Chapter 2: Molecular Structure and Bonding
Bonding Theories

1. **VSEPR Theory**
2. **Valence Bond theory** (with hybridization)
3. **Molecular Orbital Theory** (with molecualr orbitals)

To date, we have looked at three different theories of molecular boning. They are the VSEPR Theory (with Lewis Dot Structures), the Valence Bond theory (with hybridization) and Molecular Orbital Theory. A good theory should predict physical and chemical properties of the molecule such as shape, bond energy, bond length, and bond angles.Because arguments based on atomic orbitals focus on the bonds formed between valence electrons on an atom, they are often said to involve a *valence-bond* theory. The valence-bond model can't adequately explain the fact that some molecules contains two equivalent bonds with a bond order between that of a single bond and a double bond. The best it can do is suggest that these molecules are mixtures, or hybrids, of the two Lewis structures that can be written for these molecules.

This problem, and many others, can be overcome by using a more sophisticated model of bonding based on **molecular orbitals**. Molecular orbital theory is more powerful than valence-bond theory because the orbitals reflect the geometry of the molecule to which they are applied. But this power carries a significant cost in terms of the ease with which the model can be visualized.

One model does not describe all the properties of molecular bonds. Each model desribes a set of properties better than the others. The final test for any theory is experimental data.

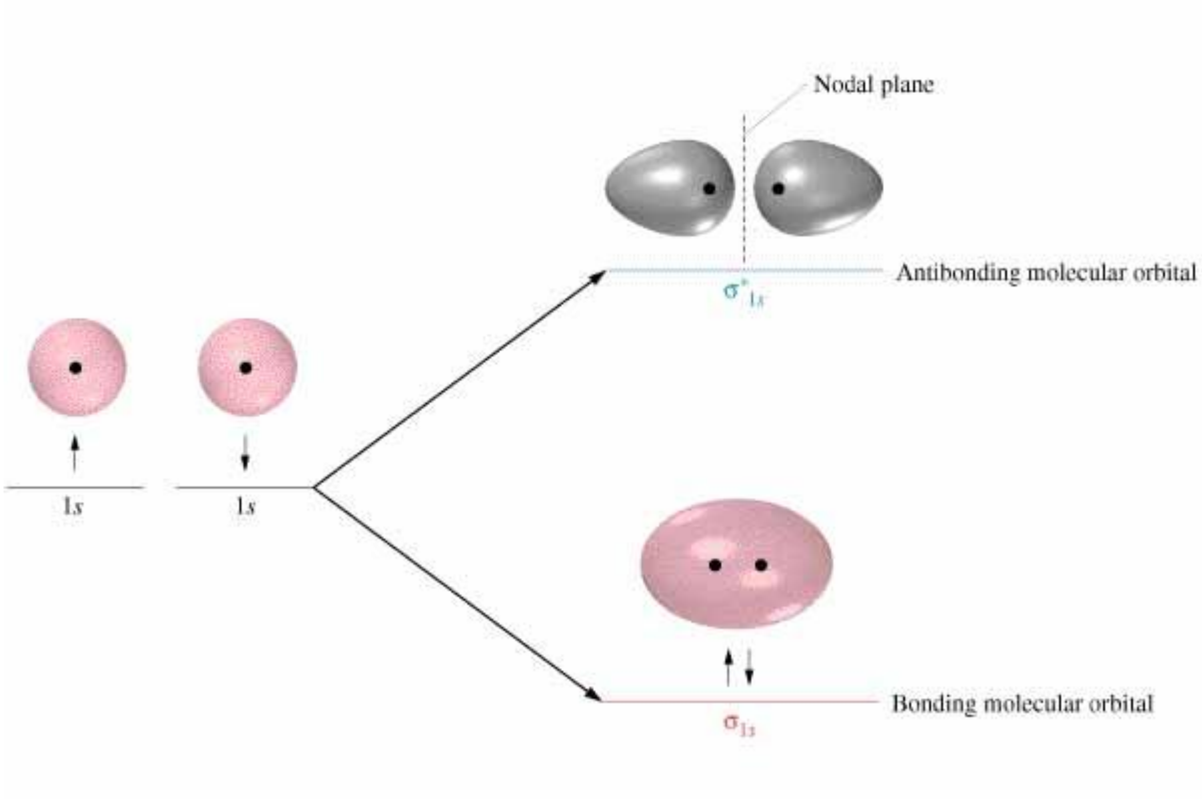
Introduction to Molecular Orbital Theory

The Molecular Orbital Theory does a good job of predicting elctronic spectra and paramagnetism, when VSEPR and the V-B Theories don't. The MO theory does not need resonance structures to describe molecules, as well as being able to predict bond length and energy. The major draw back is that we are limited to talking about diatomic molecules (molecules that have only two atoms bonded together), or the theory gets very complex.

The MO theory treats molecular bonds as a sharing of electrons between nuclei. Unlike the V-B theory, which treats the electrons as localized baloons of electron density, the MO theory says that the electrons are delocalized. That means that they are spread out over the entire molecule.

Forming Molecular Orbitals

Molecular orbitals are obtained by combining the atomic orbitals on the atoms in the molecule. Consider the H_2 molecule, for example. One of the molecular orbitals in this molecule is constructed by adding the mathematical functions for the two 1*s* atomic orbitals that come together to form this molecule. Another orbital is formed by subtracting one of these functions from the other, as shown in the figure below.



One of these orbitals is called a **bonding molecular orbital** because electrons in this orbital spend most of their time in the region directly between the two nuclei. It is called a **sigma** (σ) molecular orbital because it looks like an *s* orbital when viewed along the H-H bond. Electrons placed in the other orbital spend most of their time away from the region between the two nuclei. This orbital is therefore an **antibonding**, or *sigma star* (σ*), molecular orbital.

The σ bonding molecular orbital concentrates electrons in the region directly between the two nuclei. Placing an electron in this orbital therefore stabilizes the H_2 molecule. Since the σ* antibonding molecular orbital forces the electron to spend most of its time away from the area between the nuclei, placing an electron in this orbital makes the

molecule less stable.
The MO Theory has five basic rules:

1. The number of molecular orbitals = the number of atomic orbitals combined
2. Of the two MO's, one is a bonding orbital (lower energy) and one is an anti-bonding orbital (higher energy)
3. Electrons enter the lowest orbital available
4. The maximum # of electrons in an orbital is 2 (Pauli Exclusion Principle)
5. Electrons spread out before pairing up (Hund's Rule)

Calculating Bond Order

In molecular orbital theory, we calculate bond orders by assuming that two electrons in a bonding molecular orbital contribute one net bond and that two electrons in an antibonding molecular orbital cancel the effect of one bond. We can calculate the bond order in the O_2 molecule by noting that there are eight valence electrons in bonding molecular orbitals and four valence electrons in antibonding molecular orbitals in the electron configuration of this molecule. Thus, the bond order is two.

$$\text{Bond order} = \frac{\text{bonding electrons} - \text{antibonding electrons}}{2}$$

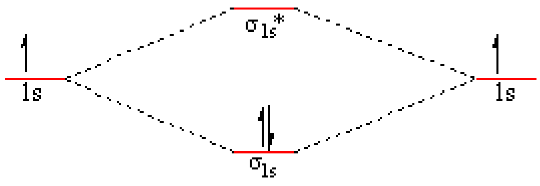
Although the Lewis structure and molecular orbital models of oxygen yield the same bond order, there is an important difference between these models. The electrons in the Lewis structure are all paired, but therecould be unpaired electrons in the molecular orbital description of a molecule. As a result, we can test the predictions of these theories by studying the effect of a magnetic field on certain molecules.

Homo Nuclear Diatmic Molecules

Molecular Orbitals of the Second Energy Level (1s and 2s only)

Molecular Orbitals for Period 1 Diatomic Molecules

Electrons are added to molecular orbitals, one at a time, starting with the lowest energy molecular orbital. The two electrons associated with a pair of hydrogen atoms are placed in the lowest energy, or σ bonding, molecular orbital, as shown in the figure below. This diagram suggests that the energy of an H_2 molecule is lower than that of a pair of isolated atoms. As a result, the H_2 molecule is more stable than a pair of isolated atoms.



We can put the Molecular Orbital Theory to use!! Would you predict that dilithium or diberylium is more likely to form, based on the diagram below?

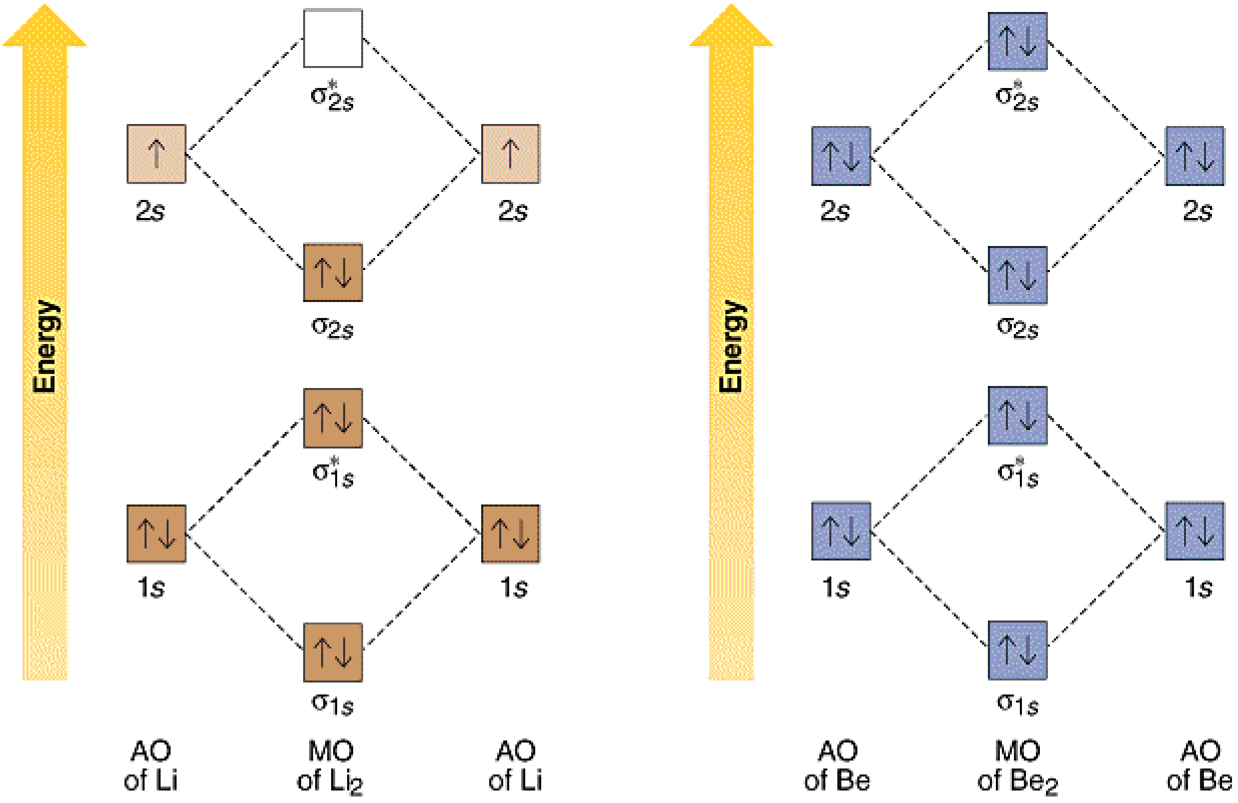
The answer is dilithium because it has a bond order of 1 which is stable and diberylium has a BO of 0 which is unstable and therefore will not form.

Using the Molecular Orbital Model to Explain Why He_2MoleculeDo Not Exist

This molecular orbital model can be used to explain why He_2 molecules don't exist. Combining a pair of helium atoms with $1s^2$ electron configurations would produce a molecule with a pair of electrons in both the σ bonding and the σ^* antibonding molecular orbitals. The total energy of an He_2 molecule would be essentially the same as the energy of a pair of isolated helium atoms, and there would be nothing to hold the helium atoms together to form a molecule.

The fact that an He_2 molecule is neither more nor less stable than a pair of isolated helium atoms illustrates an important principle: The core orbitals on an atom make no contribution to the stability of the molecules that contain this atom. The only orbitals that are important in our discussion of molecular orbitals are those formed when valence-shell orbitals are combined.

Molecular Orbitals for Period 2 Diatomic Molecules and Li_2 and Be_2 (does not exsit)



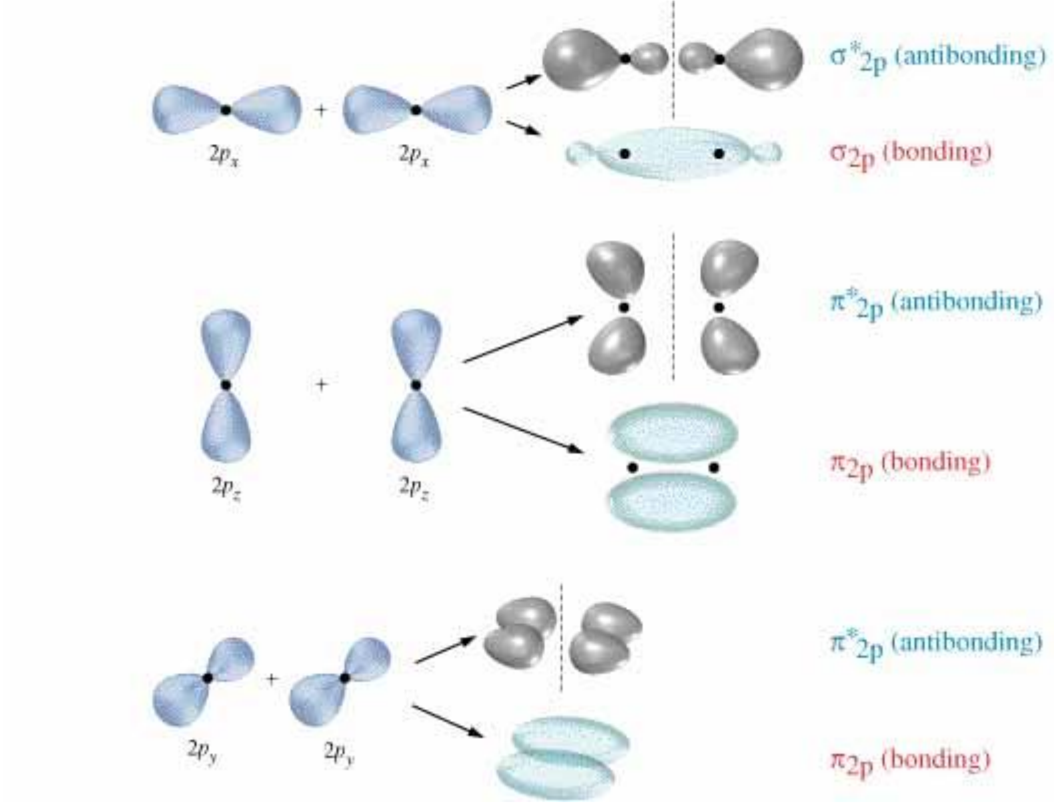
A Li_2 bond order = 1

B Be_2 bond order = 0

Homo Nuclear Diatmic Molecules

Molecular Orbitals of the Second Energy Level (2s and 2p together) ***Molecular Orbitals of the Second Energy Level***

The 2*s* orbitals on one atom combine with the 2*s* orbitals on another to form a σ_{2s} bonding and a $\sigma_{2s}*$ antibonding molecular orbital, just like the σ_{1s} and $\sigma_{1s}*$ orbitals formed from the 1*s* atomic orbitals. If we arbitrarily define the *Z* axis of the coordinate system for the O_2 molecule as the axis along which the bond forms, the $2p_z$ orbitals on the adjacent atoms will meet head-on to form a σ_{2p} bonding and a $\sigma_{2p}*$ antibonding molecular orbital, as shown in the figure below. These are called sigma orbitals because they look like *s* orbitals when viewed along the oxygen-oxygen bond.



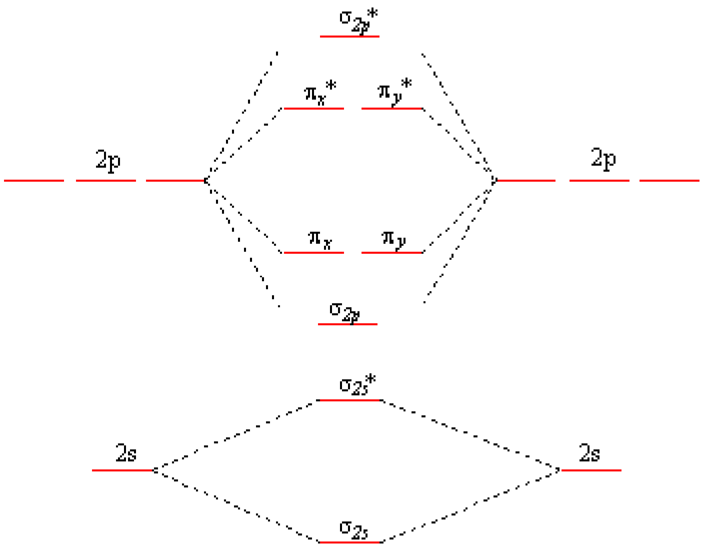
The $2p_x$ orbitals on one atom interact with the $2p_x$ orbitals on the other to form molecular orbitals that have a different shape, as shown in the figure below. These molecular orbitals are called *pi* (π) orbitals because they look like *p* orbitals when viewed along the bond. Whereas σ and $\sigma*$ orbitals concentrate the electrons along the axis on which the nuclei of the atoms lie, π and $\pi*$ orbitals concentrate the electrons either above or below this axis.

The $2p_x$ atomic orbitals combine to form a π_x bonding molecular orbital and a π_x* antibonding molecular orbital. The same thing happens when the $2p_y$ orbitals interact, only in this case we get a π_y and a π_y* antibonding molecular orbital. Because there is no difference between the energies of the $2p_x$ and $2p_y$ atomic orbitals, there is no difference between the energies of the π_x and π_y or the π_x* and π_y* molecular orbitals.

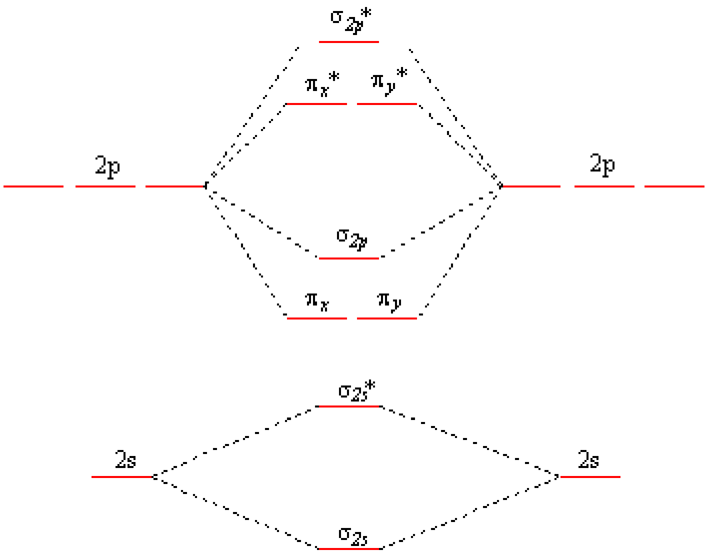
The interaction of four valence atomic orbitals on one atom (2*s*, $2p_x$, $2p_y$ and $2p_z$) with a set of four atomic orbitals on another atom leads to the formation of a total of eight molecular orbitals: σ_{2s}, $\sigma_{2s}*$, σ_{2p}, $\sigma_{2p}*$, π_x, π_y, π_x*, and π_y*.

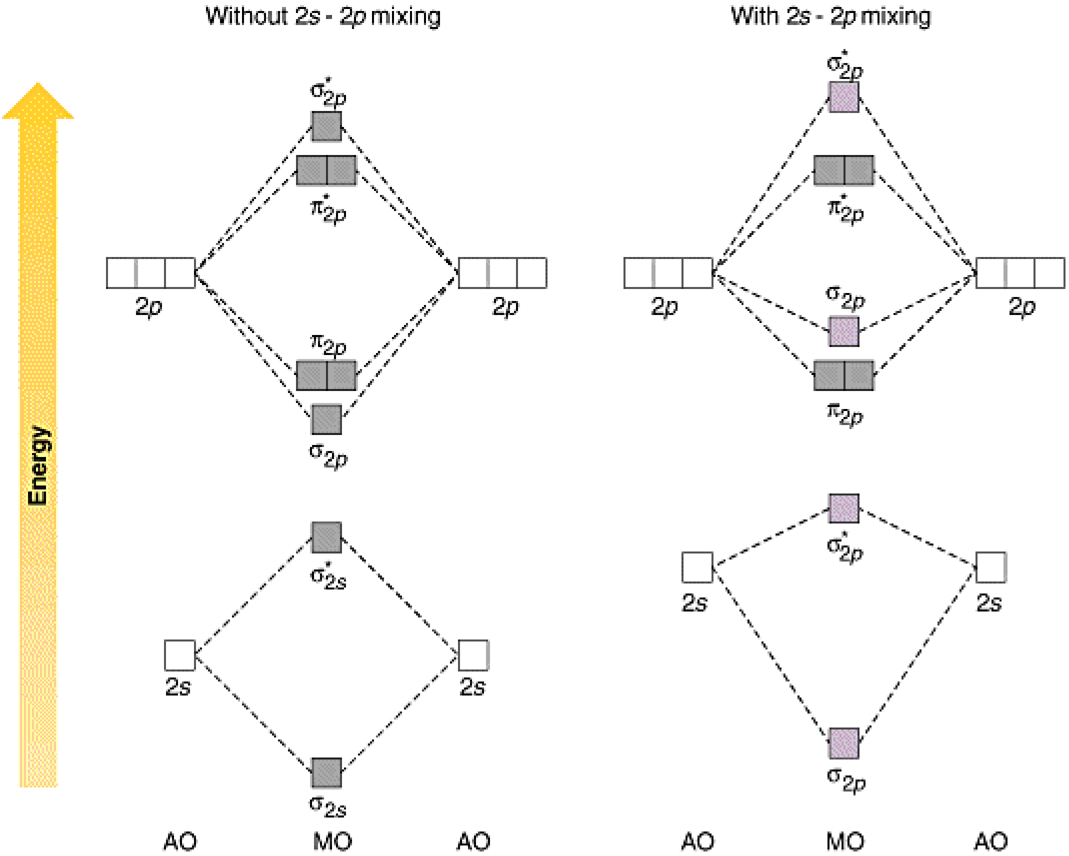
There is a significant difference between the energies of the 2*s* and 2*p* orbitals on an atom. As a result, the σ_{2s} and $\sigma*_{2s}$ orbitals both lie at lower energies than the σ_{2p}, $\sigma_{2p}*$, π_x, π_y, π_x*, and π_y* orbitals. To sort out the relative energies of the six molecular orbitals formed when the 2*p* atomic orbitals on a pair of atoms are combined, we need to understand the relationship between the strength of the interaction between a pair of orbitals and the relative energies of the molecular orbitals they form.

Because they meet head-on, the interaction between the $2p_z$ orbitals is stronger than the interaction between the $2p_x$ or $2p_y$ orbitals, which meet edge-on. As a result, the σ_{2p} orbital lies at a lower energy than the π_x and π_y orbitals, and the $\sigma_{2p}*$ orbital lies at higher energy than the π_x* and π_y* orbitals, as shown in the figure below.



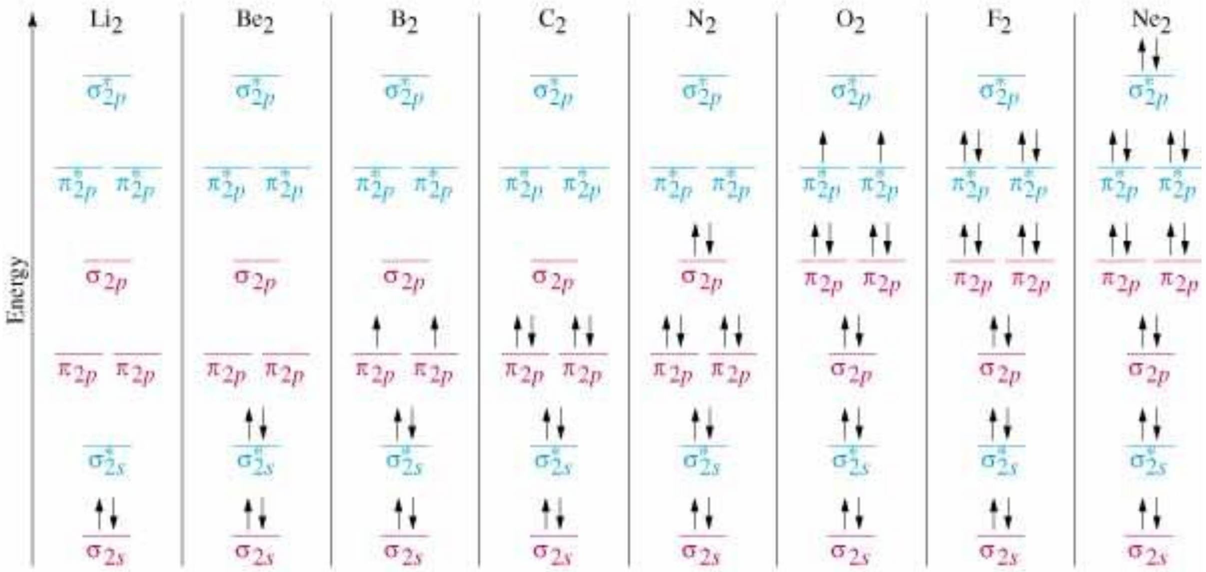
Unfortunately an interaction is missing from this model. It is possible for the 2*s* orbital on one atom to interact with the $2p_z$ orbital on the other. This interaction introduces an element of *s-p* mixing, or hybridization, into the molecular orbital theory. The result is a slight change in the relative energies of the molecular orbitals, to give the diagram shown in the figure below. Experiments have shown that O_2 and F_2 are best described by the model in the figure above, but B_2, C_2, and N_2 are best described by a model that includes hybridization, as shown in the figure below.

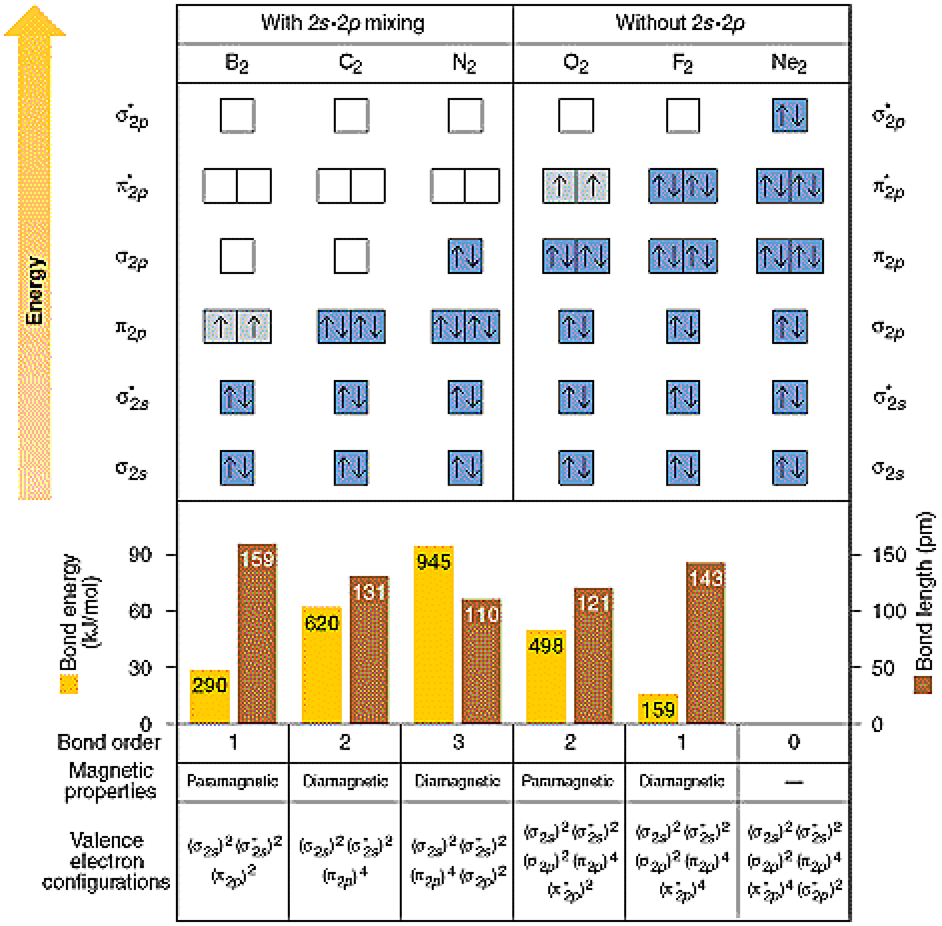

$\sigma_{2p}*$
π_x*
π_y*
2p
2p
σ_{2p}
π_x
π_y
$\sigma_{2s}*$
2s
2s
σ_{2s}



A MO energy levels for O_2, F_2, and Ne_2

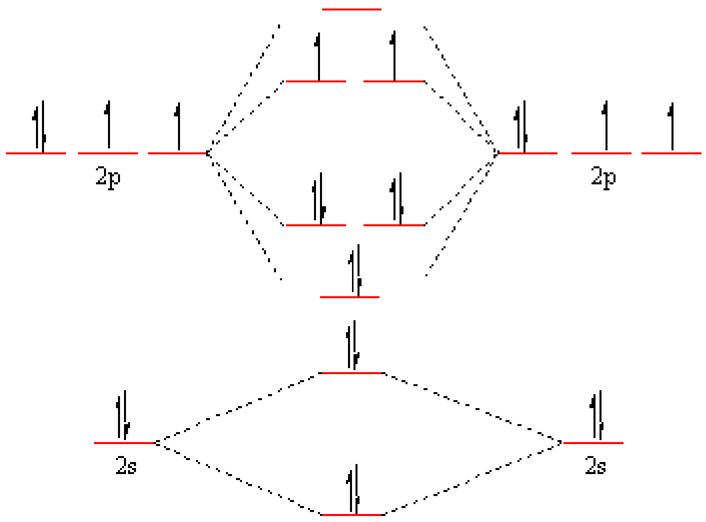
B MO energy levels for B_2, C_2, and N_2


Energy
Li$_2$
Be$_2$
B$_2$
C$_2$
N$_2$
O$_2$
F$_2$
Ne$_2$
σ^*_{2p}
π^*_{2p}
σ_{2p}
π_{2p}
σ^*_{2s}
σ_{2s}



Construct a Molecular orbital diagram for the O_2 molecule.

There are six valence electrons on a neutral oxygen atom and therefore 12 valence electrons in an O_2 molecule. These electrons are added to the diagram in the figure below, one at a time, starting with the lowest energy molecular orbital.



Because Hund's rules apply to the filling of molecular orbitals, molecular orbital theory predicts that there should be two unpaired electrons on this molecule — one electron each in the π_x^* and π_y^* orbitals.

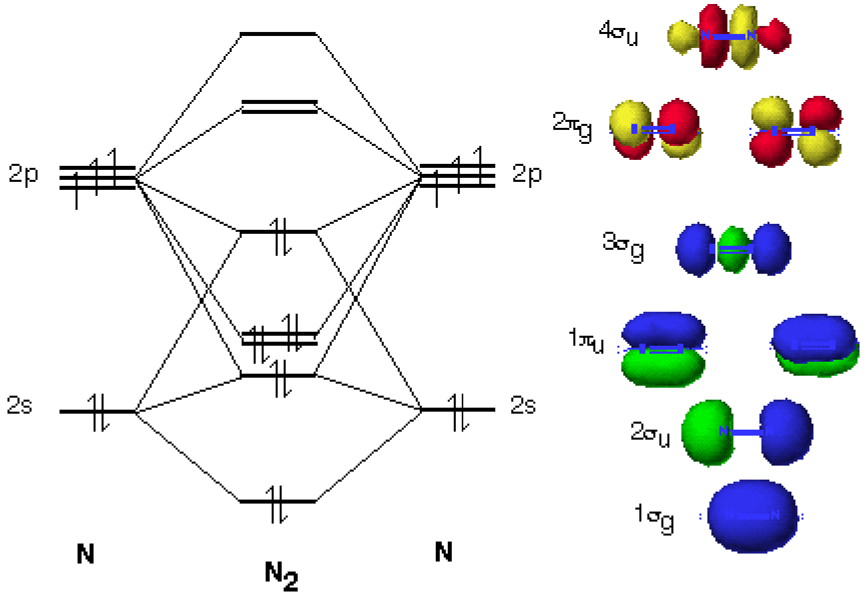
When writing the electron configuration of an atom, we usually list the orbitals in the order in which they fill.

$$\text{Pb: [Xe] } 6s^2\ 4f^{14}\ 5d^{10}\ 6p^2$$

We can write the electron configuration of a molecule by doing the same thing. Concentrating only on the valence orbitals, we write the electron configuration of O_2 as follows.

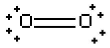
$$O_2\text{: } \sigma_{2s}^{\,2}\,\sigma_{2s}^{*2}\,\sigma_{2p}^{\,2}\,\pi_x^{\,2}\,\pi_y^{\,2}\,\pi_x^{*1}\,\pi_y^{*1}$$

Molecular Orbital diagram fro N2

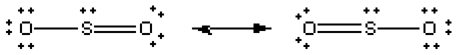


Bond Order

The number of bonds between a pair of atoms is called the **bond order**. Bond orders can be calculated from Lewis structures, which are the heart of the valence-bond model. Oxygen, for example, has a bond order of two.



When there is more than one Lewis structure for a molecule, the bond order is an average of these structures. The bond order in sulfur dioxide, for example, is 1.5 — the average of an S-O single bond in one Lewis structure and an S=O double bond in the other.



In molecular orbital theory, we calculate bond orders by assuming that two electrons in a bonding molecular orbital contribute one net bond and that two electrons in an antibonding molecular orbital cancel the effect of one bond. We can calculate the bond order in the O_2 molecule by noting that there are eight valence electrons in bonding molecular orbitals and four valence electrons in antibonding molecular orbitals in the electron configuration of this molecule. Thus, the bond order is two.

$$\text{Bond order} = \frac{\text{bonding electrons} - \text{antibonding electrons}}{2} = \frac{8 - 4}{2} = 2$$

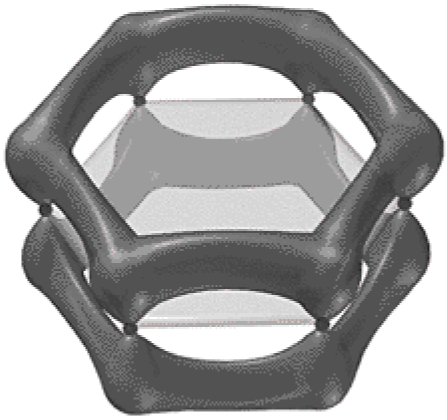
Although the Lewis structure and molecular orbital models of oxygen yield the same bond order, there is an important difference between these models. The electrons in the Lewis structure are all paired, but there are two unpaired electrons in the molecular orbital description of the molecule. As a result, we can test the predictions of these theories by studying the effect of a magnetic field on oxygen.

Atoms or molecules in which the electrons are paired are **diamagnetic** — repelled by both poles of a magnetic. Those that have one or more unpaired electrons are **paramagnetic** — attracted to a magnetic field. Liquid oxygen is attracted to a magnetic field and can actually bridge the gap between the poles of a horseshoe magnet. The molecular orbital model of O_2 is therefore superior to the valence-bond model, which cannot explain this property of oxygen.

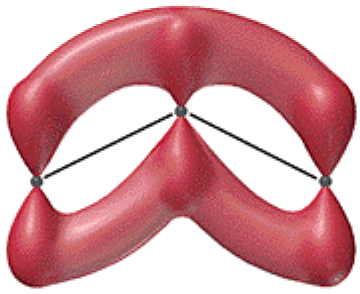
Look at the following MO diagrams for some of the period two elements. Can you tell which molecules are paramagnetic? Which molecules have the highest bond energy, which has the lowest? Rank single, double, and triple bonds in order of bond energy and bond length. (hint a BO of 1 is a single bond, 2 a double...)

Delocalized Bonding

Finaly, it was mentioned earlier that the MO Theory did not need resonance structures to explain anything. Because the MO theory holds that electrons are not held to only one position. Instead they are spread across the entire molecule. Below is a picture of Benzene and Ozone. You can see that rather than having two resonance structures, we can picture one structure with the electrons dispersed over the entire molecule.

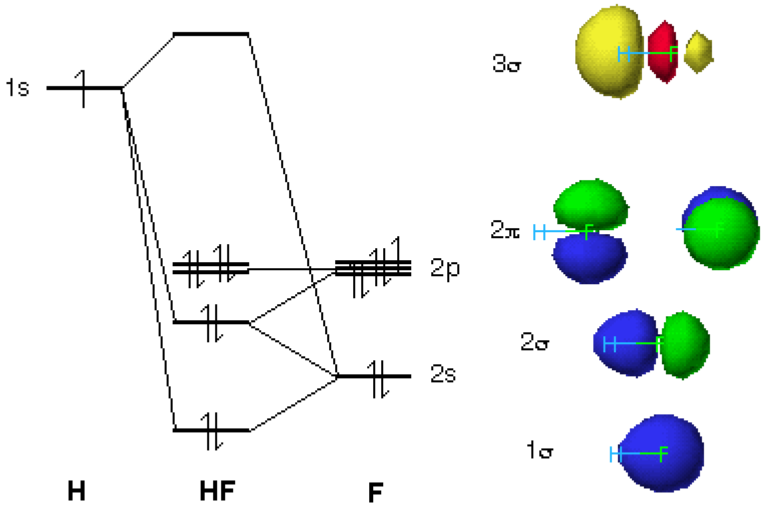


A Benzene, C_6H_6



B Ozone, O_3

Molecular Orbitals for Heteronuclear Diatomic Molecules

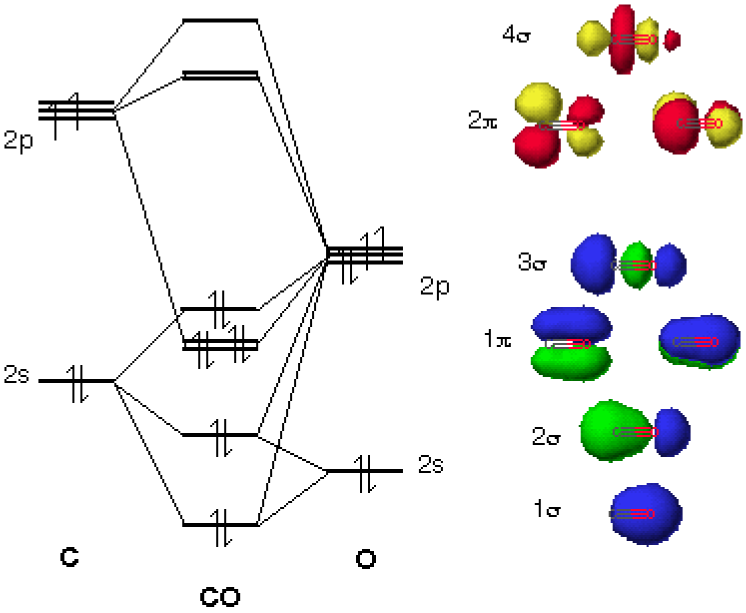


The most striking molecular orbital difference between a heteronuclear diatomic, such as HF, and the homonuclear diatomics is that the orbitals are no longer have equally density on each atom.

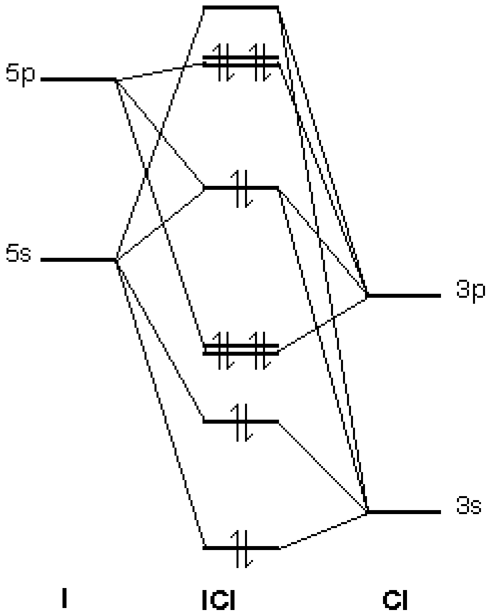
Note that the "1-sigma" and "2-sigma" molecular orbitals of Hydrogen Fluoride are mostly derived from the Fluorine 2s and 2p atomic orbitals respectively. Qualitatively, the high fluorine character of these orbitals is a consequence of the high electronegativity of fluorine as compared to hydrogen. Mathematically, the molecular orbitals have large coefficients on Fluorine and small coefficients on Hydrogen. The 1 pi orbitals are non-bonding and Fluorine 2p in character. Finally, the anti-bonding "3-sigma" orbital is primarily H 1s in character.

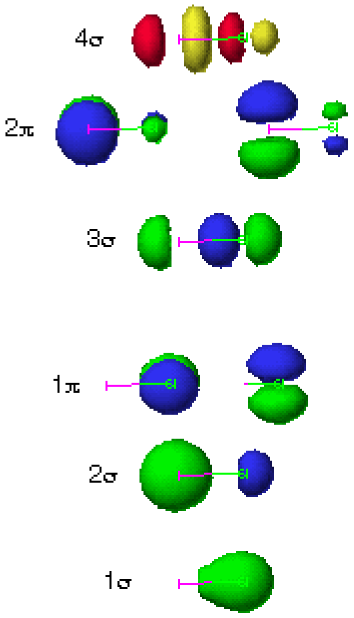
The use of nodes to give a general idea of the energy ordering still works. "1-sigma" has no nodes, "2-sigma" and "1-pi" have one node, and "3-sigma" has two nodes.

Carbon monoxide CO molecular orbital diagram



Iodine monochloride ICl molecular orbital diagram





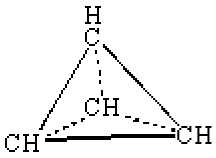
The Isolobal Analogy

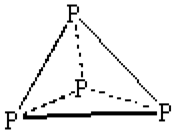
Extension of Valence Bond and Mo;ecualr Orbital theory to Complex Molecules:

Introduction

Different groups of atoms can give rise to similar shaped fragments. For example,
the C-H group and the P atom have 5 electrons and can contribute 3 electrons to a cluster,
C-H has 4+1 electrons and uses 2 electrons for the C-H bond
P has 5 electrons and uses 2 electrons for a lone pair

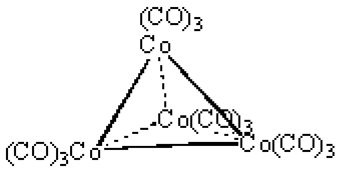
Both fragments are 3 electrons short of making maximum use of their 4 valence orbitals (s and 3× p) by achieving an octet. The clusters C_4H_4 or $(CH)_4$ (known as tetrahedrane) and P_4 have the same number of cluster electrons and therefore adopt the same shape:



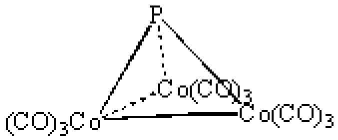


The organometallic fragment $Co(CO)_3$ has 15 electrons:
Co has 9 valence electrons and each CO donates 2e to the metal

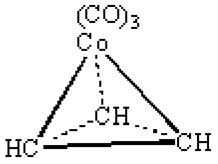
The fragment is 3 electrons short of the stable electron count for an organometallic fragment of eighteen Eighteen electrons corresponds to making maximum use of the 9 valence orbitals of the transition metal (s + 3× p and 5× d). It can achieve 18 electrons by sharing 3 electrons to make 3 covalent bonds. The $Co(CO)_3$ fragment thus has the same requirements as the C-H unit and the P atom. The cluster $[Co(CO)_3]_4$ thus also has the same tetrahedral shape as that shown by C_4H_4 and P_4. It is also possible to swap the three fragments around:



A



B



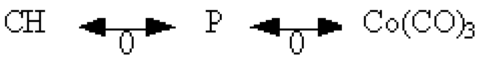
C

B and **C** are more conventionally thought of as $(\mu^3\text{-P})[\text{CoCO})_3]_3$ and $(\eta^3\text{-}C_3H_3)Co(CO)_3$ respectively but this hides the structural and electronic links between all these clusters.

The similarity between these fragments and between other groups of fragments has been investigated in detail by Roald Hoffmann. Fragments are deemed to be **isolobal** if

> "the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar"
> (R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **21**, 711, 1982)

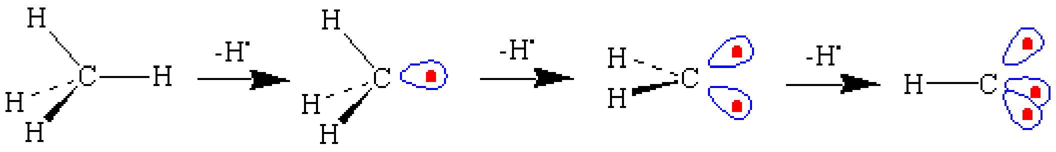
The isolobal relationship is symbolized by a double-headed arrow with a tear-drop,



The isolobal analogy relates the orbitals and bonding in inorganic, organometallic and cluster chemistry to that in organic and main group chemistry. The utility of the isolobal analogy is that one should be able to replace replace a (transition metal) ML_n fragment in a molecule with the isolobal (main group) AH_n fragment, and vice versa, to produce new molecules with very similar bonding.

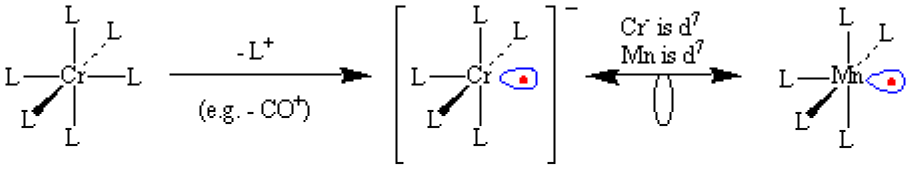
Generating isolobal fragments

Main group fragments can be generated by starting from methane, **1** (or any molecule obeying the octet rule). Homolytic cleavage of a C–H bond generates the methyl radical, **1a,**, which has one frontier orbital pointing towards the missing hydrogen with one electron in it. Homolytic cleavage of a second C–H gives methylene, **1b**, which has too singly occupied hybrids pointing towards the two vacant hydrogen positions. Removal of a third hydrogen gives methine, **1c**, with three singly occupied hybrids.



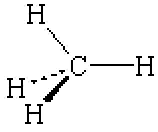
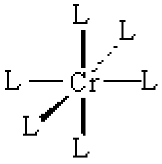
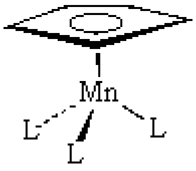
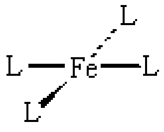
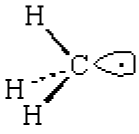
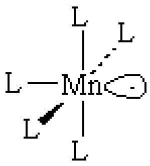
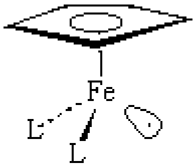
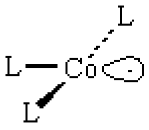
1 **1a** **1b** **1c**

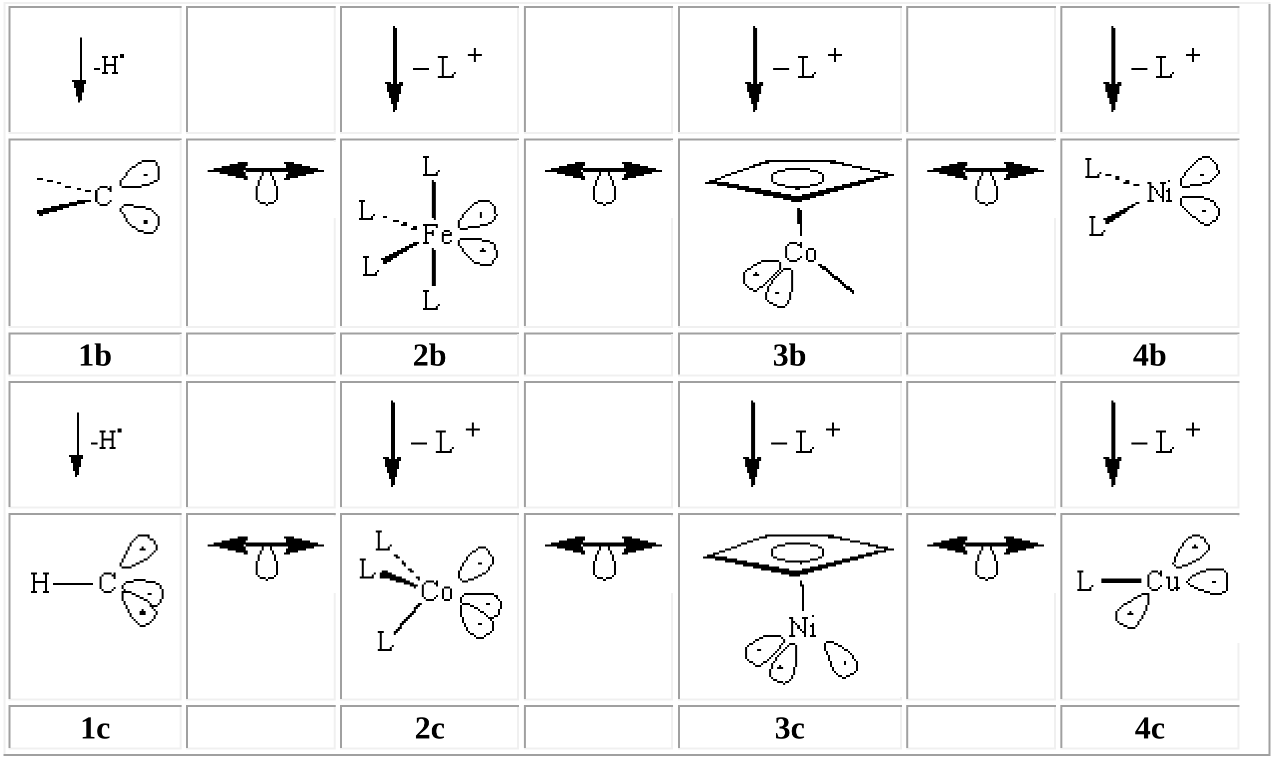
The transition metal fragments are generated in an analogous way. For example, from the starting point of CrL6, **2**, where L is a two electron donor such as CO, (or any molecule obeying the eighteen electron rule such as **3**), the fragments **2a**, **2b** and **2c** are generated by successive *homolytic* cleavage of M–L bonds on one octahedral face. As L is a two-electron donor, homolytic cleavage of CrL6 gives CrL5– and L+. To remove the charge, the metal is then replaced by Mn (the element one to the right in the 3d series):



2 **2a**

Isolobal scheme

8–electron		18–electron				16–electron
						
1		**2**		**3**		**4**
↓ $-H^{\bullet}$		↓ $-L^{+}$		↓ $-L^{+}$		↓ $-L^{+}$
						
1a		**2a**		**3a**		**4a**



As long as the electron count is maintained or consistent changes are made, the metal or main group element can be substituted. Thus,

CH_3 $\longleftrightarrow$ Me_3Sn $\longleftrightarrow$ $Mn(CO)_5$ $\longleftrightarrow$ $Fe(PPh_3)_5^+$ $\longleftrightarrow$ $Mo(CO)_5^-$

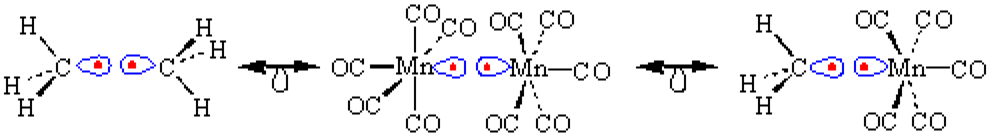
CH_3^+ $\longleftrightarrow$ BH_3 $\longleftrightarrow$ $Mn(CO)_5^+$ $\longleftrightarrow$ $Cr(CO)_5$ $\longleftrightarrow$ $Rh(PPh_3)_3^+$

CH_3^- $\longleftrightarrow$ NH_3 $\longleftrightarrow$ $Mn(CO)_5^-$ $\longleftrightarrow$ $Fe(CO)_5$ $\longleftrightarrow$ $Rh(CO)_5^+$

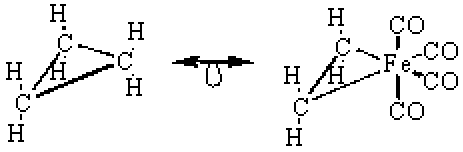
It should be noted that the main use of the isolobal analogy is in generating alternative fragments *in molecules*. The geometry of the fragment *in a molecule* not as an isolated species is important. Thus, CH_3 and BH_3 are considered as pyramidal (not planar) species and $Cr(CO)_5$ is considered as a square-based pyramid (not trigonal bipyramid).

Applications of Isolobility

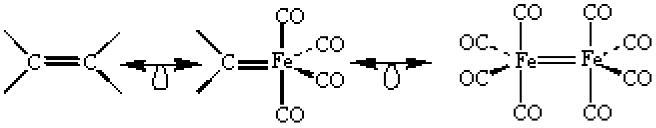
The isolobal analogy between CH_3 and d^7 MnL_5 implies similar bonding in the following compounds:

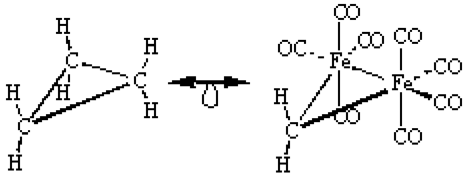


The isolobal relationship of CH_2, with $Fe(CO)_4$ generates the compounds illustrated below. The transition metal molecule has been drawn as a metallocyclopropane. A more common description is to consider it as an ethene complexes, $(\eta 2–C_2H_4)Fe(CO)_4$. The isolobal relationship shows that cyclopropane itself can be consider as $(\eta 2–C_2H_4)CH_2$.



Other known compounds generated using this relationship include:





Here are some common isolobal fragments

Molecular orbital theory

Introduction

Modern chemistry has depended upon the use of models of increasing comlexity. Atoms can be represented as spheres connected by cyclinders or sticks. In order to understand the mechanism of many reactions, **Lewis Theory**, developed by Robinson and Ingold, can provide a succesful answer.

Lewis Theory uses curly arrows to denote electron migration during a chemical reaction and has led to a greater understanding of the factors controlling chemical reactions.

Pauling with others, developed Resonance Theory, which provided the rationale to an all-embracing orbital theory. The use of "canonical forms" and "resonance hybrids", alonng with extensive use of curvy arrows has provided the fundamental background to modern organic theory, but for *eg*. Diels-Alder and pericyclic reactions, the curly arrow format is not very clear and in some instances the reactions are described as no-machanism reactions. Woodward and Hoffmann showed that by examining the interaction of the frontier molecular orbitals (ie. the Highest Occupied, **HOMO** and Lowest Unoccupied, **LUMO**) both the regio- and

stereospecificity could be accountred for.
Woodward and Hoffmann work was assimilated into general organic reaction theory.

3.7 An introduction to the theory of Linear Combination of Atomic Orbitals (LCOA)

A theory which treats bonding as an over lapping of ligand orbitals with those of the central atom.

By summing the original wavefunctions for the bonding orbitals in constituent species, "hybrid" molecular orbitals of the compound can be generated. These new orbitals have an intermediate character between the original s, p, and d orbitals (if available) in the outer energy level, and produce additional bond sites. The hybridization is named on the basis of the orbitals involved, and the hybrid wavefunction is the (renormalized) sum of the individual wavefunctions, where each addition may be with an arbitrary sign. The composite wavefunctions with differing signs are orthogonal, since

$$\int(\psi_1+\psi_2)(\psi_1-\psi_2)^*\,dV = \int(|\psi_1|^2+\psi_1\psi_2^*-\psi_1^*\psi_2-|\psi_2|^2)\,dV. \quad (1)$$

But

$$\int \psi_1\psi_2^*\,dV = \delta_{1,2}, \quad (2)$$

so

$$\int(\psi_1+\psi_2)(\psi_1-\psi_2)^*\,dV = (1+0+0-1)=0. \quad (3)$$

The simplest example is s^2-hybridization. There are two possible combinations,

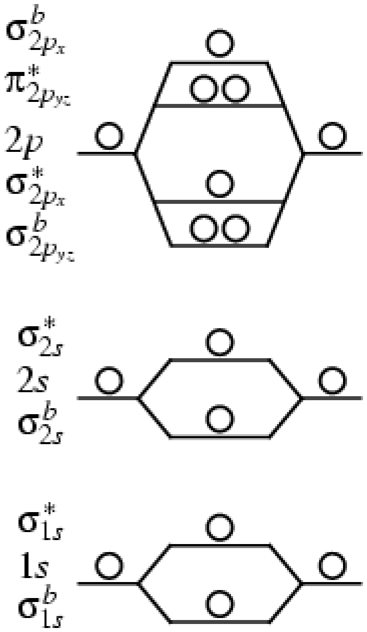
$$\psi_1 = \frac{1}{\sqrt{2}}(\psi_{s,1}+\psi_{s,2}) \qquad \sigma_{1s}^b \quad (4)$$

$$\psi_2 = \frac{1}{\sqrt{2}}(\psi_{s,1}-\psi_{s,2}) \qquad \sigma_{1s}^*, \quad (5)$$

where the wavefunctions on the right are the solutions to Schrödinger's equation, and the normalization constants are needed so that the hybrid wavefunction is normalized. ψ_1 has the electron density is greatest between the two nuclei. It will therefore bind the nuclei together, and is called a bonding molecular orbital. ψ_2 has the electron density greatest on the sides of the nuclei. It will therefore pull the nuclei apart, and is called an antibonding molecular orbital. In some instances, a nonbonding molecular orbital may be generated for which the electron density is uniformly distributed between and on the sides of the nuclei. A measure of the stability of a compound based on the occupancy of its molecular orbitals is given by the body order.

$$[\text{bond order}] \equiv \tfrac{1}{2}([\#\text{BMO electrons}] \; -[\#\text{ABMO electrons}]).$$

More complicated bonding interactions will involve s, p, and d orbitals. For a homonuclear diatomic compound with hybrid orbitals constructed from $1s$, $2s$, and 2p orbitals, the molecular orbital have the following form.



For heteropolar molecules or more complicated systems, the molecular orbital energy diagram can be quite complex. The molecular orbitals for the CO_2 (O_1=C=O_2) molecules are given by, in order of increasing energy

$$\begin{cases} \sigma_s & \mathrm{C}(2s) + \mathrm{O}_1(p_z) - \mathrm{O}_2(p_z) \\ \sigma_p & \mathrm{C}(2p_z) - \mathrm{O}_1(p_z) - \mathrm{O}_2(p_z) \end{cases}$$

$$\begin{cases} \Pi_x & \mathrm{C}(2p_x) + \mathrm{O}_1(p_x) + \mathrm{O}_2(p_x) & \Pi_x = \Pi_y \\ \Pi_y & \mathrm{C}(2p_y) + \mathrm{O}_1(p_y) + \mathrm{O}_2(p_y) & \Pi_x = \Pi_y \end{cases}$$

$$\begin{cases} n_1 & \mathrm{C}(2p_x) + \mathrm{O}_1(p_y) + \mathrm{O}_2(p_y) & n_1 = n_2 \\ n_2 & \mathrm{C}(2p_y) + \mathrm{O}_1(p_x) + \mathrm{O}_2(P_x) & n_1 = n_2 \end{cases}$$

$$\begin{cases} \Pi^*_x & \mathrm{C}(2p_x) - \mathrm{O}_1(p_x) - \mathrm{O}_2(p_x) & \Pi^*_x = \Pi^*_y \\ \Pi^*_y & \mathrm{C}(2p_y) - \mathrm{O}_1(p_y) - \mathrm{O}_2(p_y) & \Pi^*_x = \Pi^*_y \end{cases}$$

$$\sigma^*_p \qquad \mathrm{C}(2p_z) + \mathrm{O}_1(p_z) + \mathrm{O}_2(p_z)$$

$$\sigma^*_s \qquad \mathrm{C}(2s) - \mathrm{O}_1(p_z) + \mathrm{O}_2(p_z)$$

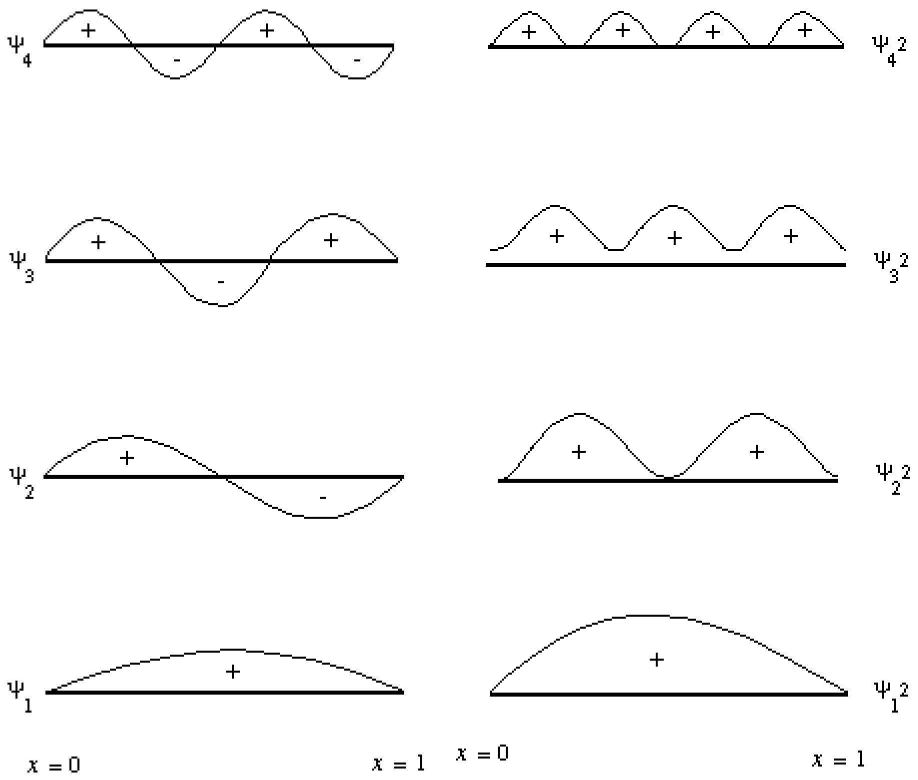
There are 12 electrons in the valence shell, so the levels are filled through the nonbonding orbitals. The compound is therefore stable, with a bond order of 4. For an even more complicated example, consider benzene. For certain compounds, electrons are delocalized. Such compounds have an extremely large number of molecular orbitals. The result, as the number of levels goes to infinity, is a band of bonding orbitals, and band of antibonding orbitals (known as the conduction band, since free electrons will exist here), possibly overlapping or possibly separated by a gap. In metals, the levels overlap, and the bonding orbitals are completely filled. In semiconductors, the levels are separated by a small "forbidden zone." The addition of a small amount of energy will therefore remove an electron from the filled bonding orbital, through the forbidden zone, and into the conduction band.

Atomic and Molecular Orbitals

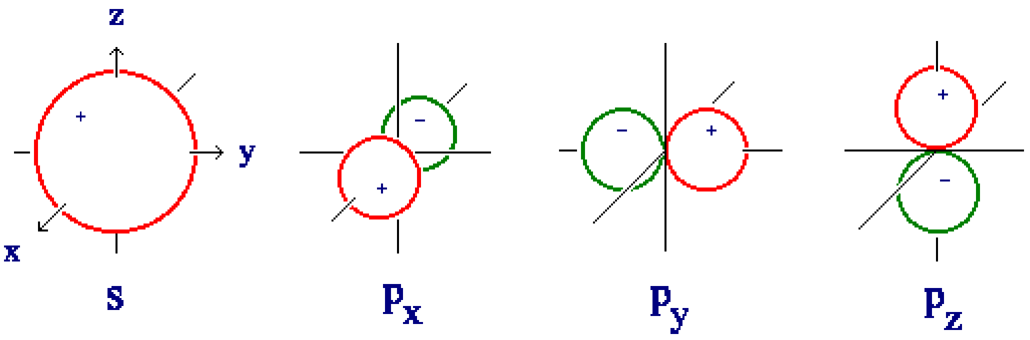
By sharing electron, molecules can form bonds, and it is possible to regard the sharing of two electrons by two atoms as constituting a chemical bond. Atoms can share one, two or three electrons (forming single, double and triple bonds).

A hydrogen atom consists of a nucleus (a *proton*) and an *electron*. It is not possible to accurately determine the position of the electron, but it is possible to calculate the probability of findng the electron at any point around the nucleus. With a hydrogen atom the probability distribution is spherical around the nucleus and it is possible to draw a spherical boundary surface, inside which there is a 95% possibility of finding the electron. The electron has a fixed energy and a fixed spatial distribution called an *orbital*. In the helium atom there are two electrons associated with the helium nucleus. The electrons have the same spatial distribution and energy (*ie*. they occupy the same orbital), but they differ in their spin (Pauli exlusion principle). In general: electrons in atomic nuclei occupy orbitals of fixed energy and spatial distribution, and each orbital only contains a maximum of two electrons with anti-parallel spins.

In physics, periodic phenomena are associated with a "wave equation", and in atomic theory the relevant equation is called the "Schrödinger Equation". The wave equation predicts discrete solutions in one dimension for a particle confined to a box with infinite walls, The solutions can be shown as in the figure below:

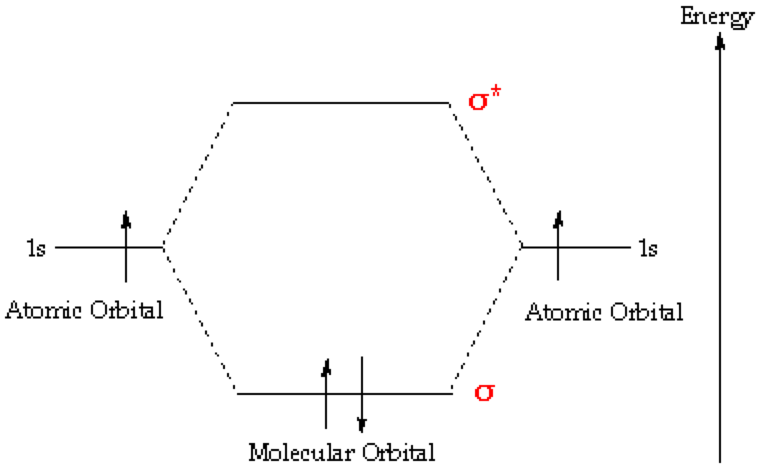


ψ_1 - ψ_4 represent solutions of increasing energy. In three dimensions, the equation determines the energy and defines the spatial distribution of each electron. Solutions of the wave equations in three-dimensions allows calculation of the "shape" of each orbital. The first five solutions of the wave equation for an electron associated with a proton can be shown in the figure below:



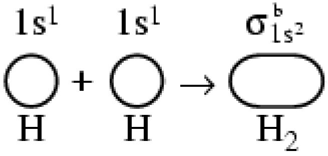
In the hydrogen atom, the *1s* atomic orbital has the lowest energy, while the remainder (*2s*, $2p_x$, $2p_y$ *and* $2p_z$) are of equal energy (*ie*.**degenerate**), but for all other atoms, the *2s* atomic orbital is of lower enegry than the $2p_x$, $2p_y$ *and* $2p_z$ orbitals, which are degenerate.

In atoms, electrons occupy **atomic orbitals**, but in molecules they occupy similar **molecular orbitals** which surround the molecule. The simplest molecule is hydrogen, which can be considered to be made up of two seperate protons and electrons. There are two molecular orbitals for hydrogen, the lower energy orbital has its greater electron density between the two nuclei. This is the **bonding** molecular orbital - and is of lower energy than the two *1s* atomic orbitals of hydrogen atoms making this orbital more stable than two seperated atomic hydrogen orbitals. The upper molecular orbital has a node in the electronic wave function and the electron density is low between the two positively charged nuclei. The energy of the upper orbital is greater than that of the *1s* atomic orbital, and such an orbital is called an **antibonding** molecular orbital. Normally, the two electrons in hydrogen occupy the bonding molecular orbital, with anti-parallel spins. If molecular hydrogen is irradiated by ultra-violet (UV) light, the molecule may absorb the energy, and promote one electron into its antibonding orbital (σ^*), and the atoms will seperate. The energy levels in a hydrogen molecule can be represented in a diagram - showing how the two 1s atomic orbitals combine to form two molecular orbitals, one bonding (σ) and one antibonding (σ^*). This is shown below - by clicking upon either the σ or σ^* molecular orbital in the diagram - it will show graphically in a window to the right:

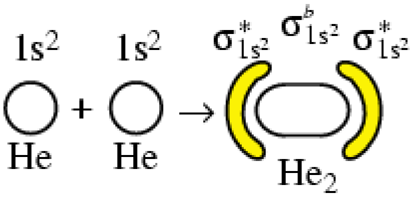


3.8 Homonuclear diatomic molecules

A diatomic hydrogen molecule fills the σ^b_{1s} orbital, and so has a bond order of 1 and is stable.



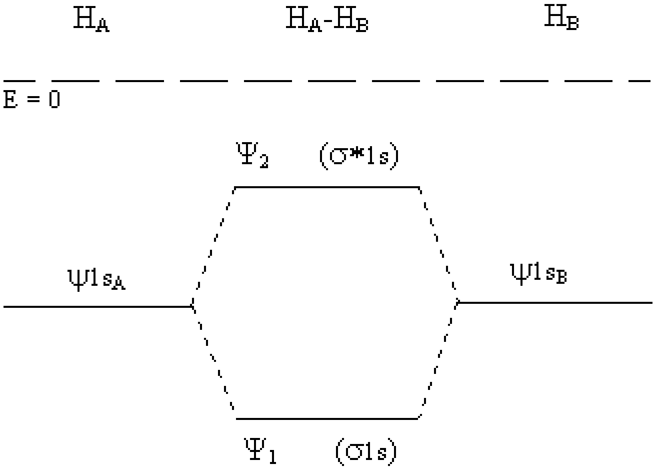
A diatomic helium molecule fills both the σ^*_{1s} and σ^b_{1s} orbitals, so it has a bond order of zero and is not stable.



Diatomic molecules H_2 and He_2

The probability plot for Ψ_2^2 is also shown in Figure 4. What would be its equation? (The

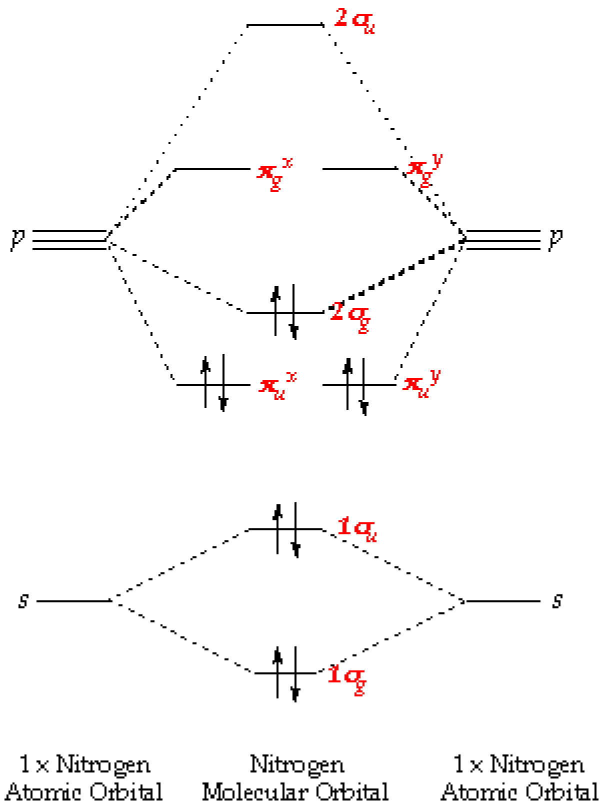
equivalent of equation 3) What do you notice about the electron density between the nuclei as compared to two individual hydrogen atoms simply placed side by side?
Further insight into the bonding of H_A and H_B can be obtained by considering the energies of the electrons in Ψ_1 and Ψ_2 compared to their energies in the non-interacting atoms. This can be done by plugging the LCAO wave functions for the molecule back into the appropriate Scrödinger equation (just as it can be done for the individual atoms using the atomic wave functions). The results are shown in Figure 5, where Ψ_1 and Ψ_2 are sometimes renamed σ(1s) and σ*(1s), respectively, to indicate the type of molecular orbital and their parentage.



These molecular orbitals are useful for any molecule, or molecule-ion, using only 1s orbitals for bonding. Several possibilities are: H_2^+, H_2, H_2^-, H_2^{2-}, He_2^+ and He_2. The positive molecule-ions are unstable, but have been detected in the gas phase under high energy conditions. The negative molecule-ions and He_2 have not been observed.

Nitrogen:

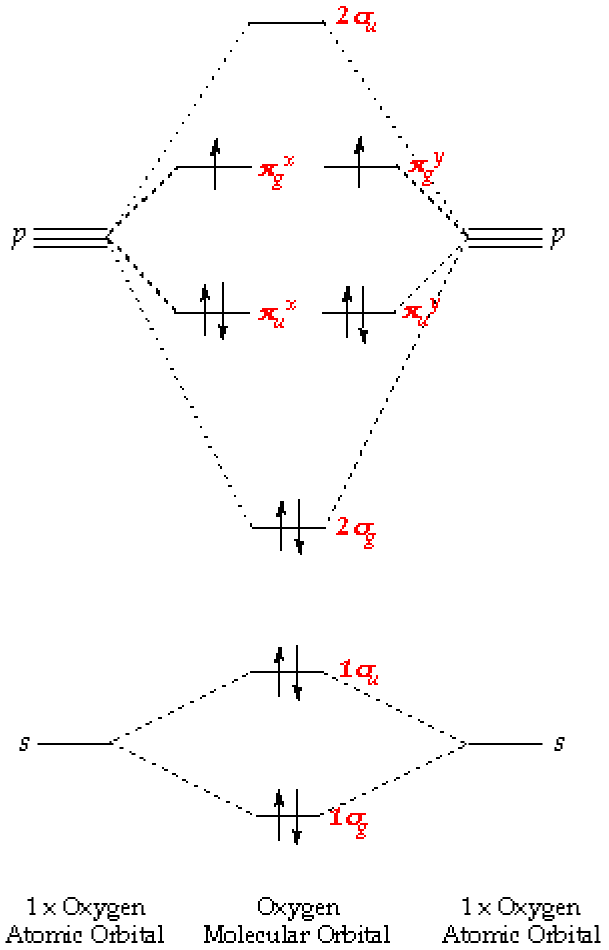
This molecule has ten electrons. The atomic orbitals combine to produce the following molecular orbital diagram:



Here the $2\pi_g$ orbital is occupied by two electrons to give a total bond order of three. This corresponds well with the Lewis structure (N≡N), although the orbital approach tells us that there is one σ and two π.

Oxygen:

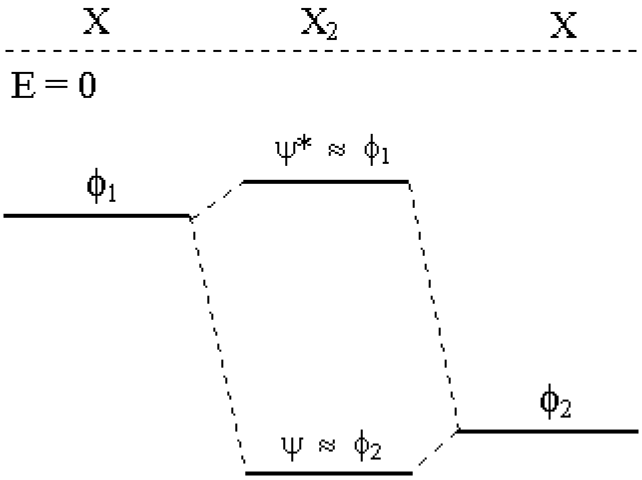
This molecule has twelve electrons, two more than nitrogen - and these extra two are placed in a pair of degenerate π_g orbitals. The atomic orbitals combine to produce the following molecular orbital diagram:



Comparison of the above energy level diagram wit hthat for nitrogen - you can see that the $2\sigma_g$ level lies lower than π_u. Here, we are starting to fill the anti-bonding orbitals originating from the *p* orbital interactions and so the bond order decreases from three to two.
The lowest energy arrangment (Hund's rule) - has a single electron, each with parallel spins, in each of the π_g^x and π_g^y orbitals. This produces a paramagnetic molecule, with a double bond and has two unpaired electrons.

3.9 Heteronuclear diatomic molecules

If the molecule is heteronuclear, the parent atomic orbitals will have different energy levels. The more easily ionized (less electronegative) atom will have the atomic orbital level closer to E = 0 in the arrangement depicted below:



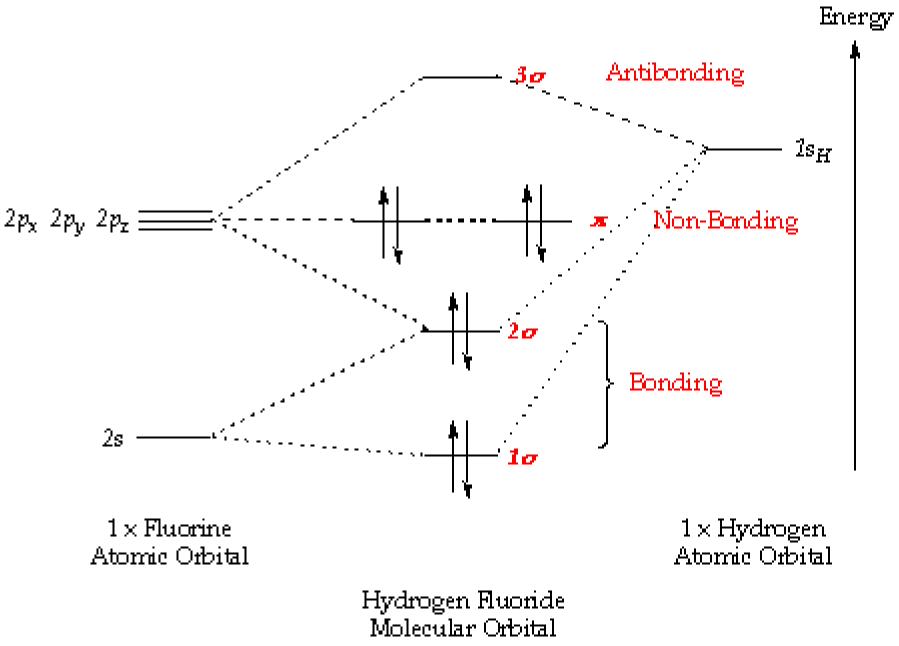
The bonding molecular orbital has an energy and a wave function which approximates the more electronegative atom. The antibonding molecular orbital will have an energy and wavefunction which resembles that of the less electronegative atom. As an example, consider the molecule hydrogen chloride. The hydrogen 1s orbital (one electron) would be ϕ_1 and the chlorine 3p orbital that bonds with it (one electron) will be ϕ_2. The molecular orbital ψ will look very much like the chlorine 3p orbital and will end up holding *both* electrons, while the ψ^* orbital will look like the original H 1s orbital and will end up empty. Thus, the molecular orbital theory correctly represents $H^{\delta+}Cl^{\delta-}$. (Note that the above is a rather treatment because it ignores the possible involvement of the 3s orbital of Cl.)

A_2 Molecules

Hydrogen Fluoride:

A simple diatomic molecule is Hydrogen fluoride. There are eight valence electrons which occupy four molecular orbitals. The two highest energy MO's are degenerate, are π-type and have no electron density associated with the hydrogen atom, *ie*. they are Non-Bonding Orbitals (NBO) and in Lewis Theory are represented as two "*Lone Pairs*". Another important difference between Hydrogen Fluoride and previous molecules is that the electron density is not equally distributed about the molecule. There is a much greater electron density around the fluorine atom. This is because fluorine is an exremely electronegative element, and in each bonding molecular orbital, fluorine will take a greater share of the electron density.

For the energy diagram and pictorial view of the orbitals - please see below:



3.10 Bond properties in the molecular orbital formalism

Bond Lengths and Covalent Radii There are several points to be made here:
Bond lengths are derived from the sums of covalent radii. The covalent radi can be obtained in the first instance by taking half the length of a homonuclear bond:

$d_{Cl\text{-}Cl}$ (in Cl_2) = 1.988 Å therefore r_{Cl} = 0.99 Å
$d_{C\text{-}C}$ (in diamond) = 1.54 Å therefore r_C(single bond) = 0.77 Å
Predicted $d_{C\text{-}Cl}$ = r_C(single bond) + r_{Cl} = 0.99 + 0.77 = 1.76 *vs* actual 1.77 Å

Naturally, the observed bond lengths will vary a little from compound to compound depending on the other atoms bonded to the two participating in the bond under consderation.
The observed bond length will be a function of the bond order for example:
$d_{N\&o\rho\delta\mu;N}$ = 1.10 Å $d_{N=N}$ = 1.25 Å $d_{N\text{-}N}$ = 1.45 Å
Double- and triple-bond radii are approximately 0.87 and 0.78 times the single-bond radius.

The single-bond covalent radius of an atom is influenced by the type of hybrids that it is using. The more p-character in the hybrid, the larger will be the radius:

$r_C(sp^3)$ = 0.77 Å $r_C(sp^2)$ = 0.73 Å $r_C(sp)$ = 0.70 Å
If the electronegativity of the bound atoms differs substantially, that is the bonds have substantial ionic character, then the bonds will be shorter than predicted by the covalent radii:
In CF_4 the C-F bondlength is 1.32 Å (predicted 1.44 Å)
In SiF_4 the Si-F bond length is 1.54 Å (predicted 1.81 Å)
In SiF_4 some of this shortening is said to involve π-bonding between empty silicon d-orbital and filled fluorine p-orbitals.

Overlap of Orbitals

Bonding overlap. All parts of the atomic orbitals which overlap each other have the same sign (colour). The electon density is raised in such areas of overlap by $2\psi_1.\psi_2$ relative to the simple sum: $\psi_1^2 + \psi_2^2$ which leads to an attractive component to the interation between the two atom concerned.

Antibonding overlap. All overlapping parts of the atomic orbitals have opposite signs. A node is formed in such regions so the electron density goes to zero at the node. Such molecular orbitals, when occupied by electrons, contribute a repulsive component to the interaction between the two atoms concerned.

Non-bonding overlap. If there some areas of overlap where the signs are the same and others where they are opposite, the net contribution of such a molecular orbital to the interaction between the two atoms would be zero. For this reason such molecular orbital combinations are not constructed.

The σ,π and δ Notation

The "bottom line" is that a σ-molecular orbital has no node which passes through all the nuclei involved, a π-molecular orbital has one such node, and a δ-molecular obrbital has two such nodes.

Molecular orbitals of polyatomic molecules

3.11 The construction of molecular orbitals

Orbitals for selected molecules

This section illustrates pictorially molecular orbitals for several organic and inorganic molecules. If possible - the energy level diagram is included and clicking upon the relelvant level will generate the accompanying molecular orbital in the right-hand frame. Please choose from:

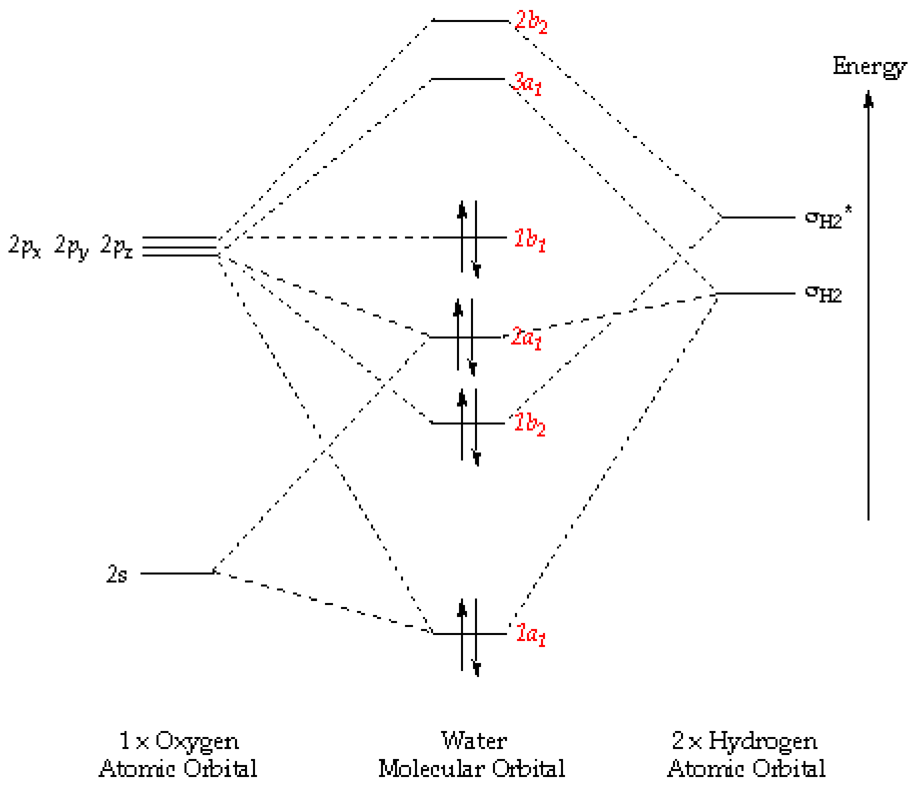
3.12 Polyatomic molecules in general

Saturated molecules

These are molecules in which all valence electrons are involved in the formation of single bonds. There are no non-bonded lone pairs. These molecules are generally less reactive than either electron-rich or electron-deficient species, with all occupied orbitals having relatively low energies.

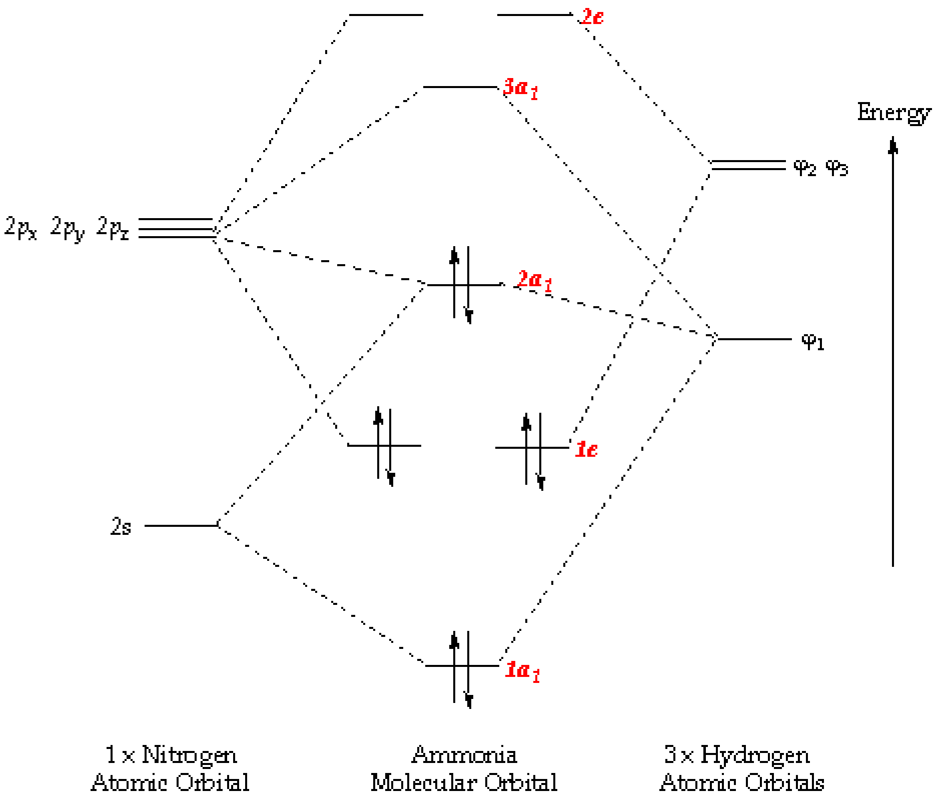
Water:

In the water molecule the highest occupied orbital, ($1b_1$) is non-bonding and highly localized on the oxygen atom, similar to the non-bonding orbitals of hydrogen fluoride. The next lowest orbital ($2a_1$) can be thought of as a non-bonding orbital, as it has a lobe pointing away from the two hydrogens. From the lower energy bonding orbitals, it is possible to see that oxygen also takes more than its "fair share" of the total electron density.



Ammonia:

Ammonia has two pairs of degenerate orbitals, one bonding and one antibonding, and like hydrogen fluoride and water has a non-bonding orbital (*$2a_1$*). This highest occupied orbital has a lobe pointing away from the three hydrogens, and corresponds to a lone pair orbital localized upon the nitrogen, whereas the three lowest energy MO's lead to the description of the three N-H bonds of the Lewis structure. The lone pair is relatively high in energy, and is responsible for the well known Lewis base properties of ammonia.

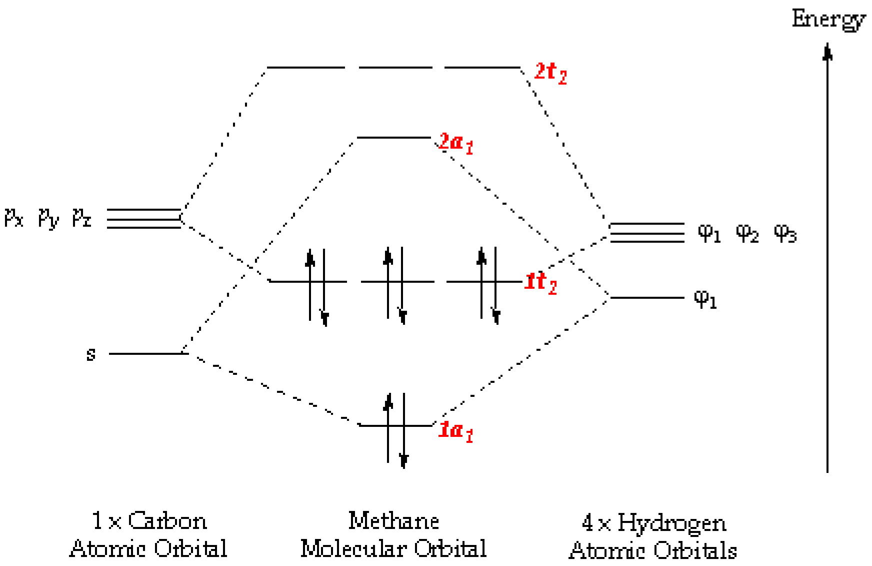


The next molecule in the series HF, H_2O and H_3N, is H_4C (methane) - which was discussed earlier - and unlike the other three molecules has no non-bonding orbitals.

Methane:

The valence molecular orbitals of methane are delocalized over the entire nuclear skeleton - that is, it is not easy to assign any one orbital to a particular C-H bond. It is possible to see how complex the orbital structure becomes with the increase in energy. Methane has four valence molecular orbitals (bonding), consisting of one orbital with one nodal plane (lowest occupied) and three degenerate (equal energy) orbitals that do have a nodal plane.

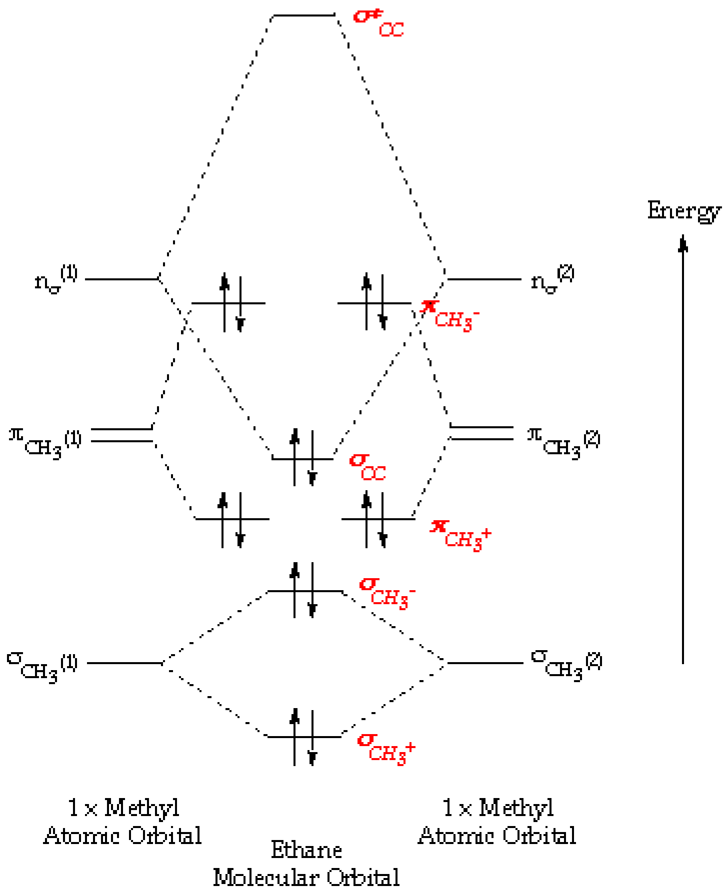
For the energy diagram and pictorial view of the orbitals - please see below:



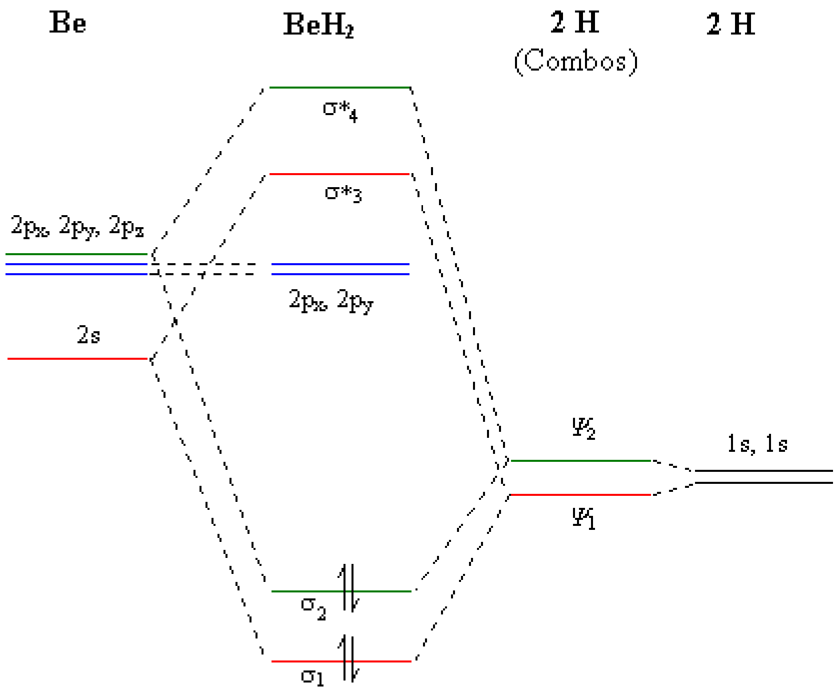
Ethane:

The ethane molecule has fourteen valence electrons occupying seven bonding molecular orbitals. As can be seen from the energy diagram - four of the molecular orbitals occur as degenerate pairs. Like in methane - the molecular orbitals of ethane show increasing nodal structure with increasing orbital energy.

For the energy diagram and pictorial view of the orbitals - please see below:



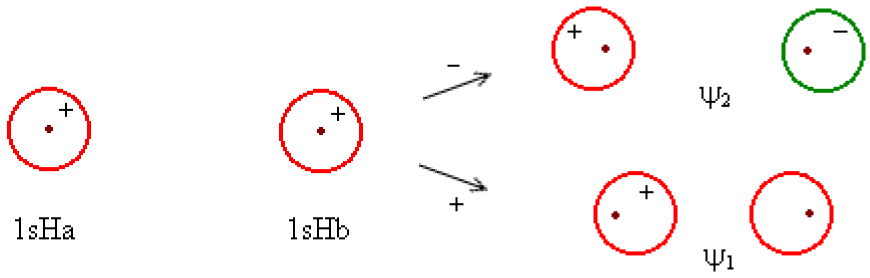
A Linear Triatomic - BeH_2



The central atom is Be and the ligands are the H's.

The atomic energy levels are shown under Be and 2H in the figure above. Note the hydrogen orbitals are shown to have a lower energy than the beryllium orbitals because the non-metal, hydrogen, is more electronegative (harder to ionize than the metal, Be.

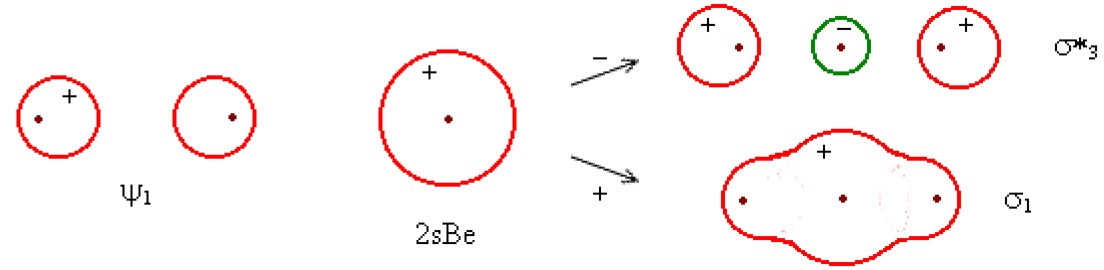
There are two linear combinations of the two hydrogen 1s orbitals:
$\psi_1 = 1/\sqrt{2}(\psi_{1sHa} + \psi_{1sHb})$ and $\psi_2 = 1/\sqrt{2}(\psi_{1sHa} - \psi_{1sHb})$



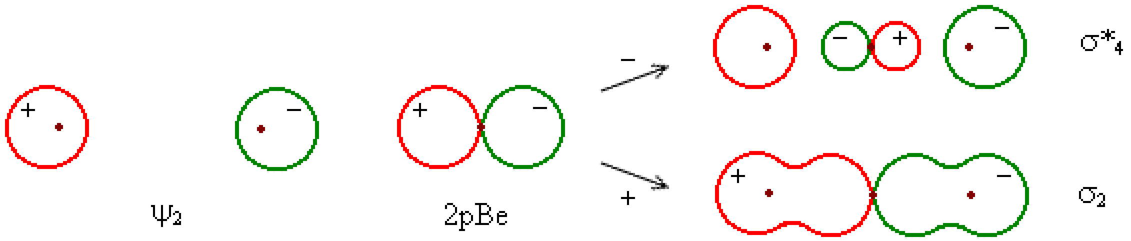
- The energy levels that these combinations might have is shown below 2H(combos).

The beryllium 2s orbital is of the correct symmetry to form combinations with ψ_1 and the Be 2p orbital directed along the internuclear axis (say z) is of the correct symetry to form combinations with ψ_2:

$\sigma_1 = 1/\sqrt{2}(\psi_1 + \psi_{2sBe})$ and $\sigma*_3 = 1/\sqrt{2}(\psi_1 - \psi_{2sBe})$



$\sigma_2 = 1/\sqrt{2}(\psi_2 + \psi_{2pzBe})$ and $\sigma*_4 = 1/\sqrt{2}(\psi_2 - \psi_{2pzBe})$

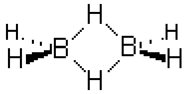


The beryllium $2p_x$ and $2p_y$ orbitals do not have matching symmetry ligand combinations.

- These molecular orbitals, including the localized $2p_x$ and $2p_y$ orbitals, are shown under BeH_2 on the energy level diagram.
- As shown on the energy level diagram, the 4 valence electrons electrons are found in σ_1 and σ_2 molecular orbitals which are both bonding 3-centre orbitals.The bond order for one Be-H connection will be:

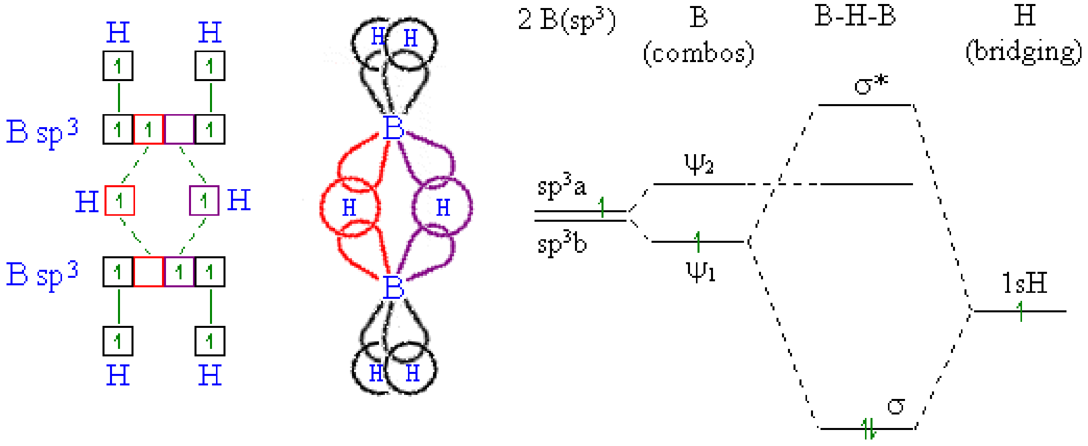
B.O = ((# bonding electrons)/2)/(# of 2-centre bonds) = (4/2)/(2) = 1

An Electron Deficient Molecule witn Bridging Hydrogen - Diborane, B_2H_6



Diborane has the structure shown on the right. At first sight, it seems to have 8 bonds, but between the two boron atoms and the 6 hydrogen atoms, there are only 12 electrons - enough to make only 6 "conventional" 2-centre - 2-electron bonds.

The figure below shows how this situation is handled using molecular orbital theory:

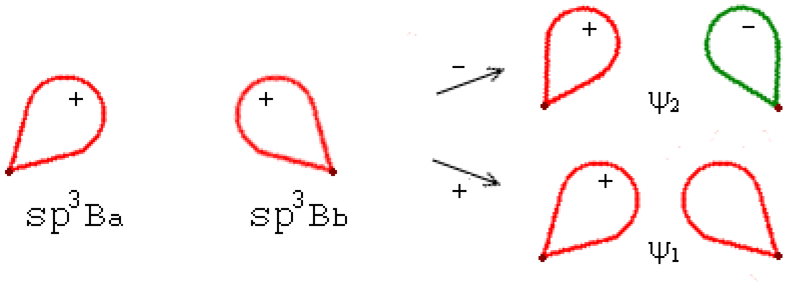


- On the left side of the diagram there is a modified valence bond diagram for the whole molecule. The various orbitals are colour-coded to the structural diagram in the centre of the diagram. Notice that the boron atoms are assigned sp^3 hybridization based on their (predicted) approximately tetrahedral geometry. Although molecular orbital theory could be used to describe the bonding in the whole molecule, and without invoking hybridization in a separate step, here it is only used for the hydrogen bridges.

- The molecular orbital energy level diagram on the right-hand side of the diagram treats only one of the two hydrogen bridges (red or purple). The orbitals used are: one sp^3 hybrid on each boron and the bridging hydrogen's 1s orbital. There are 2 electrons assigned to this system.

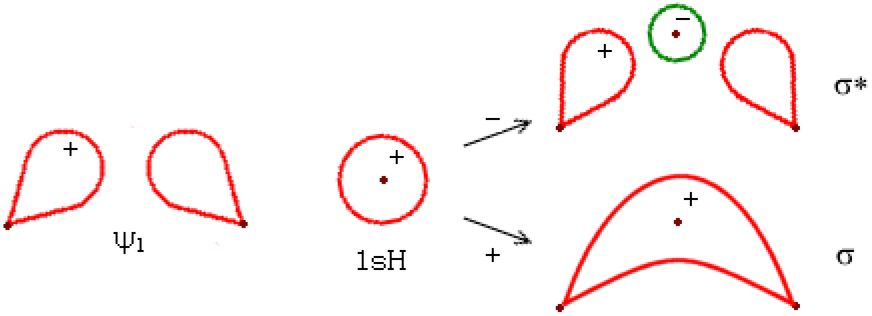
- The boron atoms are considered to be ligating hydrogen, so their orbitals are first combined to give two linear combinations:

$\psi_1 = 1/\sqrt{2}(\psi_{sp^3 Ba} + \psi_{sp^3 Bb})$ and $\psi_2 = 1/\sqrt{2}(\psi_{sp^3 Ba} - \psi_{sp^3 Bb})$



The hydrogen 1s orbital can be combined with ψ_1 yielding a bonding and an antibonding combination. The other ligand combination, ψ_2 is not used.

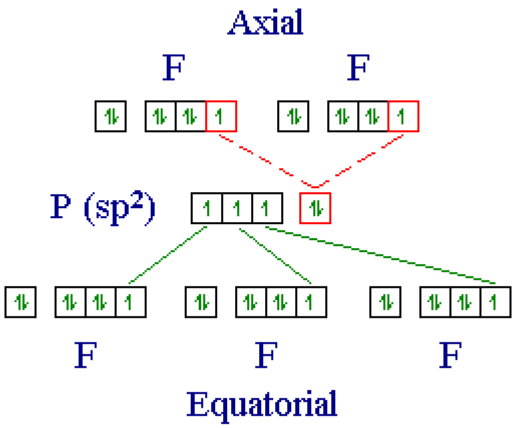
$\sigma = 1/\sqrt{2}(\psi_1 + \psi_{1sH})$ and $\sigma* = 1/\sqrt{2}(\psi_1 - \psi_{1sH})$

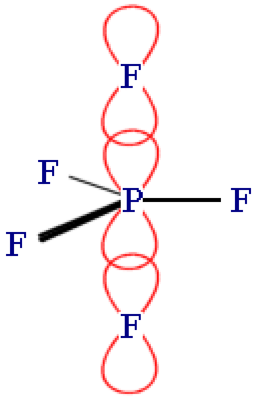


- The two electrons end up in the σ orbital delocalized over the entire bridge, i.e. contributing to 2 connections, so the bond order in any one of the B-H$_{bridging}$ bonds is ½. (The B-H$_{terminal}$ bonds are "normal" 2-electron - 2-centre Lewis bonds.)

Phosphorus Pentachloride - Without Using Those 3d Orbitals!

In pure valence bond theory, the bonding in PF_5 requires the use of the 3d orbitals of phosphorus to allow the creation of 5 normal 2-centre - 2-electron bonds. It is possible to avoid this strategy (which has been challenged as unrealistic) by using three-centre bonding described by molecular orbital theory. Valence bond theory accounts for the bonding of the fluorines in equatorial sites by employing sp^2 hybrids on phosphorus. The axial system only is described by molecular orbital theory. The diagram below sets up the situation:

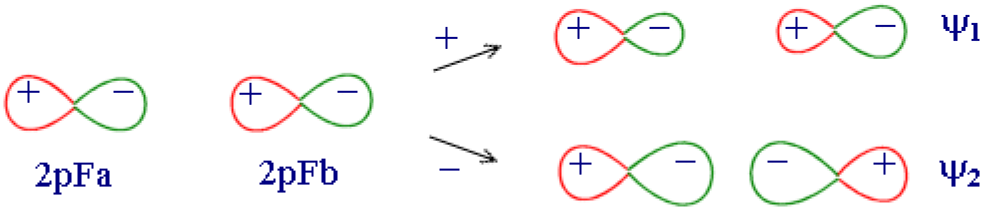




The 2p orbitals oriented along the molecular axis on the two fluorines are first combined:

$\psi_1 = 1/\sqrt{2}(\psi_{2pFa} + \psi_{2pFb})$ and $\psi_2 = 1/\sqrt{2}(\psi_{2pFa} - \psi_{2pFb})$

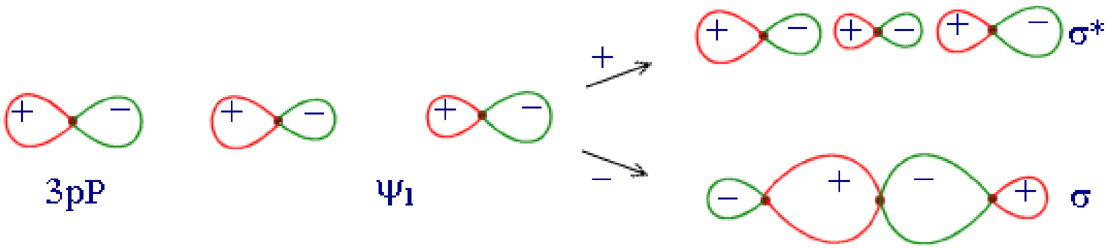
The diagram below shows the combinations graphically.



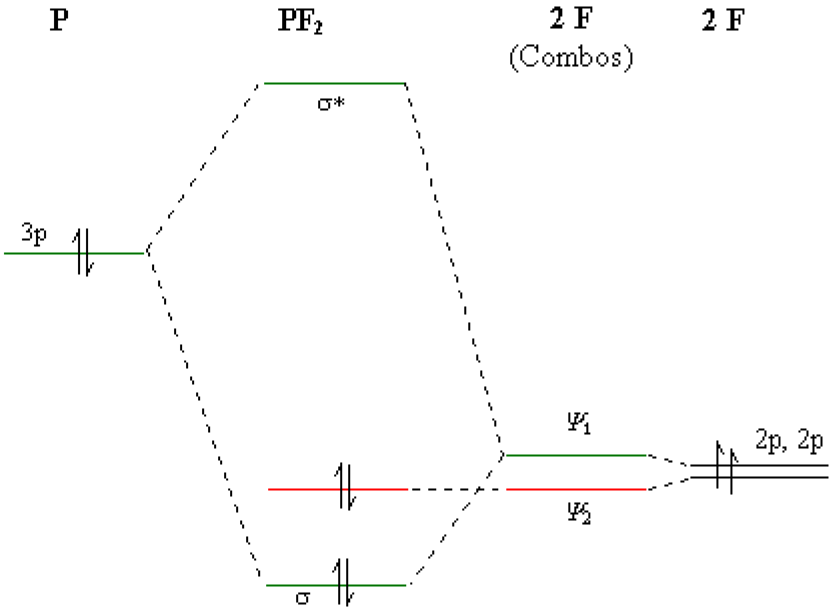
- The 3p orbital of phosphorus (remaining unhybridized) can be combined with the ligand combination ψ_1 to yeld a bonding and and antibonding combination. The ligand combination, ψ_2, remains unused in this simplified treatment.

$\sigma = 1/\sqrt{2}(\psi_1 + \psi_{3pP})$ and $\sigma* = 1/\sqrt{2}(\psi_1 - \psi_{3pP})$

The diagram below show these combinations graphically.



The diagram below shows the energy levels in the axial orbital system only. There are two electrons in the bonding orbital (σ) which leads to a bond order of ½ in each phosphorus - fluorine "connection", since the two non-bonding electrons (in ψ_2) do not contribute. Therefore, the axial bonds are expected to be weaker than the equatorial bonds. This is supported by the experimental evidence.



3.13 Molecular shape in terms of molecular orbitals

The Delocalized Approach to Bonding: Molecular Orbital Theory

In molecular orbital theory, molecular orbital wavefunctions are constructed by taking linear combinations of atomic orbitals. If there are only two atoms involved, this means the sum and the difference of the atomic orbital wavefunctions. If there are more than two atoms involved, the combinations are formed in a more complicated way, and usually the symmetry properties of the molecular or molecular ion are used to simplify the problem. (Of course, this does not simplify much if the mathematical theory which covers symmetry (group theory) has not been covered!) The first part deals with diatomic species. This is followed by several more complicated sample systems.

Molecules and Ions with double bonds

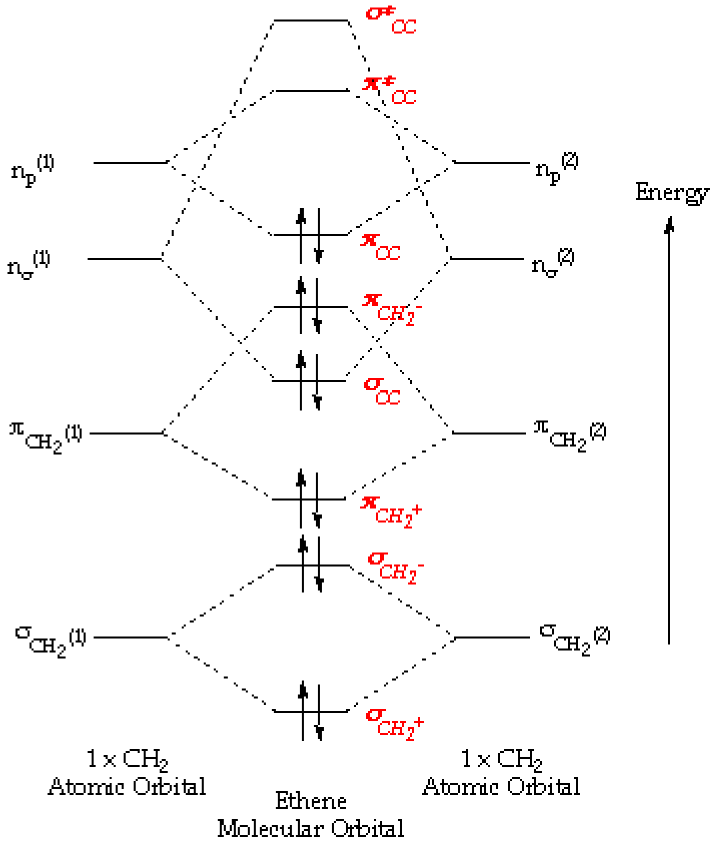
In molecules where the number of bonding electron pairs exceeds the number of unions between atoms, the extra electrons occupy higher energy molecular orbitals than the orbitals found in molecules where the number of bonding electron pairs equals the number of unions between atoms. These are double bonds, and the orbitals have a nodal plane containig the atoms sharing these π-type orbitals.

Ethene:

The simplest alkene is ethene. Its chemistry is dominated by two "*frontier orbitals*", that is the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). For the ethene orbital energy diagram these are shown as π_{CC} for the HOMO, and $\pi^{*}{}_{CC}$ for the LUMO.

An important property of the ethene molecule, and alkenes in general is the existence of a high barrier to rotation about the C=C which tends to hold the molecule flat.

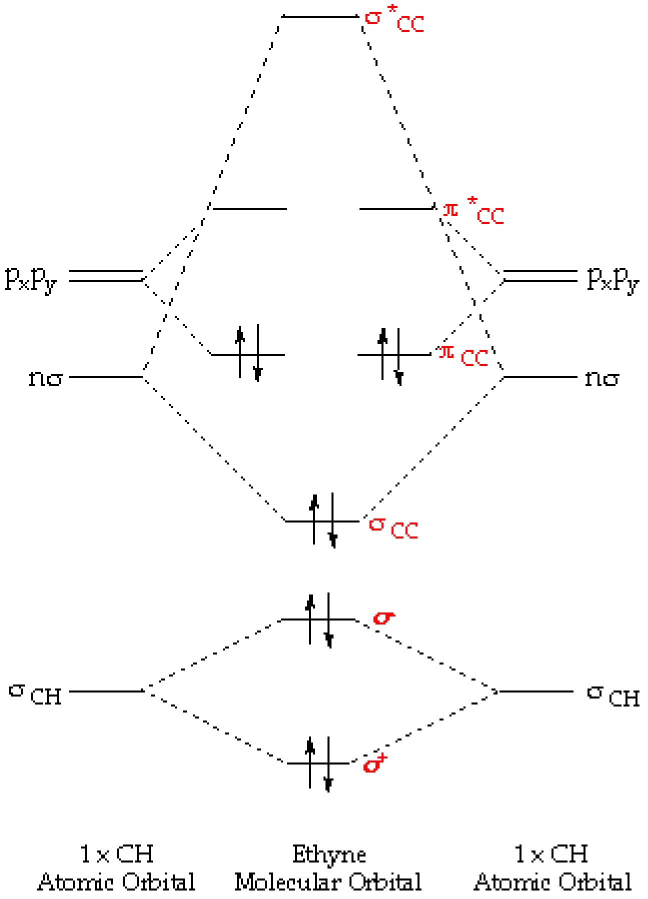
For the energy diagram and pictorial view of the orbitals - please see below:



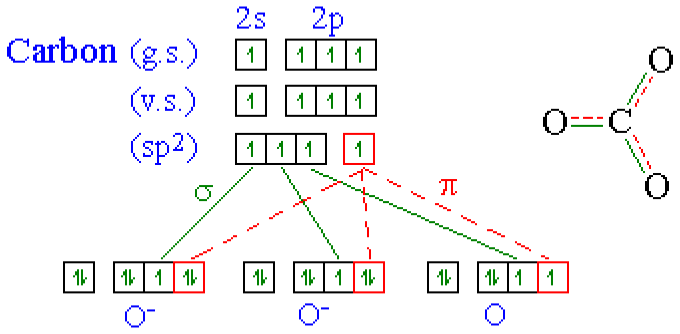
Molecules with triple bonds

Ethyne:

For the energy diagram and pictorial view of the orbitals - please see below:



A Trigonal-planar molecule/ion - CO_3^{2-} (or NO_3^- or BF_3 which are isoelectronic)



This is a case where the σ-bonding is usually handled with valence bond theory. If the three-fold axis of the molecule/ion is considered the z axis, the σ-bond framework involves hybridizing the carbon 2s $2p_x$ and $2p_y$ orbitals (sp^2) and using them to attach the oxygens by a 2p orbital lying in the molcular plane. This accounts for 6 of the valence electrons.

The π-bonding molecular orbitals are formed from the carbon and three oxygen $2p_z$ orbitals and there will be six more electrons to accomodate.

Therefore:

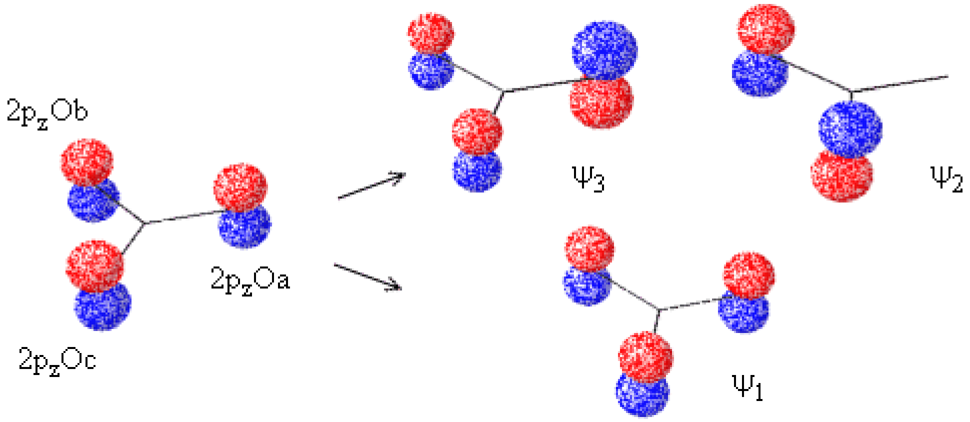
- The central atom is carbon and the ligands are oxygen.

- The atomic orbitals used for the π-bonding system *only* are shown under C and 2O¯, O in the energy level diagram below (f). The oxygen p-orbitals lie at a lower energy than those of carbon because oxygen is more electronegative.The three oxygen $2p_z$ orbitals *must* form three linear combinations:

$\psi_1 = 1/\sqrt{3}\psi_{2pzOa} + 1/\sqrt{3}\psi_{2pzOb} + 1/\sqrt{3}\psi_{2pzOc}$

$\psi_2 = 1/\sqrt{2}\psi_{2pzOb} - 1/\sqrt{2}\psi_{2pzOc}$ (no contribution from O_A)

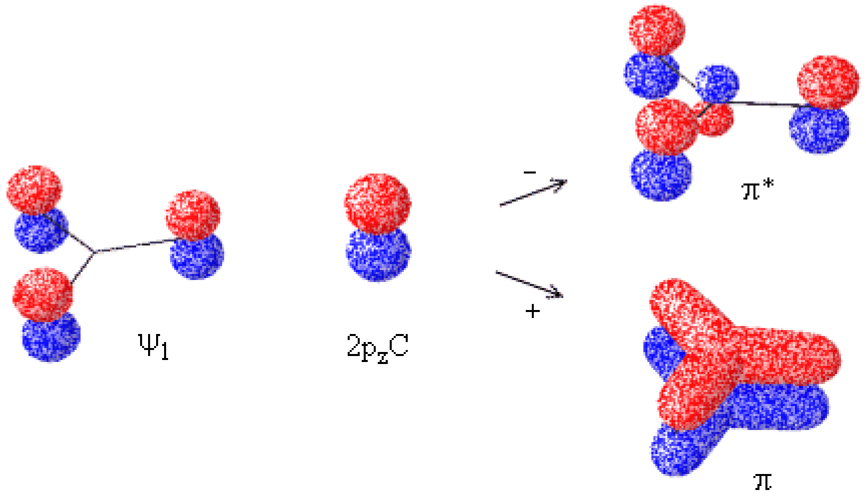
$\psi_3 = \sqrt{(2/3)}\psi_{2pzOa} - 1/\sqrt{6}\psi_{2pzOb} - 1/\sqrt{6}\psi_{2pzOc}$



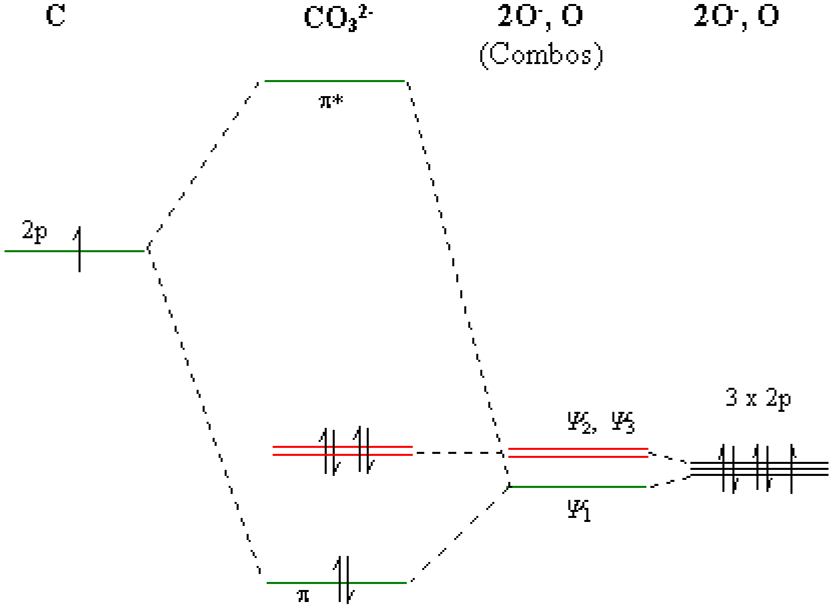
- The energy level that these combinations would have is shown below 2O¯, O (combos) in the figure below.
- The carbon $2p_z$ orbital is of the correct symmetry to combine with ψ_1.

$\pi_1 = 1/\sqrt{2}(\psi_1 + \psi_{2pzC})$ and $\pi^*_4 = 1/\sqrt{2}(\psi_1 - \psi_{2pzC})$

This is the only combination involving the carbon so ψ_2 and ψ_3 remain *non-bonding* relabelled as π_2 and π_3.



The resulting molecular orbitals are shown under CO_3^{2-} on the energy level diagram below.



The 6 electrons occupy π_1, ψ_2 and ψ_3 as shown in the energy level diagram. The only bonding π-orbital, π_1 contains 2 electrons spread over 4 centres involved in 3 C-O connections. The non-bonding ψ_2 and ψ_3 orbitals have no contribution. Therefore, the bond order for each carbon - oxygen connection is 1/3. Do not forget the σ-bonds which were not included in this scheme.

Conjugated and aromatic molecules

π bonds in close proximity will often interact. Some of the delocalized molecular orbitals that result will be stabilized, while others will be destabilized. The individual combinations may be polarized, providing an increase in wave function amplitude on some centers at the expense of a decrease in amplitude on others. This gives rise to the possibility of more varied reactivity patterns than are observed for simple alkenes.

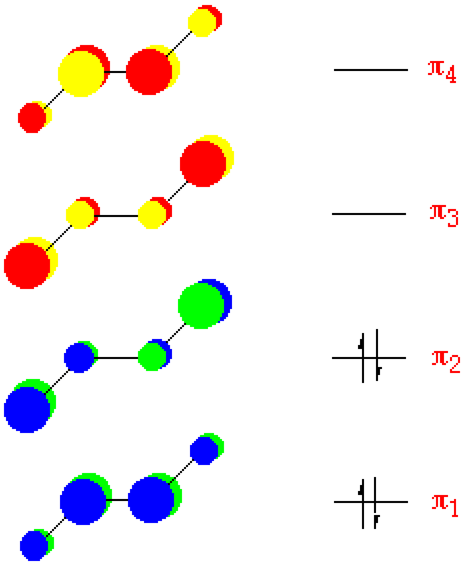
Aromatic molecules exhibit a wide range of reactivity patterns toward both electron rich and electron deficient species. These mainly depend on the structures and energies of the frontier π-type molecular orbitals, the HOMO and LUMO. Except for non-bonded lone pairs, the σ framework plays little role in the overall reactivity.

***trans*-1,3-Butadiene**:

The energies of the π-molecular orbitals of conjugated molecules like butadiene, (see below) - occur in pairs, with their energies equal to $(\alpha \pm x\beta)$, where α and β are constants. For each bonding orbital of and energy $\alpha - x\beta$ there is a corresponding antibonding orbital of energy $\alpha + x\beta$. The π-molecular orbitals are extended over the whole molecule.

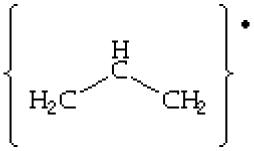
For butadiene, the π manifold contains four electrons, leading to an electronic configuration of $\pi_1^2\pi_2^2$.

For the energy diagram and pictorial view of the π-molecular orbitals - please see below:

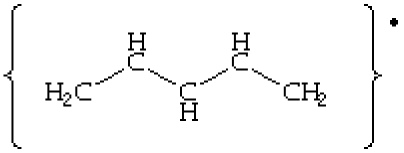


Allyl radical

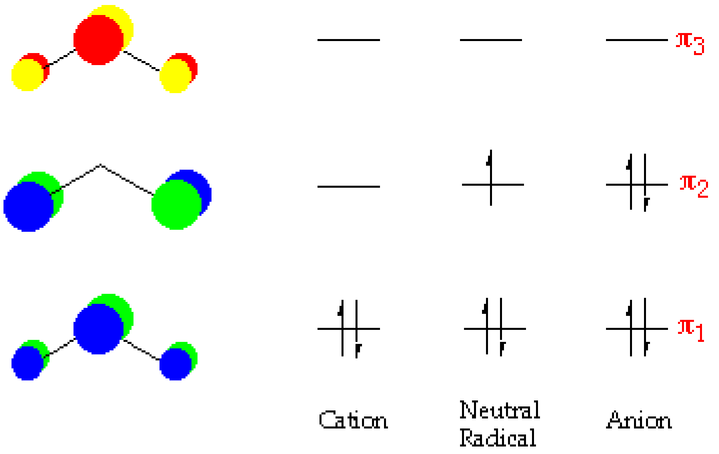
The radicals allyl:



and pentadienyl:

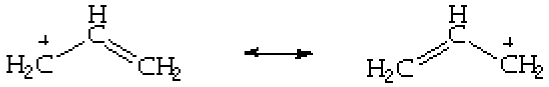


have the same arrangement of π-orbitals, (ie. the occur in pairs of energy $\alpha \pm x\beta$), but because there is an odd number of carbon atoms in the conjugate chain, there must be a non-bonding orbital with energy $x=0$. Also, because of the pairing properties of the π-molecular orbitals of conjugated chains, there will be a node at every alternate carbon atom in the non-bonding orbital. This is important for the unpaired electron of allyl, which will occupy this non-bonding orbital. If an electron is added to the allyl radical to form the anion, the negative charge will appear at the terminal carbon atoms. If the unpaired electron is removed forming the cation, the resulting positive charge is also spread over the termial carbon atoms.
There are three π-molecular orbitals for allyl, the π_1 is bonding, the π_2 orbital is non-bonding and the π_3 is anti-bonding. In the neutral allyl species - there are a total of seventeen valence electrons - of which three fill the π-orbital manifold. A pictorial representation of the energy diagram for the neutral, cationic and anionic allyl species are shown below - (*orbitals are shown only for the cationic species*):

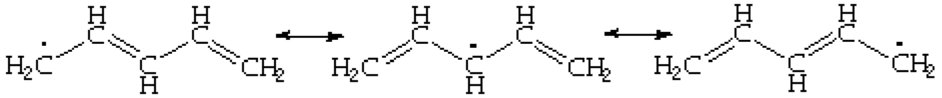


In the pentadienyl anion, the negative charge is centred on the carbon atoms in the 1,3 and 5 position - similarly with the positive charge for the cation.

These ions are represented in resonance theory as two or three canonical forms:



Resonance structures for the allyl cation



Resonance structures for the pentadienyl radical

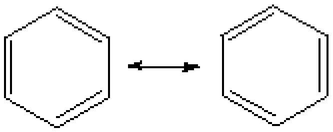
The delocalisation of π-electrons is associated with a lowering of the orbital energy. Therefore the total energy of the occupied π-orbitals of butadiene is lower in energy then two isolated ethene-type double bonds.

Bonding in benzene

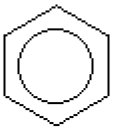
From the above diagram it can be seen that the lowest lying orbital, π_1, the orbital coefficients are such that the bonding charachter between each pair of adjacent carbon atoms is equal. In π_2 bonding only occurs between atoms C_2 and C_3 and between C_5 and C_6 since the coefficients on C_1 and C_4 are zero. In π_3, C_1, which is bonded to C_2 and C_6 and C_4 is bonded to C_3 and C_5, there are anti-bonding interactions between C_2 and C_3 and between C_5 and C_6. Therefore if we consider the pair of orbitals π_2 and π_3 the contribution to the C-C π bonding is equal for each bond. Since there are three occupied bonding orbitals and six CC linkages - the π bond order is

$^1/_2$. This description is in accord with the two resonating mesomeric forms (or Kekulé structures in a) below in which single and double bond characters alternate around the ring. Conventionally, the diagram in b) is used to show that the six electrons are delocalized around the ring:

a)



b)



$C_7H_7^+$ (tropyllium) and $C_8H_8^{2+}$

Do them yourself!

The molecular orbital theory of solids

Metallic Bonding

The third major type of chemical bond is the bond between two metal atoms. Metals lose electrons and cannot normally accept them. This means that, in a metallic bond, there are no atoms to accept the electrons. Instead, the electrons are given up to a "sea" of electrons that surrounds the metal atoms. In a way, this is similar to ionic bonding, except that the "ions" are electrons. The attraction between the electrons and the metal ions keeps the metal together.

The metals are the most numerous of the elements. About 80 of the 100 or so elements are metals. You know from your own experience something about how metallic atoms bond together. You know that metals have substance and are not easily torn apart. They are ductile and malleable. That means they can be drawn into shapes, like the wire for this paper clip, and their shape can be changed. They conduct heat and electricity. They can be mixed to form alloys.How is it that metallic bonding allows metals to do all these things?

The nature of metals and metallic atoms is that they have loosely held electrons that can be taken away fairly easily. Let's use this idea to create a model of metallic bonding to help us explain these properties. I will use potassium as an example. Its valence electron can be represented by a dot. When packed in a cluster it would look like this (also in example 31 in your workbook). The valence electron is only loosely held and can move to the next atom fairly easily. Each atom has a valence electron nearby but who knows which one belongs to which atom. It doesn't matter as long as there is one nearby.

Metals are held together by delocalized bonds formed from the atomic orbitals of all the atoms in the lattice. The orbitals spread over many atoms and blend into a band of molecular orbitals. The range of energies of these orbitals are closely spaced. The band is composed of as many levels as there are contributing atomic orbitals and each level can hold electrons of opposite spin. The idea that the molecular orbitals of the band of energy levels are spread or delocalized over the atoms of the piece of metal accounts for bonding in metallic solids. This theory of metallic bonding is called the band theory. The band is split into two regions, the upper portion being the empty levels or the antibonding and the lower portion is the filled levels or the bonding orbitals. In a metal the band of energy levels is only partly filled. The highest filled level right before going to the empty level is called the Fermi level. The trend of melting points of the transition metals is based on the electrons in the metal.

Bonding Models for Metals

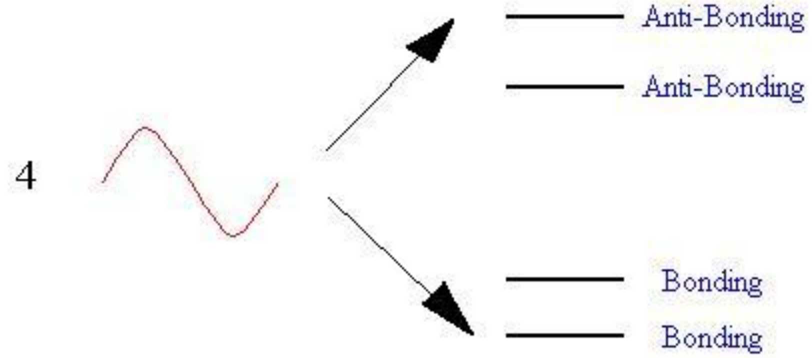
Molecular orbital bands

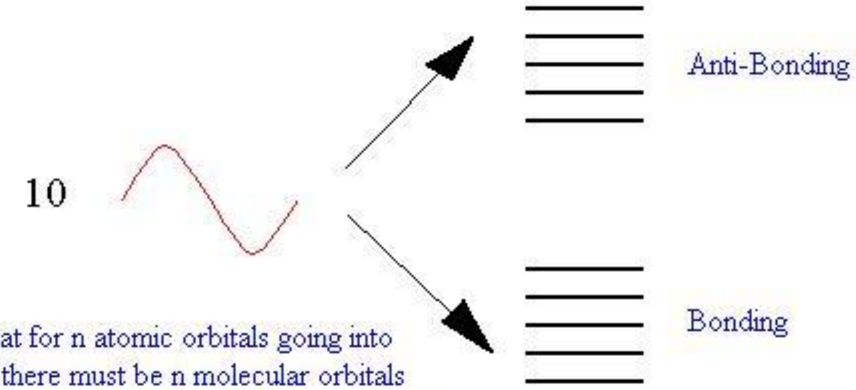
Band Theory of Bonding in Solids

Bonding in solids such as metals, insulators and semiconductors may be understood most effectively by an expansion of simple MO theory to assemblidges of scores of atoms. If we recall, in simple MO theory we assumed that atomic orbitals on two atoms could come together to form bonding and antibonding orbitals.

If we bring three atoms together we can create a string of atoms with bonding that connects all three. Here we have a bonding orbital, an antibonding orbital, and a curious critter called a nonbonding orbital. Essentially a nonbonding orbital is an orbital that neither increases nor decreases the net bonding in the molecule. The important feature here is that three atomic orbitals in must give three molecular orbitals out. The total number of orbitals must remain constant.

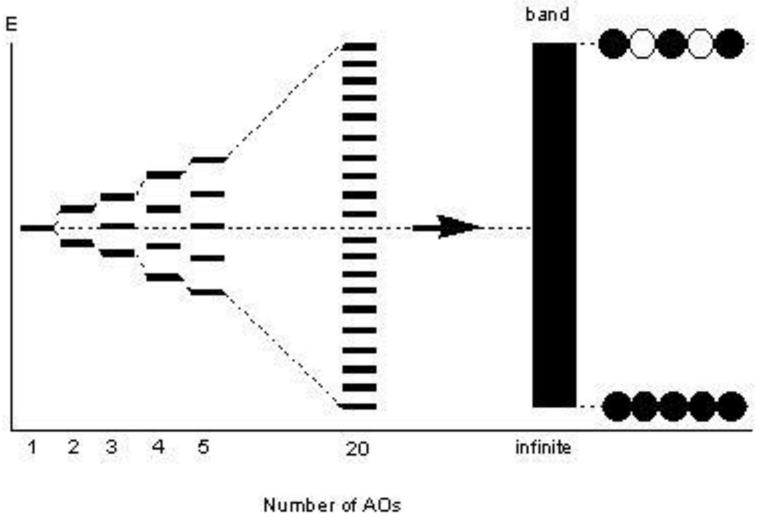
Now let's expand these idea by considering combinations of four and ten atoms. As shown below, four atoms (four atomic orbitals) will give four molecular orbitals, two bonding and two antibonding. Notice that the two bonding (and two antibonding) orbitals are not exactly the same energy. The lower bonding orbital is slightly more bonding than the other (and one antibonding orbital is slightly more antibinding than the other). For the ten atoms we'd get a set of five bonding and five antibonding orbitals, each slightly different in energy.



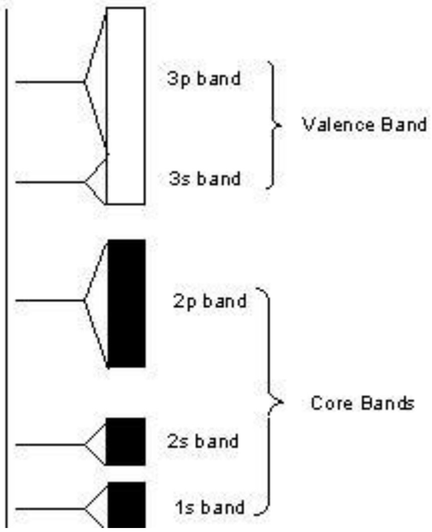


Notice that for n atomic orbitals going into the bond there must be n molecular orbitals produced. If n is even, then there will be n/2 bonding and n/2 antibonding orbitals. If n is uneven there will be a nonbonding orbital.

Band Formation in A Linear Chain
Core and Valence Bands for a Period 3 Metal



Core and Valence Bands for a Period 3 Metal



If we now jump to a huge number of atoms, n, where n is perhaps as big as Avogadro's number, we can see that we're going to have a nhge number of bonding and antibonding orbitals. These orbitals will be so close together in energy that they begin to blur creating bands of bonding and bands of antibonding orbitals. It is the existance of these bands of orbitals that underlie our understanding of the properties of solids.

Notice, by the way, that there is some point at which the properties of an assemblidge of atoms makes a transition from separate discrete orbitals (and hence quantum properties like atoms), to bands of orbitals. The technology built upon tiny clusters called nanodots in which groups of atoms with perhaps twenty atoms acts like a quantum object is built upon this concept. By the time one has even a tiny cluster of atoms such as the submicron objects in a computer chip, the properties are best described by band theory.

MO Theory of Solids. Consider a linear chain of n identical atoms, each bringing in a valence s orbital for MO formation. If n = 2, 2 MOs are formed, one bonding and one antibonding. If n = 3, we obtain 3 MOs, bonding, nonbonding, and antibonding. If we run n right up to Avogadro's number, we expect to obtain No MOs, ranging from fully bonding (+++++...) to fully antibonding (+-+-+-...), with a whole bunch of other MOs between these extremes. This is shown in Figure MO-20. The energy spacing between lowest and highest MOs is determined primarily by the overlap between neighboring atoms, so will stay finite even though the number of atoms in the
chain reaches toward the infinite! We thus have a huge number of MOs crammed into a finite energy interval. They will be so close together in energy that they will form, for all practical purposes, a continuous band of energy levels. For this reason the MO theory of solids is often called Band Theory. A very important result of this treatment is that each of the MOs in the band is delocalized over all of the atoms in the chain.

The same ideas apply to a 3-dimensional, close-packed aggregate of atoms. A band of MOs will be formed from each type of valence AO on the atoms. Thus we obtain an s band, a p band, a d band, and so on, as shown in Figure MO-20. All of the MOs are delocalized over all of the atoms in the aggregate, so electrons in them can be considered to be everywhere at once! The highest filled band of MOs is called the valence band; the lowest unfilled band is called the conduction band; and the energy separation between the top of the valence band and the bottom of the conduction band is called the band gap. A partially filled band is simultaneously the valence band and the conduction band, so in this case the band gap is essentially zero.

Now let's apply this picture to understand the electronic nature of the various classes of materials given above.

A conductor (which is usually a metal) is a solid with a partially full band, as shown in the Figure. An electron in the highest occupied MO is easily promoted to the next higher empty delocalized MO, where it is then free to roam over the whole solid lattice under the influence of an applied electric field; i.e., the solid conducts electricity due to this facile electron movement. The high reflectivity of metals is also due to the availability of a proliferation of empty MOs above the HOMO. Electrons in the filled MOs of the partially-filled band can absorb and then re-emit light of many wavelenths in making transitions to empty MOs in the band. This gives the metal surface a shiny reflective appearance. An example of a conductor is Na metal. It has an s band consisting of N MOs, where N is the number of Na atoms in the crystal. The band contains N electrons
(one from each Na atom) arrayed in N/2 pairs. These N/2 pairs go in the N/2 bonding MOs, which leaves N/2 antibonding MOs empty but readily accessible. Thus Na exhibits the characteristic properties of a metal, and is a conductor.

An insulator is a solid with a full band and a large band gap, as shown in Figure MO-21. The MOs in the conduction band are so high in energy that they are not thermally populated by the Boltzmann distribution, and there is no conductivity at ordinary temperatures. An example of an insulator is solid carbon in the diamond modification. Diamond consists of a covalently bonded network of carbon atoms (a fcc array of C atoms with more C atoms in half the tetrahedral holes), constructed from sp3 hybrid orbitals. N carbon atoms contribute 4N sp3 hybrids, which overlap strongly to give 2N bonding MOs and 2N antibonding MOs which are separated in energy by 5.47 eV from the bonding MOs. The 4N electrons exactly fill the band of bonding MOs. The antibonding band is not thermally accessible, so diamond does not conduct.

3.15 Semiconduction

A semiconductor is a solid with a full band and a small band gap, as shown in the Figure. There is a small thermal population of the conduction band at normal temperature, hence a small conductivity. For example, silicon has a diamond modification similar to that of carbon, but a band gap of only 1.12 eV, due to poorer overlap of the sp^3 hybrids of the larger Si atoms. Since the antibonding band will be occupied to a small extent via the Boltzmann distribution, Si exhibits a small conductivity at room T.

The group 4A elements, which have a number of valence electrons equal to twice the number of MOs in the bonding band, are uniquely structured to show semiconductivity. The elements C through Sn all exhibit a diamondlike crystal form, but with a band gap which decreases in magnitude for the larger atoms as orbital overlap becomes weaker. The trend in band gap down family 14 is shown below:

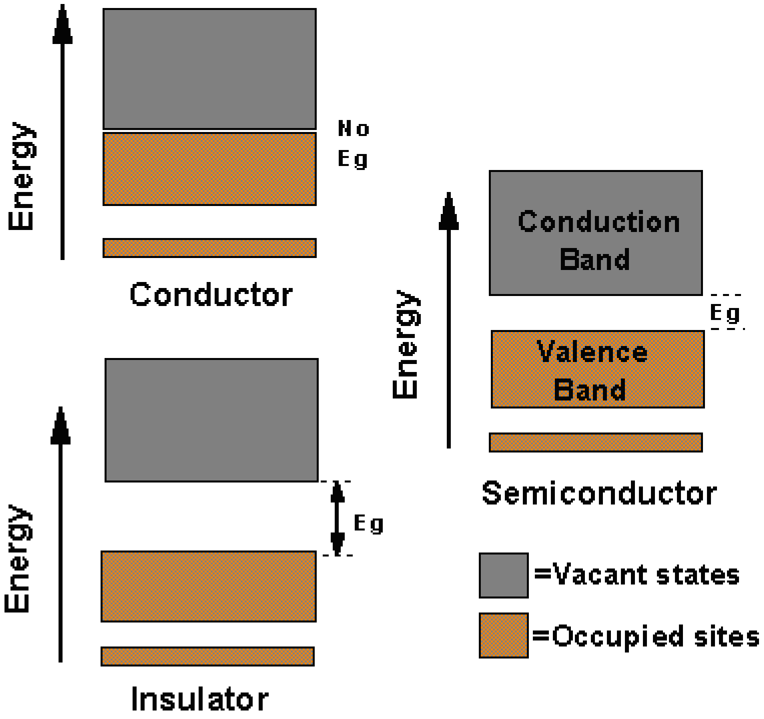
Element	**Band Gap**
C	5.47
Si	1.12
Ge	0.66
Sn	0

Thus Si and Ge are semiconductors at room T, and Sn is a conductor. Pure compounds which are electronically analogous to the group 14 elements are also semiconductors. These include the compounds boron nitride, BN, and gallium arsenide, GaAs. Note that these compounds contain one element from group 13 and one element from group 15, in a 1:1 stoichiometric ratio. They thus have exactly the same number of valence electrons as a group 14 element, and will arrange these electrons in a group-14 type band structure. They are often called 3-5 compounds, to indicate that they consist of elements taken from groups 13 and 15. Similarly, 2-6 compounds such as ZnS and CdS (both of which have the zincblende structure, which is analogous to the diamond structure) function as semiconductors. Generally, band gaps vary with position in the periodic table, but tend to decrease with increasing MW of the semiconductor.

The temperature dependence of conductivity is readily understood within the framework of band theory. For a conductor, promotion of electrons is facile within a band at any T. However, As T increases, vibrational motions of the metal atoms in the lattice increases and interferes with the motion of the conducting electrons. The result is a decrease in conductivity as T increases. For a semiconductor, an increase in T causes an exponential increase in the population of the conduction band, because of the Boltzmann distribution. Therefore the conductivity of semiconductors increases dramatically with T. Because an insulator is actually a semiconductor with a large band gap, the conductivity of an insulator should also increase markedly if the temperature is made high enough.

Because of the very large number of atoms that interact in a solid material, the energy levels are so closely spaced that they form bands. The highest energy filled band, which is analogous to the highest occupied molecular orbital in a molecule (HOMO), is called the valence band. The next higher band, which is analogous to the lowest unoccupied molecular orbital (LUMO) in a molecule, is called the conduction band. The energy separation between these bands is called the energy gap, E_g.

Idealized representation of energy bands and gaps



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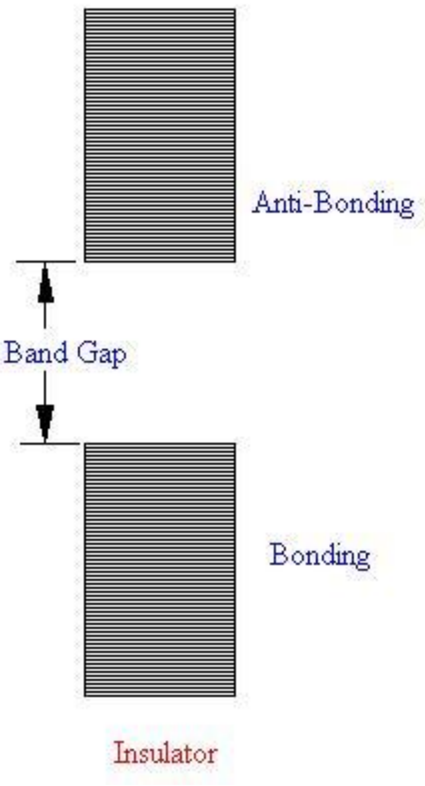
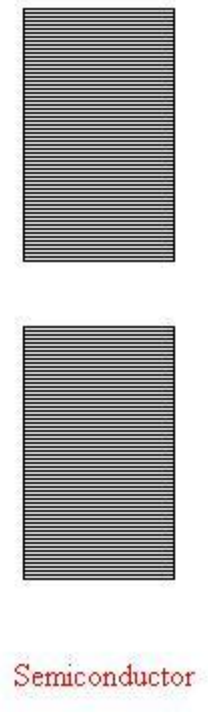
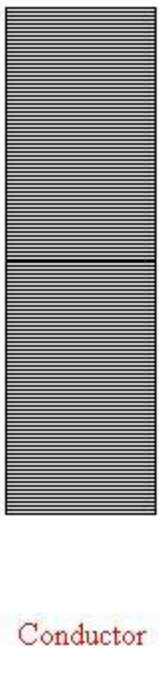
The filling of these bands and the size of the energy gap determine if a material is a conductor (a metal), a semiconductor, or an insulator. In metals there is no energy gap between filled and unfilled energy levels. A significant number of electrons are thermally excited into empty levels, creating holes in the filled band. The electrons in a conduction band and the holes in a valence band can move throughout the material, allowing it to easily conduct electricity. In semiconductors E_g is small, but large enough so that a fairly small number of electrons are in the conduction band due to thermal energy, and these materials conduct poorly. In insulators E_g is large so that electrons are not promoted to the conduction band due to thermal energy, and these materials do not conduct electricity.

Three categories of materials may be easily understood by the energy gap between the bonding bands and the antibonding bands. If there is a large gap in energy, the material is called an insulator. If the gap is finite, but small, then the material is a semiconductor, and if there is effectively no gap between the bands, the materials are called conductors. These properties arise because electrons that enter the antibonding band are free to move about the crystal. Such behavior is associated with electrical conduction. To give you an idea of the energies involved, the band gap in diamond is 502 kJ/mol, while that in Si is 100 kJ/mol and that in Ge is 67 kJ/mol. Diamond is an insulator while the other two materials are semiconductors.



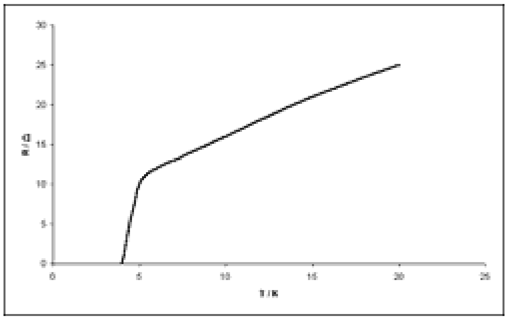




3.16 Superconduction

The Discovery of Superconduction

Before the discovery of superconduction, it was already known that cooling a metal increased its conductivity - due to decreased electron-phonon interactions (detailed in the Theory section). After the 'discovery' of liquified helium, allowing objects to be cooled to within 4K of absolute zero, it was discovered (by Onnes, 1911) that when mercury was cooled to 4.15K, its resistance suddenly (and unexpectedly) dropped to zero (i.e. it went superconducting).

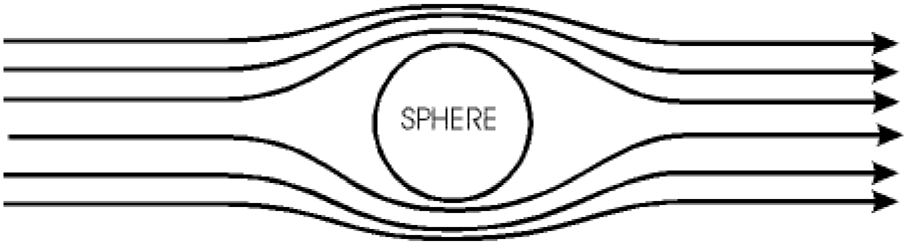


Left: When Onnes cooled mercury to 4.15K, the resistivity suddenly dropped to zero

In 1913, it was discovered that lead went superconducting at 7.2K. It was then 17 years until niobium was found to superconduct at a higher temperature of 9.2K.
Onnes also observed that normal conduction characteristics could be restored in the presence of a strong magnetic field.

The Meissner Effect

It was not until 1933 that physicists became aware of the other property of superconductors - perfect diamagnetism. This was when Meissner and Oschenfeld discovered that a superconducting material cooled below its critical temperature in a magnetic field excluded the magnetic flux. This effect has now become known as the Meissner effect (- you can see a QuickTime video of this in action from this link).



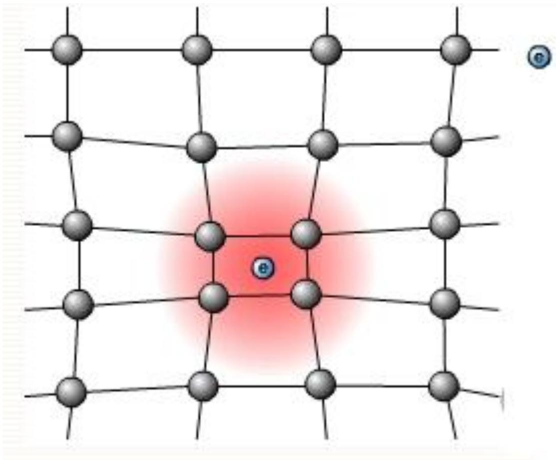
Above: The Meissner effect - a superconducting sphere in a constant applied magnetic field excludes the magnetic flux

The limit of external magnetic field strength at which a superconductor can exclude the field is known as the ***critical field strength,*** $\boldsymbol{B_c}$.
Type II superconductors have two critical field strengths; $\boldsymbol{B_{c1}}$, above which the field penetrates into the superconductor, and $\boldsymbol{B_{c2}}$, above which superconductivity is destroyed, as per B_c for Type I superconductors.

Theory of Superconduction

Fritz and Heinz London proposed equations to explain the Meissner effect and predict how far a magnetic field could penetrate into a superconductor, but it was not until 1950 that any great theoretical progression was made, with Ginzburg-Landau theory, which explained superconductivity and provided derivation for the London equations.

Ginzburg-Landau theory has been largely superseded by BCS theory, which deals with superconduction in a more microscopic manner.
BCS theory was proposed by J. **B**ardeen, L. **C**ooper and J. R. **S**chrieffer in 1957 - it is dealt with in the Theory section. BCS suggests the formation of so-called 'Cooper pairs', and correlates Ginzburg-Landau and London predictions well.



Cooper pair formation - electron-phonon interaction: the electron is attracted to the positive charge density (red glow) created by the first electron distorting the lattice around itself. However, BCS theory does not account well for high temperature superconduction, which is still not fully understood.

High Temperature Superconduction

The highest known temperature at which a material went superconducting increased slowly as scientists found new materials with higher values of T_c, but it was in 1986 that a Ba-La-Cu-O system was found to superconduct at 35K - by far the highest then found. This was interesting as BCS theory had predicted a theoretical limit of about 30-40K to T_c (due to thermal vibrations). Soon, materials were found that would superconduct above 77K - the melting point of liquid nitrogen, which is far safer and much less expensive than liquid helium as a refrigerant. Although high temperature superconductors are more useful above 77K, the term technically refers to those materials that superconduct above 30-40K.
In 1994, the record for T_c was 164K, under 30GPa of pressure, for $HgBa_2Ca_2Cu_3O_{8+x}$.
Recommended Questions from Shriver and Atkins:

	"Exercises"
3.1 - 3.5	These are important.
3.6	Important. Ignore the bit about the vapour phase.
3.7 - 3.11	Aklthough not explicitly covered in the course, you should be able to tackle these.
3.12, 3.13	These are important.
3.14	Important. Assume S_2 and Cl_2 are like their equivalents in the first row.
3.15	Important.
3.16 - 3.28	These are beyond the scope of this course.
	"Problems"
3.1	You should be able to answer this.
3.2	You would be able to do this, but in is not explicitly covered in the course.
3.3	You should be able to do this by adding on top of to the 1s - 1s

interaction, the diagram for the homonuclear diatomic molecules of the first row (which use 2s and 2p interactions).

3.4 - 3.15 These are beyond the scope of this course.

Some Answers and Questions

1. What holds molecules together?
2. What are the electrons doing in the molecule?
3. What insight do these considerations give concerning the chemical and physical properties of the molecule?
4. Can we predict existence and structures of molecules?

The first objective is to derive *molecular* orbitals into which we can place all the electrons in the molecule in much the same way as we do for atoms. (Using the Aufbau Principle.) To obtain these molecular orbitals, we use a method called the linear combination of atomic orbitals (LCAO). As the name implies, the molecular orbitals are made by adding or subtracting the atomic orbitals. The simplest example is obtained by considering the hydrogen molecule, H_2, which we write as H_A-H_B, using the subscripts A and B to label the two atoms. LCAO theory states that one of the molecular orbitals can be written as:

$$\Psi_1 = c.\psi_{1sA} + d.\psi_{1sB}$$

The constants c and d are weighting constants indicating the relative amounts of each atomic orbital that will be used. For H_2, where the two hydrogen atoms are equivalent, c = d, and we can replace them by a single "normalizing" constant N:

$$\Psi_1 = N.(\psi_{1sA} + \psi_{1sB}) = (1/\sqrt{2}).(\psi_{1sA} + \psi_{1sB})...(1)$$

(If the probability of finding the electron in such an orbital somewhere in all space is to be equal to 1, N = $1/\sqrt{2}$.)

So far we have done nothing difficult, but simply assumed that equation 1 represents our MO. Use the applet to have a look at what this orbital looks like. You can adjust the distance between the nuclei to see what happens as the atomic orbital ovelap more and more. Figure 2 gives a rather crude picture of what you should see.

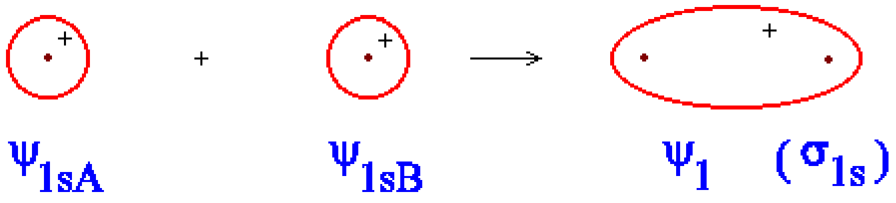


Figure 2

Since ψ_{1sA} and ψ_{1sB} are positive everywhere, their sum must be too. Just as for the atomic orbitals, the value of Ψ^2 gives the probability of finding the electron in a small region, or the electron density at a point. This particular orbital is referred to as a bonding molecular orbital for reasons that will shortly be explained.

There is another linear combination that we should have considered according to LCAO theory:

$$\Psi_2 = (1/\sqrt{2}).(\psi_{1sA} - \psi_{1sB}) \text{ ....}(2)$$

Use the applet to have a look at what this combination looks like. Figure 3 shows a crude representation of what you should see. This combination is referred to as antibonding. Whenever we combine two atomic orbitals in a way which produces a change in the sign of Ψ between the two component atomic orbitals, anti-bonding results.

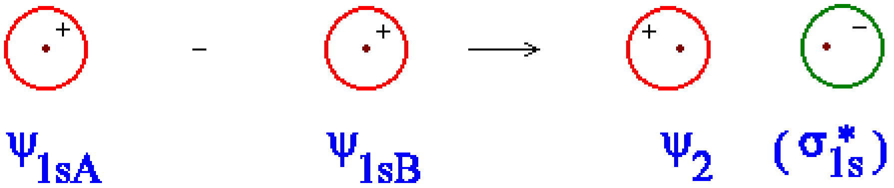


Figure 3

We can better understand the difference between Ψ_1 and Ψ_2 by examining the electron density or probability. For the bonding combination this is given by:

$$\Psi_1^2 = \&\text{frac12;}(\psi_{1sA} + \psi_{1sB})^2 = \&\text{frac12;}(\psi_{1sA}^2 + \psi_{1sB}^2 + 2.\psi_{1sA}\psi_{1sB}) \text{ ..}(3)$$

If we compare this to the electron density contribution from two individual hydrogen atoms, ½($\psi_{1sA}^2 + \psi_{1sB}^2$), it is obvious that the electron density has been increased by a amount $\psi_{1sA}\psi_{1sB}$. This effect, which accounts for the bonding because the negatively charged electrons hold the positively charged nuclei together, is illustrated in Figure 4.

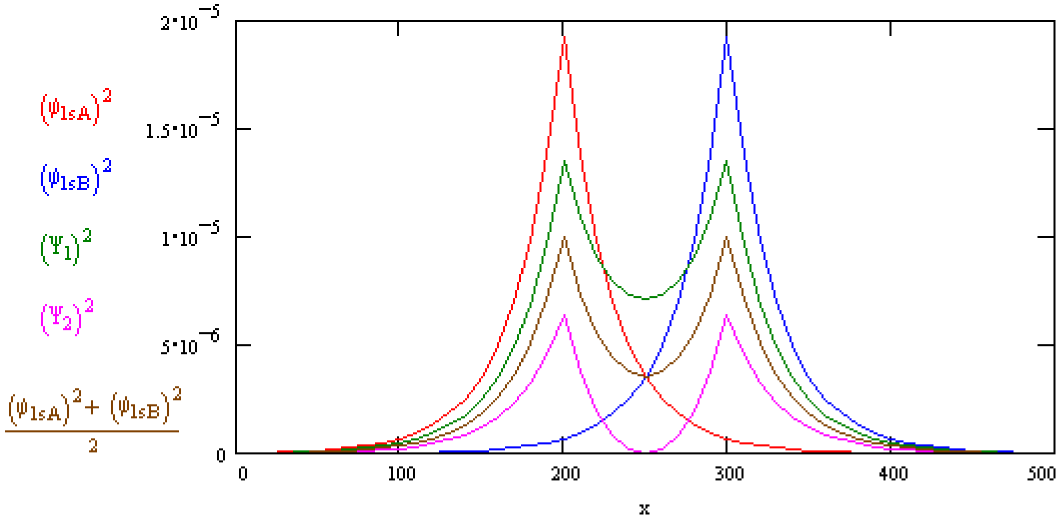


Figure 4

Question 1. The probability plot for Ψ_2^2 is also shown in Figure 4. What would be its equation? (The equivalent of equation 3) What do you notice about the electron density between the nuclei as compared to two individual hydrogen atoms simply placed side by side?

Further insight into the bonding of H_A and H_B can be obtained by considering the energies of the electrons in Ψ_1 and Ψ_2 compared to their energies in the non-interacting atoms. This can be done by plugging the LCAO wave functions for the molecule back into the appropriate Scrödinger equation (just as it can be done for the individual atoms using the atomic wave functions). The results are shown in Figure 5, where Ψ_1 and Ψ_2 are sometimes renamed σ(1s) and σ*(1s), respectively, to indicate the type of molecular orbital and their parentage.

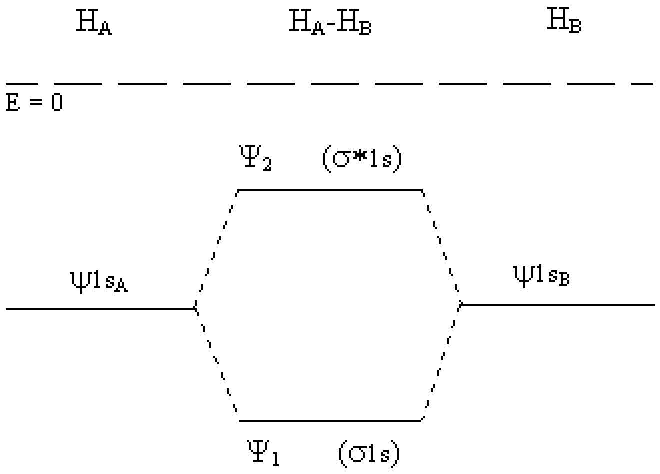


Figure 5

These molecular orbitals are useful for any molecule, or molecule-ion, using only 1s orbitals for bonding. Several possibilities are: H_2^+, H_2, H_2^-, H_2^{2-}, He_2^+ and He_2. The positive molecule-ions are unstable, but have been detected in the gas phase under high energy conditions. The negative molecule-ions and He_2 have not been observed.

Question 2. Using Figure 5, comment on the observations about the stability of the diatomic species listed above. (Would you expect all the negative molecule-ions to be unstable? Are there other species not listed which might be observed? Your answer should make reference to the electronic configuration and bond orders in these species

Second Row : Homonuclear Diatomics

Second row atoms have 2s and 2p orbitals available for use in bonding. As in the case of two atoms with 1s orbitals interacting, two atoms with 2s orbitals interacting lead to two molecular orbitals called σ(2s) and σ*(2s).

The symbol σ is used when the molecular orbital has no nodal plane which contains *both* nuclei. For the bonding combination, there is only one region of high electon density between the two nuclei. If there is a single nodal plane containing *both* nuclei, the orbital is of type π. In this case, the bonding combination will have two regions of high electron density separated by the node. There are rare cases in certain transition metal compounds, where two nodes per molecular orbital contain both nuclei. These are designated δ orbitals.

In valence bond theory terms, a single bond would have only a σ symmetry bond. A double bond consists of a σ and a π bond, a triple bond would have a σ and two π bonds, and the esoteric quadruple bond has one σ, two π and one δ combination. In a multiple bond, the various orbitals co-exist in the same region of space between the nuclei. Do not mistake the two regions of overlap of a π-bonding orbital for a double bond!

Use the applet to display the molecular orbitals derived from the 2s atomic orbitals on two atoms.

Question 3. Prepare sketches of the σ(2s) and σ*(2s) orbitals similar to Figures 2 and 3. Do not attempt to copy all shading; just show all the nodes and the phase (sign) of Ψ. Do they differ at all from figures 2 and 3?
Next use the computer program to display the overlap of two $2p_x$ orbitals. (The x axis is taken as the internuclear axis by the computer program.)

Question 4. Prepare crude sketches of the resulting orbitals. Which combination, the sum or the difference, corresponds to the bonding combination this time? What would be the names for these orbitals?
Now use the applet to examine the molecular orbitals that result from the linear combinations of the $2p_y$ orbitals. (Note that the results would be the same for the combinations of $2p_z$ orbitals, which, if you have time you can check by varying the value of z.)

Question 5. Once again prepare simplified sketches of what you see. Give the proper labels for the two combinations, including the * to indicate which is the antibonding orbital.

At this point you should have seen all the all the molecular orbitals formed by pairs of 2s and 2p orbitals. We can construct an energy level diagram to illustrate the relative energies of all these molecular orbitals and the atomic orbitals from which they are derived (Figure 6).

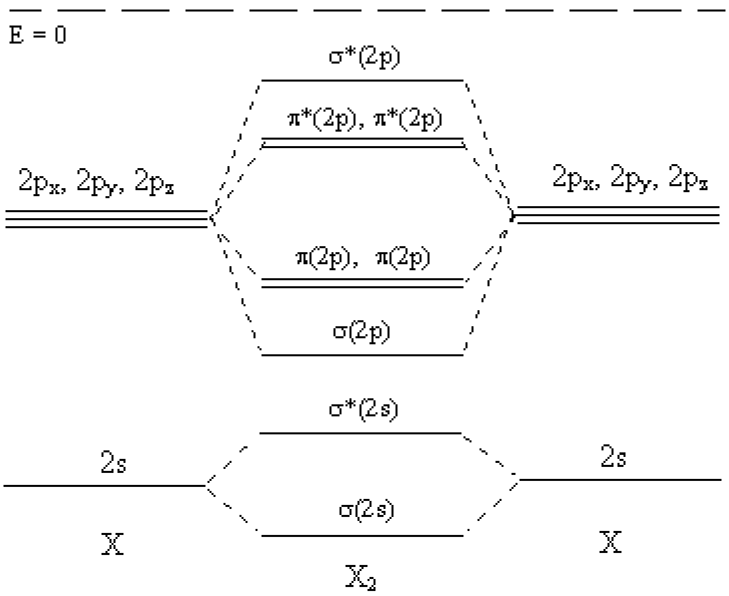


Figure 6

Question 6. What is the bond order in Li_2 and O_2?

What homonuclear molecule-cation and molecule-anion species should have the same bond order as O_2? Consider cases between X_2^{2-} and X_2^{2+} where X = Li to Ne.

Predict which two second-row elements are unlikely to give a diatomic molecule. Does simple Lewis bonding theory agree with your predictions?

Figure 6 does not quite tell the whole story. It can be refined a little by considering some other types of combination. Use the computer program to examine the linear combination of a 2s orbital on one atom with a $2p_x$ orbital on the other.

Question 7. Again sketch the results. There is no special way to label these combinations, but say if they are of type σ or π, and whether they are bonding or antibonding.

Use the computer to form a combination of a 2s orbital on one atom with a $2p_y$ orbital on the other.

Question 8. Sketch the resulting orbital. Can you classify this orbital as σ or π and bonding or antibonding? Explain. Go back to the beginning of this section if you are not sure.

Your answers to questions 7 and 8 should have convinced you that an LCAO of the type illustrated in question 7 is a reasonable combination, but that the other combination, described in question 8, is not useful. (Such a combination is called nonbonding.)

The results of including the additional overlap of 2s with 2p orbitals is shown in Figure 7. The main changes are shown in red.

- There is also a little contribution from the 2s orbitals to the most antibonding molecular orbital (at the top of the diagram), and a little contribution by the 2p orbitals to the most bonding molecular orbital (at the bottom).
- The main changes are that the orbital which was labelled σ(2p) and was below the π(2p) levels is now shown above the π(2P) and is now identified as σ*(2s,2p) while what was σ*(2s) has become σ(2s,2p)..

The difference does not affect our predictions for any of the stable homonuclear diatomic molecules, but it does slightly change our predictions for some of the more exotic species such as B_2, which can be detected in boron vapour.

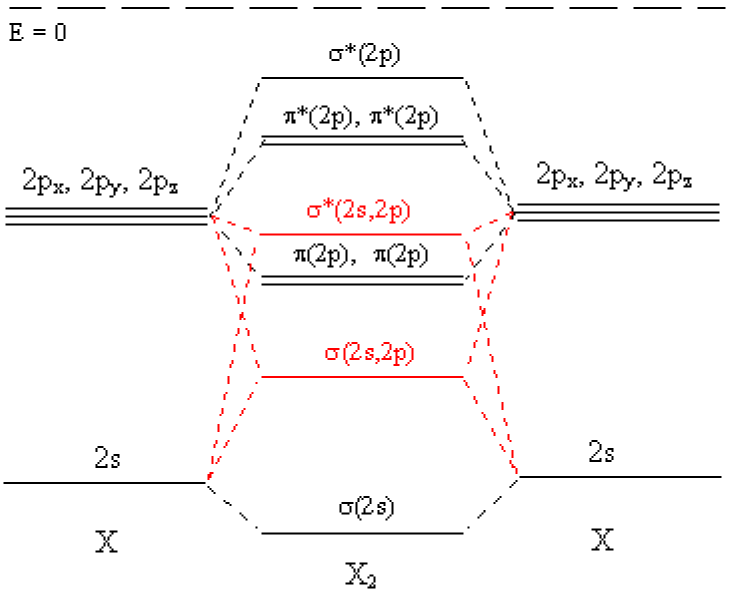


Figure 7

In actual fact the extent of the 2s - 2p interaction changes from Li_2 to F_2, becoming gradually less important, so that we should use the "improved" diagram (Figure 7) for Li_2 to N_2 and Figure 6 for O_2 F_2 (and cations of Ne_2). Figure 8 below shows what happens to the molecular orbitals as we cross the period.

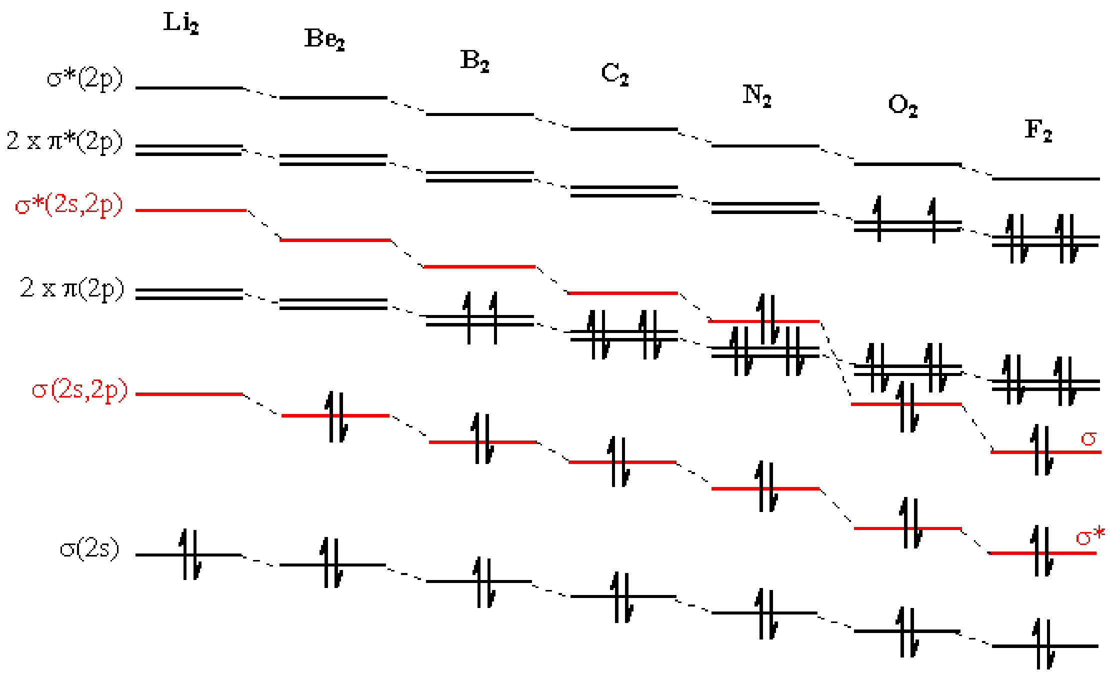


Figure 8

Question 9. What *is* the difference for B_2?
Question 10.
Go back and *briefly* answer, in the context of the homonuclear diatomic molecules, the four questions which were posed at the beginning of this lab.

Feel free to play with the applet to examine some of the other combinations of atomic orbitals that are possible. Because the projection direction is down the z-axis certain combinations cannot be displayed.