Chapter 5 – Bonding Models in Inorganic Chemistry: 2 The Covalent Bond

Lewis Structures

Read this section as a review. It is assumed that you remember this. (pp 138-9)

Valance Bond (VB) Theory

VB theory begins with the assumption that the atomic orbitals of two bound atoms overlap to form a bond. Mathematically, atomic orbitals overlap by multiplying the wave functions.

Thus for H_2: $\psi_{H2} = \psi_{A(1)}\psi_{B(2)}$

where $\psi_{A(1)}$ refers to the first hydrogen atom (A) and its electron (1), and

where $\psi_{B(2)}$ refers to the second hydrogen atom (B) and its electron (2).

This is simple enough, but turns out to be very inaccurate because it's too simplistic. Indeed, the very definition of a covalent bond as a "shared" pair of electrons suggests a problem with this equation. For this reason, modifications to correct for inaccuracies in this equation are added. For example, the initial equation includes the assumption that each electron remains completely associated with the nucleus to which it was initially assigned. In fact, there is no reason why the electrons cannot switch positions. i.e. An electron exactly half-way between the nuclei doesn't remember to which nucleus it was originally associated and is equally likely to go to either nucleus. Likewise, while energetically unfavorable, there is no reason why both electrons cannot be on the same nucleus for brief periods. The result can be thought of as an ionic correction (i.e. H^+ H^-). Including these corrections into the equation yields:

$$\psi = \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} + \lambda\psi_{A(1)}\psi_{A(2)} + \lambda\psi_{B(1)}\psi_{B(2)}$$

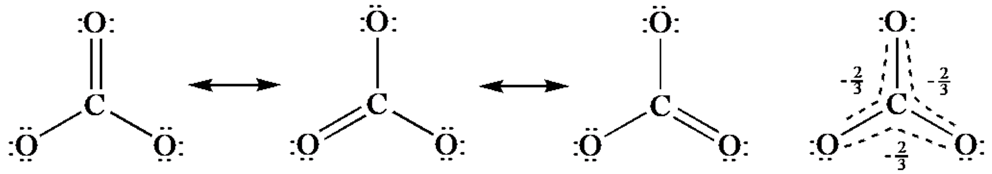
where $\lambda << 1$

A third correction allows for the electrons shielding each other. These corrections yield about 85% of the experimental energy and come within 0.008 Å of the experimental bond length. Other, more involved corrections, provide more accurate predictions. The best wave function to date has over 100 terms and is accurate to within 0.002%. It's worth noting that, unlike the sum you've been shown here, not all of those one hundred terms have physically explainable meanings.

Resonance occurs when more than one energetically reasonable structure can be drawn for a molecule. There are two possible types of resonance structures. One takes charge separation into account. For example, for the HCl molecule there will be a significant ionic contribution from H^+Cl^-. There will also be a very small contribution by H^-Cl^+. Mathematically this is expressed as

$$\psi = a\psi_{cov} + b\psi_{H^+Cl^-} + c\psi_{H^-Cl^+} \quad \text{where } a > b >> c.$$

The second resonance type is more familiar. The book uses a classic example, the carbonate ion. Here three equivalent structures can be drawn.



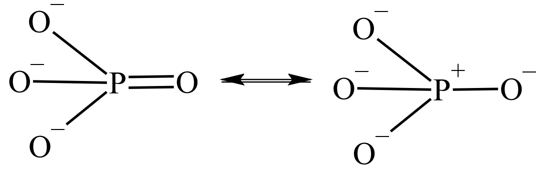
I II III average

$$\psi = d\psi_I + e\psi_{II} + f\psi_{III} \quad \text{where } d = e = f \text{ since the structures are equivalent}$$

Here the double bond is delocalized over 4 atoms. In the case of carbonate all three structures are equivalent so each contributes equally to the actual structure. As we will see next, this is not necessarily so. When structures contribute different amounts, the relative contributions must be determined.

General rules to yield resonance structures include:

1) The number of bonds should be maximized consistent with other structure drawing rules. (e.g. no pentavalent carbons)
2) The atoms must always occupy the same relative positions.
3) Formal charges on atoms should be minimized and should be placed reasonably according to atom electronegativities. (e.g. negative charges on more electronegative atoms).



Opposite charges should reside as close to each other as possible.

4) The number of unpaired electrons should be the same (usually zero).

Formal Charges

These are charges (Q) assigned to covalently bound atoms as if each atom possessed half of the electrons in the bonds it makes (i.e. each atom has the same electronegativity).

$Q = N_{AE} - N_{LPE} - \frac{1}{2}N_{BPE}$

N_{AE} = number of atomic electrons
N_{LPE} = number of lone pair electrons
N_{BPE} = number of bonding pair electrons

Example: CH_4 $Q_C = 4 - 0 - \frac{1}{2}(4 \times 2) = 0$
$Q_H = 1 - 0 - \frac{1}{2}(1 \times 2) = 0$

Remember that formal charges are just that: a formality, they should not be taken literally. Nonetheless, formal charges really do tell us something about the charge distribution within a molecule. Typically, you can do this by simply looking at electronegativities, but that doesn't always work. For example, the formal charges on carbon monoxide are reversed from the electronegativities (p. 148) resulting in a nearly non-polar molecule. Thus, if the formal charges are reversed (based on electronegativity) bond polarity will be reduced. Conversely, if they align as expected, the bond will be more polar than expected based on electronegativity alone. Nonetheless, while formal charges may provide you information about where nucleophilic or electrophilic attack may occur, these sites should not be viewed as ionic. On p. 148 the book shows a way to calculate formal charges that is interesting, but not required.

Hybridization

This is a central feature of VB theory. We will first address how, then why.

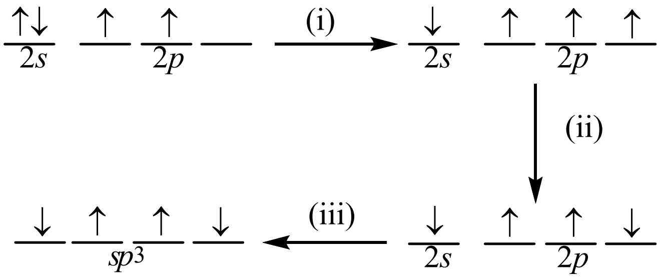
Hybridization can be viewed as a three-step process.

i) Promote paired electrons into their own atomic orbital

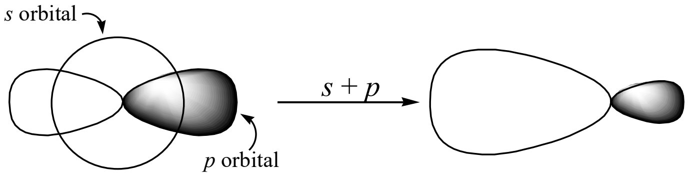
ii) Randomize the spins

iii) Mix the orbitals

Pictorially for carbon:



But why does this occur or, more specifically, why is it energetically favorable? First look at the shape of the hybrid on p. 150. It is formed by adding the wave functions of an *s* and a *p* orbital (to yield an *sp* hybrid, note the picture below does not illustrate the actual shape well).



Where the signs of the wave functions are the same, the waves add (constructive interference) and a large lobe is created. Where the signs are opposite they cancel (destructive interference) and a small lobe is generated. The resulting hybrid has a huge, broad lobe for overlap and consequently larger bond energies are obtained. An interesting feature of these orbitals is their shape (p. 150). As you can see, they are blunter than *p* orbitals, which also provides for their improved overlap. See Table 5-3 on p. 153: hybrid-H bonds 410-500 kJ/mol *vs*. *p*-H at 335 kJ/mol. The extent of overlap decreases according to the series: $sp > sp^2 > sp^3 >> p$, due to shape. There are 6 sets of hybrid orbitals.

sp - linear (2)
sp^2 - trigonal (3)
sp^3 - tetrahedral (4)
sp^2d – square planar (4)
sp^3d - trigonal bipyriamidal (5)
sp^3d^2 - octahedral (6)

All except sp^3d yield a set of equivalent orbitals, sp^3d can be thought of as a combination of 3 sp^2 and 2 dp hybrids. Of these, sp^2d may be new to you because it is sometimes not taught/emphasized in freshman chemistry. Finally, like atomic orbital subshells, overlaying all of the orbitals of a given hybrid set generates a spherical distribution of electron density. (The Orbitron is an award winning website at the University of Sheffield that can help visualize many of these concepts.)

Read the rest of this section on your own.

Molecular Orbital (MO) Theory

There is a major conceptual difference between VB and MO theory. In VB theory we talk of overlapping orbitals to form a bond and this seems to be intuitively reasonable. While qualitatively the process seem very similar, MO theory uses the atomic orbitals of its constituent atoms to create MOs are that are completely new entities, although the MOs frequently resemble the atomic orbitals. This is reasonable since core electrons are not involved in bonding and even valence electrons are not going to be completely separated from the parent atomic orbital. One thing to remember is that **each atomic orbital will give rise to one MO**. The Orbitron website has nice images of both atomic and molecular orbitals. It is linked on the 448 webpage as well as here.

There are many methods of generating MOs and the one we will use is linear combinations of atomic orbitals. We will use H_2 as an example with ψ_A and ψ_B representing the electrons on the respective hydrogen atoms. There are two possible linear combinations

$\psi_b = \psi_A + \psi_B$ (ψ_b = bonding MO, sum is a constructive interaction)

$\psi_a = \psi_A - \psi_B$ (ψ_a = antibonding MO, difference is a destructive interaction)

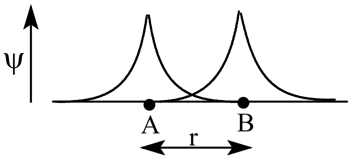
For H_2^+ (1 electron system) $\psi_{H2} = \psi_b = \psi_A + \psi_B$

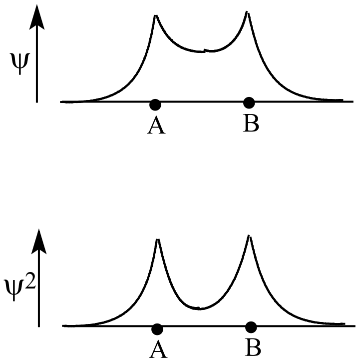
For H_2 (2 electron system) $\psi_{H2} = \psi_b^2 = (\psi_A + \psi_B)^2$

$$= \psi_{A(1)}\psi_{A(2)} + \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} + \psi_{B(1)}\psi_{B(2)}$$

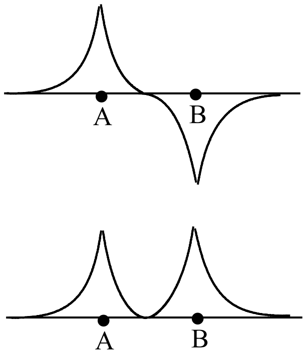
Note how similar this is to the VB equation. Here the ionic contribution is weighted too heavily, but this can be corrected for.

ψ_A and ψ_B can be represented pictorially (p.155) by:





$\psi_A + \psi_B$



$\psi_A - \psi_B$

At the center points the values of ψ^2 can be easily calculated:

$(\psi_A + \psi_B)^2 = \psi_A^2 + 2\psi_A\psi_B + \psi_B^2 = 4\psi_A^2$ (since $\psi_A = \psi_B$ for H_2)

$(\psi_A - \psi_B)^2 = \psi_A^2 - 2\psi_A\psi_B + \psi_B^2 = 0$

Molecular orbitals may be divided into three categories:

bonding MOs – the signs of the interacting wave functions are the same, the interaction is a net attraction. When A and B are the same element, there is a maximum electron density in the center. (The peaks over A and B arise from core electrons.)

antibonding MOs – the signs of interacting wave functions are opposed, so the interaction is **repulsive**. That is, the atoms are pushed apart. This is because electron density is forced from between the nuclei and the nuclear charges are not screened from each other. When A and B are the same element, there is no electron density in the center resulting in the nuclei repelling each other.

nonbonding MOs – occurs for lone pairs and when half of interacting wave functions have the same sign and half are opposed (e.g. ⊕ ⊕ – *vs.* ⊕ – –). If the signs of the end functions are fixed and opposed the middle is irrelevant. Nonbonding is no **net** interaction or overlap.

Skip normalization through end of section (pp. 156-157 (top)).

Symmetry and Overlap - Read on your own.

Symmetry of MOs

Sigma (σ) bonds possess no nodes that include the internuclear axis. Pi (π) bonds possess 1 node that includes the internuclear axis. Delta (δ) bonds possess 2 nodes that include the internuclear axis. Antibonding orbitals are designated with an asterisk *. Note the symmetry of the MO is the same as the atomic orbital of analogous designation: i.e. $\sigma \approx s$ = gerade, $\pi \approx p$ = ungerade. (From the German for "even" and "odd," respectively.)

MOs in Homonuclear Diatomics

These are the simplest molecules and will be discussed before heteronuclear diatomic molecules and polyatomic molecules.

There are two criteria for formation of a bond:

1) There must be net positive interaction between the orbitals of interacting atoms. (i.e. the signs of the wave functions must be the same)
2) The orbitals must have roughly equal energies. (i.e. 1*s* interacts well with 1*s*, 2*s* with 2*s*, 2*p* with 2*p*, etc.) We shall soon see that if necessary, any two valence atomic orbitals with the proper symmetry will combine. Generally speaking, as the energy difference between the atomic orbitals that form a bond increases (e.g. 1s/1s vs. 1s/2s), the bond energy decreases. For example, H-F → H-I is 570, 432, 366, 298 kJ/mol.

A bonding interaction is expressed as: $\sigma_{1s} = \psi_{1sA} + \psi_{1sB}$ or $\sigma_{1s} = 1s_A + 1s_B$

where A & B are labels used to designate the atoms of a homonuclear diatomic molecule

An antibonding interaction is expressed as: $\sigma_{1s}^* = \psi_{1sA} - \psi_{1sB}$ or $\sigma_{1s}^* = 1s_A - 1s_B$

These expressions are very similar in presentation to those in H_2 and are identical mathematically. The level of bonding interaction between 2 atoms is described by bond order, which is similar to the number of bonds in a molecule.

B.O. = 1/2 (number of bonding electrons - number of antibonding electrons)

Examples of some homonuclear diatomic molecules include:

H_2: σ_{1s}^2 B.O. = ½(2 - 0) = 1

He_2: $\sigma_{1s}^2\ \sigma_{1s}^{*2}$ B.O. = ½(2 - 2) = 0 This “molecule” does not exist.

B_2: KK $\sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi_{2p}^2$ B.O. = ½(4 - 2) = 1 (KK refers to core e^- in the molecule)

C_2: KK $\sigma_{2s}^2\ \sigma_{2s}^{*2}\ \pi_{2p}^4$ B.O. = ½(6 - 2) = 2

N_2: KK $\sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2p}^2\ \pi_{2p}^4$ B.O. = ½(8 - 2) = 3

O_2: KK $\sigma_{2s}^2\ \sigma_{2s}^{*2}\ \sigma_{2p}^2\ \pi_{2p}^4\ \pi_{2p}^{*2}$ B.O. = ½(8 - 4) = 2

There are several points worthy of note.

1) Fractional bond orders are possible. e.g. Li_2^+: $\sigma_{2s}^2\ \sigma_{2s}^{*1}$ B.O. = ½ (2 - 1) = ½. This ion actually exists with a longer bond length than Li_2. Valence bond theory does not have any formal way of dealing with fractional bonds.

2) You would expect the B_2 molecule would begin by filling a σ_{2p} before the π_{2p} but the reverse is observed. This is because the energy gap between 2*s* and 2*p* is not large, and for the σ_{2p} bond the 2*s* can mix in. This has the effect of raising the energy of the σ_{2p} orbital. Note on Fig. 5.13 (p. 165) mixing with the σ^*_{2s} also occurs. You may remember from 211, this unexpected, and confusing, situation when learning about B_2 – N_2 vs. O_2 – Ne_2.

3) When filling MOs the same rules apply as for atomic orbitals. Thus, for a pair of orbitals, the first electron goes in either orbital, the second in the other orbital. This suggests that C_2 and O_2 should be paramagnetic, which is experimentally observed.

Bond Lengths and Ionization Energies

As was mentioned for Li_2, experimental evidence for the MO model of molecules comes from bond lengths. Ionization energy provides further supporting evidence.

An example from the book:

	B.O.	Bond Length
O_2^+	2.5	112 pm
O_2	2	121 pm
O_2^-	1.5	126 pm
O_2^{2-}	1	149 pm

The book shows you that the ionization energy of NO (894 kJ/mol) is much smaller than that of either an isolated nitrogen atom (1402 kJ/mol) or an oxygen atom (1314 kJ/mol). On first consideration, one would expect the ionization energy of NO to be slightly less than average of these values. This is because the ionization of an electron from the molecule would spread the charge over two centers. The ionization energies of the component atoms are comparable, so the charge would be shared roughly equally and, so, the ionization of the molecule would be a little lower than the average of the ionization energies. Yet it is about 35% less. Why? The electron is taken out of a high energy antibonding orbital. (An aside, based on electronegativities, one would expect oxygen to have a higher ionization energy than nitrogen. Why are the values reversed?)

Electron Density in Li_2 - F_2: Read this section on your own

MOs in Heteronuclear Diatomic Molecules

The most important difference between heteronuclear and homonuclear diatomic molecules is that the bonding atoms in the former have different electron affinities and ionization energies. Hence, they have differing tendencies to gain or lose electrons.

The component atoms in homonuclear diatomic molecules are the same so their IEs and EAs are the identical, which results in the equal sharing of electron density. In heteronuclear bonds the electron density is shared unequally and is measured in terms of electronegativity. Greater electronegativity is a greater tendency for an atom to attract electrons from an atom to which it is bound.

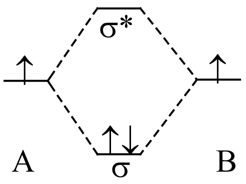
This is represented in equation form by

$\psi_b = a\psi_A + b\psi_B$ and $\psi_a = b\psi_A - a\psi_B$

where $a = b$ in a homonuclear diatomic molecule and $b > a$ if B is more electronegative than A. Note that atom B contributes more to the bonding MO than A, but the converse is true for the antibonding MO. The result is that the greater the difference in electronegativity between two atoms, the more the product MO will be like the parent atomic orbital of the more electronegative atom. (The logical extreme is $a = 0$ and $b = 1$ in a hypothetical purely ionic bond.)

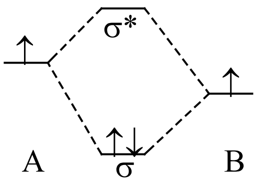
This last point relates the relative covalency/ionicity of a bond to MO theory. If $a = b$, the bond is completely covalent. As the difference increases, ionicity increases. Small a/b differences result in a polar covalent bond, large differences cause an ionic bond.

This can be seen pictorially as follows:



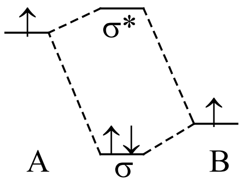
pure covalent

a = b



polar covalent

b > a



ionic

b >> a

It is worth noting that, on the one hand, there is no “magic” value of a/b that leads a bond to be thought of as ionic *vs*. covalent, but on the other there is a relatively narrow range of values that would indicate the transition from polar covalent to ionic bonding. Similarly, many bonds that are empirically treated as nonpolar are actually minimally polar because “a” does not exactly equal “b.” The C-H bond is an example of this situation. One more thing needs to be considered. What about orbitals not used in bonding? These orbitals, particularly if they are in a region of space away from bonding, remain largely unchanged. These are one of the two major types of nonbonding orbitals and correspond to lone pairs in valence bond theory.

Molecular Orbitals in Triatomic Molecules and Ions

We’ll work through the two triatomic species used by the book: BeH_2 and NO_2^+.

The valence shell of beryllium consists of the 2*s* and 2*p* orbitals. Recall from earlier that their energies are similar. Thus, if conditions are right both may be involved in bonding.

First, assume a linear geometry (it’s least crowded) with H-Be-H along the *z*-axis. Then p_x and p_y cannot participate in bonding because they are perpendicular to the bonding axis (and *s* orbitals can't π-bond).

There are two approaches to how the MOs can be constructed. One is an intuitive method which you would probably use at this point. That is, select an orbital on beryllium and match it with an appropriate hydrogen orbital. This turns out to be quite difficult with larger molecules and is not generally used.

A second approach is to treat all atoms bound to the central atom as a group. The difference will seem trivial for BeH_2, however this method is necessary for large molecules. In this approach, the hydrogens can be in-phase ($\psi_{H1} + \psi_{H2}$) or out-of-phase ($\psi_{H1} - \psi_{H2}$). The in-phase combination interacts constructively with 2*s*. The out-of-phase with 2*p*. Antibonding orbitals are obtained by reversing the signs on the hydrogen atoms. See pictures on p. 176 of the textbook.

Thus: $\psi_g = a\psi_{2s} + b(\psi_{H1} + \psi_{H2})$

$\psi_u = c\psi_{2p} + d(\psi_{H1} - \psi_{H2})$

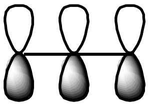
$\psi_g{}^* = b\psi_{2s} - a(\psi_{H1} + \psi_{H2})$

$\psi_u{}^* = d\psi_{2p} - c(\psi_{H1} - \psi_{H2})$

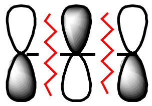
The NO_2^- ion contains 2 types of bonding: σ and π. The sigma bonds will require the *s* and 1 *p* orbital on the nitrogen. Since the nitrogen will have a lone pair, a second *p* orbital is needed. The net effect is a set of orbitals that is essentially equivalent to sp^2.

The π system can be treated similarly to the σ system in BeH_2. That is, the oxygen *p*-orbitals can be treated as a group: $\psi_{O1} + \psi_{O2}$ or $\psi_{O1} - \psi_{O2}$

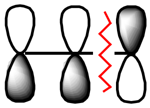
$\psi_b = a\psi_N + b(\psi_{O1} + \psi_{O2})$



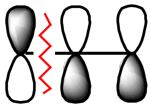
$\psi_b = b\psi_N - a(\psi_{O1} + \psi_{O2})$



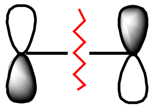
The third orbital is a little different because the same result is obtained whether ψ_N is added or subtracted.



$\psi_n = \psi_N + (\psi_{O1} - \psi_{O2})$



$\psi_n = \psi_N - (\psi_{O1} - \psi_{O2})$



$\psi_n = \psi_{O1} - \psi_{O2}$

(or $\psi_n = \psi_{O1} - \psi_{O2} \pm \psi_N$ as your book puts it.)

This is the second type of nonbonding orbital mentioned earlier in the notes. Skip the symmetry discussion from the middle of p. 178 - 182 (top).

Electronegativity

This is the ability of an atom in a molecule to attract electron density to itself. The Pauling scale is by far and away the most common scale and for general purposes works as well as the others. On page 187-190 five different scales are shown. The Pauling scale is based on a comparison of the bond energy of an A-B bond *vs*. the average of A-A and B-B bond energies.

Mulliken – Jaffe Electronegativity Scale

This method has the advantage of taking into account the number of things bound the atom (i.e. oxidation state) and which orbitals are involved in bonding. The values are relatively easy to calculate.

$$\chi = \tfrac{1}{2}(\mathrm{IE} + \mathrm{EA})$$

Therefore, the scale is based both on how well on atom adds an electron and how well it holds onto its own electrons. Read through the end of paragraph 2 on p. 185, then skip through the text on p. 191.

Variations in Electronegativity

As you can see in Table 5.6 the electronegativity of an atom depends on its hybidization. Why? A relatively simple way to address this question involves examining hydrocarbon reactivity. The pK_a of CH_4 is about 60. For ethylene $pK_a \approx 44$, and acetylene $pK_a \approx 25$. Since carbon and hydrogen have similar electronegativities, this property cannot give rise to the acidity difference. This section discusses Bent's rule, which can be stated as "central atom *s* character concentrates in orbitals directed toward electropositive substituents." In other words, in orbitals used to bond to neighboring atoms, as the percentage of the bonding orbital that is made of *s* atomic orbital increases, the neighboring atom will hold onto its electrons more poorly.

Go back to Table 5.6. Look at the various hybrids and you will see that as *s* orbital character increases, so does electronegativity. The reason is the same as for the acidity difference. First, one will have to know what they have in common:

EN: As *s* character increases, the atom is better able to remove electron density from a neighboring atom.

acidity: As *s* character increases, the carbon is better able to stabilize a product negative charge or better it causes a larger charge separation (polarization in the C-H bond).

The *s* orbital causes this because it penetrates closer to the nucleus than do *p* orbitals. Thus, electrons in *s* orbitals experience greater nuclear attraction.

Read the rest of this section on own.

<u>Pauling's Electronegativity</u> – Read this section on your own.

<u>Other Methods of Estimating Electronegativity</u> – Skip from here to the end of the chapter.

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