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MOLECULAR ORBITAL AND VALENCE BOND THEORY:

Quantum Mechanics is a very difficult topic, with a great deal of detail that is extremely complex, yet interesting. However, in this Organic Chemistry Class we only need to understand certain key aspects of Quantum Mechanics as applied to electronic theory.

What follows is an outline of many of the important concepts, color coded to help you. The statements in red are items you need to know. Items in black are for your information, but it is not essential that you know them.

Items in purple describe what you need to be able to do, namely describe organic molecules in terms of overlap of hybridized orbital’s.

QUANTUM OR WAVE MECHANICS:

Electrons have certain properties of particles and certain properties of waves.

- Electrons have mass and charge like particles.
- Because they are so small and are moving so fast, electrons have no defined position.
Their location is best described by wave mechanics (i.e. a three-dimensional wave) and a wave equation called the Schrödinger equation.

Solutions of the Schrödinger equation are called wave functions and are represented by the Greek letter psi.

Each wave function describes a different orbital.

There are many solutions to the Schrödinger equation for a given atom.

The sign of the wave function can change from positive (+) to negative (-) in different parts of the same orbital.

This is analogous to the way that waves can have positive or negative amplitudes. The sign of the wave function does not indicate anything about charge.

The value of the square of the wave function is proportional to the probability of finding electron density at a given point in an orbital.

Note that the sign of square of the wave function is always positive, because the square of even a negative value is still positive.

In a 2p orbital, it is just as probable to find electron density in the negative lobe as it is to find electron density in the positive lobe.

A node is any place in an orbital at which the value of the wave function is zero.

A nodal surface or nodal plane are surfaces or planes where the value of the wave function is zero. There is absolutely no electron density at a node, a nodal surface, or a nodal plane.

The Schrodinger equation can in principle describe covalent bonding, but, even with powerful computers the equation is too complicated to be solved exactly for large molecules.
MOLECULAR ORBITAL THEORY OF COVALENT BONDING:

Molecular orbital theory assumes that individual electron pairs are found in molecular orbitals that are distributed over the entire molecule.

Molecular orbitals are analogous to atomic orbitals and are described by the following four rules:

- First, combination of n atomic orbitals in a molecule or ion forms n molecular orbitals, each of which extends over the entire molecule or ion.
  
  The number of molecular orbitals is equal to the number of atomic orbitals combined, because atomic orbitals can be combined by both in phase and out of phase addition.
  
- Second, molecular orbitals, just like atomic orbitals, are arranged in order of increasing energy.
  
- Third, filling of molecular orbitals is governed by the same principles as the filling of atomic orbitals.
  
- Electrons are placed in molecular orbitals starting with the lowest energy orbitals first.
  
  - A molecular orbital cannot hold more than two electrons.
  
  - Two electrons in the same molecular orbital have opposite spins.
  
  - When two or more degenerate (same energy) molecular orbitals are available, one electron is placed in each before any one of them gets two electrons.
  
- When two atomic orbitals combine to form a molecular orbital, the wave functions are combined both in phase and out of phase to create one bonding molecular orbital and one antibonding molecular orbital, respectively.
  
  - A bonding molecular orbital occurs when the electron density of the orbital is concentrated between the atomic nuclei.
Electrons in bonding molecular orbitals stabilize covalent bonds because they serve to offset the repulsive forces of the positively-charged atomic nuclei. Both nuclei are attracted to the electrons between them.

- The energy of a bonding molecular orbital is lower than the energy of the uncombined atomic orbitals.
- An antibonding molecular orbital (designated with an *) occurs when the electron density of the orbital is concentrated in regions of space outside the area between the atomic nuclei.
- Electrons in antibonding molecular orbitals do not stabilize covalent bonds because the electrons are not positioned to offset the repulsive forces of the positively charged atomic nuclei.
- The energy of an antibonding molecular orbital is higher than the energy of the uncombined atomic orbitals.

- A sigma bond occurs when the majority of the electron density is found on the bond axis.
  For example, a sigma bond results from the overlap between two 1s orbitals.
  - Because rotating sigma bond does not decrease the overlap of the orbitals involved (sigma bonds have cylindrical symmetry), a sigma bond can rotate freely about the bond axis.

- A pi bond occurs when the majority of the electron density is found above and below the bond axis.
  - For example, a pi bond results from the overlap of two 2p orbitals that are parallel to each other, and orthogonal to the sigma bond that exists between the two atoms.
  - Because rotating a pi bond by 90° destroys the orbital overlap, pi bonds cannot rotate around the bond axis.

- An electronic ground state occurs when all of the electrons are in the molecular orbitals of lowest possible energy.
An electronic excited state occurs when an electron in a lower lying orbital is promoted to an orbital that is higher in energy. This can occur when light is absorbed by a molecule.

**VALENCE BOND THEORY OF COVALENT BONDING:**

For elements more complicated than hydrogen, it is helpful to combine (hybridize) the valence atomic orbitals on a given atom before looking for overlap with orbitals from other atoms.

For C, N, and O hybridization means the 2s atomic orbital is combined with one, two, or all three 2p atomic orbitals.

The results of the orbital combinations are called hybrid orbitals, the number of hybrid orbitals are equal to the number of atomic orbitals combined.

- An sp^3 hybrid orbital is the combination of one 2s orbital with three 2p orbitals.
- Four sp^3 orbitals of equivalent energy are created.
- Each sp^3 orbital has one large lobe and a smaller one of opposite sign pointing in the opposite direction (with a node at the nucleus). The large lobes point to different corners of a tetrahedron (109.5° bond angle). This explains the tetrahedral structure of molecules like methane, CH_4.
- An sp^2 hybrid orbital is the result of combining the 2s orbital with two 2p orbitals. (Fig. 1.14 in text)
- Three sp^2 orbitals of equivalent energy are created.

Each sp^2 orbital has one large lobe and a smaller one of opposite sign pointing in the opposite direction (with a node at the nucleus).

The large lobes point to a different corner of a triangle (120° bond angle). This explains the trigonal planar structure of molecules like formaldehyde, CH_2=O.

The left over 2p orbital lies perpendicular of the plane formed by the three sp^2 orbitals.

An sp hybrid orbital is the combination of one 2s orbital with one 2p orbital.
Two sp orbitals of equivalent energy are created.

Each sp orbital has two lobes of opposite sign pointing in opposite directions (with a node at the nucleus). The lobes with like sign point in exactly opposite directions (180° bond angle). This explains the linear structure of molecules like acetylene.

The two left over 2p orbitals are orthogonal to each other, and orthogonal to the two sp hybrid orbitals as well.

Carbon atoms in molecules are either sp³, sp², or sp hybridized. 1s orbitals are not considered for hybridization with C, N, or O because the 1s orbitals do not participate in covalent bonding.

The hybridization of a given atom (sp³, sp², or sp) determines the geometry and type of bonds made by that atom. The important parameters associated with each hybridization state of carbon are listed in the following table:

<table>
<thead>
<tr>
<th>Hybridization State</th>
<th># of Hybrid Orbitals</th>
<th># of 2p Orbitals</th>
<th># of Groups</th>
<th># of ( \pi ) Bonds</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp³</td>
<td>4</td>
<td>0</td>
<td>4</td>
<td>4</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>sp²</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>Trigonal Planar</td>
</tr>
<tr>
<td>sp</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>Linear</td>
</tr>
</tbody>
</table>

You should make similar tables for N and O atoms.

- Bonding in complex molecules can be qualitatively understood as overlap of hybrid orbitals.
Organic chemistry is primarily concerned with two types of covalent bonds, namely sigma (σ) bonds and pi (π) bonds.

A sigma bond can be formed in a variety of ways.

A sigma bond results from the overlap between an s orbital and any other atomic orbital.

A sigma bond also results from the overlap of an sp³, sp², or sp hybrid orbital and any s, sp³, sp², or sp hybrid orbital along the bond axis.

Because rotating a sigma bond along the bond axis does not decrease any orbital overlap, there is only a small barrier to rotation. Thus, single bonds rotate extremely rapidly around the bond axis.

This explains why molecules with only sigma bonds are highly flexible, able to adopt an almost infinite number of rapidly interconverting conformations in solution.

A double bond in molecules such as H₂C=CH₂ can be understood in terms of:

One sigma bond formed by sp² hybridized orbitals on each carbon atom.

One pi bond formed between the 2p orbitals on each carbon atom.

Because rotating a pi bond by 90° destroys the orbital overlap, there is a large barrier to rotation and for all practical purposes double bonds cannot rotate around the bond axis. A triple bond in molecules such as acetylene can be understood in terms of:

One sigma bond formed by sp hybridized orbitals on each carbon atom.

Two orthogonal pi bonds formed between the two orthogonal 2p orbitals on each carbon atom. Because rotating a pi bond by 90° destroys the orbital overlap, triple bonds also cannot rotate around the bond axis.

The pictures below are intended to help you visualize pi bonds in double and triple bonds.

Upper Molecule: The pi bonding orbital of ethylene ("hot dog bun"), formed from the overlap of the 2p atomic orbitals on each carbon atom.
The sigma bonding orbital ("hot dog meat"), formed from overlap of sp³ hybridized orbitals on each carbon atom, is NOT shown.

Lower Molecule: The two pi bonding orbitals of acetylene ("two hot dog buns"), formed from the overlap of both 2p atomic orbitals on each carbon atom (gray atom in figure).

The sigma bonding orbital ("hot dog meat"), formed from overlap of sp hybridized orbitals on each carbon atom, is NOT shown.

The two pi bonds are orthogonal to each other, because the two 2p orbitals on each carbon atom are orthogonal.

It is absolutely essential that students understand bonding in complex molecules in terms of the overlap of hybrid orbitals.

This orbital picture of molecules forms the theoretical foundation for understanding the reactions of the different functional groups discussed in the rest of the semester. Do not go any further until these concepts are thoroughly understood.

For example, below we show how we want you to think about the electronic structure of molecules according to the valence bond approach.

In the boxes are shown the hybridization state of selected atoms. You should be able to assign the correct hybridization state of all atoms in organic molecules.
You also should be able to describe all of the bonds in a molecule in terms of the overlap of hybridized orbitals, including appropriate designations for sigma or pi bonds.

A useful format for describing selected bonds is shown here in which the type of bond is indicated (sigma or pi) as well as which hybridized orbitals (Csp³, H1s, etc.,) overlaps to create the bond.

You may become confused when valence bond theory and molecular orbital theory are presented together. It is important to keep the following points in mind when learning about these two theories.

These two theories are complimentary, and are used for different purposes.

Valence bond theory and molecular orbital theory are best thought of as different approximations for the electronic structure of molecules.

Despite the apparent differences, the approaches almost always yield the same predictions of molecular structure and reactivity, the molecular orbital calculations are simply more detailed.

In other words, if you add up the electron densities in all of the calculated molecular orbitals, you find that the majority of electron density is localized between bonded atoms as predicted by valence bond theory.

The bottom line: Valence bond theory provides a good qualitative description of sigma bonding in molecules for use in routine situations.

Molecular orbital theory is usually reserved for detailed computer calculations when more quantitative results are required or when describing pi bonding and charge delocalization, including aromaticity and resonance.

**Molecular Structure and Bonding Theories:**

- VSEPR Theory
- Valence Bond theory (with hybridization)
- Molecular Orbital Theory (with molecular orbitals)

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 contain two equivalent bonds with a bond order between that of a single bond and a double bond.

The best it can do is suggested 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 describes 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 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 drawback is that we are limited to talking about diatomic molecules 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.

**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 1s 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 fig.

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 $\text{H}_2$ molecule. Since the $\sigma^*$ 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:**

- The number of molecular orbitals = the number of atomic orbitals combined.
- Of the two MO's, one is a bonding orbital (lower energy) and one is an antibonding orbital (higher energy).
- Electrons enter the lowest orbital available.
- The maximum # of electrons in an orbital is 2 (Pauli Exclusion Principle).
- 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 $\text{O}_2$ 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 there could 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.

**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.

![](image)

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 He₂ Molecule Do Not Exist:

- This molecular orbital model can be used to explain why He₂ molecules don't exist. Combining a pair of helium atoms with 1s² 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 He₂ 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 He₂ 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 Li₂ and Be₂ (does not exist)
Molecular Orbitals of the Second Energy Level (2s and 2p together)

- The 2s orbitals on one atom combine with the 2s orbitals on another to form a $\sigma_{2s}$ bonding and a $\sigma_{2s^*}$ antibonding molecular orbital, just like the $\sigma_{1s}$ and $\sigma_{1s^*}$ orbitals formed from the 1s 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 $\sigma_{2p}$ 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 \(\pi\) orbitals because they look like \(p\) orbitals when viewed along the bond. Whereas \(\sigma\) and \(\sigma^*\) orbitals concentrate the electrons along the axis on which the nuclei of the atoms lie, \(\pi\) and \(\pi^*\) orbitals concentrate the electrons either above or below this axis.

The 2p\(_x\) atomic orbitals combine to form a \(\pi_x\) bonding molecular orbital and a \(\pi_x^*\) antibonding molecular orbital.

The same thing happens when the 2p\(_y\) orbitals interact, only in this case we get a \(\pi_y\) and a \(\pi_y^*\) 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 \(\pi_x\) and \(\pi_y\) or the \(\pi_x^*\) and \(\pi_y^*\) molecular orbitals.

The interaction of four valence atomic orbitals on one atom (2s, 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: \(\sigma_{2s}, \sigma_{2s}^*, \sigma_{2p}, \sigma_{2p}^*, \pi_x, \pi_y, \pi_x^*, \text{ and } \pi_y^*\).

There is a significant difference between the energies of the 2s and 2p orbitals on an atom. As a result, the \(\sigma_{2s}\) and \(\sigma_{2s}^*\) orbitals both lie at lower energies than the \(\sigma_{2p}, \sigma_{2p}^*, \pi_x, \pi_y, \pi_x^*, \text{ and } \pi_y^*\) orbitals.

To sort out the relative energies of the six molecular orbitals formed when the 2p 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 $\sigma_{2p}$ orbital lies at a lower energy than the $\pi_x$ and $\pi_y$ orbitals, and the $\sigma_{2p}^*$ orbital lies at higher energy than the $\pi_x^*$ and $\pi_y^*$ orbitals, as shown in the figure below.

Unfortunately an interaction is missing from this model. It is possible for the $2s$ 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.
Without $2s \cdot 2p$ mixing

With $2s \cdot 2p$ mixing

MO energy levels for $O_2$, $F_2$, and $Ne_2$

MO energy levels for $B_2$, $C_2$, and $N_2$
**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.

\[ \text{O} = \text{O} \]

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.

\[ \text{S} = \text{O} \leftrightarrow \text{S} = \text{O} \]

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.

**Delocalized Bonding:**

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.

![Benzene and Ozone](image.png)
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