

Chapter 31

ORBITALS, Part 2

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We continue with the Valence Bond Approach.

All of the Examples in the prior Chapter involved single bonds and lone pairs. Now we need to bring multiple bonds into the picture and show how these are handled. First, I need to introduce some new terminology.

31.1 Bond orbital type

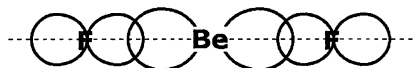
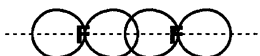
We distinguish bonding orbitals by a classification which uses the lower case, Greek letters sigma, σ , and pi, π . We base this distinction on the orbital's position relative to a bond axis. A "bond axis" is simply an imaginary line which runs through the two nuclei of a bond. A σ orbital lies on the bond axis and includes (at least part of) the bond axis. A π orbital lies on two sides of the bond axis.

We need some pictures.

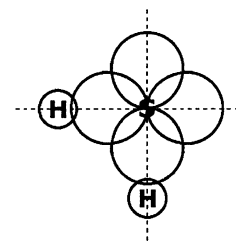
Let's go back to the simplest case, the H_2 molecule. Here's the picture with the overlapping $1s$ orbitals. I've added the bond axis as a dashed line. The bond orbital lies on this axis and encompasses this axis; therefore, this orbital is classified as σ . We refer to this as a σ orbital or we can say that there is a σ bond in H_2 .



σ -type orbitals are the most common and they can arise from numerous kinds of orbital interactions. Let's look at several more examples which we discussed last Chapter, now with the bond axis. This is depicted at left for F_2 ; we see that the bonding orbital lies on the bond axis so that this gives a σ bond. At right, the two bond axes in H_2S are shown; both of those bonds are σ .



At left again, we have the two bond axes for BeF_2 ; since the molecule is linear, the two bond axes are on the same line. Both bonds in BeF_2 are σ .



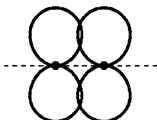
All bonds in all Examples in Chapter 30 were σ bonds. Furthermore, they were single bonds. From all cases covered so far, we can note the following generalities for the Valence Bond Approach.

1. σ bonds can be formed by using a valence AO of s or p type or by using any type of hybrid orbital.
2. Hybrid orbitals can form σ bonds or they can hold lone pairs.
3. All single bonds in a Lewis structure are σ type.

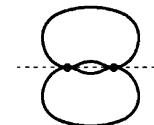
Caution! "Sigma" and "single" sound close to each other, but they are separate terms with their own definitions. Don't confuse them.

Now, π . These are present in all double and triple bonds. Let's see how these arise.

We discussed the nose-to-nose p -to- p interaction in the last Chapter and it is shown again in the diagram above for F_2 . This interaction will always give a σ bond. In addition to nose-to-nose, there's another way for p 's from two atoms to interact, and that is side-to-side; I show this at left with the bond axis drawn in. This side-to-side p -to- p interaction gives another



kind of bonding orbital, which is pictured on the right. There are two parts (lobes) to this one bonding orbital; the shape of each part is referred to as kidney-bean shape. The two parts of the orbital lie on two sides of the bond axis, so this a π orbital.



Actually, the bond axis lies in a nodal plane of this orbital, with the plane slicing between the two lobes (perpendicular to the page as drawn). I had mentioned back in Section 21.6 that p atomic orbitals had nodal planes; π molecular orbitals also have a nodal plane, and the bond axis lies in that nodal plane.

This is the simplest way to form a π orbital and it will be the only way within the coverage here. Our hybrid orbitals will not do π ; they'll only do σ bonds or they'll hold lone pairs. There is an important consequence to note. If an atom has sp^3 hybridization, then all of its valence p orbitals are involved in those interactions and there are no more p AOs available for π . Thus, atoms with sp^3 hybridization cannot form π bonds. On the other hand, if an atom has sp or sp^2 hybridization, then it still has leftover (unhybridized) p AOs which are available for π .

OK, so how do you know which bonds are σ and which are π without drawing things out all the time?

That's easy: it's in the Lewis structure.

31.2 Serving up some pi

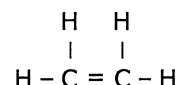
We continue into VBA, now adding π to the menu. Atoms which can form π bonds by using p orbitals are limited to those which have sp or sp^2 hybridization.

In the last Chapter when we discussed sp and sp^2 hybridization, we saw that sp -hybridized atoms still have two of their original p AOs available, perpendicular to the hybrids; we also noted that sp^2 -hybridized atoms have one original p AO available, perpendicular to the plane of the hybrid orbitals. I told you to flag those parts (" p AO") and I told you to remember this for later. Later is now. Also in the last Chapter, we covered cases of sp and sp^2 hybridized atoms but none of those had π bonds. Now, let's start into some cases which do.

We start with ethylene, C_2H_4 . I'm numbering this as Example 5, continuing the Example numbers with the number sequence from the last Chapter. We're still doing the same Steps as before; those haven't changed. If you haven't gotten the Steps down yet, bookmark that page from the last Chapter for handy reference.

Example 5. C_2H_4 .

► Step 1. Lewis. We did the Lewis structure for ethylene in Chapter 26.



► Step 2. Both carbons are central atoms; we assume that each is hybridized. The hydrogens are not hybridized.

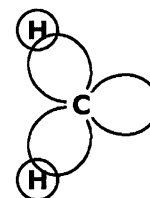
This is our first Example in which more than one atom is hybridized in the molecule. This doesn't really change anything. Just consider one atom at a time.

► Step 3. The left carbon is bonded to three other atoms and it has zero lone pairs. The sum is three; this indicates sp^2 hybridization. It's the same analysis for the right carbon: sp^2 hybridization. Each carbon's hybrid orbitals are in trigonal planar orientation.

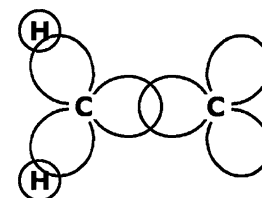
► Step 4. The four hydrogens use their $1s$ orbitals.

► Step 5.

Part a. Start with the left carbon and its three hybrids. Two of the carbon HOs interact with the hydrogen $1s$ orbitals to give two CH σ bonds.

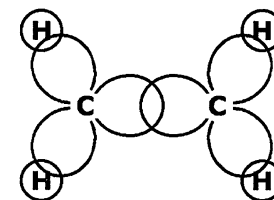


The third HO from the left carbon interacts with a hybrid from the carbon on the right. This gives a CC σ bond.



The carbon on the right uses its two other hybrids to interact with hydrogen $1s$ orbitals, thus giving two more CH σ bonds.

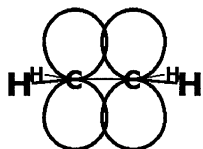
Part b. This Part is not needed.



Here's the partial summary so far.

There are a total of four CH σ bonds, each arising from $(C)sp^2 + (H)1s$.
There is one CC σ bond, arising from $(C)sp^2 + (C)sp^2$.

That's not everything. This accounts for five bond pairs in the molecule, but the Lewis structure says there are a total of six bond pairs as shown by six bond dashes. Notice that the Lewis structure says that the CC bond is a double bond; we must yet account for the second shared pair in this bond.



Each carbon atom still has one remaining $2p$ orbital. This orbital is oriented perpendicularly to the plane of the hybrids. This is shown at left but I've flipped the molecule so that you are looking at its edge. For clarity, the σ bonds from above are now just drawn as lines. In this view, you can see both carbon's $2p$ orbitals as they interact side-to-side, forming the π bond.

Now we can give the full summary.

There are four CH single bonds, all of σ type; each arises from $(C)sp^2 + (H)1s$.
There is one CC double bond composed of one σ orbital and one π orbital. The σ component arises from $(C)sp^2 + (C)sp^2$. The π component arises from $(C)2p + (C)2p$.

All electrons in the Lewis structure have now been accounted for. We're done.

Let me make two notes here.

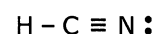
First, it is important to note that the C=C double bond in ethylene is composed of one σ bond and one π bond. This is very general: every double bond in a Lewis structure will be composed of one σ bond and one π bond.

Second, both of the carbons in ethylene have their own, separate, trigonal planar hybrids. There is a catch to note with this arrangement: the trigonal planes of both carbons are required to lie flat with each other because of the π bond. If the separate trigonal planes of the two carbons were not flat with each other, then the $2p$ atomic orbitals could not align properly side-to-side, and this would screw up the π interaction. Thus, the π bond forces the carbons and all of their attached hydrogens to be in one big plane. This is general: for two sp^2 atoms which are connected by a double bond, both of their trigonal planes will lie flat with each other. For ethylene, the whole molecule is planar.

Next.

Example 6. Hydrogen cyanide.

► Step 1. We did the Lewis structure in Chapter 26.



► Step 2. Carbon is a central atom, so we assume that it is hybridized. Nitrogen is terminal and triply-bonded, so we assume that it is also hybridized. The H is not hybridized.

The nitrogen here is our first example of a multiply-bonded terminal atom. This falls under the second assumption of our Hybridization Guidelines.

► Step 3. The carbon atom is bonded to two atoms and it has no lone pairs. The sum is two, so sp hybridization is adopted; the two HOs are in linear orientation. The nitrogen is bonded to one other atom and it has one LP. The nitrogen hybridization is also sp , giving two linear HOs.

► Step 4. Hydrogen uses its $1s$.

► Step 5.

Part a. We'll start with the carbon and its two hybrids. One hybrid interacts with the hydrogen $1s$ to give a CH σ bond.



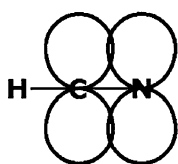
The second HO from carbon interacts with a hybrid from the nitrogen. This gives a CN σ bond.



Part b. The other sp hybrid on nitrogen is used for its lone pair, which is indicated by the two big dots.



The Lewis structure says that the CN bond is a triple bond; so far, we've only accounted for one of the three bond pairs between C and N. The carbon and the nitrogen atoms each have two remaining $2p$ AOs.



These orbitals are oriented perpendicularly to the sp hybrids. This sets up two, side-to-side interactions between C and N. One of these is on the left; the second is on the right, with the orbitals pointing perpendicular to the page. These interactions give two, equal π bonds.



Here's the summary for hydrogen cyanide.

There is one CH single bond; it is σ type and it arises from $(C)sp + (H)1s$.

There is one CN triple bond, composed of one σ and two π 's. The σ component arises from $(C)sp + (N)sp$. Two π components arise from separate combinations of $(C)2p + (N)2p$.

Nitrogen has one lone pair in an sp hybrid.

This accounts for all electrons in the Lewis structure.

The breakdown of the triple bond is general: in every Lewis structure, triple bonds are composed of one σ bond and two π bonds.

As you can see by the ethylene and hydrogen cyanide cases, it is the Lewis structure which first indicates the presence of π bonds. EVERY MULTIPLE BOND IN A LEWIS STRUCTURE INVOLVES ONE OR TWO π BONDS. Thus, the bond orders in a Lewis structure also tell us bond type. Here are the overall results from all Examples so far.

All single bonds in a Lewis structure are composed of one σ bond only.

All double bonds in a Lewis structure are composed of one σ bond and one π bond.

All triple bonds in a Lewis structure are composed of one σ bond and two π bonds.

Notice that every connection in a Lewis structure is at least σ . These relationships are extremely important. Know them.

This concludes the introduction to multiple bonds and to σ and π types. The types described here constitute the most common bonds for covalent bonding between Main Group elements. These are the limit of our coverage here.

I need to mention a bit about delocalization (resonance). I had made the point in Chapter 28 that VSEPR does not care about resonance; since the hybridization of central atoms is based on VSEPR, then the hybridization of central atoms does not care about resonance either. Thus, you can determine the hybridization of a central atom from any resonance structure. On the other hand, terminal atom hybridizations and the rest of VBA does depend on resonance. This could complicate things but, once again, we are only doing VBA for one Lewis structure. Thus, if you did have equivalent resonance structures for a particular polyatomic unit, then you would just do VBA for one of those. (You'll see that in Example 8 momentarily.)

Alright, let's ease up on some of our Approach. All six of our Examples so far illustrated all of Steps 1 - 5, but this is not always needed for every problem which you might encounter. It is common for many instructors to just ask for parts of this treatment. Having gone through all of the Steps, hopefully it will be easier to understand the parts. Here're some samples of questions which you can encounter.

- In BeF_2 , what atoms are hybridized and what are the hybridizations?
- In HCN , what bond types (σ , π) make up the CN bond?
- How many π bonds are in C_2H_4 ?
- In SCl_3^+ , what kind of orbital on sulfur holds the lone pair?
- For NH_3 , what orbitals of N and H combine to make the NH bond?

We've done these compounds in our prior Examples, so each question is answered within the fuller details of those Examples. You can flip back in this Chapter and in the prior Chapter to find the answers. Notice that, if you can work through Steps 1 - 5 as we've been doing so far, then you can answer questions of these types for other polyatomic units. And you may not need all of Steps 1 - 5 to do this.

Let's run through two more Examples, answering only specific questions related to each case.

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Example 7. HNO. This molecule is a bit of an oddity. It's somewhat related to NO but it's diamagnetic, while NO is paramagnetic. Thus, HNO can react quite a bit differently from NO. Who cares? Your body does. Like NO, HNO has also been found to be produced and needed by humans and by other organisms. The discovery of the biological importance of NO was a bit of a surprise, but the discovery of the biological roles for HNO was a bigger surprise. It's somewhat ironic that nowadays we know so

much about huge biological molecules but some of the biggest surprises are often the little things. Now, draw the Lewis structure for HNO. Then, answer the following questions.

How many π bonds are in the molecule? _____

What orbitals interact to form the HN bond? (H) _____ + (N) _____

What type of orbitals hold the oxygen lone pairs? _____

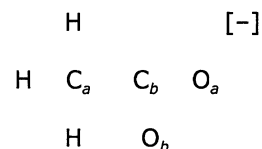
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Here's space for you to do the Lewis structure.

Fill in the blanks to the above questions. Here are possible answers for those blank spaces. One of the entries below will be used twice. Two of the entries below are wrong. Put the correct ones in the blanks above.

sp two sp^2 $1s$ one

OK, let's do one final Example.

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Example 8. Acetate, CH_3CO_2^- . Start with a Lewis structure; here's the setup. Both carbons in acetate are bonded to each other. The three hydrogens are terminal to one of the carbons (labeled C_a); the two oxygens (labeled O_a and O_b) are terminal to the other carbon (C_b). I will also tell you that there are two equivalent resonance structures. Just draw in one resonance structure and work with that. Then answer the questions below.



What is the hybridization of C_a ? _____

One O is hybridized. Which hybridization is used? _____

What orbitals interact to form each of the CH bonds? (C_a) _____ + (H) _____

What orbitals interact to form the CC bond? (C_a) _____ + (C_b) _____

How many total σ bonds are in the molecule? _____

.....
That's enough Examples.

With this, we wrap up our coverage of VBA. We've covered the derivation of σ bond orbitals using hybridized and unhybridized orbitals; we've also covered the derivation of π bond orbitals from p AOs. We've limited our coverage to the basics of Main Group compounds just to keep things at a manageable level. Other things are still possible, such as π bonds between p and d orbitals, but we're not doing that here. If you ever venture into bonding in the d -block or f -block, then still more opportunities arise. For example, transition metals can form sd^n hybrids whereas Main Group compounds only do sp^n hybrids. In fact, transition metals can use various d orbitals to form σ bonds, π bonds and even δ bonds. What's a δ bond? It's an orbital with parts on four sides of the bond axis. Where do you find δ bonds? They're present in quadruple, quintuple and sextuple bonds. I briefly mentioned in Chapter 25 that there are some bonds with orders of four, five and six. A quadruple bond is composed of one σ , two π and one δ . A quintuple bond is composed of one σ , two π and two δ . A sextuple bond is composed of two σ , two π and two δ .

But let's not go there.

31.3 Another point for emphasis

Now that we have completed orbitals, at least using Valence Bond, I would like to return to an important point about bond polarity which was made at the end of Chapter 25. Here's what we did back then.

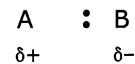
“ ▶ Consider a separate atom A and a separate atom B which will come together and share two electrons, forming a single bond. (For simplicity, I'm leaving out all lone pair electrons here.)



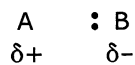
▶ Suppose atoms A and B are the same element. Under these conditions, the electronegativities are identical. The covalent bond is truly nonpolar and the share is exactly even.



▶ Now suppose that A and B are different elements, with B slightly more electronegative than A. Under these conditions, the covalent bond is slightly polar and B has slightly more than an even share of both electrons.



▶ Now we take B to be considerably more electronegative than A. Under these conditions, the bond is considerably polar and B is assuming a much larger portion of the shared electrons. Atom A is losing out considerably on the share.



These pictures are figurative only but, by scooting the dots over toward B, I hope you get the sense of the uneven share. The real story lies with orbitals. Since we aren't doing orbitals until Chapter 30, let me just point out that shared electrons are really in an orbital and that, as B becomes more and more electronegative than A, then the bond orbital field is becoming more and more concentrated on B. THIS IS THE ACTUAL DESCRIPTION. Moving the dots is useful for figurative purposes, but it's the concentration of the orbital field which matters. ”

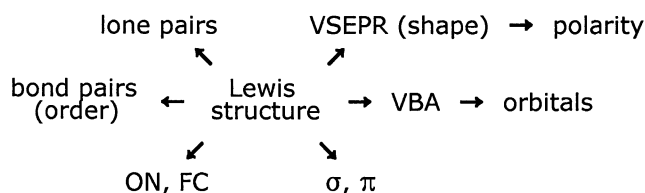
Having now seen what some of these orbitals arise from and look like, it is useful to repeat this for emphasis. In general, bonding orbitals are more concentrated on the more electronegative atom in the bond. By being stronger on the more electronegative atom, the orbital field places more of the negative charge of the shared electrons on the more electronegative atom. This is a big part of bond polarity. And, as we have seen and as we will continue to see, bond polarity is very important.

I'm not adding to this at this time. I'm simply restating this within the orbital context which we have just completed. THIS IS FOR EMPHASIS. It's important.

We now conclude the Valence Bond Approach and we conclude a major undertaking in general.

31.4 Stage 4

We are now at the final Stage of the schematic which we began in Chapter 26. From this, you can clearly see the central importance of the Lewis structure to so many different aspects of the polyatomic unit. Let's summarize this. Directly from the Lewis structure, we see where the lone pairs are, we see where the bond pairs are, and we see the bond orders.



The Lewis structure also provides for the determination of oxidation number and of formal charge. The Lewis structure provides an entry into the VSEPR system for doing shapes and this then leads to molecular polarity. The Lewis structure also provides an entry into the Valence Bond Approach for providing the orbital description of the polyatomic unit. Although VBA tells us about σ and π bonding orbitals, the Lewis structure provides a shortcut and tells us where these are directly.

This is a lot of stuff. It's a lot of important stuff. Remember this schematic. I don't care how you do it. You can put a big arrow in the margin. You can paste a gold star to this page. Or you can highlight it in Tyrian purple. I don't care. Just remember it, or at least remember where to find it.

This is a good time for a brain break. The next Chapter is real different.

Problems

1. True or false.
 - a. Double bonds have two π bonds.
 - b. Hydrogen cannot form a π bond.
 - c. Nose-to-nose p -to- p interaction gives a σ bond.

- d. An atom with sp^2 hybridization can form at most two π bonds.
2. In each of the following, how many total σ bonds and how many total π bonds are there?
- a. PF_3 b. BrO^- c. CO_2 d. $HCCH$
3. For each of the following, describe how the bond orbitals arise and identify the bonds as σ or π type.
- a. CO b. H_3SiCl c. $HNNH$
4. Acrylonitrile is a reactant for making some common types of plastic and rubber materials. The Lewis structure is shown at right. Answer the following questions.
- a. What are the shapes at each of the central atoms?
- b. What atoms are hybridized and what is their hybridization?
- c. How do the bond orbitals arise and are they σ or π ?
- d. What type of orbital holds the lone pair?

