Chy 475—Amar
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Hydrogen atom

Let us return to our model for the Hamiltonian operator for a two particle system, only now we shall take one of the particles to be a proton of mass, m_p and the other an electron of mass m_e with charges +e and –e respectively. So the classical energy is given by the kinetic energies of the two particles and the potential energy of the two charges a distance *r* apart:

$$E = \frac{1}{2m_p}\vec{p}^{\,2}_{proton} + \frac{1}{2m_e}\vec{p}^{\,2}_{electron} - \frac{e^2}{4\pi\varepsilon_0 r}$$

The corresponding quantum mechanical Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m_p}\left[\frac{\partial^2}{\partial x_p^2} + \frac{\partial^2}{\partial y_p^2} + \frac{\partial^2}{\partial z_p^2}\right] - \frac{\hbar^2}{2m_e}\left[\frac{\partial^2}{\partial x_e^2} + \frac{\partial^2}{\partial y_e^2} + \frac{\partial^2}{\partial z_e^2}\right] - \frac{e^2}{4\pi\varepsilon_0 r}$$

which can be written out in vector operator notation (del-squared):

$\hat{H} = -\frac{\hbar^2}{2m_p}\nabla_p^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\varepsilon_0 r}$ which we now use to solve a six-dimensional differential equation: $\hat{H}\Psi(\vec{r}_p,\vec{r}_e) = E\Psi(\vec{r}_p,\vec{r}_e)$

The problem is that this equation is not separable in this coordinate system because of the Coulomb interaction term with

$$r = \left(\left(x_e - x_p\right)^2 + \left(y_e - y_p\right)^2 + \left(z_e - z_p\right)^2\right)^{1/2}$$

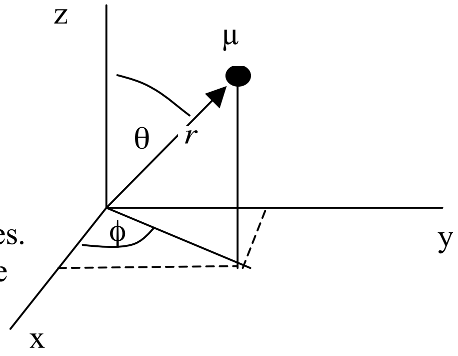
Now we can simplify the problem by converting the kinetic energy of the two particles to those for the center-of-mass coordinate and the inter-particle coordinate:

$$\hat{H} = -\frac{\hbar^2}{2M}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{e^2}{4\pi\varepsilon_0 r} \quad \text{where } M = m_e + m_p \text{ and } \mu = \frac{\mathrm{m_e m_p}}{\mathrm{m_e + m_p}}$$

This equation is partially separable as it stands and we can separate the center-of-mass motion from the internal motion and focus on the 3-dimensional interparticle coordinate:

$$\hat{H}\Psi(\vec{r}_\mu) = E\Psi(\vec{r}_\mu) \quad \text{or}$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla_r^2 - \frac{e^2}{4\pi\varepsilon_0 r}\right]\Psi(\vec{r}_\mu) = E\Psi(\vec{r}_\mu)$$



If we now rewrite the kinetic energy operator in spherical polar coordinates instead of Cartesian coordinates. This allows us to separate the *r* stretch coordinate from the tranverse (angular) coordinates, θ and ϕ, obtaining an "electronic" Hamiltonian that is separable:

$$\hat{H}^{el} = -\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}r^2\frac{\partial}{\partial r} + \sin\theta\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial^2\phi}\right] - \frac{e^2}{4\pi\varepsilon_0 r}$$

and

$$\hat{H}^{el}R_{nl}(r)Y_{lm}(\theta,\phi) = E_{nlm}R_{nl}(r)Y_{lm}(\theta,\phi)$$

We will next look at the eigenvalues and eigenfunction solutions of this equation.

Energy eigenvalues are given by:

$$E_{nlm} = E_n = -\frac{\mu e^4}{2n^2\hbar^2} = -\frac{1}{n^2}R_H$$

which agrees with the Bohr result. Notice that the eigenvalue which could in principle depend on all three quantum numbers *n,l* , and *m* depends only on *n* (in the absence of an external field). In this equation,

n is called the principal quantum number [*n*=1,2,3,…]
l is called the angular quantum number [*l*=0,1,…,(*n*-1)]
m is called the magnetic quantum number [*m*=-*l*,-*l*+1,…,-1,0,1,…*l*-1,+*l*]

If each combination of possible values of the quantum numbers corresponds to a separate state, we see that energy levels corresponding to *n* have n^2 degenerate states (with electron spin, this number becomes $2n^2$).

Hydrogen atom eigenfunctions are a product of a radial part and an angular part. Together we call this the "spatial" part of the wavefunction (as opposed to the "spin" part which we will discuss separately)

The angular functions, $Y_{lm}(\theta,\phi)$, are called the spherical harmonics. The first few are given in the first two columns of the following Table. The first few radial functions are given in the last two columns of the Table.

Y_{00}	$\frac{1}{(4\pi)^{1/2}}$		R_{10}	$2\left(\frac{1}{a}\right)^{3/2} e^{-r/a}$
Y_{11}	$\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{i\phi}$		R_{20}	$2^{-1/2}\left(\frac{1}{a}\right)^{3/2}\left(1-\frac{r}{2a}\right)e^{-r/2a}$
Y_{10}	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$		R_{21}	$(24)^{-1/2}\left(\frac{1}{a}\right)^{5/2} re^{-r/2a}$
Y_{1-1}	$\left(\frac{3}{8\pi}\right)^{1/2}\sin\theta e^{-i\phi}$		R_{30}	$\frac{2}{3\sqrt{3}}\left(\frac{1}{a}\right)^{3/2}\left(1-\frac{2r}{3a}+\frac{2r^2}{27a^2}\right)e^{-r/3a}$
Y_{22}	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{2i\phi}$		R_{31}	$\frac{8}{27\sqrt{6}}\left(\frac{1}{a}\right)^{3/2}\left(\frac{r}{a}-\frac{r^2}{6a^2}\right)e^{-r/3a}$
Y_{21}	$\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{i\phi}$		R_{32}	$\frac{4}{81\sqrt{30}}\left(\frac{1}{a}\right)^{7/2} r^2 e^{-r/3a}$
Y_{20}	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$			
Y_{2-1}	$\left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta e^{-i\phi}$			In the above, $a=\frac{\hbar^2 4\pi\varepsilon_0}{\mu e^2}$
Y_{2-2}	$\left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta e^{-2i\phi}$			

How should all these formulae be changed if hydrogen atom is replaced by a hydrogenic atom or ion such as He^+?