Mon: Read 8.1

Tues: HW

Hydrogen atom radial wavefunction

Solving the angular part of the Schrödinger equation gave solutions constrained by

$$l = 0, 1, 2, \ldots \quad \rightsquigarrow \quad C = -\hbar^2 l(l+1)$$

$$m_l = -l, -l+1, \ldots, l-1, l.$$

Then the radial part of the TISE becomes:

$$\boxed{\frac{-\hbar^2}{2m_e}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{\hbar^2 l(l+1)}{2m_e r^2}R - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}R = ER}$$

The solutions will clearly depend on l. There are general techniques for solving such equations. We definitely require that the solution decay as $r \to \infty$. A promising candidate is: $e^{-r/\text{const}}$. We will see that solutions have the form

$$R(r) = (\text{polynomial in } r) \times e^{-r/\text{const}}$$

We will try the simplest possibility

$$R(r) = Ae^{-r/a_0}$$

where A, a_0 are constants.

1 Hydrogen atom ground state

Consider a possible solution to the radial part of the TISE,

$$R(r) = Ae^{-r/a_0}$$

where A and a_0 are constants.

a) Show by substitution that this is a solution to the radial part of the TISE and give conditions for l, a_0 and E that guarantee this.

b) Using $m_e = 9.11 \times 10^{-31}$ kg, $e = 1.6 \times 10^{-19}$ C, $\epsilon_0 = 8.85 \times 10^{-12}\ \mathrm{C^2/Nm^2}$ and $\hbar = 1.05 \times 10^{-34}$ Js determine the energy in units of eV.

Answer: a) $\frac{dR}{dr} = -\frac{1}{a_0} Ae^{-r/a_0} = -\frac{1}{a_0} R \Rightarrow r^2 \frac{dR}{dr} = -\frac{r^2}{a_0} R$

$$-\frac{d}{dr}\left(\frac{r^2 R}{a_0}\right) = -\frac{2rR}{a_0} + \frac{r^2}{a_0}\frac{dR}{dr}$$

$$= -\frac{2rR}{a_0} + \frac{r^2}{a_0^2} R.$$

Substituting gives:

$$-\frac{\hbar^2}{2m_e}\left(\frac{1}{r^2}\right)\left(-\frac{2r}{a_0}\cancel{R} + \frac{r^2}{a_0^2}\cancel{R}\right) + \frac{\hbar^2 l(l+1)}{2m_e r^2}\cancel{R} - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\cancel{R} = E\cancel{R}$$

$$\Rightarrow \underbrace{\frac{1}{r}\left[\frac{2\hbar^2}{2m_e a_0} - \frac{e^2}{4\pi\epsilon_0}\right]}_{0} + \underbrace{\frac{1}{r^2}\left[\frac{\hbar^2 l(l+1)}{2m_e r^2}\right]}_{0} - \underbrace{\left[\frac{\hbar^2}{2m_e a_0^2} + E\right]}_{0} = 0$$

The conditions are:

1) $\frac{\hbar^2 l(l+1)}{2m} = 0 \Rightarrow l = 0$

2) $$\frac{\hbar^2}{m_e a_0} = \frac{e^2}{4\pi\epsilon_0} \Rightarrow a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$$

3) $$E = -\frac{\hbar^2}{2m_e a_0^2} \Rightarrow E = -\frac{m_e^2 e^4 \hbar^2}{2m_e (4\pi\epsilon_0)^2 \hbar^4}$$

$$\Rightarrow E = -\frac{m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2}$$

b) $$E = -2.2\times10^{-18}\,J = -2.2\times10^{-18}\,J \times \frac{1\,eV}{1.6\times10^{-19}\,J} = -13.7\,eV.$$

Thus we have a solution for $l=0$, $m_l=0$:

$$R(r) = A e^{-r/a_0}$$

where

$$\boxed{a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}}$$

is the Bohr radius and the energy is −13.7eV. The remaining solutions yield:

1) solutions are labeled by l and an integer $n = 1, 2, 3, \ldots$
2) for each n possible values of l are:

$$l = 0, 1, \ldots, n-1$$

3) for n the energies are

$$E_n = \frac{-m_e e^4}{2(4\pi\epsilon_0)^2 \hbar^2} \frac{1}{n^2}$$

These match the Bohr model and thus the observed spectrum. We thus have

Applying the Schrödinger equation to the hydrogen atom predicts the (broad) spectrum correctly.

Although this is true we will see that the Schrödinger equation reveals a richer range of states and degeneracies that are associated with angular momentum.

We can now list states using

$n = 1, 2, 3, \ldots \longrightarrow l = 0, 1, 2, \ldots, n-1 \rightsquigarrow m_l = -l, -l+1, \ldots, l-1, l$

	$l=0$ (s states	$l=1$ p states			$l=2$ d states				
$n=3$	$l=0$, $m_l=0$	$m_l=-1$	$m_l=0$	$m_l=1$	$m_l=-2$	-1	0	1	2
$n=2$	$l=0$, $m_l=0$	$m_l=-1$	$m_l=0$	$m_l=1$					
$n=1$	$l=0$, $m_l=0$								

] degenerate energy level

The associated radial wavefunctions are labeled by n, l. and the lowest few are in Table 7.4

e.g.

$$R_{2,0} = \frac{1}{(2a_0)^{3/2}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$$

Radial wavefunctions and probability

We know that the wavefunction gives probability densities. Then

$$\text{Prob}\begin{bmatrix} \text{particle in range} \\ r \to r+dr \\ \theta \to \theta+d\theta \\ \phi \to \phi+d\phi \end{bmatrix} = |\Psi(r,\theta,\phi)|^2 r^2 \sin\theta \, dr d\theta d\phi$$

$$= |R(r)|^2 |\Theta(\theta)|^2 |\Phi(\phi)|^2 r^2 \sin\theta \, dr d\theta d\phi$$

$$= \left[r^2|R|^2 dr\right]\left[|\Theta|^2 \sin\theta \, d\theta\right]\left[|\Phi|^2 d\phi\right]$$

If we only want the probabilities with which various values of r occur we can integrate.

$$\text{Prob}\left[r \to r+dr\right] = r^2|R|^2 dr \underbrace{\int_0^{\pi} |\Theta|^2 \sin\theta \, d\theta \int_0^{2\pi} |\Phi|^2 d\phi}_{\Theta,\ \Phi \text{ normalized so this } = 1}$$

This gives the radial probability density

$$\boxed{P(r) = r^2 |R(r)|^2}$$

so that

$$\boxed{\text{Prob}\left[r_1 \le r \le r_2\right] = \int_{r_1}^{r_2} P(r) dr = \int_{r_1}^{r_2} r^2 |R|^2 dr}$$

We can use this to answer questions about likely locations of electrons

Example: Suppose $n=1, l=0$. Determine

a) the most probable location of the electron

b) the expectation value of r.

Answer: Here $R(r) = \underbrace{\frac{1}{(a_0)^{3/2}}}_{\text{normalization!}} 2e^{-r/a_0}$

$$\Rightarrow \quad P(r) = r^2 |R(r)|^2 = r^2 \frac{1}{a_0^3} 4e^{-2r/a_0} = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

a) Most probable requires max $P(r)$.

$$\frac{dP}{dr} = 0 \Rightarrow \frac{d}{dr} \cancel{\frac{4}{a_0^3}} r^2 e^{-2r/a_0} = 0$$

$$\Rightarrow \cancel{2}re^{-2r/a_0} + r^2\left(-\frac{2}{a_0}\right) e^{-2r/a_0} = 0$$

$$\Rightarrow r - \frac{r^2}{a_0} = 0 \Rightarrow r = 0 \text{ or } \boxed{r = a_0}$$

b)
$$\langle r \rangle = \int_0^\infty r P(r)\, dr = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0}\, dr$$

$$= \frac{4}{a_0^3} \frac{3!}{(2/a_0)^4} = \frac{4 \times 6}{16} a_0 = \frac{24}{16} a_0$$

$$\langle r \rangle = \frac{3}{2} a_0$$

So we see that the size of the atom is roughly the Bohr radius.