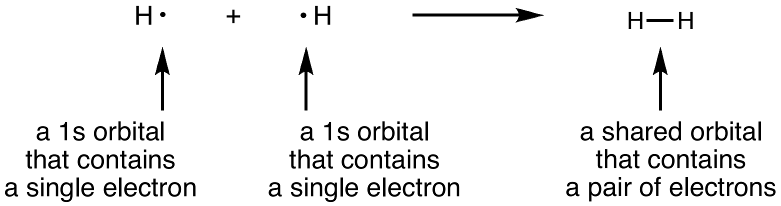
Molecular Orbitals and Curved Arrows

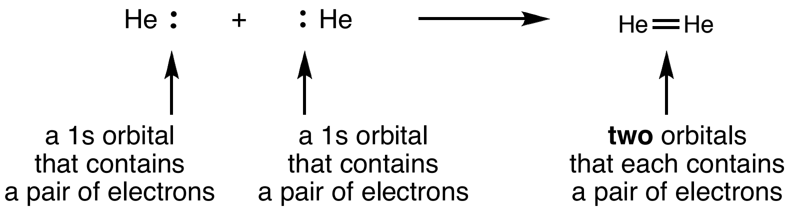
Introduction

At this point, you've seen the Lewis theory of covalent bonding, in which covalent bonds result from the sharing of electrons between atoms, and all atoms seek to complete an "octet" of electrons (or, in the case of hydrogen, a "duet" of electrons). This theory is remarkably successful in explaining why various compounds have the structures that they do and in predicting the geometry and reactivity of many molecules. However, the Lewis theory was developed before the advent of quantum mechanics, and some of the basic results of the Lewis theory are in direct conflict with quantum mechanics. For instance, consider the formation of a hydrogen molecule from two hydrogen atoms. According to quantum mechanics, every electron must reside in an orbital, and each orbital can contain either zero, one, or two electrons. Thus, each H atom has a single electron in a 1s orbital, and the resulting H_2 molecule has a pair of electrons that must reside in some sort of "shared" orbital:


H•
+
•H
H—H
a 1s orbital that contains a single electron
a 1s orbital that contains a single electron
a shared orbital that contains a pair of electrons

This interpretation, however, violates one of the basic principles of quantum mechanics, which is that in any process, the *total number of orbitals cannot change*. We can't have a process that starts with *two* orbitals (one on each atom) and ends up with *one* shared orbital. Somehow, our final product (the H_2 molecule) must have *two* orbitals. It turns out that the "missing" orbital is extremely important in chemical reactions, but Lewis theory gives no indication that this missing orbital exists.

Moreover, although the "octet rule" does give excellent predictions of the structures of the vast majority of all chemical compounds, there is no explanation within Lewis theory of *why* the presence of eight electrons is preferred. Lewis theory cannot truly *explain*, for instance, why we can't form a molecule He_2 by combining the electrons in two He atoms:



Indeed, the combination of two He atoms to form an He_2 molecule (with a double bond) seems perfectly reasonable from the simple vantage of "sharing electrons." One would think that if sharing *one* pair of electrons (in H_2) is good, then sharing *two* pairs of electrons (in He_2) must be even better. Of course, the molecule He_2 is not stable, but Lewis theory cannot explain *why* this molecule does not exist.

We thus need a better theory of covalent bonding. This theory is known as **molecular orbital theory**, and it will explain the two puzzles we have posed here:

- How can the H_2 molecule contain the *two* orbitals required by quantum mechanics, when it has only *one* pair of electrons?
- Why is it impossible for two He atoms to combine to form a stable He_2 molecule?

Moreover, we will see that simple molecular orbital theory is crucial for **understanding and predicting the reactions of organic molecules**. Without this theory, organic chemistry appears to be a vast uncharted jungle of confusing and unrelated reactions; with molecular orbital theory, you will see that this vast jungle has an incredibly beautiful and simple road map. Discovering this road map is the key to success in your study of organic chemistry.

2.1. Molecular Orbitals: Building the Covalent Bond

We seek a theory of covalent bonding that is based in quantum mechanics. We already showed that the principles of quantum mechanics can explain the electronic structure and energy levels of single atoms. Once we knew the orbitals (or wavefunctions, ψ) then we could calculate the energy levels of any atom and determine the electron distribution around the atom. For a hydrogen atom we could solve the Schrödinger equation without any approximations, just using mathematics. In principle, quantum mechanics can be applied directly to molecules, just as it was to atoms. The structures of molecules as simple as H_2 and as complicated as DNA are ultimately the result of quantum mechanics. Unfortunately, coming up with accurate and appropriate orbitals for molecules is more difficult than coming up with orbitals for a single atom. Even for a molecule as simple as H_2 this is impossible, because there are simply "too many parts" in a hydrogen molecule: there are *two* nuclei and *two* electrons. Each of the electrons in the hydrogen molecule interacts simultaneously with the two atomic nuclei and the other electron, and there are simply too many interactions ('variables') for us to solve the resulting equations without recourse to some sort of approximation.

When we make a hydrogen molecule from two hydrogen atoms we combine the nuclei and electrons from the atoms into the molecule. In the simplest and most convenient (for our purposes) approximation for the orbitals of the hydrogen molecule we do the same – we combine the atomic orbitals of the two hydrogen atoms to give us new **molecular orbitals**. In the jargon of quantum mechanics this process of building approximate molecular orbitals from atomic orbitals is known as 'linear combination of atomic orbitals' (sometimes abbreviated as 'LCAO'). We know what the atomic orbitals of hydrogen look like, and all we need to know are the rules we must obey when we combine them. Luckily these rules are few in number, and as we will be using them many times throughout the book it is important that you become familiar with them. We develop some of these rules as we analyze the hydrogen molecule, and then generalize them.

The two electrons in our two hydrogen atoms are in 1s energy levels, so the simplest approach to the molecular orbitals of the hydrogen molecule is to take these 1s orbitals and combine them. We can do this by placing two atomic nuclei 0.74 Å apart (the observed distance between the nuclei of the hydrogen molecule) and then plotting each 1s orbital using the nuclei as the origin (Fig. 2.01). As you can see the value of the 'new' molecular orbital in the region between the nuclei (between the dashed lines in Fig. 2.01) is very high, which means that if we convert this orbital into an electron distribution, the electrons in this new orbital are likely to be found there – exactly as observed in the hydrogen molecule. Moreover as the electrons would interact with both nuclei this molecular orbital will be much lower in energy than the two hydrogen 1s orbitals.

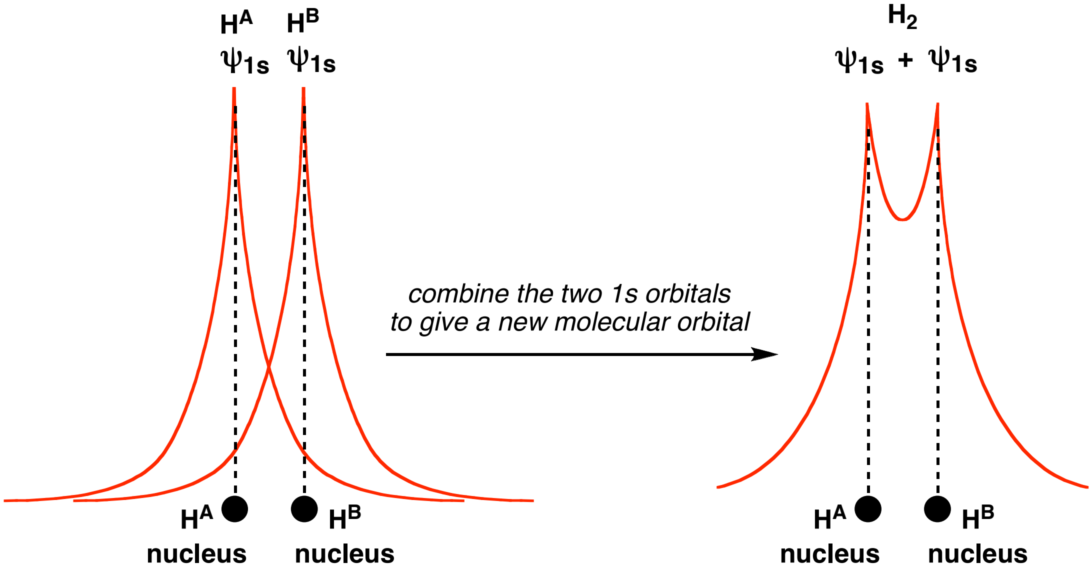

H^A
H^B
ψ_{1s}
ψ_{1s}
H_2
$\psi_{1s} + \psi_{1s}$
combine the two 1s orbitals to give a new molecular orbital
H^A nucleus
H^B nucleus
H^A nucleus
H^B nucleus

Figure 2.01

This is not the whole story; we must be careful that we take into account one of the unusual aspects of quantum mechanics, that the ‘absolute’ sign of an individual orbital is not important (ψ is entirely equivalent to $-\psi$), but the *relative* sign of *two* orbitals is extremely important. One consequence of this is that we cannot ignore the alternative of combining two 1s hydrogen orbitals with *opposite relative sign*. Instead of *adding* the two orbitals, we could just as well *subtract* them. This is illustrated pictorially in Fig. 2.02 and leads to a very different ‘new’ molecular orbital.

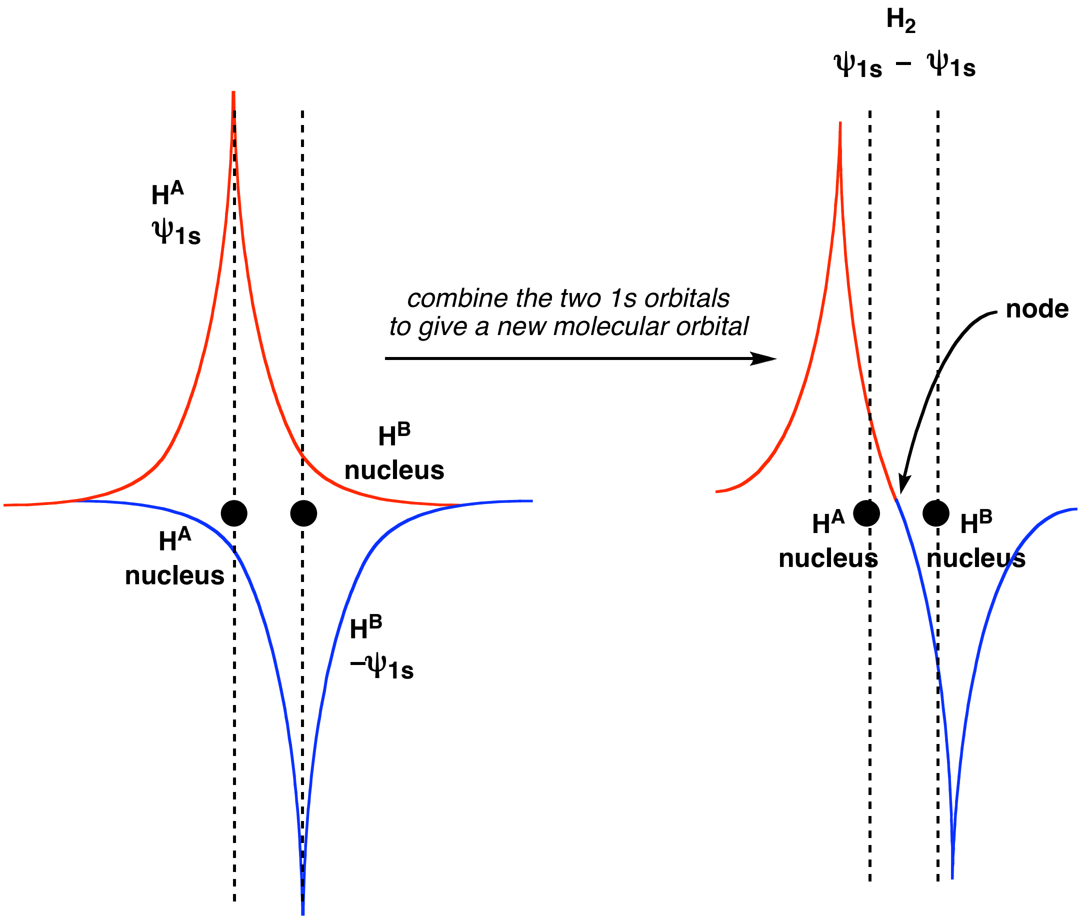
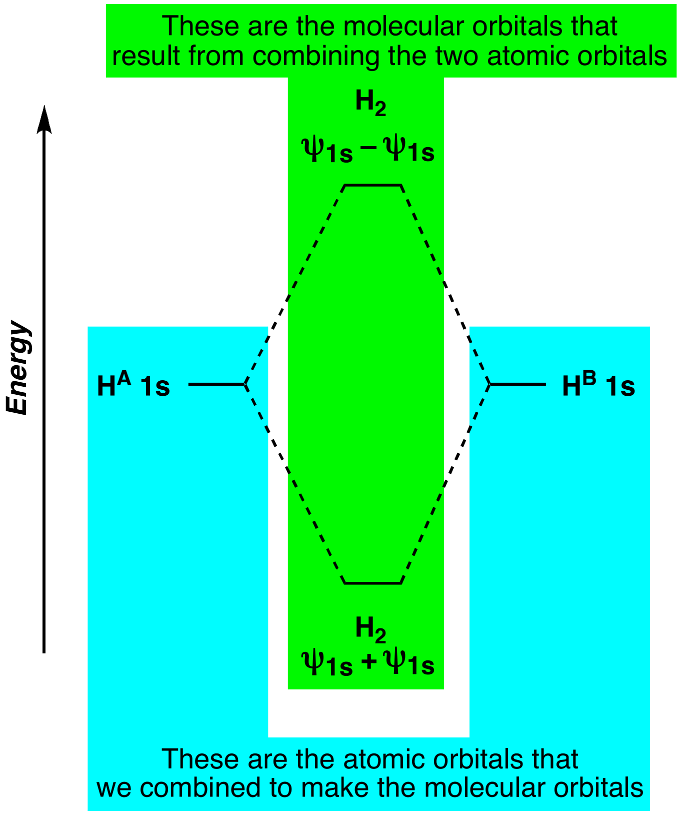

H2
ψ1s – ψ1s
H^A
ψ1s
combine the two 1s orbitals
to give a new molecular orbital
node
H^B
nucleus
H^A
nucleus
H^B
–ψ1s
H^A
nucleus
H^B
nucleus

Figure 2.02

This ‘new’ molecular orbital is very different to the one that we obtained previously by combining two 1s orbitals with the same sign. Electrons in the molecular orbital shown in Fig. 2.02 would spend very little of their time in the region between the two nuclei – indeed there is a *node* at the mid-point of the nuclei. This means that at no particular time will both electrons interact strongly with both nuclei. As a consequence there will be very little electron density between the two nuclei, so they will repel each other very strongly. The energy of this orbital will be much higher than that of the two individual (non–interacting) hydrogen atoms.

By combining our two hydrogen 1s atomic orbitals in the two ways that quantum mechanics requires, we have generated two ‘new’ molecular orbitals. We have thus answered the first puzzle posed in the introduction to this chapter: we started with two atomic orbitals, and we have constructed *two* molecular orbitals: one by adding the orbitals with the same sign, and one by adding the orbitals with opposite signs. One of these is much lower in energy than the orbitals of the two isolated hydrogen atoms, and the other is much higher in energy than the orbitals two isolated hydrogen atoms. We can represent this using a simple ‘orbital energy diagram’ as shown in Fig. 2.03.


These are the molecular orbitals that result from combining the two atomic orbitals
H_2
$\psi_{1s} - \psi_{1s}$
Energy
H^A 1s
H^B 1s
H_2
$\psi_{1s} + \psi_{1s}$
These are the atomic orbitals that we combined to make the molecular orbitals

How to read this type of orbital energy diagram:
"If we take two hydrogen 1s orbitals and combine them to make molecular orbitals of the hydrogen molecule, we get two molecular orbitals. One of these is lower in energy than the 'starting' atomic orbitals and one is higher energy."

Figure 2.03

We will use this type of orbital energy diagram a lot and so it’s important that you understand what it means. It is really a shorthand way of representing the fact that when we combine the two atomic orbitals to make the ‘new’ molecular orbitals of the hydrogen molecule, we get two molecular orbitals, one of which is *lower* in energy than the original atomic orbitals and one of which is *higher* in energy than the original atomic orbitals.

You might think that after all this we have not made much headway towards explaining why the hydrogen atoms combine to make a hydrogen molecule. After all we appear to have generated one new molecular orbital that is low energy and another that is high energy, and so they should cancel each other out. However, this is not the case because so far we have not assigned any electrons to the molecular orbitals. A key point to remember about orbitals (atomic or molecular) is that an orbital only ‘counts’ towards the energy of the system if it has one or two electrons in it. Empty orbitals (atomic or molecular) contribute nothing to the energy – if they are devoid of electron density then they are irrelevant with respect to the energy!

If this seems a little odd to you then consider a hydrogen atom. We know that there are several allowed energy levels for the electron in a hydrogen atom, and that in its ground state the electron is in the lowest (1s) energy level. The higher energy 2s orbital is ‘available’ but empty and so makes no contribution to the energy. If we wanted to promote the ground state electron to the 2s orbital we would need to provide just the right amount of energy (ΔE in Fig. 2.04). If we did this then the resulting hydrogen atom would not be in its ground state, and it would rapidly and spontaneously revert its ground state – the electron would move to the 1s energy level emitting the energy that we provided (Fig 2.04).

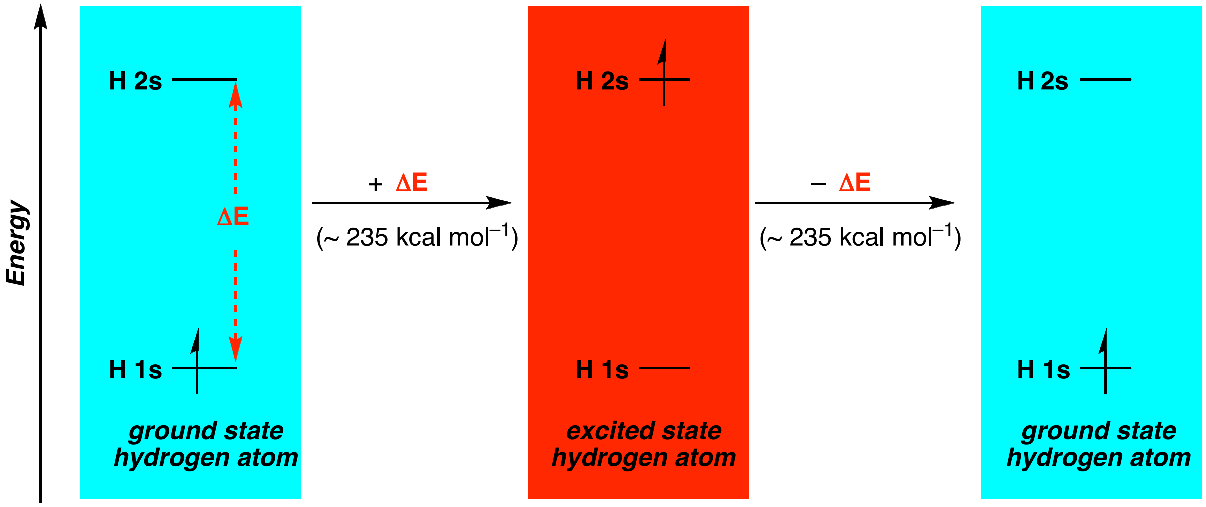


Figure 2.04

The electronic structure of the hydrogen molecule is analogous to that of the hydrogen atom shown in Fig. 2.04 in that we have two orbitals (molecular orbitals of course), one low energy and one high energy, and the ground state of the molecule will be that in which the electrons occupy the lowest energy orbital. The rules for filling molecular orbitals are no different to those for filling atomic orbitals – we fill the lowest energy orbitals first and orbitals can contain no more that two electrons whose spins must be opposite. We have two electrons to accommodate (one from each hydrogen atom) so the ground state of the hydrogen molecule is as shown in Fig. 2.05. Note that the higher energy molecular orbital, just like the 2s orbital of the hydrogen atom is 'available' but empty and contributes nothing towards the total energy.

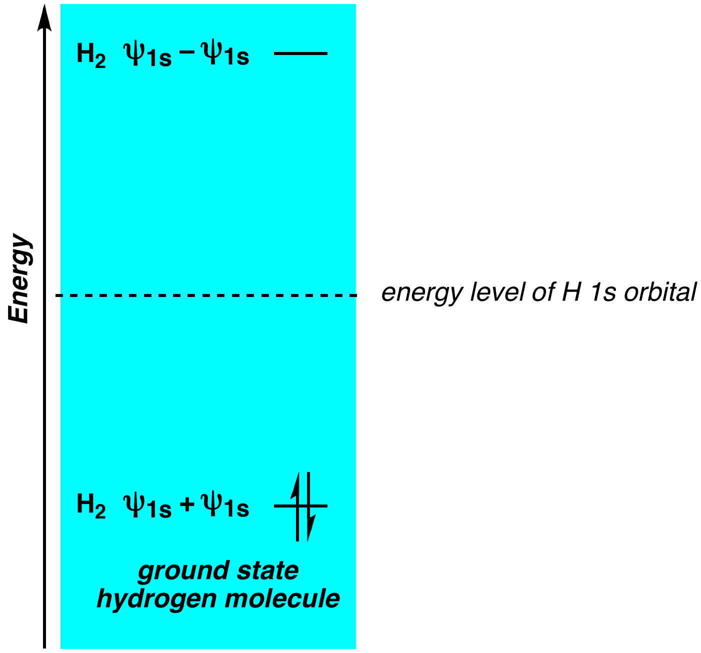

H_2 $\psi_{1s} - \psi_{1s}$
Energy
energy level of H 1s orbital
H_2 $\psi_{1s} + \psi_{1s}$
ground state hydrogen molecule

Figure 2.05

The two electrons in the low energy orbital of the hydrogen molecule are to be found most of the time between the two nuclei, and as such constitute the 'bonding electron pair' of the hydrogen molecule. In essence they are the covalent bond. Not unsurprisingly this low energy orbital is usually known as the 'bonding orbital'. What about the higher energy orbital of the hydrogen molecule? Of course being empty it contributes nothing to the energy, but it does have a name. It is often referred to as the 'antibonding orbital'. Whenever we combine two 1s orbitals we will get the same general pattern, a low energy bonding molecular orbital and a high energy antibonding orbital.

This immediately allows us to see why helium atoms behave quite differently to hydrogen atoms. A collection of helium atoms remains just that – no He_2 molecules are formed. The two electrons in a ground state helium atom are both in the 1s level. If a He_2 molecule was to form, we would get the same pattern of molecular orbitals as for the hydrogen molecule – a low energy bonding molecular orbital and a high energy antibonding molecular orbital (Fig. 2.06). The molecular orbital pattern is the same as for hydrogen but of course each helium atom has two electrons and so the helium molecule would need to accommodate these four electrons in its available molecular orbitals. This means that both the bonding and the antibonding molecular orbitals will be filled. The energy of the bonding orbital is lowered less than that of the antibonding orbital is raised (relative to the energy of the electrons in a helium atom), because in the bonding orbital the electrons must stay close to each other and so there is more electron–electron repulsion (in the antibonding orbital the electrons are on average much further apart). All this means the helium molecule would be higher in energy than two isolated helium atoms and so does not form spontaneously.

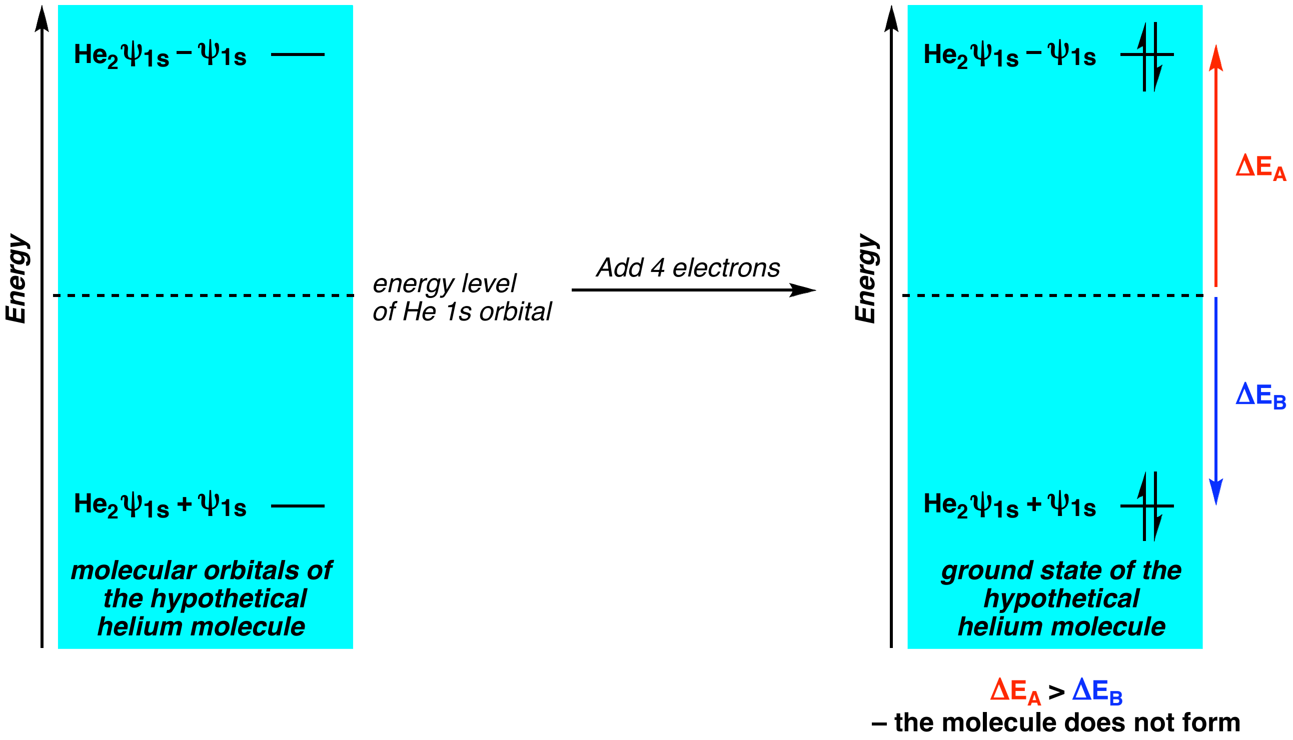
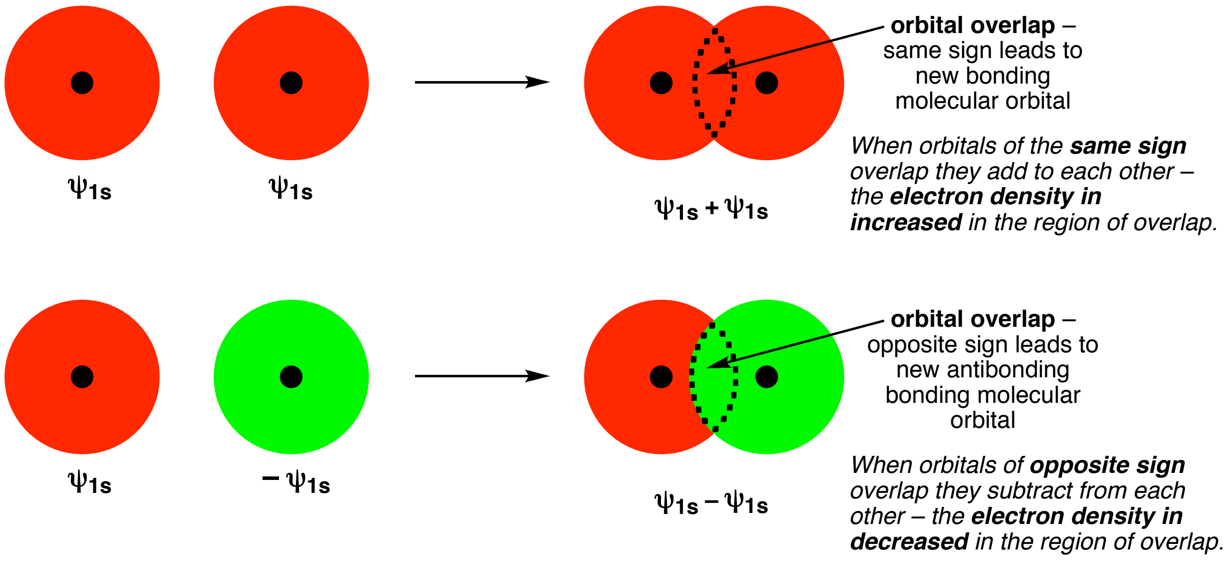

Energy
He_2 $\psi_{1s} - \psi_{1s}$
He_2 $\psi_{1s} + \psi_{1s}$
molecular orbitals of the hypothetical helium molecule
energy level of He 1s orbital
Add 4 electrons
Energy
He_2 $\psi_{1s} - \psi_{1s}$
He_2 $\psi_{1s} + \psi_{1s}$
ground state of the hypothetical helium molecule
ΔE_A
ΔE_B
$\Delta E_A > \Delta E_B$
– the molecule does not form

Figure 2.06

We have spent quite a lot of time discussing hydrogen and helium, neither of which is an organic compound! They are of course the simplest systems we could have chosen to illustrate the important ideas behind covalent bonding. Very soon we will study the bonding in organic molecules, but before that we will generalize the rules for combining orbitals so that we can apply the ideas we developed in this section to organic molecules in general.

Often when we discuss combining orbitals we speak of ‘overlap’ (illustrated pictorially in Fig. 2.07 for two 1s orbitals). This type of pictorial representation is extremely useful when thinking about covalent bonds and we will use it a lot in the rest of the book, so it’s important that you are clear about how to construct and interpret them. We need to know the ‘shape’ of the ‘starting’ orbitals, which we can represent very simply because all we need to know is where the (majority of the) orbital is located with respect to the atomic nucleus. We can use simple geometric shapes that correspond to the orbital – in Fig. 2.07 we use a circle for an s orbital. We also need to be aware of the relative sign and any nodes (sign changes) in the starting orbitals, and we will represent one sign as a red orbital and the other as green (as we discussed, it does not matter what the absolute signs are – we have taken red as positive and green as negative).



*When orbitals of the **same sign** overlap they add to each other – the **electron density in increased** in the region of overlap.*

*When orbitals of **opposite sign** overlap they subtract from each other – the **electron density in decreased** in the region of overlap.*

Figure 2.07

The pictorial representations of the molecular orbitals (Fig. 2.07) show in essence the ‘component parts’ of the molecular orbitals – viewing the starting orbitals as the components. It is often very useful to use this view, and provided you know the shapes of the starting orbitals you don’t need to guess the ‘real shapes’ of the molecular orbitals.

Sometimes it is useful and instructive to show these ‘real shapes’ and it is not difficult to draw simple approximate shapes by considering where areas of electron density are raised or lowered by the overlap. The relationship between the ‘component parts’ view and ‘real shapes’ of the molecular orbitals from Fig. 2.07 is illustrated in Fig. 2.08.

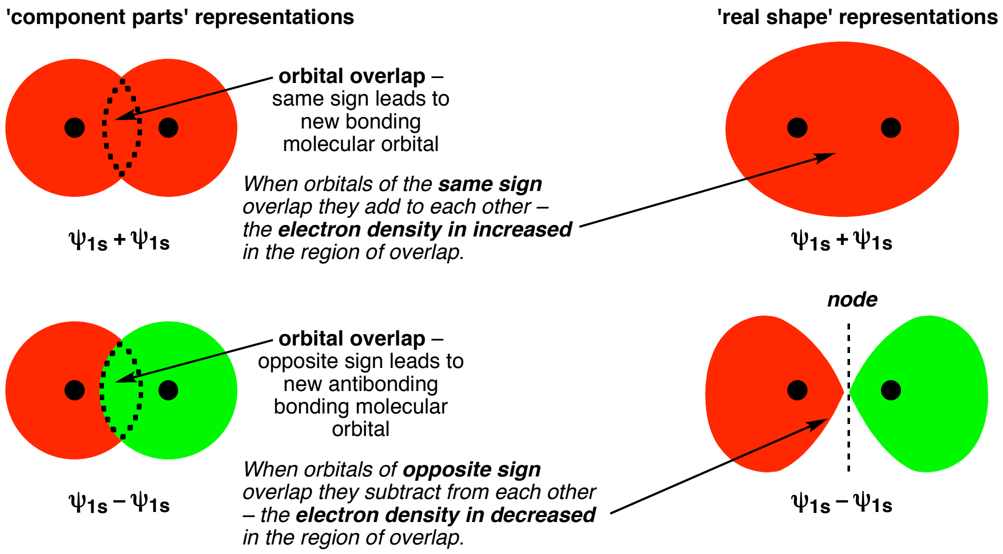
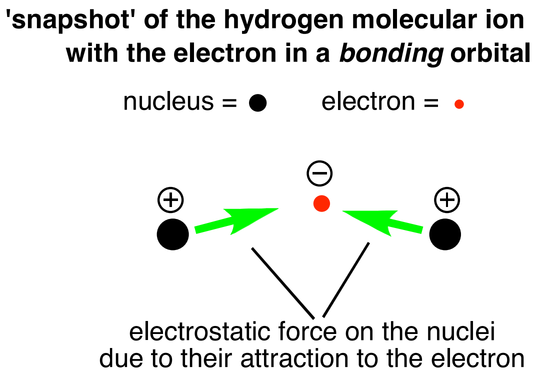

'component parts' representations
'real shape' representations
orbital overlap – same sign leads to new bonding molecular orbital
When orbitals of the same sign overlap they add to each other – the electron density in increased in the region of overlap.
$\psi_{1s} + \psi_{1s}$
$\psi_{1s} + \psi_{1s}$
node
orbital overlap – opposite sign leads to new antibonding bonding molecular orbital
When orbitals of opposite sign overlap they subtract from each other – the electron density in decreased in the region of overlap.
$\psi_{1s} - \psi_{1s}$
$\psi_{1s} - \psi_{1s}$

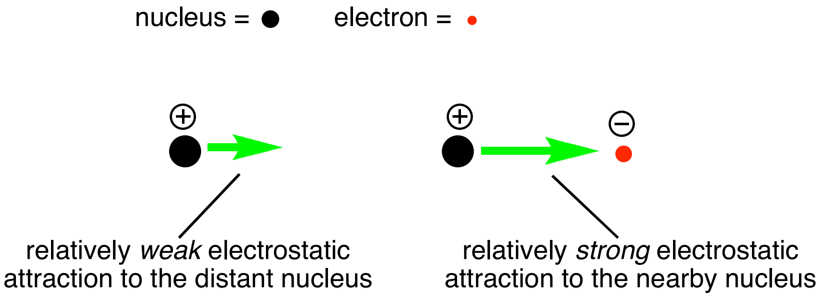
Figure 2.08

Now that you have seen the shapes of these bonding and antibonding orbitals, we can offer a more intuitive explanation of why they are called “bonding” and “antibonding.” The term “antibonding,” in particular, tends to cause much confusion among chemistry students. Consider the simple “snapshot” of the H_2 molecule that we discussed in Chapter 1. Indeed, let us simplify the picture even further and consider the H_2^+ molecular ion, which contains only *one* electron and *two* nuclei. If that electron is in a *bonding* orbital, it is most likely to be found between the nuclei, where the wavefunction is greatest. Thus, a likely “snapshot” of an electron in a bonding orbital would be as follows:


'snapshot' of the hydrogen molecular ion (H_2^+) with the electron in a *bonding* orbital
nucleus = ●
electron = ●
⊖
⊕
⊕
electrostatic force on the nuclei due to their attraction to the electron

Imagine that the electron in the above figure is momentarily "frozen" in this snapshot. What will be the forces *on the nuclei* due to their attraction to the electron? The nucleus on the left will feel a force toward the right (as indicated by the green arrow in the above figure), while the nucleus on the right will feel a force toward the left. The result of these two forces is that the nuclei are drawn *closer together*: the presence of electron density *between* the nuclei pulls the nuclei together, resulting in a chemical bond. Thus, when a molecular orbital has its greatest electron density *between* the nuclei, we call that orbital a *bonding* orbital.

Now consider the same H_2^+ molecular ion, but let's put the electron into the *antibonding* molecular orbital. The antibonding orbital has its greatest electron density *outside* the nuclei, so the electron is most likely to be found outside the nuclei, rather than in the space between them:



'snapshot' of the hydrogen molecular ion (H_2^+)
with the electron in an *antibonding* orbital

nucleus = ●
electron = •
⊕
⊕
⊖
relatively *weak* electrostatic attraction to the distant nucleus
relatively *strong* electrostatic attraction to the nearby nucleus

If the electron is, say, to the *right* of the two nuclei (as in the above figure), it will exert a relatively strong electrostatic force on the nucleus close to it and a relatively weak electrostatic force on the more distant nucleus. (Recall that the strength of electrostatic forces decreases with distance.) Although both forces pull the nuclei in the same direction, since the forces have different strengths they serve to pull the two nuclei *apart* from one another. You can best appreciate this point if you imagine that the electron is stationary and only the nuclei can move: the nucleus on the right will move quickly towards the electron, while the nucleus on the left will move slowly towards the electron.

Thus, any electron density *outside* the region between the nuclei will actually pull the two nuclei apart: this is what is meant by an *antibonding* orbital! Any molecular orbital that has its greatest electron density outside the region between the nuclei will be an *antibonding* orbital. We can finally understand why the He_2 molecule is unstable: it has two electrons in a bonding orbital (pulling the nuclei together) and two electrons in an antibonding orbital (pulling the nuclei apart), and the electrons in the antibonding orbital win this "tug-of-war" and pull the two He atoms apart. This description of bonding and antibonding orbitals is highly simplified; we discussed in Chapter 1 that the electrons in an atom or molecule never sit still. The basic conclusion, however, is correct: any electron density in a bonding orbital will hold the atoms together, while any electron density in an antibonding orbital will pull the atoms apart.

We can quantify this "tug-of-war" between bonding electrons and antibonding electrons by defining the **bond order** of a molecule or ion. The bond order is defined as follows:

$$\textbf{bond order} = \frac{(\#\text{ of } e^- \text{ in bonding orbitals}) - (\#\text{ of } e^- \text{ in antibonding orbitals})}{2}$$

This expression says that any electrons in bonding orbitals will *increase* the bond order, while any electrons in antibonding orbitals will *decrease* the bond order. The overall bond order can be positive, negative, or zero. If the bond order is positive, then the bonding electrons outweigh the antibonding electrons and the molecule will be stable; otherwise, the antibonding electrons outweigh the bonding electrons and the molecule will not be stable.

2.2. Constructing Molecular Orbitals from Hybridized Orbitals

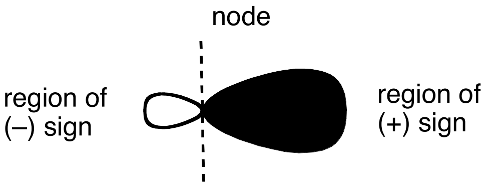
In this course, we will take an approach to molecular orbitals that may be somewhat different from the approach used in your general chemistry course. We will construct our molecular orbitals from atomic orbitals that are *already hybridized*. You will find that it is *simpler* to make molecular orbitals out of hybridized orbitals than it is to use unhybridized atomic orbitals. Note that, once you have hybridized the orbitals for each atom, **the only orbitals that can form molecular orbitals are hybridized orbitals and leftover (unhybridized) p-orbitals.**

The rules for making molecular orbitals (MO's) out of hybridized orbitals are:

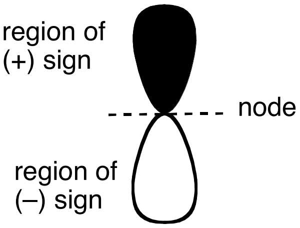
a) **Hybridized orbitals** can combine "end-on" to make **sigma**-type molecular orbitals.
b) **Unhybridized *p*-orbitals** can combine "side-on" to make **pi**-type molecular orbitals.
c) Each pair of orbitals combines to make a **bonding** MO *and* an **antibonding** MO.

Let's look at some examples. First, recall the shapes of the orbitals:

hybridized orbital (sp, sp^2, or sp^3):

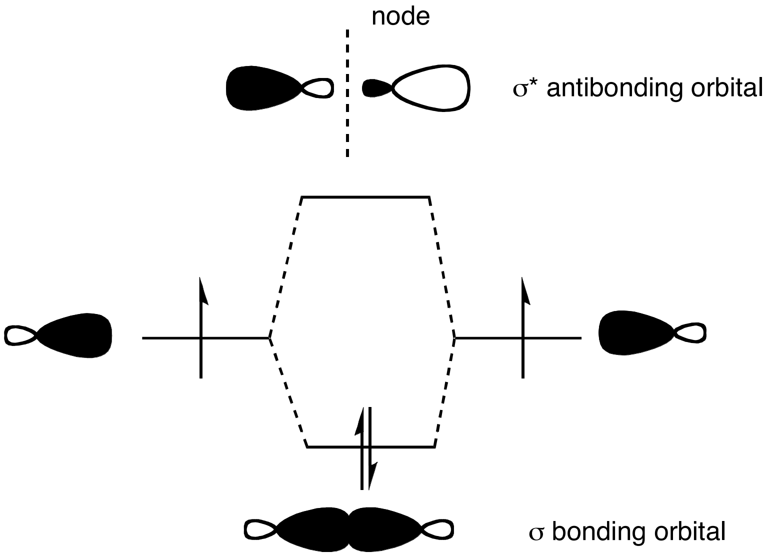


unhybridized p-orbital:



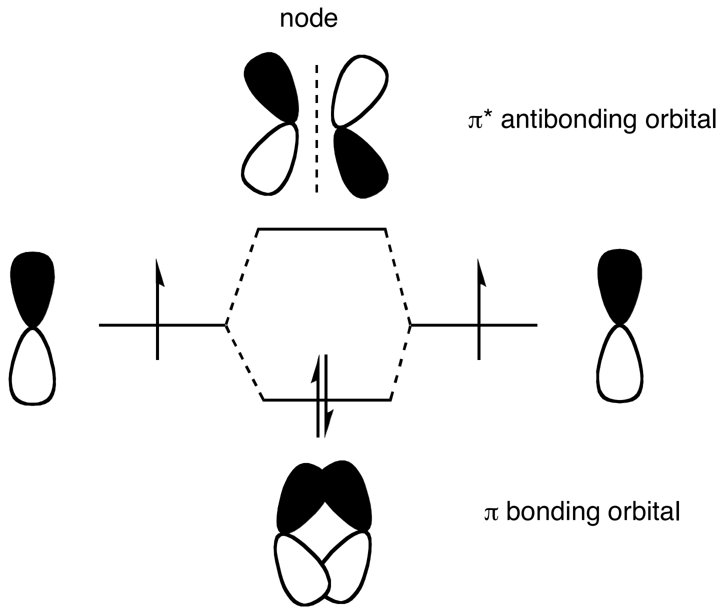
Note that the hybridized orbitals all have roughly the same shape: they each consist of two "lobes," one of which is *much larger* than the other. Between these two lobes, there is a node: the two lobes have opposite signs, as indicated by the shaded (positive sign) and unshaded (negative sign) regions. A p-orbital, on the other hand, has two lobes that are the *same size*. As with the hybridized orbitals, there is a node between these lobes; the two lobes are of opposite sign.

These orbitals combine to form molecular orbitals. We can **combine two hybridized orbitals to make a σ bonding orbital and a σ* antibonding orbital**:



As discussed in the example of the covalent bonding in H_2, the σ *bonding orbital* is constructed from a combination of the two hybridized orbitals “in phase”—with the same sign in the region between the nuclei. Thus, there is *no node* between the nuclei and the bonding orbital has lower energy than the individual hybridized orbitals. Conversely, the σ *antibonding orbital* is constructed from a combination of the two hybridized orbitals “out of phase”—with *opposite* signs in the region between the nuclei. Thus, there is a *node*—a region of zero electron density—between the nuclei. The antibonding orbital therefore has higher energy than the individual hybridized orbitals.

Instead of combining hybridized orbitals to create a σ-bond, we can combine unhybridized *p*-orbitals to create a π-bond. The **two p-orbitals combine to make a π bonding orbital and a π* antibonding orbital**:



You should recall from our discussion of Lewis structures that a single bond is a σ-bond, a double bond is a combination of a σ-bond plus a π-bond, and a triple bond is a combination of a σ-bond plus *two* π-bonds. Thus, you won't see a π-bond between two atoms unless there is *also* a σ-bond between them. These are the most important molecular orbitals for you to know: the sigma bonding (and antibonding) orbitals, and the pi bonding (and antibonding) orbitals.

There are several important features to note about these **energy-level** diagrams:

- The *node* in the *antibonding orbital* results from the fact that the two orbitals have *opposite sign* in the region of overlap. (We use the convention that a filled lobe has positive sign, while an unfilled lobe has negative sign.) This "negative overlap" results in *destructive interference* in the region between the nuclei, so there is no electron density in that region (the node).

- The antibonding orbital is always *raised in energy* compared with the atomic orbitals. Recall that orbitals with more nodes have higher energies than orbitals with fewer nodes.

- The bonding orbital is always *lowered in energy* compared with the atomic orbitals: the region of overlap (where the orbitals have the same sign) results in *constructive interference* and lowers the energy of the orbitals.

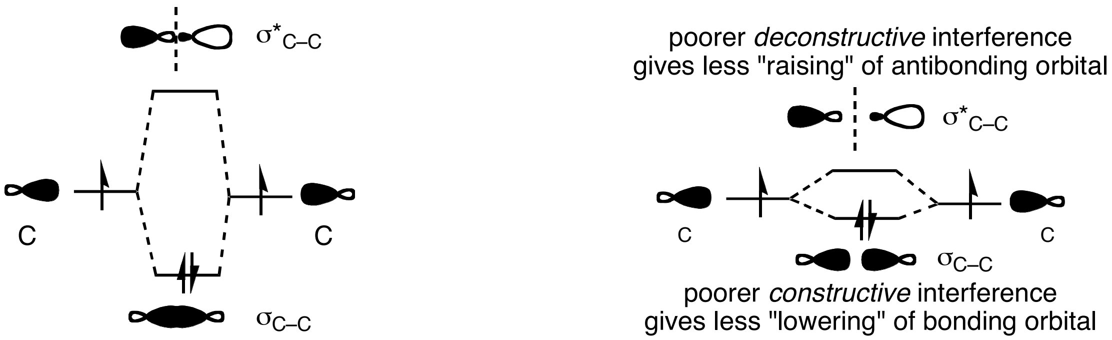
- The amount that the antibonding orbital is raised is slightly *greater* than the amount that the bonding orbital is lowered. (Look closely at the diagrams: can you see this?)

- The amount of energy raising and lowering is *greater* for sigma bonds than for pi bonds. This is because sigma bonds have better orbital overlap than pi bonds.

The amount of raising and lowering of the energies of the molecular orbitals is primarily determined by two factors: the *geometric overlap* of the atomic orbitals, and the *difference in energy* between the atomic orbitals. Let's examine each of these factors:

First, consider the effect of **geometric overlap**. Imagine taking a molecule of ethane ($H_3C–CH_3$) and stretching the C–C bond. What will happen to the energies of the molecular orbitals as we stretch that bond?

$H_3C–CH_3$ --- stretch ----> H_3C————CH_3



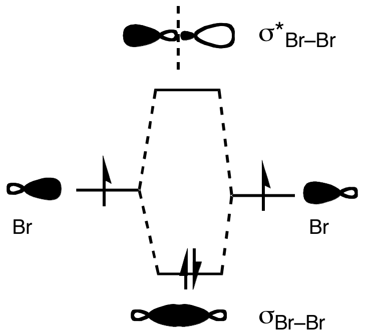
poorer *deconstructive* interference gives less "raising" of antibonding orbital

poorer *constructive* interference gives less "lowering" of bonding orbital

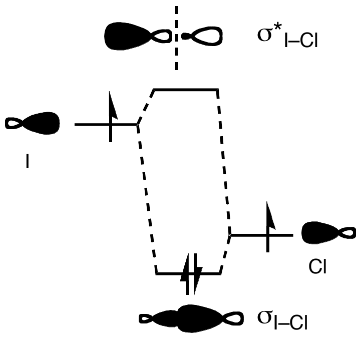
We see that as we stretch the bond, the geometric overlap between the sp^3-hybridized orbitals becomes smaller and smaller, so the splitting in energy between the σ bonding orbital and the σ* antibonding orbital decreases. If we streched the bond to an infinite distance, there would be no splitting—and no bond!

Now, consider the effect of the **difference in energy** between the orbitals. Compare the molecule Br_2 (Br–Br), in which the two atomic orbitals have the same energy, with the molecule ICl (I–Cl), in which the two atomic orbitals have different energies:

Br–Br


$\sigma^*_{\text{Br–Br}}$
Br
Br
$\sigma_{\text{Br–Br}}$

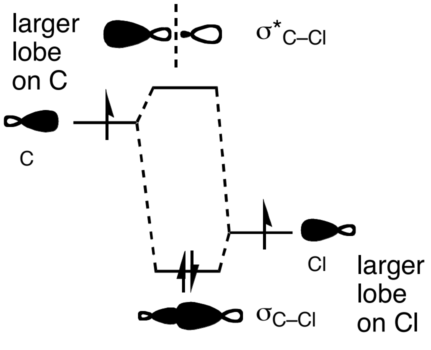
I–Cl


$\sigma^*_{\text{I–Cl}}$
I
Cl
$\sigma_{\text{I–Cl}}$

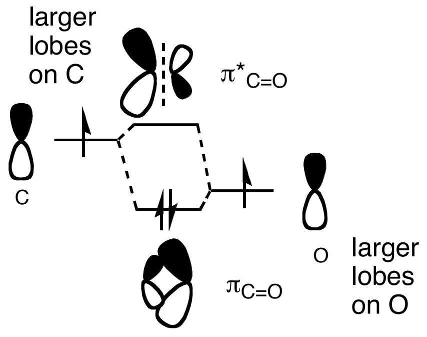
We see that orbitals that are **close in energy** give rise to a **large change in energy** between the atomic orbitals and the resulting molecular orbitals. (*Question*: Why are the chlorine orbitals lower in energy than the iodine orbitals?)

When the orbitals of the two atoms have different energies (e.g. they come from atoms with different electronegativities), the resulting molecular orbital will be asymmetric. Look at the asymmetric σ (sigma) orbitals in $H_3C–Cl$, and the asymmetric π (pi) orbitals in $H_2C=O$:

$H_3C–Cl$


larger lobe on C
$\sigma^*_{\text{C–Cl}}$
C
Cl
larger lobe on Cl
$\sigma_{\text{C–Cl}}$

$H_2C=O$


larger lobes on C
$\pi^*_{\text{C=O}}$
C
O
$\pi_{\text{C=O}}$
larger lobes on O

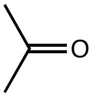
The bonding orbital always has a larger lobe near the more electronegative atom (where there is more electron density). Thus, the rules of quantum mechanics require that the **antibonding orbital must have a larger lobe near the less electronegative atom**. In both of the above diagrams, the antibonding orbital has a larger lobe on the carbon atom. This asymmetry will be extremely important in determining how molecules react.

Practice Problem 2.2: Construct a simple molecular orbital "splitting diagram" for the specified bonds in each of the following species. The splitting diagram should include the atomic orbitals for the atoms involved in the bond and the resulting molecular orbitals. Try to illustrate the correct *relative* energies of the orbitals involved. Include "cartoon orbitals" that represent the general shape (and, when relevant, the asymmetry) of the resulting molecular orbitals.

the C–H σ-bond in CH_3Cl

the C–Cl σ-bond in CH_3Cl

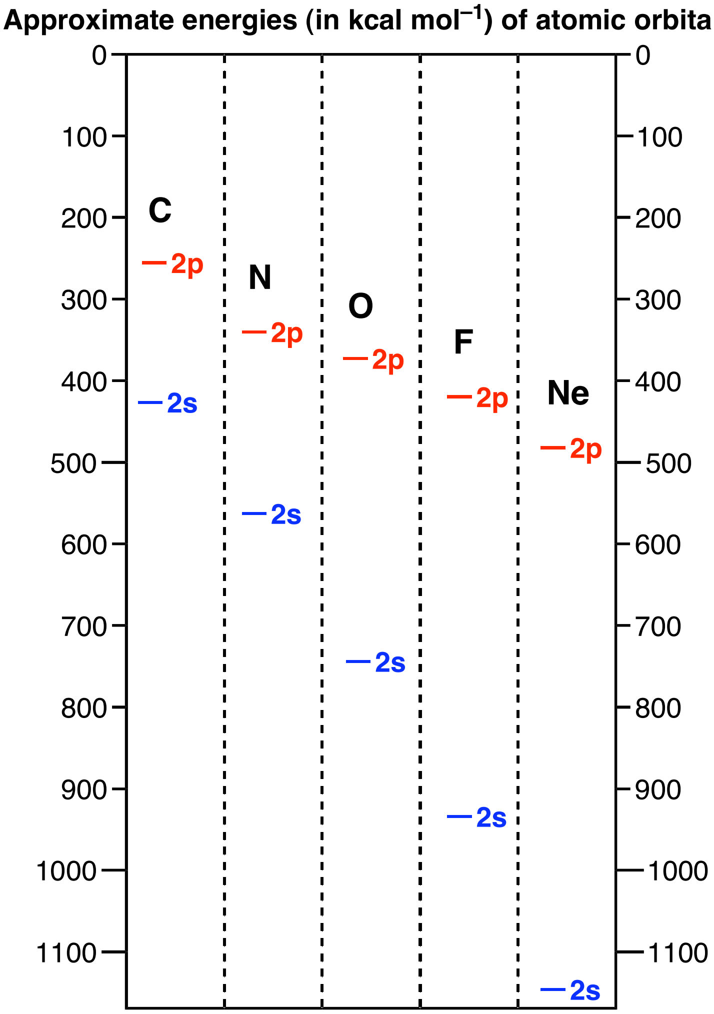
the C=C π-bond in $H_2C{=}CH_2$

the C=O π-bond in 

the **two** C=N π-bonds in $H_3C-C\equiv N$

2.3. The Energies of Atomic and Molecular Orbitals

We learned in Chapter 1 that the electronegativity of an atom influences the energies of its orbitals: more electronegative atoms have lower-energy orbitals. Since we are constructing molecular orbitals from *hybridized* orbitals, we should also determine how the hybridization of an atom affects the energies of its orbitals. Recall the energies of the *s* and *p* orbitals we saw in Chapter 1:



We described hybridized orbitals as *mixtures* of the basic atomic orbitals. For instance, an *sp* hybrid orbital is a mixture of one *s*-orbital and one *p*-orbital. Likewise, an sp^3 hybrid orbital is a mixture of one *s*-orbital and *three p*-orbitals. In quantum mechanics, when you mix atomic orbitals of different energy, the *average* energy of the mixed orbital (technically called the "expectation value" of the energy") is given simply by the weighted average of the energies of the individual orbitals. So, the energy of an *sp*-

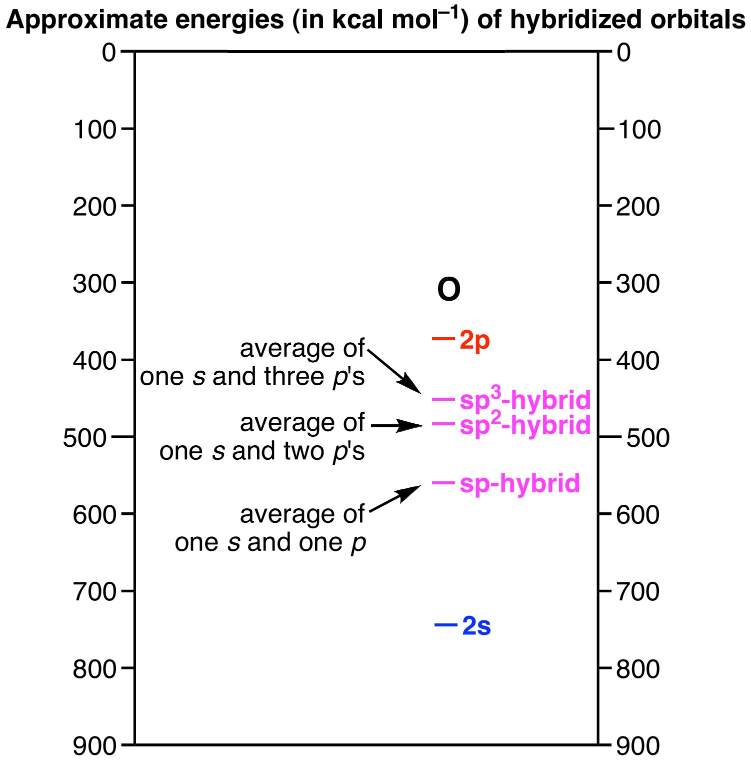
hybridized orbital is equal to the average of the energy of one *s* and one *p* orbital. Consider oxygen as an example. The energies of the 2*s* and 2*p* orbitals in oxygen are –740 and –364 kcal/mol, respectively. An *sp*-hybridized orbital will have an energy that is the average of these two energies:

$$\text{energy of } sp\text{-hybridized oxygen orbital} = \frac{(-740) + (-364)}{2} = -552 \text{ kcal/mol}$$

You will often hear chemists say that an *sp*-hybridized orbital is 50% *s* and 50% *p* in character; these percentages correspond to the weights of the energies in the above formula. Likewise, the energy of an sp^3-hybridized orbital is equal to the average of the energy of one *s* and three *p* orbitals:

$$\text{energy of } sp^3\text{-hybridized oxygen orbital} = \frac{(-740) + 3(-364)}{4} = -458 \text{ kcal/mol}$$

Chemists often refer to an sp^3-hybridized orbital as 25% *s* and 75% *p* in character; again, these percentages correspond to the weights of the energies in the above formula. The diagram below shows the approximate energies of the hybridized orbitals of oxygen in comparison to the atomic orbitals:



As you can see from this diagram, the *sp*^{2}- and sp^3-hybridized orbitals are fairly close in energy, while the *sp*-hybridized orbital is significantly lower in energy than the other two. The important take-home message is that **hybridized orbitals with more *s*-character are lower in energy than hybridized orbitals with more *p*-character.** In other words, for all atoms, the energies of their hybridized orbitals follow the order $sp < sp^2 < sp^3$. You will sometimes hear chemists say that *sp*-hybridized atoms are effectively *more electronegative* than *sp*^{3}-hybridized atoms. This statement is reasonable, if somewhat oversimplified: you can think of "electronegativity" as a measure of the energy of electrons in an orbital, with more electronegative orbitals having lower energies.

We have now seen *two* factors that affect the energies of atomic orbitals: electronegativity and hybridization. There is a *third* factor that is also quite significant: the effect of *charge* on orbitals: specifically, the effect of *formal charge*. Atoms that have a *positive* formal charge will have orbitals that are *lower* in energy, while atoms that have a *negative* formal charge will have orbitals that are *higher* in energy. This trend should make sense; an atom with a greater positive charge will have a greater electrostatic attraction for its electrons, so their overall energy will be lower. Confusingly, this trend is often expressed by saying that an atom with a positive formal charge is *more electronegative* than a neutral atom, and an atom with a negative formal charge is *less electronegative* than a neutral atom.

There are thus three factors that affect the energies of atomic orbitals: electronegativity, hybridization, and formal charge. These factors are summarized in the following table:

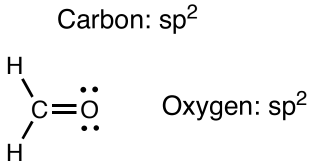
	Low energy orbitals result from:	**High energy** orbitals result from:
Electronegativity	**high** electronegativity	**low** electronegativity
Hybridization	***sp***-hybridization	***sp*^{3}**-hybridization
Formal Charge	**positive** formal charge	**negative** formal charge

You should commit these trends to memory, but you should also understand (and be able to explain) the reasons behind these trends.

2.4. Molecular Orbitals for Simple Molecules

Now that you can construct a molecular orbital for a particular bond in a molecule, let's learn how to determine *all* the important valence molecular orbitals for a molecule. First we'll walk through an example. Let's determine all the molecular orbitals for the molecule formaldehyde, $H_2C{=}O$.

Step 1. Draw the Lewis structure for the molecule, including any important resonance structures. Determine the hybridization of all the atoms in the structure.



Step 2. Make a list of all the molecular orbitals in the molecule. For every bond in the Lewis structure, there will be **two** molecular orbitals: a bonding orbital and an antibonding orbital. In addition, every **nonbonded** orbital in the molecule will correspond to a single nonbonded molecular orbital. (Lone pairs and vacant p-orbitals are examples of nonbonded orbitals). At this point, *count* to make sure you have the correct total number of molecular orbitals:

(Total # of orbitals) = (# of hydrogen atoms) + (4 × (# of other atoms))

Question: Can you explain where this formula comes from?

For formaldehyde, $H_2C{=}O$, we have the following orbitals (in **no particular order**):

$$2\ \sigma_{C\text{–}H}\ ,\ 2\ \sigma^*_{C\text{–}H}\ ,\ \ \sigma_{C\text{–}O}\ ,\ \ \sigma^*_{C\text{–}O}\ ,\ \ \pi_{C=O}\ ,\ \ \pi^*_{C=O}\ ,\ \ 2\ nb_O$$

Note that there are a total of 10 molecular orbitals = (2 H atoms) + 4 × (2 other atoms)
The nonbonding orbitals on O (nb_O) are the two lone pairs on the oxygen atom.

Step 3. Group the orbitals together and rank their energies according to the following general guidelines:

(High energy)

σ^*

π^*

nb

π

σ

(Low energy)

For formaldehyde, we obtain the following groups of orbitals, with a rough order of energies:

(High energy)

σ^*	2 $\sigma^*_{C–H}$, $\sigma^*_{C–O}$
π^*	$\pi^*_{C=O}$
nb	2 nb_O
π	$\pi_{C=O}$
σ	2 $\sigma_{C–H}$, $\sigma_{C–O}$

(Low energy)

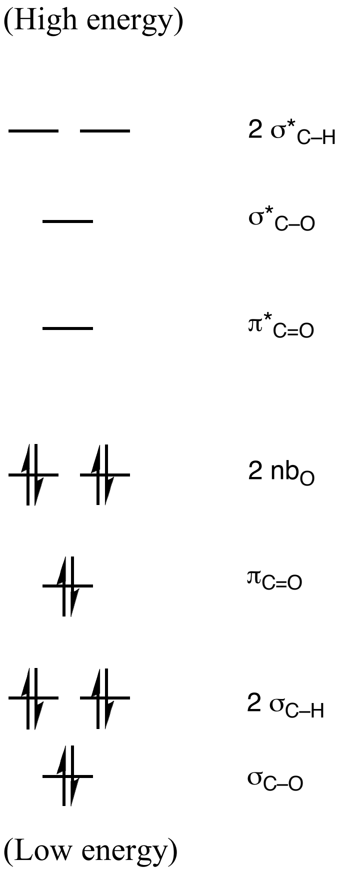
Step 4. *Within* each of the above groups, rank the energies of the orbitals based on the electronegativities of the atoms involved. (Recall that more electronegative atoms have orbitals that are lower in energy.) For formaldehyde, we obtain the following list of orbitals, with an *approximate* ordering of energy levels:

(High energy)

σ^*	2 $\sigma^*_{C–H}$ $\sigma^*_{C–O}$
π^*	$\pi^*_{C=O}$
nb	2 nb_O
π	$\pi_{C=O}$
σ	2 $\sigma_{C–H}$ $\sigma_{C–O}$

(Low energy)

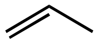
Step 5. Draw horizontal lines to represent each orbital, and fill the orbitals with the correct number of electrons. (You may wish to refer back to the Lewis structure to count the total number of valence electrons in the molecule. Formaldehyde has 12 valence electrons.) Be sure to add electrons starting with the lowest-energy molecular orbital, and observe the Pauli principle (each orbital can have at most 2 electrons, with opposite spins). This diagram shows all the valence orbitals in the molecule, ordered based on energy, and filled with the correct number of electrons. It is usually called as an "**energy-level diagram**." You may wish to also draw "cartoon" representations of each of the orbitals, just to remind yourself what each of the orbitals looks like.

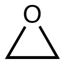


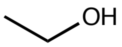
Step 6. Check your energy-level diagram:

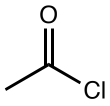
- Does it have the correct number of orbitals?
- Does it have the correct number of electrons?
- Are *all* the bonding orbitals filled with electrons? (They should be!)
- Are *all* the antibonding orbitals vacant? (They should be!)
- Count the total number of filled bonding orbitals:
  is that equal to the total number of bonds in the Lewis structure?

Practice Problem 2.4: For each of the following species, draw a complete Lewis structure, showing all atoms and lone pairs, and then construct an energy-level diagram for the valence molecular orbitals for the species. Be sure to **check** your MO diagram using the guidelines given above!









$Br-C\equiv N$

2.5. Reactions Between Molecules: Frontier Orbitals

Now that we can determine all the molecular orbitals for a given molecule, we can begin to answer the central question in chemistry: **What happens when molecules react, and why?** Consider the following general chemical reaction:

$$A + B \rightarrow C + D$$

You should visualize this reaction as follows: A molecule of A collides with a molecule of B. Most of the time, those two molecules just bounce off of each other and emerge unchanged. When A and B collide in the *correct orientation* with *sufficient energy*, they can *react* during that collision, and molecules of C and D will emerge from the collision. As an analogy, consider a pickpocket walking through a crowd. Most of the time, the pickpocket bumps into someone and nothing happens. Sometimes, if the situation is just right, the pickpocket bumps into someone and steals his wallet. After that collision, the pickpocket now has the wallet and the victim does not. That type of collision, in which the two species that *emerge* from the collision are different from those that *entered* the collision, is analogous to a chemical reaction.

So, we want to ask: what happens when two molecules, A and B, collide? Well, *all* of the orbitals of A interact with *all* of the orbitals of B molecule to form a whole set of *new* orbitals. Then the electrons slosh around in all of these new orbitals and redistribute themselves. Sometimes, the electrons can distribute themselves into new orbitals that correspond to the products, C and D. In that case, these new products emerge from the collision, and we say that a chemical reaction has occurred.

Although that description is generally accurate, it's not very helpful to us in determining what happens when molecules A and B collide. Each of these molecules will have many molecular orbitals, and the number of *interactions* between those orbitals will be an even larger number. Although computers can keep track of all those interactions, you or I would have quite a hard time doing so. So we make a dramatic simplification: we focus on the interactions between a very small number of orbitals, known as the **frontier orbitals**. This approach, developed in the 1950's by Kenichi Fukui, of Kyoto University in Japan, and extended in the 1960's by Roald Hoffmann, of

Cornell University, in Ithaca, New York, was so important that these two scientists received the Nobel Prize in Chemistry in 1981 for their work. **Understanding the interactions of frontier orbitals is the key to understanding chemical reactivity**. Here are some excerpts from the press release of the 1981 Nobel Prize Committee (emphasis added):

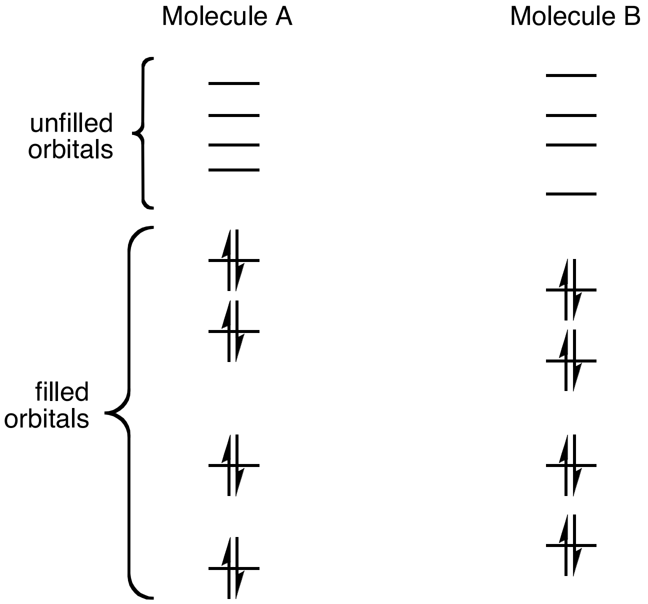
> The Prizewinners' work aims at theoretically **anticipating the course of chemical reactions**. It is **based on quantum mechanics** (the theory whose starting point is that the smallest building blocks of matter may be regarded both as particles and as waves), which attempts to explain how atoms behave...
>
> [In the 1950's], Fukui showed that certain properties of the orbits of the most loosely bound electrons and of the "most easily accessible" unoccupied electronic orbits had **unexpectedly great significance for the chemical reactivity of molecules**. He called these orbits "**frontier orbitals**." Fukui's earlier frontier orbital theory attracted only little attention at first. In the mid-1960s, Fukui and Hoffmann discovered—almost simultaneously and independently of each other—that symmetry properties of frontier orbitals could explain certain reaction courses that had previously been difficult to understand. This gave rise to unusually intensive research activity—both theoretical and practical—in many parts of the world, as Fukui and other researchers developed the **frontier orbital theory** into a highly powerful **tool for understanding the reactivity of molecules**...
>
> A characteristic feature of Fukui's and Hoffmann's method of attacking difficult and complicated problems is that they **succeeded in making generalizations through simplifications**. In this lies the key to the strength of their theories. The theoretical models that Fukui and Hoffmann introduced have been in many branches of chemistry since the 1970s. Their method of conceiving of the course of chemical reactions is **utilized nowadays, for example, by chemists studying life processes and by chemists making new drugs**.

Kenichi Fukui

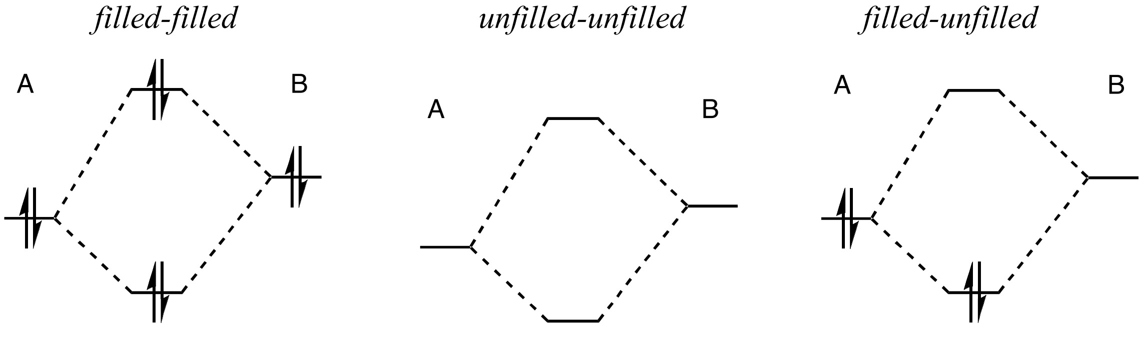
Roald Hoffmann

For you, as a student, the most important message is that the theory of frontier orbitals will allow you to **anticipate the course of chemical reactions**. That means that you can **predict** what will happen in an organic reaction—you don't have to memorize every reaction. Let's see how to use this amazing tool!

We know that molecule A and molecule B will each have many molecular orbitals. Roughly half of the orbitals (the ones lowest in energy) will be filled with electrons, while the others will be unfilled. We can imagine that the molecular orbitals for these species might look something like this:

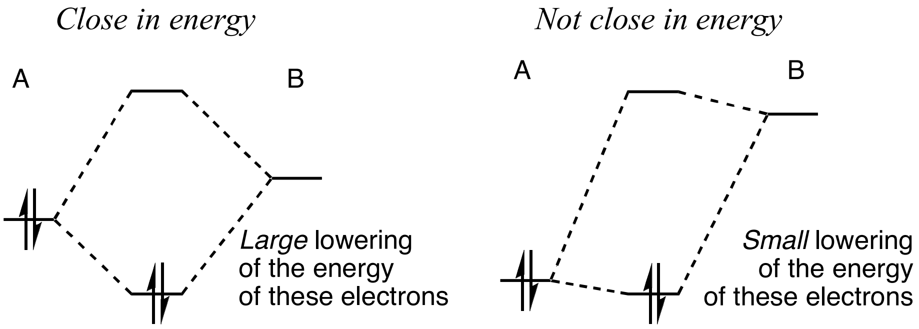

Molecule A
Molecule B
unfilled orbitals
filled orbitals

Now allow all of these orbitals to interact with one another. There are essentially three types of interactions: interactions betweeen two filled orbitals, interactions between two unfilled orbitals, and interactions between a filled orbital and an unfilled orbital:


filled-filled
unfilled-unfilled
filled-unfilled
A
B
A
B
A
B

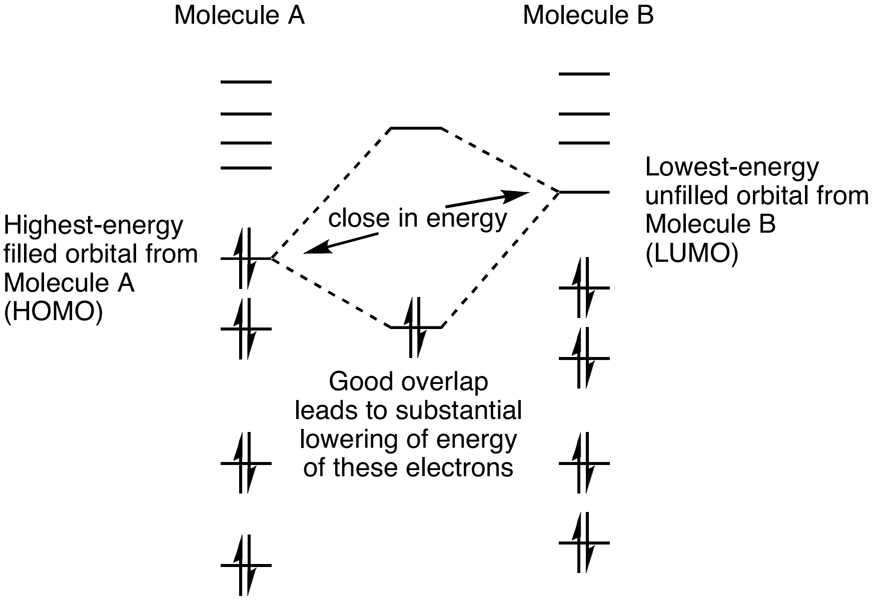
When two filled orbitals interact, two electrons go up in energy and two electrons go down in energy, but the total energy of the electrons doesn't change very much. In fact, the antibonding orbital is raised in energy more than the bonding orbital is lowered in energy, so the total energy is actually increased: this is an *unfavorable* interaction. When two unfilled orbitals interact, no electrons change energy at all, so this interaction has no effect on the reaction. However, when a filled orbital interacts with an unfilled orbital, the result is a net *lowering* of the total energy of the electrons. This observation is the first rule of frontier orbitals: **the most important interactions are those between a filled orbital and an unfilled orbital.** We can usually *ignore* all the other interactions.

Now consider all of the possible interactions between filled orbitals and unfilled orbitals. We learned earlier that large splittings in the energy between the bonding and antibonding orbitals result from two factors: orbitals that have favorable geometric overlap and orbitals that are are close in energy. The issue of geometric overlap is absolutely important: if two orbitals can't overlap, they can't interact. Recall, though, that two molecules can collide in many different orientations. Often, at least one of those orientations will allow the orbitals in question to overlap. So we must consider the energies of the orbitals. If two orbitals are close in energy, there will be a large splitting between the bonding and antibonding orbitals. For an interaction between filled and unfilled orbitals, a large splitting will lead to a large lowering of the energy of the electrons. Consider two possible interactions between a filled orbital from molecule A and an unfilled orbital from molecule B:


Close in energy
A
B
Large lowering of the energy of these electrons
Not close in energy
A
B
Small lowering of the energy of these electrons

When the filled and unfilled orbitals are close in energy, the electrons in the filled orbital end up significantly lower in energy; when the filled and unfilled orbitals have very different energies, the electrons in the filled orbital end up only slightly lower in energy.

In general, all of the filled orbitals (of both molecules) are lower in energy than all of the unfilled orbitals (of both molecules.) If *all* the orbitals of molecule A interact with *all* the orbitals of molecule B, the interaction that gives the *greatest* lowering of the energy of the electrons will be the interaction between the **filled orbital with the highest energy** and the **unfilled orbital with the lowest energy**, because those two orbitals will be *closest* in energy:


Molecule A
Molecule B
Highest-energy filled orbital from Molecule A (HOMO)
close in energy
Lowest-energy unfilled orbital from Molecule B (LUMO)
Good overlap leads to substantial lowering of energy of these electrons

These special orbitals are called the **HOMO** (Highest Occupied Molecular Orbital) and the **LUMO** (Lowest Unoccupied Molecular Orbital), respectively. Together, they are referred to as the **frontier orbitals**. (In geography, the frontier is defined as the border between the populated regions of a country and the unpopulated regions; the frontier orbitals are the orbitals at the "border" between the filled orbitals and the unfilled orbitals.) Fukui's simple but powerful idea (which won him a Nobel Prize!) was that you could ignore all the other orbitals in the molecule and focus on the frontier orbitals. Once you identify the frontier orbitals of a molecule, you can usually predict how that molecule will react.

The overlap between a filled orbital (the HOMO) of one molecule and an unfilled orbital (the LUMO) results in **donation of electrons** from the filled orbital to the unfilled orbital. We often refer to the HOMO as the **donor orbital** and the LUMO as the

acceptor orbital. These terms emphasize the *roles* that these orbitals play in a particular reaction: the electron-rich donor orbital donates electrons into the vacant acceptor orbital. The key question in predicting and understanding the results of the reaction between two molecules can be stated quite simply: Which orbital will be the donor, and which orbital will be the acceptor? Once that question is answered, you can usually predict the course of the reaction: the donor orbital will donate electrons to the acceptor orbital. Nothing could be simpler!

One of the most important skills, then, is to be able to identify quickly the frontier orbitals (the donor and acceptor orbitals) in any organic molecule. You can always write out a complete energy-level diagram, as you did in Section 2.4, and find the highest occupied MO and the lowest unoccupied MO from the diagram. There are some simple "shortcuts," however, that can allow you to find all the reasonable candidates for the frontier orbitals in any molecule. Recall that the molecular orbitals in any molecule are generally arranged as follows:

(High energy)

σ^* (unfilled)

π^* (unfilled)

nb (filled or unfilled)

π (filled)

σ (filled)

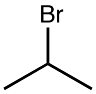
(Low energy)

First, let's consider candidates for the LUMO (the acceptor orbital). What is the *lowest possible unoccupied orbital*? The lowest orbitals are the σ- and π-bonding orbitals, but those orbitals are occupied: they are not candidates for the LUMO. The next lowest orbitals will be any unoccupied non-bonding orbitals (for instance, a vacant p-orbital). If a molecule has a vacant non-bonding orbital, that orbital is almost always the LUMO. Otherwise, the LUMO must be an antibonding orbital. Recall that more electronegative orbitals are lower in energy. Thus, the LUMO is likely to be a π^* or σ^* antibonding orbital that involves an electronegative atom—for instance, a $\pi^*_{C=O}$ or σ^*_{C-Br} orbital.

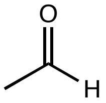
Next, consider candidates for the HOMO (the donor orbital). What is the *highest possible occupied orbital*? The highest-energy orbitals are the σ^*- and π^*-antibonding orbitals, but these orbitals do not contain any electrons: they are not candidates for the HOMO. For organic molecules, the HOMO is almost always a lone pair (a filled non-bonding orbital). Sometimes, the HOMO may be a filled π-orbital. Because orbitals involving electronegative atoms are low in energy, the HOMO is likely to be a filled π-orbital that does *not* have electronegative atoms—typically, a $\pi_{C=C}$ orbital. The following table summarizes the likely HOMO's and LUMO's for organic molecules:

Best candidates for HOMO (donor)	*Best candidates for LUMO (acceptor)*
1. Lone pairs (filled non-bonding orbitals)	1. Vacant p-orbital (non-bonding orbital)
2. π bonding orbitals: $\pi_{C=C}$	2. π^* antibonding orbitals (electroneg.)
	3. σ^* antibonding orbitals (electroneg.)

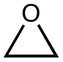
You should become adept at identifying the likely donor and acceptor orbitals *simply by looking at the skeletal structures of organic molecules*. Let's take a look at some examples. Notice that we indicate *all* the potential donors and potential acceptors for a given molecule. Our goal is not to identify the single orbital in a molecule that will interact, but rather to identify the plausible candidates based on the above table. Here are some examples of molecules with plausible donors and acceptors identified:



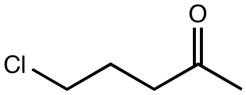
Acceptor: $\sigma^*_{C\text{–}Br}$
Donor: Br lone pairs



Acceptor: $\pi^*_{C=O}$
Donor: O lone pairs

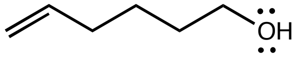


Acceptor: $\sigma^*_{C\text{–}O}$
Donor: O lone pairs



Acceptor: $\pi^*_{C=O}$ *or* $\sigma^*_{C\text{–}Cl}$
Donor: O lone pairs *or* Cl lone pairs

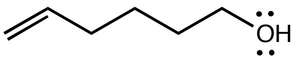
Why do we identify more than one plausible donor for a molecule? Doesn't the word "*highest*" in HOMO mean that there is only one HOMO, which should be the best donor orbital for that molecule? Yes, but you must also consider the geometry of the molecule *and* its interaction with other molecules. For instance, consider the following molecule:



Donor: $\pi_{C=C}$

Donor: O lone pairs

This molecule has *two* plausible donors: the oxygen lone pair and the alkene $\pi_{C=C}$. Why? The oxygen lone pair is the HOMO for this molecule: it is certainly higher in energy than the π-bonding orbital. You must also consider the *geometry* of the interaction, however. If another molecule collides with the *left* end of this molecule, then it will only "see" the π-bond, and it will react with that donor orbital as if it were the HOMO. If another molecule collides with the *right* end of this molecule, it will "see" the oxygen lone pair, and will react with that donor orbital:

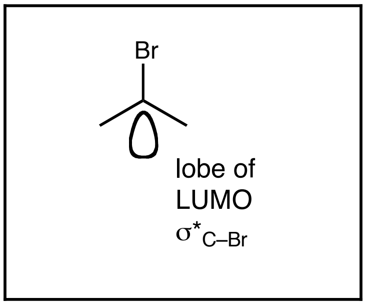


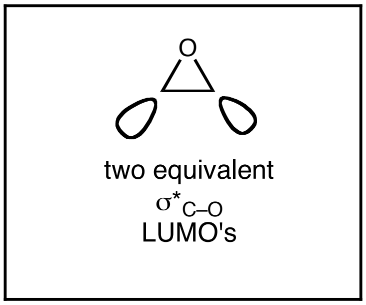
a collision with
this end of the molecule
would "see" the
$\pi_{C=C}$ as the donor

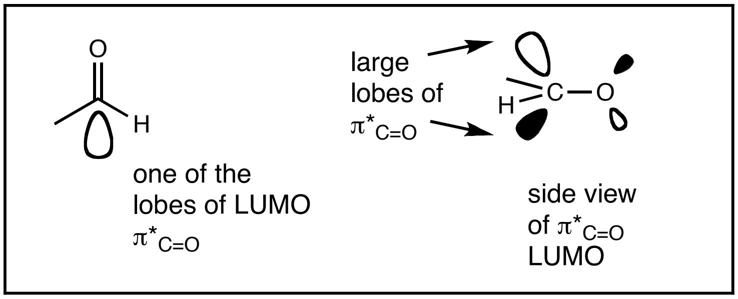
a collision with
this end of the molecule
would "see" the
O lone pairs as the donor

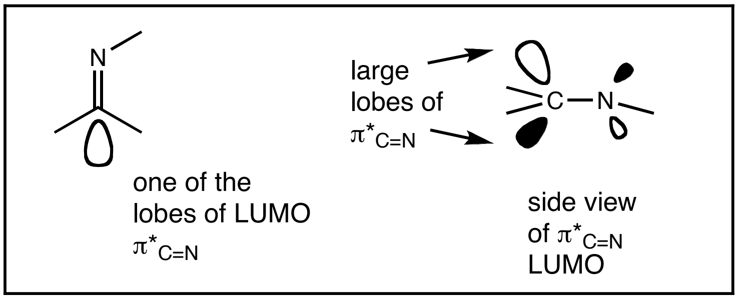
So the apparently simple question of "what is the best donor orbital for that molecule?" often must be answered: "It depends on how another molecule interacts with that molecule!" Since molecules can collide in many different ways, we should identify *all* the orbitals that could plausibly react. We will encounter many examples like this one, in which there are several plausible donors or acceptors for a given molecule, and more then one of them could react.

In addition to identifying the orbitals that could be the donor or acceptor, you should think about the *shapes* of these orbitals. In particular, for *antibonding orbitals* that are potential acceptors, you should note that the largest lobe of the orbital is actually *"behind" the less electronegative atom*. Here are some examples of molecules with antibonding orbitals as their LUMO in which the most important lobe is indicated. (For π^* orbitals, of course, there are two such lobes, above and below the plane of the paper.)

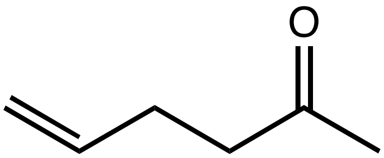

Br
lobe of
LUMO
$\sigma^*_{C\text{–}Br}$

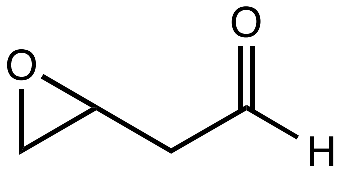

O
two equivalent
$\sigma^*_{C\text{–}O}$
LUMO's

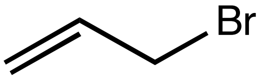

O
H
one of the
lobes of LUMO
$\pi^*_{C=O}$
large
lobes of
$\pi^*_{C=O}$
H
C
O
side view
of $\pi^*_{C=O}$
LUMO

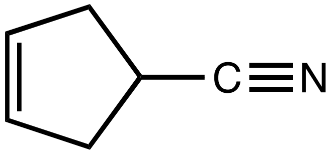

N
one of the
lobes of LUMO
$\pi^*_{C=N}$
large
lobes of
$\pi^*_{C=N}$
C
N
side view
of $\pi^*_{C=N}$
LUMO

Practice Problem 2.5: For each of the following molecules, circle the plausible donors and acceptors and provide their names (e.g. $\sigma^*_{C\text{–}Br}$, $\pi_{C=C}$, etc.). (In the case of an antibonding acceptor orbital, do not circle the bond; instead, draw a circle that represents the largest lobe of the acceptor orbital as discussed above.)









2.6. Reactions Between Molecules: Frontier Orbitals and Curved Arrows

You now have the skills to:

- List all the molecular orbitals in a molecule
- Draw the shapes of these orbitals
- Estimate the order of energies of these orbitals
- Identify the possible frontier orbitals (donor and acceptor)

Now you can learn how the frontier orbitals of two molecules interact. First, we need to introduce a bit of important terminology. In the simplest organic reactions, the (filled) donor orbital of one molecule will react with the (empty) acceptor orbital of the other molecule. In such a reaction, the molecule that is providing the electrons—the one with the donor—is called the *nucleophile*, while the molecule with a vacant orbital that can accept electrons—the one with the acceptor—is called the *electrophile*. These two words, nucleophile and electrophile, are derived from the words “nucleus” or “electron” along with the Greek suffix “philos,” meaning “friend of” or “love of.” An electrophile, with its vacant orbital, has a “love of” electrons, while a nucleophile, with its orbital full of high-energy electrons, has a “love of” the (positively-charged) nucleus. A nucleophile *has* electrons that it wants to share or donate, and an electrophile *wants* electrons.

Note that the terms HOMO and LUMO refer to *orbitals*, while the terms electrophile and nucleophile refer to *molecules* or *ions.* To be more specific, the terms electrophile and nucleophile refer to the *role* that a molecule plays in a given interaction. (Here we use the term “molecule” as a generic term to describe either a neutral or charged species.) A molecule could be a nucleophile in one reaction and an electrophile in another. As an analogy, the terms “buyer” and “seller” refer to the *role* that a person plays in an economic transaction. When I go to a car dealer to buy a new car, I play the role of buyer, and the car dealer is the seller. When the car is old and I want to get rid of it, I can go back to the dealer and sell it back as a used car; now I am the seller and the dealer is the buyer. The terms electrophile and nucleophile are analogous: the nucleophile is often referred to as the *electron donor* in a reaction, while the electrophile is the *electron acceptor*.

In analyzing a reaction between two molecules, you must decide which molecule will act as the nucleophile and which will act as the electrophile. Usually, the molecule with the "highest HOMO" (i.e. the highest-energy donor orbital) will be the nucleophile, and the molecule with the "lowest LUMO" (i.e. the lowest-energy acceptor orbital) will be the electrophile. Likewise, molecules with a negative charge (anions) are likely to be nucleophiles, while molecules with a positive charge (cations) are likely to be electrophiles.

You can now learn how to *predict* what will happen when two molecules react with one another. The general strategy is:

1. Identify the plausible donor and acceptor orbitals for the molecules.

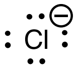
2. Determine which molecule will be the nucleophile and which will be the electrophile.

3. Have the donor orbital of the nucleophile react with the acceptor orbital of the electrophile.

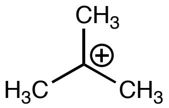
What does it mean for the donor to "react with" the acceptor? That phrase means that electrons from the donor orbital "flow" or "donate" into the acceptor orbital. To keep track of this flow of electrons, organic chemists use a simple but powerful tool known as *cuvred arrows*; the process of drawing curved arrows to keep track of the flow of electrons is often called *arrow pushing*. Let's look at some examples.

- **Reaction between a non-bonding donor (lone pair) and a non-bonding acceptor**:

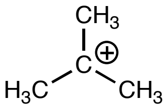
This is the simplest type of frontier orbital interaction. Consider, as an example, the reaction between the chloride ion Cl$^-$ and the tert-butyl cation, $(H_3C)_3C^+$. First, we must draw the Lewis structures and identify the plausible donor and acceptor orbitals for these species:



HOMO: Cl lone pair

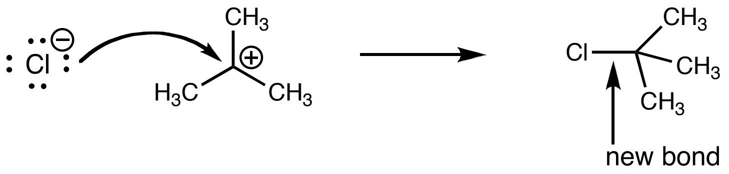


LUMO: nonbonding p orbital
on positively-charged carbon atom

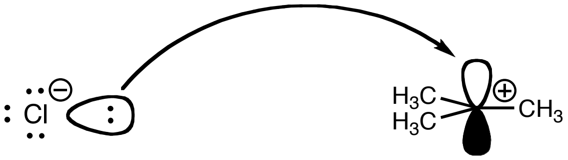


(This is the complete Lewis
structure of the cation)

We can use curved arrows to show the flow of electrons from the donor (HOMO) to the acceptor (LUMO). This donation of electrons results in the **formation of a new bond**:



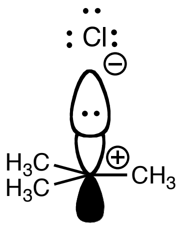
Keep in mind the orbitals involved here:



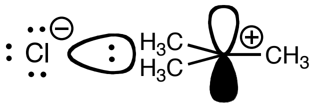
lone pair donor

vacant orbital acceptor

Note that, when the two species interact, they must interact in such a way that the donor orbital can *overlap* with the acceptor orbital. That is:



correct orientation
of reactants has *good*
overlap between
donor and acceptor



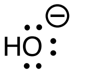
incorrect orientation
of reactants has *poor*
overlap between
donor and acceptor

That's it! That's one of the simplest reactions in organic chemistry. In this example, there is no ambiguity: the chloride ion has only one possible donor, and the cation has one obvious acceptor. Also note that the combination of *two* non-bonding orbitals results in *one* new bond (which has a bonding orbital and an antibonding orbital). (Recall that a combination of *n* orbitals must yield *n* molecular orbitals.) This reaction is:

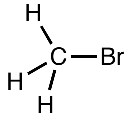
(lone pair) + (vacant orbital) → (new bond)

- **Reaction between a non-bonding donor (lone pair) and an antibonding acceptor**:

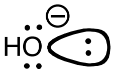
This is an extremely common type of frontier orbital interaction in organic chemistry. As an example, consider the reaction between the hydroxide ion (OH^-) and methyl bromide (CH_3Br). Again, we must first draw Lewis structures and identify the frontier orbitals:

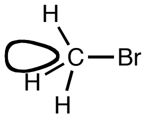


HOMO: O lone pair



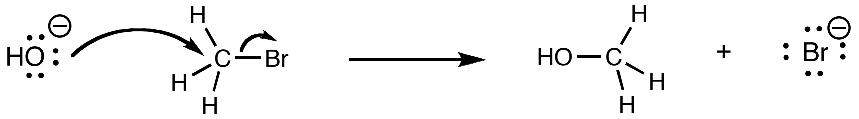
LUMO: σ^*_{C-Br}
HOMO: Br lone pairs (not shown)





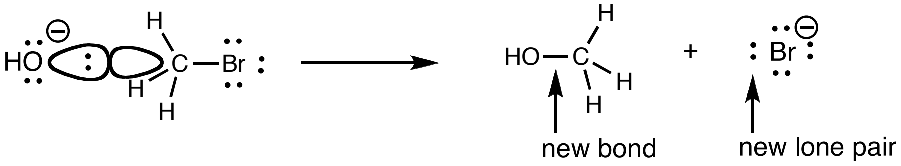
(largest lobe of σ*orbital
is *behind* the carbon atom!)

We use curved arrows to show the flow of electrons from the donor into the acceptor. The electrons from the donor interact with the **large lobe** of the acceptor (the lobe "behind" the carbon atom). In addition, note that **donating electrons into an antibonding orbital breaks the bond that is associated with that orbital**:



Why does the σ_{C-Br} bond *break* in this reaction? Recall from our earlier discussion that the presence of electron density in an antibonding orbital tends to pull the nuclei *apart* from one another; that is why the orbital is called "antibonding." As electrons from the donor (the lone pair on oxygen) start to overlap with the antibonding acceptor orbital, this *weakens* the C–Br bond, until eventually this bond *breaks*. **It is always the case that donating electrons into an antibonding orbital must break the bond that is associated with that orbital!**

In this reaction, the HOMO of OH^- must overlap with the LUMO of CH_3Br:

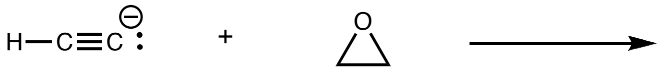


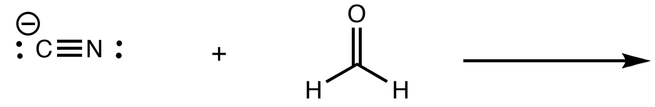
Observe how the curved arrows help to keep track of where the electrons are going. This reaction can be thought of as:

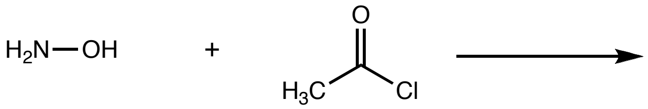
(lone pair) + (antibonding orbital) → (new bond) + (new lone pair)

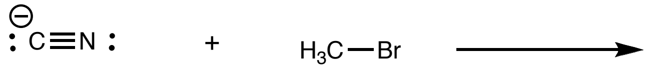
Now see if *you* can predict how the following molecules will react. If you can make these predictions successfully, you're well on your way to understanding organic chemistry!

Practice Problem 2.6: For each of the following pairs of molecules, find the donor and acceptor orbitals of the molecules, identify which molecule will be the electrophile and which will be the nucleophile, show how the molecules would react using curved arrows, and show the product that would result from that single step of reaction.









2.7. Proton-Transfer Reactions: Frontier Orbitals of Brønsted Acids and Bases

In your previous chemistry courses, you encountered the concept of acids and bases. One of the most commonly-used definitions of acids and bases is known as the Brønsted-Lowry acid-base theory. In this theory, an **acid** is defined as a species that can **donate a proton** (H^+), while a **base** is defined as a species that can **accept a proton**. One of the basic concepts of this theory is that every acid has a **conjugate base** that results from the "loss" of a proton from that acid. Here are some common Brønsted acids and their conugate bases:

Brønsted Acid	*Conjugate Base*
H_2O	OH^-
H_3O^+	H_2O
NH_4^+	NH_3
H_2S	HS^-
HF	F^-
HCl	Cl^-

Conversely, every Brønsted base has a **conjugate acid** that results from adding a proton to that base. Here are some common Brønsted bases and their conjugate acids:

Brønsted Base	*Conjugate Acid*
OH^-	H_2O
H_2O	H_3O^+
NH_3	NH_4^+
HS^-	H_2S
F^-	HF
Cl^-	HCl

You may notice that the above lists are quite similar! Every Brønsted acid is the conjugate acid of a Brønsted base, and every Brønsted base is the conjugate base of a Brønsted acid.

When a Brønsted acid reacts with a Brønsted base, a proton (H^+) can be transferred from the acid to the base. Such a reaction is called a **proton-transfer reaction**. Here are some examples of proton-transfer reactions:

$$\mathrm{HF} + \mathrm{NH_3} \rightleftharpoons \mathrm{F^-} + \mathrm{NH_4^+}$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

$$H_2S + OH^- \rightleftharpoons SH^- + H_2O$$

The products of any proton-transfer reaction are the **conjugate acid and conjugate base** of the reactants. For example, in the reaction:

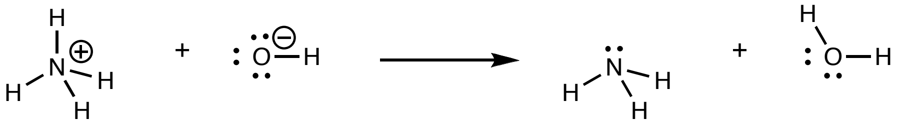
$$HF + NH_3 \rightleftharpoons F^- + NH_4^+$$

the product F^- is the conjugate base of the acid HF, and the product NH_4^+ is the conjugate acid of the base NH_3.

The nature of a proton-transfer reaction can be seen more clearly if we write out the complete Lewis structures for the reactants and products. For instance, for the reaction between the ammonium ion and the hydroxide ion:

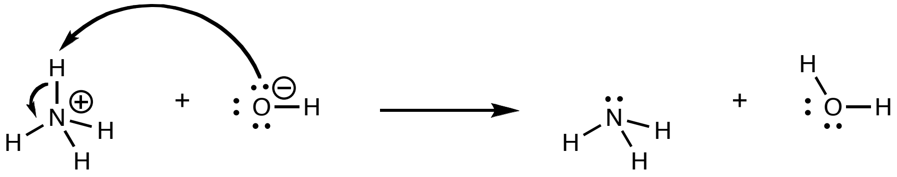
$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

the complete Lewis structures are:

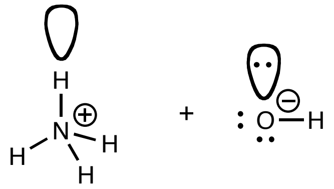


If you write out the Lewis structures for any Brønsted proton-transfer reaction, you will notice that **Brønsted bases always have lone pairs**, and it is the lone pair on the Brønsted base that accepts the proton from the Brønsted acid.

We can use curved arrows to follow the motion of the electrons in an acid-base reaction. (From now on in the text, when we use the generic terms "acid" or "base," we always mean "Brønsted acid" or "Brønsted base.") For the reaction between the ammonium ion and the hydroxide ion, the curved arrows are:



Note that the arrows follow the motion of the *electrons*, not the motion of the proton that is being transferred! You should be able to identify the frontier orbitals of these species and explain the reaction in terms of a donor-acceptor interaction. The frontier orbitals of the reactants are:



Brønsted Acid
(Proton Donor)
has an
acceptor orbital:
$\sigma^*_{H\text{–}N}$

Brønsted Base
(Proton Acceptor)
has a
donor orbital:
O lone pair

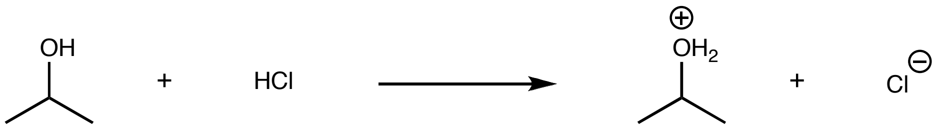
The hydroxide ion (OH^-) is the nucleophile, with a lone pair as its donor orbital; the ammonium ion (NH_4^+) is the electrophile, with a σ* antibonding orbital as its acceptor. Note that the **largest lobe of the antibonding orbital** is, as usual, *behind* the less electronegative atom (the hydrogen atom). As the curved arrows show, the donation of electrons from the HOMO (donor orbital) of OH^- into the antibonding $\sigma^*_{H\text{–}N}$ orbital breaks the H–N bond.

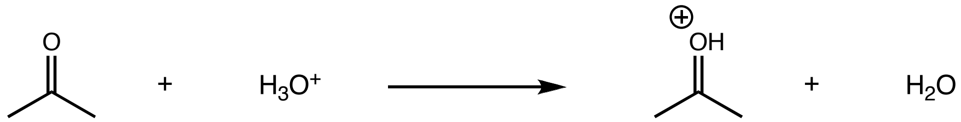
We can define Brønsted acids and bases in terms of their frontier orbitals:

- A Brønsted acid has a $\sigma^*_{H\text{–}Y}$ orbital as an acceptor orbital, in which Y is an atom that is more electronegative than H. It will transfer that proton when a filled orbital donates into that vacant antibonding orbital.
- A Brønsted base has a filled orbital (usually a lone pair) as a donor orbital that can accept a proton. It will accept a proton when that filled orbital donates into the $\sigma^*_{H\text{–}Y}$ antibonding orbital of a Brønsted acid.

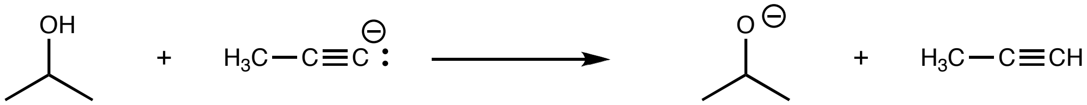
Note that the *proton donor* has an *acceptor orbital*: it is an *electron-pair acceptor*. Likewise, the *proton acceptor* has a *donor orbital*: it is an *electron-pair donor*. The concept of electron-pair donors and acceptors form the basis of the Lewis theory of acids and bases, which is a more general theory than the Brønsted-Lowry theory. Don't get confused between these two descriptions of a proton-transfer reaction: in the Brønsted view, it is the *proton* that is transferred, while in the Lewis (or molecular orbital) view, it is the *pair of electrons* that are transferred from one species to the other during the reaction.

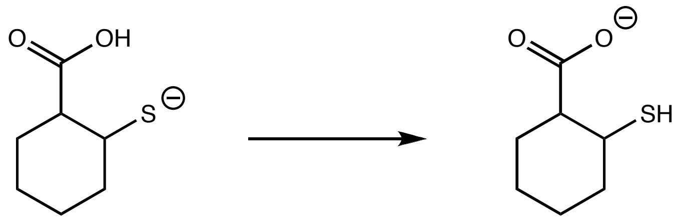
Practice Problem 2.7: For each of the following acid-base reactions, draw complete Lewis structures of the reactants, draw curved arrows to explain the proton transfer that occurs, and identify the HOMO and LUMO involved in the proton transfer.


OH
+
HCl
OH2
+
Cl



$$H_3C-C\equiv CH \quad + \quad NH_2^- \longrightarrow H_3C-C\equiv C\!:^{\ominus} \quad + \quad NH_3$$


OH
+
H3C—C≡C:
O
+
H3C—C≡CH



2.8. Electrophiles, Nucleophiles, Acids, and Bases

We have discussed two roles that a molecule can play in a chemical reaction:

- An **electrophile** is a molecule with a low-energy acceptor orbital that accepts electrons into that orbital from a donor orbital of another species.
- A **nucleophile** is a molecule with a high-energy donor orbital that donates electrons from that orbital into the acceptor orbital of some other species.

Although a **Brønsted acid** is merely a special type of electrophile (in which the acceptor orbital is a σ^*_{H-Y} antibonding orbital), you should consider such an acid to be in a category by itself. We will use the classical definition of a Brønsted acid as a proton donor, although we *understand* that it is a proton donor because it has a σ^*_{H-Y} antibonding orbital.

Likewise, although a **Brønsted base** is merely a special type of nucleophile (in which the donor orbital of the nucleophile donates into a σ^*_{H-Y} antibonding orbital and acquires the proton from that antibonding orbital), you should consider such a base to be in a category by itself. We think of a base as a proton acceptor, but we *understand* that it can accept a proton because it has a donor orbital that can donate into a σ^*_{H-Y} antibonding orbital of another molecule (the Brønsted acid).

In any organic reaction, each molecule usually plays one of the above four roles: the molecule acts as an electrophile, as a nucleophile, as an acid, or as a base. Indeed, the main questions you should ask upon encountering any molecule or any reaction are the **four basic questions of organic reactivity**:

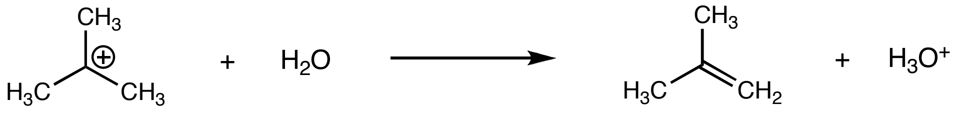
- Can the molecule act as an electrophile?
- Can the molecule act as a nucleophile?
- Can the molecule act as an acid?
- Can the molecule act as a base?

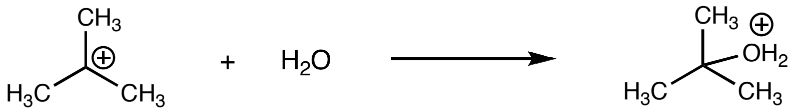
Once you have answered those basic questions, you have an excellent chance of being able to *predict* how that molecule will react: electrophiles react with nucleophiles, and acids react with bases.

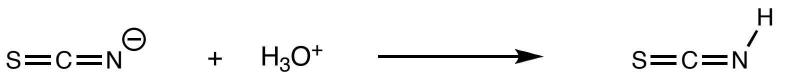
We conclude this chapter by examining some molecules that can exhibit *different reactivity* depending on their role as an electrophile, nucleophile, acid, or base. See if you can identify the role that each species is playing in the following reactions:

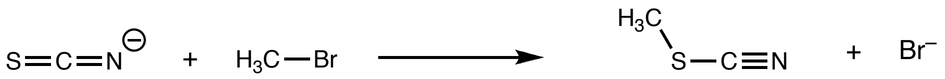
Practice Problem 2.8: For each of the following reactions:

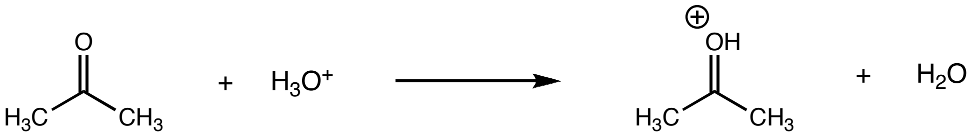
- Draw the curved arrows that show how the reaction takes place.
- Identify the donor and acceptor orbitals of the interacting species.
- Identify each species as an electrophile, a nucleophile, an acid, or a base.
  (Be sure to consider the *role* that the species is playing in the reaction!)
- Notice that the *same species* can play different roles in different reactions!

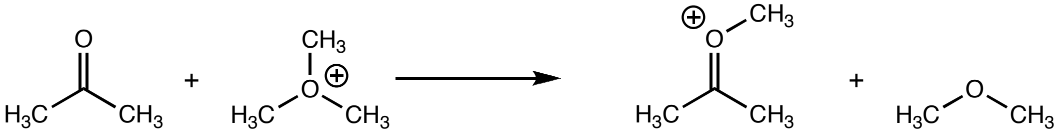

CH3
H3C
CH3
+ H2O
CH3
H3C
CH2
+ H3O+

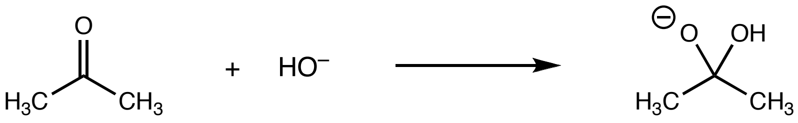

CH3
H3C
CH3
+ H2O
CH3
OH2
H3C
CH3

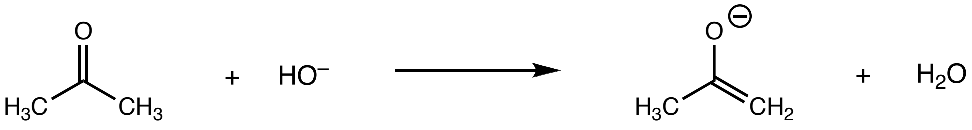

S=C=N
+ H3O+
H
S=C=N


S=C=N
+ H3C—Br
H3C
S—C≡N
+ Br−


O
H3C
CH3
+ H3O+
OH
H3C
CH3
+ H2O


O
H3C
CH3
+
CH3
O
H3C
CH3
CH3
O
H3C
CH3
+
O
H3C
CH3


O
H3C
CH3
+ HO−
O
OH
H3C
CH3


O
H3C
CH3
+ HO−
O
H3C
CH2
+ H2O