analysis techniques that any function can be written as a power series. Thus we know

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

- Now we must determine the coefficients $(c_0, c_1, c_2, \ldots)$ We see

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

- Plugging these equations into the radial equation for $v(\rho)$ we have

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

- Dividing through by p^j, we have

$$j(j+1)c_{j+1} + 2(l+1)(j+1)c_{j+1} - 2jc_j + (\rho_0 - 2(l+1))c_j = 0$$

- And solving for c_{j+1} we have

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

- Let us consider large values of j. Then

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

- Now suppose this approximation was exact. Then

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

- and then we would have

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

- But this would mean

$$u(\rho) = c_0 \rho^{l+1} e^{\rho}$$

- so $u(\rho)$ displays asymptotic behavior, which is what we were trying to get rid of.

- It now seems that there is only one way to deal with this issue - The series must be finite.
- There must exist a maximum j such that

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

- This implies

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

- We now define the **principal quantum number**, n, to be

$$n \equiv j_{max} + l + 1$$

- Note that

$$\rho_0 = 2n$$

- Recall that energy depends on ρ_0

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

- Therefore we have at last determined the allowed energies to be

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2} = \frac{E_1}{n^2} \qquad \text{where } n \in \{1, 2, 3, \ldots\}$$

- Recall

$$\rho_0 \equiv \frac{me^2}{2\pi\epsilon_0\hbar^2\kappa} \qquad\qquad \rho_0 = 2n$$

- Combining these we have

$$\kappa = \left(\frac{me^2}{4\pi\epsilon_0\hbar^2}\right)\frac{1}{n} = \frac{1}{an}$$

- where a is the Bohr Radius

$$a = \frac{4\pi\epsilon_0\hbar^2}{me^2} \approx 5.29 \times 10^{-11}\mathrm{m}$$

- Recalling the definition of ρ we also now see

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

- So far we have three quantum numbers, n, l, and m. The spatial wave functions for hydrogen are labeled

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)Y_l^m(\theta,\phi)$$

- Recall from **section 4.1**

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

- The ground state is the case where $n = 1$. Using our best approximations for the physical constants we have

$$E_1 = -\left[\frac{m}{2\hbar}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right] = -13.6\text{eV}$$

- As expected, the binding energy, or the energy necessary to ionize a a Hydrogen atom in the ground state, is 13.6 eV

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

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

- Normalizing we have

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

- Thus $c_0 = \frac{2}{\sqrt{a}}$. Also, $Y_0^0 = \frac{1}{\sqrt{4\pi}}$, so the ground state of hydrogen is

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

Thank you!