

# Chemical Bonding Review

Chem. 142 S2006

## Molecular Shapes: Valence Shell Electron Pair Repulsion

In order to predict molecular shape, we assume the valence electrons of each atom in the molecule repel one another.

When this occurs, the molecule adopts a 3D geometry that minimizes this repulsion where:

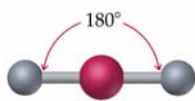
$$lp-lp > lp-bp > bp-bp$$

This process is known as: Valence Shell Electron Pair Repulsion (VSEPR) theory.

A molecule can be described in terms of the distribution of the bonding atoms about the central atom: *Molecular Geometry* (MG)

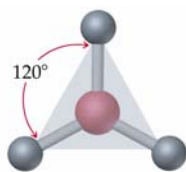
A molecule can be described in terms of the distribution of the bonding pair electrons (bp) and lone pair electrons (lp) about the central atom: *Electronic Geometry* (EG)

There are five fundamental shapes that describe the electronic geometries for molecular shape:



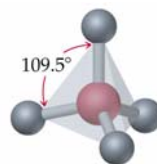
Linear

2 pairs of electrons



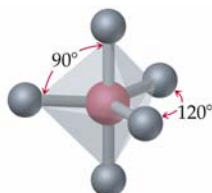
Trigonal planar

3 pairs of electrons



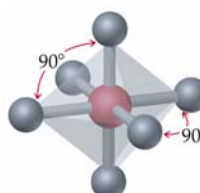
Tetrahedral

4 pairs of electrons



Trigonal bipyramidal

5 pairs of electrons



Octahedral

6 pairs of electrons

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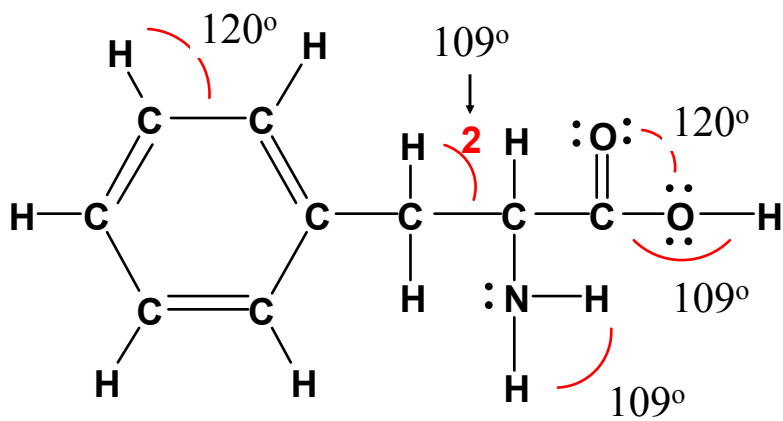
### Summary of VSEPR Molecular Geometries

Electron Groups	Lone Pairs	Bonds	Geometry	Examples
2	0	2	Linear	BeCl <sub>2</sub>
3	0	3	Trigonal planar	BF <sub>3</sub>
3	1	2	Bent	SO <sub>2</sub>
4	0	4	Tetrahedral	CH <sub>4</sub>
4	1	3	Trigonal pyramidal	NH <sub>3</sub>
4	2	2	Bent	H <sub>2</sub> O
5	0	5	Trigonal bipyramidal	PCl <sub>5</sub>
5	1	4	See-saw	SF <sub>4</sub>
5	2	3	T-Shaped	ClF <sub>3</sub>
5	3	2	linear	I <sub>3</sub> <sup>-</sup>
6	0	6	Octahedral	SF <sub>6</sub>
6	1	5	Square pyramidal	SbCl <sub>5</sub> <sup>2-</sup>
6	2	4	Square planar	XeF <sub>4</sub>

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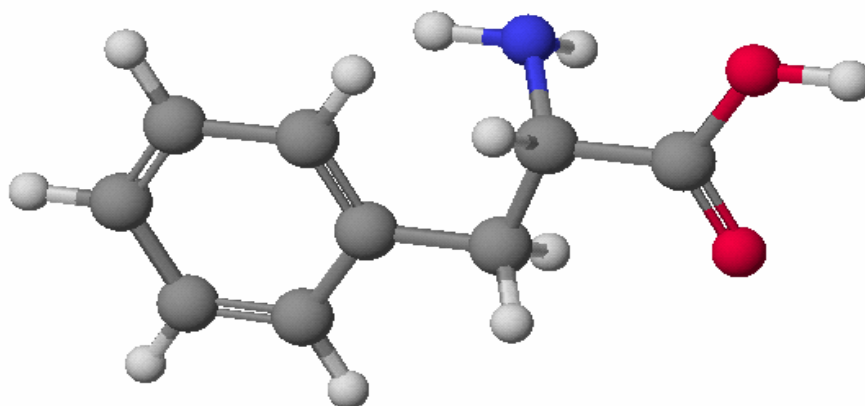
What are the approximate bond angles at each number?  
*Remember, the 2-D Lewis structure is not to scale...*



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Here is the 3-D rendering showing the true bond angles.



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## Bonding Theories for Covalent Molecules (1):

### Valence Bond Theory

*VSEPR* → predicts the 3-dimensional molecular (*MG*) and electronic (*EG*) geometries of a large number of covalent compounds and polyatomic anions.

*Valence Bond (VB)* theory describes these geometries in terms of the bonding orbitals used by the atoms in these molecules.

Valence bond theory states that bonding in covalent compounds occurs via the *overlap* of two half-filled orbitals of the bonding atoms.

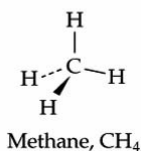
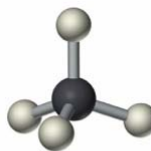
In order to achieve the correct bond angles as predicted by VESPR, the atomic orbitals on each bonding atom “mix” to form new “hybrid” bonding orbitals.

### *Valence Bond Terminology:*

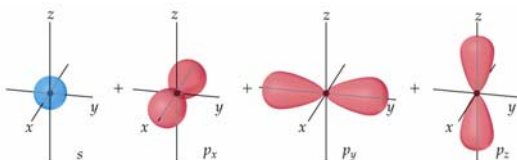
<i>Overlap:</i>	two orbitals existing in the same region of space
<i>lp:</i>	lone pair of electrons (non-bonding)
<i>bp:</i>	bonding pair of electrons (result of orbital overlap)
<i>Central atom:</i>	the atom of concern in a molecule
<i>hybridization:</i>	the linear combination of atomic orbitals
<i>hybrid orbital:</i>	bonding orbitals that arise from the mixing of AO's.
<i>σ-bond:</i>	(sigma bond) overlap of orbitals along the bond axis
<i>π-bond:</i>	(pi bond) overlap of orbitals above and below the bond axis.
<i>single bond:</i>	one σ-bond
<i>double bond:</i>	one σ-bond & one π-bond
<i>triple bond:</i>	one σ-bond & two π-bonds

## Consider methane: CH<sub>4</sub>

We know that methane has a tetrahedral molecular geometry.



If the H-atoms were to bond via overlap with the carbon valence orbitals, this geometry could not be attained.



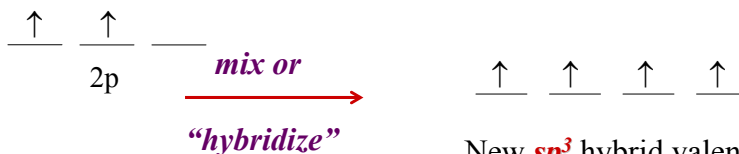
These atomic orbitals would result in the wrong bond angles.

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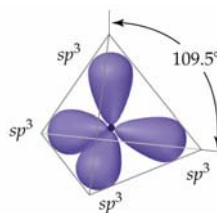
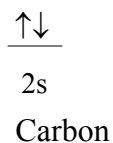
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In order to attain the needed geometry, the *atomic orbitals* (AO's) mix or *hybridize* to form new *valence bond* orbitals.

This *hybridization* determines by the electron domain geometry for the central atom.

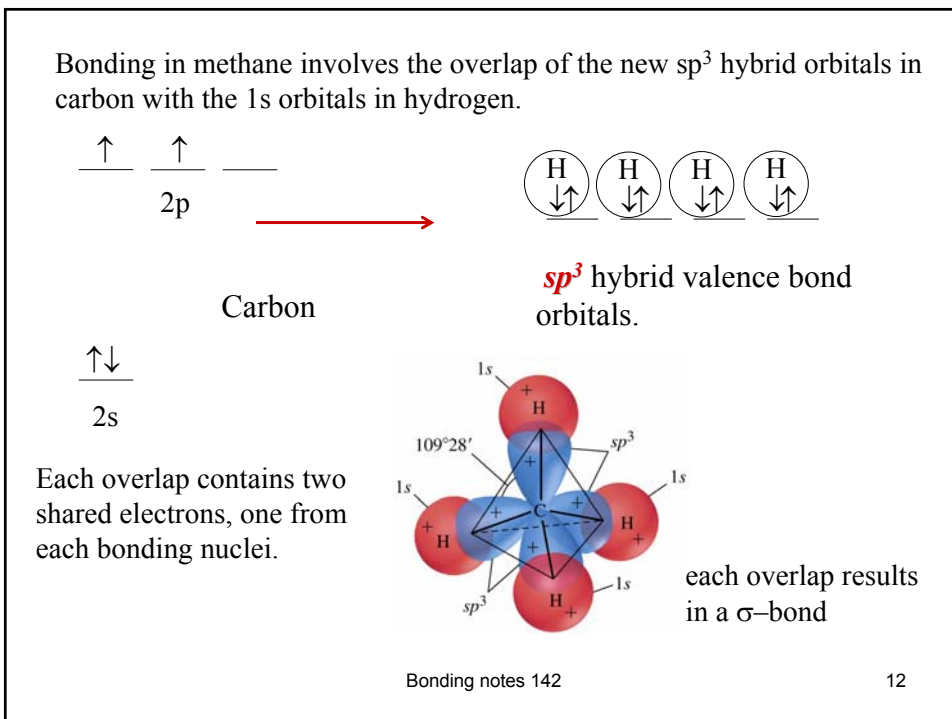
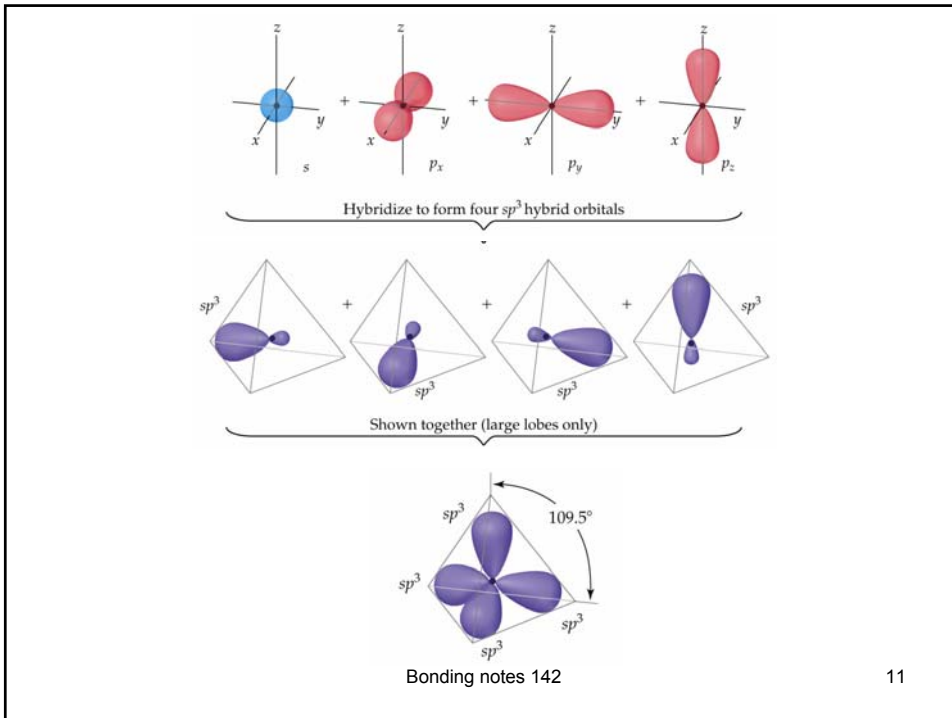


New *sp<sup>3</sup>* hybrid valence bond orbitals.

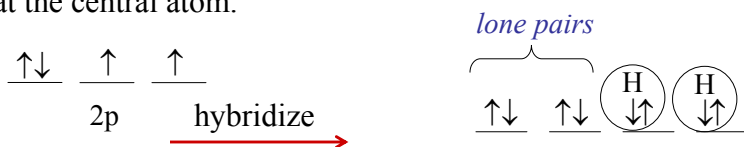


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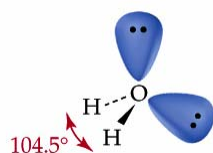
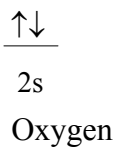
10



From this we can say that any molecule that has an **electronic geometry** that is **tetrahedral** in shape must involve  $sp^3$  hybridization at the central atom.



New  $sp^3$  hybrid valence bond orbitals.



$H_2O$

EG: **Tetrahedral**

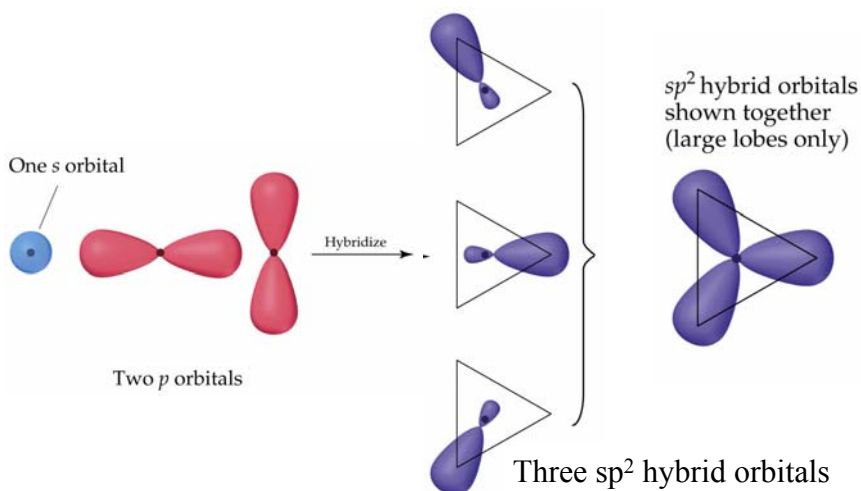
MG: **Bent**

Hybridization:  $sp^3$

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### $sp^2$ hybridization



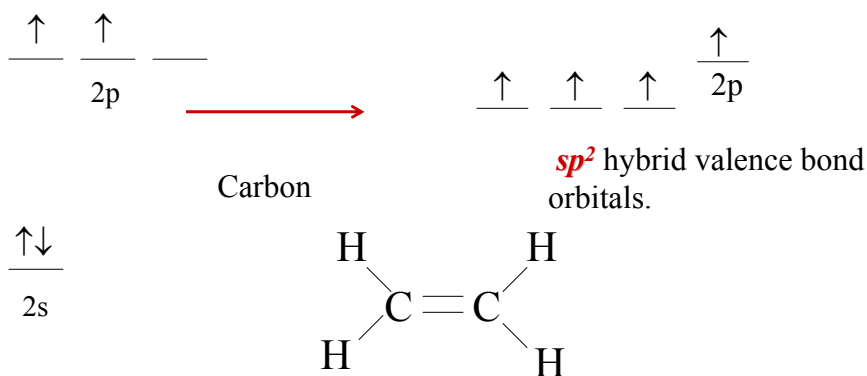
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An example of  $sp^2$  hybridization is given by  $C_2H_4$  (ethene)

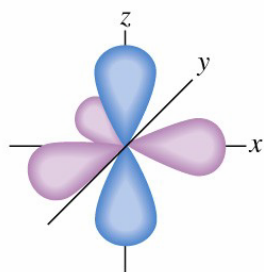


Each  $sp^2$  orbital can form a  $\sigma$ -bond, two with each of the H's and one with the other carbon.

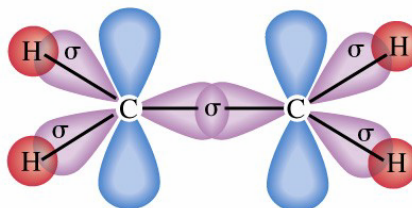
The left over p-orbitals on each carbon overlap to form the  $\pi$ -bond (second half of the double bond).

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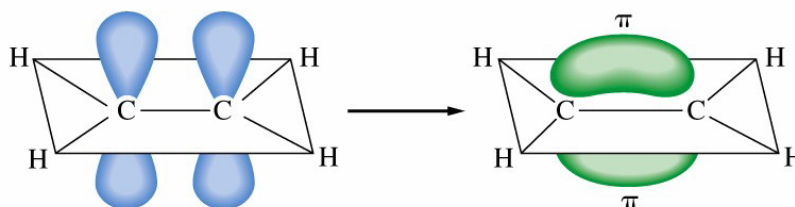
17



The set of orbitals  $sp^2 + p$



Sigma ( $\sigma$ ) bonds



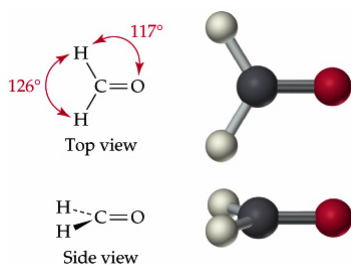
Overlap of p orbitals leading to pi ( $\pi$ ) bond

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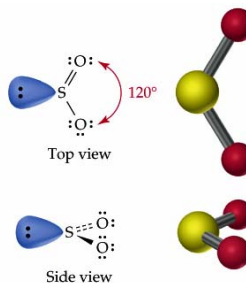
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Other examples of molecules with  $sp^2$  hybridization are:

$CH_2O$  formaldehyde



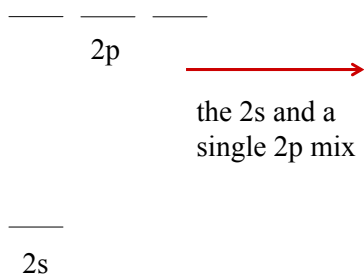
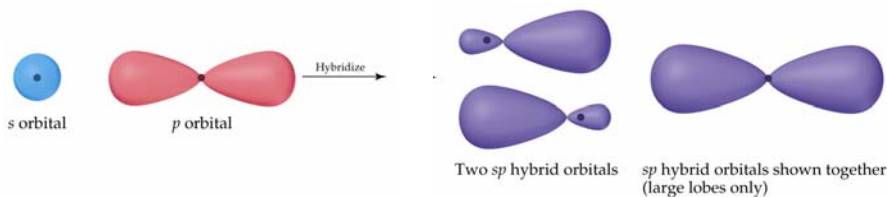
$SO_2$  sulfur dioxide



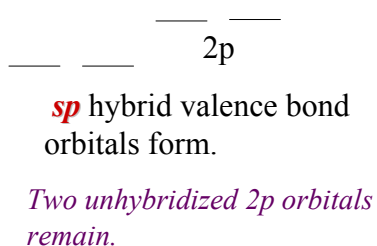
**Conclusion:** When a central atom has a *trigonal planar* electronic geometry (EG), it is most likely to bond through  $sp^2$  hybridization.

Compounds containing double bonds ( $\sigma + \pi$ ) most often have  $sp^2$  hybridization.

### $sp$ Hybridization



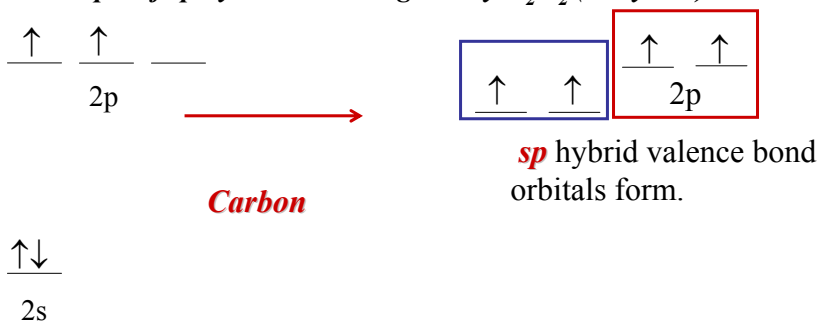
the 2s and a  
single 2p mix



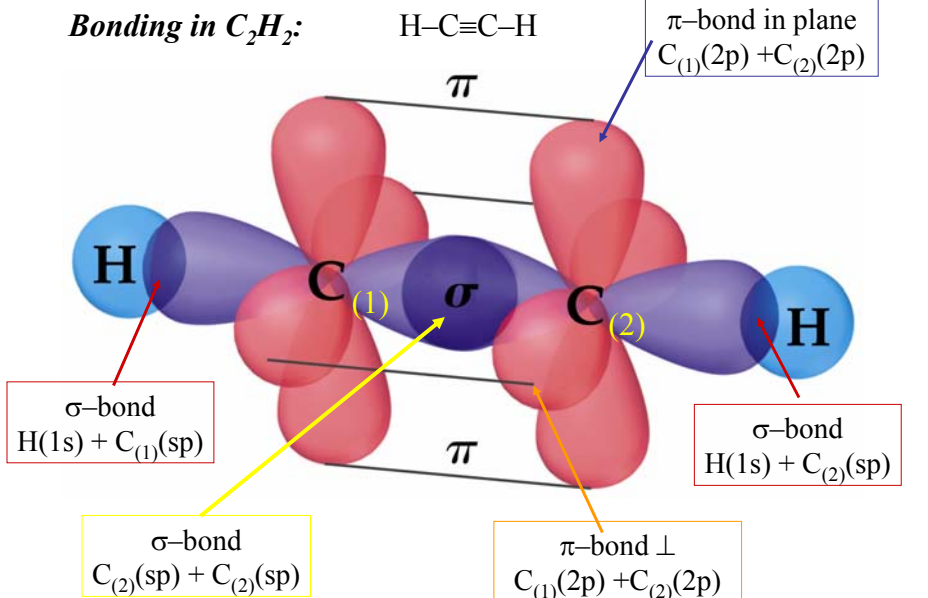
The  $sp$  orbitals spread out to form a **linear** geometry (directed away from one another) leaving the p orbitals perpendicular to the molecular axis.

The  $sp$  orbitals can form  $\sigma$ -bonds or hold lone pairs. One of the p orbital can form the  $\pi$ -bond in a double bond or the two p's can form the  $\pi$ -bonds in a triple bond.

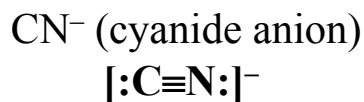
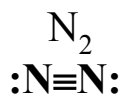
*An example of  $sp$  hybridization is given by  $C_2H_2$  (acetylene)*



**Bonding in  $C_2H_2$ :**



*Other examples of molecules with sp hybridization are:*



**Conclusion:** When a central atom has a *linear* electronic geometry (EG) with no lone pairs, it is most likely to bond through sp hybridization.

Compounds containing triple bonds ( $\sigma + 2\pi$ ) or adjacent double bonds ( $\text{CO}_2$ ) have sp hybridization.

### **Molecular Orbital (MO) Theory (Ch. 10.3)**

*Lewis dot, VESPR & Valence Bond (VB)* theories all do a good job at predicting the shapes and bonding in covalent molecules.

Chemists however sometimes require another theory of bonding that explains phenomenon such as *paramagnetism* in covalent molecules or why certain species form unstable compounds while others don't.

To address such issues, we can describe bonding from a perspective of *Molecular Orbitals*.

In MO theory, the *atomic orbitals* on individual atoms combine (*constructively and destructively*) to produce new *molecular orbitals* that give rise to bonding and anti-bonding orbitals that exist between nuclei.

**Molecular Orbital Theory (10.3) has several advantages and differences over VESPR & VB theory:**

- **MO** does a good job of predicting electronic spectra and paramagnetism, when *VSEPR* and the **VB** theories don't.
- The **MO** theory like **VB** theory, predicts the bond order of molecules, however it does not need resonance structures to describe molecules
- MO theory treats molecular bonds as a sharing of electrons between nuclei. Unlike the VB theory, which treats the electrons as *localized hybrid orbitals* of electron density.
- **MO** theory says that the electrons are *delocalized*. That means that they are spread out over the entire molecule.

The main drawback to our discussion of **MO** theory is that we are limited to talking about *diatomic molecules* (molecules that have only two atoms bonded together), or the theory gets very complex.

**MO Theory: Considered a molecule A-B**

When two *wave functions* (orbitals) on different atoms add constructively they produce a new MO that promotes bonding given by:



When two *wave functions* (orbitals) on different atoms add destructively (subtract) they produce a new MO that promotes anti-bonding bonding given by:

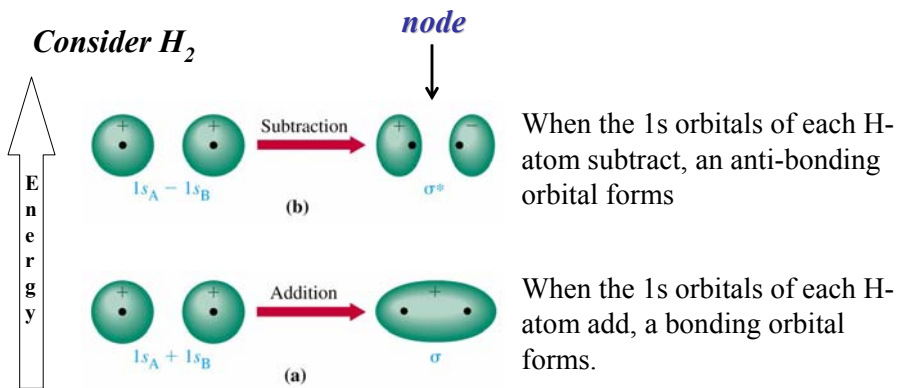


The “*bonding*” MO ( $\Omega_{AB}$ ) is lower in energy than the “*anti-bonding*” MO ( $\Omega_{AB}^*$ ).

### MO Theory:

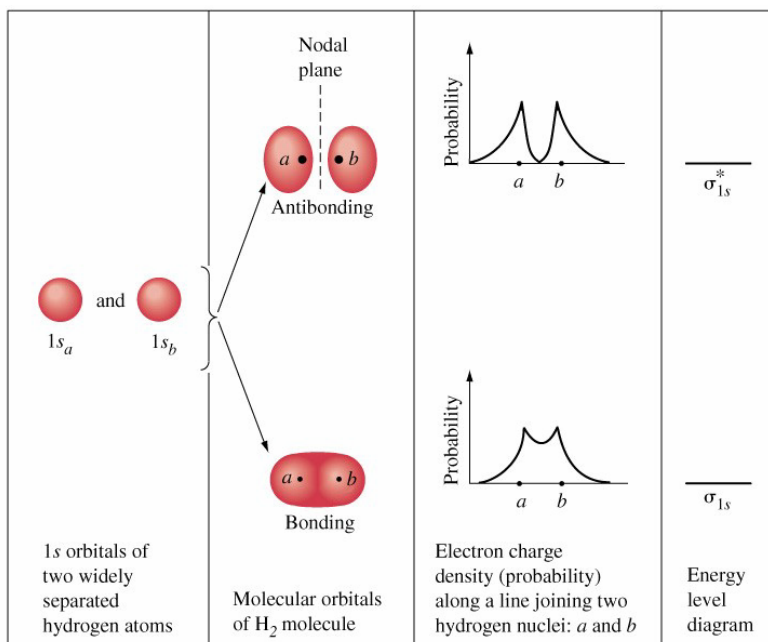
The lower energy *bonding molecular* orbital (1) stabilizes the molecule is.

The higher energy *anti-bonding molecular orbital* (2) destabilizes the molecule.



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### Terminology in MO theory:

**$\sigma$ -bonding orbital:** stabilizing MO that exists between nuclei.

**$\sigma^*$ -anti-bonding orbital:** destabilizing MO that exists between nuclei.

**$\pi$ -bonding orbital:** stabilizing MO that exists above and below the inter nuclear axis.

**$\pi^*$ -anti-bonding orbital:** destabilizing MO that exists above and below the inter nuclear axis.

**node:** region of zero probability

**ground state:** lowest energy configuration of electrons in a molecule

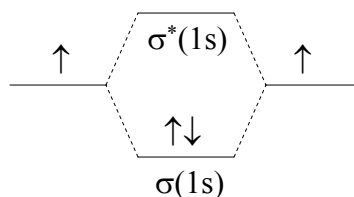
**excited state:** electron(s) moved to higher energy MO's

$$BO = \frac{\# \text{ of bonding electrons in MO's} - \# \text{ of anti-bonding electrons in MO's}}{2}$$

### MO Diagrams:

Once again we consider the simplest molecule,  $H_2$ .

When two hydrogen atoms combine the 1s orbitals on each can add or subtract to form a  $\sigma(1s)$  bonding or  $\sigma^*(1s)$  anti-bonding orbital.



Each H-atom has one *1s* electron that can contribute to the MO bonding and anti-bonding MO's.

Just as in the electron configurations of atoms, the electron fill from the lowest energy MO first (*Aufbau principle*) only pairing when forced to (*Hund's rule*). Each MO can only hold two electrons of opposite spin (*Pauli principle*)

### ***Bond Order:***

From this we find that the bonding in  $H_2$  is described by:

$$BO = \frac{\# \text{ of bonding electrons in MO's} - \# \text{ of anti-bonding electrons in MO's}}{2} = \frac{2-0}{2} = 1$$

Bond Order = 1 (single bond)

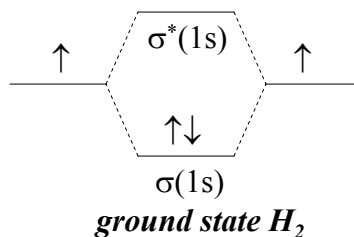
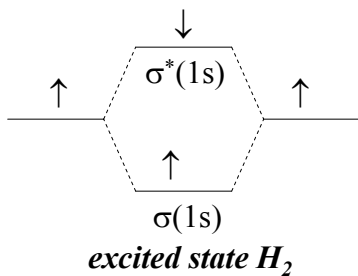
MO electron configuration of:  $\sigma^2(1s)$

One also sees that the molecule ( $H_2$ ) is ***diamagnetic*** (no unpaired electrons)

### ***Excited States:***

What happens to a  $H_2$  molecule if one of the electrons is excited to the anti-bonding orbital?

$$BO = \frac{2-0}{2} = 1$$



$$BO = \frac{1-1}{2} = 0$$

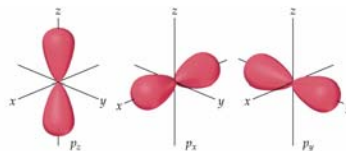
The molecule falls apart!

***Photodissociation***

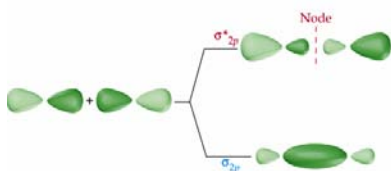


## MO's arising from the p-orbitals

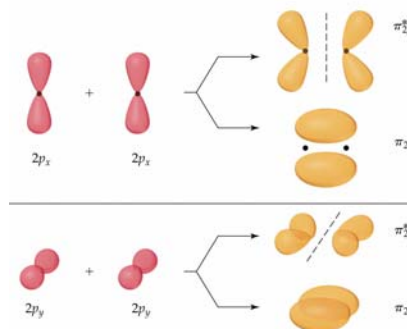
Recall that the three p-orbitals are all perpendicular to one another.



End on addition gives rise to  $\sigma$  &  $\sigma^*$  bonds



Sideways addition gives rise to two sets of  $\pi$  &  $\pi^*$  bonds

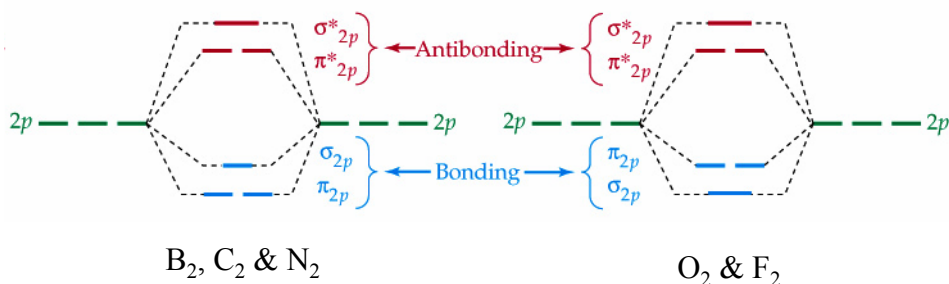


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## The MO correlation diagram for the 2p atomic orbitals

The three 2p orbitals on each side combine to form six new Molecular Orbitals that can accommodate up to 12 electrons.

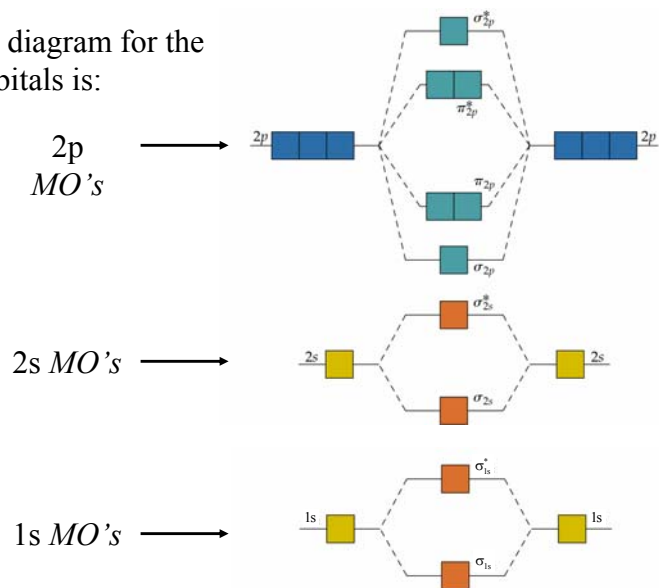


Experimentally, it is seen that the  $\sigma_{2p}$  & the  $\pi_{2p}$  MO's switch for  $B_2$ ,  $C_2$  &  $N_2$  (see page 349-50)

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The overall MO diagram for the 1s, 2s and 2p orbitals is:



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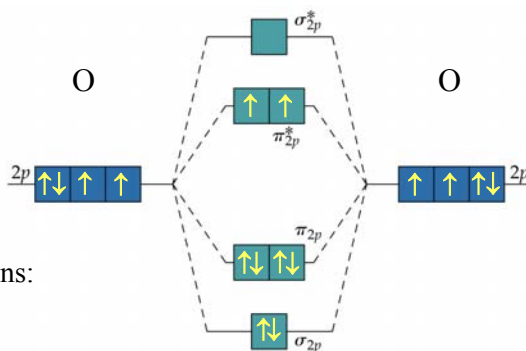
### Bonding in O<sub>2</sub>

Since the 1s and 2s MO's are full, they do not contribute any net bonding

Any net bonding will be determined by the 2p MO's.

Each O-atom has four 2p electrons:

The electrons fill the MO's fill by the Aufbau principle and Hund's rule:

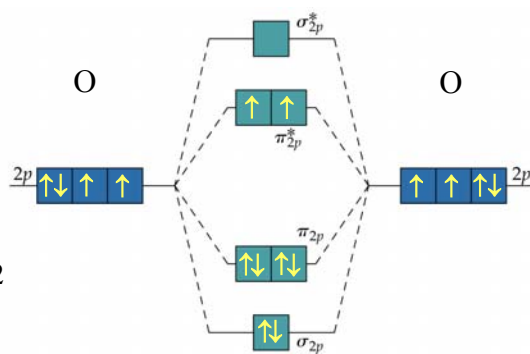


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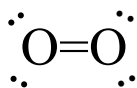
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$$BO = \frac{6 - 2}{2} = 2$$

*double bond*



This agrees with the Lewis dot structure:

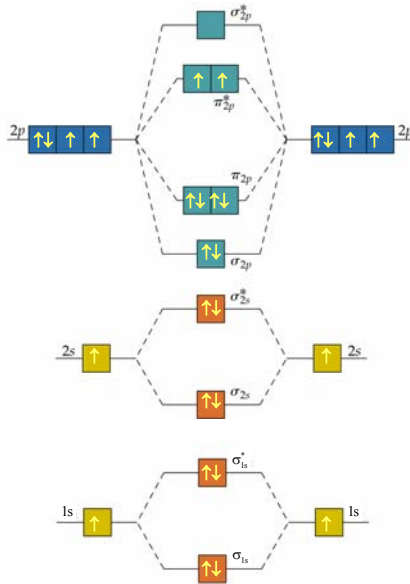
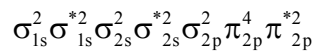


However, VB theory did not tell us that the molecule is paramagnetic!





Molecular Orbital configuration for O<sub>2</sub>



## Bonding in $O_2^{2-}$

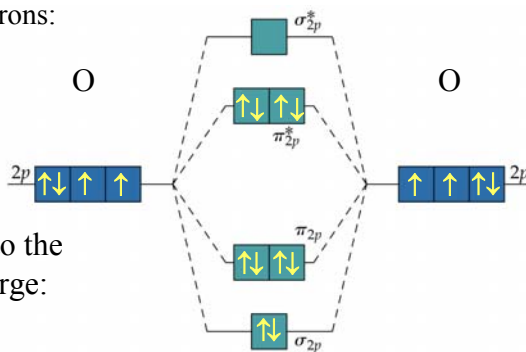
Each O-atom has four 2p electrons:

The electrons fill the *MO*'s fill by the Aufbau principle and Hund's rule:

Add in two more electrons to the lowest open *MO* for the charge:

$$BO = \frac{6 - 4}{2} = 1$$

The peroxide ion has a single bond and is diamagnetic!



	Large 2s-2p interaction			Small 2s-2p interaction		
	$B_2$	$C_2$	$N_2$	$O_2$	$F_2$	$Ne_2$
$\sigma_{2p}^*$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
$\pi_{2p}^*$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
$\sigma_{2p}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
$\pi_{2p}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
$\sigma_{2s}^*$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
$\sigma_{2s}$	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>

Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—