

VSEPR theory

Valence shell electron pair repulsion

Covalent Bond Theories

1. VSEPR (valence shell electron pair repulsion model).

A set of *empirical* rules for predicting a molecular geometry using, as input, a correct Lewis Dot representation.

2. Valence Bond theory.

A more advanced description of orbitals in molecules. We emphasize just one aspect of this theory: Hybrid atomic orbitals.
Works especially well for organic molecules, which is the reason we don't scrap it entirely for MO theory.

3. Molecular Orbital theory.

The most modern and powerful theory of bonding. Based upon QM.

On the Value of Lewis Structures

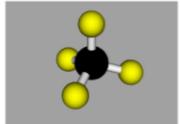
A Lewis structure is a **two-dimensional** (2D) representation of a molecule.

Lewis structures are used in conjunction with valence shell electron-pair repulsion (VSEPR) theory to predict the **three-dimensional** (3D) shapes of molecules.

We first consider Lewis structures for molecules with **single bonds** (bond order = 1).

Molecular Shape

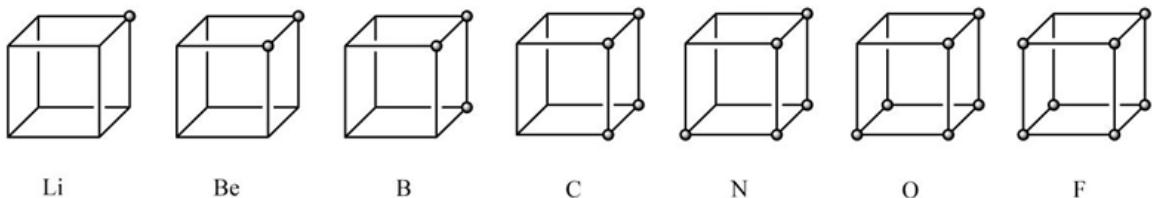
BUT, molecules are 3 dimensional!



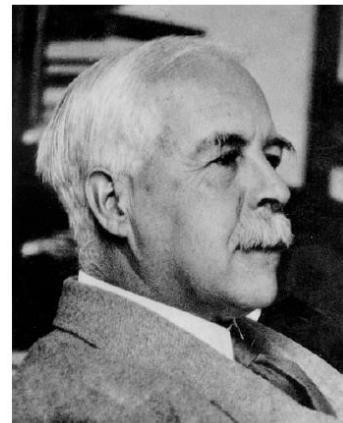
- in 3D it is:
a tetrahedron!

- = coming out of page
- = going into page
- = flat on page

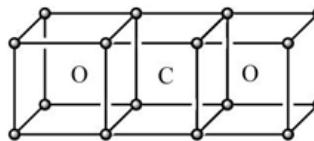
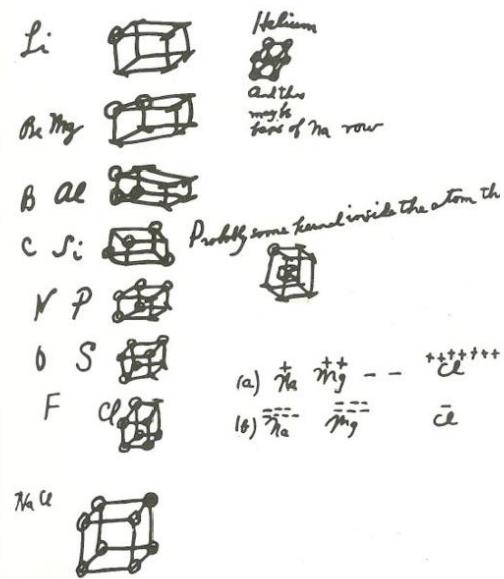
One of the most important discoveries of the 20th century was Lewis's description of the chemical bond as a shared pair of electrons. This remarkably brilliant idea connected some of the most important inventions in chemistry from the 19th century; like the Mendeleev's periodic table of elements and the van 't Hoff's formulation of the tetrahedral carbon. Lewis's idea also laid down the foundation of some advanced theoretical models for chemical bonding used today. The cubical atoms and the concept of shared electron pairs proposed by Lewis in 1919 can be illustrated as shown below.



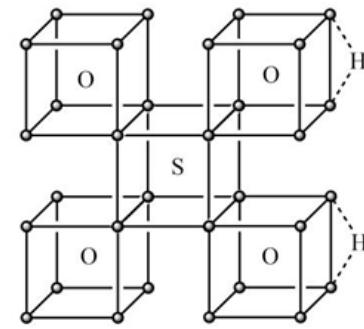
G. N. Lewis tried to develop a geometrical model for atoms and chemical bonding -- but failed.



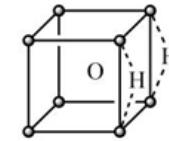
G. N. Lewis
1875-1946



CO₂

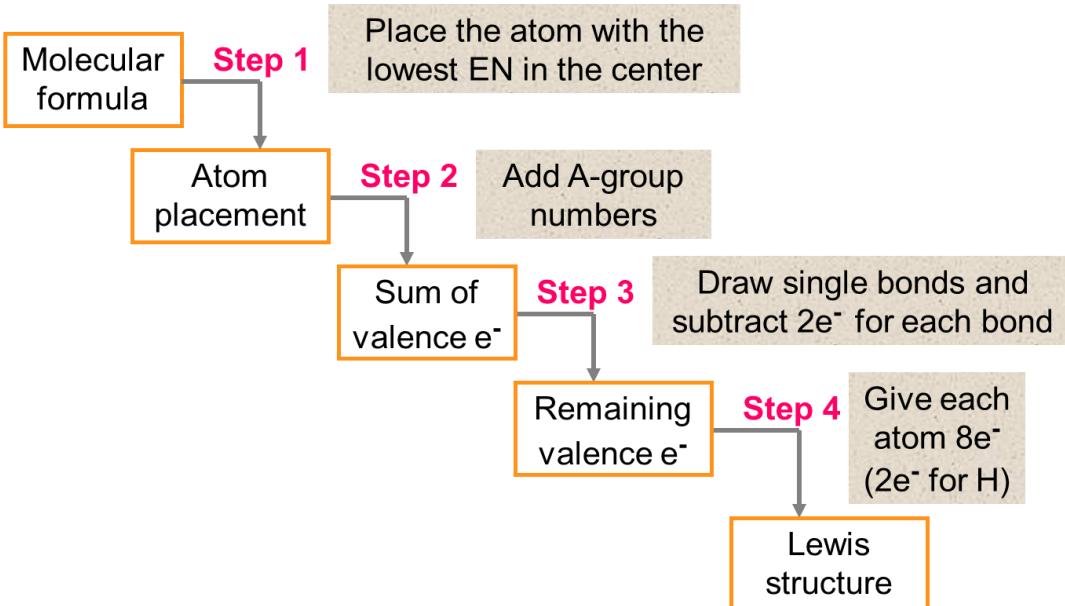


H₂SO₄



H₂O

Steps to convert a molecular formula into a Lewis structure

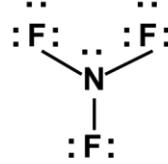
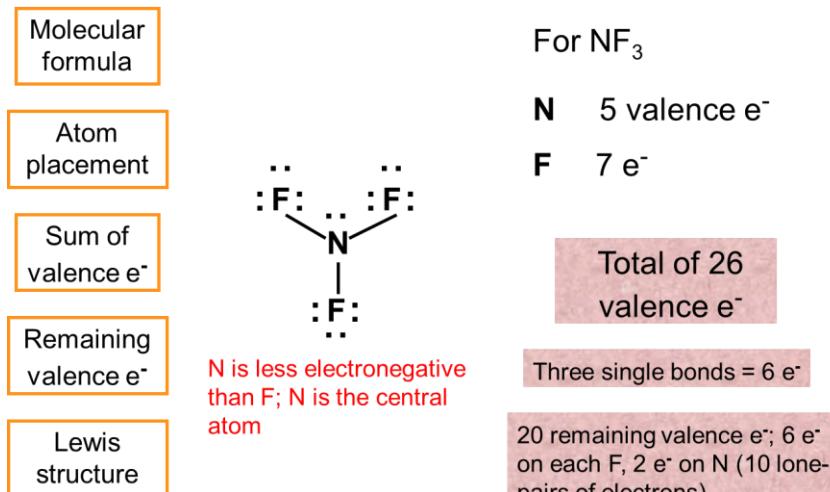
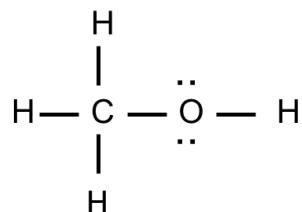


PROBLEM: Write the Lewis structure for methanol (molecular formula, CH_4O), a compound used as a gasoline additive/alternative in auto engines.

SOLUTION: Hydrogen can have only one bond. Thus, C and O must be next to each other, with H filling in the bonds.

There are $4(1) + 1(4) + 1(6) = 14$ valence electrons.

C has 4 bonds and O has 2. O has two pairs of unshared e^- .



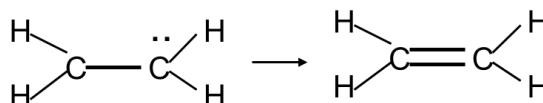
PROBLEM: Write Lewis structures for the following:

(a) Ethylene (C_2H_4), an important reactant in the manufacture of polymers

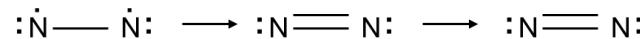
(b) Nitrogen (N_2), the most abundant atmospheric gas

PLAN: For molecules with multiple bonds, **Step 5** follows the other steps in Lewis structure construction. If a central atom does not have 8 e^- (an octet), then electrons can be moved to form a **multiple bond**.

SOLUTION: (a) There are $2(4) + 4(1) = 12$ valence electrons. H can have only one bond per atom.



(b) N_2 has $2(5) = 10$ valence electrons. Therefore, a **triple bond** is required to make the octet around each N.



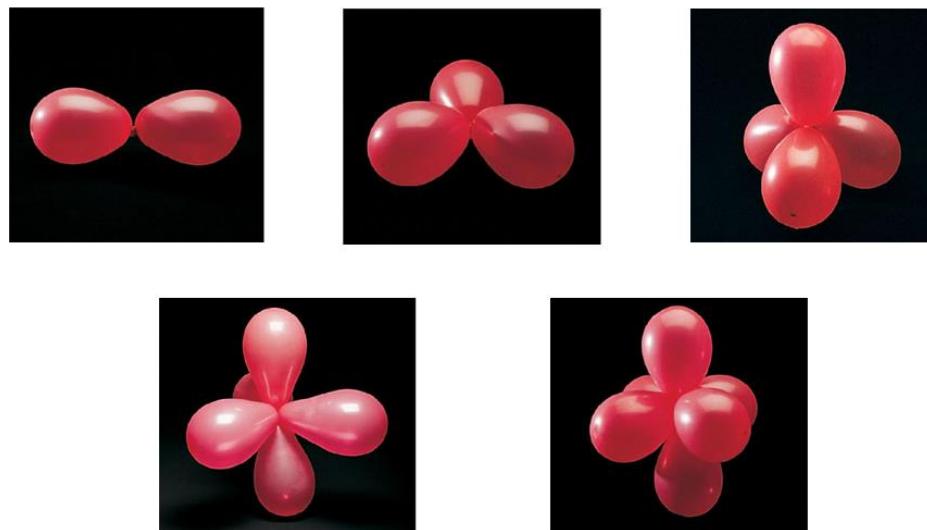
The valence-shell-electron-pair-repulsion (VSEPR) theory is actually the successor of Lewis's idea which also says that the covalent bond can be portrayed as a shared electron-pair. Now, although Lewis's model explained the correlation between valence and bonding in an extremely beautiful manner, it had no theoretical basis at that time. Later in 1924, Wolfgang Pauli rationalized the electron pairing by proposing the Pauli exclusion principle. Now being an extension of the Lewis idea, the VSEPR theory also finds its roots in the Pauli exclusion principle. The initial formulation of the VSEPR model was actually carried out by two British chemists, Nevil Sidgwick and Herbert Powell, who correlated the number of valence shell electron pairs of the central atom in a molecule to the bonding profile around.

Gillespie and Nyholm devised a simple scheme for geometry based on the Lewis dot structure (VSEPR).

Valence shell electron pair repulsion (VSEPR) theory is a model in chemistry used to predict the shape of individual molecules based upon the extent of electron-pair electrostatic repulsion. It is also named Gillespie-Nyholm* theory after its two main developers. The acronym "VSEPR" is pronounced "vesper" for ease of pronunciation.



A balloon analogy for the mutual repulsion of electron groups

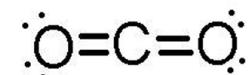


*Ronald J. Gillespie and Ronald S. Nyholm
University College, London, 1957.

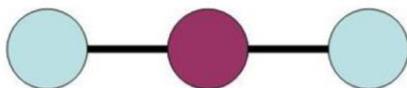
Ronald J. Gillespie
1924 -

Basic postulate

- The definite shape of any covalent molecule depends on the number of pairs of electrons in the central atom
- Covalent bonds are formed due to the sharing of electrons and the covalent bonds arrange themselves around the central atom.
- Electron pairs repel one another and arrange themselves as far apart from each other as possible. An electron pair may be involved in forming a bond, in which case the pair is called a BOND PAIR (BP), or may not be involved, in which case the pair is called a LONE PAIR (LP).
- Repulsion between electron pairs on the outer shell of the central atom in a molecule is in the order of
- LP:LP>LP:BP>BP:BP



Two pairs of electrons
Both bonding



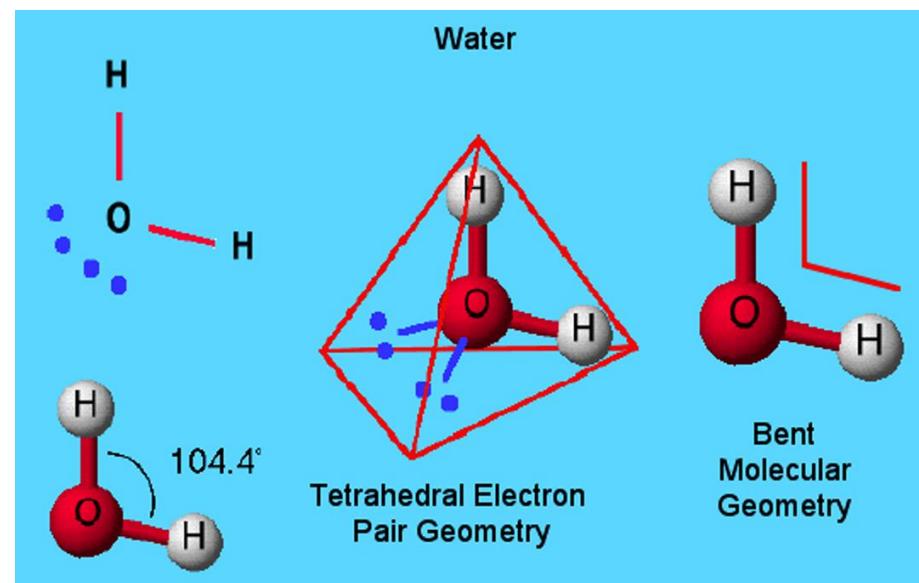
Linear
Bond angle 180°
eg BeCl₂

2) Bent



- Example: H₂O

****Notice electron pair repulsion!!!**

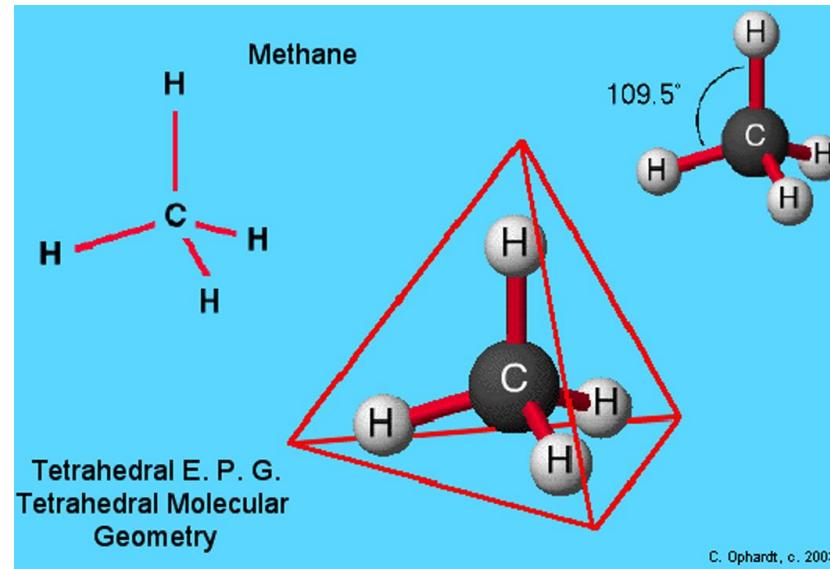
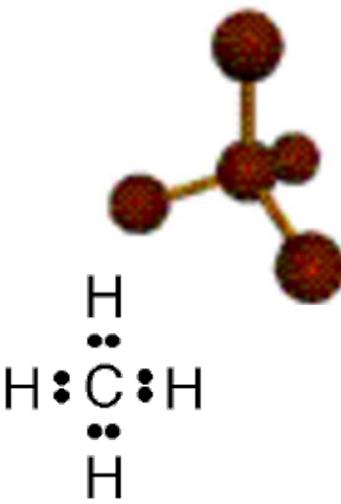


5 Basic Molecule Shapes

1) Linear

- Example: CO₂

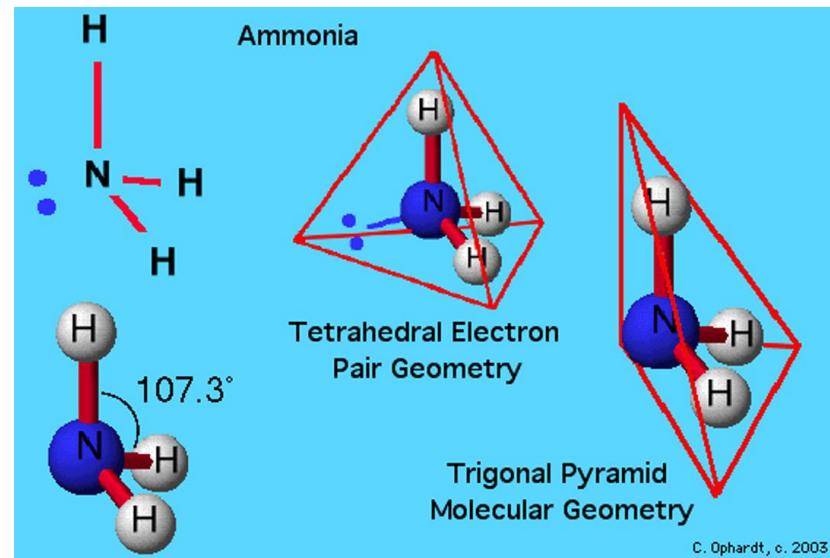
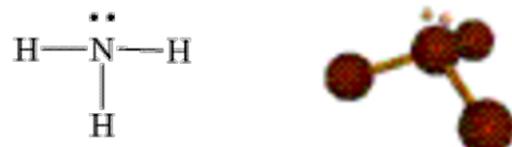
3) tetrahedral



How 109.5 deg?

- example: CH_4

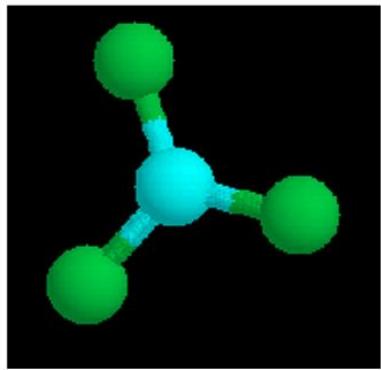
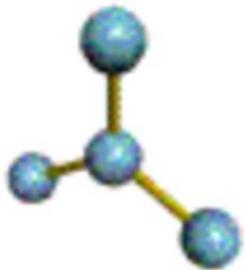
4) Pyramidal



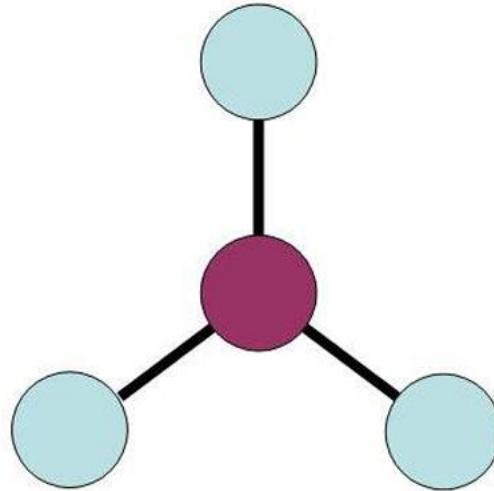
- Example: NH_3

(note: unshared pair of electrons repels, but is not considered part of overall shape; no atom there to contribute to the shape)

5) Trigonal planar

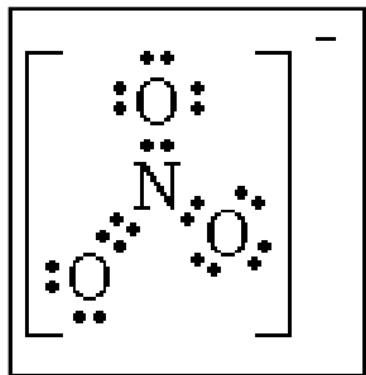


Three pairs of electrons
All bonding



Trigonal planar
Bond angle 120°
eg BF_3

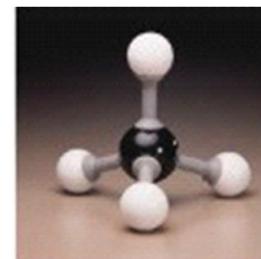
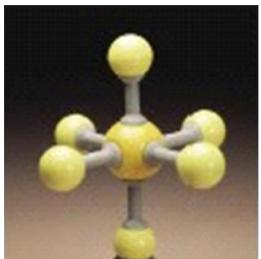
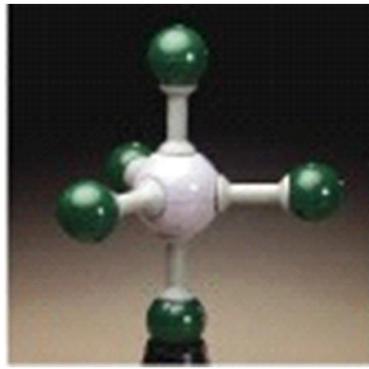
- Example: NO_3^-



Electron pairs (bonding and nonbonding electrons) repel one another, as a result , the electron pairs remain as far apart as possible from another as possible to minimize the repulsion.

- Two electron pairs in the valence orbital are arranged **linearly**
- Three electron pairs are organized in a **trigonal planar** arrangement
- Four electron pairs are organized in a **tetrahedral** arrangement
- Five electron pairs are arranged in a **trigonal bipyramidal**
- Six electron pairs are organized in an **octahedral** arrangement

Electron pairs assume orientations about an atom to minimize repulsions.



The repulsion of lone pair electrons is greater than the repulsion of bond pair electrons

The nonbonding electron pairs are as important as bonding electron pairs in determining the structure.

Nonbonding electrons take up more space in the valence shell than the bonding electrons.

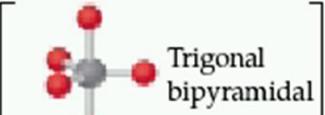
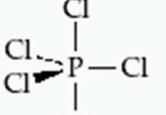
If one or more of the electron pairs are lone pairs, the distribution of electron pair and the geometrical shape of the molecule must be different.

The bond angles decrease as the number of nonbonding electron pairs increases

Repulsion strengths

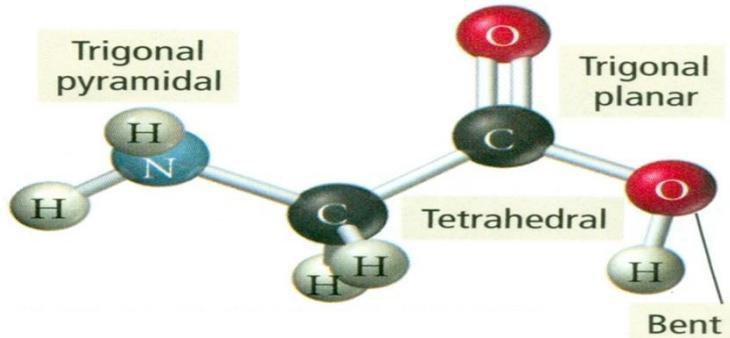
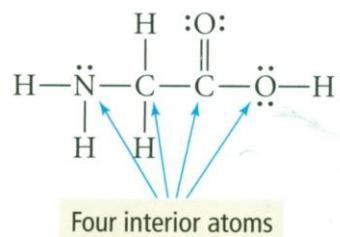
lone pair -lone pair > lone pair e-bond pair > bond pair-bond pair

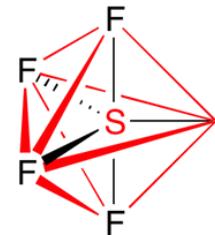
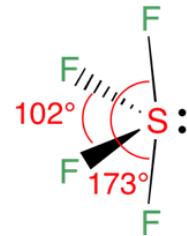
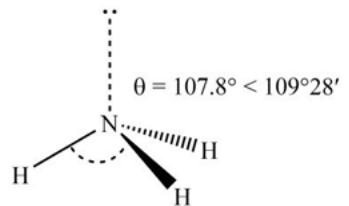
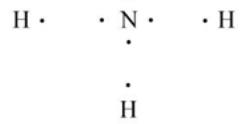
Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
2	0	2	 Linear	<chem>O=C=O</chem>
3	0	3	 Trigonal planar	<chem>H3C=O</chem>
			 Bent	<chem>O=S(=O)O</chem>
	1			
4	0	4	 Tetrahedral	<chem>CH4</chem>
			 Trigonal pyramidal	<chem>NH3</chem>
	1		 Bent	<chem>OH2</chem>
	2			

Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
5	0	5	Trigonal bipyramidal	
4	1	5	Seesaw	
3	2	5	T-shaped	
2	3	5	Linear	

Number of Bonds	Number of Lone Pairs	Number of Charge Clouds	Molecular Geometry	Example
6	0	6	Octahedral	
5	1	6	Square pyramidal	
4	2	6	Square planar	

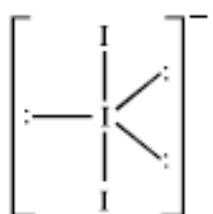
Predict the shape



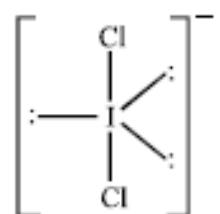


The F–S–F angle involving the axial F atoms is 102°

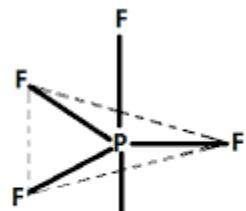
The red lines outline a **trigonal bipyramidal**.
Black lines show the electron pairs



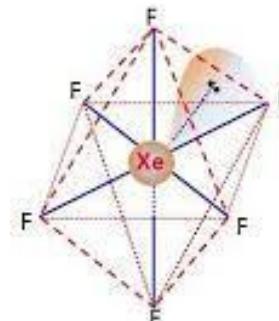
Linear
 $[I-I \leftarrow I^-]$



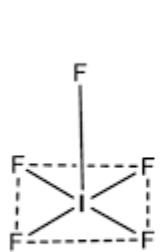
Linear
 $[Cl-Cl \leftarrow Cl^-]$



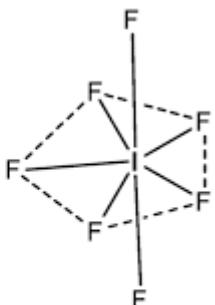
Structure of PF_5 (Trigonal bipyramidal shape)



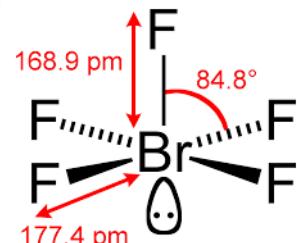
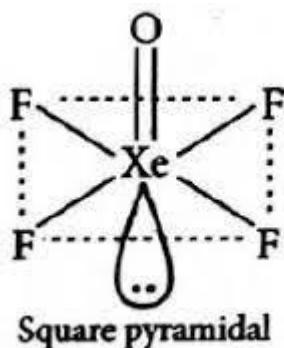
Geometri molekul XeF_6 : oktaedral terdistorsi
Distorted octahedral

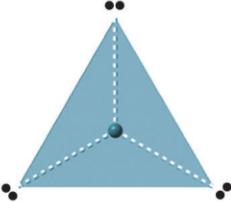
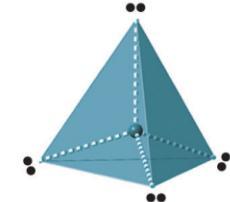
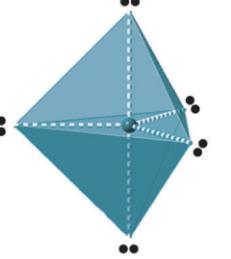
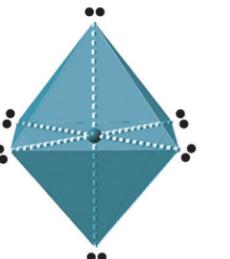
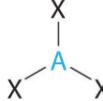
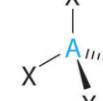
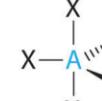
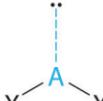
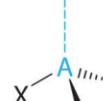
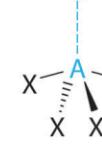
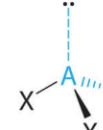
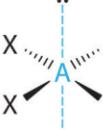
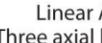


Strucuture of IF_5



Strucuture of IF_7



Electron Groups	2	3	4	5	6
Molecular Geometry					
	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Zero Lone Pairs	$X-A-X$				
	Linear AX_2	Trigonal planar AX_3	Tetrahedral AX_4	Trigonal bipyramidal AX_5	Octahedral AX_6
One Lone Pair					
		Bent (V-shaped) AX_2E	Trigonal pyramidal AX_3E	Seesaw AX_4E One axial lone pair	Square pyramidal AX_5E
Two Lone Pairs					
			Bent (V-shaped) AX_2E_2	T-shaped AX_3E_2 Two axial lone pairs	Square planar AX_4E_2
Three Lone Pairs					
				Linear AX_2E_3 Three axial lone pairs	

Molecule	SN	Number of lone pairs	Geometry	shape	Example
MA ₂	2	0	Linear		CO ₂
MA ₃	3	0	Trigonal planar	Trigonal planar	SO ₃
	3	1		angular	SO ₂
MA ₄	4	0	Tetrahedral	Tetrahedral	CH ₄
		1		Trigonal pyramidal	NH ₃
		2		Angular	H ₂ O
MA ₅	5	0	Trigonal bipyramidal	Trigonal bipyramidal	AsF ₅
		1		Seesaw	SF ₄
		2		T-shaped	ClF ₃
		3		linear	XeF ₂
MA ₆	6	0	Octahedral	Octahedral	SF ₆
		1		Square pyramidal	BrF ₅
		2		Square planar	XeF ₄

➤ ***Limitations of VSEPR Theory***

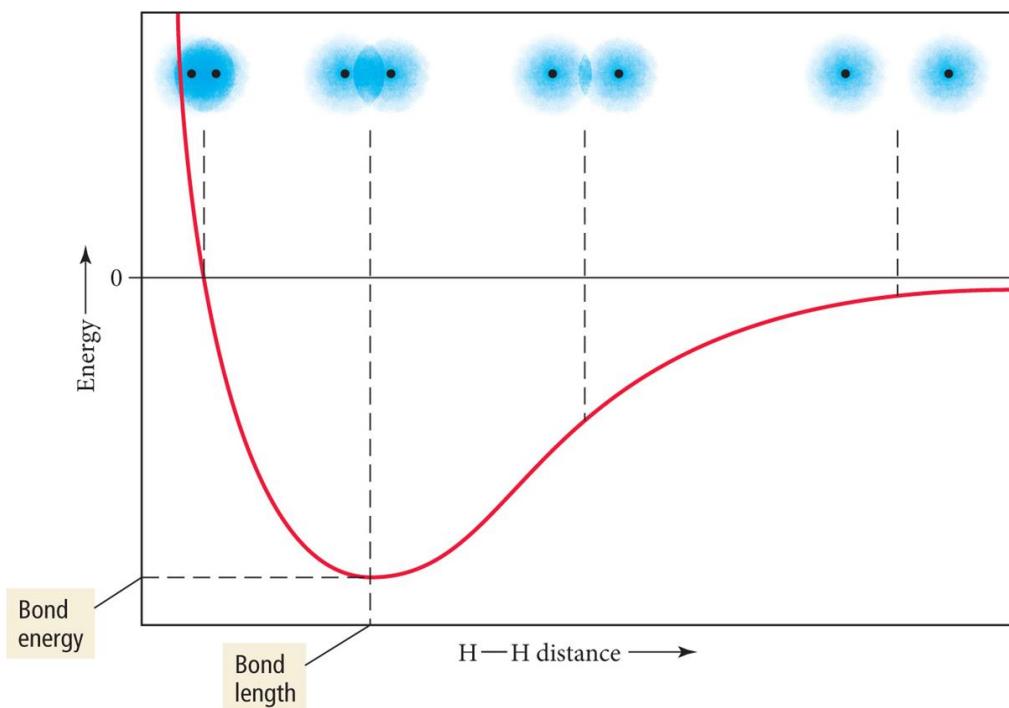
The VSEPR theory is pretty much successful in explaining a wide range of geometries in main group chemistry but there are some serious limitations also for which it offers no rational solution. Some of the most common limitations of the VSEPR theory are given below.

1. The valence-shell-electron-pair-repulsion theory has no sound explanation for molecular geometries having very polar bonds; like Li_2O is linear whereas its counterpart H_2O is bent in nature.
2. The VSEPR theory offers no solution for molecular geometries with a high magnitude of π -cloud delocalization.
3. It does not consider the “inert pair effect”, and thus fails to rationalize the bonding characteristic in molecular geometries possessing the same. For example, $[\text{SeCl}_6]^{2-}$, $[\text{TeCl}_6]^{2-}$ and $[\text{BrF}_6]^-$ are expected to adopt a pentagonal bipyramidal structure due to seven electron pair domains but are found to be octahedral systems.
4. It fails to predict the structure of transition metal complexes. For example, many bivalent complexes of nickel are square-planar and not tetrahedral.
5. The VSEPR theory does not consider the wave function treatment of chemical bonds and therefore fails to explain many bond length and bond angle variations. For example, the bond C–Cl bond length decreases as we move from CH_3Cl to CCl_4 , which is unexpected because of the larger size of Cl in comparison to H.
6. Also magnetic behaviour like - paramagnetic behaviour of O_2 can not be explained.

Valence Bond Theory

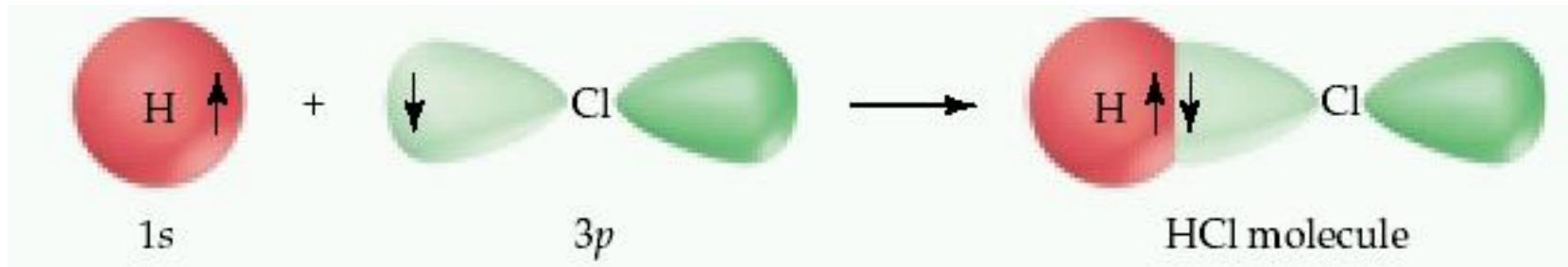
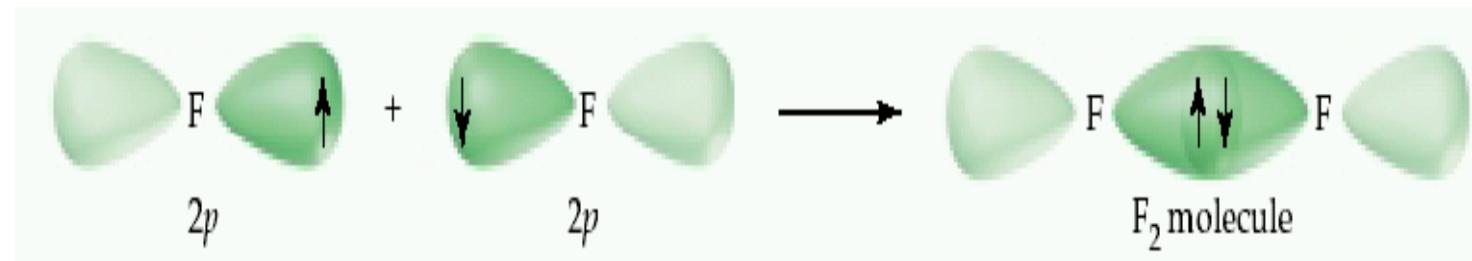
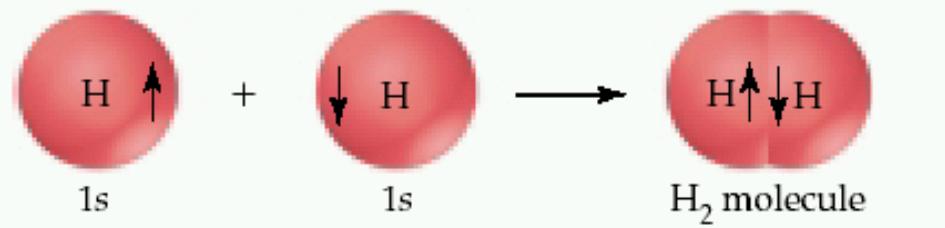
- Linus Pauling and others applied the principles of quantum mechanics to molecules.
- They reasoned that **bonds** between atoms would **occur when the orbitals** on those atoms **interacted** to make a bond.
- The kind of interaction depends on whether the **orbitals align** along the axis between the nuclei, or outside the axis.

Interaction Energy of Two Hydrogen Atoms

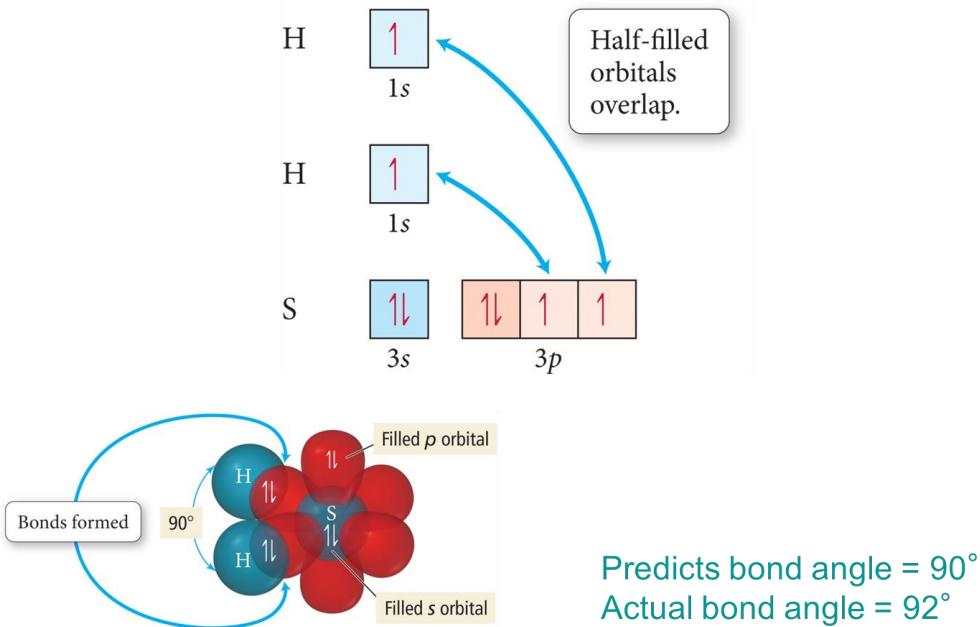


- As two atoms approached, the half-filled valence atomic orbitals on each atom would interact to form **molecular orbitals**.
 - Molecular orbitals are **regions of high probability of finding the shared electrons** in the molecule.
- The **molecular orbitals** would be **more stable** than the separate atomic orbitals because they would **contain paired electrons** shared by both atoms.
 - The **potential energy is lowered** when the molecular orbitals contain a total of two paired electrons compared to separate one electron atomic orbitals.

The covalent bonds are formed by overlap of atomic orbitals each of which contains one electron of opposite spin.



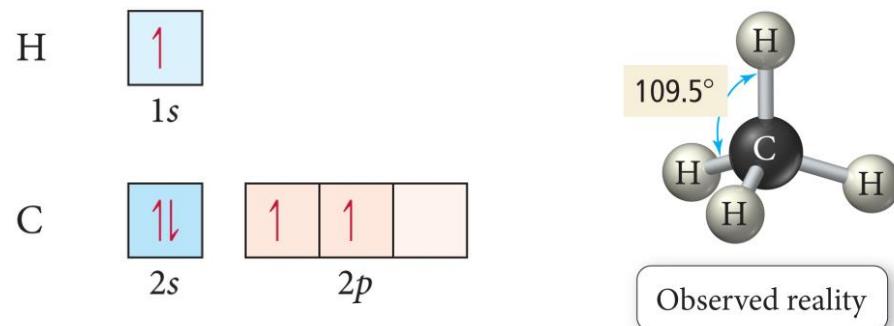
Orbital Diagram for the Formation of H₂S



Valence Bond Theory – Hybridization

- One of the issues that arises is that the number of partially filled or empty atomic orbitals did not predict the number of bonds or orientation of bonds.
 - $C = 2s^2 2p_x^1 2p_y^1 2p_z^0$ would predict two or three bonds that are 90° apart, rather than four bonds that are 109.5° apart.
- To adjust for these inconsistencies, it was postulated that the valence atomic orbitals could **hybridize** before bonding took place.
 - One hybridization of C is to mix all the 2s and 2p orbitals to get four orbitals that point at the corners of a tetrahedron. sp^3

Unhybridized C Orbitals Predict the Wrong Bonding and Geometry



Valence Bond Theory: Main Concepts

1. The valence electrons of the atoms in a molecule reside in quantum-mechanical atomic orbitals. **The orbitals can be the standard s, p, d, and f orbitals, or they may be hybrid combinations of these.**
2. A chemical **bond results** when these atomic orbitals interact and there is a **total of two electrons in the new molecular orbital**.
 - a) The electrons **must be spin paired**.
3. The **shape** of the molecule is **determined by the geometry of the interacting orbitals**.

Hybridization

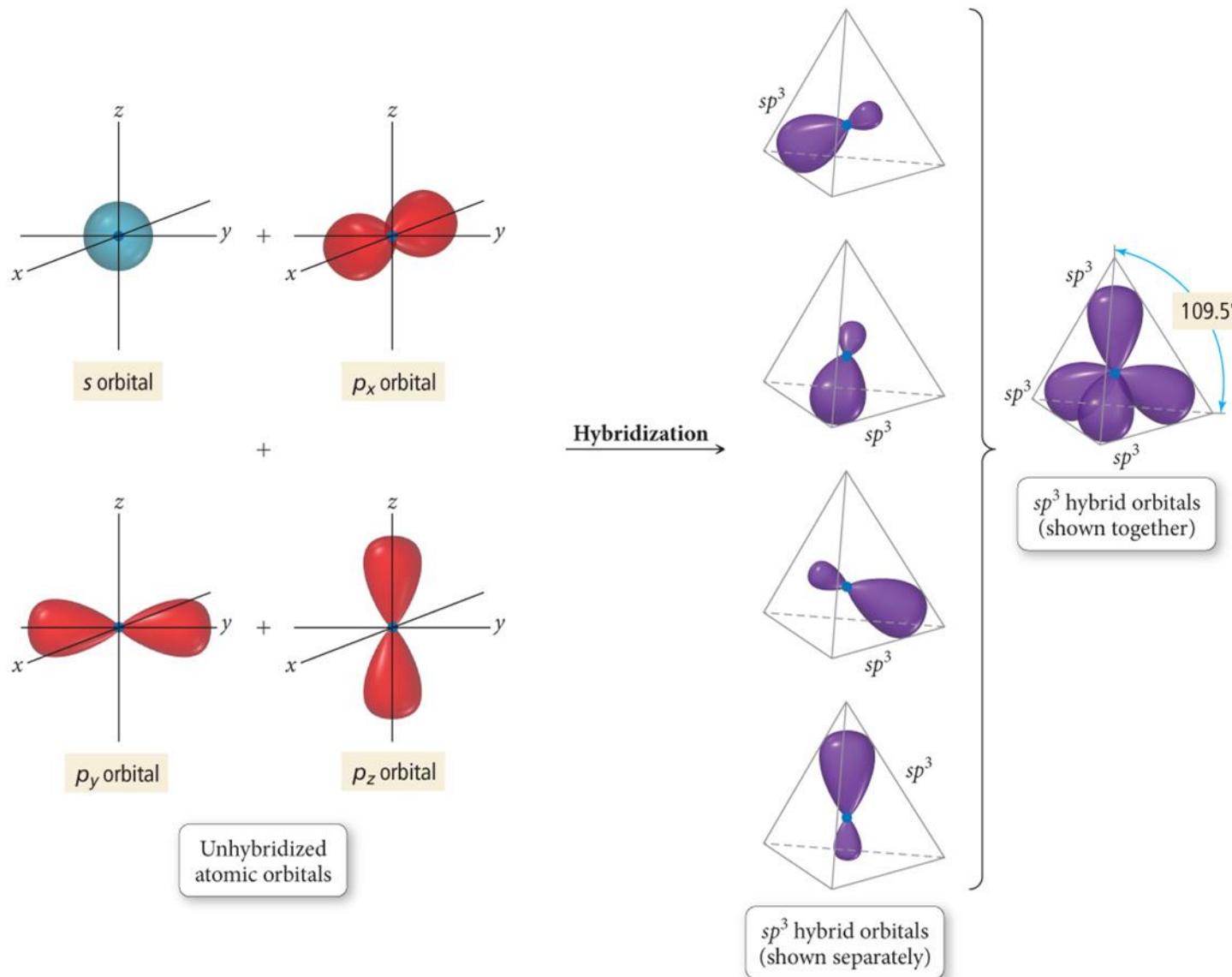
- Some atoms **hybridize** their orbitals to maximize bonding.
 - More bonds = more full orbitals = more stability
- **Hybridizing** is mixing different types of orbitals in the valence shell to make a new set of degenerate orbitals.
 - sp , sp^2 , sp^3 , sp^3d , sp^3d^2
- **Same type of atom can have different types of hybridization.** For example Carbon:
 - **C** = sp , sp^2 , sp^3

Hybrid Orbitals

- The number of standard atomic orbitals combined = the number of hybrid orbitals formed.
 - Combining a $2s$ with a $2p$ gives two $2sp$ hybrid orbitals.
 - **H cannot hybridize!**
 - Its valence shell only has one orbital.
- The number and type of standard atomic orbitals combined determines the shape of the hybrid orbitals.
- The particular **kind of hybridization** that occurs is the one that **yields the lowest overall energy** for the molecule.

Formation of sp^3 Hybrid Orbitals

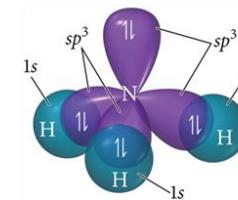
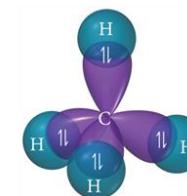
One s orbital and three p orbitals combine to form four sp^3 orbitals.



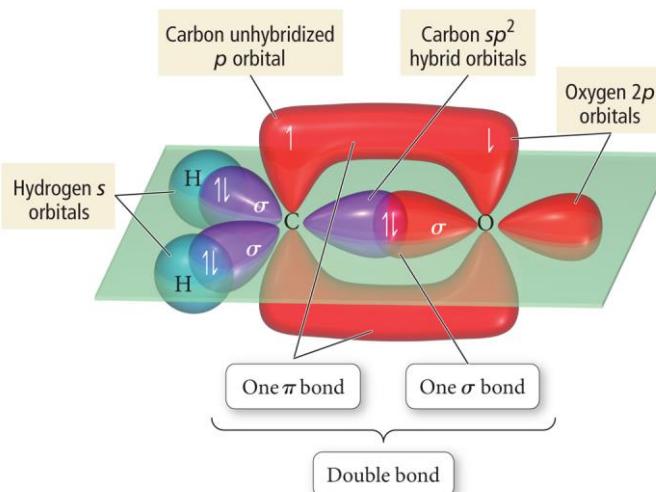
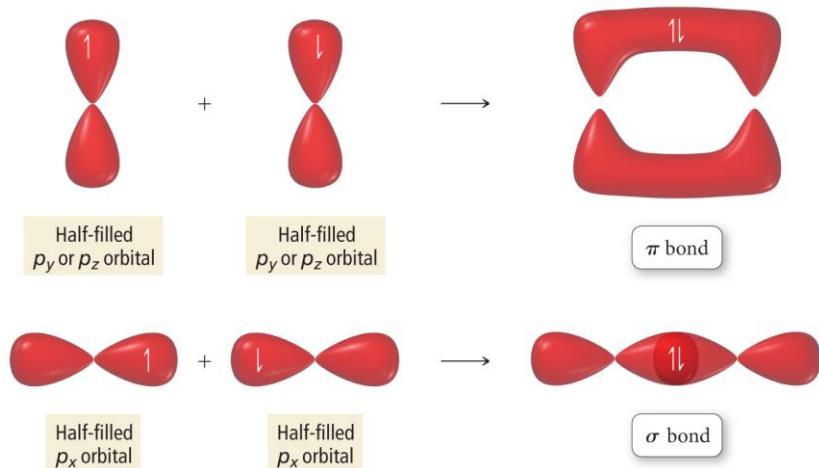
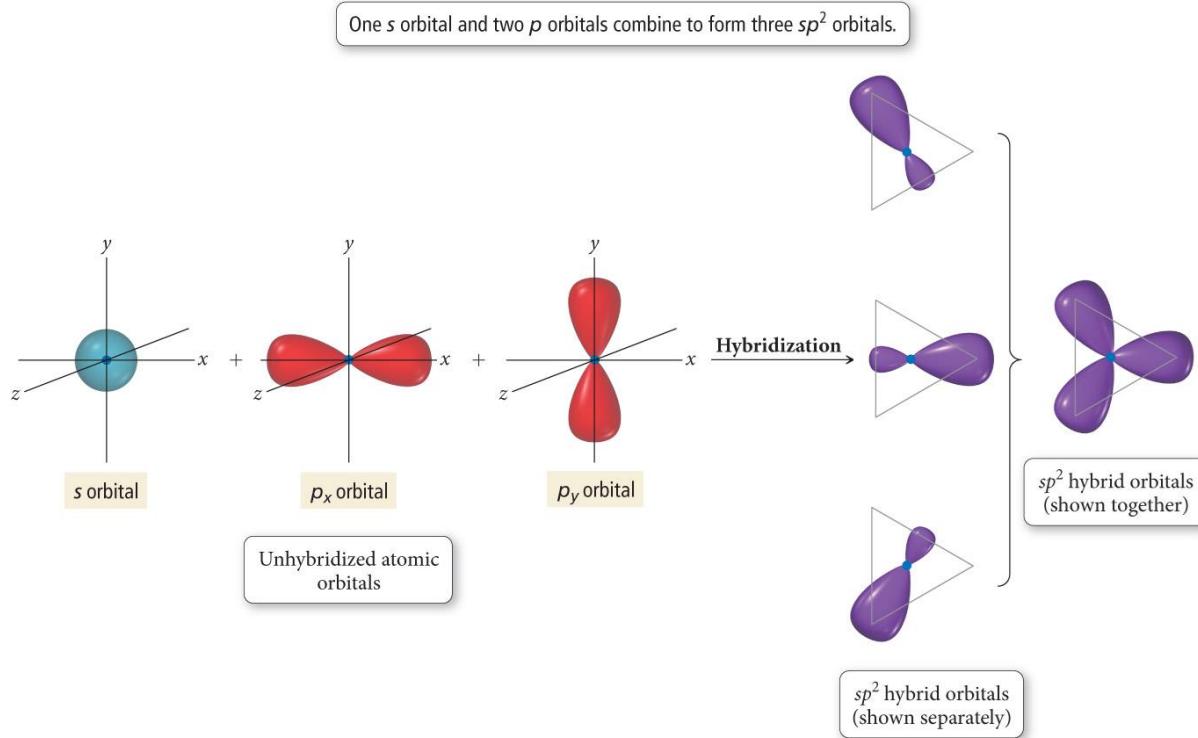
In [chemistry](#), **orbital hybridisation** (or **hybridization**) is the concept of mixing [atomic orbitals](#) to form new **hybrid orbitals** (with different energies, shapes, etc., than the component atomic orbitals) suitable for the pairing of electrons to form [chemical bonds](#) in [valence bond theory](#).

sp³ Hybridization

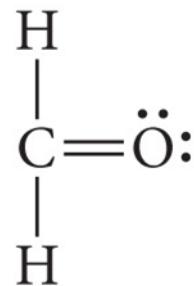
- Atom with four electron groups around it
 - Tetrahedral geometry
 - 109.5° angles between hybrid orbitals
- Atom uses hybrid orbitals for all bonds and lone pairs



Formation of sp^2 Hybrid Orbitals



- Atom with three electron groups around it
 - Trigonal planar system
 - C = trigonal planar
 - N = trigonal bent
 - O = “linear”
 - 120° bond angles
 - Flat
- Atom uses hybrid orbitals for σ bonds and lone pairs, and uses non-hybridized p orbital for π bond

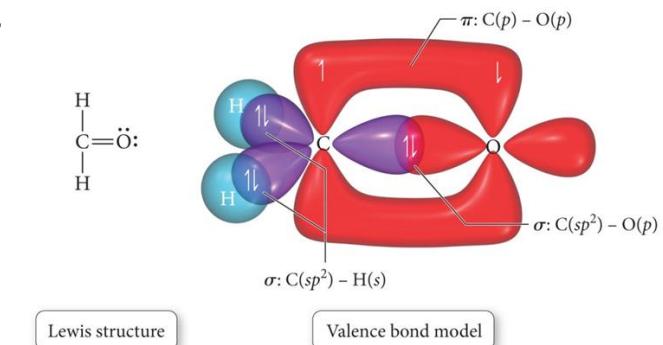


Types of Bonds

- A **sigma (σ) bond** results when the interacting atomic orbitals point along the axis connecting the two bonding nuclei.
 - Either standard atomic orbitals or hybrids
 - s to s , p to p , hybrid to hybrid, s to hybrid, etc.
- A **pi (π) bond** results when the bonding atomic orbitals are parallel to each other and perpendicular to the axis connecting the two bonding nuclei.
 - Between unhybridized parallel p orbitals
- The interaction between parallel orbitals is **not as strong** as between orbitals that point at each other; therefore, **σ bonds are stronger than π bonds**.

Orbital Diagrams of Bonding

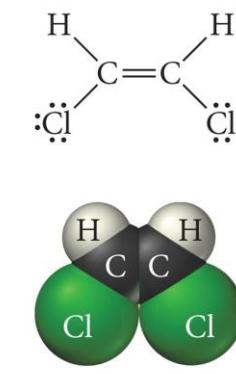
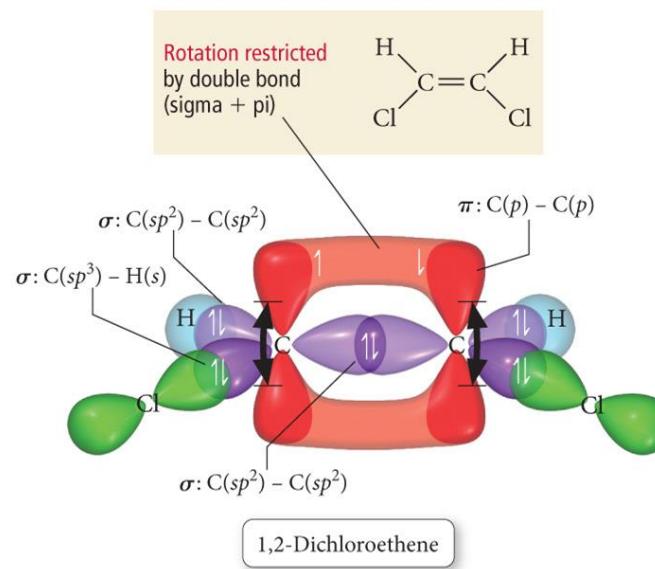
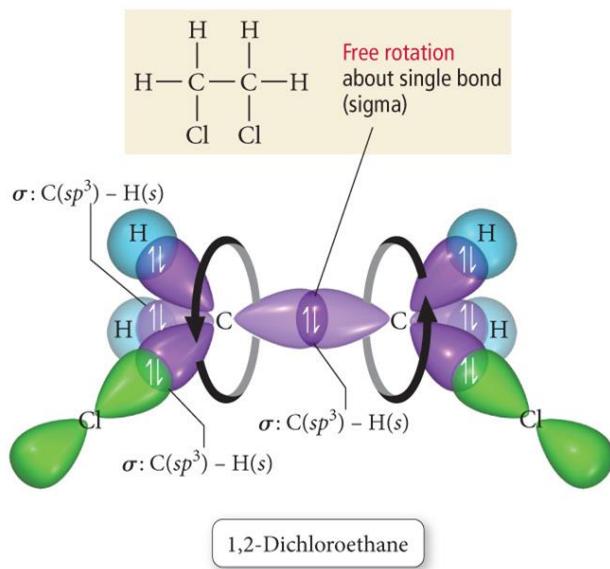
- “Overlap” between a hybrid orbital on one atom with a hybrid or nonhybridized orbital on another atom results in a σ bond.
- “Overlap” between unhybridized p orbitals on bonded atoms results in a π bond.



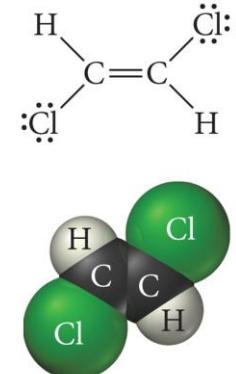
Hybrid orbitals overlap to form a σ bond. Un-hybridized p orbitals overlap to form a π bond.

Bond Rotation

- Because the orbitals that form the σ bond point along the inter-nuclear axis, rotation around that bond does not require breaking the interaction between the orbitals.
- But the orbitals that form the π bond interact **above and below** the inter-nuclear axis, so rotation around the axis requires the breaking of the interaction between the orbitals.



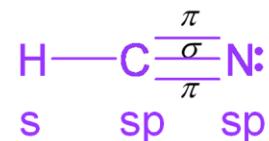
cis-1,2-Dichloroethene



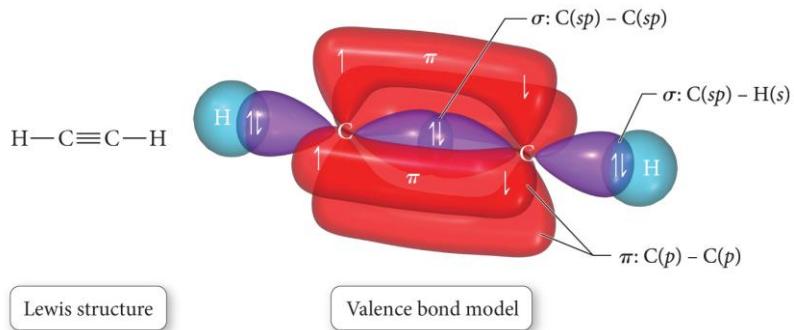
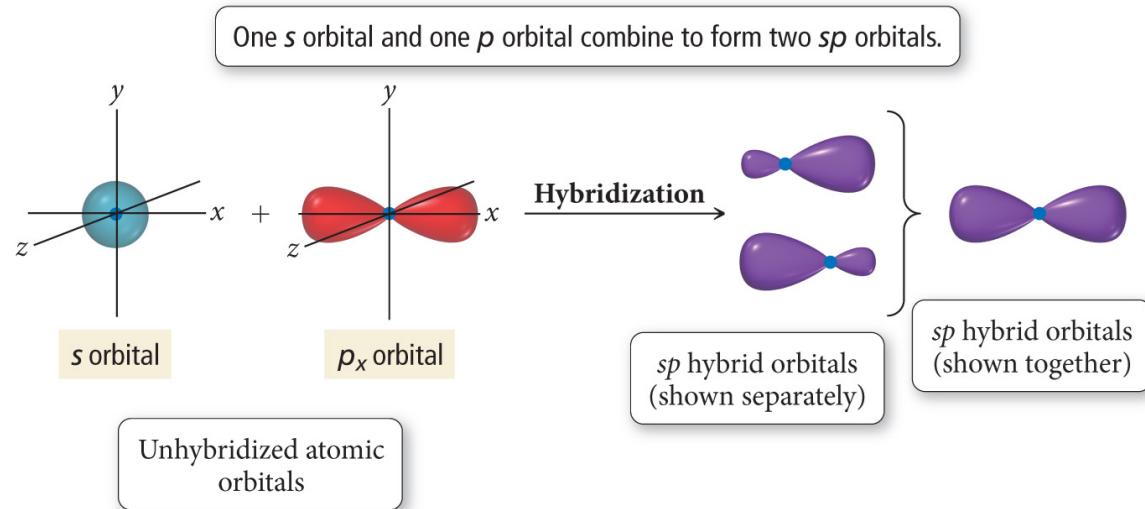
trans-1,2-Dichloroethene

sp

- Atom with two electron groups
 - Linear shape
 - 180° bond angle
- Atom uses hybrid orbitals for σ bonds or lone pairs, and uses nonhybridized p orbitals for π bonds

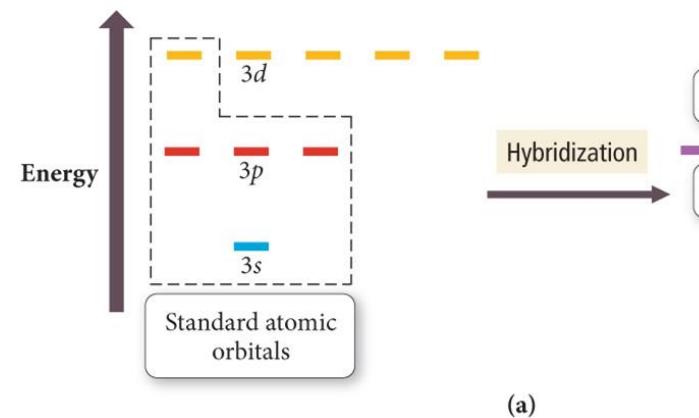
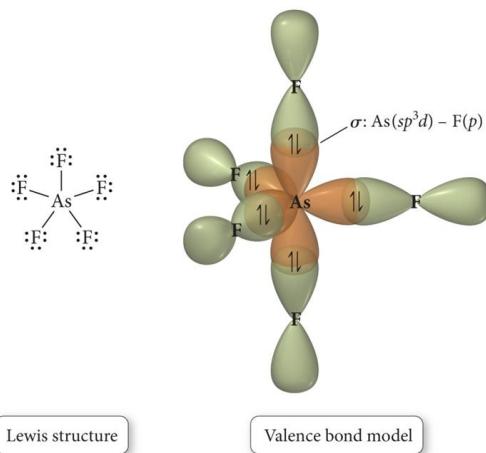


Formation of *sp* Hybrid Orbitals

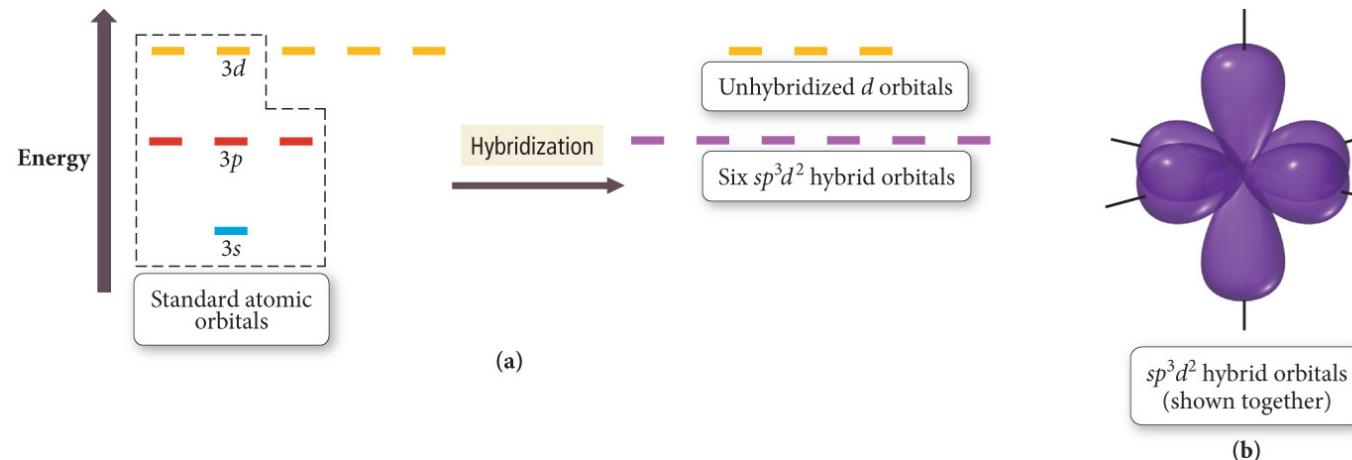


sp^3d

- Atom with five electron groups around it
 - Trigonal bipyramidal electron geometry
 - Seesaw, T-shape, linear
 - 120° and 90° bond angles
- Use empty d orbitals from valence shell
- d orbitals – used to make π bonds



sp^3d^2



- Atom with six electron groups around it
 - Octahedral electron geometry
 - Square pyramid, Square planar
 - 90° bond angles
- Use empty d orbitals from valence shell to form hybrid
- d orbitals – used to make π bonds

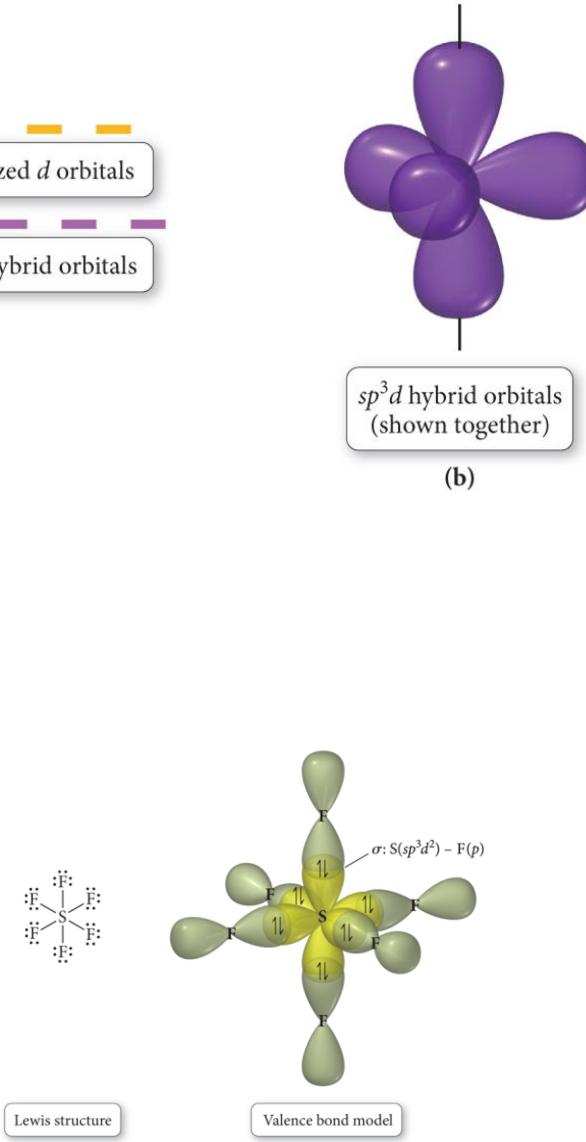
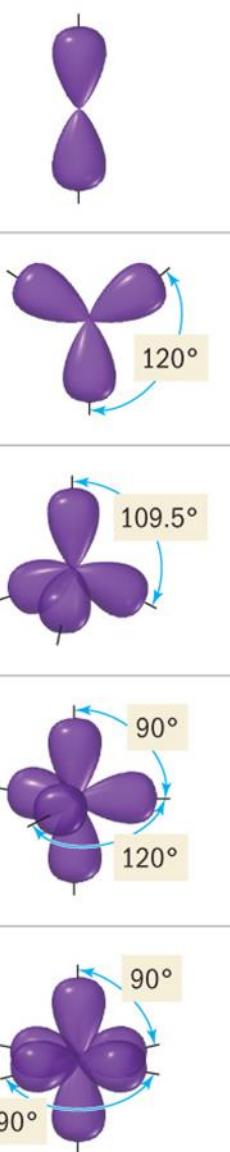


TABLE 10.3 Hybridization Scheme from Electron Geometry

Number of Electron Groups	Electron Geometry (from VSEPR Theory)	Hybridization Scheme
2	Linear	sp
3	Trigonal planar	sp^2
4	Tetrahedral	sp^3
5	Trigonal bipyramidal	sp^3d
6	Octahedral	sp^3d^2



VBT

- **Advantages:**

- VB theory predicts many properties better than Lewis theory.
 - Bonding schemes, bond strengths, bond lengths, bond rigidity

- **Disadvantages:**

- However, there are still many properties of molecules it doesn't predict perfectly.
 - Magnetic behavior of O_2
- In addition, VB theory presumes the electrons are localized in orbitals on the atoms in the molecule—it doesn't account for delocalization.

Valence Bond Theory (VBT)

1-Valence orbital theory was first proposed by **W.Heitler and F.London.**

2-The valence bond theory explains the bonding of **atomic orbitals..**

3-describes **hybrid orbitals.**

4-**Resonance** plays an important role in this theory.

5-There is no explanation of **paramagnetic** character of oxygen.

6- Calculations are simpler.

Molecular Orbital Theory (MOT)

Molecular orbital theory was proposed by **F. Hund and R.S. Mulliken**

The molecular orbital theory is based on the **molecular orbitals**

describes **bonding molecular orbitals** and **antibonding molecular orbitals.**

There is **no place of resonance** in this theory.

Good explanation of paramagnetic character of oxygen.

Calculations are very difficult

Molecular Orbital Theory

A molecular orbital describes a region of space in a molecule where electrons are most likely to be found.

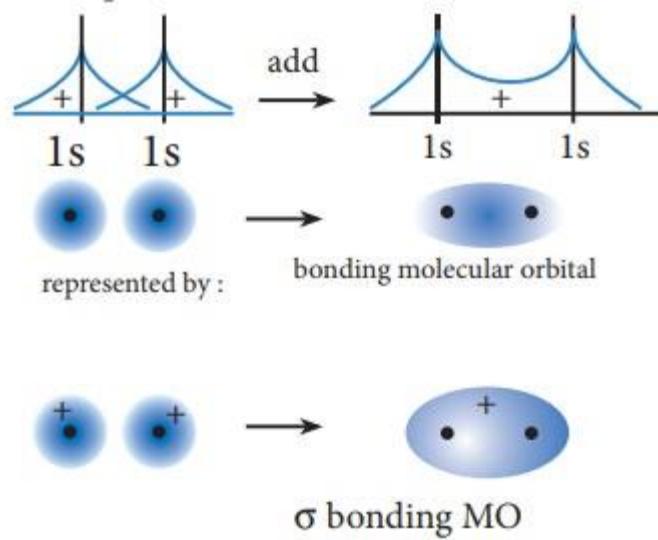
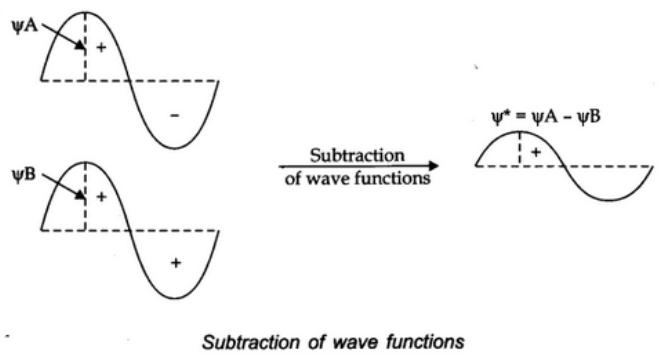
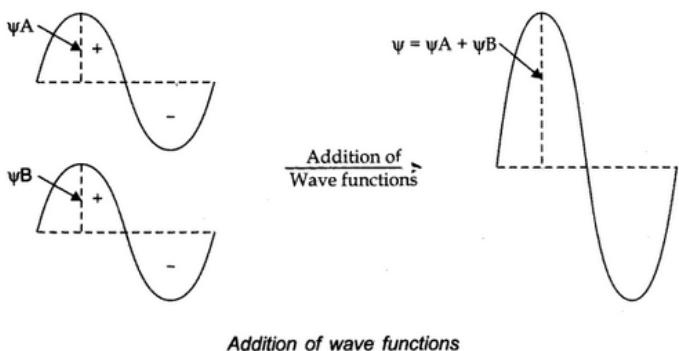
Atomic orbitals: orbitals that are localized on single atoms.

Molecular orbitals: orbitals that span two or more atoms. Constructing molecular orbitals (MOs) by overlapping atomic orbitals (AOs)

- In MO theory, Schrödinger's wave equation is used calculate a set of **molecular orbitals**.
 - In practice, the equation solution is estimated.
 - We start with good guesses from our experience as to what the orbital should look like.
 - Then we test and tweak the estimate until the energy of the orbital is minimized.
- In this treatment, the electrons belong to the whole molecule, so the orbitals belong to the whole molecule.
 - Delocalization

LCAO

- The simplest guess starts with the atomic orbitals of the atoms adding together to make molecular orbitals; this is called the **linear combination of atomic orbitals (LCAO)** method.
 - Weighted sum
- Because the orbitals are wave functions, the waves can combine either **constructively or destructively**.



Destructive interaction The two 1s Orbitals are out phase

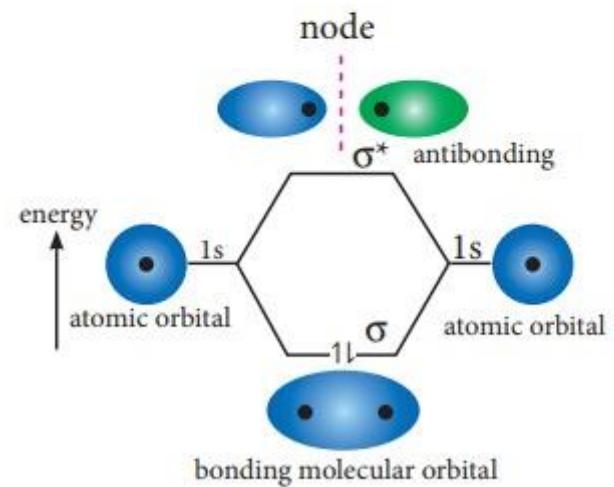
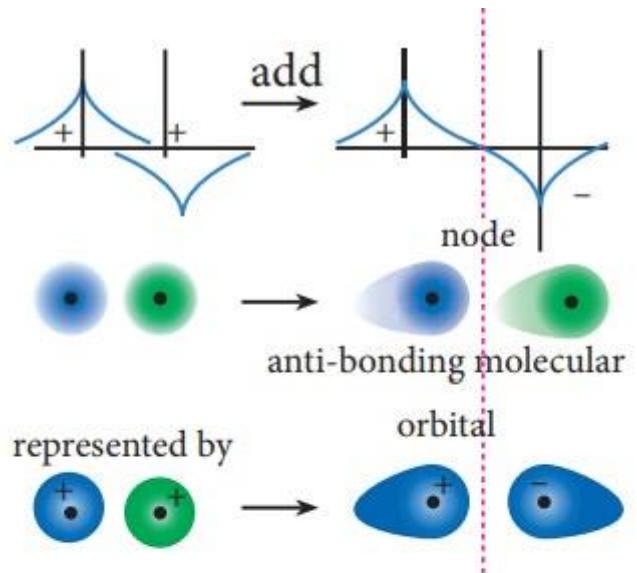


Fig 10.29 Linear Combination of atomic orbitals

We know that the atomic orbitals are represented by the wave function Ψ . Let us consider two atomic orbitals represented by the wave function ψ_A and ψ_B with comparable energy, combines to form two molecular orbitals. One is bonding molecular orbital(ψ_{bonding}) and the other is antibonding molecular orbital($\psi_{\text{antibonding}}$). The wave functions for these two molecular orbitals can be obtained by the linear combination of the atomic orbitals ψ_A and ψ_B as below.

$$\psi_{\text{bonding}} = \psi_A + \psi_B$$

$$\psi_{\text{antibonding}} = \psi_A - \psi_B$$

The formation of bonding molecular orbital can be considered as the result of constructive interference of the atomic orbitals and the formation of anti-bonding molecular orbital can be the result of the destructive interference of the atomic orbitals. The formation of the two molecular orbitals from two 1s orbitals is shown below.

Molecular Orbitals

- When the wave functions combine constructively, the resulting molecular orbital has less energy than the original atomic orbitals; it is called a **bonding molecular orbital**.

σ , π

– Most of the electron density between the nuclei

- When the wave functions combine destructively, the resulting molecular orbital has more energy than the original atomic orbitals; it is called an **antibonding molecular orbital**.

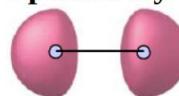
σ^* , π^*

– Most of the electron density outside the nuclei

– Nodes between nuclei

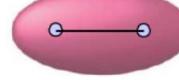
- Electrons are negatively charged
- Nuclei are positively charged

Destabilization



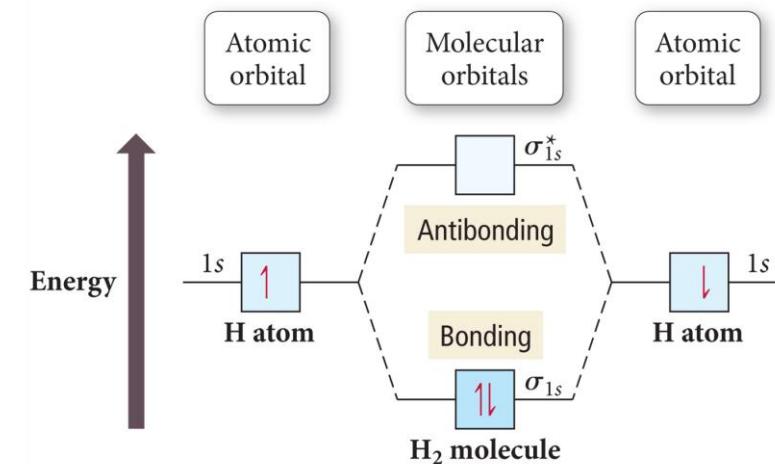
○ = + = nucleus

Stabilization

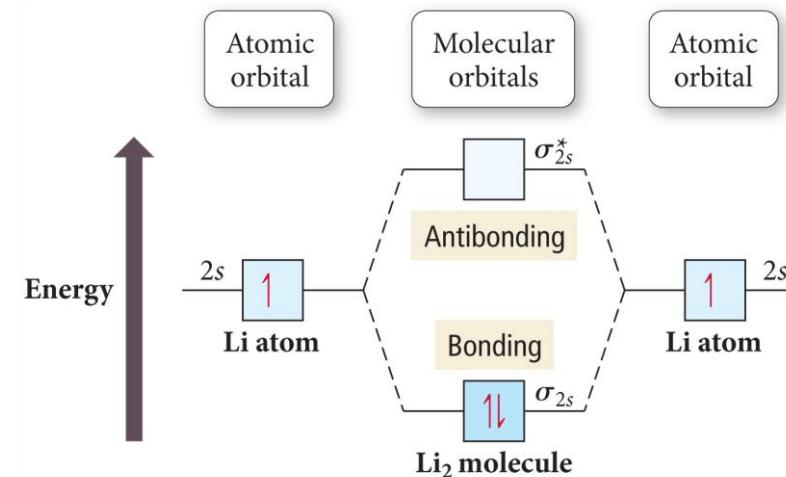


The bonding combination puts electron density between the two nuclei - **stabilization**

The antibonding combination moves electron density away from the nuclei - **destabilization**



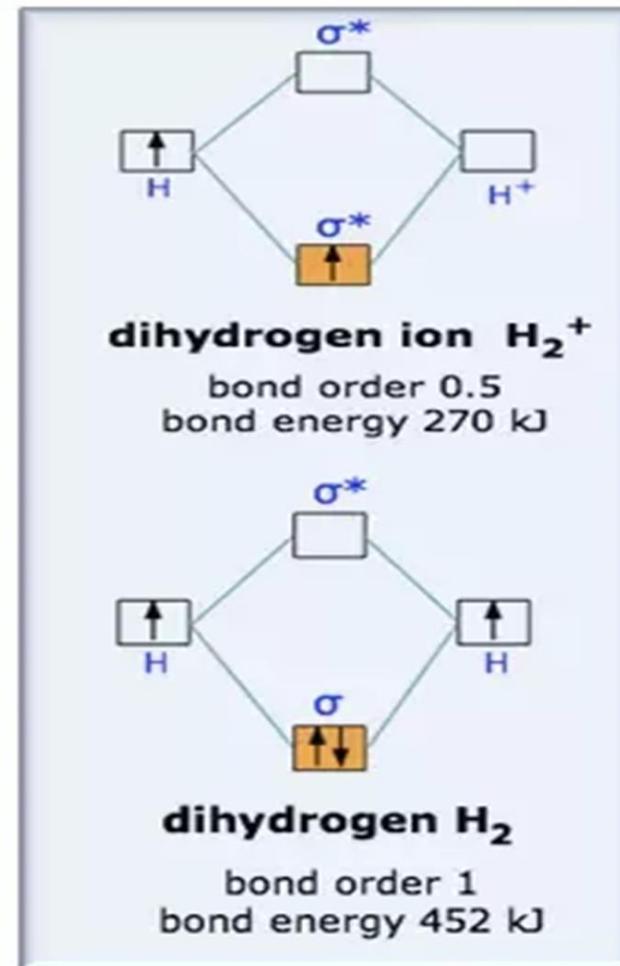
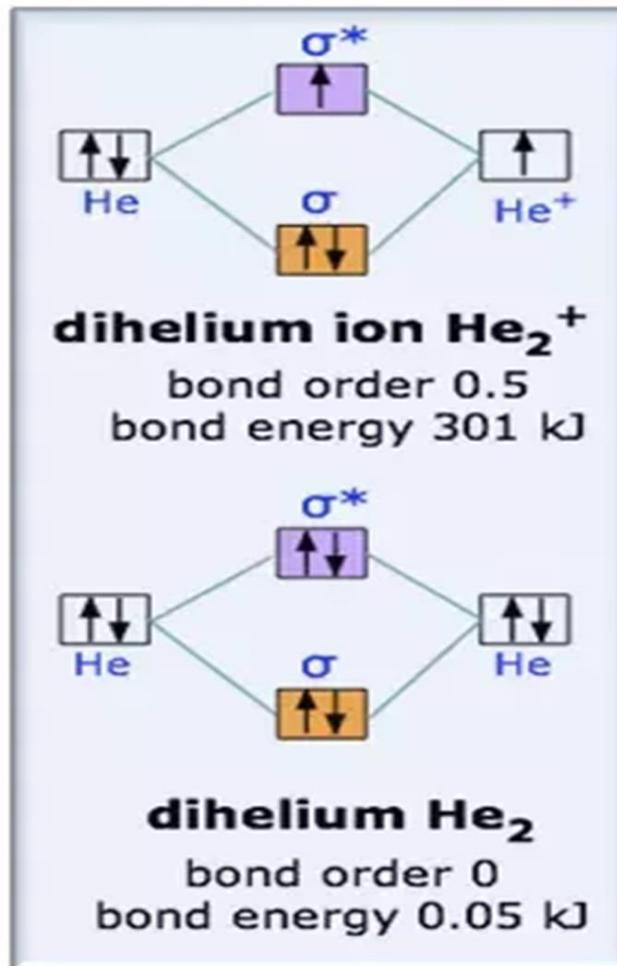
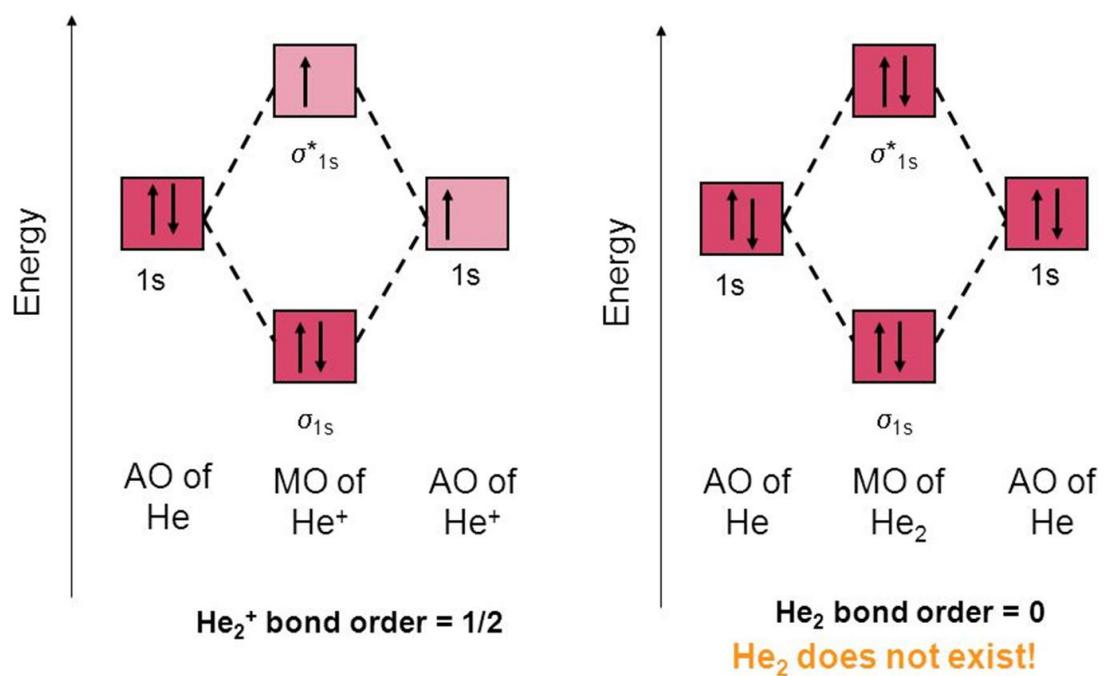
Period Two Homonuclear Diatomic Molecules



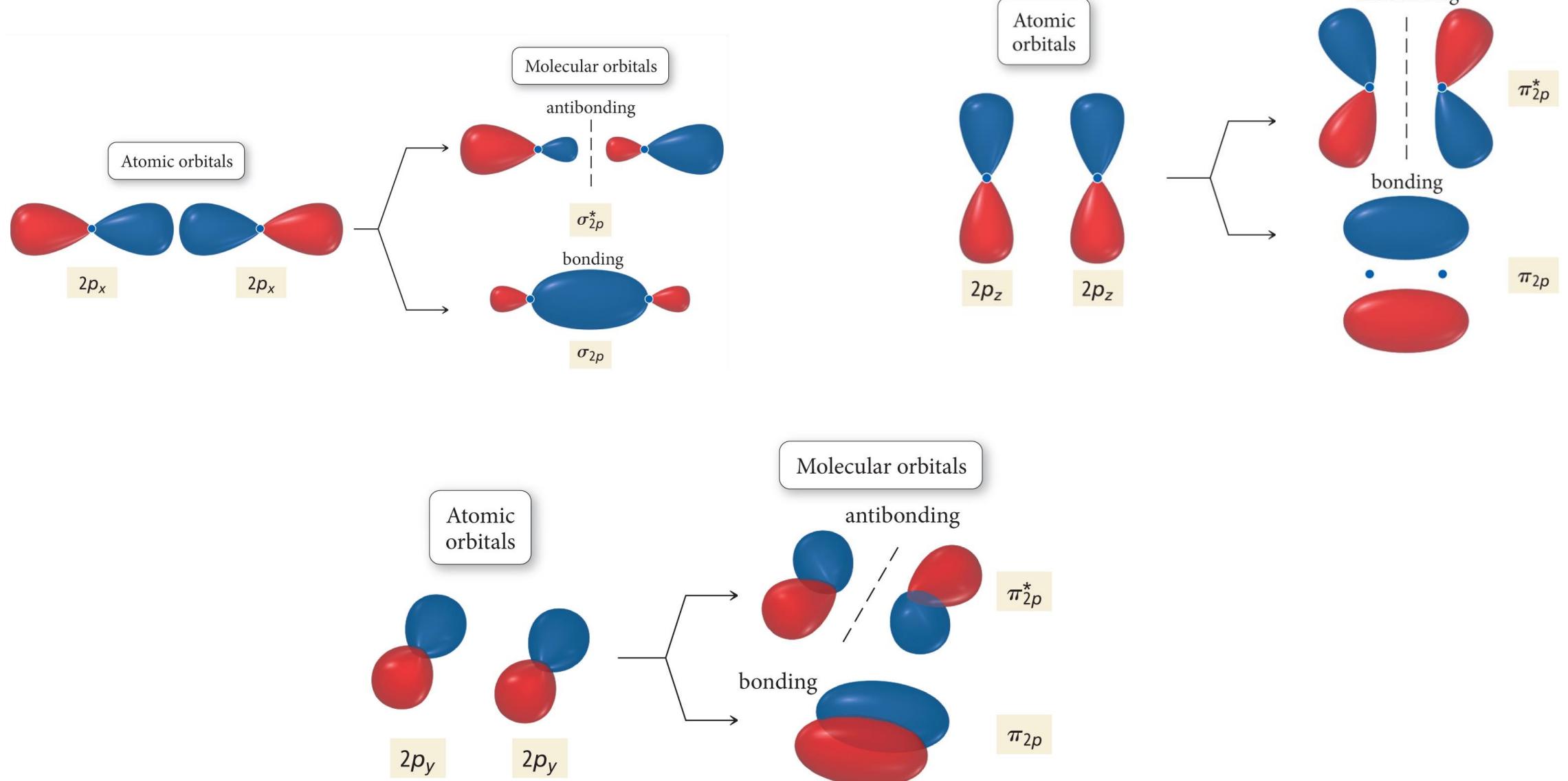
Bond Order = $\frac{\text{No. } e^- \text{ in bonding MOs} - \text{No. } e^- \text{ in antibonding MOs}}{2}$

Figure 11.16

MO diagram for He_2^+ and He_2

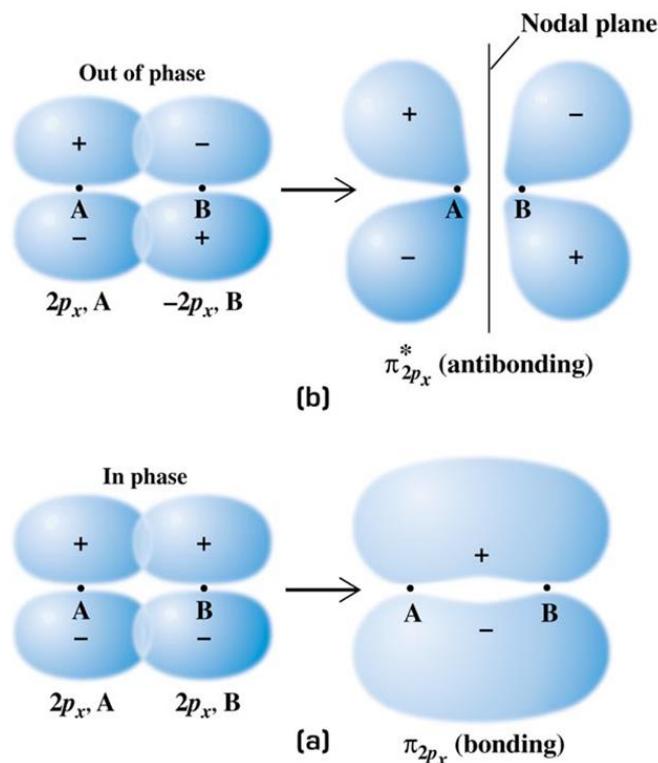


Interaction of *p* Orbitals



Constructive and destructive overlap of 2 p orbitals to form π and π^* orbitals

(a) Bonding π orbital; (b) Antibonding π^* orbital

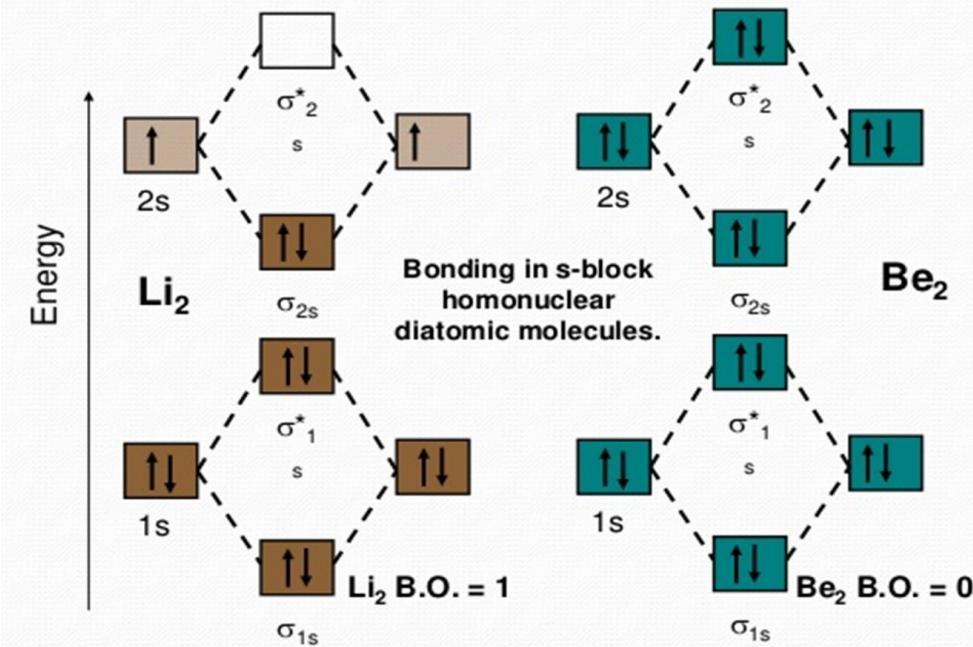


Overlap perpendicular to the internuclear axis is termed π overlap. A nodal plane that contains the bond axis. The resulting orbitals are called π and π^* orbitals

Remember: + and - refer to mathematical symbols, not charge

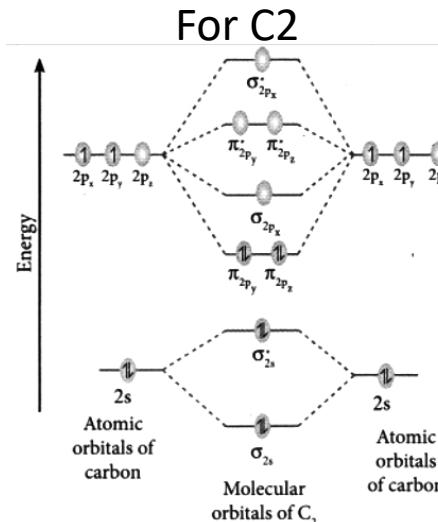
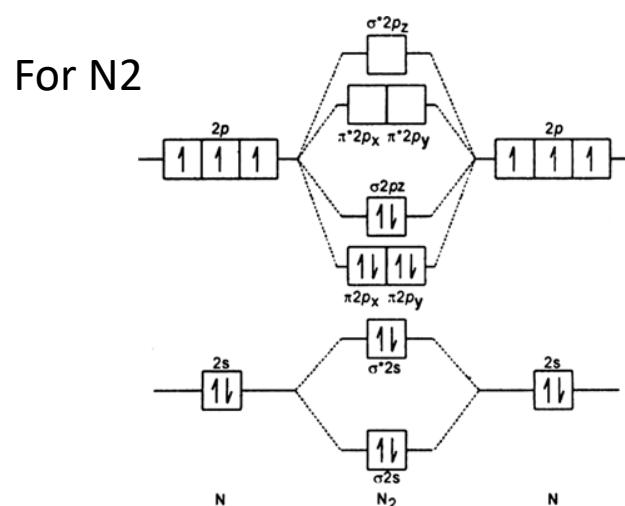
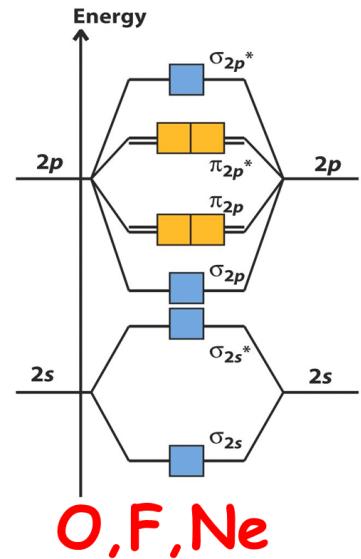
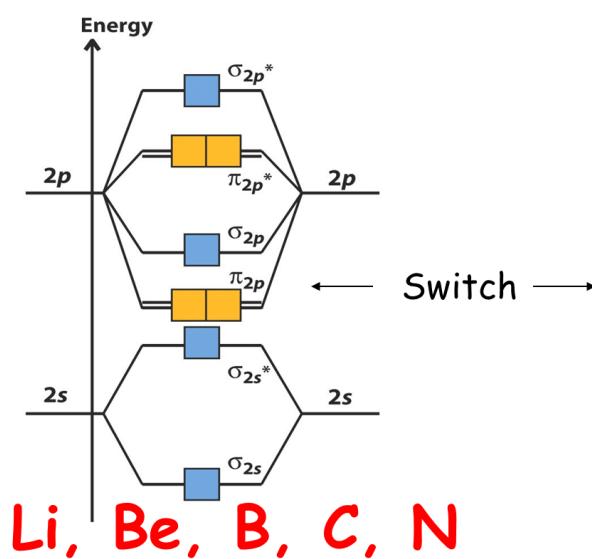
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Next Row: 2s & 2p orbitals



Orbital energies for the $3\text{Li}-{}^{10}\text{Ne}$

The relative energies are bonding **sigma < pi < antibonding pi < antibonding sigma**



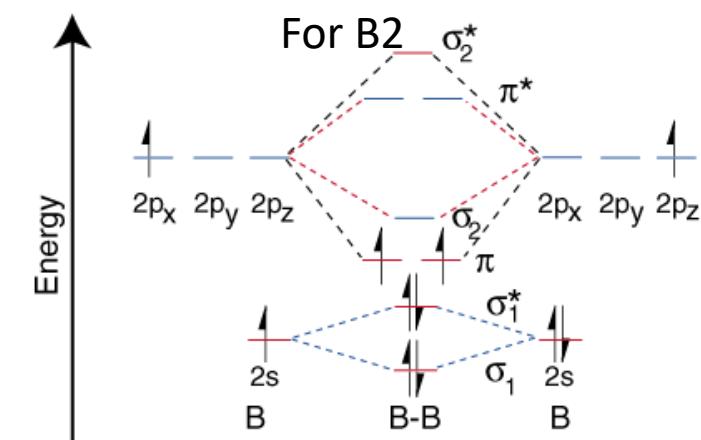
Before we can draw a molecular orbital diagram for B_2 , we must find the in-phase and out-of-phase overlap combinations for boron's atomic orbitals.

Then we rank them in order of increasing energy. We can ignore the 1s orbitals, because they do not contain the valence electrons.

Each boron atom has one 2s and three 2p valence orbitals. The 2s orbitals will overlap to form $2s\sigma$ and $2s\sigma^*$ orbitals. The 2px orbitals can overlap end-on to form $2p\sigma$ and $2p\sigma^*$ orbitals. The 2py and 2pz orbitals can overlap side-on to form degenerate pairs of $2p\pi$ and $2p\pi^*$ orbitals.

The order of energies is $2s\sigma < 2s\sigma^* < 2p\pi < 2p\sigma < 2p\pi^* < 2p\sigma^*$. We have three valence electrons from each B atom, so B_2 will have six valence electrons.

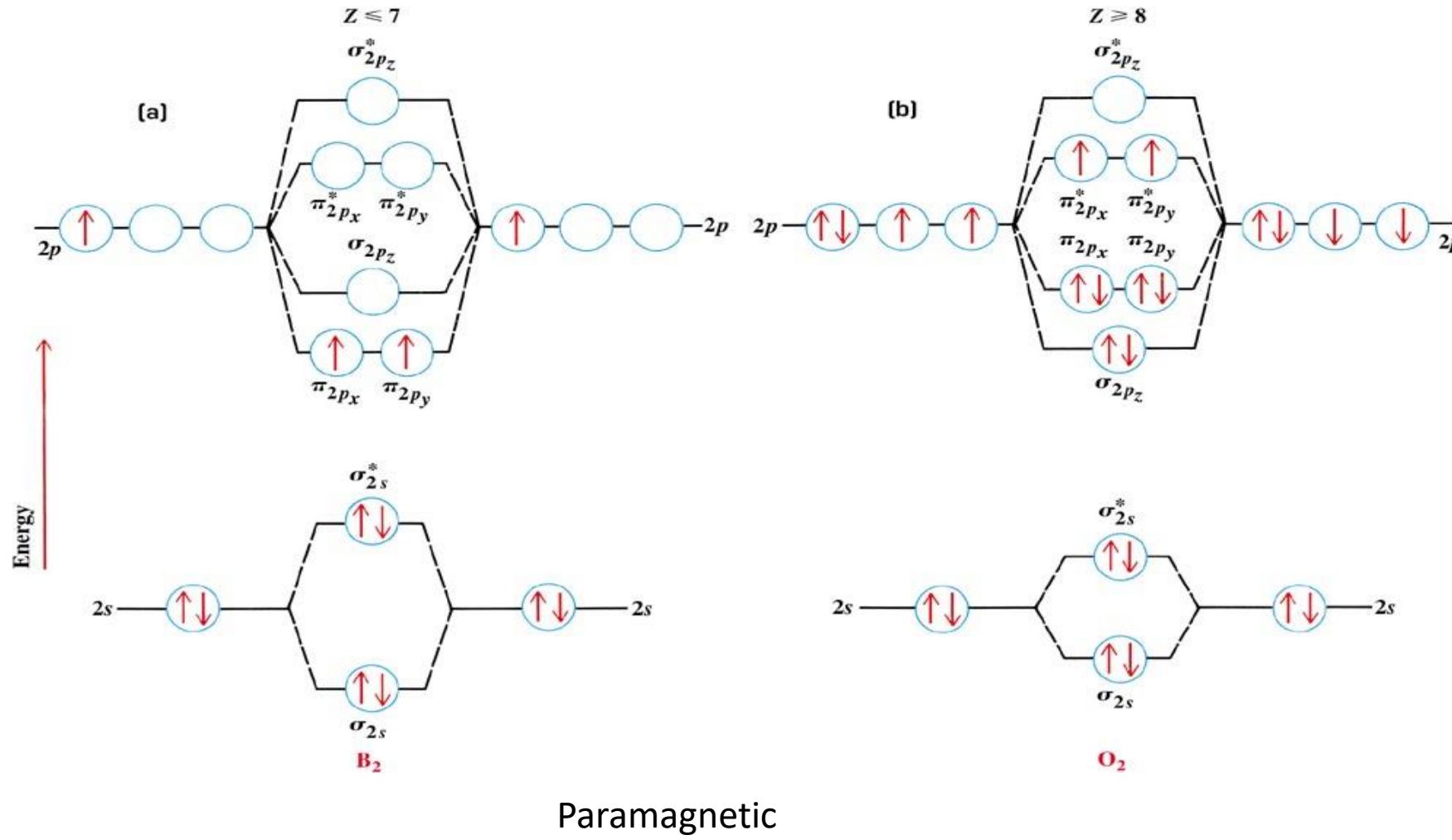
We use the Pauli Exclusion Principle and Hund's rule to fill the orbitals in an Aufbau process. The molecular orbital diagram for B_2 then becomes



Correlation diagrams for B_2 (left) and O_2 (right)

6 VE: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p}\uparrow\uparrow)^2(\pi_{2p}^*)^0(\sigma_{2p}^*)^0$

12 VE: $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^*\uparrow\uparrow)^2(\sigma_{2p}^*)^0$



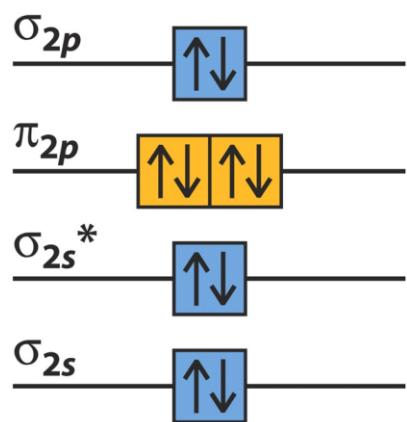
Electron configurations for the diatomic molecules: B_2 , C_2 , N_2 , O_2 , F_2 , Ne_2

VE: 6	8	10	12	14	16
Large 2s-2p interaction			Small 2s-2p interaction		
B_2	C_2	N_2	O_2	F_2	Ne_2
σ_{2p}^*	□	□	□	σ_{2p}^*	□
π_{2p}^*	□□	□□	□□	π_{2p}^*	1 1
σ_{2p}	□	□	1↓	π_{2p}	1↓ 1↓
π_{2p}	1 1	1↓ 1↓	1↓ 1↓	σ_{2p}	1↓
σ_{2s}^*	1↓	1↓	1↓	σ_{2s}^*	1↓
σ_{2s}	1↓	1↓	1↓	σ_{2s}	1↓
Bond order	1	2	3	2	1
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

▲ Figure 9.45 The second-row diatomic molecules. Molecular orbital electron configurations and some experimental data for several second-row diatomic molecules.

The molecular orbital electronic configuration of ${}^7\text{N}_2$

Group V: Valence electrons = 10. Ignore core electrons



Nitrogen, N_2

What is the bond order of N_2 ?

$$\text{BO} = 1/2(\text{N} - \text{N}^*)$$

$$\text{N} = 8, \text{N}^* = 2,$$

$$\text{N} - \text{N}^* = 6$$

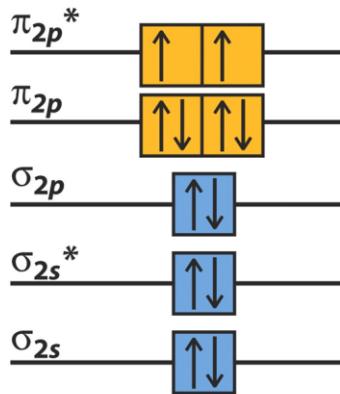
$$\text{BO} = 1/2(6) = 3$$

How does the Lewis structure compare to the MO structure?



The molecular orbital electronic configuration of ${}^8\text{O}_2$

Group VI: Valence electrons = 12. Ignore core electrons



Oxygen, O_2

What is the electronic configuration of O_2 ?

$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^* \uparrow\uparrow)^2$$

What is the bond order of O_2 ?

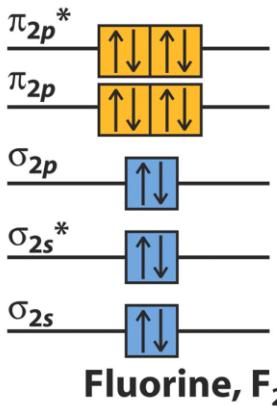
$$\text{Bond order} = 1/2(\text{N} - \text{N}^*)$$

$$1/2(8 - 4) = 2$$

O_2 possesses a net double bond and is paramagnetic

The molecular orbital electronic configuration of ${}^9\text{F}_2$

Group VII: Valence electrons = 14



Fluorine, F_2

What is the valence electronic configuration of F_2 ?

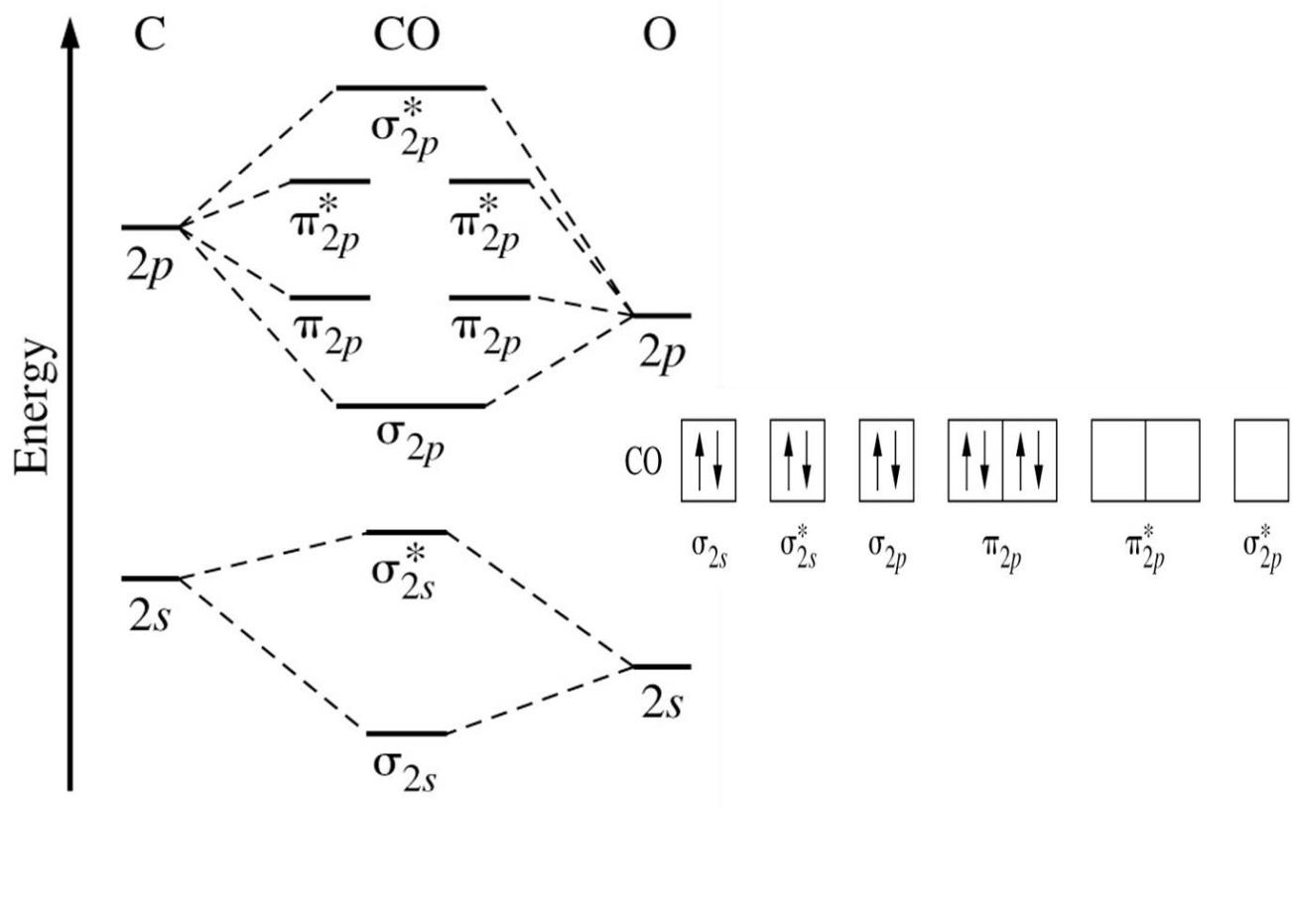
$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p})^4(\pi_{2p}^* \uparrow\uparrow)^4$$

What is the bond order of F_2 ?

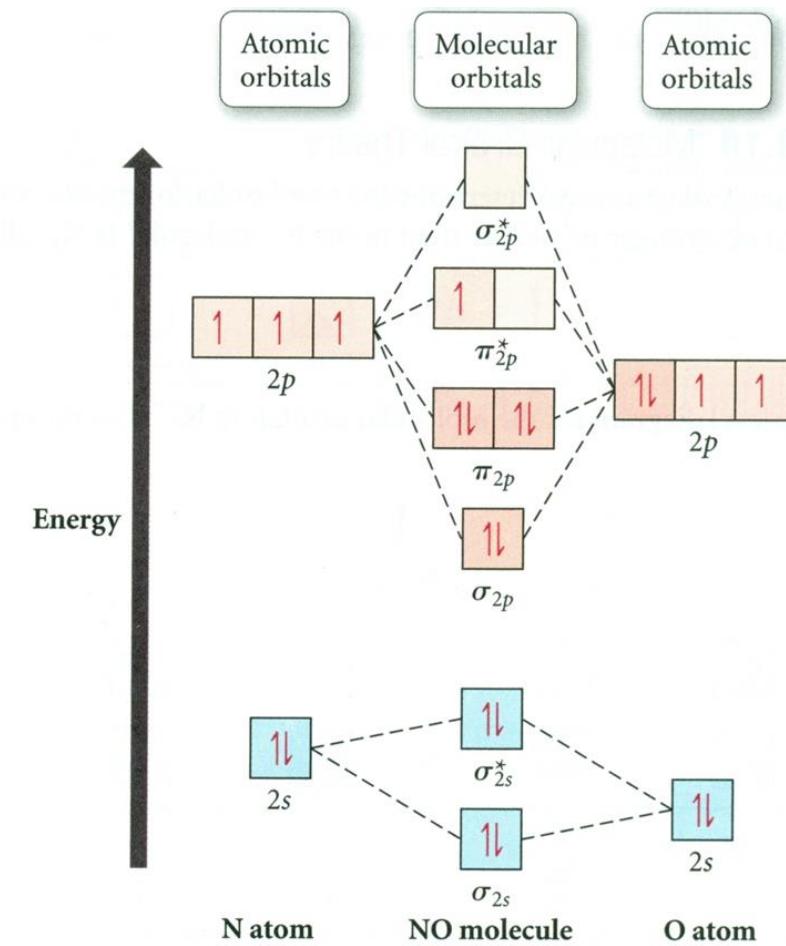
$$\text{BO} = 1/2(8 - 6) = 1$$

F_2 possesses a net single bond

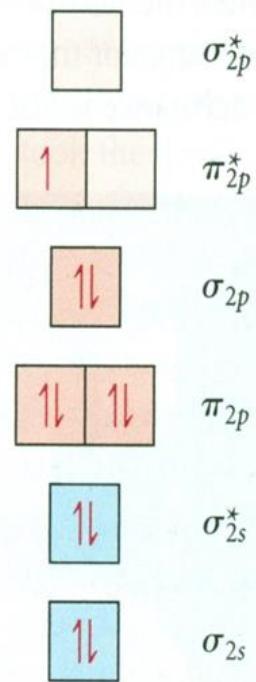
MO diagram of CO



MO diagram of NO



The N_2^- ion has 11 valence electrons (5 for each nitrogen atom plus 1 for the negative charge). Assign the electrons to the molecular orbitals beginning with the lowest energy orbitals and following Hund's rule.



Calculate the bond order by subtracting the number of electrons in antibonding orbitals from the number in bonding orbitals and dividing the result by two.

$$\text{N}_2^- \text{ bond order} = \frac{8 - 3}{2} = +2.5$$

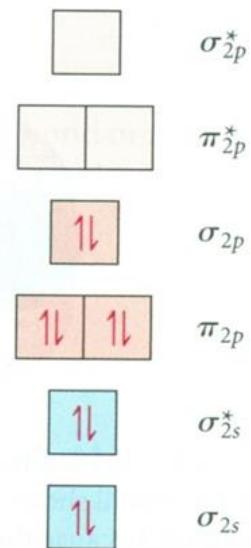
The bond order is 2.5, which is a lower bond order than in the N_2 molecule (bond order = 3); therefore, the bond is weaker. The MO diagram shows that the N_2^- ion has one unpaired electron and is therefore paramagnetic.

Determine the number of valence electrons in the molecule or ion.

Number of valence electrons

$$\begin{aligned} &= 4 \text{ (from C)} + 5 \text{ (from N)} + \\ &\quad 1 \text{ (from negative charge)} \\ &= 10 \end{aligned}$$

Write an energy level diagram using Figure 10.15 as a guide. Fill the orbitals beginning with the lowest energy orbital and progressing upward until all electrons have been assigned to an orbital. Remember to allow no more than two electrons (with paired spins) per orbital and to fill degenerate orbitals with single electrons (with parallel spins) before pairing.



Compute the bond order using the following formula:

Bond order =

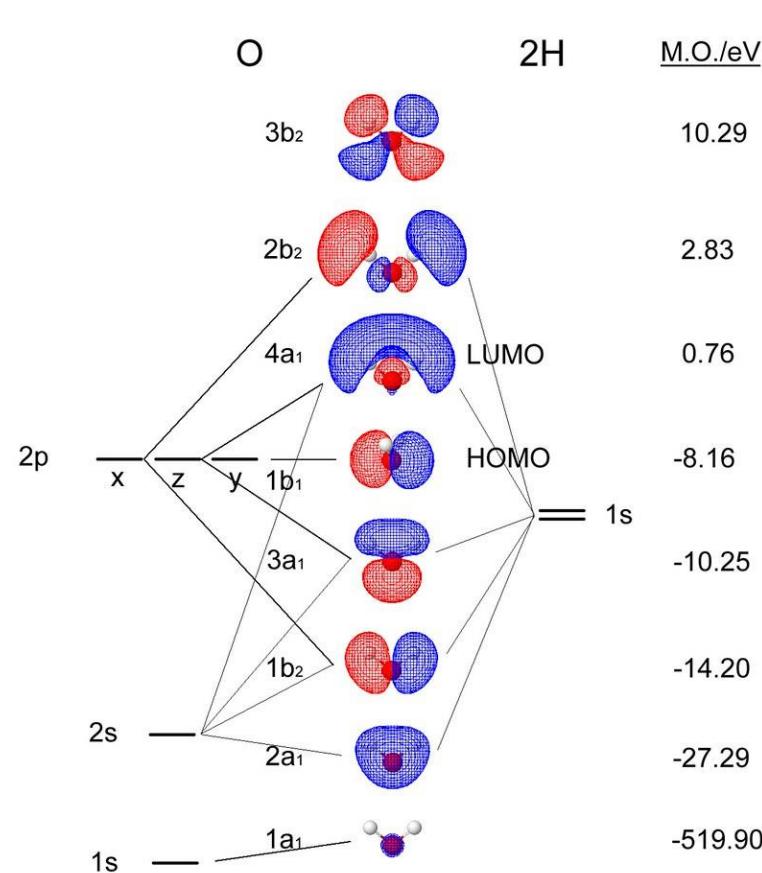
$$\frac{(\text{number of } e^- \text{ in bonding MOs}) - (\text{number of } e^- \text{ in antibonding MOs})}{2}$$

If the MO diagram has unpaired electrons, the molecule or ion is paramagnetic. If the electrons are all paired, the molecule or ion is diamagnetic.

$$\text{CN}^- \text{ bond order} = \frac{8 - 2}{2} = +3$$

Since the MO diagram has no unpaired electrons, the ion is diamagnetic.

Molecular Orbitals for Water



Orbital interaction "**topology**" as discussed above plays a most-important role in determining the orbital energy level patterns of a molecule. Symmetry also comes into play, but in a different manner. Symmetry can be used to characterize the core, bonding, nonbonding, and antibonding molecular orbitals.

In 1965 R. B. Woodward and Ronald Hoffmann of Harvard University proposed and demonstrated that concerted reactions proceed most readily when there is congruence between the orbital symmetries of the reactants and products. In other words, when the bonding character of all occupied molecular orbitals is preserved at all stages of a concerted molecular reorganization, that reaction will most likely take place. The greater the degree of bonding found in the transition state for the reaction, the lower will be its activation energy and the greater will be the reaction rate.

