The Hydrogen Atom

CHEM 361B: Introduction to Physical Chemistry

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Lecture 12

Table of contents

Learning Objectives:

- Solve the Schrödinger Equation for the Hydrogen Atom
- Discuss the solutions in order to characterize atomic orbitals

References:

- McQuarrie Chapter 6

The Hydrogen Atom

The Schrödinger equation can be solved exactly for the hydrogen atom. This solution

- plots all the orbitals (s,p,d,f, etc).
- gives the Rydberg equation.

and serve as a template to examine other, larger, more complicated atoms/molecules.

For the purposes of the calculation, assume that the proton nucleus is fixed at the origin with an electron of reduced mass μ interacting with the proton through the Coulombic potential

$$U(r) = -\frac{e^2}{4\pi\epsilon_0 r}$$

The Hydrogen Atom - Setup

Since the potential is spherically symmetric, the Schrödinger equation will be written using spherical coordinates

$$-\frac{\hbar^2}{2\mu}\nabla^2\psi(r,\theta,\phi) + U(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

or

$$-\frac{\hbar^2}{2\mu}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right]$$
$$-\frac{e^2}{4\pi\epsilon_0 r}\psi = E\psi$$

The Hydrogen Atom - Setup Simplification

Let

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

and recall that

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

and that

$$\hat{L}^2 Y(\theta,\phi) = \hbar^2\ell(\ell+1)Y(\theta,\phi)$$

then

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \left[\frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + U(r) - E\right]R(r) = 0$$

The Hydrogen Atom - Radial Solution

The solution to the previous differential equation is

$$R_{n\ell}(r) = -\left[\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right]^{1/2}\left(\frac{2}{na_0}\right)^{\ell+3/2} r^{\ell} e^{-r/na_0} L_{n+\ell}^{2\ell+1}\left(\frac{2r}{na_0}\right)$$

where $L_{n+\ell}^{2\ell+1}(x)$ is the associated Laguerre polynomial. The first few of these are

$n=1; l=0$		$L_1^1(x) = -1$	$x = 2r/a_0$
$n=2; l=0$		$L_2^1(x) = -2!(2-x)$	$x = r/a_0$
	$l=1$	$L_3^3(x) = -3!$	
$n=3; l=0$		$L_3^1(x) = -3!(3-3x+\frac{1}{2}x^2)$	$x = 2r/3a_0$
	$l=1$	$L_4^3(x) = -4!(4-x)$	
	$l=2$	$L_5^5(x) = -5!$	
$n=4; l=0$		$L_4^1(x) = -4!(4-6x+2x^2-\frac{1}{6}x^3)$	$x = r/2a_0$
	$l=1$	$L_5^3(x) = -5!(10-5x+\frac{1}{2}x^2)$	
	$l=2$	$L_6^5(x) = -6!(6-x)$	
	$l=3$	$L_7^7(x) = -7!$	

The Energy of the Hydrogen Atom

The energy from the Schrödinger equation of the hydrogen atom is

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \quad n = 1, 2, \ldots$$

where the Bohr radius, a_0, is

$$a_0 = \frac{\epsilon_0 h^2}{\pi\mu e^2}$$

From this solution there is also a limit imposed on the values of ℓ where

$$0 \leq \ell \leq n - 1$$

Recall that the energy for the hydrogen atom that Bohr calculated more than a decade before the Schrödinger equation existed was

$$E_n = -\frac{\mu e^4}{8\epsilon_0^2 h^2 n^2} \quad n = 1, 2, \ldots$$

Hydrogen-like Solutions

For every other atom, hydrogen-like orbitals can be used. Using the Helium atom as an example, its Schrödinger equation takes the form of:

$$\left(-\frac{\hbar^2}{2M}\nabla^2 - \frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2\right)\psi(r_n, r_1, r_2)$$
$$+\left(-\frac{2e^2}{4\pi\epsilon_0|r_n - r_1|} - \frac{2e^2}{4\pi\epsilon_0|r_n - r_2|} + \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|}\right)\psi(r_n, r_1, r_2)$$
$$= E\psi(r_n, r_1, r_2)$$

Hydrogen-like Solutions (cont.)

Given that $M >> m_e$ and fixing r_n to not move and let it be the origin then this simplifies to

$$-\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2)\psi(r_1, r_2) - \frac{2e^2}{4\pi\epsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right)\psi(r_1, r_2) + \frac{e^2}{4\pi\epsilon_0|r_1 - r_2|}\psi(r_1, r_2) = E\psi(r_1, r_2)$$

which can not be solved exactly due to the electron-electron repulsion term (in blue). The "2" that appears in the core-electron attraction term represents the atomic number Z in the next slide.

The Hydrogen Atom - The Full Solution

The Complete Hydrogenlike Atomic Wave Functions for $n = 1, 2,$ and 3. The Quantity Z Is the Atomic Number of the Nucleus, and $\sigma = Zr/a_0$, Where a_0 is the Bohr Radius.

$n = 1; l = 0, m = 0$	$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n = 2; l = 0, m = 0$	$\psi_{200} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma)e^{-\sigma/2}$
$l = 1, m = 0$	$\psi_{210} = \frac{1}{\sqrt{32\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\cos\theta$
$l = 1, m = \pm 1$	$\psi_{21\pm1} = \frac{1}{\sqrt{64\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta e^{\pm i\phi}$
$n = 3; l = 0, m = 0$	$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
$l = 1, m = 0$	$\psi_{310} = \frac{1}{81}\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3}\cos\theta$
$l = 1, m = \pm 1$	$\psi_{31\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3}\sin\theta e^{\pm i\phi}$
$l = 2, m = 0$	$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}(3\cos^2\theta - 1)$
$l = 2, m = \pm 1$	$\psi_{32\pm1} = \frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta e^{\pm i\phi}$
$l = 2, m = \pm 2$	$\psi_{32\pm2} = \frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta e^{\pm 2i\phi}$

Recall that

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

What n, ℓ, and m represent

The wave function ψ depends on three quantum numbers

- n - The Principle Quantum Number

  Determines the energy of the system

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \quad n = 1, 2, \ldots$$

- ℓ - Angular Momentum Quantum Number

  Determines the angular momentum of the electron around the proton

$$|L| = \hbar\sqrt{\ell(\ell+1)} \quad 0 \leq \ell \leq n-1$$

- m - Magnetic Quantum Number

  Determines the z-component of the angular momentum

$$L_z = m\hbar \quad m = 0, \pm 1, \pm 2, \ldots, \pm \ell$$

Ground State Hydrogen Problems

Given that the ground state of the hydrogen atom puts the electron in the 1s orbital find

1. the most probable radius of the electron

given that

$$\psi_{100} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

Looking at p-orbitals

p-orbitals are defined as when $\ell = 1$. Looking only at $Y(\theta, \phi)$, the first three p-orbitals are:

$$Y_1^0(\theta, \phi) = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$$

$$Y_1^{\pm 1}(\theta, \phi) = \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$$

A solution with $Y_1^0(\theta, \phi)$ is called the p_z orbital since it is real and is orientated along the z-axis. Since $Y_1^{\pm 1}$ is complex they do not directly translate to the p_x and p_y orbitals. It is customary to use the combinations:

$$p_x = \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$$

$$p_y = \frac{1}{\sqrt{2}}(Y_1^1 - Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$$

p-orbital questions

1. What is the probability of finding an electron within a sphere of radius R centred on the nucleus for a $2p_z$ orbital?

Looking at d-orbitals

When $\ell = 2$ then $m = 0, \pm 1$, and ± 2 so there are five d-orbitals. Like the p-orbitals, real functions are easier to handle so the typical convention is

$$
\begin{aligned}
d_{z^2} &= Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1) \\
d_{xz} &= \frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi \\
d_{yz} &= \frac{1}{\sqrt{2}i}(Y_2^1 - Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi \\
d_{x^2-y^2} &= \frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi \\
d_{xy} &= \frac{1}{\sqrt{2}i}(Y_2^2 - Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi
\end{aligned}
$$

Real Atomic Orbitals

$n=1,\ l=0,\ m=0;$	$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n=2,\ l=0,\ m=0;$	$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (2-\sigma)e^{-\sigma/2}$
$l=1,\ m=0;$	$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\cos\theta$
$l=1,\ m=\pm1;$	$\psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta\cos\phi$
	$\psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta\sin\phi$
$n=3,\ l=0,\ m=0;$	$\psi_{3s} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2} (27-18\sigma+2\sigma^2)e^{-\sigma/3}$
$l=1,\ m=0;$	$\psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\cos\theta$
$l=1,\ m=\pm1;$	$\psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\sin\theta\cos\phi$
	$\psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\sin\theta\sin\phi$
$l=2,\ m=0;$	$\psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}(3\cos^2\theta-1)$
$l=2,\ m=\pm1;$	$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta\cos\phi$
	$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta\sin\phi$
$l=2,\ m=\pm2;$	$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta\cos 2\phi$
	$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta\sin 2\phi$

where $\sigma = Zr/a_0$

Summary

- The Schrödinger equation can be solved explicitly for the hydrogen atom.
    - The energy found from the solution of the Schrödinger equation exactly matches the one found for the Bohr atom.
    - The quantum numbers which define atomic orbitals arise from the limits imposed through solving the Schrödinger equation.
- Due to electron-electron interactions, the Schrödinger equation cannot be solved analytically for atoms with more than one electron.
    - Numerical methods are instead used to generate wavefunction solutions for multi-electron systems
    - Hydrogen-like orbitals are also used to approximate heavier elements with one electron