Quantum Mechanics: The Hydrogen Atom

13th April 2011

I. The Hydrogen Atom

In this next section, we will tie together the elements of the last several sections to arrive at a complete description of the hydrogen atom. This will culminate in the definition of the hydrogen-atom orbitals and associated energies. From these functions, taken as a complete basis, we will be able to construct approximations to more complex wave functions for more complex molecules. Thus, the work of the last few lectures has fundamentally been aimed at establishing a foundation for more complex problems in terms of exact solutions for smaller, model problems.

II. The Radial Function

We will start by reiterating the Schrodinger equation in 3D spherical coordinates as (refer to any standard text to get the transformation from Cartesian to spherical coordinate reference systems). Here, we have not placed the constraint of a constant distance separting the masses of the rigid rotor (refer to last lecture); furthermore, we will keep in the formulation the potential $V(r, \theta, \phi)$ for generality.

Thus, in spherical polar coordinates, $\hat{H}(r, \theta, \phi)\psi(r, \theta, \phi) = E\psi(r, \theta, \phi)$ becomes:

$$E\psi(r, \theta, \phi) =$$
$$\left[\frac{-\hbar^2}{2\mu} \left(\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 sin\theta} \frac{\partial}{\partial \theta} \left(sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right) + V(r, \theta, \phi) \right] \psi(r, \theta, \phi)$$

Now, for the hydrogen atom, with one electron found in "orbits" (note the quotes!) around the nucleus of charge $+1$, we can include an electrostatic potential which is essentially the Coulomb potential between a positive and negative charge:

$$V(|\mathbf{r}|) = V(r) = \frac{-Ze^2}{4\pi\epsilon_o r}$$

where Z is the nuclear charge (i.e, $+1$ for the nucleus of a hydrogen atom). **It is important to note that the Coulomb potential as we have written it here is simply a function of the magnitude of the position vector between the 2 masses (i.e, between the electron and nucleus). There**

is no angular dependence!.

Recall:

$$\hat{L}^2 = -\hbar^2 \left(\frac{1}{sin\theta} \frac{\partial}{\partial\theta} \left(sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{sin\theta} \frac{\partial^2}{\partial\phi^2} \right)$$

is the total angular momentum squared operator (function of θ and ϕ only!). Thus, we can rewrite the Schrodinger equation as:

$$\left(\frac{-\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] + \frac{1}{2\mu r^2} \hat{L}^2 + V(r,\theta,\phi) \right) \psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

Thus, the wavefunction can be written in a form that lends to separation of variables. Recalling that the **spherical harmonics** are eigenfunctions of the angular momentum operator:

$$\psi(r,\theta,\phi) = R(r)Y_l^m(\theta,\phi) \quad Separation \ of \ Variables$$

$$\hat{L}^2 \left[R(r) \ Y_l^m(\theta,\phi) \right] = \hbar^2 l(l+1) \ [R(r) \ Y_l^m(\theta,\phi)] \quad l = 0,1,2,...$$

Accounting for separation of variables and the angular momentum results, the Schrodinger equation is transformed into the **Radial equation for the Hydrogen atom**:

$$\left(\frac{-\hbar^2}{2\mu} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right] R(r) + \left[\frac{\hbar^2 \ l \ (l+1)}{2\mu r^2} - \frac{Z \ e^2}{4\pi\epsilon_0 r} \right] R(r) \right) = E \ R(r)$$

The solutions of the radial equation are the Hydrogen atom radial wavefunctions, R(r).

II. Solutions and Energies
The general solutions of the radial equation are products of an exponential and a polynomial. The eigenvalues (energies) are:

$$E = \frac{-Z^2 e^2}{8\pi\epsilon_o a_o n^2} = \frac{-Z^2 \mu e^4}{8\epsilon_o^2 h^2 n^2} \quad n = 1,2,3,..$$

The constant a_o is known as the Bohr Radius:

$$a_o = \frac{\epsilon_o h^2}{\pi\mu e^2}$$

The energy is quantized and dependent only on the pricipal quantum number, n. This quantization arises from the restriction that R(r) be well behaved at large separations, r (vis-a-vis, $R(r) \rightarrow 0$ as $r \rightarrow \infty$).

The Radial eigenfunctions are:

$$R_{nl}(\frac{r}{a_0}) = A_{nl} \left(\frac{Zr}{a_0} \right)^l L_{nl} \left(\frac{r}{a_0} \right) exp^{\frac{-Zr}{na_0}}$$

$$n = 1; \quad l = 0; \quad L_{11} = 1$$

$$n = 2; \quad l = 0; \quad L_{21} = (2 - x) \quad x = (\frac{r}{a_0})$$

$$n = 2; \quad l = 1; \quad 1$$

How to normalize:

Spherical Harmonics:

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \, sin\theta \, Y_l^{m*}(\theta, \phi) Y_l^m(\theta, \phi) = 1$$

Radial Wavefunctions:

$$\int_0^{\infty} dr \, r^2 R_{nl}^*(r) R_{nl}(r) = 1$$

The total hydrogen atom wavefunctions are:

$$\psi(r, \theta, \phi) = R_{nl} Y_l^m(\theta, \phi)$$

Table 1. Nomenclature and Ranges of H-Atom quantum numbers

Name	Symbol	Allowed Values
principle quantum number	n	1,2,3,....
angular momentum quantum number	l	0,1,2,...,n-1
magnetic quantum number	m	$0, \pm 1, \pm 2, \pm 3, ..., \pm l$

energies: depend on "n" $\quad E = \frac{-Z^2 e^2}{8\pi\epsilon_o a_o n^2}$.

angular momentum: depends on "l" $\quad |L| = \hbar\sqrt{l(l+1)}$

$L_{z-component}$**: depends on "m"** $\quad L_z = m\hbar$

Total H atom wavefunctions are normalized and orthogonal:

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \, sin\theta \int_0^{\infty} dr r^2 \psi_{nlm}^*(r,\theta,\phi)\psi_{n'l'm'}^*(r,\theta,\phi) = \delta_{nn'}\delta_{ll'}\delta_{mm'}$$

Lowest total Hydrogen atom wavefunctions: $n = 1$ and $n = 2$ (define $\sigma \equiv \frac{Zr}{a_o}$)

Table 2. Hydrogen Atom Wavefunctions

n	l	m	ψ_{nlm}	Orbital Name
1	0	0	$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_o}\right)^{\frac{3}{2}} e^{-\sigma}$	ψ_{1s}
2	0	0	$\psi_{200} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_o}\right)^{\frac{3}{2}} (2-\sigma)e^{\frac{-\sigma}{2}}$	ψ_{2s}
	1	0	$\psi_{210} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_o}\right)^{\frac{3}{2}} \sigma e^{\frac{-\sigma}{2}} cos\theta$	ψ_{2p_z}
	1	± 1	$\psi_{21\pm 1} = \frac{1}{\sqrt{64\pi}} \left(\frac{Z}{a_o}\right)^{\frac{3}{2}} \sigma e^{\frac{-\sigma}{2}} sin\theta e^{\pm i\phi}$	

Transforming to real functions via normalized linear combinations

| | 1 | ± 1 | $\psi_{2p_x} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_o}\right)^{\frac{3}{2}} \sigma e^{\frac{-\sigma}{2}} sin\theta cos\phi$ | $\psi_{2p_x} = \frac{1}{\sqrt{2}}\left(\psi_{21+1} + \psi_{21-1}\right)$ |
| | 1 | ± 1 | $\psi_{2p_y} = \frac{1}{\sqrt{32\pi}} \left(\frac{Z}{a_o}\right)^{\frac{3}{2}} \sigma e^{\frac{-\sigma}{2}} sin\theta sin\phi$ | $\psi_{2p_y} = \frac{1}{\sqrt{2}}\left(\psi_{21+1} - \psi_{21-1}\right)$ |

Thus, we have come to the point where we can connect what we already know
from previous analysis:

Table 3. Quantum numbers

$n = 1, 2, 3, ...$	$l = 0, 1, 2, ..., n-1$	$m = 0, \pm1, \pm2, ..., \pm l$	Orbital
1	0	0	$1s$
2	0	0	$2s$
2	1	0	$2p_z$
2	1	+	$2p_x$
2	1	-	$2p_y$

What are the degeneracies of the Hydrogen atom energy levels? Recall they are dependent on the **principle quantum number only**.

III. Spectroscopy of the Hydrogen Atom

Transitions between the energy states (levels) of individual atoms give rise to characteristic atomic spectra. These spectra can be used as analytical tools to assess composition of matter. For instance, our knowledge of the atomic composition of the sun was in part aided by considering the spectra of the radiation from the sun. For the Hydrogen atom, early scientists observed that the emission spectra (generated by exciting hydrogen atoms from the ground to excited states), gave rise to specific lines; the spectra were **NOT** continuous. The understanding of the quantum mechanical nature of the hydrogen atom helps us understand how these lines arise.

Series of lines in the hydrogen spectrum, named after the scientists who observed and characterized them, can be related to the energies associated with transsitions from the various energy levels of the hydrogen atom. The relation, simple enough as it is, turns out to accurately predict the spectral lines. The equation relating the wavelength (and thus energy via $E = h\nu$) associated with a transition from a state n_1 to another tate n is given by:

$$\frac{1}{\lambda} = R_{Rydberg} \left(\frac{1}{n_1^2} - \frac{1}{n^2} \right) \quad n_1 = 2; \; Balmer \; Series$$

$$n_1 = 1; \; Lyman \; Series$$

$$n_1 = 3; \; Paschen \; Series$$