

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)

Valence 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 : $\Psi_{H_2} = \Psi_{A(1)}\Psi_{B(2)}$

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. 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 $\lambda \ll 1$

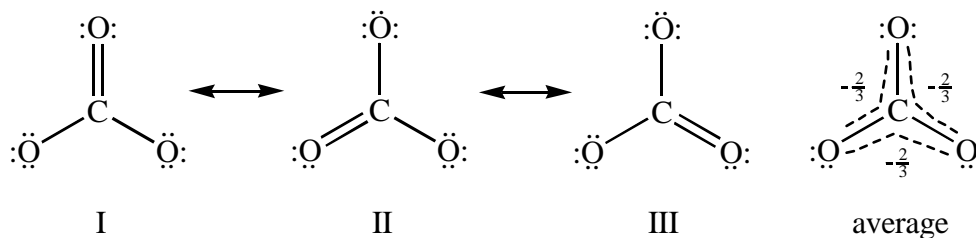
A third correction allows for the electrons shielding each other. These corrections yield about 85% of the experimental energy and come within 0.008 Å of the experimental bond length. Other, more involved corrections, provide more accurate predictions. The best wave function to date has over 100 terms 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 $\text{H}-\text{Cl}^+$. Mathematically this is expressed as

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

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

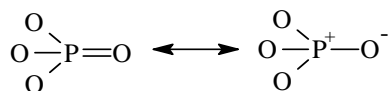


$$\psi = d\psi_{\text{I}} + e\psi_{\text{II}} + f\psi_{\text{III}} \quad \text{where } d = e = f \text{ since the structures are equivalent}$$

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 assigned to covalently bound atoms as if each atom possessed half of the electrons in the bonds it makes.

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

N_{AE} = number of atomic electrons

N_{LPE} = number of lone pair electrons

N_{BPE} = number of bonding pair electrons

Example: CH_4 $Q_{\text{C}} = 4 - 0 - \frac{1}{2}(4 \times 2) = 0$

$Q_{\text{H}} = 1 - 0 - \frac{1}{2}(1 \times 2) = 0$

Remember that formal charges are just that: a formality, they should not be taken literally. Formal charges really 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. 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.

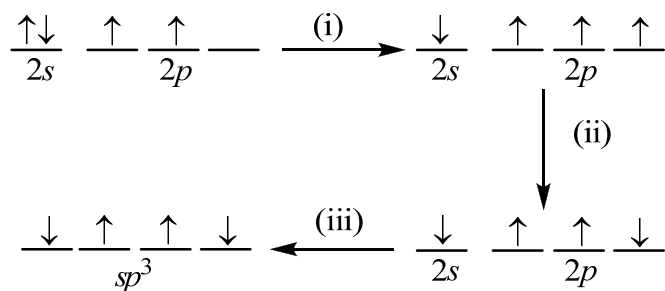
Hybridization

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

Hybridization can be viewed as a three step process.

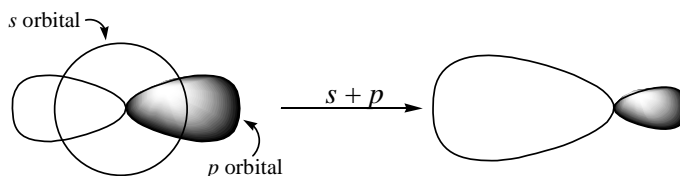
- i) Promote paired electrons into its own atomic orbital
- ii) Randomize the spins
- iii) Mix the orbitals

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).



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 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: $sp > sp^2 > sp^3 \gg p$, due to shape. There are 6 sets of hybrid orbitals.

sp - linear (2)

sp^2d - square planar (4)

sp^2 - trigonal (3)

sp^3d - trigonal bipyramidal (5)

sp^3 - tetrahedral (4)

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 is probably new to you because it is often not taught 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. In contrast, while MO theory uses the atomic orbitals of its constituent atoms, the product MOs are thought of as 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

$$\psi_b = \psi_A + \psi_B \quad (\psi_b = \text{bonding MO, sum is a constructive interaction})$$

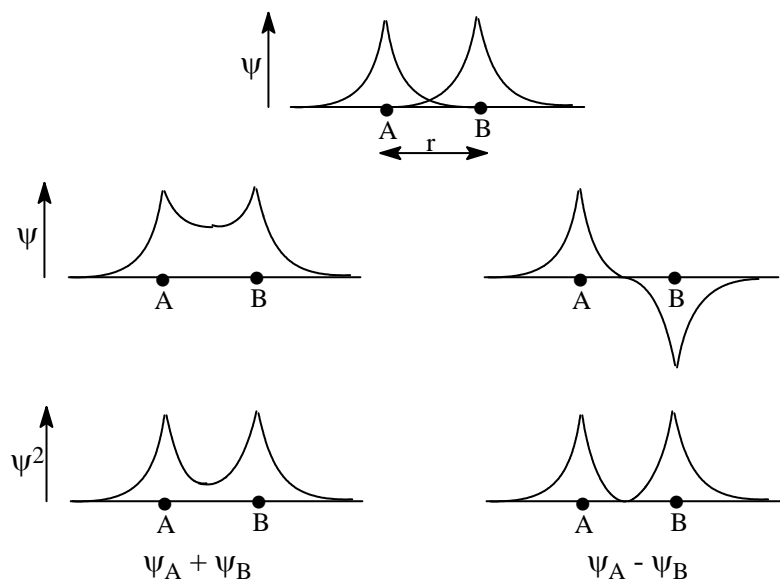
$$\psi_a = \psi_A - \psi_B \quad (\psi_a = \text{antibonding MO, difference is a destructive interaction})$$

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

$$\begin{aligned} \text{For } H_2 \text{ (2 electron system)} \quad \psi_{H_2} &= \psi_b^2 = (\psi_A + \psi_B)^2 \\ &= \psi_{A(1)}\psi_{A(2)} + \psi_{A(1)}\psi_{B(2)} + \psi_{A(2)}\psi_{B(1)} + \psi_{B(1)}\psi_{B(2)} \end{aligned}$$

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:



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

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

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

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.

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.

nonbonding MOs - occurs for lone pairs and when half of interacting wave functions have the same sign and half are opposed (e.g. $\oplus \oplus -$ vs. $\oplus - -$). 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. $\sigma \approx s = \text{gerade}$, $\pi \approx p = \text{ungerade}$.

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. $1s$ interacts with $1s$, $2s$ with $2s$, $2p$ with $2p$, 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, $\text{H-F} \rightarrow \text{H-I}$ 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.

$$\text{B.O.} = 1/2 (\text{number of bonding electrons} - \text{number of antibonding electrons})$$

Examples of some diatomic molecules include:

$$\text{H}_2: \sigma_{1s}^2 \quad \text{B.O.} = 1/2(2 - 0) = 1$$

$$\text{He}_2: \sigma_{1s}^2 \sigma_{1s}^{*2} \quad \text{B.O.} = 1/2(2 - 2) = 0 \quad \text{This "molecule" does not exist.}$$

$$\text{B}_2: \text{KK } \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^2 \quad \text{B.O.} = 1/2(4 - 2) = 1$$

$$\text{C}_2: \text{KK } \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2p}^4 \quad \text{B.O.} = 1/2(6 - 2) = 2$$

$$\text{N}_2: \text{KK } \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \quad \text{B.O.} = 1/2(8 - 2) = 3$$

$$\text{O}_2: \text{KK } \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p}^2 \pi_{2p}^4 \pi_{2p}^{*2} \quad \text{B.O.} = 1/2(8 - 4) = 2$$

There are several points worthy of note.

- 1) Fractional bond orders are possible. e.g. $\text{Li}_2^+ : \sigma_{2s}^2 \sigma_{2s}^{*1}$ B.O. = $1/2 (2 - 1) = 1/2$. 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 $2s$ and $2p$ is not large, and for the σ_{2p} bond the $2s$ 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.
- 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 also provides further supporting evidence.

An example from the book:

	<u>B.O.</u>	<u>Bond Length</u>
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. A result is 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.

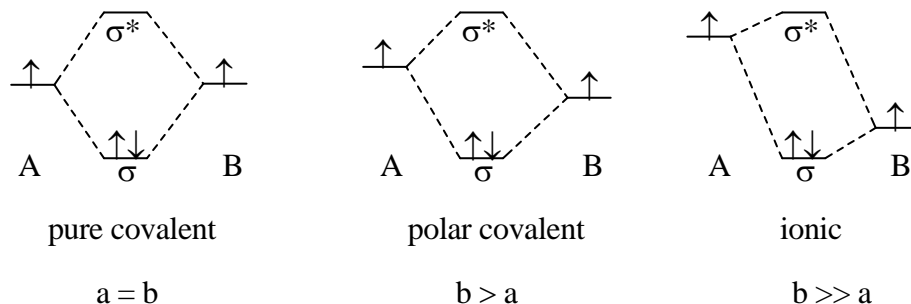
This is represented in equation form by

$$\psi_b = a\psi_A + b\psi_B \quad \text{and} \quad \psi_a = b\psi_A - a\psi_B$$

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. At small differences a bond is polar covalent, at large differences a bond is ionic.

This can be seen pictorially as follows:



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 .” 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 use the two triatomic species used by the book: BeH_2 and NO_2^+ .

The valence shell of beryllium consists of the $2s$ and $2p$ 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 it is necessary for large molecules. In this approach, the hydrogens can be in-phase ($\psi_{\text{H1}} + \psi_{\text{H2}}$) or out-of-phase ($\psi_{\text{H1}} - \psi_{\text{H2}}$). The in-phase combination interacts constructively with $2s$. The out-of-phase with $2p$. Antibonding orbitals are obtained by reversing the signs on the hydrogen atoms.

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

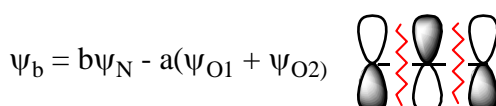
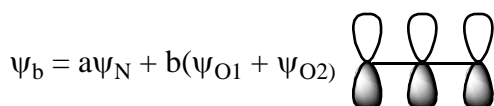
$$\psi_u = c\psi_{2p} + d(\psi_{\text{H1}} - \psi_{\text{H2}})$$

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

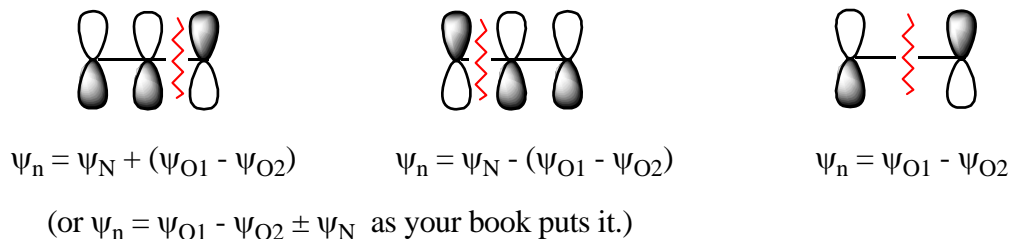
$$\psi_u^* = d\psi_{2p} - c(\psi_{\text{H1}} - \psi_{\text{H2}})$$

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 which 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: $\psi_{\text{O1}} + \psi_{\text{O2}}$ or $\psi_{\text{O1}} - \psi_{\text{O2}}$



The third orbital is a little different because the same result is obtained whether ψ_{N} is added or subtracted.



This is the second type of nonbonding orbital. 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.

$$\chi = \frac{1}{2}(\text{IE} + \text{EA})$$

Therefore, the scale is based both on how well an 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 hybridization. Why? A relatively simple way to address this question involves examining hydrocarbon reactivity. The pK_a of CH_4 is about 60. For ethylene $\text{pK}_a \approx 44$, and acetylene $\text{pK}_a \approx 25$. Since carbon and hydrogen have similar electronegativities, this property cannot give rise to the acidity difference.

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.

Pauling's Electronegativity – Read this section on your own.

Other Methods of Estimating Electronegativity – Skip from here to the end of the chapter.

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