THE HYDROGEN ATOM

The H atom can be described as heavy, motionless nucleus (the proton) around which a much lighter particle (the electron) rotates. Both proton and electron have a charge of the same absolute value, e.

Coulomb's law states that the potential energy is:

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

We can write Schrödinger's equation, and separate the time and spatial parts of the equation, since $V(r)$ does not depend on time. We look for stationary states satisfying:

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V(r)\psi = E\psi$$

where ∇^2 is a 3D Laplacian operator. We notice that the potential energy depends only on r, which suggests to use spherical coordinates.

The Laplacian is hideous:

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

It is a good exercise to derive it explicitly (or verify that it collapses to $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ in cartesian coordinates) once in your lifetime.

The good thing is that, since V depends on r only, we can imagine that:

$$\psi(r, \theta, \phi) = R(r)\,Y(\theta, \phi)$$

will be a viable form for solutions.

We can work out the separation between R and Y, and use the quantity $\ell(\ell+1)$ as separation constant. Explicitly:

$$-\frac{\hbar^2}{2m}\nabla^2(RY) + VRY = ERY$$

$$\downarrow$$

$$-\frac{\hbar}{2m}\left[\frac{Y}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{R}{r^2\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right]$$

Dividing by RY and multiplying by $-2mr^2/\hbar^2$:

$$\underbrace{\frac{1}{R}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} - \frac{2mr^2}{\hbar^2}(V(r)-E)}_{\text{depends only on } r} + \underbrace{\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right)}_{\text{depends only on } \vartheta \text{ and } \phi} = 0$$

I can solve separately:

a) $$\frac{1}{R}\frac{\partial}{\partial r}r^2\frac{\partial R}{\partial r} - \frac{2mr^2}{\hbar^2}(V(r)-E) = \ell(\ell+1)$$

b) $$\frac{1}{Y}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial Y}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2}\right) = -\ell(\ell+1)$$

The best part is that the second equation can be further split:

$$Y(\theta,\phi) = \Theta(\vartheta)\,\Phi(\phi)$$

Multiply b) by $\sin^2\theta$:

$$\underbrace{\frac{1}{\Theta}\left(\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\Theta}{\partial\vartheta}\right) + \ell(\ell+1)\sin^2\vartheta}_{\text{depends only on } \vartheta} + \underbrace{\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2}}_{\text{depends only on } \phi} = 0$$

Solve separately using m^2 as separating variable:

c) $$\frac{1}{\Theta}\left(\sin\theta\frac{\partial}{\partial\theta}\sin\theta\frac{d\Theta}{d\vartheta}\right) + \ell(\ell+1)\sin^2\theta = m^2$$

d) $$\frac{1}{\Phi}\frac{\partial^2\Phi}{\partial\phi^2} = -m^2$$

Now I start from d) and solve back to $\psi(r,\theta,\phi) = R(r)\,\Theta(\theta)\,\Phi(\phi)$

$\Phi(\phi)$ is easy: $\dfrac{\partial^2 \Phi}{\partial \phi^2} = -m^2 \Phi \implies \Phi(\phi) = e^{im\phi}$

it makes sense to ask that $\Phi(\phi + 2\pi) = \Phi(\phi) \Rightarrow m$ must be integer

$\Theta(\theta)$ not so easy:

$$\sin\theta \frac{\partial}{\partial\theta} \sin\theta \frac{\partial \Theta}{\partial \theta} + \left[\ell(\ell+1)\sin^2\theta - m^2\right]\Theta = 0$$

The solution are the $P_\ell^m(\cos\theta)$ functions, that can be obtained as follows:

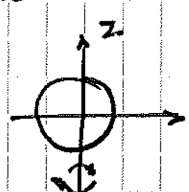
$$P_\ell^m(x) = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_\ell(x) \qquad \text{[associated Legendre function]}$$

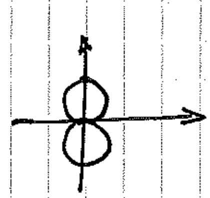
this tells me $|m| \le \ell$, or $P_\ell^m(x) = 0$

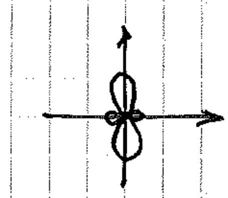
where $P_\ell(x) = \dfrac{1}{2^\ell \ell!}\left(\dfrac{d}{dx}\right)^{\ell}(x^2-1)^\ell$ [Legendre polynomial]

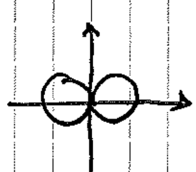
this suggests ℓ integer ≥ 0

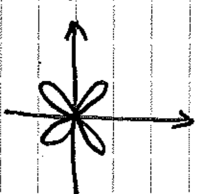
Examples:

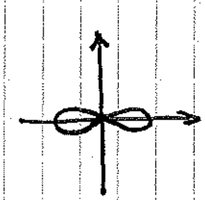
P_0^0 

P_1^0 

P_2^0 

P_1^1 

P_2^1 

P_2^2 

The <u>normalized</u> angular wave functions are called spherical harmonics:

$$Y_\ell^m(\theta,\phi) = \begin{matrix} (-1)^m & \text{if } m>0 \\ 1 & \text{if } m<0 \end{matrix} \cdot \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\; e^{im\phi}\, P_\ell^m(\cos\theta)$$

How about the radial part? If I replace $R = r \cdot u(r)$, I get:

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

A solution can be obtained in the form of a power series, with a recursion formula defining the coefficients. Suffice to say that we end up getting:

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

where $\rho = r/an$ (a being the Bohr radius: $\frac{4\pi\varepsilon_0\hbar^2}{me^2} = 0.5\cdot 10^{-10}\,m$)

and $v(\rho)$ is a polynomial of degree $n-l-1$, whose coefficients satisfy the recursion formula:

n must be $\geq l+1$, otherwise $R_{nl}(r)$ explodes at $\rho \to 0$

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

Interestingly, we find that the energy E depends exclusively on n (and not on l):

$$E_n = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2\cdot\frac{1}{n^2} \qquad E_1 = -13.6\text{ eV}$$

How degenerate are the energy levels? For any n, l can take the values 0, 1, 2... n-1; for each l, m can take the values $-l, -l+1, .., 0, 1, .. l-1, l$. Hence, I have:

$$\text{degeneracy}(n) = \sum_{l=0}^{n-1}(2l+1) = \underline{n^2}$$

[find and show example of wavefunctions of hydrogen]