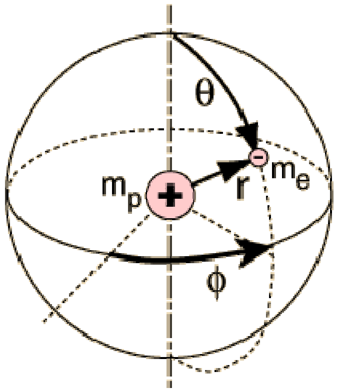
Lecture 19

The hydrogen atom



Heavy proton (put at the origin), charge e and much lighter electron, charge -e.

Potential energy, from Coulomb's law

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

Our mission is to find the allowed energies E and the corresponding wave functions
While there are both continuum (E> 0) and bound (E < 0) states for the Coulomb potential, we will only consider bound states now. Since this potential is spherically symmetric, we were looking for the wave function in a form

$$\psi_{n\ell m}(r,\theta,\phi) = R_{n\ell}(r)\,\underbrace{Y_\ell^m(\theta,\phi)}_{\text{spherical harmonics}}$$

We solved the radial equation and found the radial functions

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

where $v(\rho)$ is a power series

$$v(\rho) = \sum_{j=0}^{j_{max}} c_j \rho^j \qquad j_{max} = n - \ell - 1$$

principal quantum number

The coefficients of this power series are given by

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

C_0 is determined from the normalization condition.

We found the energies to be

$$\boxed{E = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots}$$

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

Ground state energy of hydrogen

Now we can write down actual wave functions.

First, we need to express ρ via r:

$$\rho = Kr, \quad K = \underbrace{\left(\frac{me^2}{4\pi\varepsilon_0\hbar^2}\right)}_{1/a}\frac{1}{n} = \frac{1}{an}$$

$$a \equiv \frac{4\pi\varepsilon_0}{me^2}\hbar^2 = 0.529 \times 10^{-10}\,m$$

[or a_0] Bohr radius

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

Let's get some lower functions.

1 **Ground state of hydrogen: n=1, l=0, m=0.**

$$\psi_{100}(r, \theta, \phi) = R_{10}(r)\underbrace{Y_0^0(\theta, \phi)}_{=\frac{1}{\sqrt{4\pi}}}$$

Exercise 1: find R_{10} and normalize it.

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

Plug in $\begin{cases} n=1 \\ l=0 \\ j=0 \end{cases} \Rightarrow$ get $c_1 = 0.$

$j_{max} = n-l-1$

$j_{max} = 0$

$$v(\rho) = \sum_{j=0}^{j_{max}} c_j \rho^j = c_0 \quad [\text{constant}]$$

$$R_{nl} = \frac{1}{r}\rho^{l+1} e^{-\rho} v(\rho) \Rightarrow R_{10} = \frac{1}{r}\rho\, e^{-\rho} c_0$$

$$R_{10} = \frac{1}{r}\frac{r}{\underbrace{an}_{n=1}} e^{-\frac{r}{an}\,\leftarrow n=1} c_0 = \frac{c_0}{a} e^{-r/a}$$

Normalization:

$$\int_0^\infty |u|^2 dr = 1$$

$$\int_0^\infty |R_{10}|^2 r^2 dr = \frac{|c_0|^2}{a^2}\int_0^\infty e^{-2r/a} r^2 dr$$

$$= |c_0|^2 \frac{a}{4} = 1 \Rightarrow$$

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

$$Y_0^0 = \frac{1}{\sqrt{4\pi}} \Rightarrow \boxed{\psi_{100}(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}}$$

Exercise 2: find R_{20} and R_{21}, don't need to normalize.

① $\ell = 0$, $n = 2$ $\quad c_{j+1} = \frac{2(j+\ell+1-n)}{(j+1)(j+2\ell+2)} c_j$.

$j = 0$ $\quad c_1 = \frac{2(0+0+1-2)}{1(2)} = -c_0$

$c_2 = 0$ since $j_{max} = n - \ell - 1 = 1$

$$\boxed{v(\rho) = c_0(1-\rho)} \quad R_{n\ell} = \frac{1}{r}\rho^{\ell+1} e^{-\rho} v(\rho) \quad \rho = \frac{r}{an} = \frac{r}{2a}$$

$$R_{20} = \frac{1}{r}\left(\frac{r}{2a}\right) e^{-r/2a}\left(1-\frac{r}{2a}\right)c_0 \quad \boxed{R_{20} = \frac{c_0}{2a}\left(1-\frac{r}{2a}\right) e^{-r/2a}}$$

② $\ell = 1$, $n = 2$ $\Rightarrow j_{max} = 1$ $\quad v(\rho) = c_0$

$\rho = \frac{r}{2a}$

$$R_{21} = c_0 \frac{1}{r}\left(\frac{r}{2a}\right)^2 e^{-r/2a} \Rightarrow \boxed{R_{21} = \frac{c_0}{4a^2} r e^{-r/2a}}$$

We can see now that for a given value of n, these values of l are possible:

$$\boxed{\ell = 0, 1, 2, \dots n-1}$$

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

If, for example, you try to take $n = \ell \Rightarrow$

$$n = j_{max} + n + 1 \qquad j_{max} < 0 .$$

Now we can calculate degeneracy of the level E_n:
For each n, there are l=0... n-1 and for each l, there are 2 (l +1) values of m:

$$d(n) = \sum_{\ell=0}^{n-1} (2\ell + 1) = n^2$$

The polynomial that is determined by our recursion formula is knows as associate Laguerre polynomial (up to normalization).

$$v(\rho) = L^{2\ell+1}_{n-\ell-1}(2\rho)$$

$$L^{p}_{q-p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x)$$

where $L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q \left(e^{-x} x^q\right)$ is called

the qth Laguerre polynomial.

The normalized hydrogen wave functions are

$$\boxed{\psi_{n\ell m} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^\ell \left[L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{na}\right)\right] Y_\ell^m(\theta,\phi)}$$

Note: the energies depend only on n.

Orthogonality:

$$\int \psi^*_{n\ell m}\, \psi_{n'\ell' m'}\, r^2 \sin\theta\, dr\, d\theta\, d\phi = \delta_{nn'}\, \delta_{\ell\ell'}\, \delta_{mm'}$$

Simulations:

Models of the hydrogen atom

http://phet.colorado.edu/new/simulations/index.php?cat=Quantum_Phenomena

Hydrogen atom orbitals:

http://www.falstad.com/mathphysics.html

Mathematical formulas

$$\sin(a \pm b) = \sin a \cos b \pm \cos a \sin b$$
$$\cos(a \pm b) = \cos a \cos b \mp \sin a \sin b$$

$$c^2 = a^2 + b^2 - 2ab\cos\theta$$

$$\int x \sin(ax)\,dx = \frac{1}{a^2}\sin(ax) - \frac{x}{a}\cos(ax)$$

$$\int x \cos(ax)\,dx = \frac{1}{a^2}\cos(ax) + \frac{x}{a}\sin(ax)$$

$$\int_0^\infty x^n e^{-x/a}\,dx = n!\,a^{n+1}$$

$$\int_0^\infty x^{2n} e^{-x^2/a^2}\,dx = \sqrt{\pi}\,\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1}$$

$$\int_0^\infty x^{2n+1} e^{-x^2/a^2}\,dx = \frac{n!}{2}\,a^{2n+2}$$

$$\int_a^b f\,\frac{dg}{dx}\,dx = -\int_a^b \frac{df}{dx}\,g\,dx + fg\Big|_a^b$$