

Chapter 11 Theories of Covalent Bonding

Chapter Outline

11.1 Valence Bond (VB) Theory and Orbital Hybridization

- The Central Themes of VB Theory
- Types of Hybrid Orbitals

11.2 The Mode of Orbital Overlap and the Types of Covalent Bonds

- VB Treatment of Single and Multiple Bonds
- Orbital Overlap and Molecular Rotation

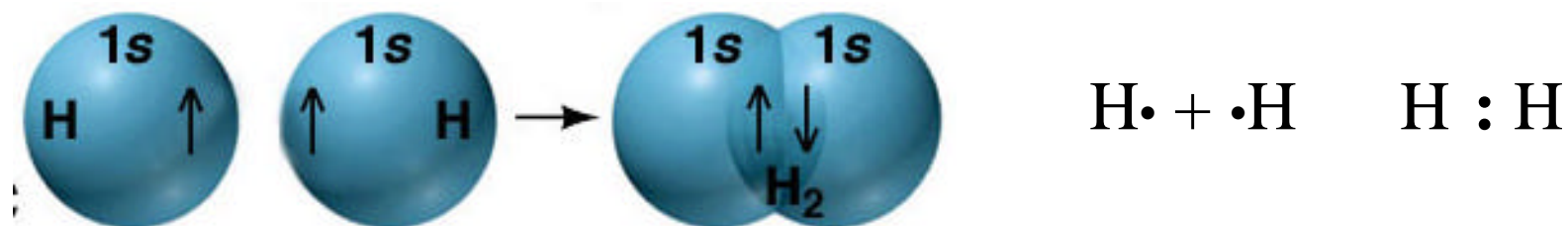
11.3 Molecular Orbital (MO) Theory and Electron Delocalization

- The Central Themes of MO Theory
- Homonuclear Diatomic Molecules of the Period 2 Elements
- Some Heteronuclear Diatomic Molecules
- MO Descriptions of Ozone and Benzene

Concept 11-1. The main ideas of valence bond theory, orbital overlap, opposing electron spins, and hybridization as a means of rationalizing molecular shapes orbitals.

Valence Bond Theory and Orbital Hybridization

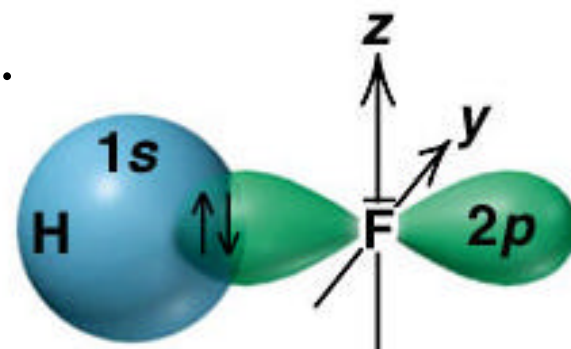
- VB theory bases molecular shape on orbital characteristics.
- In VB model, a covalent bond forms as orbitals from two atoms **overlap** and a pair of electrons occupies space between the nuclei.



- Three central ideas of VB theory :

1. **Opposing spins of the electrons must pair.**

The overlapping orbitals have a capacity of two electrons that must have opposite spins.

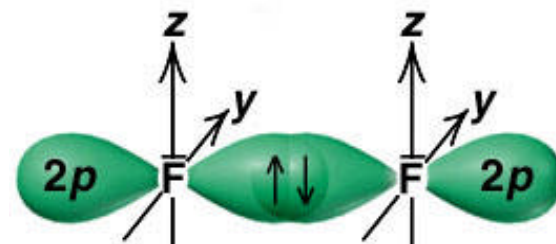


2. **Maximum overlap** of bonding orbitals.

The **bond strength** depends on attraction of the nuclei for the shared electrons, so the greater the orbital overlap, the stronger the bond.

3. Hybridization of atomic orbitals.

- Bonding in molecules like HF and F₂ results from direct overlap of s and p orbitals of atoms.



- Shapes of many polyatomic molecules/ions aren't easily explained using s orbitals and dumb-bell-shaped, perpendicular p orbitals.

Consider methane molecule: 4 H atoms bonded to a carbon.

- A ground-state carbon atom ([He] 2s²2p²) is not well suited to form four bonds.



- Linus Pauling proposed that the valence atomic orbitals in the molecule are different from those in the isolated atoms.
- He mathematically combined atomic orbitals in an atom to create new atomic orbitals with better characteristics for bonding.

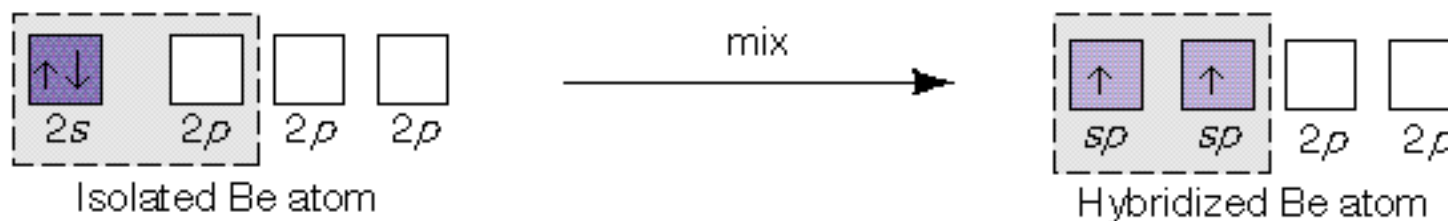
- Orbital mixing is called hybridization, and the mixed atomic orbitals are called **hybrid orbitals** (HO). Two key points are:
 - The number of hybrid orbitals obtained always equals the number of atomic orbitals (AO) mixed.
 - The type of HO's obtained varies with the types of AO's mixed.

Concept 11-2. How orbitals mix to form hybrid orbitals with different spatial orientations

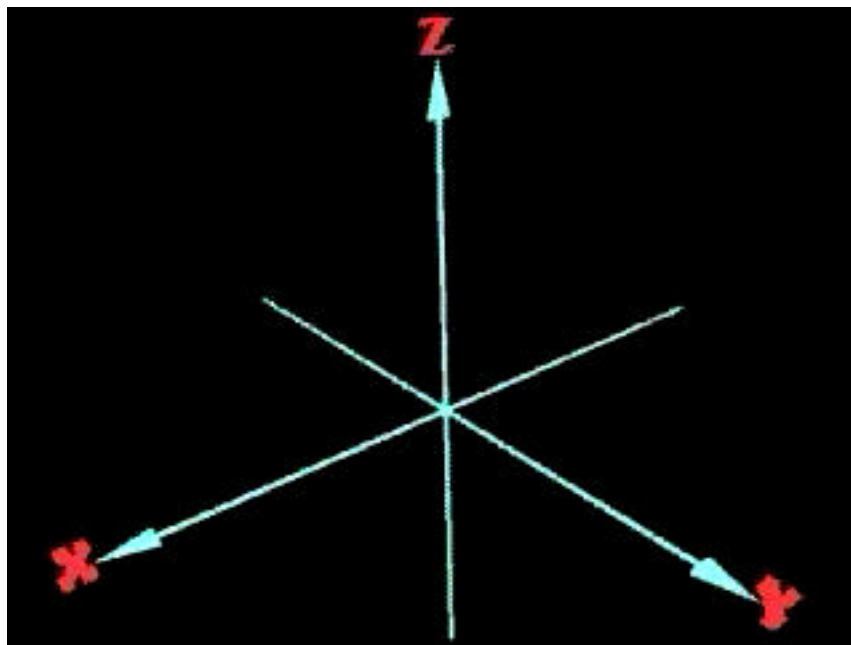
- The type of HO is picked after we know the molecular shape.

sp hybridization When two electron groups surround the central atom, as in AX_2 molecules like $BeCl_2(g)$, a **linear** shape is found.

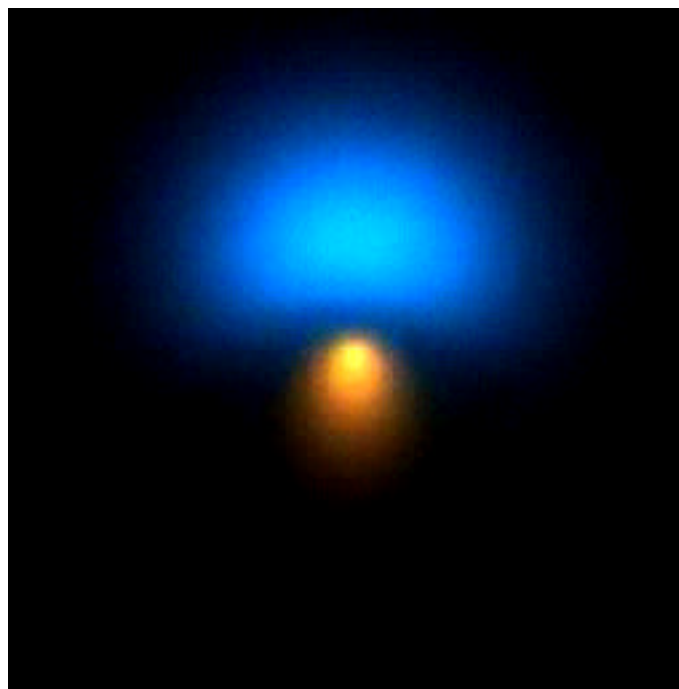
- VB theory proposes that mixing one s and one p AO on the central atom gives two equivalent **sp hybrid orbitals** that lie 180° apart.

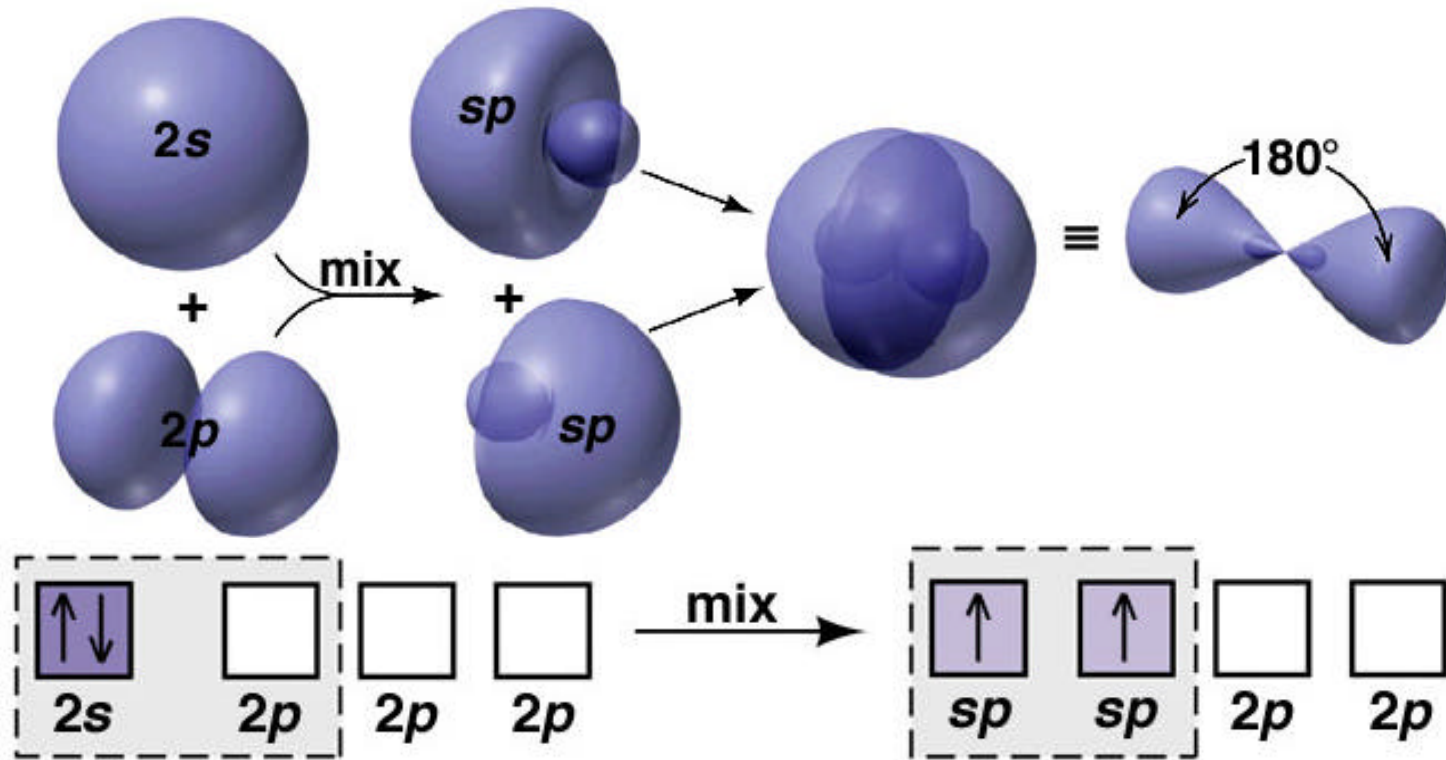


Animation of sp hybrid orbital formation

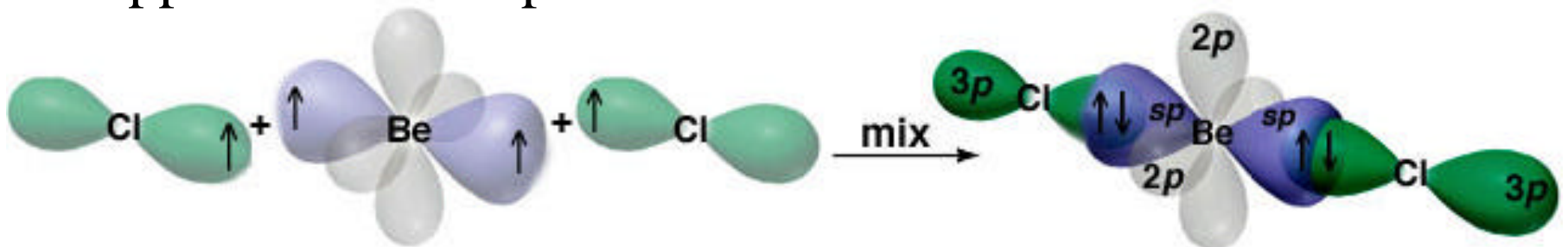


An accurate quantum mechanical representation of an sp HO



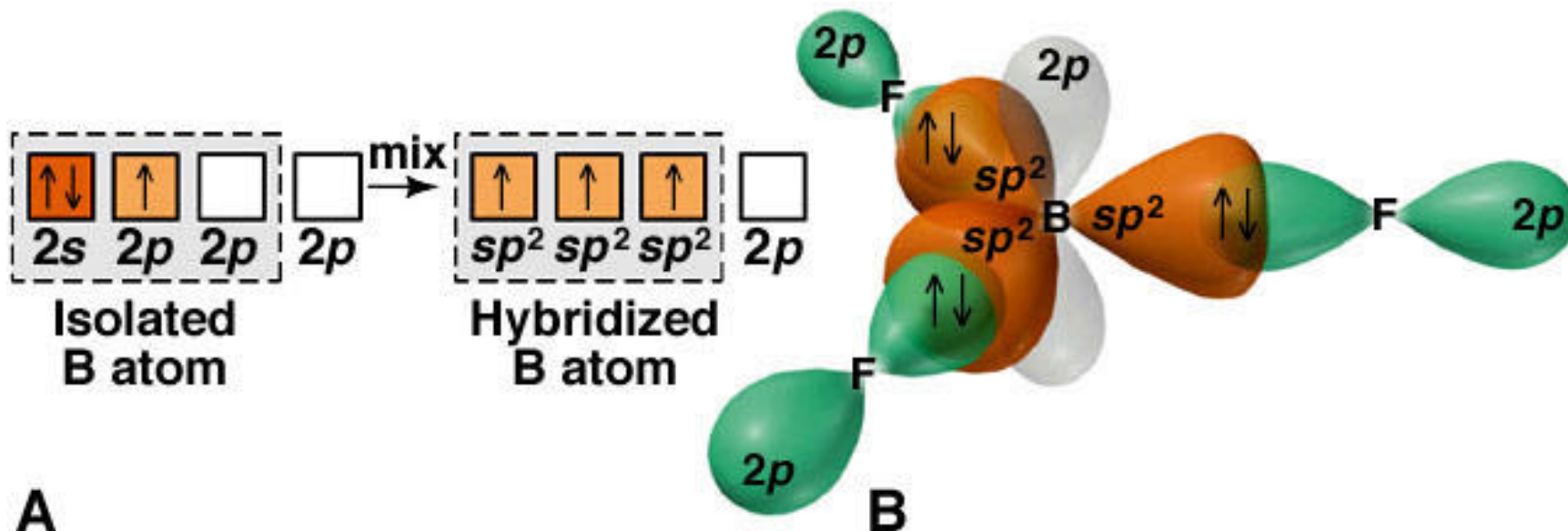


- The paired 2s electrons in the Be atom occupy sp HO's. These then form the Be–Cl bonds.
- The 4 valence e⁻ (2 from Be + 1 from each Cl) occupy the overlapped orbitals in pairs.



sp^2 hybridization. To explain a **trigonal planar molecule**, mix one s and two p orbitals of the central atom to give three sp^2 HO's.

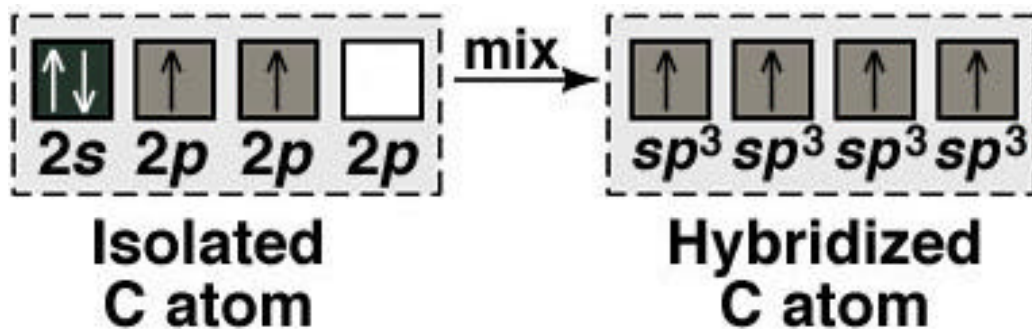
- VB theory shows the B atom in BF_3 molecule to be sp^2 hybridized.



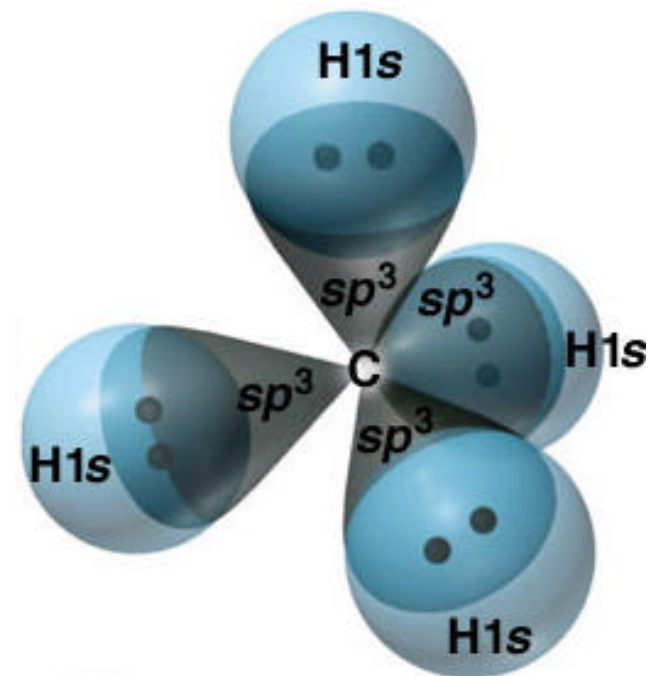
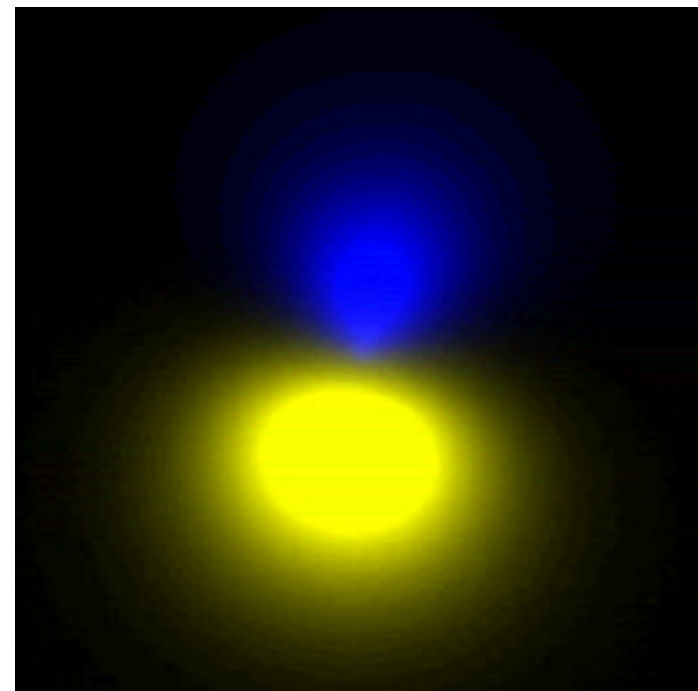
- The three sp^2 orbitals point to the corners of an equilateral triangle; the third, unhybridized 2p orbital lies perpendicular to the plane.
- The six valence electrons—three from B and one from each of the three F atoms—make up three bonding pairs.

sp^3 hybridization. In AX_4 shapes with a tetrahedral electron-group arrangement, one s and three p orbitals of the central atom are mixed.

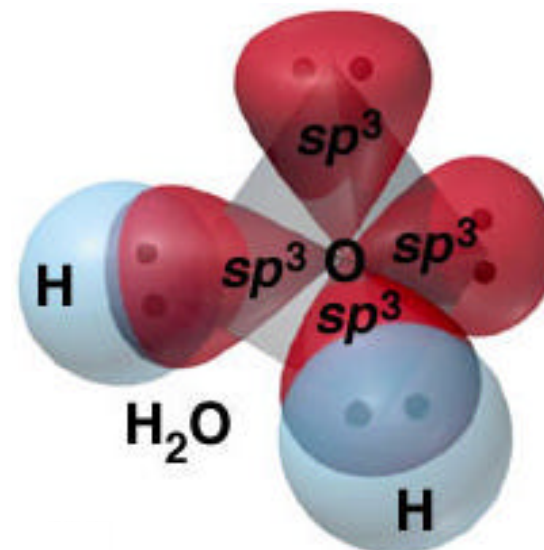
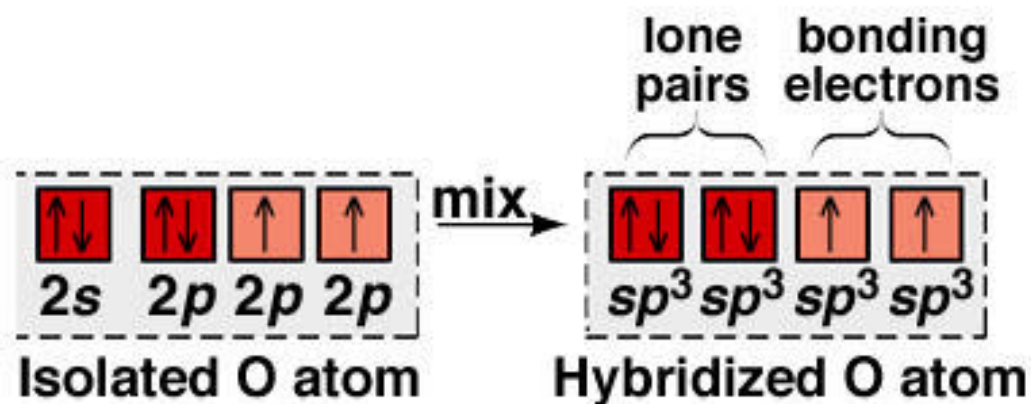
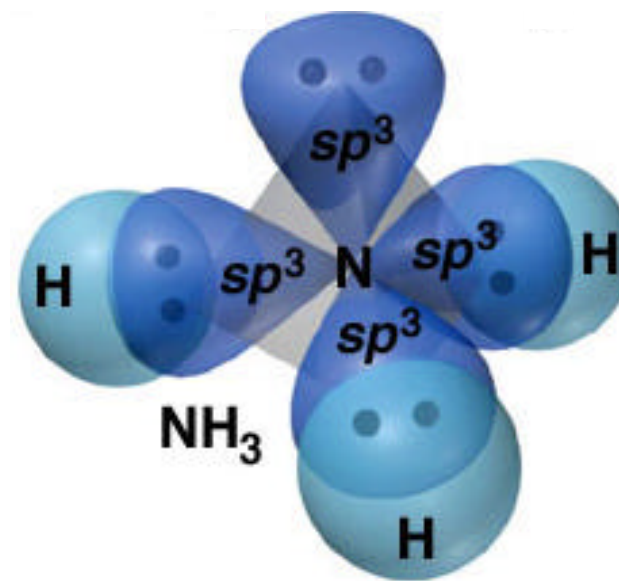
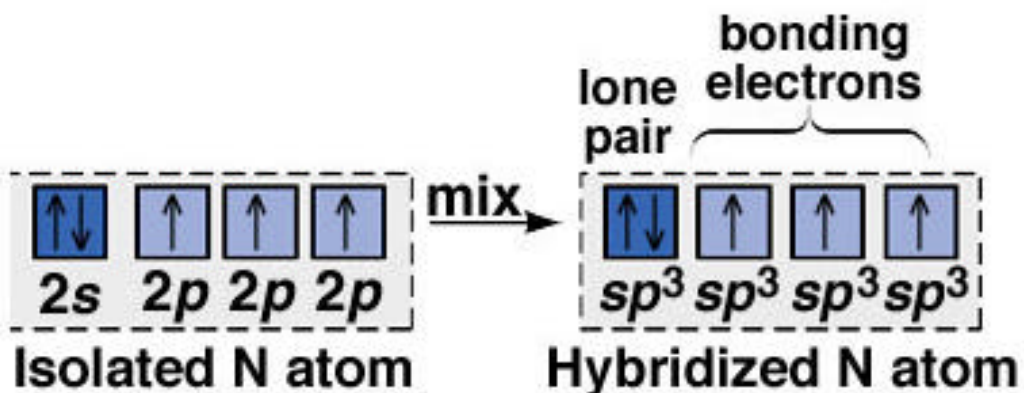
- Forms **four sp^3 hybrid orbitals**, which point toward the corners of a tetrahedron.
- Carbon in methane is sp^3 hybridized.



- Its 4 valence electrons, 2- 2s and 2- 2p, half fill the four sp^3 hybrids.
- These overlap the 1s orbitals on 4 H atoms and form 4 C–H bonds.

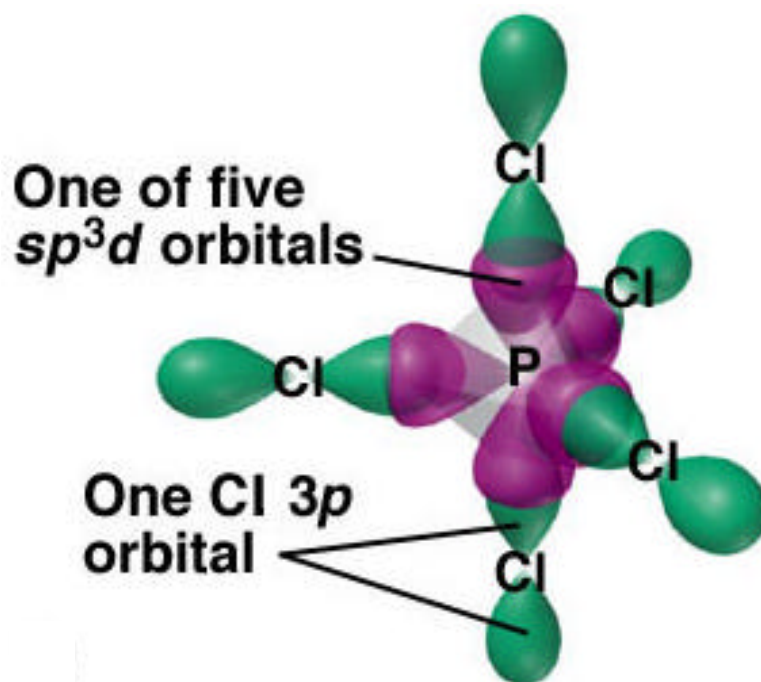
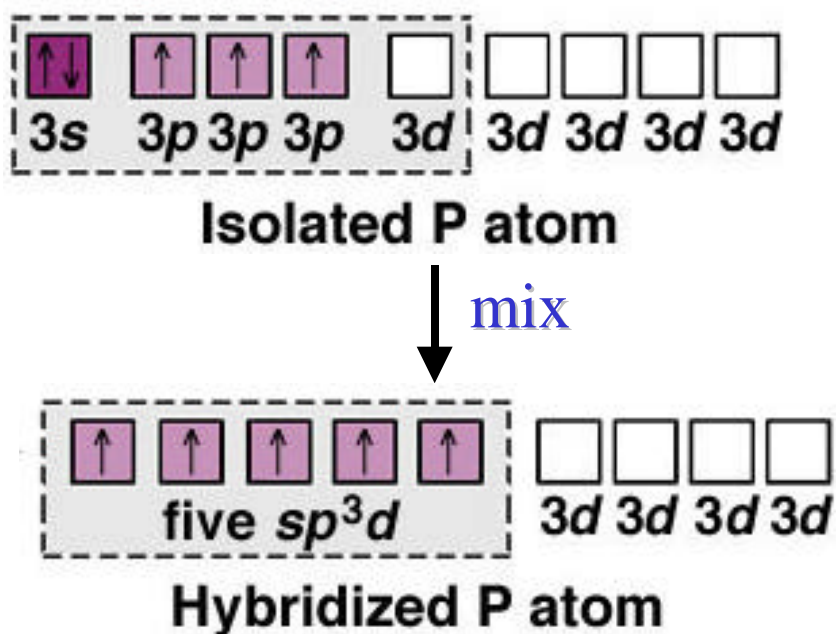


- In NH_3 , a lone pair fills one of the four sp^3 orbitals, whereas in H_2O , lone pairs fill two of them.

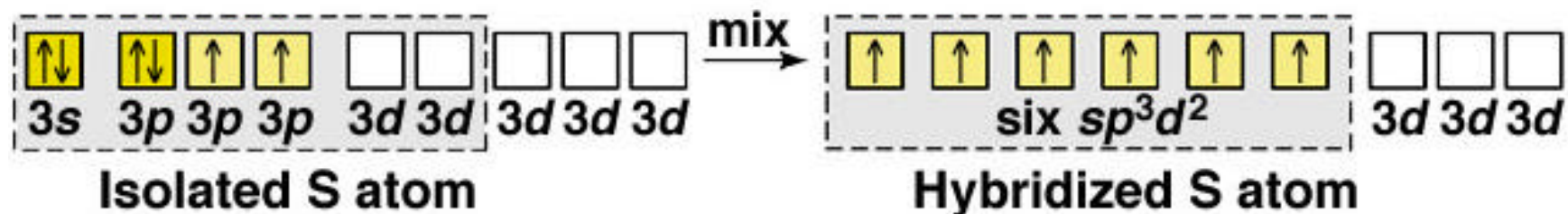


sp^3d hybridization. Trigonal bipyramidal molecules have central atoms from Period 3 or higher, so d orbitals can be hybridized.

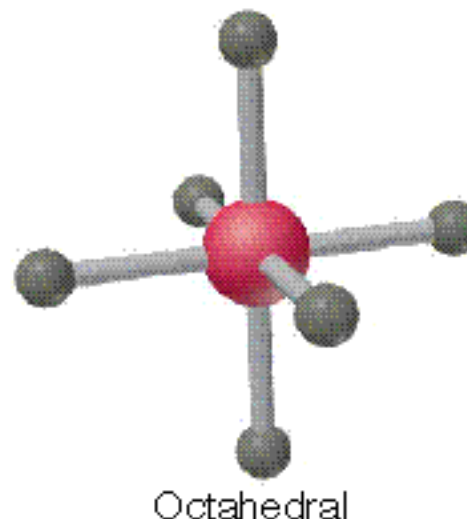
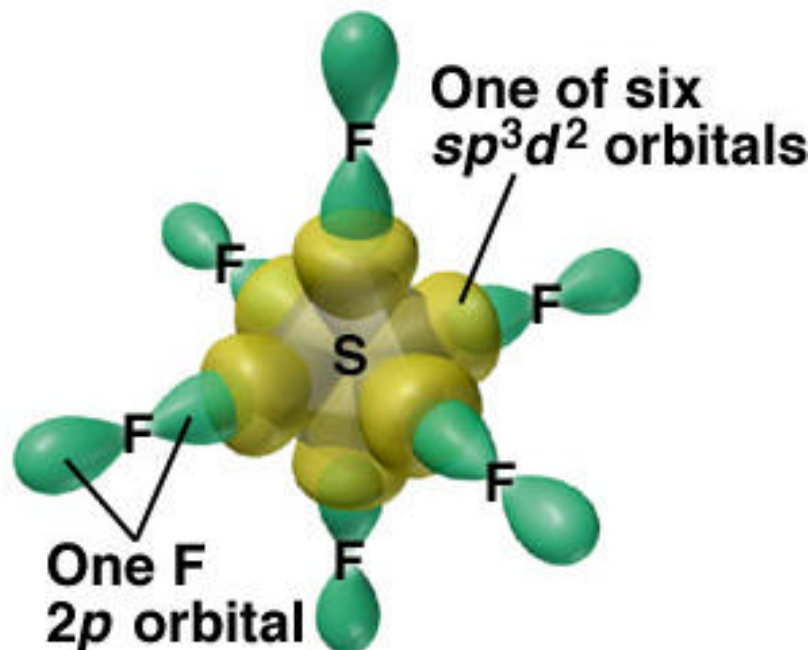
- In PCl_5 molecule, VB indicates that 3s, three 3p, and one of the five 3d orbitals of the P atom mix and form five **sp^3d hybrid orbitals**.
- Each sp^3d hybrid orbital overlaps a 3p orbital of a Cl atom.
- The five valence electrons of phosphorus, together with one from each of the five Cl atoms, pair up to form five P–Cl bonds



sp^3d^2 hybridization. For octahedral SF_6 , VB mixes the 3s, three 3p, and two 3d AO's of the central S atom forming **six sp^3d^2 HO's**.



- These point to the corners of an octahedron.
- Sulfur's 6 valence electrons half fill the HO's, each of which overlaps a half-filled 2p orbital of an F atom forming six S–F bonds.

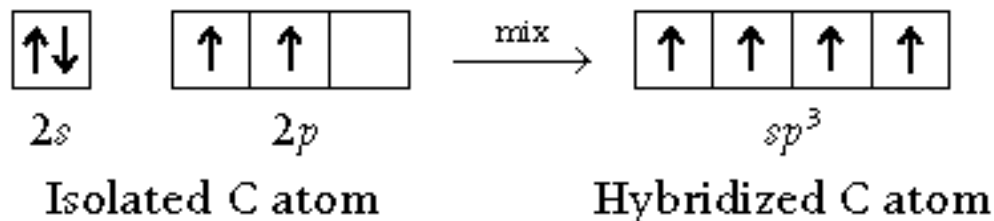


Postulating the Hybrid Orbitals in a Molecule

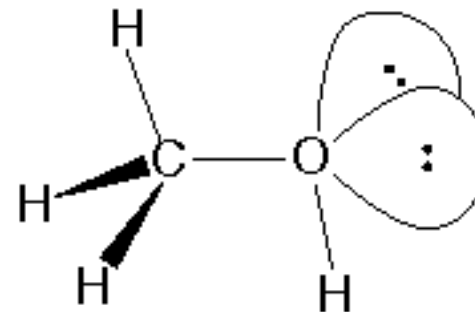
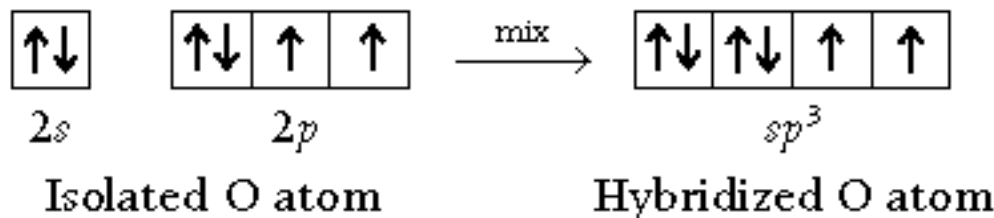
Problem: Describe how mixing AO's on the central atoms leads to the HO's in : (a) Methanol, CH_3OH (b) Sulfur tetrafluoride, SF_4

Plan: Find the number and arrangement of electron groups around central atoms and postulate the type of HO's needed. Write the box diagram for central atoms before and after orbitals are hybridized.

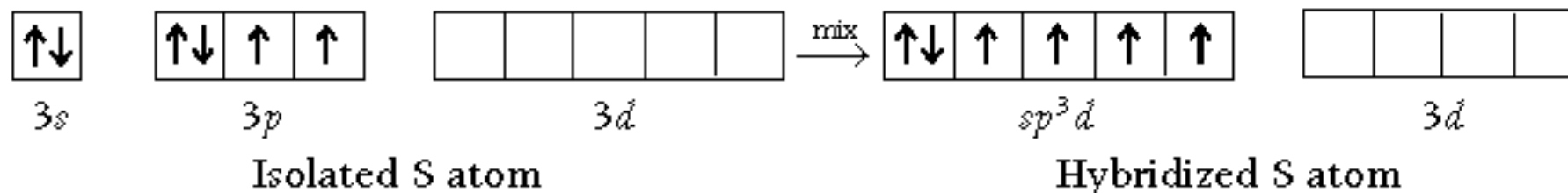
Solution: (a) CH_3OH The C is AX_4 and the O is AX_2E_2 so central atoms are sp^3 hybridized. The C atom has 4 half-filled sp^3 orbitals:



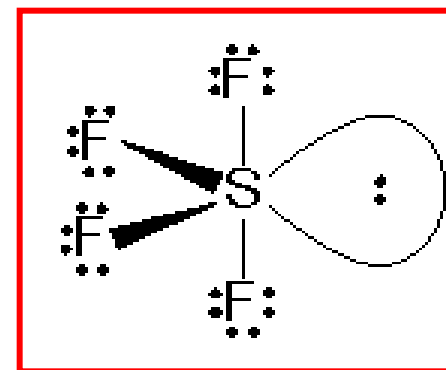
The O atom has two half-filled sp^3 HO's and two filled with lone pairs:



(b) SF_4 Molecular shape is seesaw. The central S atom is surrounded by five electron groups, which requires sp^3d hybridization.



One hybrid orbital is filled with a **lone pair** and four form S–F bonds.

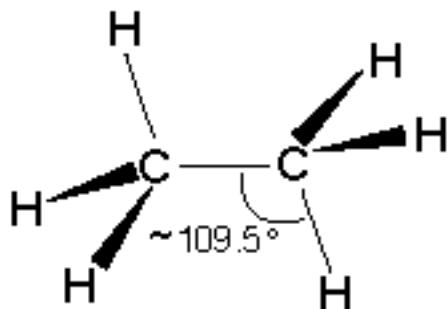


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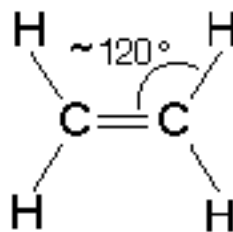
- H_2S molecule has a 92° bond angle, near the 90° angle between p AO's. Such angles occur in most hydrides with **large central atoms**.
- As the central atom becomes larger, electron repulsions decrease. Hybridization is not needed to explain the bond angles.

Concept 11-3. The distinction between end-to-end and side-to-side overlap and the origin of sigma (σ) and pi (π)

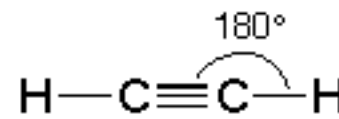
- VSEPR model predicts different shapes for the ethane (C_2H_6), ethylene (C_2H_4) and acetylene (C_2H_2) molecules.



ethane



ethylene

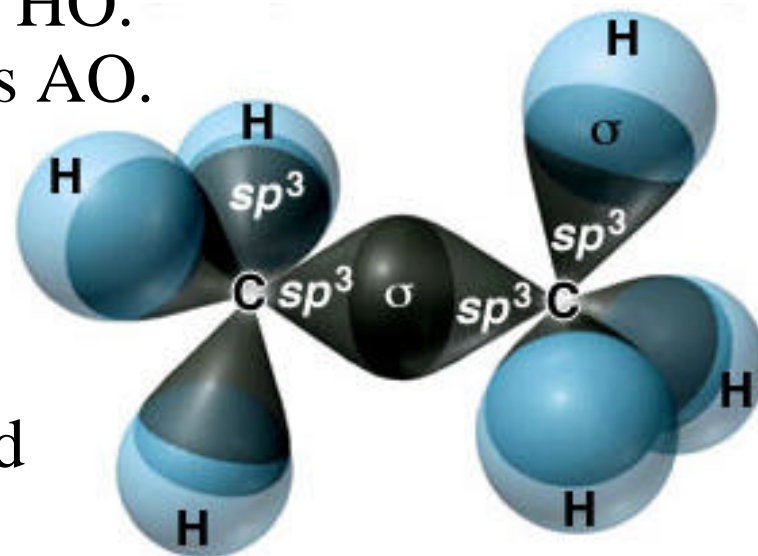


acetylene

- **Ethane:** **C–C bond:** C sp^3 HO - C sp^3 HO.
C–H bonds: C sp^3 HO - H 1s AO.

- Both have **end-to-end** overlap; highest electron density along the bond axis.

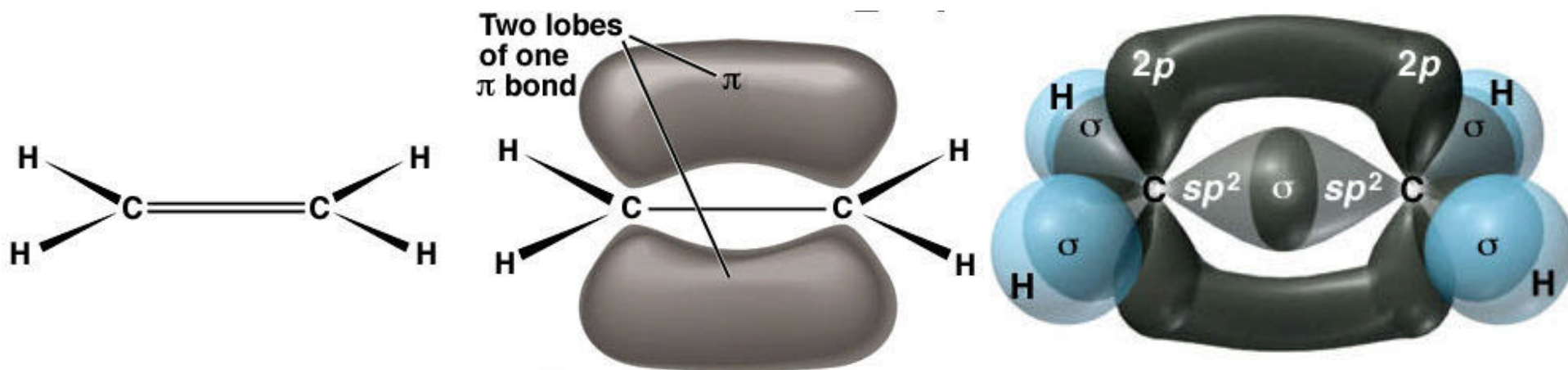
- **End to end overlap** \rightarrow sigma (σ) bond



Concept 11-4. How two modes of orbital overlap lead to single, double, and triple bonds

- **Ethylene** contains a carbon-carbon **double** bond. Each C atom is **AX₃**, so C forms three sp^2 HO's.

↑	↑	↑	↑
sp^2	sp^2	sp^2	p
- Each carbon uses the three sp^2 HO's to form sigma bonds; unhybridized 2p orbital lies perpendicular to the sp^2 plane.
- The π -bonded C atoms hold their half-filled unhybridized 2p AO's close together so they overlap **side to side** and form a **pi** (π) bond.

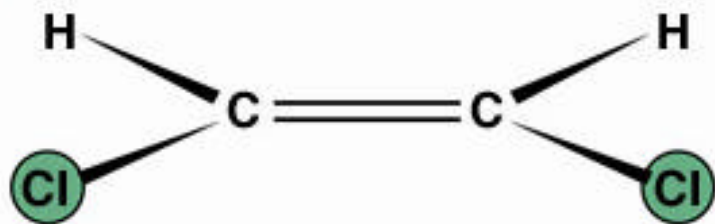


- A π bond has lobes **above** and **below** the σ -bond axis. One π bond holds 2 electrons that move through both regions.

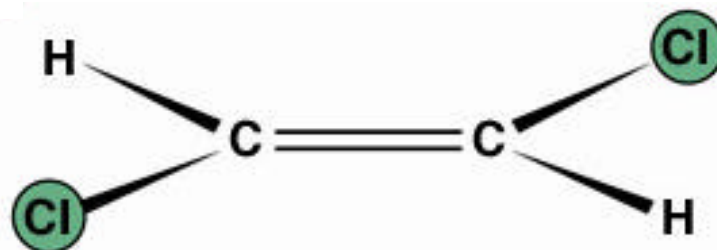
- Side-to-side overlap is not as extensive as end-to-end overlap, so a **bond is weaker than a bond**.
- As a result, the C=C bond energy of 614 kJ/mol is 80 kJ/mol less than twice that of the C–C bond (347 kJ/mol).

Concept 11-5. Why π bonding restricts rotation around double bonds.

- There is **free rotation** of the atoms around a σ bond because the extent of overlap is not affected.
- However, p orbitals must be parallel to engage in side-to-side overlap, so a π bond **restricts the rotation** of the atoms.
- This explains the existence of separate cis and trans structures in double-bonded molecules, such as dichloroethylene.

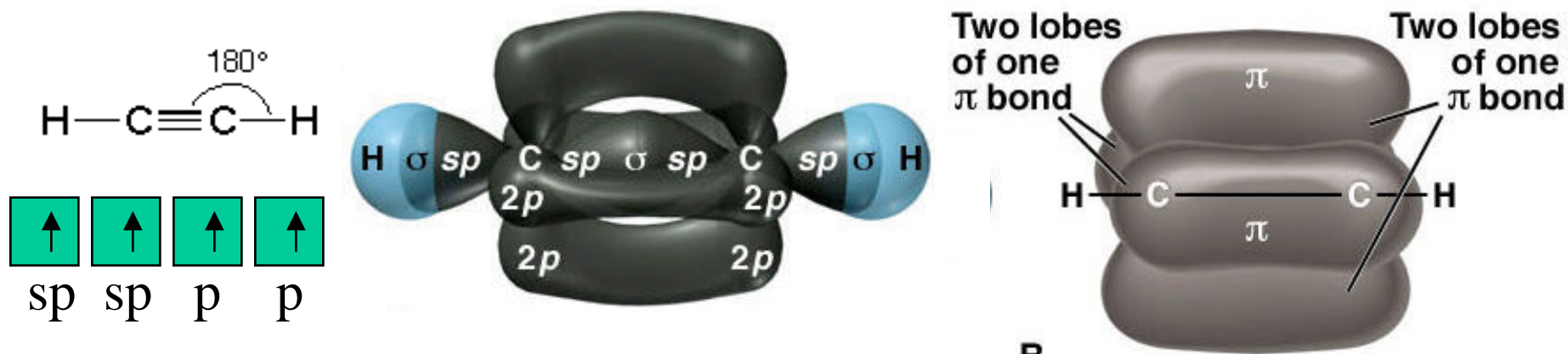


cis-dichloroethylene



trans-dichloroethylene

- The C-C bond in **acetylene** consists of **one** and **two** bonds. For linear shape, each C uses 2 sp HO's for C-C and C-H bonds.
- Two 2p orbitals on each C are unhybridized forming **two** bonds.



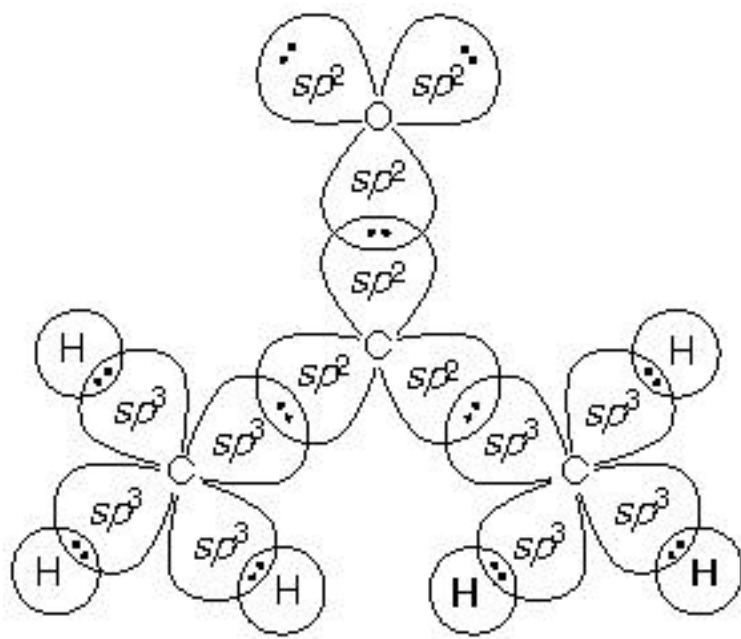
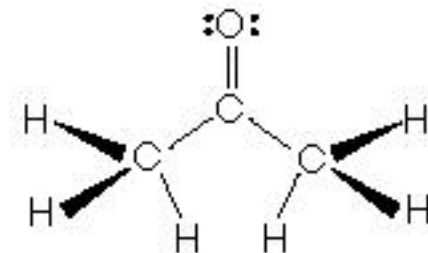
- Side-to-side overlap of the pairs of 2p AO's gives a pair of bonds, oriented at 90° to one another.
- Lobes of one bond are **above** and **below** the bond. Lobes of the other bond are **in front of** and **behind** the bond.

Describing the Bonding in Molecules with Multiple Bonds

Problem: Describe the bonds and orbitals in acetone, $(\text{CH}_3)_2\text{CO}$.

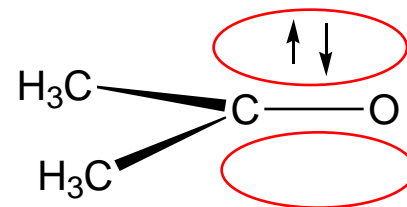
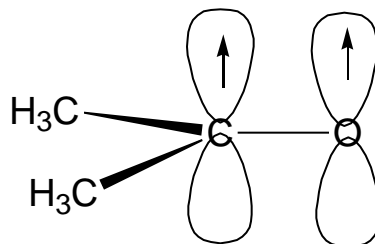
Solution: Each C of the two CH_3 groups are AX_4 so use sp^3 HO's and the middle C is AX_3 so uses sp^2 HO's.

The O atom is sp^2 hybridized also. Two of its sp^2 orbitals hold lone pairs; the third forms a π bond with the third sp^2 orbital of the middle C atom.



σ bonds

The unhybridized, half-filled p orbitals on C and O form a **π bond**.



Molecular Orbital (MO) Theory and Electron Delocalization

Concept 11-6. The distinction between the localized bonding of VB theory and the delocalized bonding of MO theory.

- In **MO theory**, a molecule is a collection of nuclei with the electrons in orbitals that are **delocalized** over the structure.
- Just as atoms have AO's of a given energy and shape, molecules have **molecular orbitals (MO's)** of certain energies and shapes.

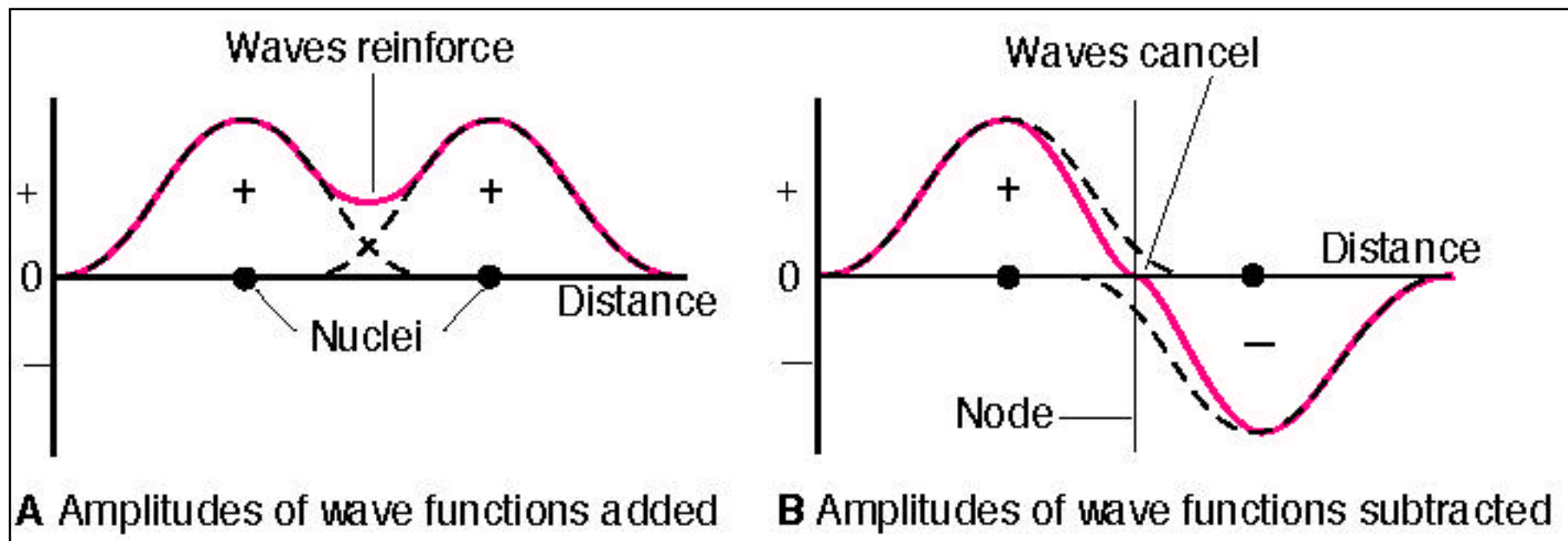
Concept 11-7. How addition or subtraction of AOs form bonding or antibonding MO's.

- In the LCAO approximation, used to obtain energies and shapes of MOs, MOs are derived from a **Linear Combination of AO's**.
- LCAO combines atomic orbitals (atomic wave functions) of nearby atoms to form the molecular orbitals (molecular wave functions).

- H_2 molecule: two H nuclei lie near each other so their AOs **overlap**.
- Adding their wave functions together forms a **bonding MO**, which allows a region of higher electron density between the nuclei.

$$\text{AO of } H_A + \text{AO of } H_B = \text{bonding MO of } H_2$$

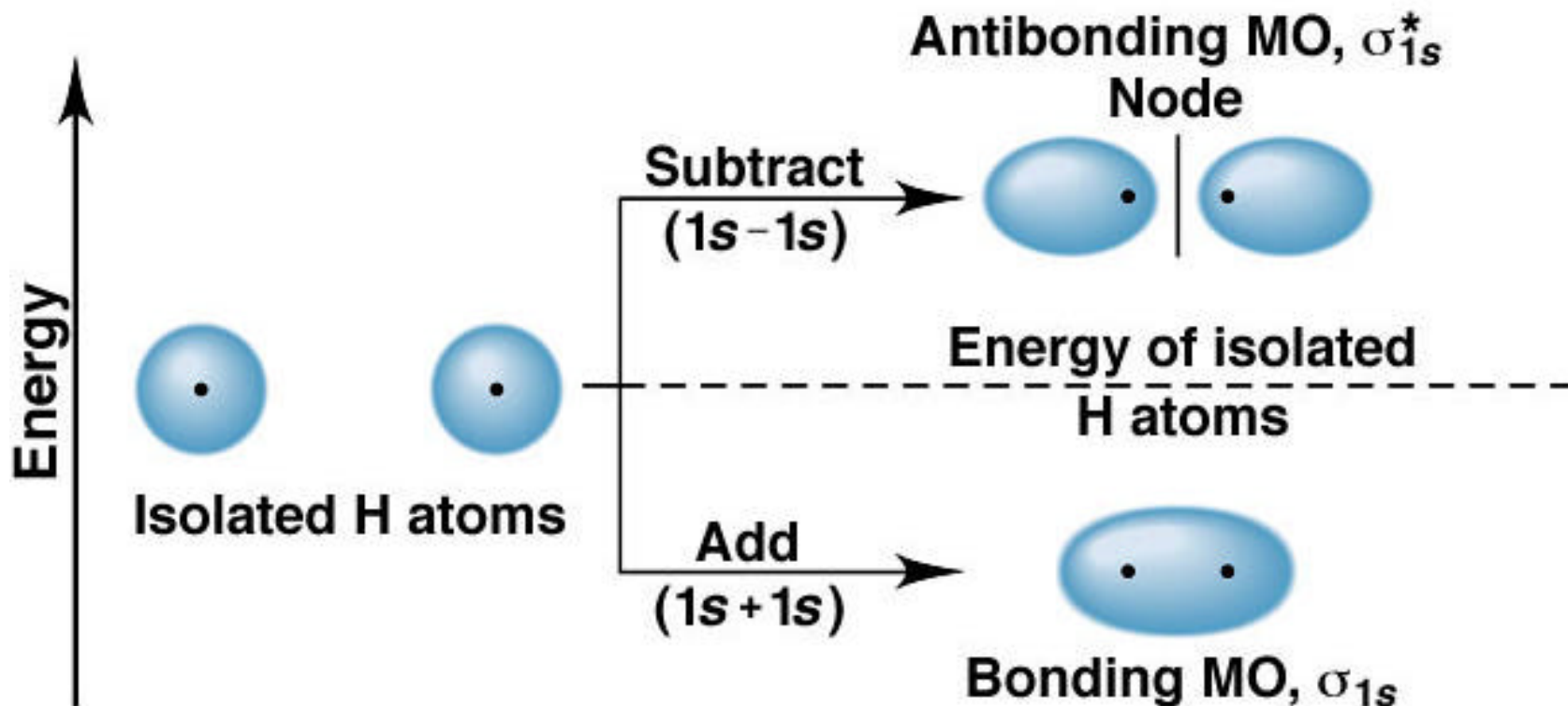
$$\text{AO of } H_A - \text{AO of } H_B = \text{antibonding MO of } H_2 \quad (\text{less } e^- \text{ density between nuclei})$$



- The number of AOs combined always equals the number of MOs formed: **two H AOs** form **two H_2 MOs**.

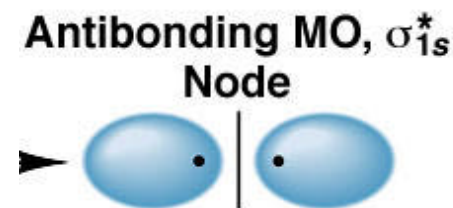
Concept 11-8. Shapes of MOs formed from combinations of two s orbitals and combinations of two p orbitals

- 1s AOs of H atoms have same energy, so they interact strongly.



- Charge delocalization lowers the energy of the bonding MO. When electrons occupy σ_{1s} , H_2 is more stable than the separate H atoms.

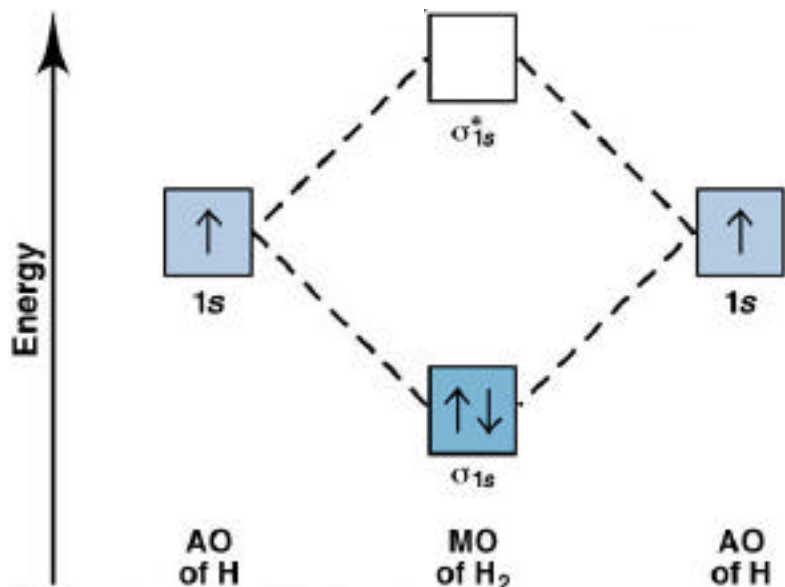
- Antibonding MO (σ_{1s}^*) has a node between the nuclei and most of its electron density outside the internuclear region.
- This increases **nuclear repulsions** making the antibonding MO higher in energy than the isolated AOs.
- When the antibonding orbital is occupied, the molecule is less stable than when the orbital is empty.



Filling molecular orbitals with electrons. Electrons fill MOs in the same way that they fill AOs:

- Orbitals are filled in order of increasing energy.
- An MO has a maximum capacity of 2 electrons with paired spins.
- Orbitals of equal energy are half filled, with spins parallel, before any is filled with two electrons.

MO energy diagrams show the relative energy and number of electrons in each MO and the AOs that originally held the electrons.



Concept 11-9. How MO bond order predicts the stability of molecules.

- The MO **bond order** is the number of electrons in bonding MOs minus the number in antibonding MOs, divided by two:

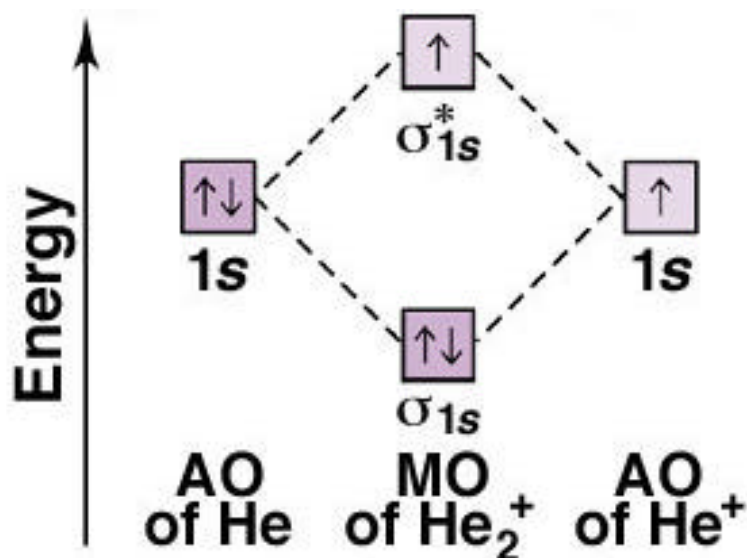
$$\text{Bond order} = \frac{1}{2}[(\text{no. of } e^- \text{ in bonding MO}) - (\text{no. of } e^- \text{ in antibonding MO})]$$

Thus, for H_2 , the bond order is $1/2(2 - 0) = 1$.

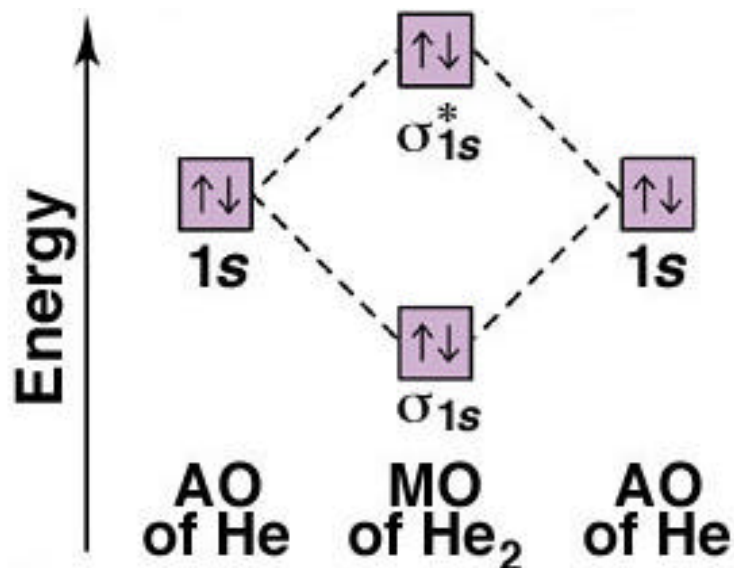
- A bond order greater than zero indicates that the molecule or ion is stable relative to the separate atoms.
- The higher the bond order, the stronger is the bond.

- **MO electron configuration:** symbol of each occupied MO shown in parentheses with the number of its electrons written as a superscript.
- The MO electron configuration of H_2 is $(\sigma 1s)^2$.

An early success of MO theory was in predicting the existence of He_2^+ , which is composed of two He nuclei and three electrons.



He_2^+ bond order is
 $1/2 (2 - 1) = 1/2$



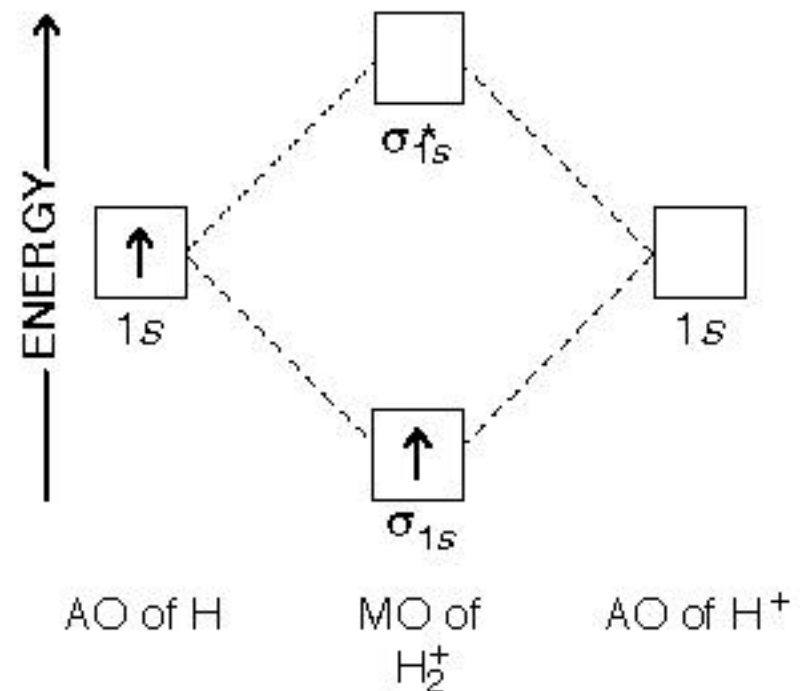
He_2 bond order is
 $1/2 (2 - 2) = 0$

Predicting Species Stability Using MO Energy Diagrams

Problem: Use MO diagrams to predict whether H_2^+ and H_2^- exist. Determine their bond orders and electron configurations.

Plan: These ions use $1s$ orbitals to form MOs, so the MO diagrams are like that of H_2 . Determine the number of electrons in each, place them in bonding and antibonding MOs and find the bond orders.

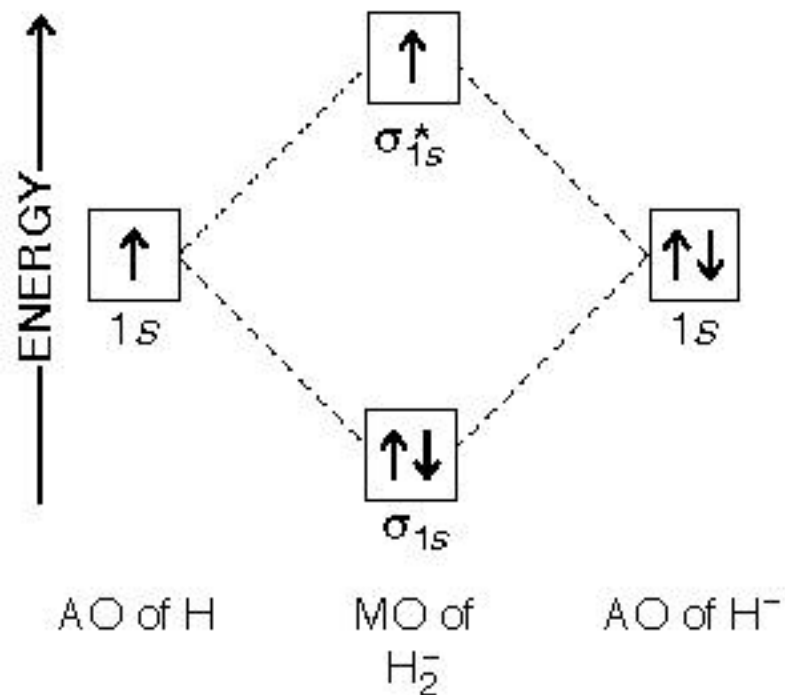
Solution: For H_2^+ the bond order is $1/2(1 - 0) = 1/2$, so we predict that H_2^+ does exist.



Since H_2 has two e^- , H_2^- has three e^- .

The bond order is $1/2(2 - 1) = 1/2$, so we predict that H_2^- also exists.

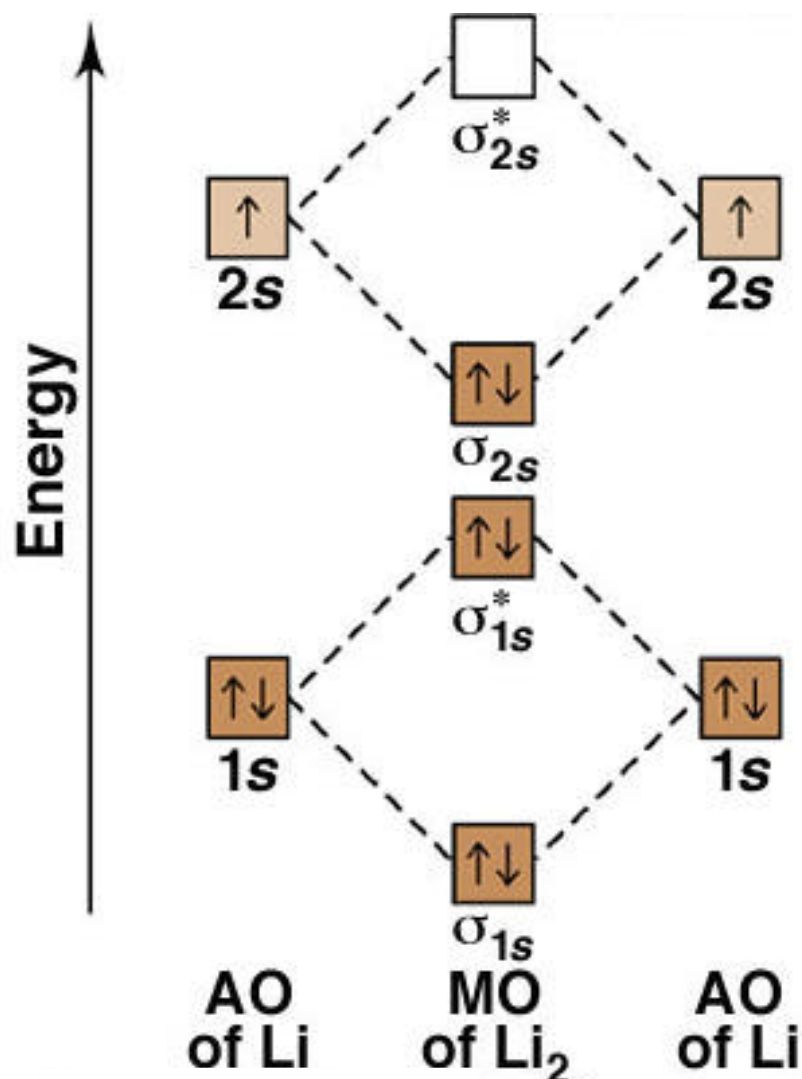
Concept 11-10. How MO theory explains the bonding and properties of the diatomic molecules of Period 2



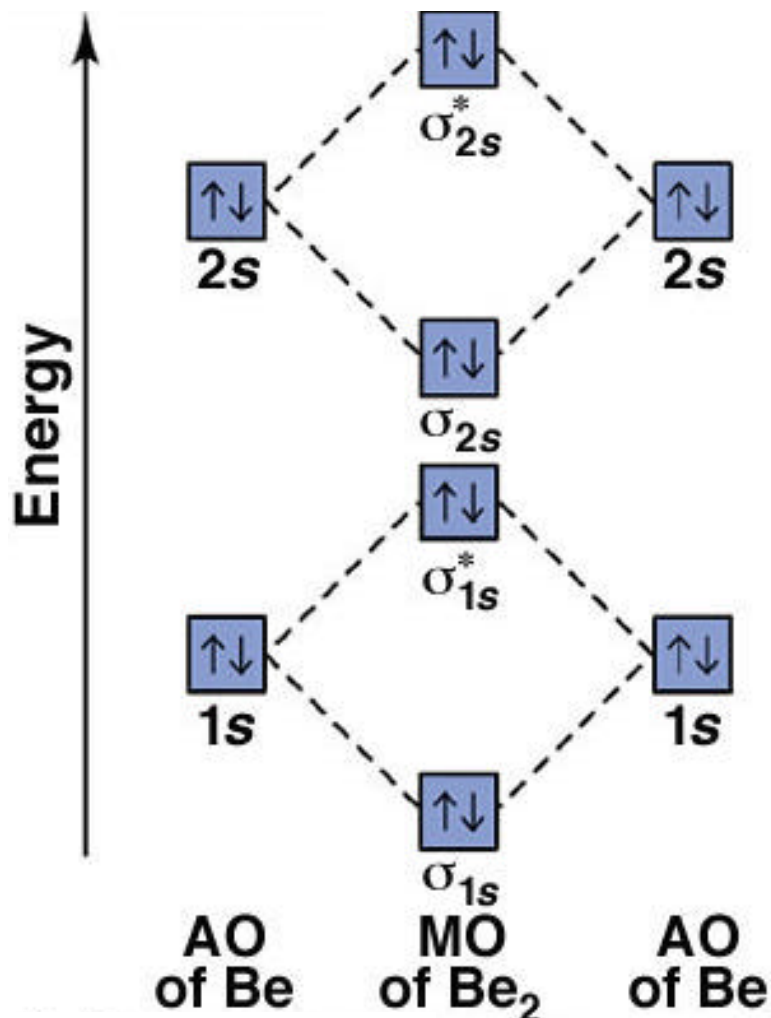
- The s-block diatomic molecules, Li_2 and Be_2 , use their valence **2s AO's** to form molecular orbitals.
- Like the MOs formed from 1s orbitals, those formed from 2s atomic orbitals are **σ MO's**.
- A 2s AO is higher in energy than a 1s, so the **2s** and ***2s** MOs are higher in energy than the 1s and ***1s** MOs.

- Dilithium has 4 electrons in bonding MOs and 2 in antibonding MOs, so its bond order is $\frac{1}{2}(4 - 2) = 1$.

- Electron configuration is $(1s)^2(\sigma^*1s)^2(\sigma 2s)^2$.



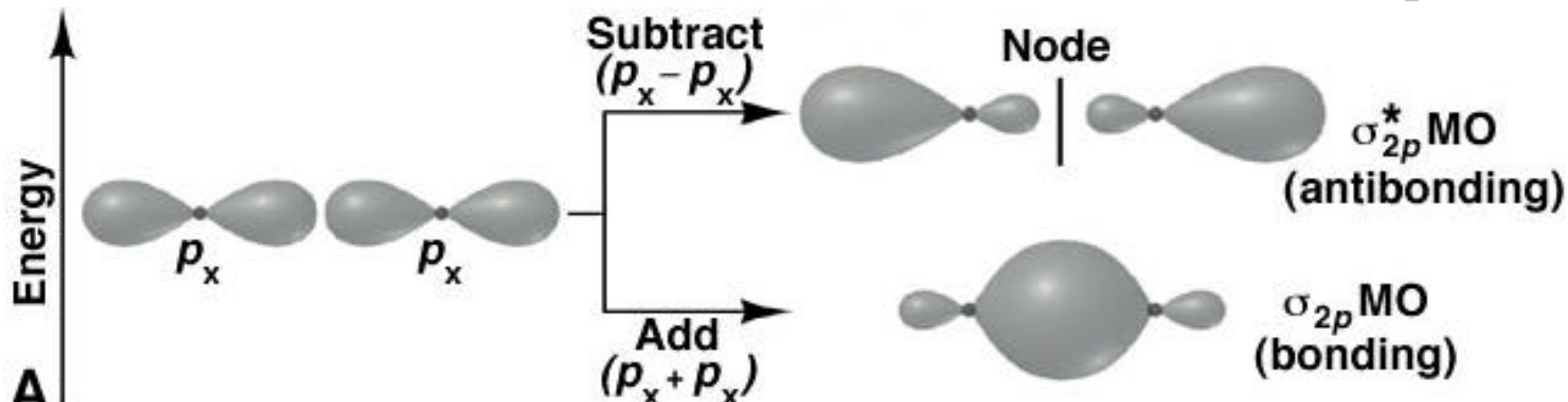
- Usually show only configuration of the MOs formed from valence electrons: $(\sigma 2s)^2$.



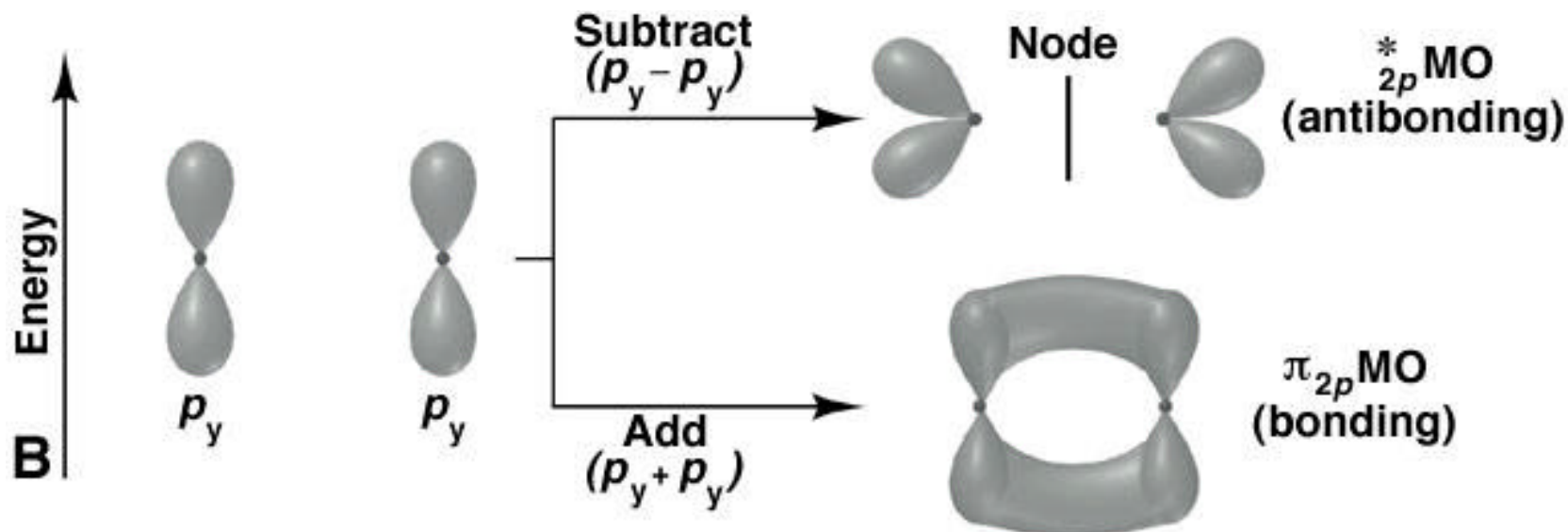
- The MO diagram for Be_2 has filled $2s$ and σ_{2s}^* MOs.
- The bond order is $\frac{1}{2}(4 - 4) = 0$.
- The compound, Be_2 has never been observed.

Molecular orbitals from atomic p-orbital combinations.

- End-to-end overlap of p AOs gives two MOs, the $2p$ and $*2p$.



- Side-to-side combination gives a pair of pi () MOs, $2p$ and $*2p$.

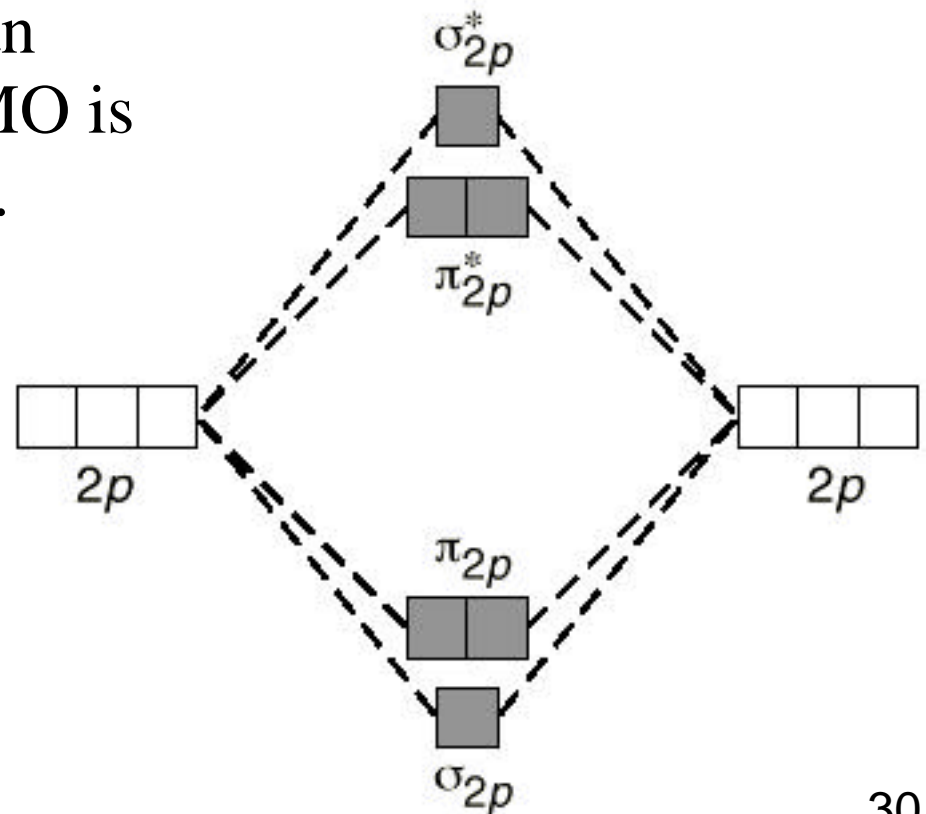


- Another pair of MO's from the two p_z AO's; same energy as p_y MO's

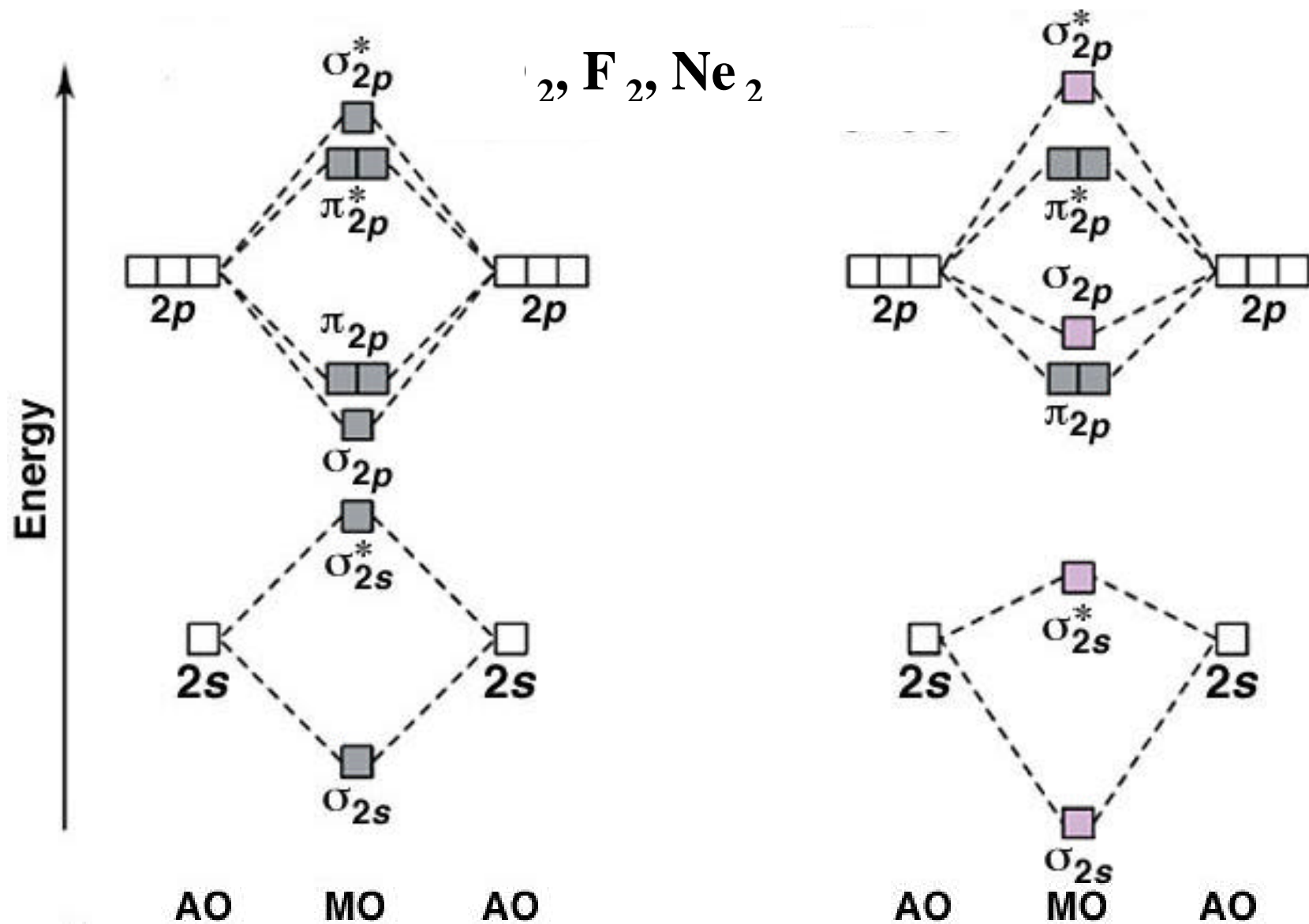
Energy level diagram

- MOs from 2p AOs are higher in energy than MOs from 2s AOs because 2p AOs are higher in energy than 2s AOs.
- Bonding MOs are lower in energy than antibonding MOs, so σ_{2p} is lower in energy than σ_{2p}^* and π_{2p} is lower than π_{2p}^* .
- 3. End-to-end overlap is greater than side-to-side overlap, so the σ_{2p} MO is lower in energy than the π_{2p} MO.
- The energy order for MOs derived from 2p orbitals is:

$$\sigma_{2p} < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}^*$$



- The MO energy order depends on how close the s and p AOs are in energy. If they do not interact, order is: $\sigma_{2p} < \pi_{2p} < \pi_{2p}^* < \sigma_{2p}^*$

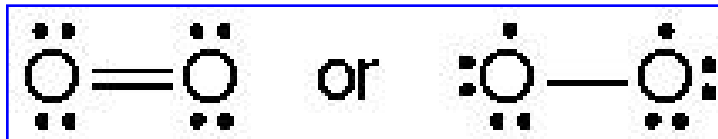




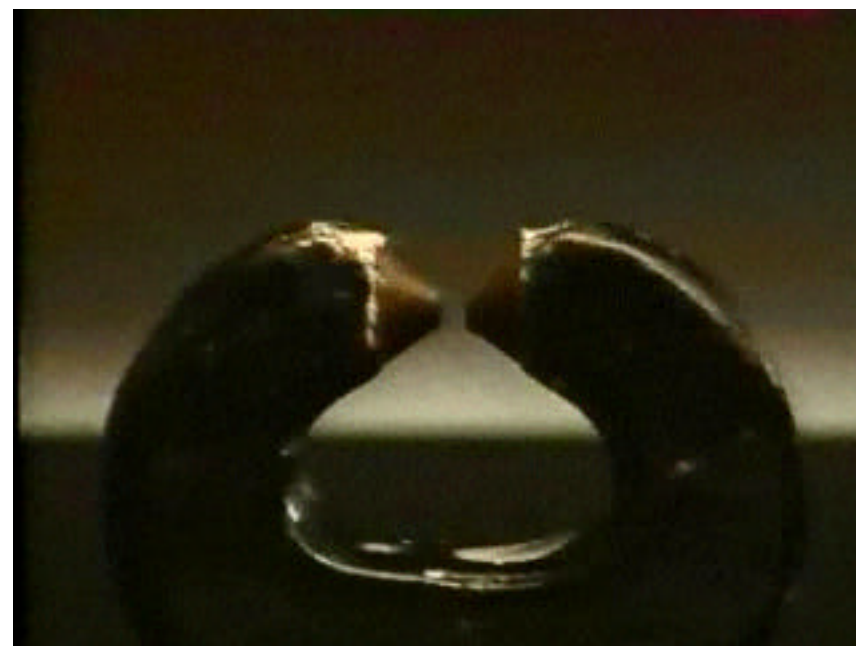
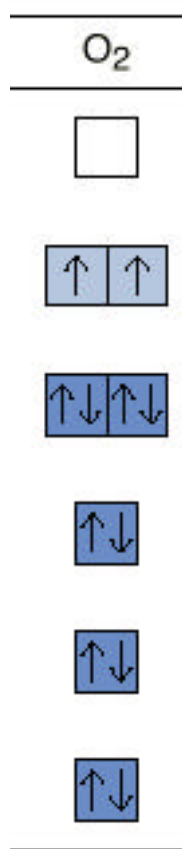
		With 2s-2p mixing			Without 2s-2p mixing				
		B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂		
σ_{2p}^*		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	σ_{2p}^*	
π_{2p}^*		<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	π_{2p}^*	
σ_{2p}		<input type="checkbox"/>	<input type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	π_{2p}	
π_{2p}		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	σ_{2p}	
σ_{2s}^*		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	σ_{2s}^*	
σ_{2s}		<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	σ_{2s}	

- O₂ molecule, by experiment, is **paramagnetic**.

- O₂ has two possible Lewis structures:



- O₂ bond energy = 498 kJ/mol suggests a double bond in O₂.



- By MO theory the bond order of O₂ is **2**:

$$\text{B.O.} = 1/2(8 - 4) = 2].$$

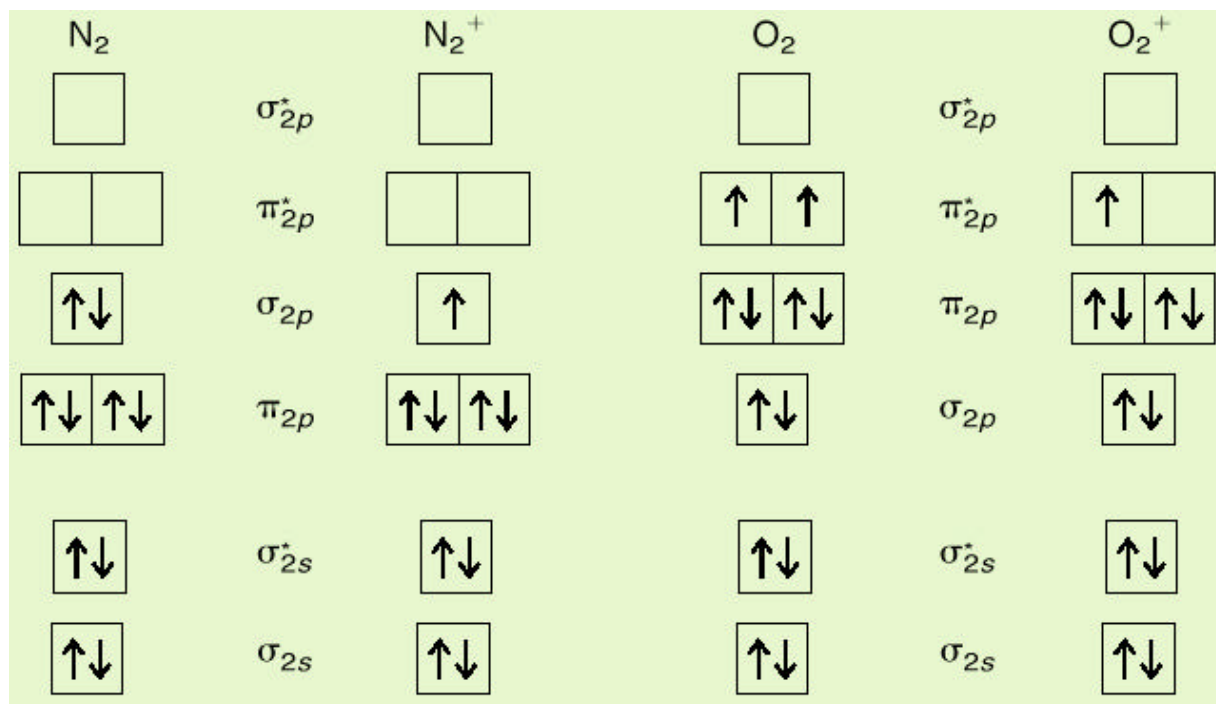
- The two electrons with highest energy occupy the two ***2p MOs** with unpaired spins, making the molecule **paramagnetic**.

Using MO Theory to Explain Bond Properties

Problem: Consider this data for homonuclear diatomic species:

	N_2	N_2^+	O_2	O_2^+
Bond energy (kJ/mol)	945	841	498	623
Bond length (pm)	110	112	121	112
No. of valence electrons	10	9	12	11

Why does bond energy **decrease** from N_2 to N_2^+ but **increase** from O_2 to O_2^+ ?



$$\frac{1}{2}(8 - 2) = 3 \quad \frac{1}{2}(7 - 2) = 2.5 \quad \frac{1}{2}(8 - 4) = 2 \quad \frac{1}{2}(8 - 3) = 2.5$$

Predicted order of bond energy: $\text{N}_2 > \text{N}_2^+$ and $\text{O}_2^+ > \text{O}_2$ 34