

We enter into our last phase of discussion of the polyatomic unit: orbitals. We will cover different kinds of bonding orbitals and nonbonding orbitals which are present in polyatomics. We will also cover a strange, new kind of orbital, the antibonding orbital. What is an antibonding orbital? Bad news, that's what it is.

We are beginning a string of four Chapters regarding orbitals in polyatomic units. Why is this so important? That's a good question. After all, we already know the basics of the covalent bond: it's the sharing of electrons. We already know how many electrons are shared and how many are not shared: that's in the Lewis structure. We can already predict the shapes of many polyatomics: that's VSEPR. We already know so much about the polyatomic unit. So why are orbitals so important to add at this time? You already know the answer: electrons do chemistry! Not only do electrons do chemistry, but electrons in different kinds of orbitals can do different kinds of things. As such, a discussion of orbitals is important in characterizing the polyatomic unit itself.

As we go through these parts, we are still doing covalent bonds. Later in this stretch, at the end of Chapter 33, we will finally cover metallic bonding. Metallic bonding is an extreme case of covalent bonding. We're just not ready for that yet.

30.1 VBA and/or MOA

The two most common approaches for describing orbitals in polyatomics are the Valence Bond Approach (VBA) and the Molecular Orbital Approach (MOA). These two are the standard tools of the trade for describing polyatomic orbitals and how these orbitals arise. Why are there two? As tools of the trade, sometimes one works better than the other. The Valence Bond Approach is much easier to work with at our level of coverage, even for complicated molecules; on the other hand, at this level, it has limitations and it doesn't quite explain everything. In comparison, the Molecular Orbital Approach can give better answers for some things but it gets complicated even for simple molecules. The bottom line is this: MOA is good, but it can be very tedious; VBA is fast and convenient, and it's usually good enough. By "fast", I mean VBA is fast compared to MOA; it may not seem fast to you, especially at first.

In both methods, the general picture is the same regarding the origin of the orbitals in a polyatomic: an orbital of one atom interacts with the orbital(s) of some other atom(s) to produce a bonding orbital, a nonbonding orbital, or an antibonding orbital. In essence, this interaction involves the merging of 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.

By the way, in its most general sense, the term "molecular orbital" (MO) can refer to bonding, nonbonding or antibonding orbitals in a polyatomic unit. This is a generic term which can be used with either approach: we can use this term when we are using the Valence Bond Approach or when we are using the Molecular Orbital Approach. The term "atomic orbital" (AO) will remain one of the *s* or *p* or *d* or other types, as discussed for isolated atoms in Chapter 21.

As you might see here, we'll be using a bunch of initials for things. Let me restate these at this time for clarity. We will use "AO" for an atomic orbital of the original *s*, *p*, etc. type, as introduced in Chapter 21. We will use "MO" for an orbital in a polyatomic unit. "MOA" is for the Molecular Orbital Approach to bonding. "VBA" refers to the Valence Bond Approach to bonding. If you get confused by these initials, circle this paragraph for handy reference.

Like any orbital, all molecular orbitals are field regions in three dimensional space. Each can hold two electrons max. If there are two electrons in the 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. This much is the same as for simple atomic orbitals. The shape of the molecular orbital fields, however, will be different from those of typical atomic orbitals; we shall see these as we go.

Let me illustrate a few things at this time with the simplest case possible: the bonding orbital in H₂. We shall describe this bonding orbital as arising from the interaction of valence orbitals from the two H atoms.



To begin, we start with two separate H atoms, each with 1s¹ configuration. 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 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 electrostatic attraction between each nucleus and each electron and this helps, but this is enhanced by a contraction of the orbital which brings the electrons closer to each nucleus. Furthermore, the electrons have more favorable energies as a consequence of being spread over more than one atom. Thus, various factors come into play. The important part is that this is a bond and now we have a molecule of H₂. As with any orbital holding two electrons, the two electrons are spin-paired and so H₂ 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. Keep in mind the general result:

MOLECULAR ORBITALS ARISE FROM THE INTERACTION OF ORBITALS FROM DIFFERENT ATOMS.

This applies for both the Valence Bond Approach and the Molecular Orbital Approach. Although this much is the same for the two, things can get different otherwise. This is where I will start to separate VBA and MOA. For starters, the typical coverage of Valence Bond does not do antibonding orbitals. The Molecular Orbital Approach includes antibonding even at its most basic level; our coverage in this text will include bonding and antibonding orbitals.

Let's get started. First, a warning: since we are again dealing with the quantum realm, some things may seem strange. They are.

We begin with Valence Bond.

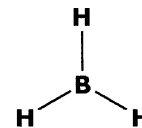
30.2 The Valence Bond Approach

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 minor, 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, I will exclude all cases of expanded valence from coverage. Here, we stick to polyatomics with atoms of octet or less. As you can guess, there are more layers of complexity to VBA but we're not doing everything.

OK, let's start. For our VBA coverage, we consider only valence shell *s* and *p* orbitals from the atoms involved. One or more valence orbitals from one atom will interact with one or more valence orbitals from another atom.

In order to do Valence Bond for a molecule or polyatomic ion, you begin with a Lewis structure and specific shape information, including bond angles if possible. The specific shape information can be determined experimentally or it can be predicted by VSEPR. The Lewis structure tells us about lone pairs and bond orders; VBA will accommodate all such lone pairs and bond pairs with the appropriate orbitals. VBA will also need to provide those orbitals in a manner to accommodate the shape and bond angles. Typically, the bond angles predicted by VSEPR are assumed to apply but those aren't always correct, as noted in the last Chapter. We'll see how the various factors fall into place as we go along here.

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 accommodates 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. The actual directions derive from vector algebra of the x and y components for p_x and p_y , but there's more to the story due to the wave math.) Each of the three mixed orbitals is then used to form a bond to one H atom. What happened to the third p orbital, p_z ? It's still there but it's not used in the mix; it is not involved in the bonding in this particular molecule.

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. Usually, a superscript of one is not shown but sometimes this is written as s^1p^2 . The superscripts 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, we can mathematically derive a fractional mix of valence atomic orbitals 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 range of angles.

Time to introduce some terminology.

This mathematical mixing is called "hybridization". Each fractional combination of 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 . HO will refer to some mathematical mix of these.

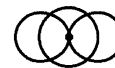
Before continuing, we need to discuss more of the hybridization sets which are possible, and that is where we go now. We will cover three standard hybridization sets but many hybridization sets are actually possible. For our purposes here, we select the three which correspond to the angles within the 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

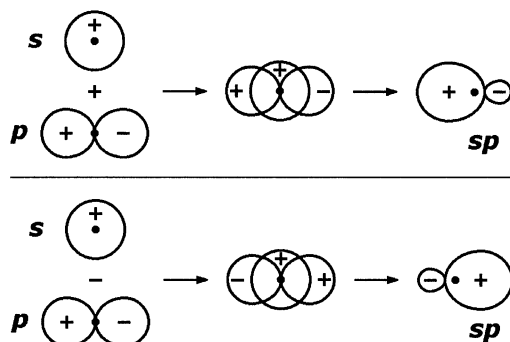
sp. This is the simplest of our hybridization sets. *sp* hybridization involves the mathematical mixing of an atom's valence *s* orbital and one of its three valence *p* orbitals;



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 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.

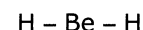


At right, I show a hybrid orbital with an incomplete loop at the nucleus, such as that shown at right. No, it doesn't show the node but we really don't need that for our purposes anyway. I will follow this pictorial format for the other hybridizations, also.



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: BeH₂. We did BeH₂ using VSEPR in Chapter 28. The Lewis structure is at right; the shape is linear.



In BeH₂, 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: (Be)*sp* + (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 full 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.

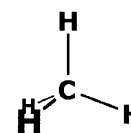
Returning to BH_3 as our example for sp^2 , we can represent each bonding interaction as follows.



Each 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 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 VB 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 the full steps for doing the Valence Bond Approach.

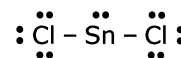
- **Step 1.** You must start with the Lewis structure of the polyatomic unit.
- **Step 2.** Identify which atoms are hybridized and which are not.
Use the assumptions from the Hybridization Guidelines which you circled earlier (or your instructor's guidelines if provided) for this part.
- **Step 3.** 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 fairly full (qualitative) treatment of the use of 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 full treatment, 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.

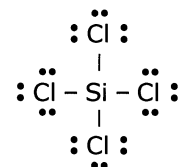
Before jumping into the whole shebang, let's see a few examples with Step 3 by itself. For purposes of these examples, we will simply determine the hybridization of the central atom, using the table above. We'll roust up some Lewis structures from the last several chapters and put them to more work here.



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.

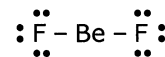


Silicon has four atoms bonded to it and it has zero lone pairs. The sum is four. Four hybrid orbitals are needed and these are provided by sp^3 hybridization. Silicon is sp^3 hybridized.

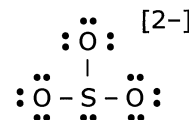




The beryllium has two atoms bonded to it and it has zero lone pairs. The sum is two. Two hybrids are needed, and this requires sp hybridization.



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?



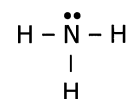
Now let's start with Examples using all of Steps 1 - 5. Be ready to flip back to the Steps in order to follow as we go.

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Example 1. Ammonia.

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► 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? Hydrogen will use its $1s$ orbitals.

► 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 $(\text{N})sp^3 + (\text{H})1s$.

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 back 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.

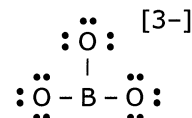
There are two BeF bonds, each derived from $(\text{Be})sp + (\text{F})2p$.

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 $(\text{B})sp^2 + (\text{O})2p$.

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 stepping out 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° - 93° 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

1. True or false.
 - a. Molecular orbitals arise from the interaction of orbitals from different atoms.
 - b. Hydrogen cannot hybridize.

- c. Fluorine will always hybridize in order to form bonds.
 - d. sp^3 hybridization gives three hybrid orbitals.
 - e. The bond angles for sp^2 hybrids are 109.5° .
2. 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
 3. 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
 4. 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. $GaBr_3$