Chapter 2 – The Structure of the Atom

Since the book assumes you have a background in quantum chemistry, we will go over some of what you will need to begin Chapter 2. At this point, it would behoove you to go back and read your general chemistry text on topics concerning atomic structure.

A prime mission of inorganic chemistry is to understand the bonding in molecules. In large measure, to understand bonding is to understand reactivity. Now for a quick review of general chemistry.

By the late 19th century it was known that the atom contained electrons. The discovery of the nucleus and protons in the early 20th century required a model of the atom classical physics could not provide. The first real model to describe the atom with some accuracy was proposed by Neils Bohr and is the familiar electron traveling around a nucleus in circular orbits. This model employed several assumptions, including energy quantization. Unfortunately, it had two significant problems: (1) it only worked for one electron atoms and, (2) there were no good justifications for the assumptions beyond that they seemed to work. A better description of the atom was developed when it was realized that electrons behaved both as particles and as waves. This is called particle/wave duality.

What we will now do is discuss how this dual nature of the electron affects the structure of the atom.

An early contribution to the study of wave mechanics (the study of electrons in atoms as waves) was made by Louis de Broglie. He proposed that the electron wave obeyed the relationship $p\lambda = h$ (p = momentum). That is to say, the higher the momentum of an electron the shorter is its wavelength. As p^2 is directly proportional to kinetic energy, this means long wavelength electrons have low kinetic energy and short wavelength electrons have high kinetic energy.

A second major contribution was made by Werner Heisenberg who realized that it is impossible to know both the position and momentum of a particle precisely. He proposed that $(\Delta p)(\Delta x) \geq \frac{1}{2}h/2\pi$. This tells us that the more accurately you determine the momentum of a particle the less precisely you know its position (and vice-versa). This is reasonable because in order to

determine the position or momentum of a particle there must be an interaction with the particle. The interaction will cause the energy of the particle to change and this will cause some uncertainty in the result. In other words, in order for the particle to reveal information about itself, its energy must change.

Now, what can we say about the electron wave? In 1926, Erwin Schrödinger proposed an equation to describe the electron wave.

$$H\Psi = E\Psi$$

where Ψ is the wave function, H is called a Hamiltonian and performs a transformation on Ψ such that it is regenerated and multiplied by a constant E (that equals the energy of the system). Remember, that Ψ is simply an amplitude and has **no** physical reality.

In the case of an atom in 3-dimensions the Schrödinger equation becomes:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

This equation is very difficult to solve for an atom (e.g. the potential energy of the electron, V, changes with distance from the nucleus) and doing so isn't really necessary for this course. However, a hypothetical example that can be solved by hand is the particle-in-a-box. We will solve this problem in 1-dimension. Converting it to 3-dimensional space is quite easy. *See separate handout*.

Now, the major differences between the particle-in-a-box and an atom are

a) The potential energy in the box is limited to 2 values, eliminating a gradient.

b) The total distance of the box is fixed.

Conceptually, however, the problems are the same and, as a result, their solutions are related.

The Hydrogen Atom

Solving the Schrödinger equation for the hydrogen atom is very similar to doing so for the particle-in-a-box. In addition to the 3 requirements placed on the particle-in-a-box, a 4th one is required for the hydrogen atom. The total probability must equal 1. (i.e. There is a 100% probability of finding the electron on the atom.)

The results for the hydrogen atom can be summarized as follows:

    a) 3 quantum numbers are generated n (principle), ℓ (angular momentum), m_ℓ (magnetic) since the equation is solved in three dimensions.

    b) Instead of solving it in Cartesian coordinates (x, y, z) it is easier to solve and interpret in polar coordinates (ϕ, θ, r). Thus, the solutions have the form $\psi = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi)$ Generally the latter two functions are grouped together because the atom is 3-dimensional and one angle occurs in a plane, while the other occurs out of that plane: $\psi = R \cdot [\Theta, \phi]$.

The Radial Wave Function

We will now look at the two parts separately, taking the radial part first. This is the distance function.

Radial wave equations are shown for the 1s, 2s and 2p orbitals on page 11 of your book. The exact equations are not important to this course, but the general forms shown below are (where e.g. "K_{1s}" is a constant):

$R_{1s} = K_{1s}e^{(-Zr/a_0)}$

$R_{2s} = K_{2s}(2 - Zr/a_0)e^{(-Zr/2a_0)}$

$R_{2p} = K_{2p}re^{(-Zr/2a_0)}$

Not surprisingly, for the 1s orbital we find that the wave function, and hence the probability (ψ^2) of finding the electron, drops off as the electron moves further from the nucleus. Since exponential functions tend to change much more rapidly than do linear ones, the trend of lower electron density with increasing distance is always true at large distances. At small distances variations occur.

A second important point should be noted in the R_{2s} equation. When $Zr/a_0 = 2$, $R_{2s} = 0$. This is a place where the wave function calculates to zero. That is, the electron cannot exist there. This point is called a <u>radial node</u>. While it may seem odd that the electron may exist on either side of the node but not at it, remember the electron is just as much a wave as it is a particle. Recall from the particle-in-a-box handout, the solution was a cosine function, which naturally has a value of zero at

$^\pi/_2$ and $^{3\pi}/_2$. Since the wave function describing the electron is similar, the existence of a node is reasonable.

It is essentially impossible to think of an electron as a standing wave and it is still relatively difficult to treat each point along the wave. A conceptually easier way of looking at the atom is in terms of thin shells centered on the nucleus. Since the electrons on all atoms are spherically distributed, the probability of finding an electron at any point, distance r from the nucleus, is given by $P = 4\pi r^2 R^2$ where $4\pi r^2$ is the surface area of a sphere. Thus, for a 1*s* orbital:
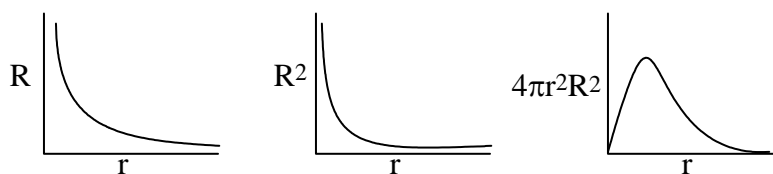

The volume element solves an apparent problem: earlier it appeared as if the electron spent most of the time in the nucleus, which we know is not true.

On page 13 the radial probability functions for the *1s - 3d* orbitals are shown. As you see, a *3s* orbital has two radial nodes, *3p* has 1 node, and *3d* has 0 nodes. Therefore, in general, there are (n - ℓ - 1) radial nodes per orbital.

Angular Wave Functions

The angular wave function yields the shape of the orbital (*s*, *p*, *d*, *f*) and its orientation in space (e.g. p_x, p_y, p_z). Unlike R, $\Theta\Phi$ is independent of n. As n increases, the sizes of the orbitals change, but not the shapes.

The angular wave functions for 3 orbitals, *s*, p_z, and d_{z^2} are shown on p.15. Note for the *s* orbital, $\Theta\Phi$ is a constant. This means there is no angular dependence and a sphere is generated. The *p* orbital takes the form A•cosθ. If the function is plotted on polar graph paper, one obtains a figure that looks something like the 2-lobe form you are used to seeing. It also gives rise to the plus and minus signs you have seen placed in orbitals earlier. Squaring this function yields a diagram (shown below) that shows the probability of finding the electron and is the shape of the orbital you are familiar with seeing.
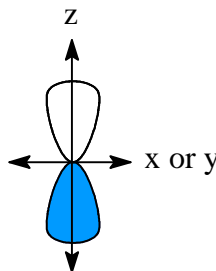
There are two things worth mentioning here. The first has to do with the +/- signs (or the white/blue shading in the figure). These signs refer to the amplitude of the wave function, <u>not</u> the charge on the electron. Electrons are <u>always</u> negatively charged. When a cosine function is drawn on Cartesian graph paper, the wave undulates above and below the zero line. When the wave is above the line the amplitude is positive; when it is below the line the amplitude is negative. If you look at the plot of a cosine function on polar graph paper you will see how the two lobes have either fully positive or negative amplitudes. The second point has to do with the various pictorial representations of orbitals shown in the book (in particular on p. 16). The simplest drawings (e.g. Figure 2.9a-c) give you a very qualitative view of the orbital, perhaps including the sign of the wave function. They are the easiest to draw. Electron density diagrams (e.g. Figure 2.7a) have the advantage of showing either (from a particle perspective) where the electron spends relatively more of the time or (in the wave view) where the amplitude is greatest. Contour diagrams (e.g. Figure 2.7b, 2.8) have the advantage of providing all of the information provided by the other types of figures and the location of the nodes as well.

The wave function for a d-orbital, $A(B \cdot \cos^2\theta - 1)$, yields 4 lobes. Each type of orbital has a fixed number of <u>angular nodes</u> associated with it. Number angular nodes $= \ell$. One feature of d orbitals that everyone notices is the odd shape of the d_{z^2} orbital relative to the other 4 orbitals. Why is it that the d_{xy}, d_{xz}, d_{yz}, and $d_{x^2-y^2}$ orbitals all have 4 lobes while the d_{z^2} orbital consists of a double lobe with a torus about the center? The answer lies in a mathematical curiosity. When the Schrödinger equation for $\ell = 2$ is solved, one obtains six solutions, not five. Physical reality allows only five orbitals, so the d_{z^2} orbital is a result of the "averaging" of two of the solutions.

Notice how on moving from any position (x, y, z) on an s orbital to a position on the other side of the nucleus $(-x, -y, -z)$, the sign of the wave function remains the same (positive). In contrast, the sign changes in the p-orbital. Orbitals that do not change signs on opposite sides of the nucleus

have <u>gerade</u> (even) symmetry. Those whose wave function changes signs are <u>ungerade</u>. *S* and *d* orbitals are gerade, while *p* and *f* orbitals are ungerade. This feature will become important when we discuss bonding.

Energies of Orbitals

The energies of the electrons in hydrogen atom orbitals are determined solely by the principle quantum number, n, which may have any integral value (1, 2, 3 ...). When n = ∞ the electron is lost and the atom is ionized. The <u>angular momentum q.n.</u>, ℓ, represents the shape of the orbital and may have integral values of 0 to (n - 1). Commonly, letters are used to represent this quantum number. $0 = s, 1 = p, 2 = d, 3 = f, 4 = g, ...$

The <u>magnetic q.n.</u> m_ℓ, gives the number of each type of orbital and its orientation in space. There are $(2\ell + 1)$ of each type of orbital and the orientations are designated by $m_\ell = \ell ... -\ell$. In the absence of an external magnetic field (or other perturbing force) the orbitals with the same n and ℓ are equal in energy or <u>degenerate</u>. (In the presence of a magnetic field the orbitals differ in energy, hence the name *magnetic* q.n.). It turns out that when all of the m_ℓ orbitals are combined for any ℓ value, the product orbital has spherical symmetry just like an *s* orbital. That is, at any distance, r, from the nucleus, ψ^2 is the same, regardless of the angle.

There is a summary of the rules just discussed on the top of p. 20.

The Polyelectronic Atom

Now what happens when atoms possessing more than one electron are considered? The wave functions for such atoms cannot be determined exactly. This is because 3 (or more) interactions occur simultaneously. For helium, the nucleus is attracted to each electron and the electrons repel one another. The problem is that the wave equation that describes the motion of each particle must include terms for interactions with the other two particles, both of which move independently. Hence, there is no exact solution. The most common approximation is done by first assigning reasonable wave functions to each of the electrons. One is refined, while the others are held constant. This is done sequentially and repeatedly until the energy of the system changes by an

insignificant amount. Of course, "insignificant" is a relative term and different people will select different values to terminate the calculation. Nonetheless, over a very broad range of cut-off values, the appearance of orbitals does not change appreciably.

It has been found the orbitals in multi-electron atoms are very similar to those in the hydrogen atom and are thus called hydrogen-like orbitals. Unlike for hydrogen, in multi-electron atoms different orbital types differ in energy if they are occupied. For any principle q.n. *s < p < d < f.* We'll get to why later.

The general energy ordering of orbitals is shown in the middle of p. 21 and in the diagram at the top of p. 22. For the most part, the order follows increasing n, then ℓ. That is *1s < 2s < 2p < 3s...* the two exceptions being n*d* is always higher that (n + l)*s* and n*f* always follows (n + l)*d*^{1}.

Electron Spin and the Pauli Principle

Rotating a magnetic field establishes an electric field. This is how hand crank generators operate. The opposite is also true, a spinning charged particle generates a magnetic field. It was known that some atoms interacted with a magnetic field suggesting the electrons were spinning. When the Schrödinger equation is solved with time included, a new quantum number is produced. It can have only two values, ±½. (Classically, clockwise/counter-clockwise spins) This quantum number was assigned to "spin" because the electron behaves as if it were spinning. In reality, the nature of this q.n. is more complicated because waves don't "spin," at least not in the classical sense.

Atoms with all electrons spin paired (equal number of each) are diamagnetic. Those with one or more unpaired electrons are paramagnetic. The Pauli exclusion principle tells us that no two electrons may have the same 4 quantum numbers.

The Aufbau Principle and Hund's Rule

The aufbau principle describes a method for filling atomic orbitals. The atomic orbitals are filled according to the list on p. 21, that is *1s, 2s, 2p, 3s, 3p, 4s, 3d,* … Within subshells with multiple orbitals (e.g. *p, d, f*) electrons are placed singly in each orbital until all contain 1 electron, then the electrons are paired. This is because the electrons repel each other and each orbital is

directed towards a different region of space so the electrons can get away from each other.

Be able to write out the electron configuration of <u>any</u> element using the ordering on p. 21. Do not worry about the exceptions just treat them as if they were normal.

We won't deal with term symbols in this course. Hund's rule states that ground state electronic configurations have maximum spin multiplicity once the aufbau principle has been applied. What this says is that unpaired electrons in degenerate orbitals will have the same spin alignment. For example, consider 2 electrons in *2p* orbitals. The aufbau principles tells us the electrons will go in different orbitals, while Hund's rule tells us they will both be either spin up or spin down.

Periodicity of the Elements

As the book points out, the development of the periodic table is an interesting story. The same information that lead to the discovery of the periodic table is part of what makes it very useful to the practicing chemist. Knowing the position of an element tells its most stable oxidation states and the types of bonds it forms and their strength among other things. A knowledge of atomic structure makes it even more valuable.

E.g. the alkali metals: oxidation state +1 for all and ionic bonds for all elements in the group.

All transition metals have a stable +2 oxidation state except group IIIB.

We will look at this in greater detail in the lab part of the course.

Semantics, History, and Other Questions

Read on your own, but I will address one point here. Why do some chemists, myself included, not think of Zn as a transition metal? Because of its reactivity. It behaves just like Mg. What about Cu^+? Cu^{2+} meets the general criteria, as does Hg_2^{2+} and some Cd compounds. I would argue solely on the basis of chemical reactivity that zinc is only nominally a transition metal.

Shielding

Now we begin to apply some of these more abstract concepts to the physical and chemical properties of atoms.

With each successive electron added to an atom, a proton is also added. In a one electron atom or ion, the energy of attraction of an electron to a nucleus is given by

$$E = \frac{Z^2}{n^2}$$

where Z is the nuclear charge. Since Z increases faster than n, this would suggest that as one moves through the periodic table electrons are pulled increasingly closer to the nucleus and it would be more difficult to pull off an electron. Of course, this is wrong. Alkali metals are a case in point.

So why does the energy of an electron behave differently from what the equation predicts? Begin by noting that hydrogen is the only one electron element. Two factors must then be considered. First, as n increases the energy of the electron increases and this forces it away from the nucleus. The increase in distance reduces the electron nuclear attraction, but there is more to it than this. An electron with a smaller n will spend a substantial portion of the time between the nucleus and an electron with a higher n.

$$\oplus \cdots\cdots e^- \cdots\cdots e^-$$
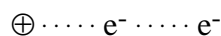
The outer electron experiences less electrostatic attraction (1 proton is partially to completely canceled) to the nucleus and is repelled by the inner electron. Thus, this electron experiences a lower _effective_ nuclear charge than the electron closer to the nucleus. As larger numbers of electrons are added the lowering of Z can be substantial. This process is called _shielding_.

The second factor that affects Z is the shape of the orbital. There are four orbital types: _s_, _p_, _d_, and _f_. The _s_ orbital is spherical with the electron density concentrated near the nucleus. In contrast, the _p_ orbital has a nodal plane passing through the nucleus. This has the effect of forcing electron density away from the nucleus. For _d_-orbitals (2 nodal planes) and _f_-orbitals (3 nodal planes) the effect is more pronounced. Orbitals that allow electron density to concentrate closer to the nucleus are said to be more _penetrating_.

Electrons in more penetrating orbitals shield other electrons better than electrons in less penetrating orbitals.

Some general trends:

1) Orbitals within the same subshell do not shield each other.

2) Orbitals with the same n shield each other poorly

3) Orbitals in the previous shell shield well.

4) Orbitals 2 or more shells lower shield completely.

e.g. Z_{eff} for Ar   1s: 17.5   2p: 14.0   3p: 6.8

                         2s: 12.2   3s: 7.8

Skip "**Slater's Rules and Modifications**."

The Sizes of Atoms:

As the book points out the size of an atom depends on how and where the measurement takes place. The specifics will be covered later but two general trends are known:

1) Atomic size increases down a group. The principal q.n. increases and the electrons are placed in successively less penetrating, better shielded orbitals. The result is the nuclear-valence electron attraction is reduced and the electron moves away. The book lists Z_{eff} for Group IA on p. 35.

2) Within a period the size of atoms <u>decreases</u> left to right. Here n remains constant. From the rules given in the shielding section, we know that electrons in orbitals of the same shell and subshell shield each other poorly. Therefore, as one moves from left to right each time an electron is added, so is a proton. Each proton adds 1 to Z, but since the new electron is not well shielded by the last electron, it experiences most of the electrostatic attraction of the new proton, and is pulled closer. Data for Group IIA are provided on p. 35.

Ionization Energy

This is the energy required to remove an electron from an isolated, gas phase atom or ion. It is <u>always</u> positive (endothermic).
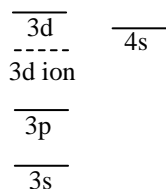
IE tends to decrease down a group because the principal q.n. increases (i.e. the size increases) and the valence electrons are well shielded. IE tends to increase right across a period. In this case, n is constant. Protons and electrons are both being added and the new electrons are poorly shielded so they are held more tightly. The increase is not smooth, however. On moving from Group IIA to IIIA or B the newest electron is placed in a different type of orbital (*p* or *d vs*. *s*). Since the *s* shields a little better than the others the increase should be a little smaller than expected.

Finally, the IE of elements with half-filled subshells (see nitrogen on p. 36) is slightly higher (more endothermic) than expected. This is because in a half-filled shell there is a uniform distribution of electrons with the same spin. This Pauli stabilization is maximized in half-filled subshells.

Ionization

This section begins by stating the obvious. For the most part, electrons are removed from an atom (ionization) in reverse order of addition. (That is: last in, first out.) The major exceptions to this rule occur in the transition metals. Here the n*s* electrons are added before the (n-l)*d* electrons and are removed first. Why?

The book gives one general explanation. Here is a plausible extension. Turn to p. 13 and look at the *3s* and *3d* orbitals. The *4s* will have a very similar diagram to the 3*s* with 4 humps with largest being a little further from the nucleus. I'll use the *3s* for my arguments since you have the picture. The line between 400 and 600 pm is the *3d* maximum. The area under the curve to left of this line is larger for *3d* than for *3s*, however the *3s* puts some electron density closer to the nucleus. Now consider an argon atom. When a proton and an electron are added where does the electron go? The space around the nucleus has 18 electrons so e⁻-e⁻ repulsions are significant. Since the *3d* electron has a higher probability of being in this region its repulsions, and hence its energy, are raised relative to *4s*. When electrons are removed from transition metals two things come into play. (1) Reduced e⁻-e⁻ repulsions lower the energy of *3d* more than *4s* and (2) higher Z_{eff} will lower the energy on the electrons that spend the greatest time near the nucleus. Thus, residual electrons wind up in *3d*. This is explained it greater detail in one of the handouts.

$$
\begin{array}{cc}
\overline{} & \\
\text{3d} & \overline{} \\
\text{-----} & \text{4s} \\
\text{3d ion} & \\
\overline{} & \\
\text{3p} & \\
\overline{} & \\
\text{3s} &
\end{array}
$$

I'd like to emphasize a point the books makes. It is the total energy of the system that matters.

Therefore, you must consider the aggregate effect of principal q.n. and orbital shape (angular momentum q.n.) on both the initial and final states (e.g. pre- and post-ionization) when considering into which orbital an electron goes or from which it is removed.

Electron Affinity

The energy released when an electron is added to the valence shell of a gas phase atom or ion is <u>electron affinity</u>. This is a great definition intuitively, the problem is its sign convention is opposite to the standard practice. We will get around this by using ΔH.

   e.g. $F_{(g)} + e^- \rightarrow F_{(g)}^-$ EA= 328 kJ/mol ΔH= -328 kJ/mol
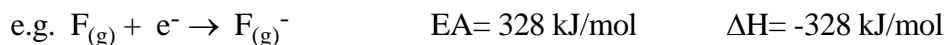
   Some general notes:

   1) The second EA of <u>all</u> atoms is <u>always</u> endothermic.

   2) The first EA of open subshell atoms is exothermic.

   3) The first EA of closed subshell atoms is zero.

   4) First EA generally become more exothermic left to right across a period.

The point made by Figure 2.13 (p. 41) is worth remembering.

August 25, 2014