8.2 Ground state of Hydrogen $Z = 1, \mu = \mu_H$

radial wavefunction R_{10}

Plot Laguerre[0,1,2*x] * x**0 * Exp[-x] x=0 to 10

probability density $|R_{10}|^2 r^2$

Plot (Laguerre[0,1,2*x] * x**0 * Exp[-x])**2 * x**2 x=0 to 10

we have $R_{10} = \frac{2}{a^{3/2}} e^{-r/a}$ and $Y_{00} = 1/\sqrt{4\pi}$ so

$$\psi_{100} = R_{10} Y_{00} = \sqrt{\frac{1}{a^3 \pi}} e^{-r/a} = R_{10} Y_{00}$$

lets calculate some expectation values. we can

$$< r >= \int \int \int (\psi_{100}^2 r r^2 \sin\theta dr d\theta d\phi = 4\pi \frac{1}{\pi a^3} \int r^3 e^{-2r/a} dr$$

standard integral $\int x^p e^{-ax} dx = p!/a^{p+1}$

$$< r >= \frac{4}{a^3} \frac{3!}{(2/a)^4} = 3a/2$$

the classically allowed region is only where $E > V$ i.e. $V = -e^2/(4\pi\epsilon_0 r)$ and E_1 (as the source is in the ground state) is

$$E_1 = -\frac{m}{2\hbar^2} \Big(\frac{e^2}{4\pi\epsilon_0} \Big)^2$$

We can simplify this as $a = 4\pi\epsilon_0 \hbar^2 / me^2$ so $V = -\hbar^2/(mar)$ and $E_1 = -\hbar^2/(2ma^2)$ so for $E > V$ we have

$$-\frac{\hbar^2}{2ma^2} > -\frac{\hbar^2}{mar}$$

$$\frac{1}{2a} < \frac{1}{r}$$

so classically we have $r < 2a$. But this is a wavefunction so there is some probability we find the electron beyond $r = 2a$ which is

$$\frac{1}{a^3\pi}\int\int\int e^{-2r/a}r^2\sin\theta dr d\theta d\phi = \frac{1}{a^3\pi}4\pi\int_{2a}^{\infty} r^2 e^{-2r/a}dr = 0.24$$

where we just do the integral numerically!

But we could have saved ourseves work on $< r >$ by using the fact that the Y_{lm} are already normalised over $\theta\phi$ integrals so

$$< f(r) >= \int\int\int R_{nl}^* Y_{lm}^* f(r) R_{nl} Y_{lm} r^2 \sin\theta d\theta d\phi = \int R_{nl}^*(f(r)R_{nl})r^2 dr$$

So lets find $< V >$ the simple way

$$< V >=< -\frac{e^2}{4\pi\epsilon_0 r} >= -\frac{e^2}{4\pi\epsilon_0}\int R_{10}^* r^{-1} R_{10} r^2$$

$$= -\frac{e^2}{4\pi\epsilon_0}\frac{4}{a^3}\int e^{-2r/a} r dr$$

$$= -\frac{e^2}{4\pi\epsilon_0}\frac{4}{a^3}\frac{1!}{(2/a)^2} = -\frac{e^2}{4\pi\epsilon_0 a} = \frac{-\hbar^2}{\mu a^2}$$

8.3 Expectation values from more complex orbitals

$\psi_{210} = R_{21}Y_{10}$, where $R_{21} = \frac{1}{\sqrt{24a^3}}\frac{r}{a}e^{-r/2a}$ and $Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$

find the probability that the electron is in the 'arctic circle' - i.e. within the range $\theta = 0 - 23.5°$.

prob=$\int_0^{23.5}\int_0^{2\pi}\int_0^{\infty} R_{21}^2 Y_{10}^2 r^2 \sin\theta dr d\theta d\phi$

$$= \int_0^{23.5}\int_0^{2\pi} Y_{10}^2 \sin\theta d\theta d\phi$$

$$= 2\pi\Big(\frac{3}{4\pi}\Big)\int_0^{23.5}\cos^2\theta\sin\theta d\theta$$
$$= \frac{3}{2}0.0762 = 0.11$$

compare to classical - we would have uniform probability with angle. so we will just integrate our angle surface element for our angle raneg. But this needs to be normalised so we divide by the integral over the total angle range.

$$= \frac{\int_0^{23.5}\int_0^{2\pi}\sin\theta d\theta d\phi}{\int_0^{\pi}\int_0^{2\pi}\sin\theta d\theta d\phi}$$
$$= \frac{2\pi 0.0829399}{2\pi 2} = 0.041$$

and we can see this by looking at the shape of the 3D orbitals....

8.4 Energy levels

Put hydrogen in some stationary state ψ_{nlm}. it should stay there forever. But perturb it slightly - maybe a collision with another atom/electron/photon then the electron may undergo a transition to another stationary state - either by absorbing energy or emitting it. such perturbationas are always present, so such tranistions - quantum jumps - are constantly occuring. But since these transitions occur between levels of fixed energy, then the emitted photon depends on the difference in energy between the initial and final states

$$E_\gamma = E_i - E_f = -13.6\Big(\frac{1}{n_i^2} - \frac{1}{n_f^2}\Big)$$

8.5 Hydrogen isoelectronic sequence

any ion with atomic number Z which is ionised so that there is only 1 electron left should be described by the same equations, but with $V(r) = -Ze^2/(4\pi\epsilon_0 r)$.

This affects both atom size and energy as $a = 4\pi\epsilon_0\hbar^2/(mZe^2)$ so this scales as $a = a_H(\mu_H/\mu)(1/Z)$ while $E_n(Z,\mu) = \frac{\mu}{\mu_H}Z^2E_{1H}/n^2$

so then we can treat ionised helium, which has more or less same mass $\mu_{He} \approx \mu_H \approx m_e$

a 1st energy level of -13.6.4 = -54.4 eV. and should have all size scales which are 2x smaller than Hydrogen.

similarly, we could have different reduced mass μ_Z e.g. for positronium where the proton is replaced by a positron so the reduced mass $\mu = M_AM_B/(M_A + M_B) = m_e/2$ then $a = a_H/\mu$ so the size scale is 2x larger, and $E \propto \mu$ so the energy is 2x smaller.

and the wavefunctions are just derived with the size scale a.

e.g.

$$\psi_{100} = (\pi a^3)^{-1/2}e^{-r/a}$$

where $a = a_H(\mu_H/\mu)(1/Z)$ so for a Hydrogen-like ion with change Z and reduced mass $\mu = \mu_H)$ $\psi(r) = (\pi(a_H^3/Z^3)^{-1/2}e^{-rZ/a_H}$ so

$$< r >= \int\int\int \psi^2 r r^2 \sin\theta d\theta d\phi = \frac{Z^3}{\pi a_H^3}4\pi \int r^3 e^{-2Zr/a_H}dr$$

$$= \frac{4Z^3}{a_H^3}\frac{3!}{(2Z/a_H)^4} = \frac{4Z^3}{a_H^3}\frac{3!}{(2/a_H)^4} = \frac{3a_H}{2Z} =< r >_H /Z$$

so as expected, all the typical sizes scale with $1/Z$

8.6 Comparison in detail with Hydrogen

The balmer line is actually 2 lines, yet our schroedinger solution did not give us this! so maybe its that hydrogen is not just proton-electron, there is some admixture of deuterium. so $\mu_d = 2m_pm_e/(2m_p + m_e)$ while $\mu_H = 2m_pm_e/(2m_p + m_e)$ so the energies will be slightly different $E_n = \frac{\mu}{\mu_H}E_{nH} = (2m_pm_e)/(2m_p + m_e)E_{nH} = 1.0003E_{nH}$ but this is a BIGGER shift than is observed,.

so where do the small line shifts come from???

To understand Hydrogen at this level of detail we have to do a lot more work - and in particular, we need to do more work on angular momentum, and especially spin angular momentum. And since we are going to be looking for TINY effects, we are going to treat these as a small perturbation so rather than solve things exactly, we are going to do perturbation theory to get approximate answers.