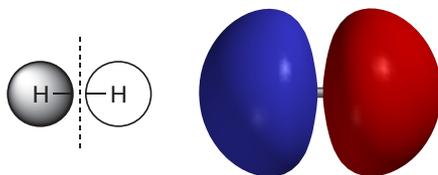


## ATOMIC AND MOLECULAR ORBITALS

Chemists have developed a variety of methods for describing electrons in molecules. Lewis structures are the most familiar. These drawings assign pairs of electrons either to single atoms (lone pairs) or pairs of atoms (bonds)\*. The quantum mechanical equivalents are atomic and molecular orbitals which arise from solution of (approximate) Schrödinger equations for atoms and molecules, respectively. Molecular orbitals are spread throughout the entire molecule, that is, they are delocalized.\*\* Because of this, they are typically more difficult to interpret than Lewis structures.

### Orbital Surfaces

Molecular orbitals may be able to provide important clues about chemical reactivity, but before we can use this information we first need to understand the fundamentals for very simple molecules. The following figure shows two representations, a hand drawing and a *Spartan*-generated image of an unoccupied molecular orbital of hydrogen molecule, H<sub>2</sub>.



unoccupied molecular orbital in hydrogen

Open *hydrogen empty* in the *topics* directory. Note that except for the colors (sign of the orbital) the two sides of the graphic are identical. The junction between red and blue regions is where the value of the orbital is zero. Close *hydrogen empty* when you are finished.

The familiar hand drawing shows the orbital as two circles and a dashed line. The circles identify regions where the orbital takes on a

\* The present discussion is limited to molecules in which all electrons are paired. Molecules with one or more unpaired electrons (radicals, triplet states, etc.) may also be treated.

\*\* Is it possible to localize molecular orbitals such that they correspond more closely to conventional Lewis structures. Because this is costly in terms of computation and to some extent "ill defined" (the need to specify what conditions are to be met) localization is only rarely performed.

significant value, either positive (*shaded*) or negative (*unshaded*). The dashed line identifies locations where the orbital's value is exactly zero (a *node*). The drawing is useful, but it is also limited. We only obtain information about the orbital in two dimensions, and we only learn the location of significant regions and not how the orbital builds and decays inside and outside of these regions.

The *Spartan*-generated image depicts the same orbital as a surface of constant value. The surface is accurate in that it is derived from an authentic (but approximate) calculated solution to the quantum mechanical equations of electron motion (the Schrödinger equation). Equally important, the image is three-dimensional, and can be manipulated and looked at from a variety of different perspectives. It is not unexpected that the orbital consists of two distinct surfaces represented by different colors. The two surfaces have the same meaning as the two circles in the orbital drawing. They identify regions where the orbital takes on a significant value, either positive (blue) or negative (red). The orbital node is not shown, but we can guess that it lies midway between the two surfaces (this follows from the fact that the orbital's value can only change from positive to negative by passing through zero).

## Atomic Orbitals

Atomic orbitals (descriptions of atoms) are the fundamental building blocks from which molecular orbitals (descriptions of molecules) are assembled. The familiar atomic orbitals for the hydrogen atom are in fact exact solutions of the Schrödinger equation which can actually be solved exactly for this one electron system. They form an infinite collection (a complete set), the lowest-energy member representing the best location for the electron, and higher-energy members representing alternative locations. Orbitals for real many-electron atoms are normally (and necessarily) assumed to be similar in form to those of hydrogen atom, the only difference being that, unlike hydrogen, more than the lowest-energy atomic orbital is utilized. In practical quantum chemical calculations, atomic orbitals for many-electron atoms are made up of sums and differences of a finite collection of hydrogen-like orbitals (see the topic *Theoretical Models*).

It is common practice to divide the full set of atomic orbitals into core and valence orbitals, and further to ignore the former. Valence orbitals for an element in the first long row of the *Periodic Table* are  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$ , and for the second long row are  $3s$ ,  $3p_x$ ,  $3p_y$  and  $3p_z$ . In the case of first-row elements, a single orbital,  $1s$ , lies underneath (is a core orbital) while in the case of second-row elements, a set of five orbitals,  $1s$ ,  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$ , lie underneath.

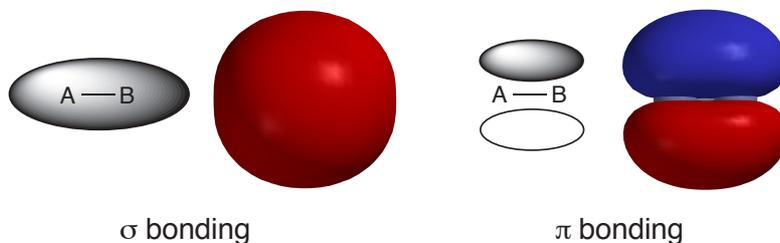
Open ***fluoride and chloride*** in the ***topics*** directory. On the top row are the four valence orbitals of fluoride anion and on the bottom row the four valence orbitals of chloride anion. You can select among them by *clicking* (left mouse button) on each in turn. First note that the three  $2p$  orbitals in fluoride are identical except for the direction in which they point. The same is true for the three  $3p$  orbitals in chloride. Next, note that the valence orbitals in chloride are larger than those in fluoride. Atoms further down in the *Periodic Table* are generally larger than analogous atoms further up. Close ***fluoride and chloride*** when you are finished.

## Orbitals and Chemical Bonds

Although molecular orbitals and Lewis structures are both used to describe electron distributions in molecules, they are used for different purposes. Lewis structures are used to count the number of bonding and non-bonding electrons around each atom. Molecular orbitals are not useful as counting tools, but orbitals and associated orbital energies are useful tools for describing chemical bonding and reactivity. This section describes a few common orbital shapes and illustrates their use.

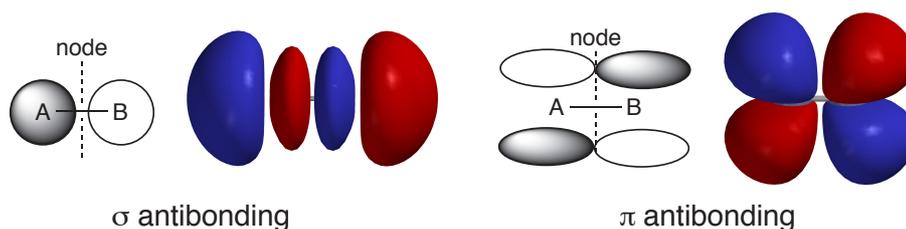
Molecular orbital surfaces can extend over varying numbers of atoms. If the orbital surface (or surfaces) is confined to a single atom or to atoms which are not close together, the orbital is regarded as non-bonding. If the orbital contains a surface that extends continuously over two neighboring atoms, the orbital is regarded as bonding with respect to these atoms. Adding electrons to such an orbital will strengthen the bond between these atoms and cause them to draw closer together, while removing electrons will have the opposite effect. Two different kinds of bonding orbitals are depicted below.

The drawing and surface on the left correspond to a  $\sigma$  bond while the drawing and surface on the right correspond to a  $\pi$  bond.



Open ***nitrogen bonding*** in the ***topics*** directory. The image on the left corresponds to the  $\sigma$  bonding orbital of  $N_2$ , while that on the right corresponds to one of two equivalent  $\pi$  bonding orbitals. Switch to a transparent or mesh model to see the underlying molecular skeleton. Note that the  $\sigma$  orbitals is drawn in a single color (insofar as NN bonding is concerned) while the  $\pi$  orbital is made up of red and blue parts. This indicates a node or a break in the latter, although not involving the NN bond. Close ***nitrogen bonding*** when you are finished.

It is also possible for an orbital to contain a node that divides the region between two neighboring atoms into separate atomic regions. Such an orbital is regarded as antibonding with respect to these atoms. Adding electrons to an antibonding orbital weakens the bond and pushes the atoms apart, while removing electrons from such an orbital has the opposite effect. The following pictures show drawings and orbital surfaces for two different kinds of antibonding orbitals. As above, the left and right-hand sides correspond to  $\sigma$  and  $\pi$  type arrangements, respectively.



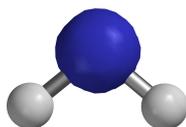
Open *nitrogen antibonding* in the *topics* directory. The image on the left corresponds to the  $\sigma$  antibonding (so-called  $\sigma^*$ ) orbital of  $N_2$  while that on the right corresponds to one of the two equivalent  $\pi$  antibonding (so-called  $\pi^*$ ) orbitals. Switch to a mesh or transparent surface to see the underlying molecular skeleton. Note that the  $\sigma^*$  orbital has a single node (change in color from red to blue) in the middle of the NN bond, while the  $\pi^*$  orbital has two nodes (one in the middle of the NN bond and to the other along the bond). Close *nitrogen antibonding* when you are finished.

To summarize, bonds can be strengthened in two different ways, by adding electrons to bonding orbitals, or by removing electrons from antibonding orbitals. The converse also holds. Bonds can be weakened either by removing electrons from bonding orbitals or by adding electrons to antibonding orbitals.

### Singlet Methylene

Molecular orbitals in molecules which contain many atoms are typically spread throughout the molecule (they are delocalized). Delocalized orbitals have complicated shapes and contain multiple interactions that may be bonding, non-bonding, antibonding, or any mixture of all three. Nevertheless, these shapes can usually be broken down into two-atom interactions and analyzed using the principles outlined earlier. This process is illustrated for a triatomic molecule, singlet methylene,  $CH_2$ . (Singlet refers to the fact that the eight electrons in this highly reactive molecule are organized into four pairs, and that each pair of electrons occupies a different molecular orbital. The lowest-energy state of methylene is actually a triplet with three electron pairs and two unpaired electrons.)

The lowest energy molecular orbital of singlet methylene is not very interesting in that it looks like a  $1s$  atomic orbital on carbon. The electrons occupying this orbital restrict their motion to the immediate region of the carbon nucleus and do not significantly affect bonding. Because of this restriction, and because the orbital's energy is very low, this orbital is referred to as a *core orbital* and its electrons are referred to as *core electrons*.



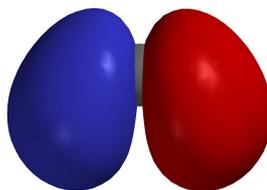
core orbital for methylene

The next orbital is much higher in energy. It consists of a single surface that is delocalized over all three atoms. This means that it is simultaneously ( $\sigma$ ) bonding with respect to each CH atom pair.



core orbital for methylene

The next higher energy orbital is described by two surfaces, a positive (blue) surface that encloses one CH bonding region and a negative (red) surface that encloses the other CH bonding region\*. Since each surface encloses a bonding region, this orbital is also ( $\sigma$ ) bonding with respect to each CH atom pair. This reinforces the bonding character of the previous orbital. The node that separates the two surfaces passes through the carbon nucleus, but not through either of the CH bonding regions, so it does not affect bonding.



core orbital for methylene

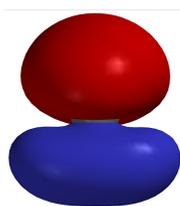
Thus, the two CH bonds in the Lewis structure for singlet methylene are replaced by two bonding molecular orbitals.\*\*

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\* While the absolute signs (colors) of a molecular orbital are arbitrary, the relative signs (colors) indicate bonding and antibonding character.

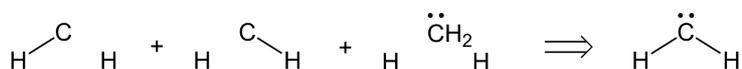
\*\* Unlike the two Lewis structures, the two CH bonding molecular orbitals reflect the fact that the two CH bonds in methylene are identical. Specifically, the square of each of the orbitals, corresponding to the electron distribution or electron density, has the same 2-fold symmetry as the molecule. The square of either the molecular orbitals themselves or a combination of so-called degenerate (same energy) molecular orbitals must have the same symmetry as the underlying nuclear skeleton.

The highest-occupied molecular orbital (the HOMO) is also described by two orbital surfaces. One surface extends into carbon's non-bonding region opposite the two hydrogens. The other surface encompasses the two CH bonding regions. Although it is hard to track the exact path of the orbital node in this picture, it happens to pass almost exactly through the carbon. This means that this particular orbital possesses only weak CH bonding character (it is H---H bonding). It turns out that the non-bonding character of the orbital is much more important than the bonding character, in that it leads to the fact that singlet methylene is able to behave as an electron-pair donor (a nucleophile).



core orbital for methylene

In addition to two CH bonds, the Lewis structure for singlet methylene shows a lone pair on carbon.



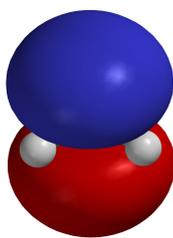
The above analysis shows that while the occupied orbitals of singlet methylene are spread over all three atoms, they are comprehensible. The orbitals divide into two groups, a single low-energy core orbital and three higher-energy valence orbitals. The latter consist of two CH bonding orbitals and a non-bonding orbital on carbon. There is no one-to-one correspondence between these orbitals and the Lewis structure. The bonding orbitals are not associated with particular bonds, and the non-bonding orbital contains bonding interactions as well.

Open ***methylene bonding*** in the ***topics*** directory. Four images appear corresponding to the core and three valence orbitals of singlet methylene. Switch to a mesh or transparent surface to see the underlying molecular skeleton. Close ***methylene bonding*** when you are finished.

Singlet methylene also possesses unoccupied molecular orbitals. The unoccupied orbitals have higher (more positive) energies than the

occupied orbitals, and these orbitals, because they are unoccupied, do not describe the electron distribution in singlet methylene.\* Nevertheless, the shapes of unoccupied orbitals, in particular, the lowest-unoccupied orbital (LUMO), is worth considering because it provides valuable insight into the methylene's chemical reactivity.

The LUMO in methylene has non-bonding character, and looks like a 2p atomic orbital on carbon. This suggests that singlet methylene should be able to behave as an electron-pair acceptor (an electrophile). Note, however, that were the molecule to accept electrons, these would go into non-bonding orbital; carbon would become more electron-rich, but the CH bonds would not be much affected.



LUMO of methylene

Open *methylene LUMO* in the *topics* directory and switch to a mesh or transparent surface to see the underlying skeleton. Close *methylene LUMO* when you are finished.

## Frontier Molecular Orbitals and Chemical Reactivity

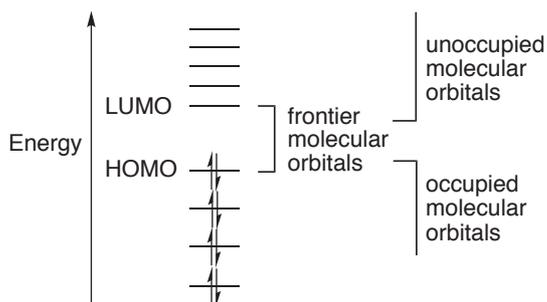
Chemical reactions often involve movement of electrons from an electron donor (base, nucleophile, reducing agent) to an electron acceptor (acid, electrophile, oxidizing agent). This electron movement between molecules can also be thought of as electron movement between molecular orbitals, and the shapes and energies of orbitals that act as electron donors or electron acceptors may provide considerable insight into chemical reactivity.

The first step in constructing a molecular orbital picture of a chemical reaction is to decide which orbitals are most likely to act as electron

\* Because Lewis structures describe electron pair bonds and non-bonding electron pairs, they may not be related to unoccupied molecular orbitals.

donors and acceptors. It is obvious that an electron-donor orbital must be drawn from the set of occupied orbitals, and an electron-acceptor orbital must be an unoccupied orbital, but there are many orbitals in each set to choose from.

Orbital energy is usually the deciding factor. The highest-energy occupied orbital (the HOMO) is most commonly assumed to be the relevant electron-donor orbital and the lowest-energy unoccupied orbital (the LUMO) is most commonly assumed to be the relevant electron-acceptor orbital. For example, the HOMO and LUMO of singlet methylene ( $\sigma$  and  $\pi$  non-bonding orbitals, respectively) would serve as the donor and acceptor orbitals. The HOMO and LUMO are collectively referred to as the *frontier molecular orbitals*, and most chemical reactions involve electron movement between them. In this way, the energy input required for electron movement is kept to a minimum.

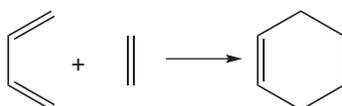


Closely related to chemical reactivity (reaction rate) is chemical selectivity. The relevant question is, where more than one combination of reagents can react, which combination will react more quickly? The answer can often be found by examining the energies of the frontier orbitals. Consider ranking the rates of a series of reagents, where chemical reaction requires electron donation from the donor's HOMO. It is reasonable to expect that the donor with the highest energy HOMO will give up its electrons most easily and be the most reactive. Electron-acceptor reagents should follow the opposite pattern. The reagent with the lowest energy LUMO should be able to accept electrons most easily and be the most reactive. For a mixture of several donor and acceptor reagents, the fastest chemical reaction

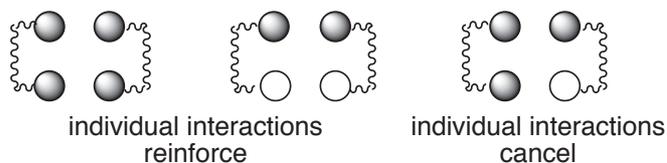
would be expected to involve the reagent combination that yields the smallest HOMO-LUMO energy gap.

### The Fukui-Woodward-Hoffmann Rules

In certain cases, multiple frontier orbital interactions must be considered. A good example is provided by so-called cycloaddition reactions, such as the Diels-Alder reaction between 1,3-butadiene and ethylene.



The key feature of this reaction is that the reactants combine in a way that allows two bonds to form simultaneously. This implies two different sites of satisfactory frontier orbital interaction (the two new bonds that form are sufficiently far apart that they do not interact with each other during the reaction). If we focus exclusively on the interactions of the terminal carbons in each molecule, then three different frontier orbital combinations made up of upper and lower components can be imagined.



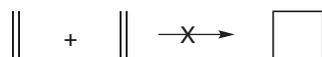
The upper orbital components are the same sign in all three combinations, meaning that their overlap is positive. In the two cases on the left, the lower orbital components also lead to positive overlap. Thus, the two interactions reinforce, and the total frontier orbital interaction is non zero. Electron movement (leading to chemical reaction) can occur. The right-most case is different. Here the lower orbital components lead to negative overlap (the orbitals have opposite signs at the interacting sites), and the total overlap is zero. No electron movement and no chemical reaction can occur in this case.

As it happens, the frontier orbital interactions in the Diels-Alder cycloaddition shown above correspond to those found in the middle

drawing, that is, the upper and lower interactions reinforce and the reaction proceeds.

Open *1,3-butadiene+ethylene* in the *topics* directory. The image on top is the LUMO of ethylene while that on the bottom is the HOMO of 1,3-butadiene. They are properly poised to interact, but you can manipulate them independently. Close *1,3-butadiene+ethylene* when you are finished.

The same arguments suggest that cycloaddition of two ethylene molecules is unlikely to occur. This is because it involves a frontier orbital interaction like that found in the right drawing.



Open *ethylene+ethylene* in the *topics* directory. The image on top corresponds to the LUMO of one ethylene while that on the bottom corresponds to the HOMO of the other ethylene. You can manipulate them independently or in concert (hold down on the **Ctrl** key while you carry out rotation and translation). Note, that in this case, the two individual atom-atom interactions cancel. Close *ethylene+ethylene* when you are finished.

The importance of orbital overlap in determining why certain chemical reactions proceed easily while other seemingly similar reactions are sluggish or do not go at all was first advanced by Fukui and then beautifully elaborated by Woodward and Hoffmann, and collectively their ideas are now known as the Fukui-Woodward-Hoffmann rules.