

Molecular Orbital Theory

To date, we have looked at three different theories of molecular bonding. 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.

WHY 3 THEORIES?

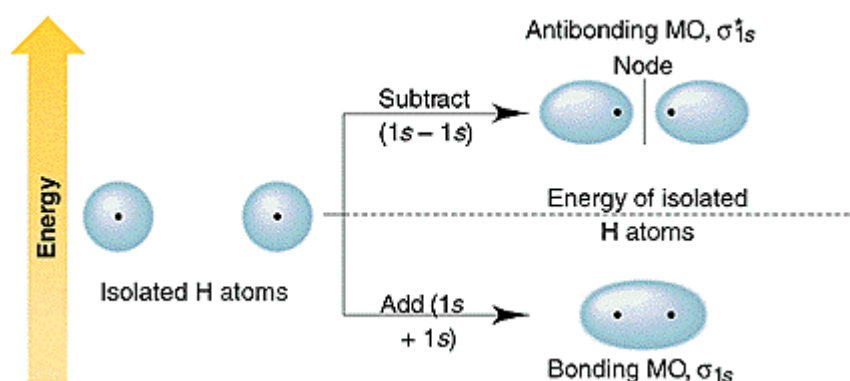
One model does not describe all the properties of molecular bonds. Each model describes a set of properties better than the others. The final test for any theory is experimental data.

The Molecular Orbital Theory does a good job of predicting electronic 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 balloons of electron density, the MO theory says that the electrons are delocalized. That means that they are spread out over the entire molecule.

Now, when two atoms come together, their two atomic orbitals react to form two possible molecular orbitals. One of the molecular orbitals is lower in energy. It is called the bonding orbital and stabilizes the molecule. The other orbital is called an anti-bonding orbital. It is higher in energy than the original atomic orbitals and destabilizes the molecule.

Below is a picture of the molecular orbitals of two hydrogen atoms come together to form a hydrogen molecule:

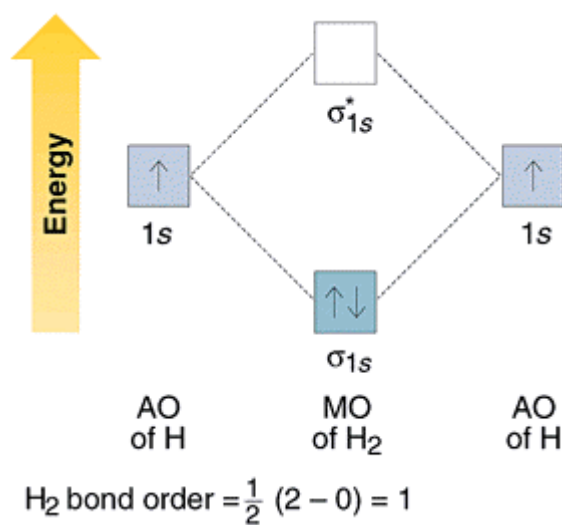


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The MO Theory has five basic rules:

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)

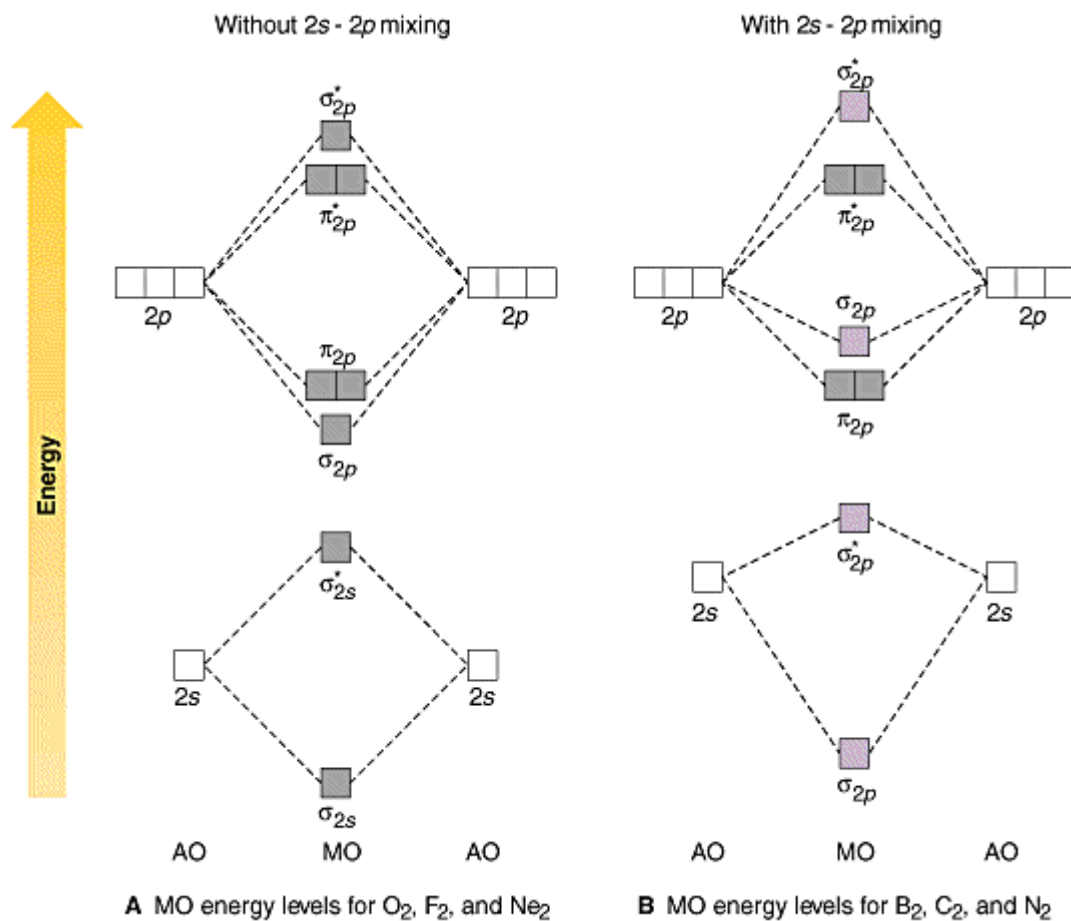
Below is a molecular orbital energy diagram for the hydrogen molecule. Notice that the two AO's or atomic orbitals combine to form 2 MO's - the bonding and the anti-bonding molecular orbitals. Also, notice that the five rules have been followed, the electrons having been placed in the lowest energy orbital(rule 3) and have paired up(rule 4) and there are only two electrons in the orbitals(rule 5).



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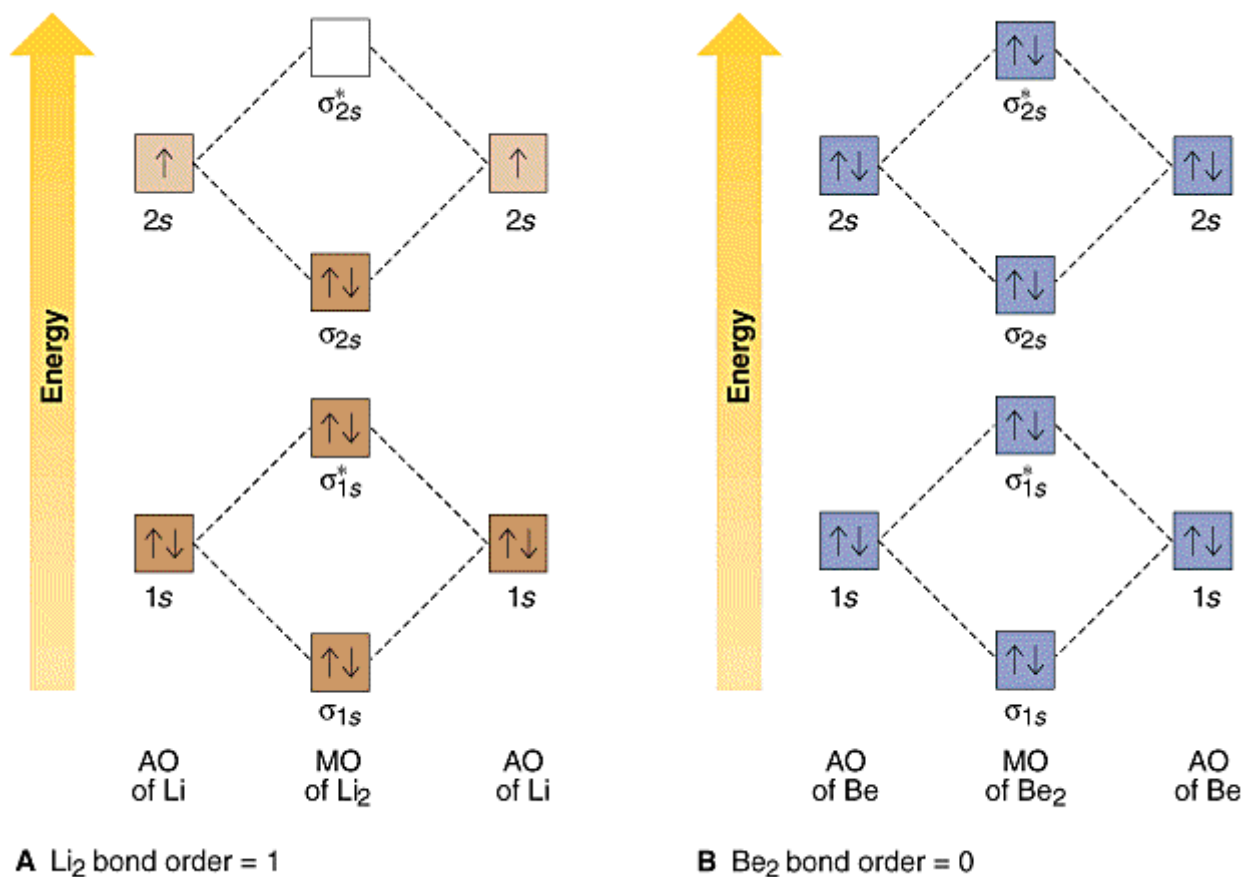
If you notice at the very bottom of the above picture, "bond order" is mentioned. If a molecule is to be stable, it must have a bond order greater than 0. Bond order is calculated as: $\frac{1}{2} (\text{\# of electrons in bonding orbitals} - \text{\# of electrons in anti-bonding orbitals})$. If the bond order is 0, the molecule is unstable and won't form. If the bond order is 1 a single bond is formed. If the BO (bond order) is 2 or 3 a double or triple bond will be formed respectively.

When the 2nd period atoms are bonded to one another, you have both 2s and three 2p orbitals to contend with. When this happens, you have twice as many MO's! Below is a diagram of the new molecular orbitals:



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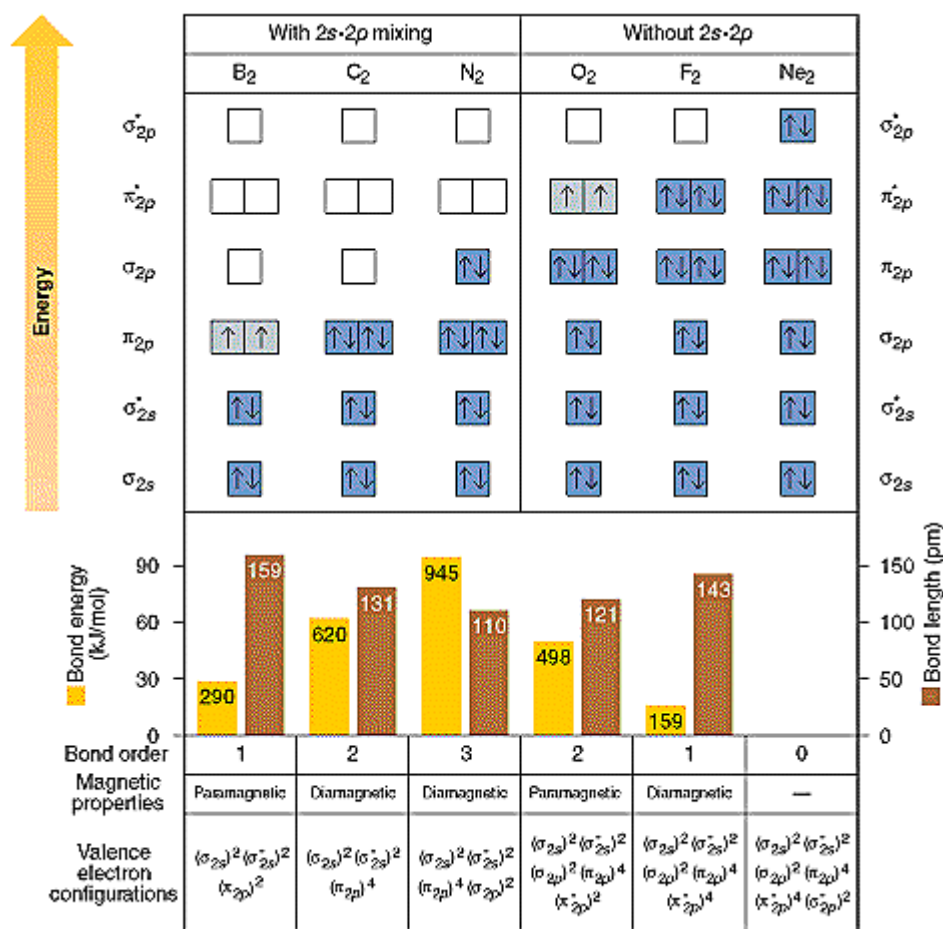
Finally, we can put the Molecular Orbital Theory to use!! Would you predict that dilithium or diberyllium is more likely to form, based on the diagram below?



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

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...)



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Finally, 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.

In valence bond theory, a single electron pair bond between two atoms is described in terms of the overlap of atomic orbitals (or in the mathematical formulation of the theory, the product of atomic orbitals) which are centred on the nuclei joined by the bond. In molecular orbital theory the bond is described in terms of a single orbital which is determined by the field of both nuclei. The two theories provide only a first approximation to the chemical bond.

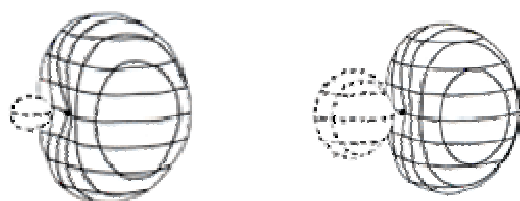
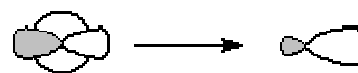
HYBRIDIZATION:

In the Valence Bond (VB) theory an atom may rearrange its atomic orbitals prior to the bond formation. Instead of using the atomic orbitals directly, mixtures of them (hybrids) are formed. For carbon (and other elements of the second row) the hybridization is limited to mixing one 2s and three 2p orbitals, as appropriate.

We recognize three basic **types** of hybridization: sp^3 , sp^2 and sp . These terms specifically refer to the hybridization of the atom and indicate the number of p orbitals used to form hybrids.

- Thus, in **sp^3 hybridization** all three p orbitals are mixed with the s orbital to generate **four new hybrids** (all will form σ type bonds or hold lone electron pairs).
- If two p orbitals are utilized in making hybrids with the s orbital, we get **three new hybrid orbitals** that will form σ type bonds (or hold lone electron pairs), and the "unused" p will participate in π type bonding. We call such an arrangement **sp^2 hybridization**.
- If only one p orbital is mixed with the s orbital, in **sp hybridization**, we produce **two hybrids** that will participate in σ type bonding (or hold a lone electron pair). In this case, the remaining two p orbitals are part of two perpendicular π systems.

The most important rule is that the number of orbitals must be preserved in the mixing process. The mixing principles can be illustrated on a simple example of one s and one p orbital making **two** equivalent sp hybrids (only one is shown here for clarity). The constructive interference of the wavefunctions at the "right" half gives a large lobe of the hybrid orbital, while the destructive interference on the left (opposite signs of the s and p wavefunctions) yields a small "tail". The second hybrid formed in this case is a 180° -rotated version of the one shown. In this case each of the two hybrids is constructed from $\frac{1}{2}$ of s and $\frac{1}{2}$ of p .



Within each **type** of hybridization, one can produce infinite number of different hybrids (mixtures). The hybrids are defined by the p to s ratio of the contributing orbitals. Thus, an sp^m hybrid is composed of $m+1$ parts: one part of s and m parts of p , and the p/s ratio is equal m , called the hybridization index. For example, an sp^3 hybrid has $\frac{1}{4}$ (25%) of s and $\frac{3}{4}$ (75%) of p . This fraction is called an s (or p) character of the orbital. Thus, an sp^3 hybrid has 25% s character.