

Hydrogen Atom, Atomic Orbitals

Pre-Quantum Atomic Structure

The existence of atoms and molecules had long been theorized, but never rigorously proven until the late 19th and early 20th centuries. (Remember, Boltzmann was criticized for insisting that atoms and molecules were real and not just “useful theoretical constructs.”) Convincing proof came from the discovery of the electron by Thomson in 1897 and the atomic nucleus by Rutherford in 1909. The Rutherford model of the atom consisted of a positively charged nucleus surrounded by the negatively charged electrons. The electrons were thought to orbit the nucleus, similar to how planets orbit the sun.

Niels Bohr took the Rutherford model one step further in his attempt to explain the observed atomic emission spectra. Experiments showed quite clearly that when a gas was subjected to an electrostatic discharge, light was emitted. However, this light consisted of a series of discrete frequencies, or colors. (This is how neon signs work, by the way.) To explain these discrete spectra, Bohr developed a model of the atom that had the electrons confined to orbits of particular energy. The only way that an electron could change its energy was to absorb enough energy to “leap” to a higher energy orbit. When an excited electron released energy to drop down to a lower energy orbit, that extra energy was carried away by the light. These discrete transitions give the emission spectrum its characteristic lines.

In order for this orbit to be stable, there needs to be a balance between the Coulombic attraction toward the nucleus and the centrifugal force pulling the electron away.

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$$

To fit the experimental data, Bohr needed to quantize the angular momentum of the different orbitals. He found that he needed Planck's constant (funny how that same number keeps showing up, isn't it?)

and the de Broglie relation, $\lambda = \frac{h}{p}$, to make this work. The length of the path around the orbital is given by $\lambda = 2\pi r$. The length of the orbit must be an integer number of de Broglie wavelengths.

$$2\pi r = n\lambda = n\frac{h}{p}$$

If we rearrange things, we have

$$mvr = n\hbar$$

Solving for the radius of the orbitals we have

$$r = \frac{\epsilon_0 \hbar^2 n^2}{\pi m e^2} = a_0$$

This is known as the Bohr radius and has a value of 5.29177×10^{-11} m.

Going through some more algebra and calculating the total energy of each orbital, we find

$$E_n = \frac{-m_e e^4}{8 \epsilon_0^2 \hbar^2 n^2}$$

The Bohr model was successful, in that it explained a great deal of experimental observations.

However, it had some very fundamental problems. First of all, there was no basis for it in classical physics. Classically, an electron traveling in a circular orbit should be radiating energy, leading to a loss of its own energy. Eventually (actually, very quickly) the electron would lose enough energy that it would crash into the nucleus. The Bohr model is based on electronic orbits, but provides no rationale for why these orbits, or in fact atoms themselves, are stable. This requires quantum mechanics.

Schrödinger Equation for the Hydrogen Atom

We have explored several model systems that can be solved analytically. Even though real systems are more complicated, the model systems are useful approximations. The hydrogen atom is the first real situation that we can actually solve exactly. A hydrogen atom consists of a single proton surrounded by a single electron. The interaction between the proton and the electron is represented by the Coulomb potential, of the form

$$V(r) = \frac{-Ze^2}{4\pi\epsilon_0 r}$$

Z is the nuclear charge, e is the elementary charge of an electron (or proton), and ϵ_0 is the permittivity of free space. This potential depends on the distance between the particles, r . (We use r because this situation has inherent spherical symmetry.) Unlike previous potentials, we choose our zero to be at infinite separation of the two particles. (This potential actually works for any hydrogen-like atom, meaning all but one of its electrons have been removed. Only Z will change.)

If we take the proton to be the origin of our coordinate system, we can write our Hamiltonian as

$$\hat{H} = \hat{T}_e + \hat{V} = \frac{-\hbar^2}{2\mu_e} \nabla_e^2 - \frac{Ze^2}{4\pi\epsilon_0 r}$$

The first term accounts for the kinetic energy of the electron and the second term is the Coulombic interaction between the electron and the nucleus. (Since we are keeping our coordinate system fixed on the nucleus, we ignore nuclear motion.)

The ∇^2 operator, known as the Laplacian, is written in Cartesian coordinates as

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In spherical coordinates, this becomes significantly more complicated

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

The portion in the square brackets is exactly the same as in our total angular momentum operator \hat{l}^2 that we encountered with the rigid rotor. It only needs the factor of $-\hbar^2$, which we have in the Schrödinger equation above.

This fact suggests that we can use separation of variables to solve this problem. Because we already know the eigenfunctions of the total angular momentum operator, the spherical harmonics, we will write the wavefunction as

$$\psi(r, \theta, \phi) = R(r) Y_l^{m_l}(\theta, \phi)$$

So we can write the Schrödinger equation as

$$\frac{1}{2\mu_e r^2} R(r) \hat{l}^2 Y_l^{m_l}(\theta, \phi) - \frac{\hbar^2}{2\mu_e r^2} Y_l^{m_l}(\theta, \phi) \frac{d}{dr} \left[r^2 \frac{dR(r)}{dr} \right] - Y_l^{m_l}(\theta, \phi) \frac{e^2}{4\pi\epsilon_0 r} R(r) = E R(r) Y_l^{m_l}(\theta, \phi)$$

This looks quite formidable, but we already know that

$$\hat{l}^2 Y_l^{m_l}(\theta, \phi) = \hbar^2 l(l+1) Y_l^{m_l}(\theta, \phi)$$

If we make this substitution, we can divide out the spherical harmonics and write

$$\frac{-\hbar^2}{2\mu_e r^2} \frac{d}{dr} \left[r^2 \frac{dR(r)}{dr} \right] + \left[\frac{\hbar^2 l(l+1)}{2\mu_e r^2} - \frac{e^2}{4\pi\epsilon_0 r} \right] R(r) = E R(r)$$

We have grouped the terms this way for a reason. The first term, involving derivatives with respect to r , relates to the kinetic energy of the electron. The second term is an *effective* potential with two parts. The first part has to do with the angular momentum of the electron and is a centripetal potential. Notice that if the electron has no angular momentum, this term doesn't contribute; $l = 0$. The second term is the same Coulombic potential from between the proton and the electron.

This differential equation can be solved through standard methods, so we'll just jump to the solutions. We already have the spherical harmonics, which give us the angular dependencies of the wavefunction.

The radial function is of the form

$$R_{n,l}(r) = - \left[\frac{4Z^3 (n-l-1)!}{n^4 a_0^3 [(n+1)!]^3} \right]^{1/2} \left(\frac{2Zr}{na_0} \right)^l e^{-Zr/na_0} L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right)$$

where $a_0 = \frac{4\pi\epsilon_0\hbar^2}{\mu_e e^2}$ is known as the Bohr radius. The functions $L_{n+l}^{2l+1} \left(\frac{2Zr}{na_0} \right)$ are known as the associated Laguerre polynomials. The first few radial functions are tabulated and plotted below.

$$\begin{aligned} R_{1,0} &= 2 \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0} & R_{2,0} &= \frac{1}{\sqrt{8}} \left(\frac{1}{a_0} \right)^{3/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0} \\ R_{2,1} &= \frac{1}{\sqrt{24}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r}{a_0} e^{-r/2a_0} & R_{3,0} &= \frac{2}{81\sqrt{3}} \left(\frac{1}{a_0} \right)^{3/2} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2} \right) e^{-r/3a_0} \\ R_{3,1} &= \frac{4}{81\sqrt{6}} \left(\frac{1}{a_0} \right)^{3/2} \left(6\frac{r}{a_0} - \frac{r^2}{a_0^2} \right) e^{-r/3a_0} & R_{3,2} &= \frac{4}{81\sqrt{30}} \left(\frac{1}{a_0} \right)^{3/2} \frac{r^2}{a_0^2} e^{-r/3a_0} \end{aligned}$$

Like the spherical harmonics, these functions are all orthogonal and normalized. Because we have three coordinates in our wavefunction, we have three quantum numbers. The possible values are:

principle quantum number	$n = 1, 2, 3, \dots$
orbital angular momentum	$l = 0, 1, 2, \dots, n-1$
magnetic quantum number	$m_l = -l, -(l-1), \dots, 0, \dots, (l-1), l$

The restrictions on the values of the quantum numbers are a result of the boundary conditions of the differential equations.

The energy of these states is given by

$$E_n = \frac{-Z^2 \mu_e e^4}{8\epsilon_0^2 \hbar^2 n^2} = \frac{-Z^2 e^2}{8\pi\epsilon_0 a_0 n^2}$$

Note that the energy only depends on the principle quantum number, n . This means that each energy level has a degree of degeneracy for the various values of l and m_l . (Compare this energy to Bohr's result above.)

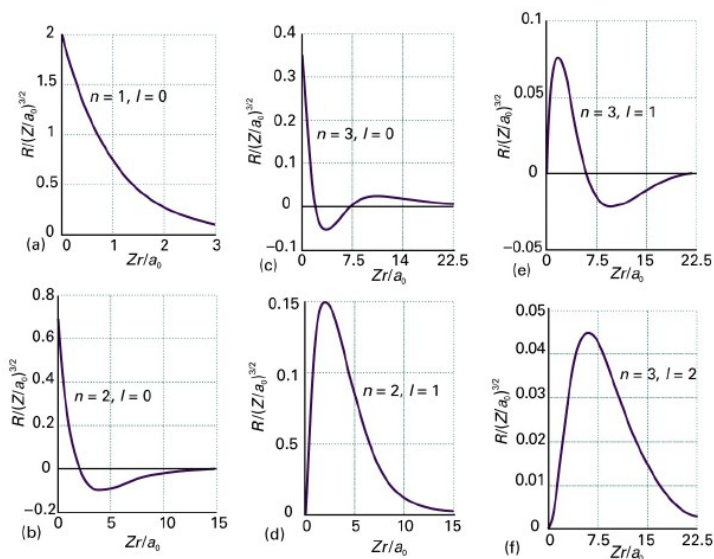


Figure 10-4
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Stability of Atoms

Now that we have the solutions for the hydrogen atom, we can comment on why atoms are stable. It all has to do with the balance between kinetic and potential energy. The Coulombic potential gets more and more negative as the distance between the electron and the nucleus decreases; being closer to the nucleus decreases the potential energy. However, recall from the particle in a box that confinement leads to higher kinetic energy; being closer to the nucleus increases the kinetic energy. The stable levels achieve a balance between the kinetic and potential energy.

Atomic Orbitals

Each of the solutions for the hydrogen atom $\psi_{n,l,m_l}(r, \theta, \phi) = R_{n,l}(r)Y_l^{m_l}(\theta, \phi)$ is known as an **atomic orbital**. As with the other wavefunctions we have seen, these functions have nodes. Because of the spherical symmetry, these nodes can either be radial, as in the radial functions plotted above, or angular, as with the spherical harmonics. The locations of these nodes give characteristic shapes to the different atomic orbitals. Atomic orbitals are typically grouped according to the angular momentum quantum number, l , with the following assignments:

$$l = \begin{array}{cccc} 0 & 1 & 2 & 3 \\ s & p & d & f \end{array}$$

(These letters are chosen for historical reasons from atomic spectra and stand for *sharp*, *principle*, *diffuse*, and *fine*.) s type orbitals have no angular nodes, so they must have spherical symmetry. They do, however, have radial nodes, as can be seen in the plots above. p type orbitals have an angular node that runs through the origin, giving them a characteristic dumbbell shape. d type orbitals have two angular nodes, so they look more complicated. You should have plots of these orbitals in your general chemistry textbook.

Multi-Electron Atoms, Pauli Principle and Electron Spin

It must be remembered that these orbitals are solutions for the hydrogen atom; they are not exact solutions for the wavefunctions of other atoms. However, they do comprise a complete mathematical set, meaning we can describe the solutions of any atom in terms of the hydrogenic orbitals. They also form a useful picture and give us a way to describe what is happening in atoms with more than one electron. The reason we can't rigidly use the hydrogen-like orbitals is because we have to include additional terms in the Hamiltonian to describe all the interactions. Also, the wavefunction needs to account for the coordinates of all the electrons.

Let's consider helium. Here we have one nucleus, with a +2 charge, and two electrons. The Hamiltonian is written as

$$\hat{H} = -\frac{\hbar^2}{2\mu_e} \nabla_{e_1}^2 - \frac{\hbar^2}{2\mu_e} \nabla_{e_2}^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

Let's briefly discuss the terms here. The first two represent the kinetic energy of electron 1 and electron 2, respectively. The next two terms are the interactions of the two electrons with the nucleus; r_1 is the distance of electron 1 from the nucleus and r_2 is the distance of electron 2 from the nucleus. If this were all we had to deal with, we could treat this with separation of variables. However, the last term accounts for the interaction between the two electrons, with r_{12} the distance between them. This term makes it impossible to analytically solve the Schrödinger equation; the solution for the first electron depends on the location of the second, and vice versa. This equation can only be solved numerically. However, we can describe the solution in terms of the hydrogenic orbitals. Mathematically, we write the solutions to the Schrödinger equation for the He atom as a linear combination of the hydrogenic atomic orbitals. Note, however, that the real orbitals are not exactly the same as they were in hydrogen. For helium, there really isn't a 1s orbital, but the first solution is dominated by the hydrogen 1s orbital; the first He orbital is 1s-like. It is also important to note that the degeneracy of the different states is broken by the interactions between the electrons; the 2s-like and 2p-like orbitals are not at exactly the same energy in helium as they were in hydrogen.

Lastly, we need to know about one more property of electrons, **spin**. Electron spin is purely a quantum mechanical property; it has no classical analog. (It arises from relativistic quantum mechanics, definitely beyond the scope of this course.) There are two possible spin states, called **spin-up** and **spin-down**, commonly represented by up and down arrows. The **Pauli exclusion principle** states that no two electrons in a quantum mechanical system can have exactly the same set of quantum numbers. For purposes of our discussion, we can take this as a postulate of quantum mechanics. Because there are two spin states, each hydrogenic orbital can contain at most two electrons.

So, using the hydrogenic orbitals and the Pauli principle, we can describe the electronic configuration of multi-electron atoms. Going back to He, we describe its electronic configuration as $1s^2$, meaning the 1s-like orbital contains two electrons. The **Aufbau principle** gives the order in which orbitals are filled as:

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s

So the configuration of boron is described as $1s^2 2s^2 2p^1$ or $[\text{He}] 2s^2 2p^1$.

The last thing that is needed to describe electronic configurations is **Hund's rule**, which states that electrons will enter unfilled orbitals before occupying part-filled orbitals. This leads to the maximum total electron spin, because the electrons can line up their spin states. Correlation of spins helps to lower the total energy of the electrons, again purely a quantum mechanical effect.

Summary

This treatment of atomic structure has covered many important ideas, most of which you should have encountered before, at least at a basic level. Quantum mechanics provides the answer for why atoms are stable. The hydrogen-like atom, meaning an atom with only one electron, is the only system that can be solved analytically without making any approximations. However, the orbitals that serve as the solutions to this problem form a useful model for describing the structure of all atoms. The additional electrons perturb the hydrogen-like orbitals, which breaks the degeneracy of the various states.

Recall also that the atomic orbitals are orthogonal to each other and form a complete set. Thus the real solutions for atoms other than hydrogen can be described in terms of the hydrogenic orbitals. This is also the mathematical basis behind the idea of “hybridized” orbitals that you learned about in organic chemistry. So long as orbitals are of the same, or very similar energy, they can mix to form new orbitals. We will talk about bonding and molecular orbitals in the next lecture.