

Chapter 30

ORBITALS, Part 1

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We enter into our last phase of discussion of the polyatomic unit: orbitals. This part of the journey was briefly mentioned when we first started into polyatomics in Chapter 25:

“ ...And, of course, there will be some new stuff, such as orbitals. Not just more atomic orbitals; we will also be doing bond orbitals. These are where the shared electrons reside in the covalent bond. Like atomic orbitals, bond orbitals are field regions but these bond orbitals surround two or more atoms and hold the polyatomic unit together. In addition to bonding orbitals, there are still other kinds of orbitals in polyatomics. ”

The other kinds of orbitals will include nonbonding orbitals and also a strange, new kind of orbital, the antibonding orbital. What is an antibonding orbital? Bad news, that's what it is.

This trek will take us through Chapter 33. At the end of Chapter 33, we will finally cover metallic bonding. Metallic bonding is an extreme case of covalent bonding. We're not ready for that yet.

30.1 Basics

Orbitals are at the very heart of the covalent bond. These orbitals share numerous similarities to atomic orbitals. Like AOs, these are three dimensional regions in space in which electrons can be found. Each can hold two electrons max. If there are two electrons in one orbital, then they must be spin-paired. The strength of the orbital field will be great in some places but this will dwindle to insignificance further and further away. Also as we had done for AOs, we want to know what types of orbitals there are, where they are located, and what are the energies of their electrons. Besides helping us to understand the bonding in a polyatomic unit, these things are also important for understanding chemical reactivity. As always: electrons do chemistry! Electrons in different types of orbitals can do different types of reactions.

We continue the practice since Chapter 25 of only considering the valence electrons from the atoms to be involved in bonding. The core electrons of the atoms do not participate; as such, they are still in their original AOs of *s*, *p*, *d*, etc. type.

Here is a general approach to the formation of a bonding orbital, described for the simplest molecule, H₂. We can describe this bonding orbital as arising from the interaction of the 1s atomic orbitals from each of the two H atoms.



To begin, we start with two separate H atoms, each with 1s¹ configuration. For as long as the atoms are too far apart for any interaction between each other, then the atomic orbitals stay their usual, spherical, 1s type.



Once the two atoms come into interaction range, the nucleus and electron of one atom sense the nucleus and electron of the other atom. Each orbital distorts toward the other atom as a result of this interaction.



As the atoms get closer, the interaction between the fields increases. This interaction results in substantial merging and overlapping of the AOs, resulting in the formation of a new field, the bonding orbital.



This interaction increases as the atoms get closer and closer. Eventually they achieve their optimum limit of approach, which corresponds to the bond length for H₂. Now you have a typical molecule of H₂.

The last orbital shown above is a bonding orbital. The bonding interaction can be derived as the sum of 1s orbitals from the two, separate hydrogen atoms. For our purposes, we will adopt a simplistic representation of this interaction as follows.



This interaction generates a bonding orbital which is now a field region encompassing both atoms of the molecule. This orbital holds the two electrons. This arrangement holds the diatomic unit together through a combination of effects, some of which are not straightforward but which are a consequence of the quantum realm. There is a stabilization brought about by the electrons spreading over two atoms instead of only one. There is electrostatic attraction between each nucleus and each electron; this is enhanced by a contraction of the orbital which brings the electrons closer overall to both nuclei. On the other hand, there is repulsion between the two electrons and between the two nuclei. Other factors also

come into play. The important part is that this is a bonding orbital and now we have a molecule of H_2 . As with any orbital holding two electrons, the two electrons are spin-paired and so H_2 is diamagnetic.

This is the simplest example to do. Once you bring in other kinds of atomic orbitals, then things can get much more complex.

Since this is still part of the quantum realm, some aspects of bonding may seem hard to understand, and many aspects of bonding are even harder to quantify. There are wavefunctions, Ψ , underlying much of this, with Ψ^2 providing the location, as done for atoms in Chapter 21. Most of the wavefunctions cannot be solved directly, so approximations are made. There have been numerous approaches over the years for approximations and we will specifically look at two of these. The Valence Bond Approach (VBA) and the Molecular Orbital Approach (MOA) were the earliest to address the nature of the covalent bond, and these continue today in numerous modifications. These are two tools of the trade and, like any set of tools, sometimes one tool works better for a particular job than the other. We start with VBA in this Chapter, and we pick up MOA in Chapter 32. We will be working on a strictly qualitative, basic level with these. In actual practice, these Approaches can involve very heavy duty computations.

Regardless of method, the general picture is the same regarding the origin of orbitals in a polyatomic: one or more orbitals of one atom interact(s) with the orbital(s) of one or more other atom(s) to produce a bonding orbital (as for H_2), a nonbonding orbital, or an antibonding orbital. This interaction essentially merges atomic orbital fields to produce new fields of bonding, nonbonding or antibonding types. Electrons in bonding orbitals hold the polyatomic together. Electrons in nonbonding orbitals constitute lone pairs. Electrons in antibonding orbitals actually oppose bonding and weaken the bond.

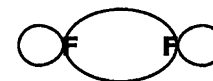
Time to get started.

30.2 The Valence Bond Approach

Let me open up with a few ground rules. Our emphasis will continue to be with Main Group compounds; for these, the bonding interactions derive from s and p orbitals of the valence shell. Although the transition elements extensively utilize d orbitals in their bonding, this is not true for Main Group compounds. There are some contributory roles for d orbital involvement in some cases of multiple bonding but that level of coverage is beyond what we need here. Thus and overall, we are excluding d . Also, due to the issues regarding expanded valence going back to Chapter 26, we will exclude all cases of expanded valence from coverage. Here, we stick to polyatomics with atoms of octet or less. Finally, we won't do antibonding orbitals with VBA; we will, however, use them with MOA in Chapter 32.

Using the Valence Bond Approach for a given polyatomic unit, one would construct a series of resonance structures, possibly several or possibly very many, which may be applicable. (The types of resonance structures involved would extend well beyond our coverage of resonance structures in Chapter 27.) One would then combine these mathematically, in variable amounts, in such a manner so as to obtain the "best" picture for that polyatomic unit. That's a loose description of the process but, for our purposes, we're going to simply work with one Lewis structure, as derived by Chapter 26 and 27 methods, and describe the bonding for that structure in a qualitative, pictorial fashion. In addition to starting with the Lewis structure, we would like to have shape and bond angle information, which can be obtained experimentally or it can be predicted by VSEPR.

Let's take a look at another diatomic. Diatomics are the easiest, since there are only two terminal atoms and there is no shape to worry about. We'll go with F_2 . We begin with the Lewis structure. The Lewis structure tells us that there is a single bond between the two F atoms and that there are three lone pairs on each F. We construct the orbitals in the molecule from the valence orbitals of the two fluorines: the valence orbitals are $2s$ and $2p$. It's the $2p$ orbital that is responsible for the bond in this case; we can formulate this in a manner parallel to the case above for H_2 . When two F atoms come together, a bond orbital arises from the interaction of a $2p$ orbital on one F and a $2p$ orbital on another F. Recall that p orbitals in an atom point in different directions (p_x , p_y , p_z); if the two F atoms point a p directly at each other, then a very strong interaction is obtained. This direction of interaction is called nose-to-nose (or, nose-to-nose p -to- p), and it is shown at left in terms of the atomic orbitals which are involved. The bond orbital which results from this interaction is depicted at right. We can depict the FF bonding orbital as arising from the interaction of the two $2p$ atomic orbitals.



The two electrons of the bond occupy this orbital. In addition, the Lewis structure says that each F has three lone pairs. These LPs are in the remaining (unchanged) $2s$ and $2p$ orbitals on each fluorine, although they're not shown in the drawings above.

The H_2 and F_2 cases are fairly straightforward: they use simple combinations of their original AOs to form bonds. Let me point out that s orbitals can bond in any direction because they are spherical, whereas p orbitals bond best only in certain directions. Thus, depending on the orbitals used, directionality can be important. Let me also point out that bonding can occur between



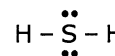
different kinds of orbitals on different atoms. For example, in the diatomic molecule HF, the bonding orbital is derived from H's $1s$ and one of F's $2p$, as shown at left.



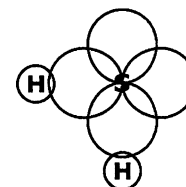
We'll see other kinds of combinations which give rise to bonding orbitals as we go.

Now let's get more complicated by bringing in a central atom. We'll do H_2S .

For this, we need Lewis and we need shape. Lewis is at right. Sulfur has octet; there are two single bonds and there are two lone pairs. VSEPR will tell you that the shape is bent and the bond angle is based on 109.5° . (H_2S is AX_2E_2 .) But I'm going to bring in the real, measured bond angle for this example, which is 92° . Although VSEPR would expect the bond angle to be less than 109.5° due to lone pair repulsion, 92° is too far off to be due to simple repulsion. So this is one of those cases in which VSEPR does not do well for bond angle although the shape is still correct.



A bond angle near 90° on a central atom with octet is a clue that the atom is using valence p orbitals to form bonds. This clue arises from the fact that the three p orbitals in a subshell lie at 90° to each other. Thus, we can say that sulfur in H_2S is using two of its $3p$ orbitals to form single bonds to the hydrogens, each of which uses $1s$. Each bonding orbital is therefore the result of interaction between one of S's $3p$ orbitals and the $1s$ of H.



Each of these orbitals holds two electrons. This uses two of sulfur's $3p$ orbitals. The other $3p$ orbital and also the $3s$ orbital will hold the lone pairs for sulfur.

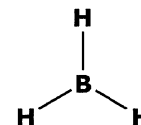
Let's summarize a few things so far.

- ▶ H forms bonding orbitals using its $1s$ orbital only. That's its only valence orbital, and that's all it can use.
- ▶ Terminal atoms other than H which form a single bond will commonly use one valence p orbital, as seen above for fluorine in F_2 and in HF. In these cases, the lone pairs on that terminal atom will be in the remaining, valence atomic orbitals.
- ▶ Central atoms with octet and with bond angles near 90° will use p valence orbitals. This is seen in H_2S above. For these cases, lone pairs are found in the remaining valence orbitals.

We'll build on this as we go. So far, things are hopefully straightforward. We can account for bond orbitals using simple atomic orbitals of s and p type. Unfortunately, things aren't always straightforward.

Let's do BH_3 .

We did the Lewis structure and the VSEPR shape for BH_3 back in Chapter 28. At that time, we derived that it had three BH single bonds, that the shape was trigonal planar, and that the bond angles were 120° . All of that holds true. Now, let's think about how the bonding orbitals arise.



For each separate bonding orbital, H will contribute its usual $1s$. This will overlap and interact with boron orbitals, but which ones? Boron's valence orbitals are $2s$ and $2p$. The $2s$ orbital is spherical; the three $2p$ orbitals are located at 90° relative to each other along the x , y and z axes. This causes a problem: given a spherical $2s$ orbital and three $2p$ orbitals at 90° , how do we end up with three bonding orbitals at 120° , all in the same plane?

That would be a very good question.

Although none of boron's valence orbitals are 120° to each other, Valence Bond Approach explains a trigonal planar shape by using a combination of boron atomic orbitals. Using the mathematics of wavefunctions, we derive a mix of the s orbital, the p_x orbital and the p_y orbital which gives three new

orbitals at 120° , all lying in the xy plane. (It's not easy to see how all of this can come out to 120° , but it does.) Each of the three mixed orbitals is then used to form a bond to one H atom, and each of the resulting bond orbitals holds two electrons. What about the third p orbital, p_z ? Nothing. It's still available, but it's not used in the mix and it is not involved in the bonding in this particular molecule. It remains an empty orbital.

Taken together, the three mixed orbitals for boron constitute an "s + two p" set, but we actually refer to this as an " sp^2 " set. In this notation, the superscripts represent how many of each orbital type are used in the set. Commonly, a superscript of one is not shown but sometimes this is written as s^1p^2 . The superscripts (other than ones) are pronounced as normal numbers, not as exponents: sp^2 is pronounced as "ess-pee-two" and not "ess-pee-squared". Notice also that the valence shell number is not included in the sp^2 designation. The designation always refers to the atom's valence shell; here for B, we know that this involves $2s$ and $2p$ orbitals.

I have used this example with BH_3 to introduce you to an important aspect in the Valence Bond Approach: for a specific atom in some polyatomic unit, a fractional mix of valence atomic orbitals can be derived in order to account for bonding at various bond angles. Although we were able to describe the bonding in H_2S earlier using simple p orbitals at 90° , the mathematics of mixing within VBA allows us to accommodate a wide range of bond angles.

Time to introduce some terminology.

This mathematical mixing is called "hybridization". Each of the resulting atomic orbitals is called a "hybrid orbital". "Hybrid" is used in its normal dictionary sense: it's a mix or a blend of things. Here, it's a mix or a blend of different atomic orbitals. In BH_3 , we say that boron is hybridized or we say that boron undergoes hybridization. There are different types of hybridization and each type is given by the set of AOs involved. In BH_3 , we derived an sp^2 set so we say that boron is sp^2 hybridized. By using three AOs, three orbital mixes are generated; each of these is called a hybrid orbital.

Each hybrid orbital is labeled by its hybridization set. Thus, we would label each of the boron hybrid orbitals in BH_3 as an sp^2 hybrid orbital. There are three of these, and the number of hybrid orbitals obtained from any set is important. The quantum realm demands orbital conservation: the number of orbitals is conserved in any mixing or in any hybridization or in any interaction whatsoever. Thus, if three AOs are put into hybridization, then three hybrids must result. If you want an easy way to keep track of this, keep an eyeball on the sum of the superscripts for the hybridization set: the superscripts in sp^2 (which can also be written as s^1p^2) give a sum of three, so this tells you that three hybrid orbitals are obtained.

For convenience, I will start abbreviating hybrid orbitals as HO. AO will continue to refer to an original atomic orbital of Chapter 21-type such as s or p .

Before continuing, we need to get more into the hybridization sets which are possible, and thither thus we go. We will cover three standard hybridization sets but many hybridization sets are actually possible. For our purposes here, we select the three which correspond to the angles within the VSEPR OLRs of linear, trigonal planar and tetrahedral. This allows us to maintain continuity to our coverage of VSEPR, at least as applied to those OLRs. Of the three standard sets, sp^2 is not the simplest, so I will back up to the simplest first.

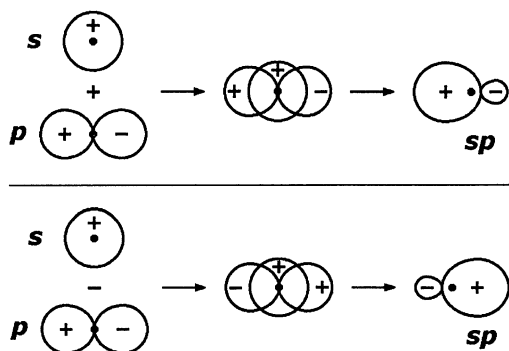
30.3 Hybridization sets

sp . This is the simplest of our hybridization sets. sp hybridization involves the mathematical mixing of an atom's valence s orbital and one of its three valence p orbitals; I show these two atomic orbitals at right. Two hybrids result: each sp hybrid is a field in the strange shapes shown at left, drawn separated from each other. Each has two lobes, one large and one small; each has a node, and the node lies a bit to the right or left of the atom's nucleus (which is shown as a dot). Both of the hybrids are the same shape but they point in exactly opposite directions. I show them together at right in the correct position relative to each other and relative to the nucleus. Since sp hybrids point at 180° relative to each other, they are linear to each other. This linear orientation will correspond to the linear VSEPR OLR.



Since these orbital shapes can seem strange to many students, I'm going to take a moment to explain this. Let's return to the notion of the amplitude of the orbital wavefunction. Back in Chapter 21 when we did the shapes of atomic orbitals, I made a brief mention that most orbitals have lobes of

positive and negative amplitude with a node in between. You flagged the paragraph by writing "orbital sign" in the margin. Go back to Chapter 21 and read that paragraph now; we need to bring this into the current picture. Using amplitude signs, we can pictorially derive one sp hybrid orbital as the additive combination of the original s and p atomic orbitals, as shown directly at left. In the regions where the s and p atomic orbital fields have the same amplitude sign, the hybrid orbital field is enhanced; in regions where the AOs are of opposite sign, the hybrid field is diminished. This is what gives the overall shape. The second hybrid orbital is derived by the subtractive combination, which is shown directly at left by reversing the signs of the p AO in the middle of the diagram. This interaction gives the second hybrid pointing in the opposite direction.



We won't belabor this +/- sign business as we go along here. I just want to show how amplitude sign sets up the shape of a hybrid orbital. This will apply for the other hybridizations, too: their hybrid orbitals will also have the same general shape, with a large lobe and a small lobe and with the node off a bit from the nucleus.

Although each sp hybrid orbital possesses a large lobe and a small lobe, it is common to neglect the small part. The reason for this is simple: by being so small, this lobe does not reach out and overlap well with orbitals from other atoms. For this reason, we will drop the small part and focus only on the larger portions. I show this at left for the two sp hybrid orbitals on a generic atom A. Be clear on the meaning here: the picture shows two, separate sp hybrid orbitals for atom A. If you're not careful on this, then the picture also looks like a single p orbital but that is not the intention here. In order to clarify the distinction from a p

orbital, I will draw a hybrid orbital with an incomplete loop at the nucleus, such as that shown at right. No, it doesn't show the node but we really don't need that for our purposes anyway. I will follow this pictorial format for the other hybridizations, also.



This concludes the introduction of sp hybrid orbitals. There's something which you must keep in mind for later. Since sp hybridization only uses one of the valence p orbitals, the other two p 's are still there, untouched. Both of those are perpendicular to the hybrid orbitals. These two remaining p AOs are yet available and they can still form bonding orbitals in some cases. We will come back to this point later in Chapter 31. Write " p AO" in the margin.

Let's do a simple example for now: BeH_2 . We did BeH_2 using VSEPR in Chapter 28. The Lewis structure is at right; the shape is linear. $\text{H} - \text{Be} - \text{H}$

In BeH_2 , the beryllium is sp hybridized. The Lewis structure shows that there are two BeH single bonds. We formulate each separate bond as arising from the interaction of the H $1s$ and one Be sp hybrid. We can write this as follows.

each BeH bonding interaction: $(\text{Be})sp + (\text{H})1s$



Each interaction gives one bonding orbital which holds two electrons. The two bonding orbitals will hold the four electrons in the Lewis structure. That's the bonding picture for BeH_2 .

As we proceed, I won't keep drawing orbitals because the pictures will start to get very complicated. Just remember: all hybrids will have the same basic shape. They will either form a bonding orbital by interacting with an orbital on an adjacent atom, or, they will hold a lone pair. We haven't done a lone pair example yet but we will get to it.

Let's move on.

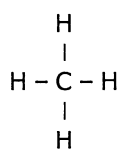
sp^2 . Our next hybridization is sp^2 , as seen previously for BH_3 . There are three sp^2 hybrid orbitals. Each hybrid orbital has the same shape and each orbital's shape is like the general shape of each sp hybrid above. The three sp^2 hybrids lie at 120° in a trigonal plane. This orientation will accommodate the trigonal planar OLR of VSEPR. There is still one original p AO available, and it lies perpendicular to the hybrid trigonal plane. Remember this also for Chapter 31; write " p AO" again in the margin here.

Returning to BH_3 as our example for sp^2 , we can represent each bonding interaction as follows.

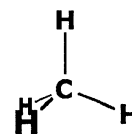
each BH bonding interaction: $(\text{B})sp^2 + (\text{H})1s$

Each bond orbital will hold two electrons; the three bonding orbitals will hold the six electrons in the Lewis structure.

sp^3 . For sp^3 hybridization, we mix the atom's valence s orbital and all three p orbitals. Four AOs go into this process, so four HOs result. By the desired mathematics of this mixing, the four hybrids are oriented in tetrahedral directions. This accommodates the tetrahedral OLR of VSEPR.



Let's consider methane, CH_4 , again. Its Lewis structure is at left and its shape is at right. The central carbon is sp^3 hybridized. The Lewis structure shows four CH single bonds. Each one of these bonds is derived from the interaction of the $1s$ orbital from one hydrogen and one sp^3 hybrid from the carbon.



each CH bonding interaction: $(\text{C})sp^3 + (\text{H})1s$

Each bonding orbital will hold two electrons, and this accounts for the eight electrons in the Lewis structure. That's the bonding story for methane.

With sp^3 hybridization, we conclude the common hybridization schemes which involve s and p combinations. Before going further, I need to bring up two aspects.

First aspect: This deals with lone pairs, which I only made brief mention of so far. In all of the examples above, all hybrid orbitals were used to form bonds to other atoms. However, that won't always be true. Sometimes, hybrid orbitals will be used for lone pair electrons. In fact, if the atom is hybridized to form bonds, then it will usually use hybrids for its lone pairs (if it has any).

Second aspect: So far, I have shown some atoms which use hybrids to form bonds and some atoms which just use s or p orbitals to form bonds. How do you know if an atom in some polyatomic unit is hybridized or not? Here are some generalities.

- First of all, hydrogen never hybridizes because it has only a single $1s$ to work with; you can be sure of this much.
- Atoms with four other atoms bonded to it will hybridize pretty much all of the time. Atoms with one, two or three atoms bonded to it may or may not hybridize.
- Elements from the Second Period are pretty much limited to hybridization when they are central atoms; however, elements from lower Periods exhibit greater diversity in their bonding and are not so restricted.

Let me illustrate the last entry using sulfur, an element in the Third Period. Sulfur is hybridized in SO_2 but it is not hybridized in H_2S . In SO_2 , the sulfur is sp^2 hybridized; in H_2S , sulfur uses regular $3p$ orbitals to form bonds, as shown earlier. How do we know this? It's in the bond angles: ultimately, bond angles tell us whether a central atom is hybridized or not. The bond angle in SO_2 is 119° , very close to the sp^2 hybrid angle. In H_2S , the bond angle is 92° , very close to the angles for $3p$ orbitals.

Unfortunately, the three generalities above don't really give us much info to go by when it comes to specific cases. So where does this put us? How can we predict whether a specific atom in some polyatomic unit is hybridized or not, without having to know experimentally measured bond angles?

It ain't easy.

The most common practice at this stage of the game is to assume VSEPR angles for central atoms, unless told otherwise. And, if you assume VSEPR angles, then you assume hybridization. As for being "told otherwise", I gave the example of H_2S and I said the angle was 92° which is nowhere close to the VSEPR angle of 109.5° . In that case, we knew sulfur did not follow the VSEPR angle, so it did not follow any of our standard hybridizations; instead, it used its simple p orbitals. As a practical point, many instructors just go with assuming hybridization, so you may not need this "told otherwise" part.

Unfortunately, that only covers central atoms. Terminal atoms may or may not hybridize, and that's a separate issue. Terminal atoms don't get a VSEPR treatment, and terminal atoms have no bond angles to clue us either way.

Given all of the peculiarities here, it is time to draw the line somewhere and set up some guidelines to go by. We'll use the following hybridization guide. Circle this part.

HYBRIDIZATION GUIDELINES: Unless there is information to the otherwise,

1. assume that central atoms are hybridized;
2. assume that multiply-bonded terminal atoms are hybridized; and,

3. assume that singly-bonded terminal atoms are not hybridized.

Notice that these are written as assumptions; exceptions can occur, such as H_2S which does not hybridize. There are other kinds of exceptions, too, and these arise from atoms which have hybridizations which are different from the ones we're covering here. We're not even going to worry about those. Just do these Guidelines, unless your instructor specifies something else to go by. As always, be careful and be clear on what s/he expects. We'll do examples for these Guidelines, so you'll see how they work.

By the way, remember that H always and only uses 1s because that's all it has for valence. I say this again for emphasis because it is so common. It's covered in the third assumption but this should be automatic.

30.4 How to use the Valence Bond Approach

So far, we've seen a few examples of the Valence Bond Approach but now we need to address how you are to determine this on your own. The starting point for all of this is the Lewis structure. Lewis tells you what atoms are central, what atoms are terminal, what bonds are single bonds, what bonds are multiple bonds, what atoms have lone pairs, etc. Lewis is also the entry point for VSEPR which provides us the shape and angle information (unless told otherwise). Thus, the Lewis structure is central to many key concepts.

Once you have the Lewis structure, you must determine which atoms are hybridized and which are not. For this part, you can follow the assumptions above or use whatever guidelines are specified by your instructor.

If an atom is hybridized, then you must determine which hybridization set is being used. Is it sp ? sp^2 ? sp^3 ? In order to answer this question, you must consider the number of hybrid orbitals necessary. The atom must have the correct number of HOs to accommodate its lone pairs and its interactions with bonded atoms. Look at the Lewis structure. Look at each hybridized atom separately, one at a time: how many lone pairs does it have and how many atoms are bonded to it? This sum is the number of hybrids required. The atom will have that hybridization which provides that number of hybrid orbitals.

If the sum is two, then two hybrids are needed. We assign sp hybridization to the atom.

If the sum is three, then three hybrids are needed. We assign sp^2 hybridization to the atom.

If the sum is four, then four hybrids are needed. We assign sp^3 hybridization to the atom.

Remember this all-important sum: the sum of the number of lone pairs plus the number of bonded atoms.

Let's see... The sum of the number of lone pairs plus the number of bonded atoms. Hmm... Does this sound vaguely familiar? Hopefully it does. We've done this already: this sum is the same number for determining the orientation of least repulsion for VSEPR. Let's go back momentarily and see how we set that up back in Section 28.2.

“ For any central atom in any polyatomic unit, its orientation of least repulsion is determined by the sum of the number of lone pairs plus the number of bonded atoms. THIS IS VERY IMPORTANT. I'll say it once more for emphasis.

THE OLR FOR ANY CENTRAL ATOM IS DETERMINED BY THE SUM OF THE NUMBER OF LONE PAIRS PLUS THE NUMBER OF BONDED ATOMS. ”

Now, this same sum is used in Valence Bond Approach to determine which hybridization set is used by an atom.

THE HYBRIDIZATION SET OF AN ATOM IS DETERMINED BY THE SUM OF THE NUMBER OF LONE PAIRS PLUS THE NUMBER OF BONDED ATOMS.

As noted previously, the hybridizations covered here are for the specific purpose of accommodating the angles in the linear, trigonal planar and tetrahedral VSEPR OLRs. This is why the same sum (lone pairs + bonded atoms) gives both the VSEPR OLR and the VBA hybridization. With that connection, we are able to realize a tremendous advantage and simplification: we can bypass the details of VSEPR and just use Lewis in order to determine the hybridization. Let's summarize the coverage so far.

SUM	HYBRID SET	NUMBER OF HOs	ORIENTATION OF HOs	VSEPR OLR
2	sp	2	linear	linear
3	sp^2	3	trigonal planar	trigonal planar
4	sp^3	4	tetrahedral	tetrahedral

The Sum column comes from Lewis; again, all of this begins with the Lewis structure. Lewis can give us the hybridization directly.

Things may seem a bit complicated but, as we go through examples, hopefully you'll see how this works out. Now we are finally able to proceed to specific steps for doing the Valence Bond Approach.

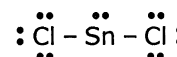
- **Step 1.** You must start with the Lewis structure of the polyatomic unit.
- **Step 2.** Identify which atoms are hybridized and which are not.
Use the assumptions from the Hybridization Guidelines which you circled earlier (or your instructor's guidelines if provided) for this part.
- **Step 3.** For atoms which are hybridized, determine the hybridization set. Find the sum of the number of bonded atoms and the number of lone pairs, and use this sum to determine the hybridization.
- **Step 4.** For atoms which are not hybridized, determine which orbitals are used. Hydrogen will always and only use 1s to form a bonding orbital. For other unhybridized atoms, we assign a valence p orbital for bonding.
- **Step 5.** Formulate the various orbitals which will account for the bond pairs and lone pairs in the Lewis structure.
 - a. Bonding orbitals arise from the interaction of AOs and/or HOs on bonded atoms.
 - b. Lone pairs reside in HOs on hybridized atoms or in AOs on unhybridized atoms.

These five Steps illustrate a useful qualitative treatment of the Valence Bond Approach at this level, but not every instructor routinely does it to this extent. That's OK. I've set this up for allowing some variation. We'll do six Examples with this method, continuing into Chapter 31. We will be using these six Examples to illustrate different aspects which can arise. Afterwards in Chapter 31, I'll show you a short format which is quite common.

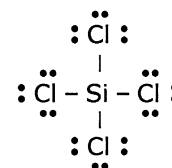
Before jumping into the whole shebang, let's see a few examples with Step 3 by itself. For purposes of these examples, we will simply determine the hybridization of the central atom, using the table above. We'll roust up some Lewis structures from the last several chapters and put them to more work here.



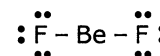
The central tin has two atoms bonded to it and it has one lone pair. The sum is three, and three hybrid orbitals are needed. Three are obtained by sp^2 hybridization, so tin is sp^2 hybridized.



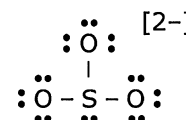
Silicon has four atoms bonded to it and it has zero lone pairs. The sum is four. Four hybrid orbitals are needed and these are provided by sp^3 hybridization. Silicon is sp^3 hybridized.



The beryllium has two atoms bonded to it and it has zero lone pairs. The sum is two. Two hybrids are needed, and this requires sp hybridization.



That's all there is to this Step 3. Here, you can do an example: SO_3^{2-} . What is the hybridization of the central atom?



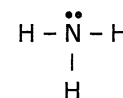
Now let's start with Examples using all of Steps 1 - 5. Be ready to flip back to the Steps in order to follow as we go.

.....

Example 1. Ammonia.

.....

- Step 1. Start with the Lewis structure.



- ▶ Step 2. Who is hybridized? From the Lewis structure, we see that nitrogen is a central atom, so we assume that it is hybridized. The hydrogens are not hybridized.
- ▶ Step 3. Determine the hybridization set. Nitrogen has three atoms bonded to it and it has one lone pair, for a sum of four. This requires four hybrid orbitals. Nitrogen will adopt sp^3 hybridization; these hybrids lie in tetrahedral orientation.
- ▶ Step 4. Are there any unhybridized orbitals for bonding? Each hydrogen will use its $1s$ orbital.
- ▶ Step 5. Formulate the required orbitals.
 - Part a. Each of the NH bonds arises from the interaction of a nitrogen sp^3 hybrid and a hydrogen $1s$. This uses three of the sp^3 HOs.
 - Part b. Since N is hybridized, its lone pair will also be in a hybrid orbital. This uses the fourth of the sp^3 HOs.

This concludes the Steps for ammonia. We can summarize as follows.

There are three NH bonds, each arising from $(N)sp^3 + (H)1s$.
There is one lone pair on N and it is in one of the sp^3 orbitals.

This accounts for all electrons in the Lewis structure. By the way, we looked at the bonding orbitals in ammonia in Chapter 29 when we talked about different repulsions and variations in bond angles. Now you can see how those bonding orbitals are derived.

For our next Example, we will bring in other kinds of terminal atoms. Watch how these are handled.

Example 2. BeF_2 . We just looked at this one above but now we'll do the whole thing.

- ▶ Step 1. Start with Lewis. Look upstairs or draw it in again.
- ▶ Step 2. Who is hybridized? Beryllium is a central atom, so we assume it to be hybridized. The fluorines are terminal atoms, bonded by single bonds. By assumption number 3 of the Hybridization Guidelines, we assume that these are not hybridized.
- ▶ Step 3. Determine the hybridization set. Beryllium has two atoms bonded to it and it has zero lone pairs. The sum is two, so two hybrid orbitals are needed. Beryllium is sp hybridized and the two hybrid orbitals are linear.
- ▶ Step 4. Are there any unhybridized orbitals for bonding? Fluorine will form a bonding orbital by using a valence $2p$ orbital.
- ▶ Step 5. Formulate the molecular orbitals.
 - Part a. Each BeF bond arises from the interaction of one Be sp hybrid and one F $2p$ orbital. I've illustrated this at right, since we haven't yet done a bond between a hybrid and a p . (It's basically the same notion of overlap as for any other combination.)
 - Part b. Since the fluorines are not hybridized, their lone pairs will be in their other valence $2s$ and $2p$ atomic orbitals (not shown in the drawing).



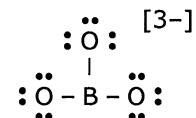
Here's the summary.

There are two BeF bonds, each derived from $(\text{Be})sp + (\text{F})2p$.
There are three lone pairs on each F; these are in the $2s$ and remaining $2p$ orbitals.

Next.

Example 3. BO_3^{3-} .

- ▶ Step 1. Lewis.



- ▶ Step 2. Who is hybridized? We assume boron to be hybridized, since it is a central atom. The oxygen atoms are terminal and bonded by single bonds; as such, we assume that they are not hybridized.
- ▶ Step 3. Determine the hybridization set. Boron is sp^2 hybridized. The three hybrids on B are in trigonal planar orientation.
- ▶ Step 4. Each oxygen atom will form a bonding orbital to boron using a $2p$ orbital.
- ▶ Step 5. Formulate the molecular orbitals.
 - Part a. Each bond arises from one B sp^2 hybrid and one oxygen $2p$ orbital.
 - Part b. The oxygen lone pairs will be in the $2s$ and the remaining $2p$ orbitals.

Summarize.

There are three BO bonds, each derived from $(B)sp^2 + (O)2p$.
 There are three lone pairs on each oxygen atom in the remaining valence atomic orbitals.

Done.

Now it's your turn.

.....
Example 4. SCl_3^+

- ▶ Step 1. Lewis, please.

- ▶ Step 2. Who's hybridized? _____
- ▶ Step 3. What kind of hybridization is utilized? _____
- ▶ Step 4. What unhybridized atomic orbitals are used for bonding? _____
- ▶ Step 5.
 - Part a. Each SCl bond arises from the interaction of one S _____ orbital and one Cl _____ orbital.
 - Part b. Are there any lone pairs? _____
 - On what atom(s)? _____
 - In what orbitals? _____

Fill in the summary here.

There are three SCl bonds, each derived from (S) _____ + (Cl) _____ .

Who's got lone pairs and in what orbitals? _____

30.5 A closing comment

This concludes this initial part of VBA but, before continuing into new turf, let me return and expand a bit on the connections between VBA, VSEPR and bond angles. This point applies to central atoms only.

All of our applications so far of Valence Bond Approach have invoked hybridization of the central atom, except for one. That exception was H_2S . For that case, Lewis tells us that sulfur has octet; VSEPR predicts a bent shape with a bond angle near 109.5° ; and, we would predict sp^3 hybridization based on the VSEPR angle. But, alas, that's not what happens. The actual bond angle of 92° tells us that sulfur uses its $3p$ orbitals to form bonds. VSEPR is right about the bent shape, but wrong about the angle.

Cases which do not follow hybridization as covered here are somewhat common for elements from the Third Period and lower in the Periodic Table. I said somewhat common, not always. Sometimes it happens and sometimes it doesn't. Other examples include other binary hydrogen compounds, such as PH_3 , AsH_3 , SbH_3 , BiH_3 , H_2Se , and H_2Te . All of these have central atoms with octet and they all have one

or two lone pairs; all would be expected to be sp^3 hybridized. But, no, they all have bond angles from $90^\circ - 93^\circ$ and so they are not hybridized. (They'll primarily use valence p orbitals for bonds.) There are also many examples for which the bond angles clearly show hybridizations other than what we cover here. For example, SnCl_2 , which we predicted earlier to be sp^2 hybridized, has a real bond angle of 98° ; that value is well removed from the sp^2 angle of 120° , so SnCl_2 is not sp^2 hybridized after all. The angle also differs considerably from 90° predicted for simple p -orbitals. This tells us that some other hybridization is probably at work for tin in this molecule.

How important is all of this stuff?

I'm trying to illustrate for you some of the many diverse ways of bonding which occur in polyatomic units. On the other hand, such diversity can also be a headache for students trying to keep things straight. So, as usual, that brings us to the bottom line. As noted back in Section 30.3:

The most common practice at this stage of the game is to assume VSEPR angles for central atoms, unless told otherwise. And, if you assume VSEPR angles, then you assume hybridization.

So, in general, go with hybridization for the central atom but be aware that other things can happen. Again, the other things are more likely for central atoms from the Third or lower Periods; central atoms from the Second Period do follow hybridization very nicely.

Although this diversity of bonding may complicate things, the other modes of bonding can still be handled by the Valence Bond Approach, even including different hybridization schemes than what we're covering here. It is actually VSEPR that suffers from this bonding diversity, as was noted in Chapter 29.

“ VSEPR is very good but it's not perfect. In many cases, VSEPR does not give the correct bond angles. Much of the reason for this is that VSEPR does not take into account the different kinds of orbitals that make up the polyatomic unit. We will see these orbitals in Chapter 30 and 31. Although the bond angles may not be right, VSEPR still gives the correct shape in the vast majority of cases, and this much is extremely important. ”

Thus, VSEPR provides a very good basis upon which we can base our Valence Bond Approach, and many instructors simply work with that much. It's not perfect, but that's OK. We're not out to be perfect here.

Problems

- True or false.
 - Molecular orbitals arise from the interaction of orbitals from different atoms.
 - Hydrogen cannot hybridize.
 - Fluorine will always hybridize in order to form bonds.
 - sp^3 hybridization gives three hybrid orbitals.
 - The bond angles for sp^2 hybrids are 109.5° .
- What is the hybridization of the central atom for each of the following VSEPR classifications?

a. AX_2E	b. AX_3E	c. AX_3	d. AX_2E_2	e. AX_4	f. AX_2
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- In each of the following, which atoms are hybridized and what is their hybridization?

a. H_2O	b. NCl_3	c. GeF_2	d. AlH_3
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- For each of the following, how do the bond orbitals arise? What orbitals on the atoms hold the lone pairs (if any)?

a. SiH_4	b. I_2	c. GaBr_3
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