

Chapter 9

Molecular Geometries and Bonding Theories

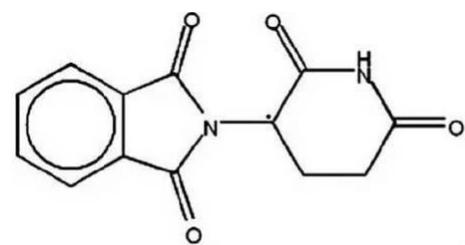
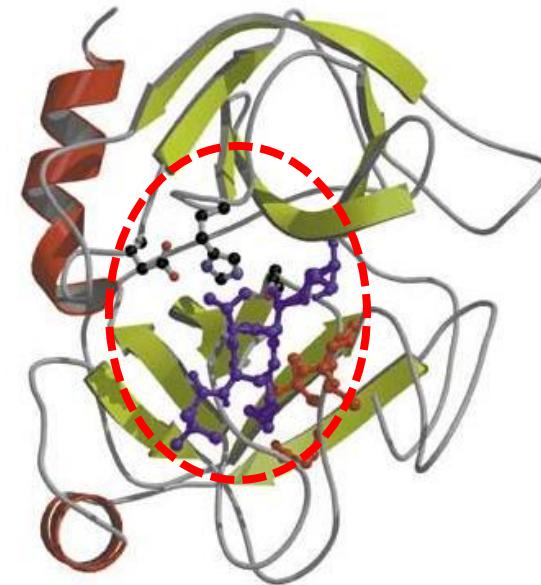
➤ Molecular Shapes

- The **geometry (几何形状)** of a molecule plays an important role in its reactivity.

- Shape
- Size
- Strength and polarity of bonds



Thalidomide

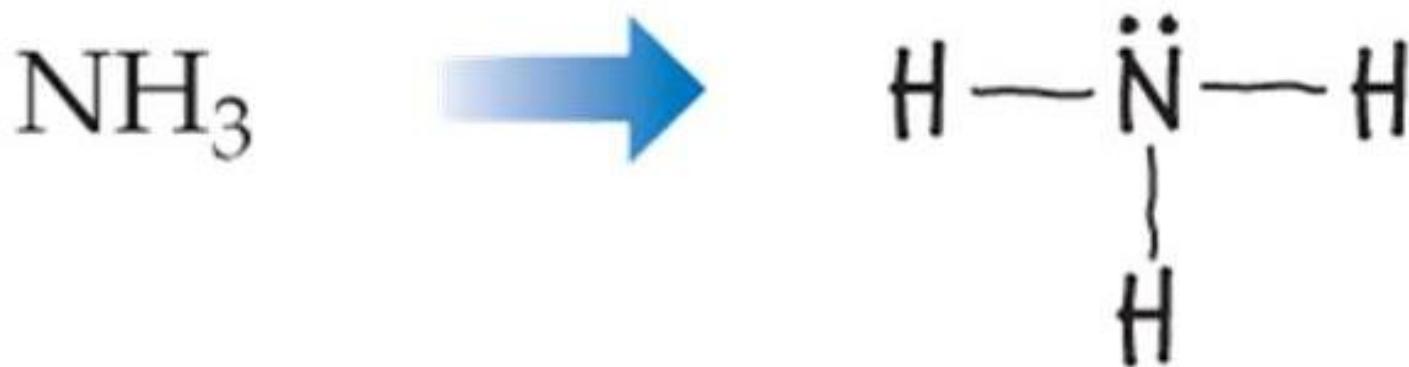


Note: • = asymmetric carbon atom



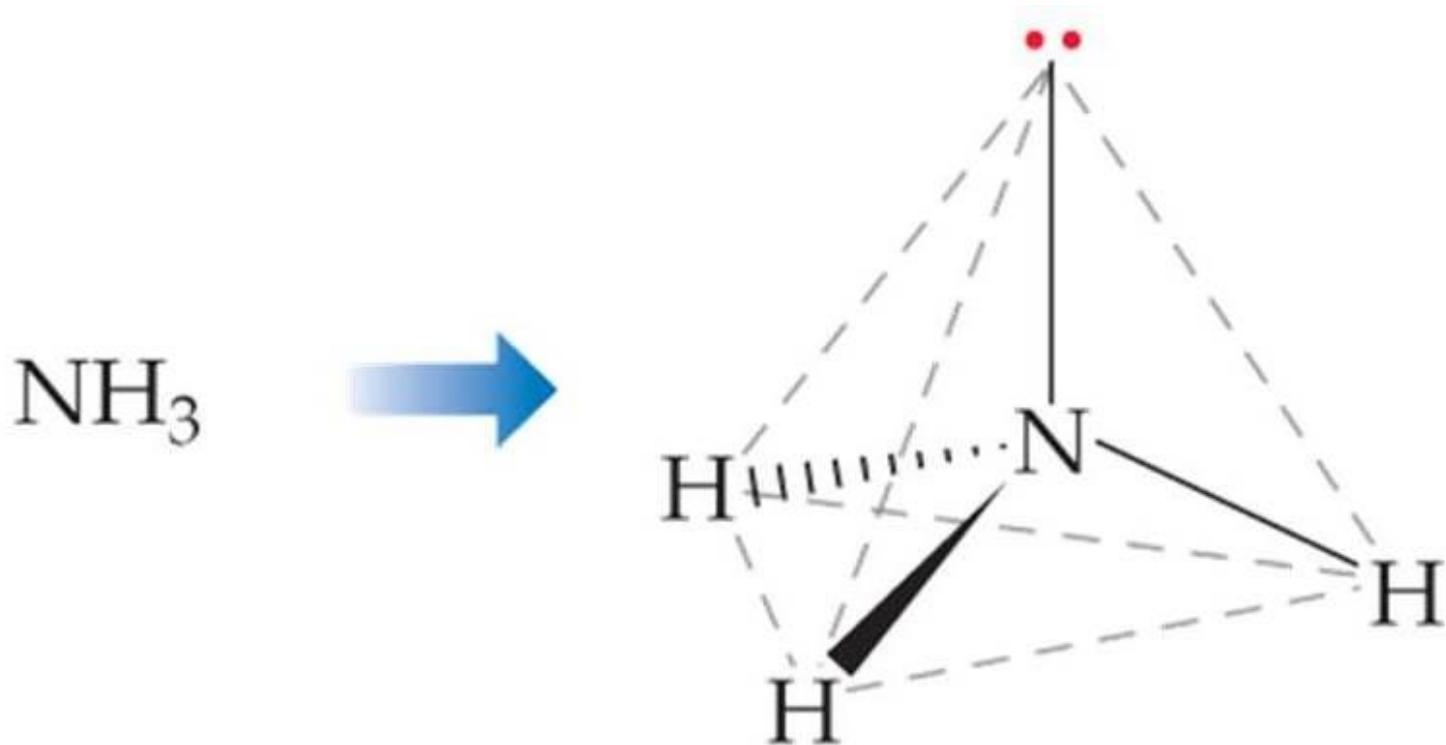
➤ Molecular Shapes

- Lewis structure helps to understand the compositions of molecules and their covalent bonds.
- Do not show the important aspects of molecules-overall shape.



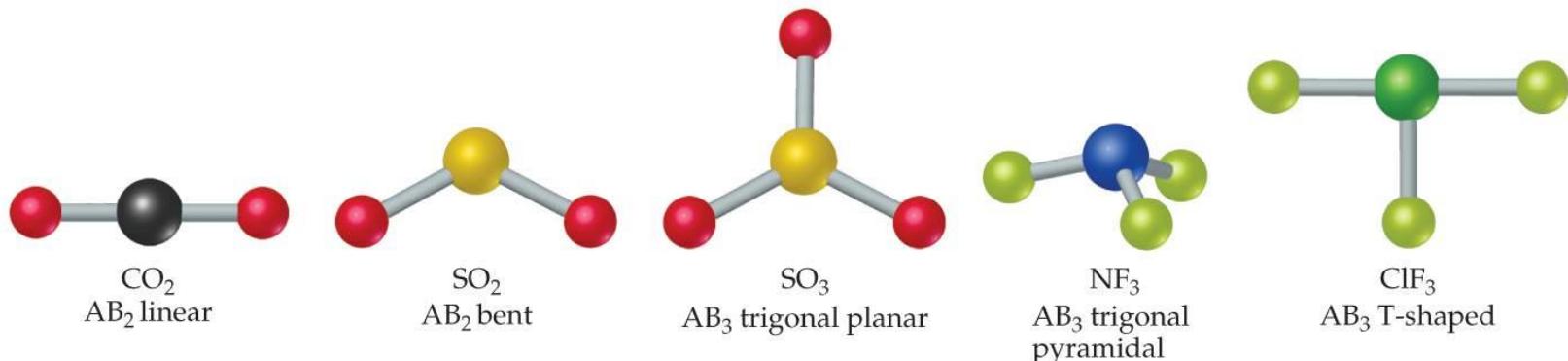
➤ Molecular Shapes

- Molecular architecture(结构): the bond angles and bond length define the shape and size of the molecule.



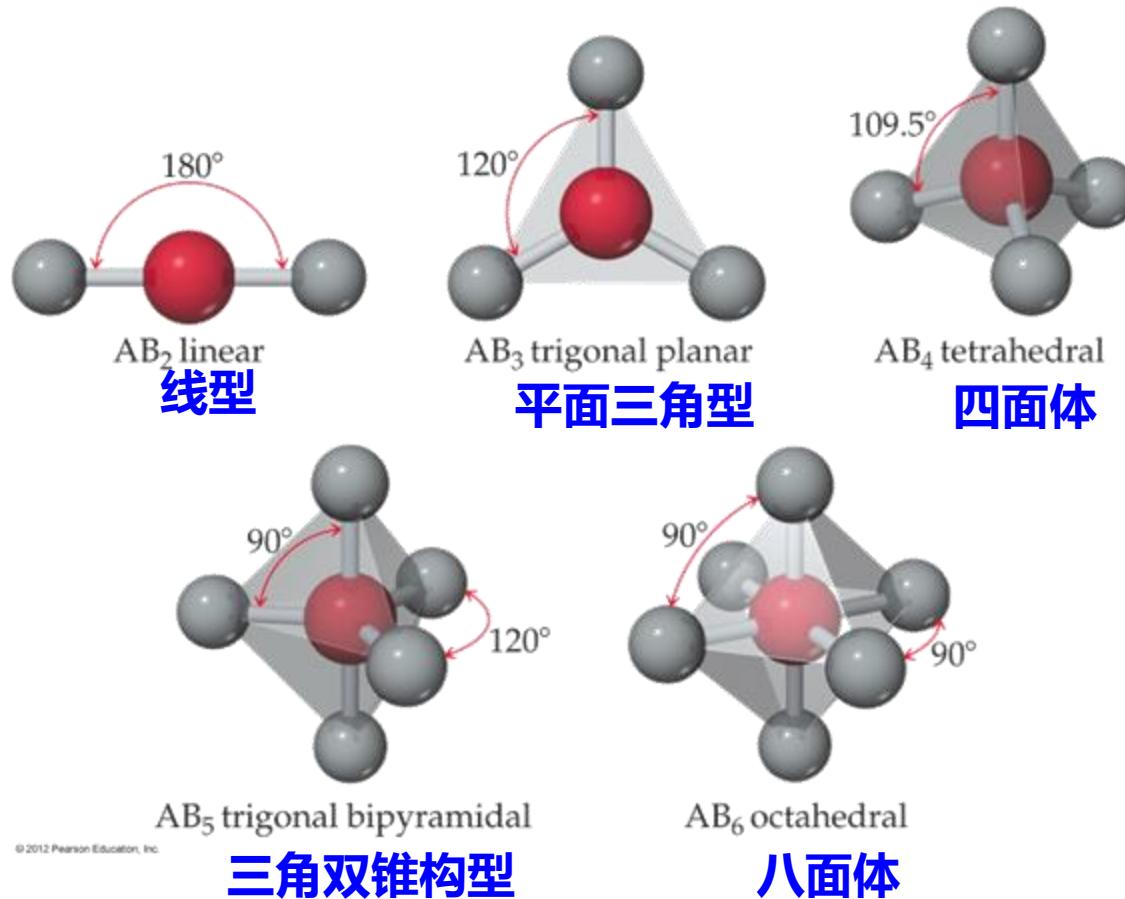
➤ Molecular Shapes

- By noting the number of bonding and nonbonding electron pairs, we can easily predict the shape of the molecule.
- Molecules AB_n : the central atom A is bonded to n B atoms.
- The shapes possible for AB_n molecules depends on the value of n .

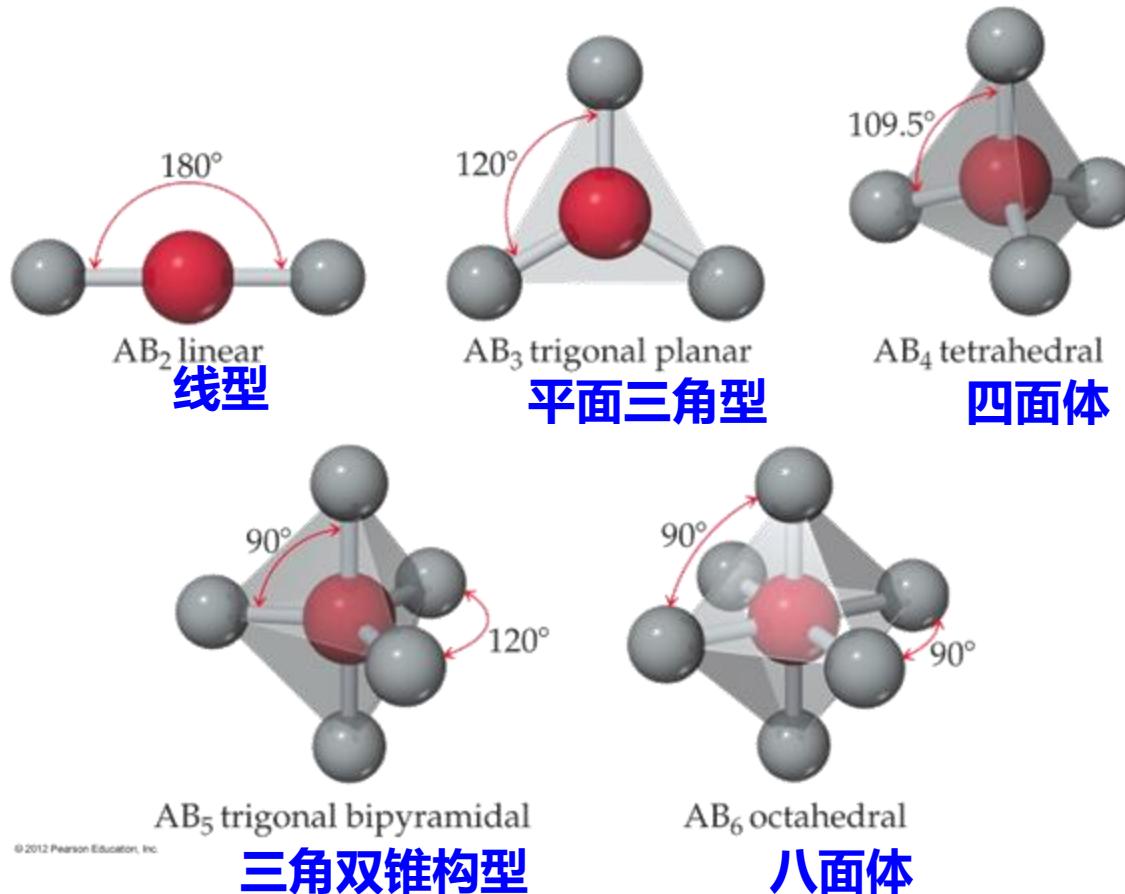


➤ What Determines the Shape of a Molecule?

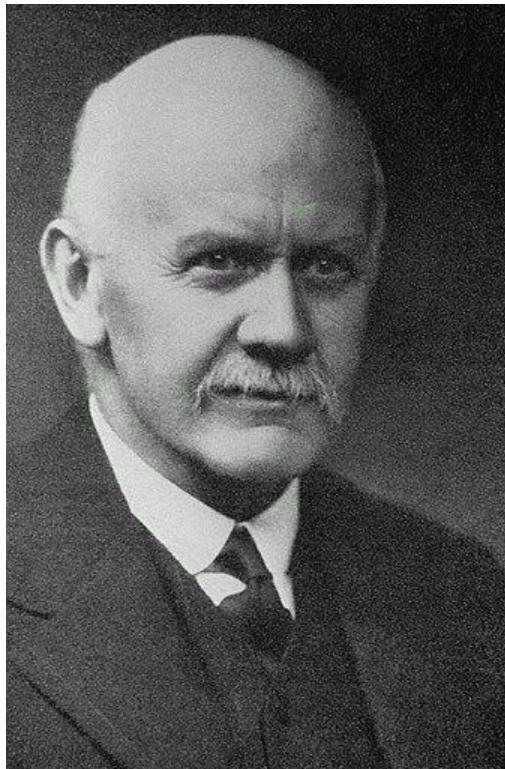
- Simply put, electron pairs, whether they be bonding or nonbonding, repel each other.



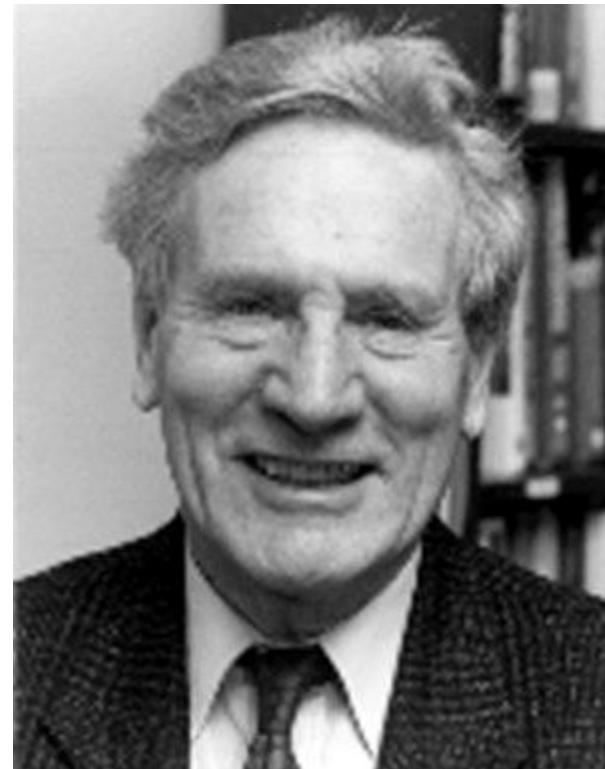
- By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.



➤ **Valence-Shell Electron-Pair Repulsion Theory
(VSEPR)价层电子对互斥理论**



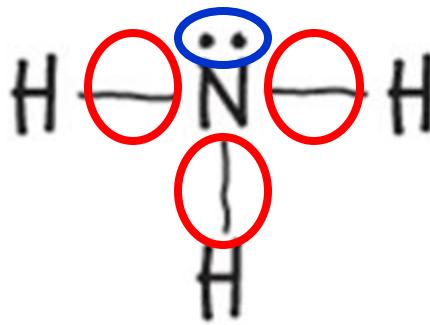
Nevil Vincent Sidgwick
(1873–1952)



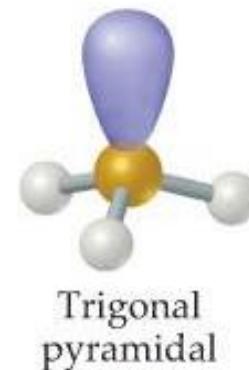
Ronald James Gillespie
(1924–1921)

➤ VSEPR Model

- A bonding pair of electrons defines a region in which the electrons are most likely to be found, such a region is an **electron domain(电子域)**.
- Likewise, nonbonding pair of electrons defines an electron domain located principally on one atom.



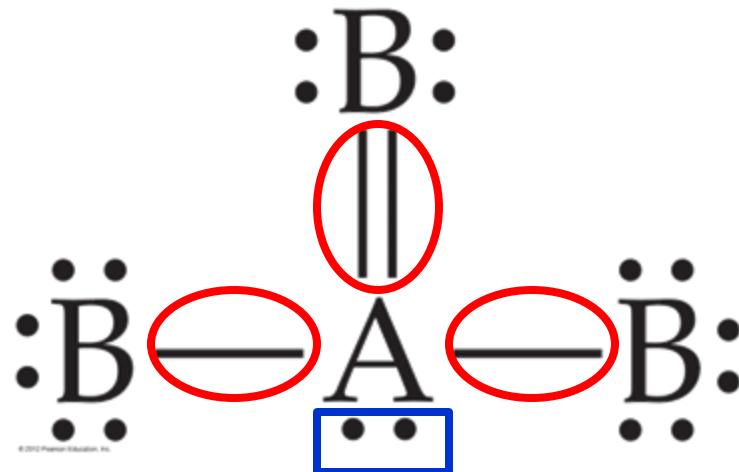
4 electron domains



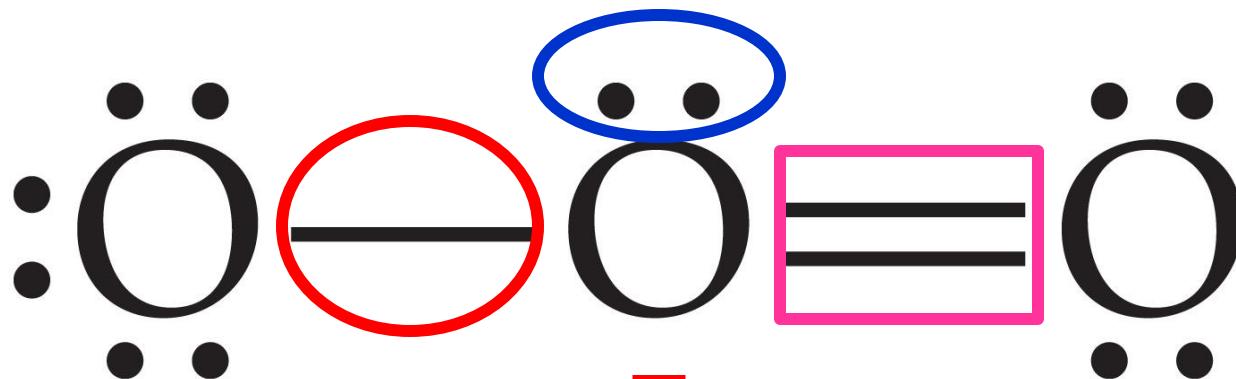
➤ Electron Domains

- We can refer to the electron pairs as **electron domains**.
- In a double or triple bond, all electrons shared between those two atoms are on the same side of the central atom; therefore, they count as one electron domain.

- The central atom in this molecule, A, has four electron domains.

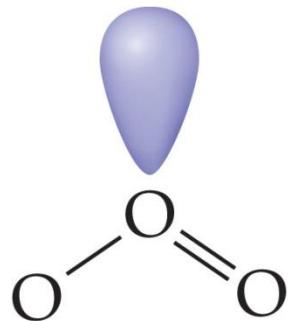
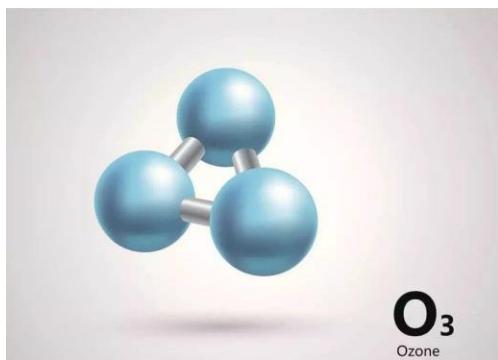


➤ Electron Domains

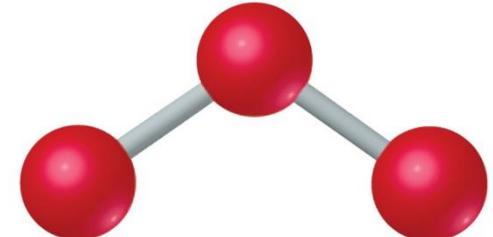


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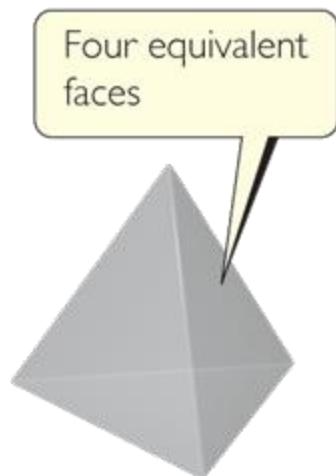
3 electron domains



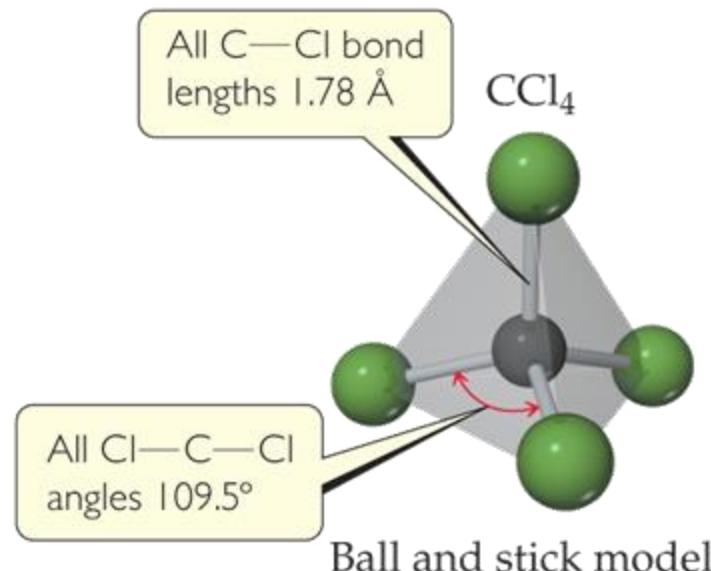
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➤ Valence-Shell Electron-Pair Repulsion Theory (VSEPR) 价层电子对互斥理论

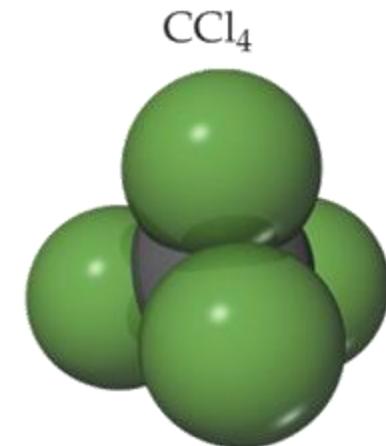


Tetrahedron



Ball and stick model

球棒模型

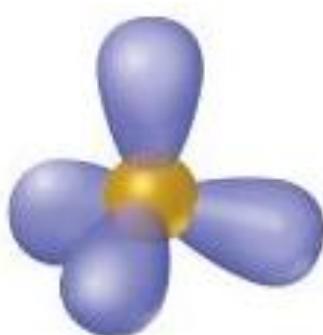


Space-filling model

空间填充模型

"The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them."

- **Electron-domain geometry:** the arrangement of electron domains about the central atom of an AB_n molecule or ion.
- **Molecular geometry:** arrangement of only the atoms in a molecule or ion-any nonbonding pairs in the molecule are not part of the description.

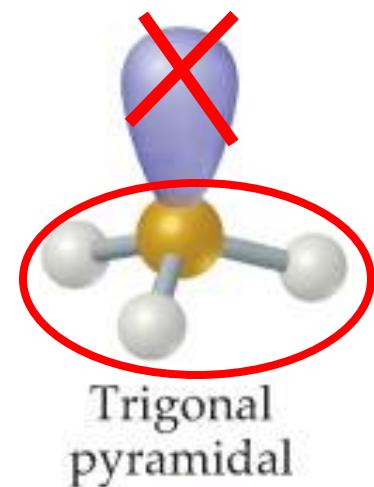


Tetrahedral

*Electron-
domain
geometry*

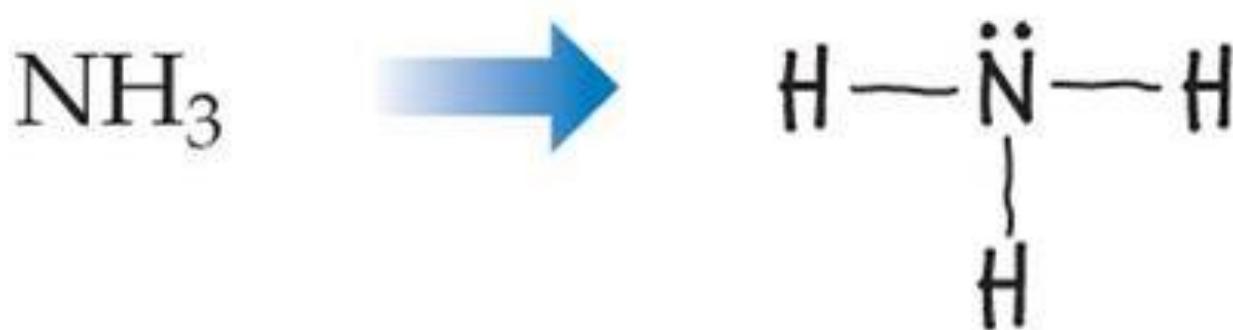


*Molecular
geometry*



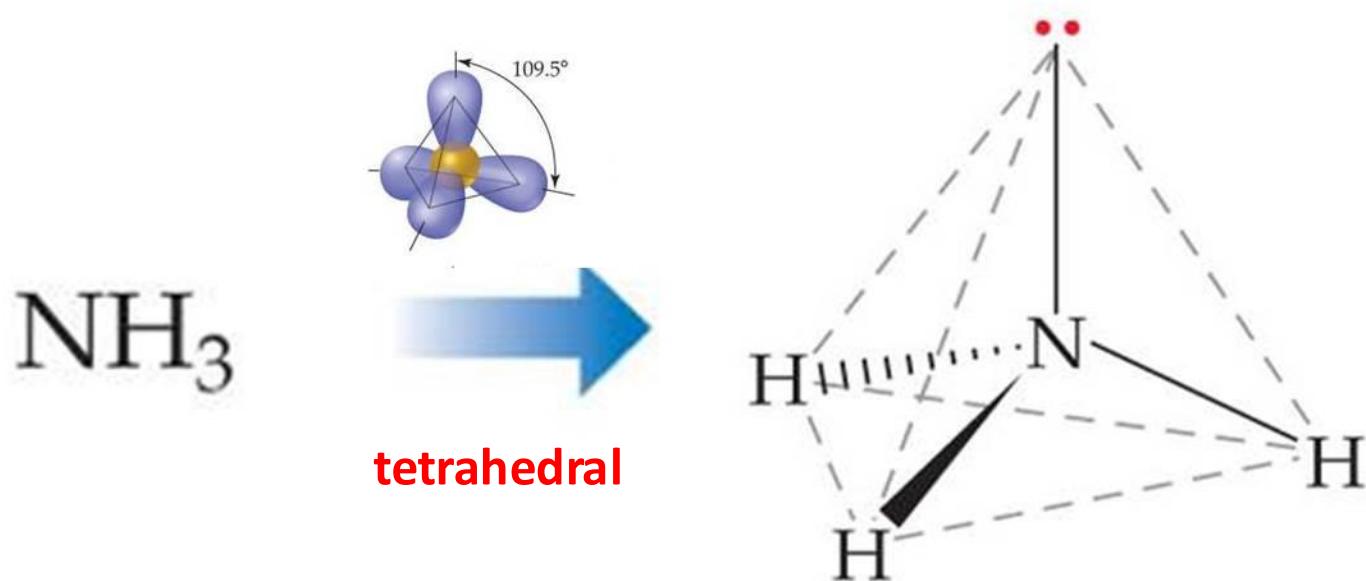
➤ The VSEPR Model

- Draw the Lewis structure of the molecule or ion, count the number of electron domains around the central atom, including nonbonding and bonding pairs of electron.

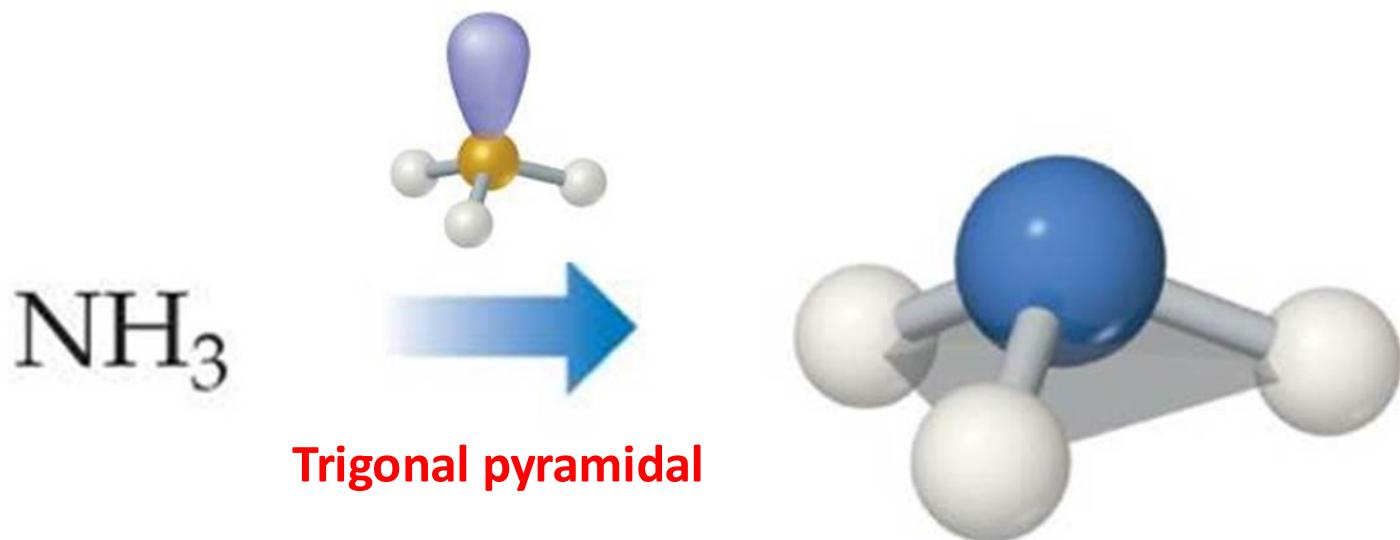


1. Draw Lewis structure

- Determine the electron-domain geometry by arranging the **electron domains** about the central atom so that the repulsions among them are minimized.

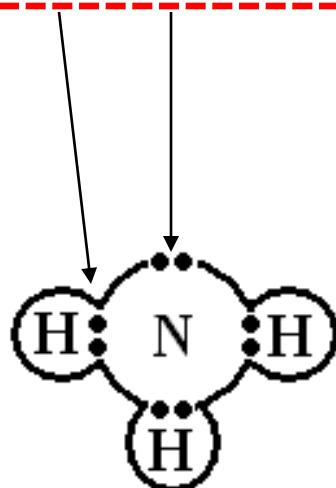


- Use the arrangement of the bonded atoms to determine the **molecular geometry**, counting only bonding electron-domain.



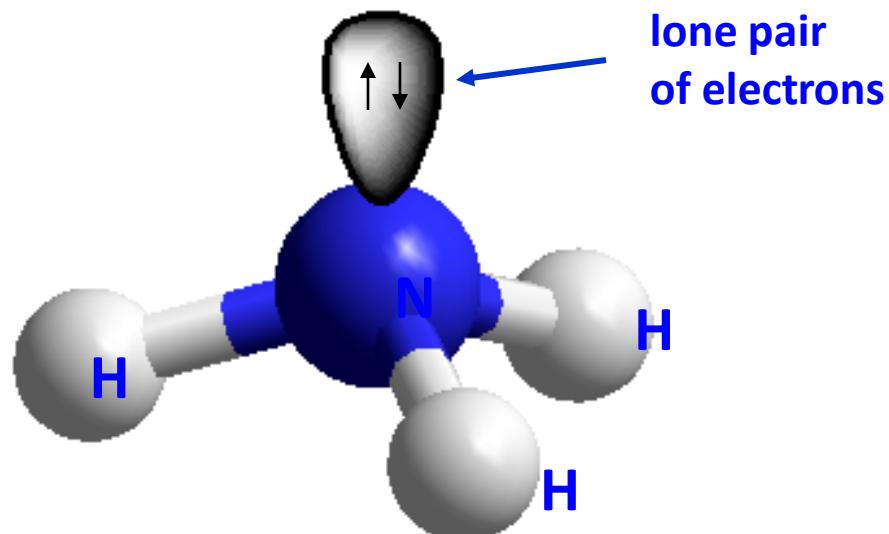
Electron Domains and Molecular Geometry

each lone pair of electrons plus each atom bonded to the central atom constitute an electron 'domain'



Lewis dot diagram
of ammonia

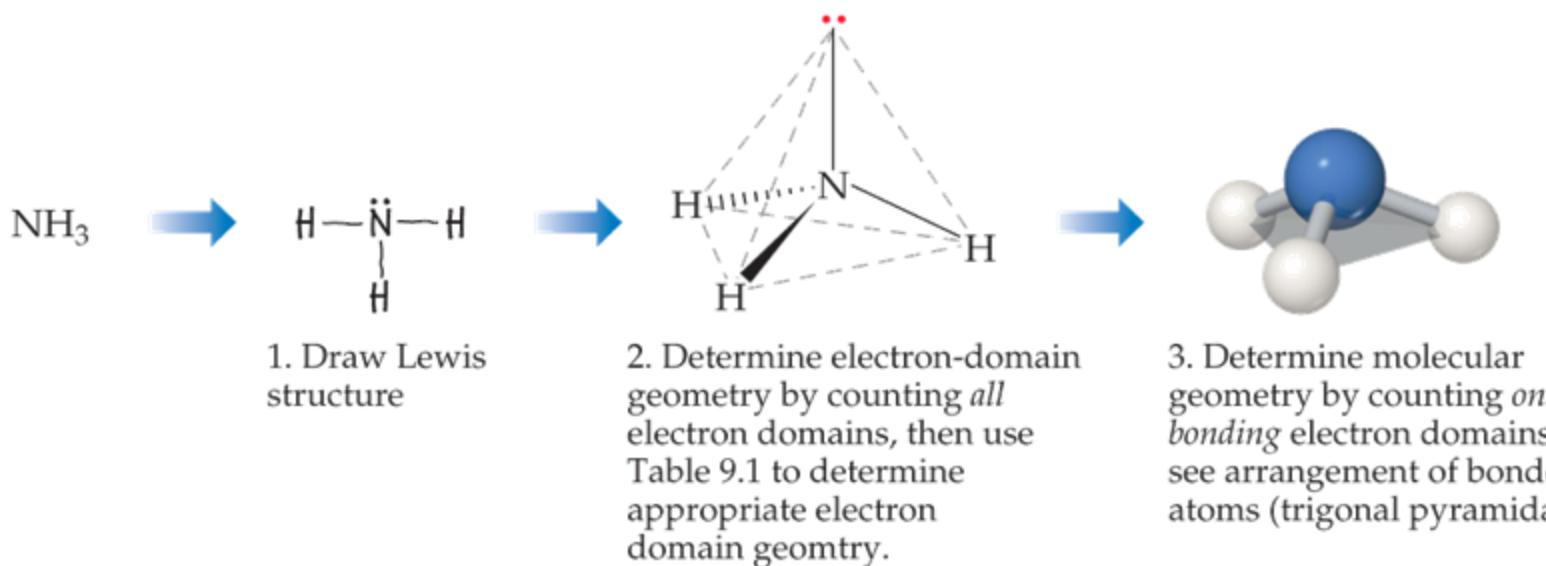
observed geometry is that where the electron domains are as far apart as possible



Ammonia trigonal pyramidal
(derived from tetrahedral geometry)

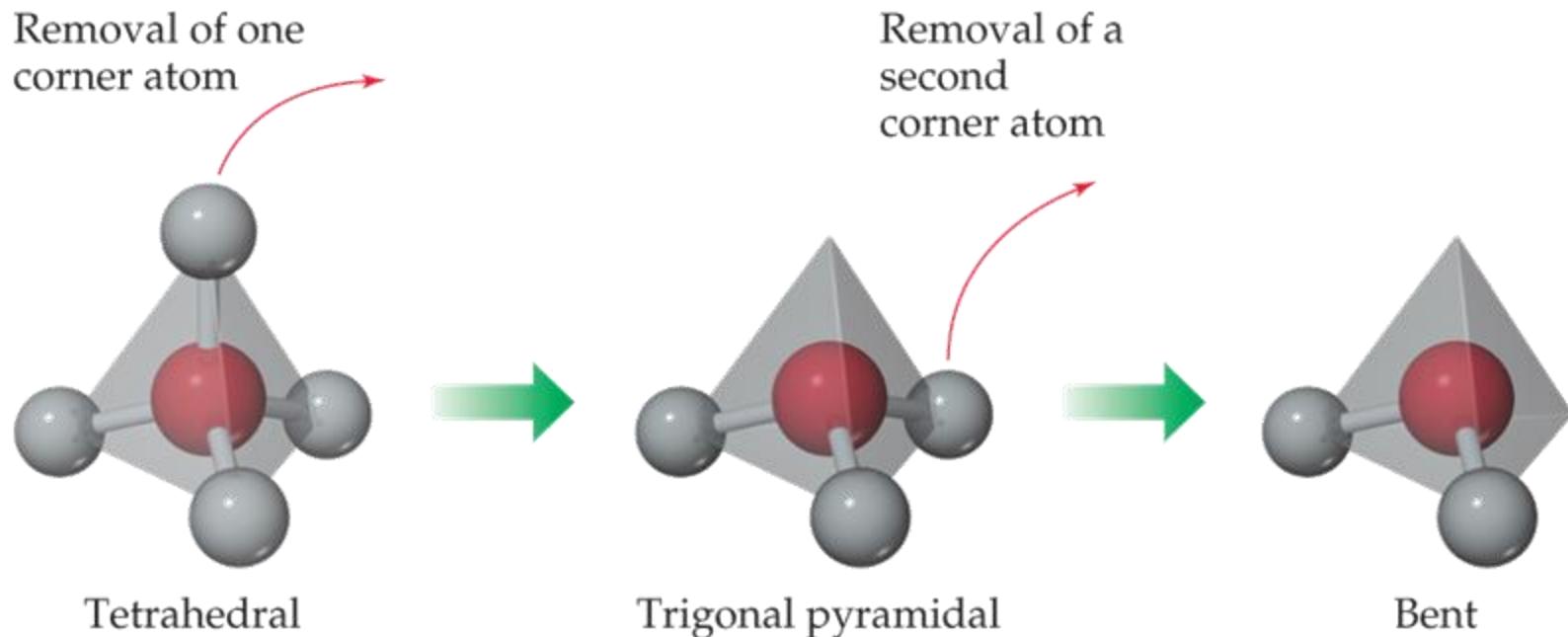
➤ Molecular Geometries

- The electron-domain geometry is often *not* the shape of the molecule, however.
- The molecular geometry is that defined by the positions of *only* the atoms in the molecules, not the nonbonding pairs.



➤ Molecular Geometries

- Within each electron domain, then, there might be more than one molecular geometry.

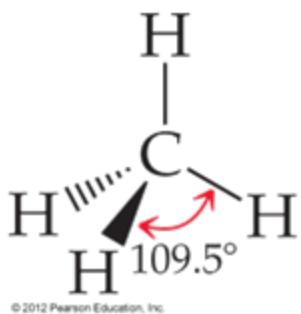
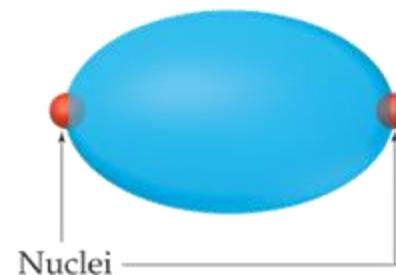


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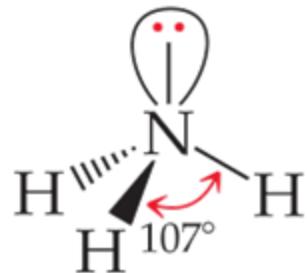
➤ Nonbonding Pairs and Bond Angle

- Nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.

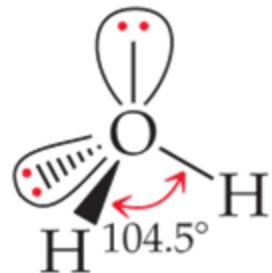
Bonding electron pair



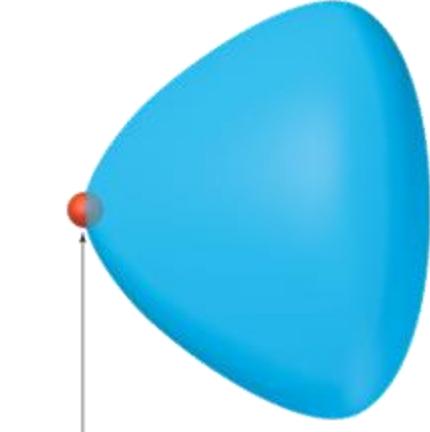
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Nonbonding pair

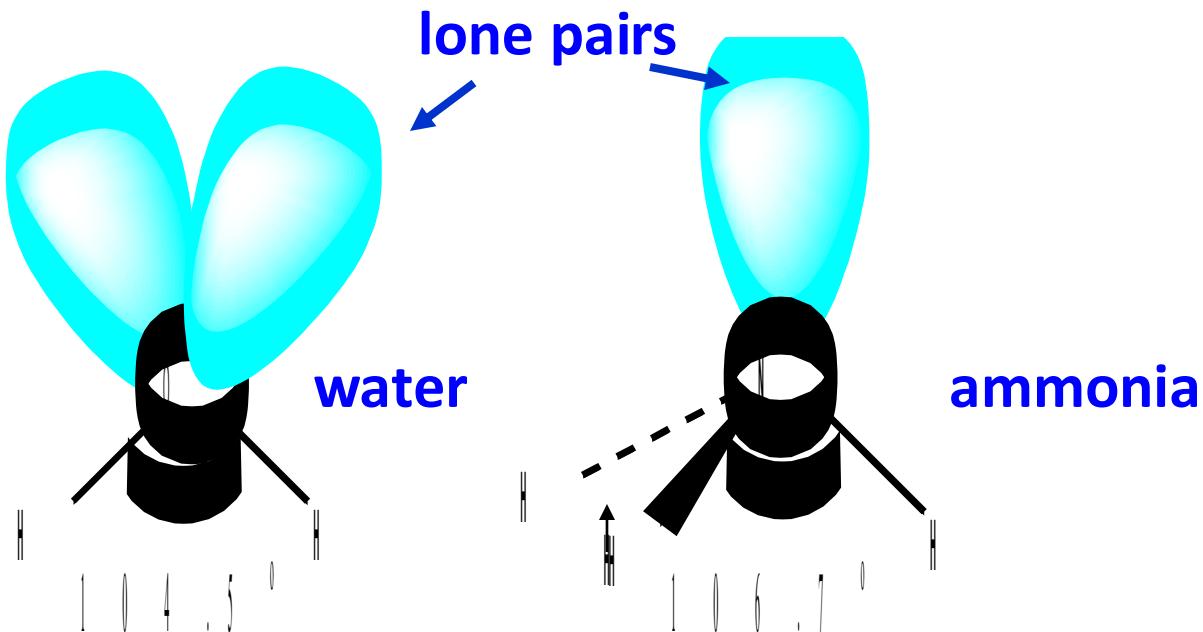


Nucleus
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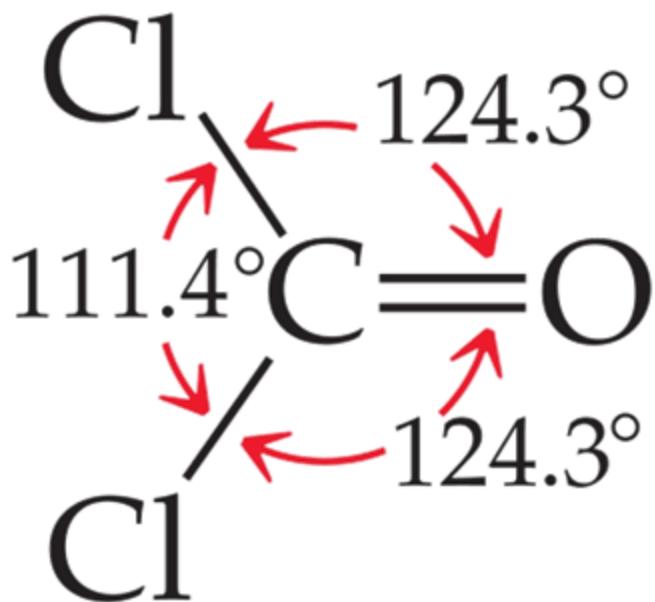
➤ Nonbonding Pairs and Bond Angle

- In VSEPR, the lone pairs appear to occupy more space than bonded electron pairs in bonds, with the result that bond angles are compressed away from the lone pairs. For example, in structures derived from tetrahedral parent geometry, such as water or ammonia, the H-O-H and H-N-H angles are compressed to be less than the 109.5° expected for a regular tetrahedron:

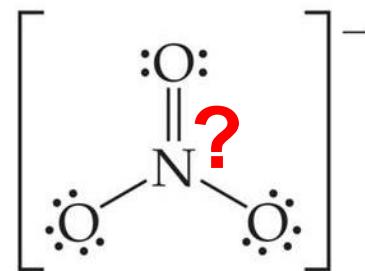


➤ Multiple Bonds and Bond Angles

- Double and triple bonds place greater electron density on one side of the central atom than do single bonds.
- Multiple bonds exert a greater repulsive force on adjacent electron domain than single bonds



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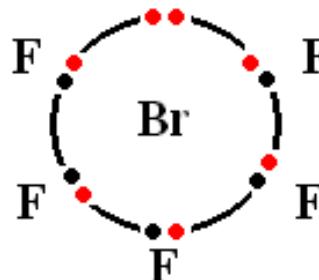
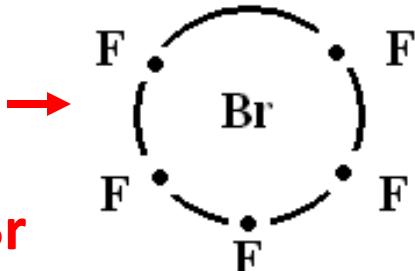


➤ Using VSEPR

□ In order to use VSEPR to predict molecular structure:

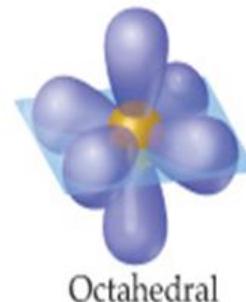
- Draw up Lewis dot diagram for the molecule or ion. The first atom (e.g. Br in BrF_5) is always the central atom. Place the other atoms around the central atom.
- If these are single bonds, contribute one electron per attached atom. Then add the valence electrons for the central atom = 7 for Br.

place 5 F
atoms
around
central Br

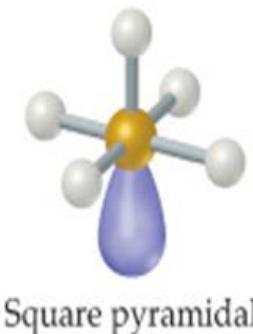


red = 7
valence
electrons
for Br

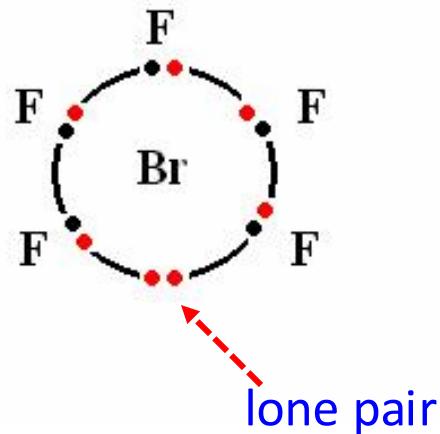
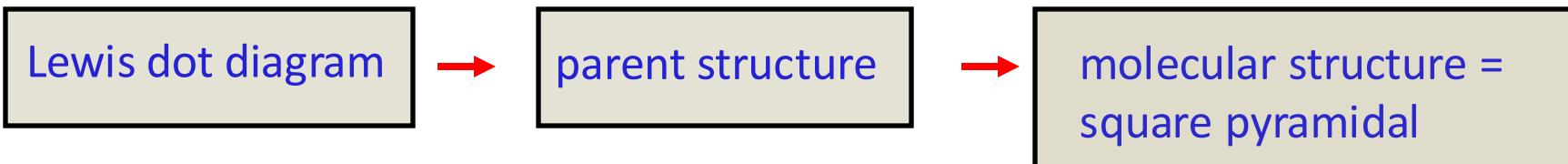
- Work out number of electron domains = valence electron pairs ('n') on central atom. For BrF_5 n = 6.
- Relate n to the type of structure predicted for that value of n. n = 6 = octahedral.



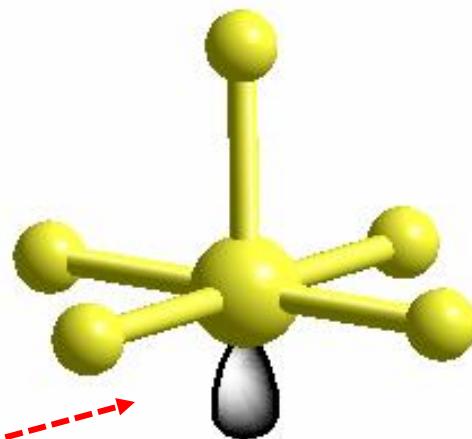
- Place lone pairs in expected positions, maximizing separation of lone pairs. For BrF_5 , there is one lone pair, so mol. structure = square pyramidal.



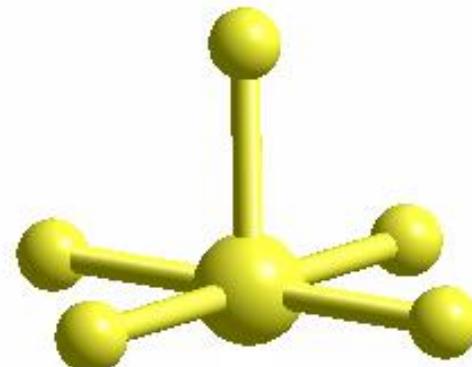
➤ Structure of BrF_5 from VSEPR



$n = 6$ from five attached atoms plus one electron pair



$n = 6$, parent structure = octahedral, but one site occupied by a lone pair

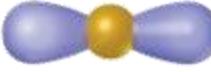


molecular or final structure – disregard the lone pair

➤ Linear Electron Domain

- In the linear domain, there is only one molecular geometry: linear.
- NOTE: If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.

TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

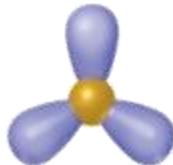
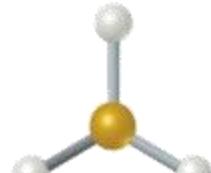
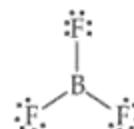
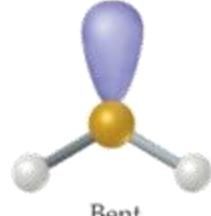
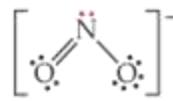
Number of Electron Domains	Electron- Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2		2	0		$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$

➤ 3 electron domains: Trigonal Planar Electron Domain

□ There are two molecular geometries:

- Trigonal planar, if all the electron domains are bonding
- Bent, if one of the domains is a nonbonding pair

TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
3	 Trigonal planar	3	0	 Trigonal planar	
2		1		 Bent	

3 electron domains

➤ 4 electron domains Tetrahedral Electron Domain

□ There are three molecular geometries:

- Tetrahedral, if all are bonding pairs
- Trigonal pyramidal, if one is a nonbonding pair
- Bent, if there are two nonbonding pairs

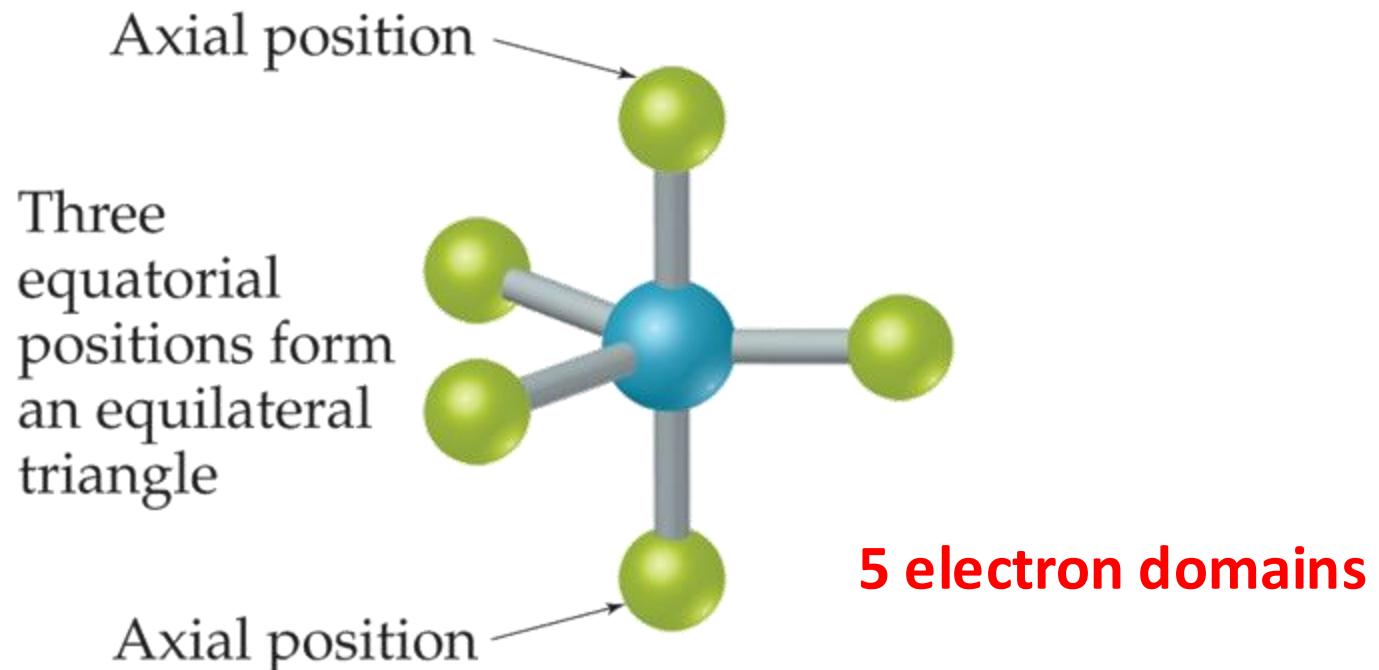
TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
4		4	0		
3		1			
2		2			

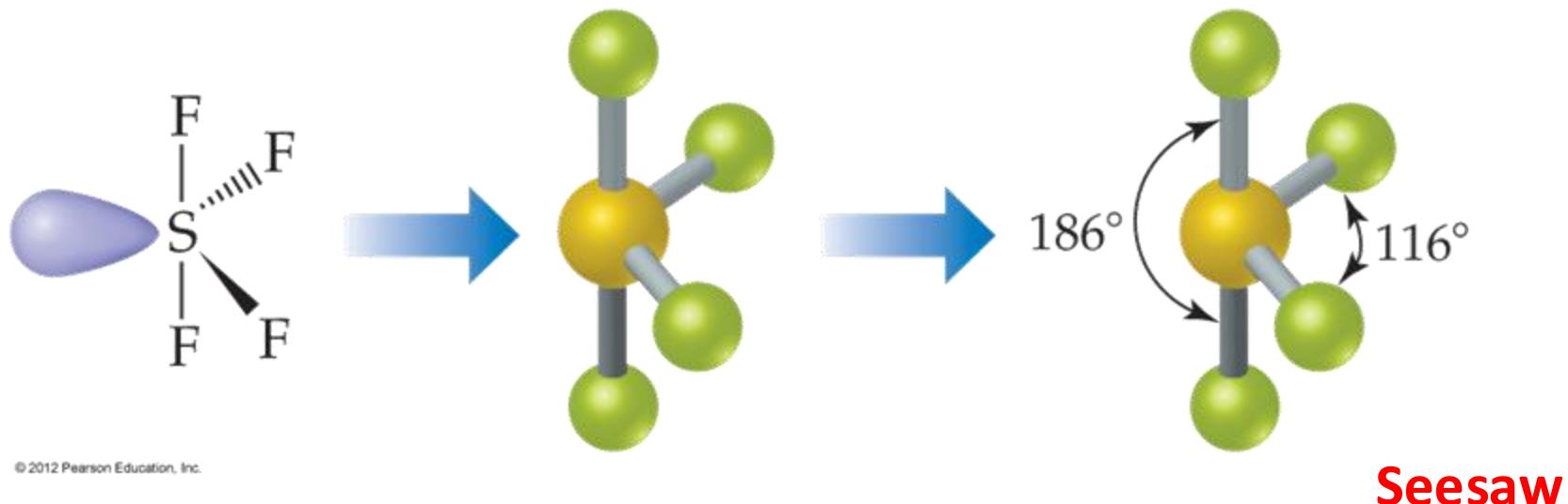
4 electron domains

➤ 5 electron domains: Trigonal Bipyramidal Electron Domain

- There are two distinct positions in this geometry:
 - Axial(轴)
 - Equatorial(赤道)



- **Trigonal Bipyramidal Electron Domain**
- Lower-energy conformations result from having **nonbonding electron pairs in equatorial**, rather than axial, positions in this geometry.

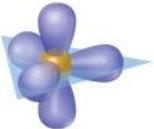
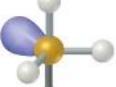
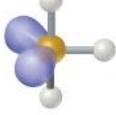
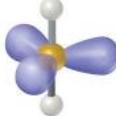


➤ Trigonal Bipyramidal Electron Domain

- There are four distinct molecular geometries in this domain:

- Trigonal bipyramidal
- Seesaw
- T-shaped
- Linear

TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0		PCl ₅
4		1			SF ₄
3		2			ClF ₃
2		3			XeF ₂

5 electron domains

➤ 6 electron domains Octahedral Electron Domain

- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:
 - Octahedral
 - Square pyramidal
 - Square planar

TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	Octahedral	6	0	Octahedral	<chem>SF6</chem>
5		1		Square pyramidal	<chem>BrF5</chem>
4		2		Square planar	<chem>XeF4</chem>

TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

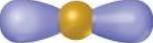
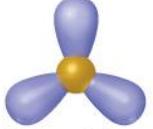
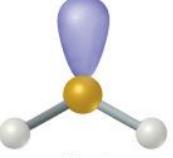
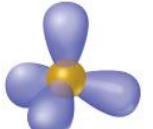
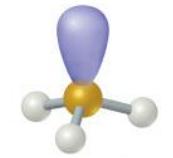
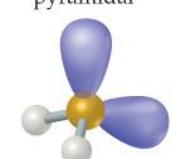
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	 Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	 Trigonal planar	3	0	 Trigonal planar	$\text{B}(\text{F})_3$
		2	1	 Bent	$[\text{N}(\text{O})_2]^-$
4	 Tetrahedral	4	0	 Tetrahedral	CH_4
		3	1	 Trigonal pyramidal	NH_3
		2	2	 Bent	H_2O

TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

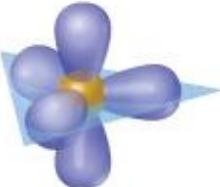
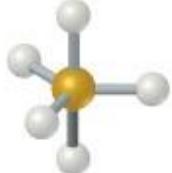
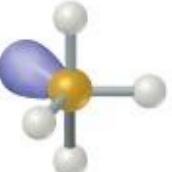
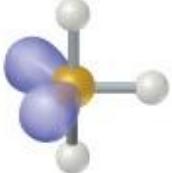
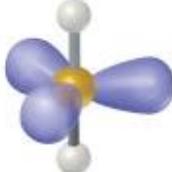
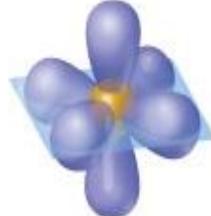
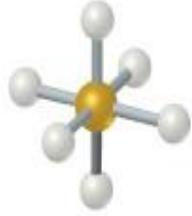
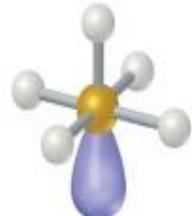
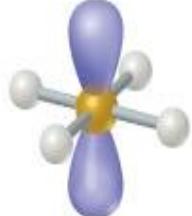
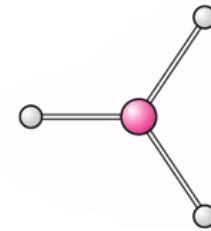
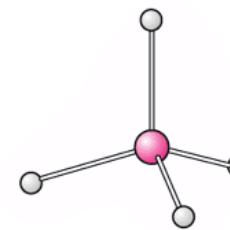
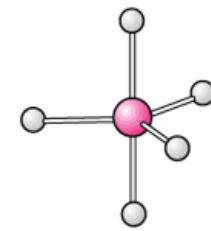
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5		5	0		PCl_5
	Trigonal bipyramidal			Trigonal bipyramidal	
		4	1		SF_4
				Seesaw 跷跷板	
		3	2		ClF_3
				T-shaped	
		2	3		XeF_2
				Linear	

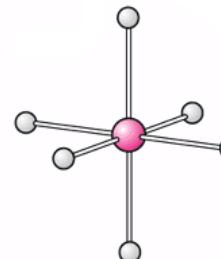
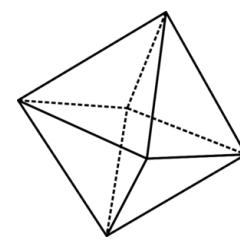
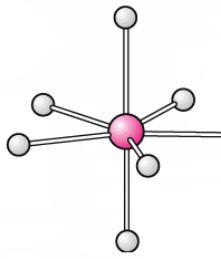
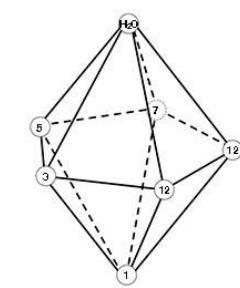
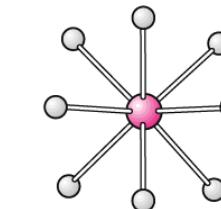
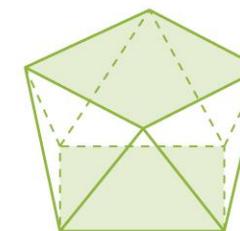
TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron- Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6		6	0		SF_6
	Octahedral			Octahedral	
5		1			BrF_5
				Square pyramidal	
4		2			XeF_4
				Square planar	

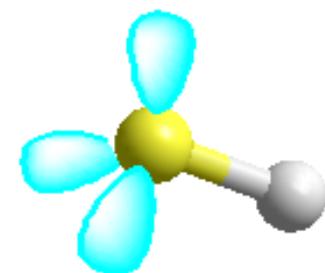
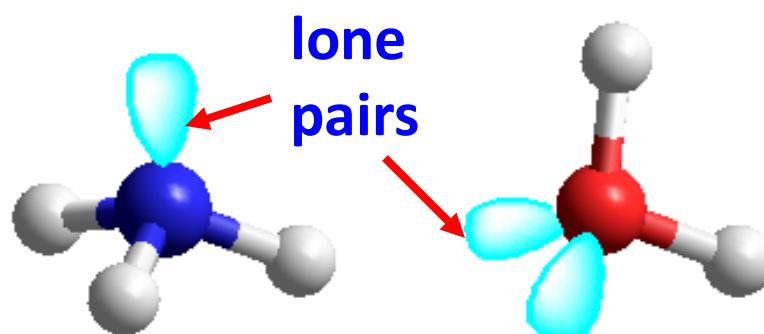
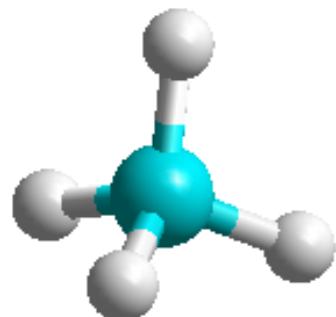
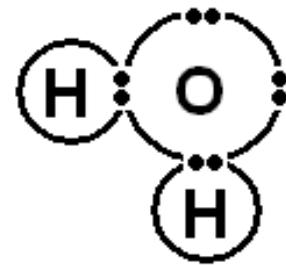
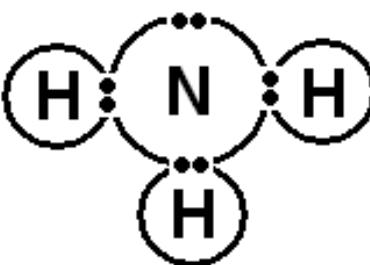
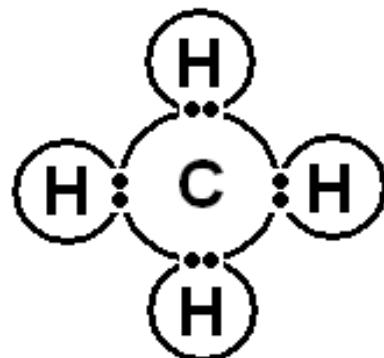
➤ Parent Shapes for EX_n Molecules ($n = 2\text{--}5$)

<u>Formula</u>	<u>n</u>	<u>shape</u>	<u>shapes of structures</u>
EX_2	2	linear	
EX_3	3	trigonal planar	
EX_4	4	tetrahedral	
EX_5	5	trigonal bipyramidal	

➤ Parent Shapes for EX_n Molecules (n = 6–8)

<u>Formula</u>	<u>n</u>	<u>shape</u>	<u>shapes of structures</u>
EX ₆	6	octahedral	 
EX ₇	7	pentagonal bipyramidal	 
EX ₈	8	square antiprismatic 四棱柱	 

Derivatives of EX_4 Geometry with Increasing Numbers of Lone Pairs



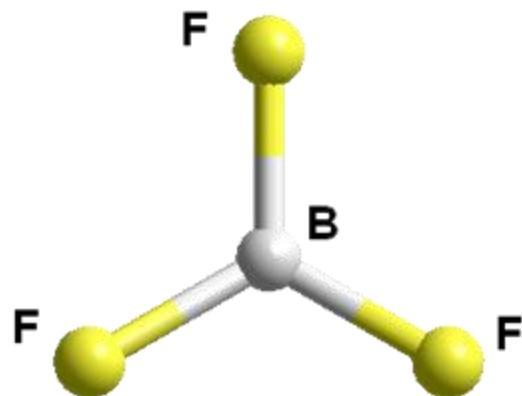
Methane
Tetrahedral

ammonia
trigonal pyramid

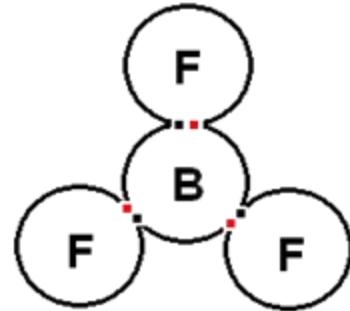
water
bent

hydrogen fluoride
linear diatomic

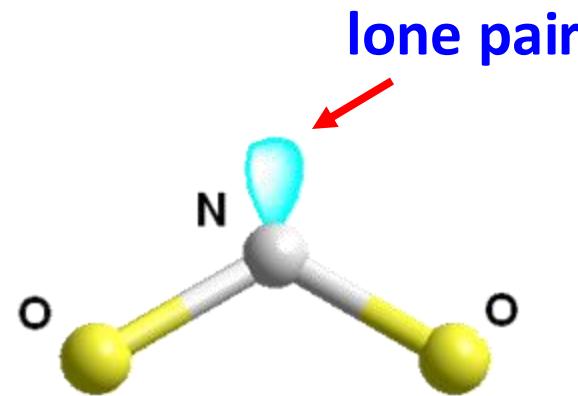
Structures Derived from Trigonal Geometry ($n = 3$)



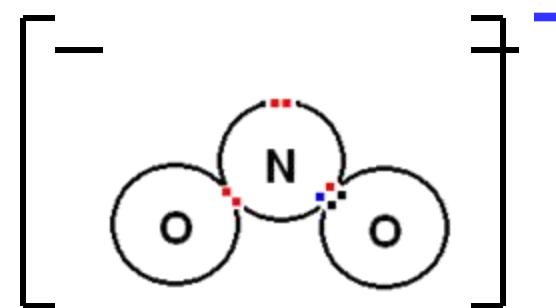
trigonal planar



boron trifluoride
trigonal planar



bent

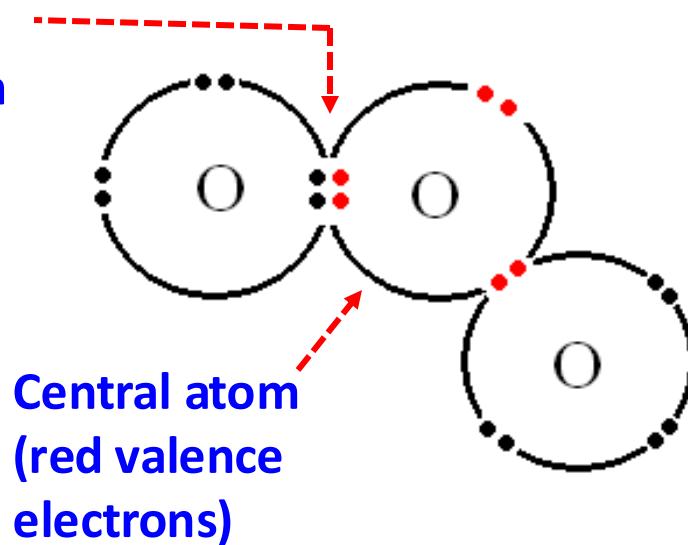


nitrite anion, NO_2^-
bent

➤ Ozone – A Bent Molecule

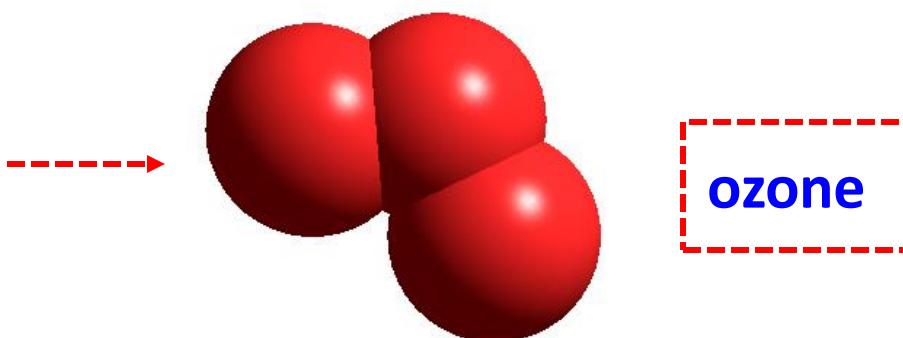
- The structure of the O_3 (ozone) molecule can be predicted using VSEPR.
- First draw up the Lewis dot diagram

Note that two pairs
of e's (double bond) still
count as only one electron
domain = one
attached O-atom



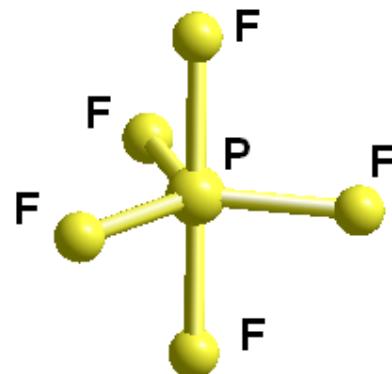
- For the valence shell of the central oxygen atom $n = 3$, so parent geometry = trigonal. The final structure is thus two-coordinate bent, as seen for the ozone molecule below:

Structure of the ozone molecule (oxygens = red atoms)

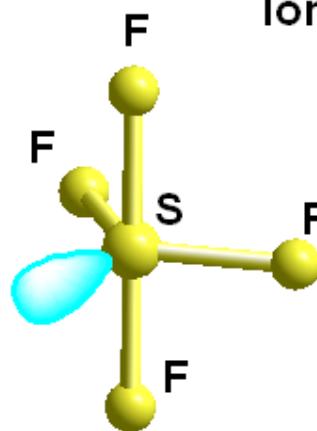


Structures Derived from TBP ($n = 5$)

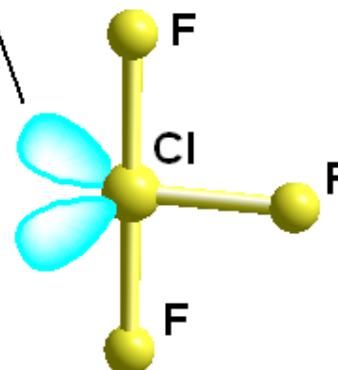
(Note: lone pairs go in the plane)



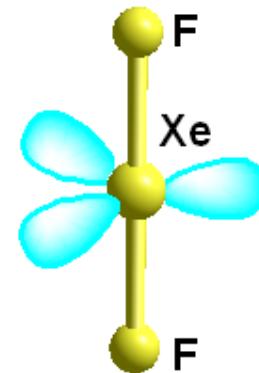
trigonal bipyramidal



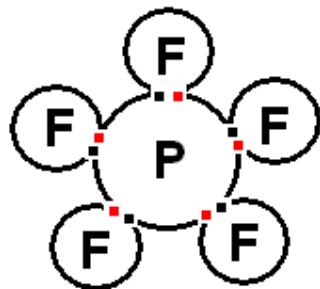
saw-horse



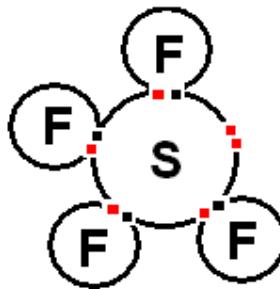
T-shaped



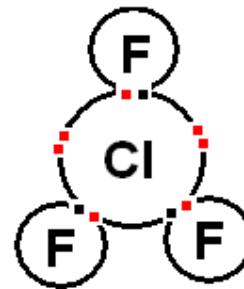
linear



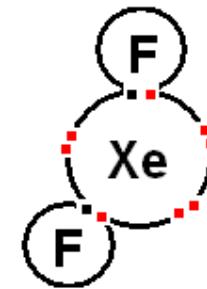
phosphorus
pentafluoride



sulfur
tetrafluoride

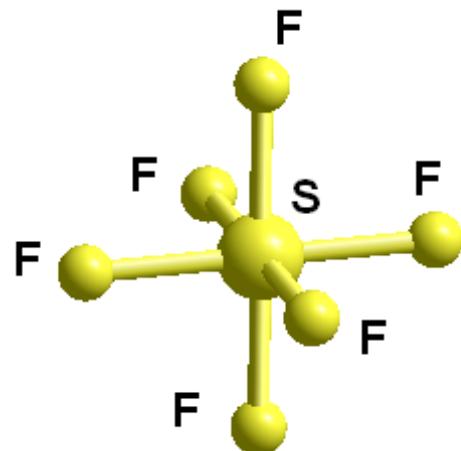


chlorine
trifluoride

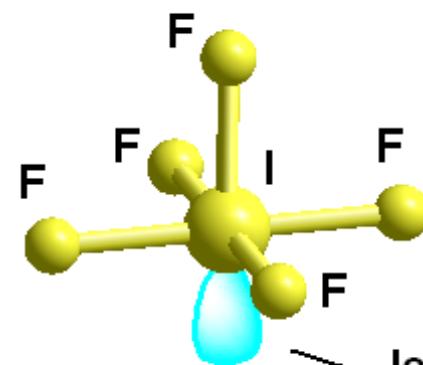


xenon
difluoride

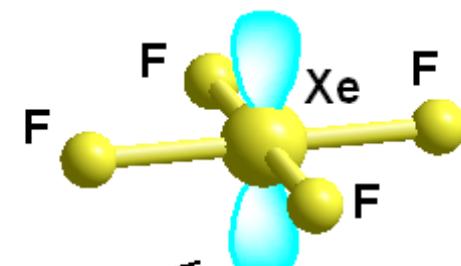
Structures Derived from Octahedron ($n = 6$)



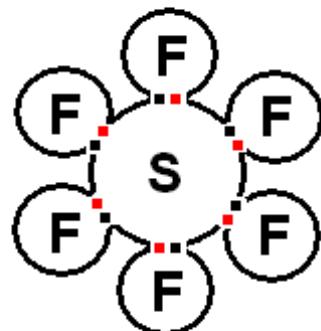
octahedral



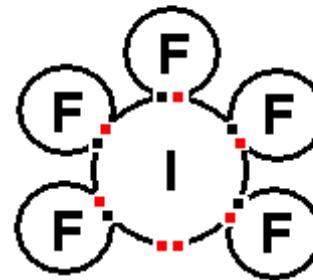
square pyramidal



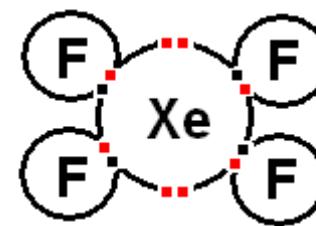
square planar



sulfur hexafluoride



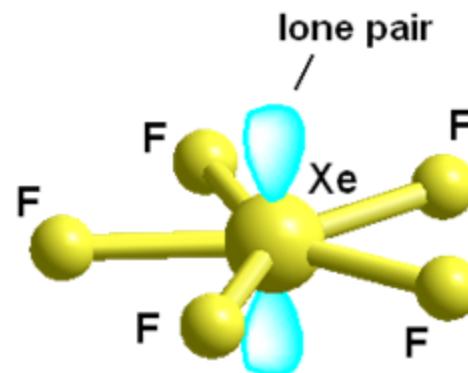
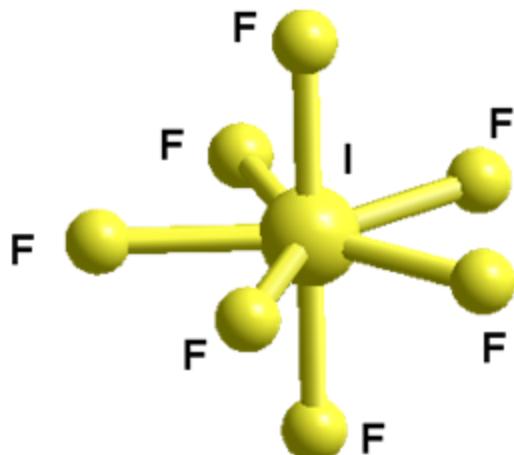
iodine pentafluoride



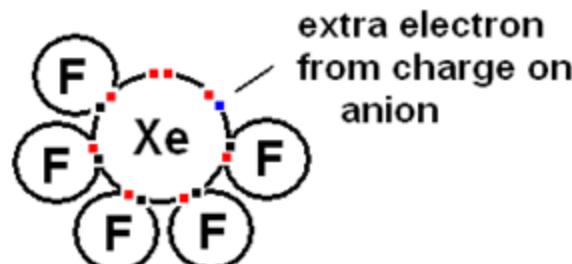
xenon tetrafluoride

Structures Derived from Pentagonal Bipyramidal ($n = 7$)

(Note: lone pairs go axial)

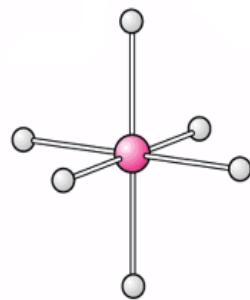
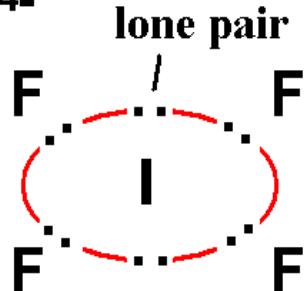


iodine heptafluoride



xenon pentafluoride anion,
 $[XeF_5]^-$

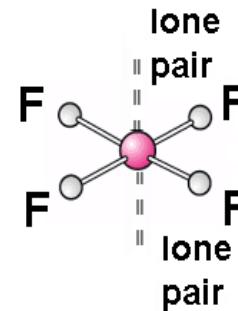
➤ Example: Iodine Tetrafluoride Anion



parent structure
= octahedral

two lone pairs plus 4 bound F atoms, $n = 6$.

two lone pairs



final structure =
square planar

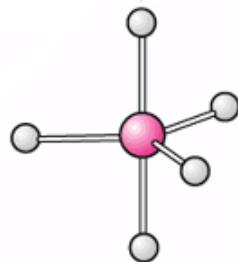
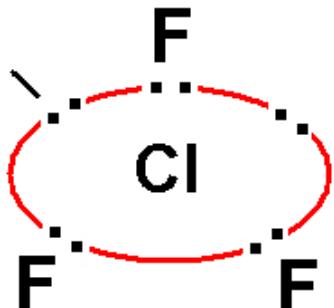
Note: The way the number of valence electrons (= 12) on the iodine is derived is from the seven valence electrons for iodine (group 7 in the periodic table), plus one each from the F-atoms, and one from the negative charge on the complex.

➤ Example: Chlorine Trifluoride

虽然把你提议的结构（三角平面）在纸面上看更对称，但它会导致 6 个强烈的90度排斥。而 T 形结构只有 4 个这样的排斥。自然界总是选择能量最低、最稳定的构型，也就是排斥力最小的构型。因此，孤对电子优先占据赤道位置，形成了 T 形结构。

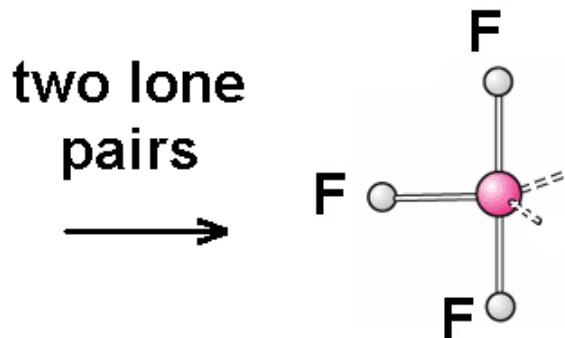


lone pair



parent structure
= TBP

two lone pairs plus 3
bound F atoms, $n = 5$
 $n = 5 = \text{trigonal}$
 bipyramidal (TBP)



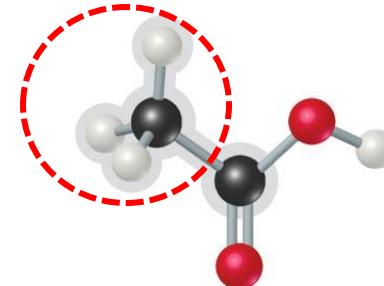
final structure =
T-shaped

注：赤道上的孤对–孤对排斥是120度，赤道上的孤对–成键排斥也是120度。120度的排斥力远小于90度的排斥力。)

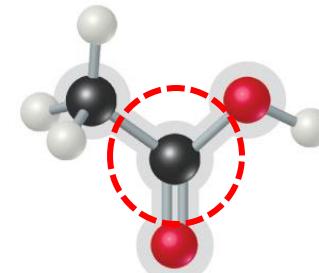
NOTE: in structures derived from a TBP parent structure, the lone pairs always lie in the plane, as seen here for the T-shaped structure of ClF_3 .

➤ Larger Molecules

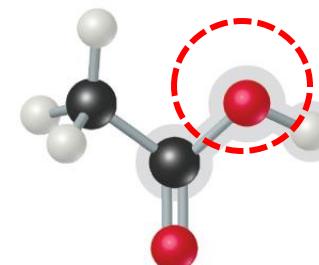
- In larger molecules, it makes more sense to talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.



Electron-domain geometry tetrahedral,
molecular geometry tetrahedral



Electron-domain geometry trigonal planar,
molecular geometry trigonal planar



Electron-domain geometry tetrahedral,
molecular geometry bent

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➤ 提出背景及基本思想

1940年， Sidgwick等人在归纳了许多已知的分子几何构型后， 提出了价层电子对互斥理论(简称VSEPR法， valence shell electron pair repulsion method)。

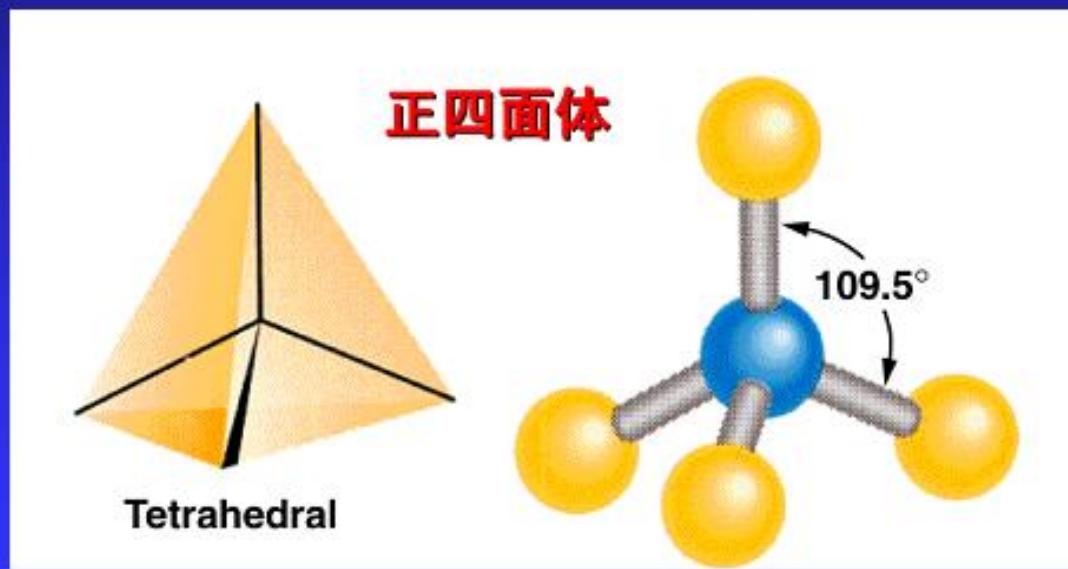
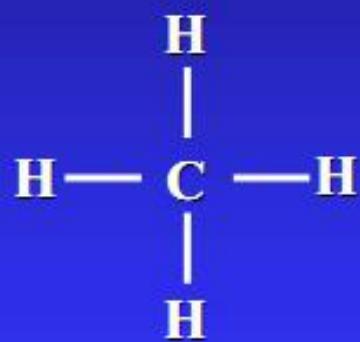
VSEPR法的基本思想是， 分子的共价键(单键、 双键或叁键)中的电子对以及孤对电子由于相互排斥作用而趋向尽可能彼此远离， 分子尽可能采取对称的结构。

利用VSEPR法， 仅需依据分子中成键电子对及孤电子对的数目， 便可定性判断和预见分子属于哪一种几何构型。

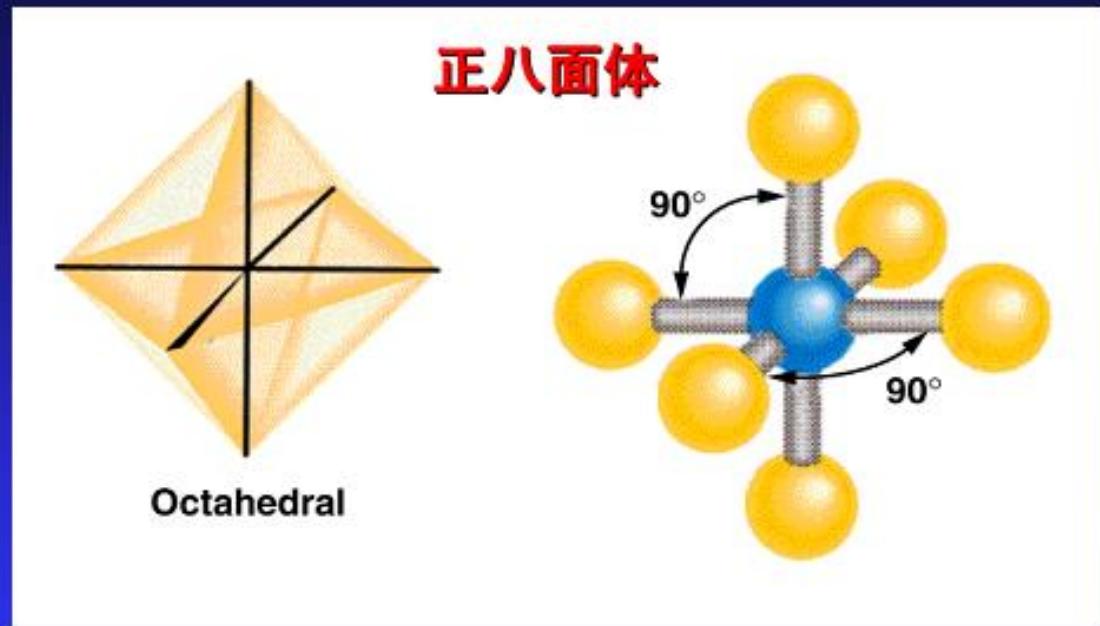
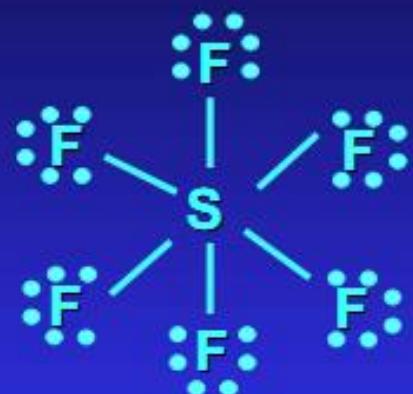
<http://www.faidherbe.org/site/cours/dupuis/vseprev.htm>

► VSEPR法的应用 —— (1) AX_n 型

分子的中心原子A周围只有n个以单键邻接的原子X(或n个单电子对)而没有孤电子对存在。此时，只要知道n的数目(1 - 6)，就可以预测分子构型和相应键角。

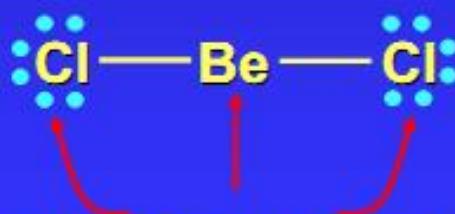
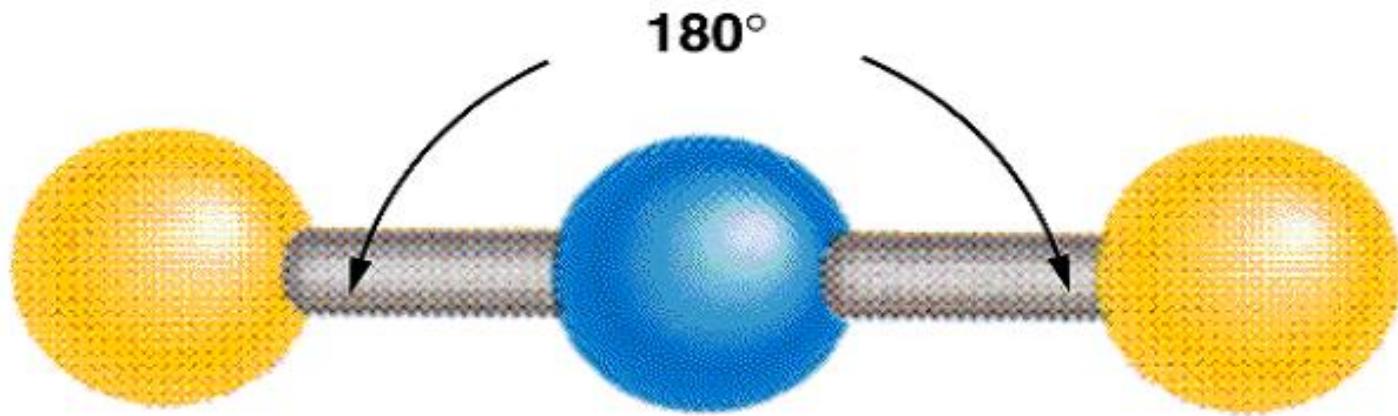


CH_4 分子的电子对几何分布和分子构型



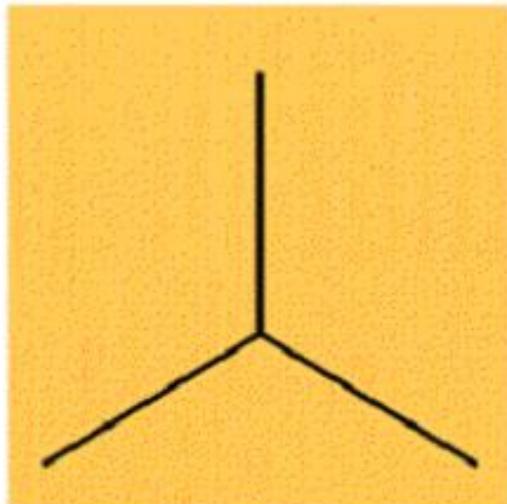
SF_6 分子的电子对几何分布和分子构型

Beryllium Chloride

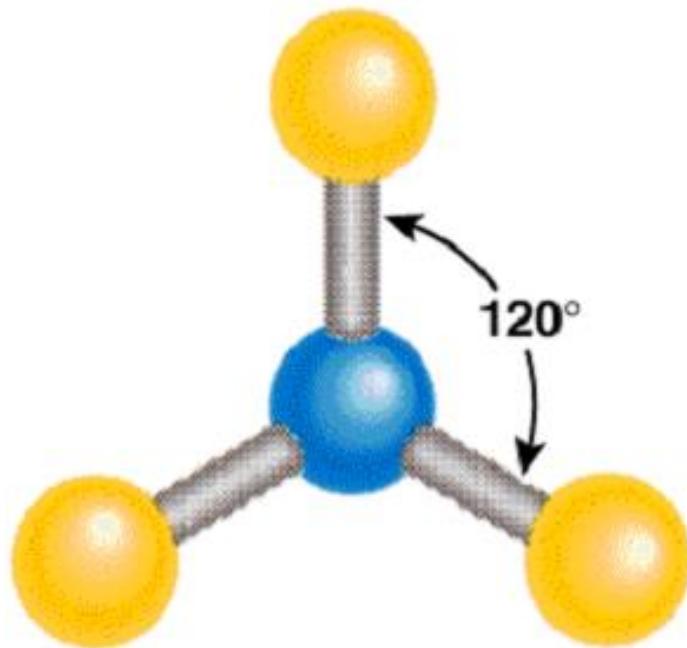


2 atoms bonded to central atom

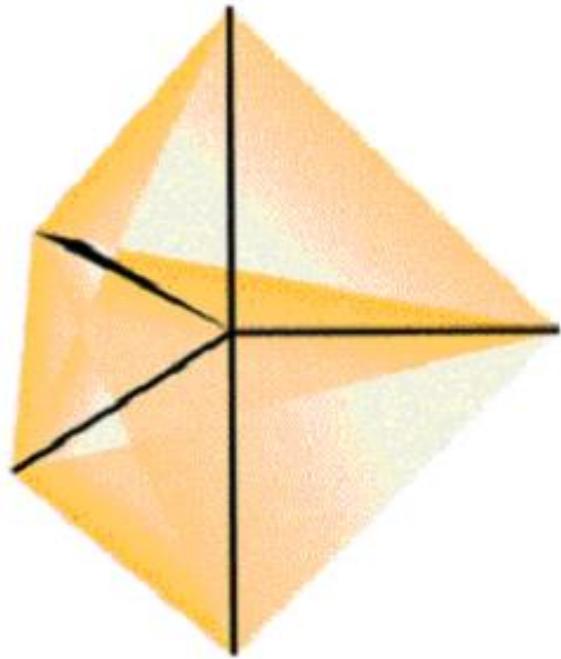
Boron Trifluoride



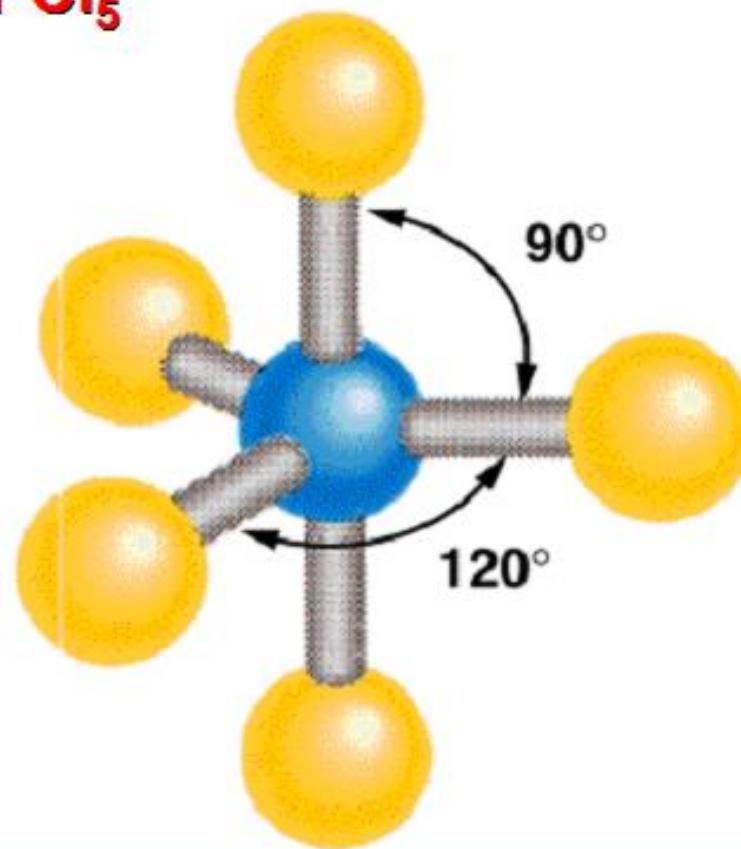
Planar



Phosphorus Pentachloride



Trigonal
bipyramidal



► VSEPR法的应用 —— (2) AX_nE_m 型

分子的中心原子A周围不仅有n个邻接原子(X)的成键电子对，还有m个孤电子对(E)。此时，预测分子构型时除需知道X的数目，还需知道E的数目及其作用。

有以下三条规则：

- 1) 有孤对电子存在，分子中价层电子对的几何分布情况一般仍然保持上述5种基本类型(电子对尽可能彼此分离)，但分子的构型就不限于这5种类型了，因为描绘分子构型时不包括孤对电子，亦即分子的形状由中心原子与相应邻接原子来决定。
- 2) 孤电子对的存在影响分子基本构型中的键角而使分子变形，这是由于孤对电子只受一个原子核的束缚，电子云偏向中心原子一侧，从而对邻近的成键电子有较强的排斥作用，使邻近键角发生变化。

3) 电子对之间的排斥力大小顺序是:

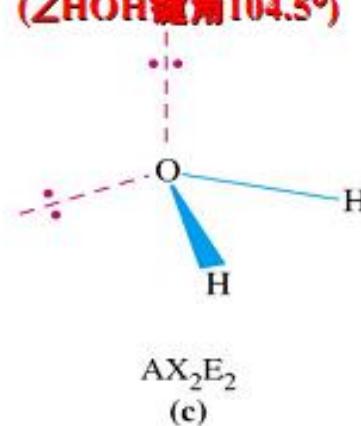
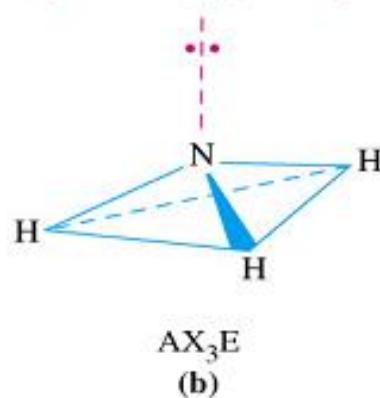
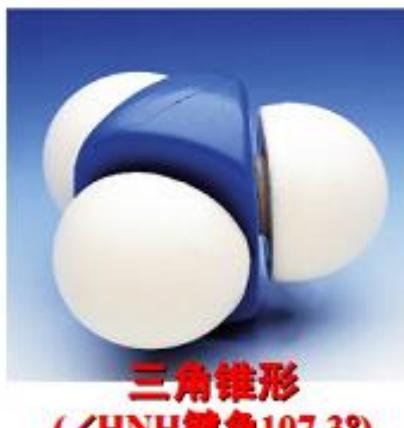
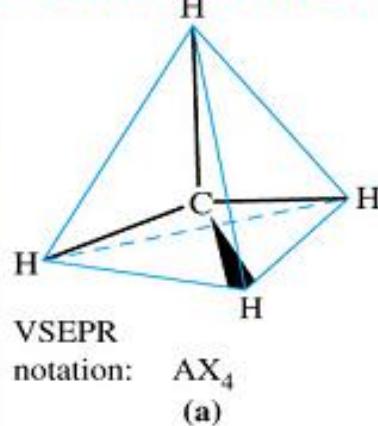
孤电子对-孤电子对 > 孤电子对-成键电子对
> 成键电子对-成键电子对

两个电子对与中心原子形成的键角不同，排斥力也不同，顺序是：

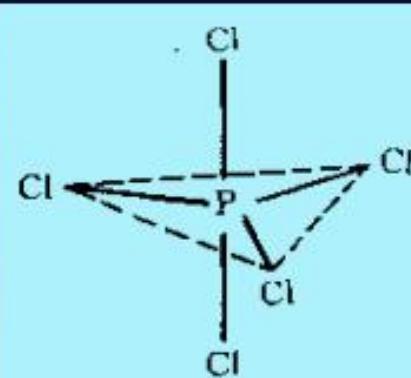
90°时的排斥力 > 120°时的排斥力 > 180°时的排斥力

因此，在分子(或离子)的几种可能的几何构型中，以含90°角孤电子对-孤电子对排斥作用和含90°角孤电子对-成键电子对排斥作用数目最少的构型是分子较稳定的构型。

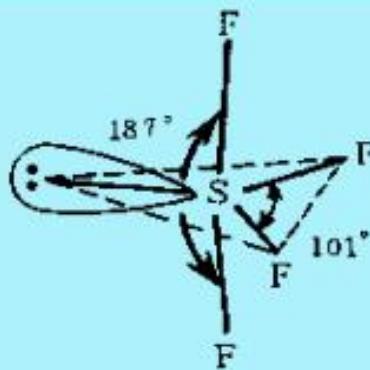
Methane, Ammonia and Water



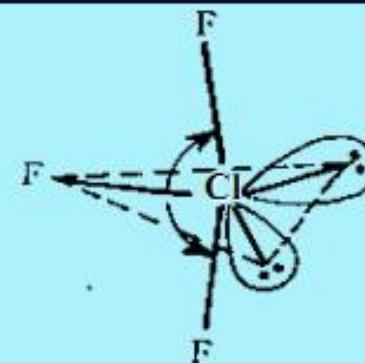
三种分子的中心原子都有4对电子，电子对几何分布都为四面体形，但因有孤电子对存在，分子构型由1种变为3种。



PCl_5 (AX_5 型)
三角双锥



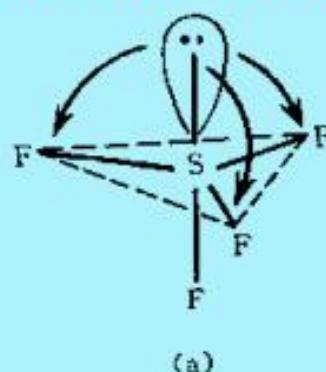
SF_4 (AX_4 型)
变形四面体



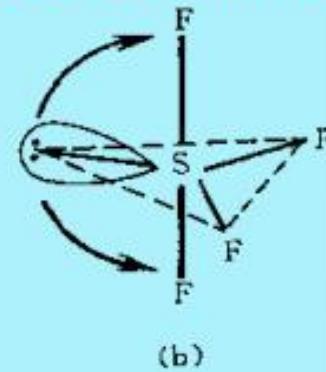
ClF_3 (AX_3E 型)
T型

PCl_5 , SF_4 , ClF_3 分子构型和键角比较

(a)和(b)为 SF_4 分子中孤电子对可能的排布方式



(a)

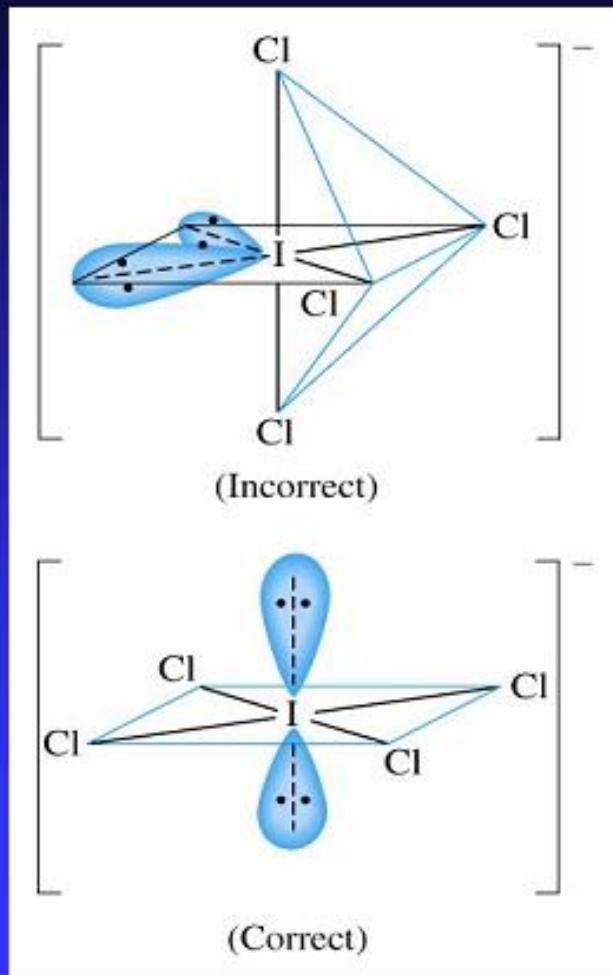


(b)

如图(a)所示，若孤电子对位于三角双锥顶部，则分子中存在3个90°角的孤电子对-成键电子对的排斥作用，不稳定。

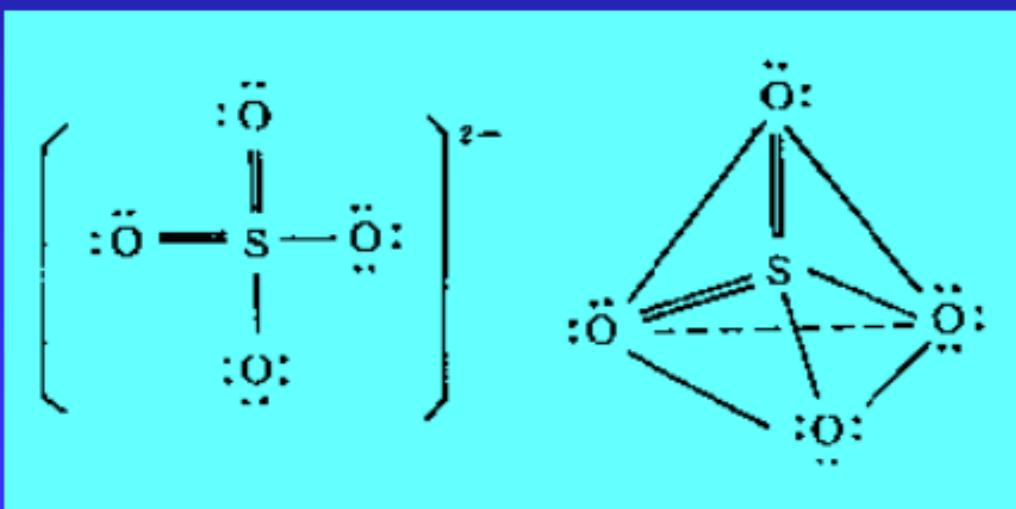
如图(b)所示，若孤电子对位于三角平面的一角，则只存在2个90°角的孤电子对-成键电子对的排斥作用，因此， SF_4 分子以此方式排列为宜。

孤电子对的存在改变了分子构型的基本类型，增加了电子对间的排斥力，影响了分子中的键角。

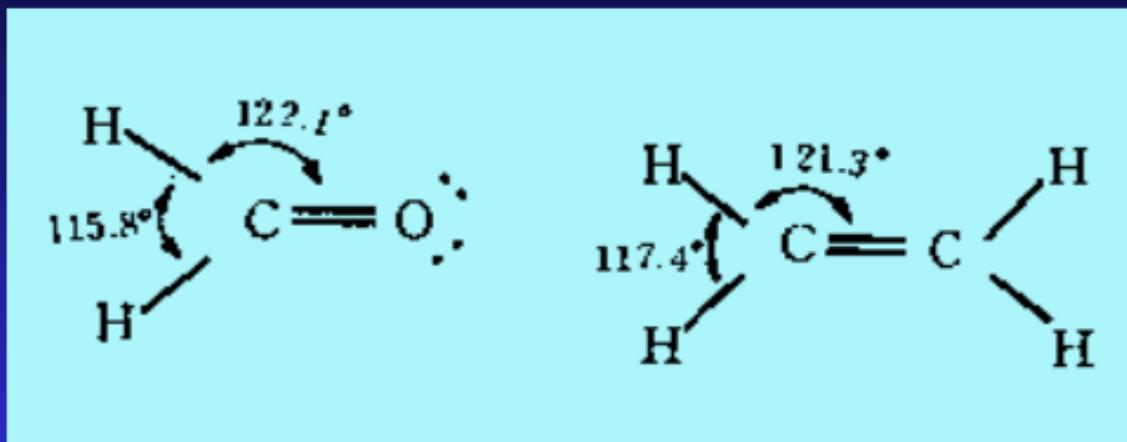


➤ VSEPR法的应用 —— (3) 具有双键或叁键的 AX_n 型

当中心原子(A)和邻接原子(X)之间通过两对电子或3对电子(即通过双键或叁键)结合成 AX_n 分子时, VSEPR法仍然适用。这时可将双键或叁键当作一个电子对来看待, 单电子键也按一个电子对对待。



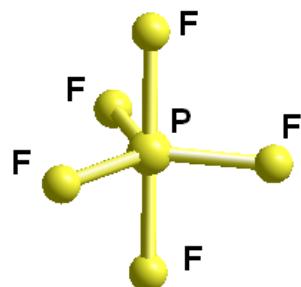
例如, AX_4 型的 SO_4^{2-} 离子, 把中心S原子周围看成有4对电子, 则可推测离子呈四面体形(见左图)。



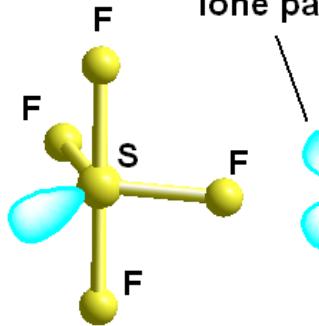
双键和叁键存在时，因分子中的多重键部分电子密度高，排斥作用更强，使相应的键角有所增加。

VSEPR 法的使用方法

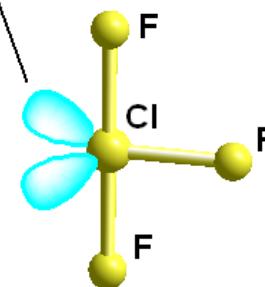
- 写出Lewis结构式
- 计算成键电子和孤对电子数目
- 确定电子对几何构型
- 确定分子构型
- 双键或叁键当作一个电子对使用
- 中心原子多于一个时可分别处理



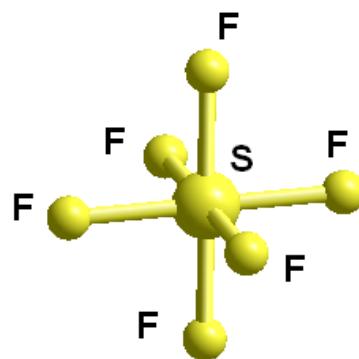
trigonal bipyramidal



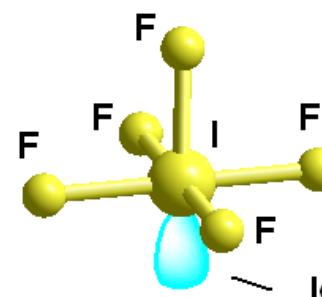
saw-horse



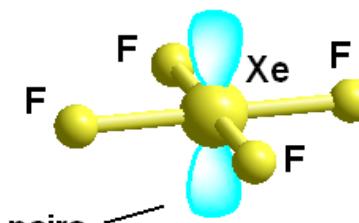
T-shaped



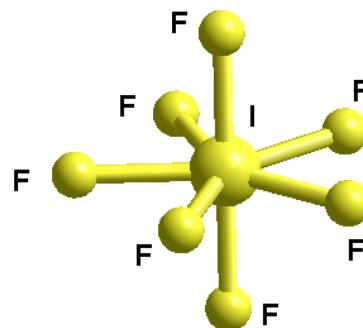
octahedral



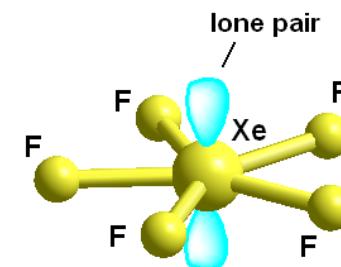
square pyramidal



square planar



pentagonal bipyramidal

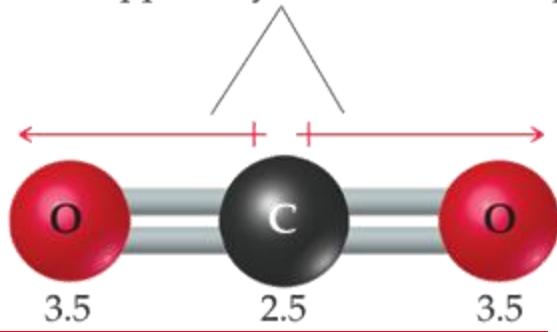


pentagonal planar

➤ Polarity

- In Chapter 8, we discussed dipoles moment.
- Bond dipole: the dipole moment due only to the two atoms in that bond
- A molecule possesses polar bonds does not mean the molecule *as a whole* will be polar.

Equal and oppositely directed bond dipoles



High electron density

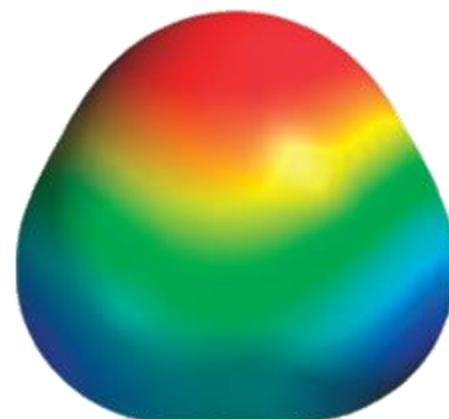
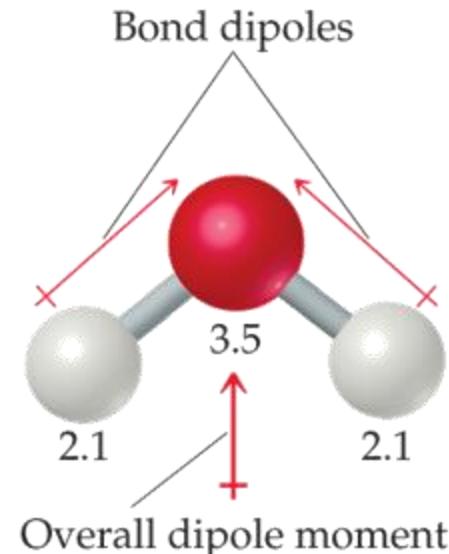
Low electron density



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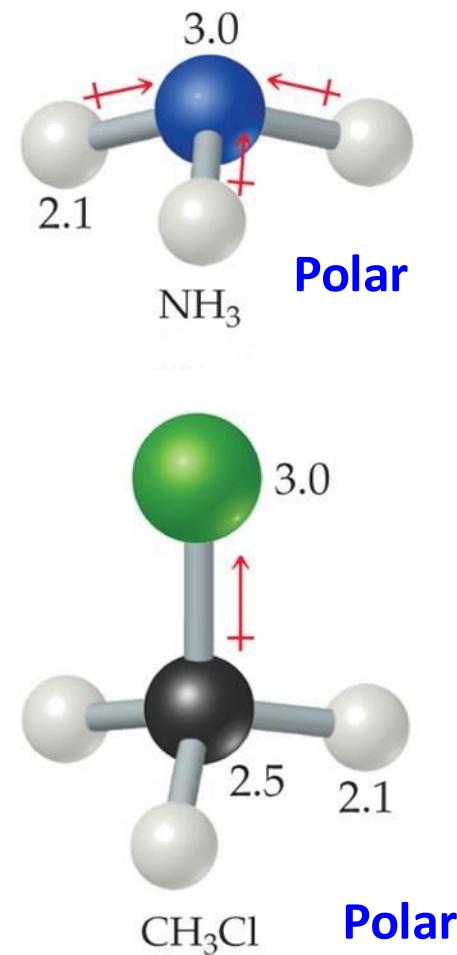
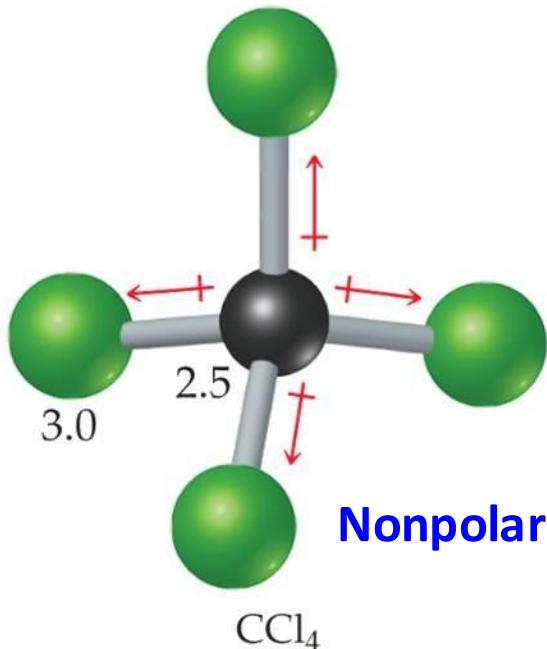
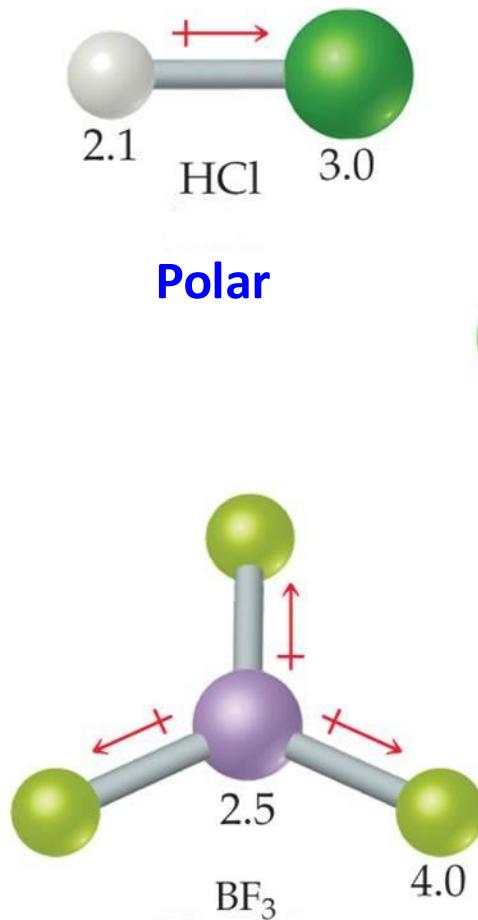
➤ Polarity

- Bond dipoles and dipole moments are vector(矢量) quantities.
- By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.



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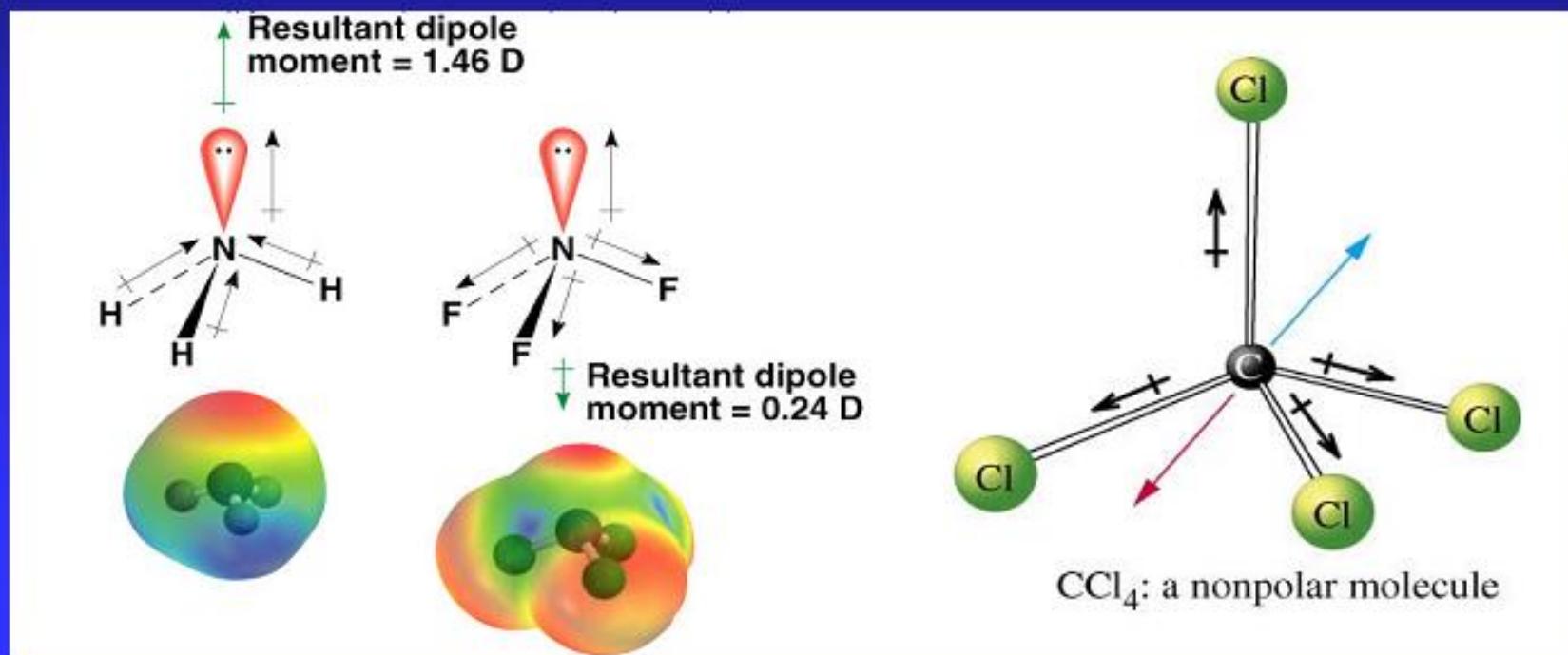
➤ Polarity

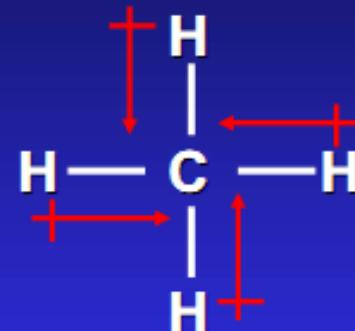
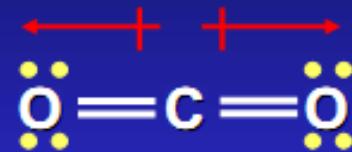


Nonpolar

➤ 键矩——双原子分子中，两个原子间的偶极矩称为键矩。原子电负性差值的大小决定双原子分子的键矩大小。

对于多原子分子来说，偶极矩是分子中所有化学键键矩的矢量和。





多数分子都可以通过测定偶极矩来判断其构型：

$\mu=0$, 分子是结构对称的非极性分子。

$\mu \neq 0$, 分子为结构不对称的极性分子，且分子的极性随偶极矩的增大而增加。

The overall shape of a molecule
is determined by its

- a. atoms.
- b. bond angles.
- c. Symmetry.
- d. electron affinity.

If a central atom is surrounded by six electron domains, the term used to describe its fundamental geometry is

- a. square planar.
- b. octahedral.
- c. square pyramidal.
- d. tetrahedral.

The geometry of the methane (CH_4) molecule is

- a. linear.
- b. trigonal bipyramidal.
- c. trigonal planar.
- d. tetrahedral.

The geometry of the phosphorus trichloride (PCl_3) molecule is

- a. tetrahedral.
- b. trigonal planar.
- c. trigonal pyramidal.
- d. trigonal bipyramidal.

The geometry of the bromine trifluoride (BrF_3) molecule is

- a. see-saw shaped.
- b. trigonal planar.
- c. pyramidal.
- d. T-shaped.

The geometry of the xenon tetrafluoride (XeF_4) molecule is

- a. square planar.
- b. tetrahedral.
- c. see-saw shaped.
- d. trigonal bipyramidal.

Formic acid (HCO_2H) has an O-C-O bond angle of (X) degrees and a C-O-H bond angle of (Y) degrees.

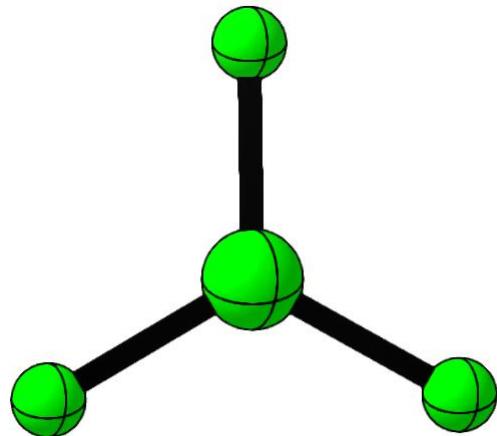
- a. $X = 180, Y = 120$
- b. $X = 120, Y = 109.5$
- c. $X = 180, Y = 109.5$
- d. $X = 109.5, Y = 109.5$

Which molecule is polar?

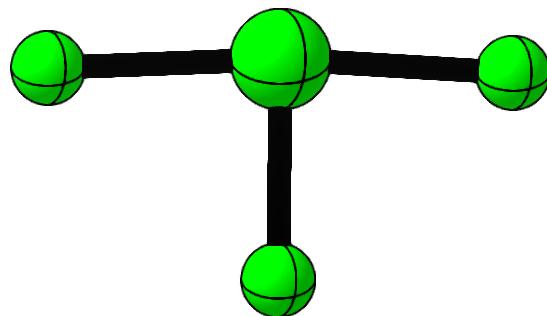
- a. CH_4
- b. BBr_3
- c. SF_6
- d. NH_3

Which molecule is nonpolar?

- a. CO_2
- b. SO_2
- c. IF_3
- d. IF_5



14.4 kcal/mol



0.0 kcal/mol

B3LYP/def2-SVP level of theory

Sample Exercise 9.1 Using the VSEPR Model

Use the VSEPR model to predict the molecular geometry of (a) O₃, (b) SnCl₃⁻.

Solution

Analyze We are given the molecular formulas of a molecule and a polyatomic ion, both conforming to the general formula AB_n and both having a central atom from the *p* block of the periodic table.

Solve

(a) We can draw two resonance structures for O₃:

Plan To predict the molecular geometries, we draw their Lewis structures and count electron domains around the central atom to get the electron-domain geometry. We then obtain the molecular geometry from the arrangement of the domains that are due to bonds.

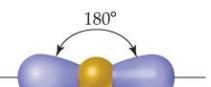
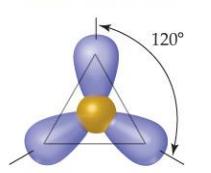
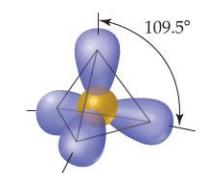
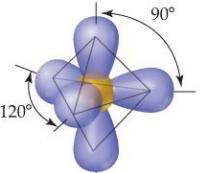
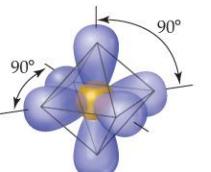


Sample Exercise 9.1 Using the VSPER Model

Continued

Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures the central O atom is bonded to the two outer O atoms and has one nonbonding pair. Thus, there are three electron domains about the central O atoms. (Remember that a double bond counts as a single electron domain.) The arrangement of three electron domains is trigonal planar (Table 9.1).

TABLE 9.1 • Electron-Domain Geometries as a Function of Number of Electron Domains

Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2	 A central yellow sphere (representing the nucleus) is surrounded by two blue lobes (representing electron domains). They are positioned along a horizontal axis, forming a 180° angle.	Linear	180°
3	 A central yellow sphere is surrounded by three blue lobes. They are positioned at the vertices of an equilateral triangle, forming 120° angles between them.	Trigonal planar	120°
4	 A central yellow sphere is surrounded by four blue lobes. They are positioned at the vertices of a regular tetrahedron, forming 109.5° angles between them.	Tetrahedral	109.5°
5	 A central yellow sphere is surrounded by five blue lobes. They are positioned in a trigonal bipyramidal arrangement, forming 120° and 90° angles between them.	Trigonal bipyramidal	120° 90°
6	 A central yellow sphere is surrounded by six blue lobes. They are positioned in an octahedral arrangement, forming 90° angles between them.	Octahedral	90°

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Sample Exercise 9.1 Using the VSPER Model

Continued

Two of the domains are from bonds, and one is due to a nonbonding pair. So, the molecule has a bent shape with an ideal bond angle of 120° (Table 9.2).

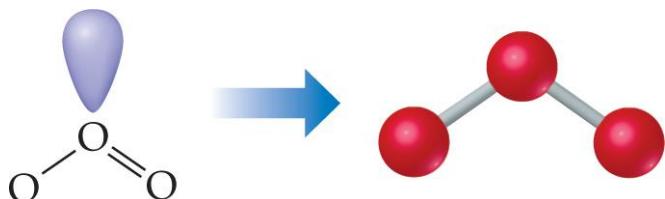


TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	Trigonal planar	3	0	Trigonal planar	$\ddot{\text{F}}\text{B}\ddot{\text{F}}$
		2	1	Bent	$[\ddot{\text{O}}=\text{N}(\ddot{\text{O}})\text{]}^-$
4	Tetrahedral	4	0	Tetrahedral	CH_4
		3	1	Trigonal pyramidal	NH_3
		2	2	Bent	H_2O

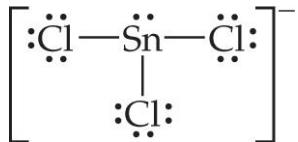
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Sample Exercise 9.1 Using the VSPER Model

Continued

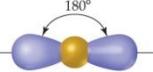
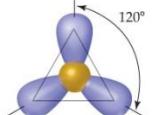
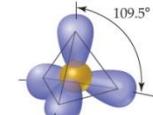
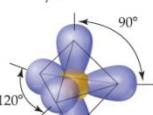
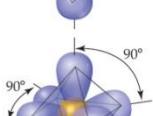
Comment As this example illustrates, when a molecule exhibits resonance, any one of the resonance structures can be used to predict the molecular geometry.

(b) The Lewis structure for SnCl_3^- is



The central Sn atom is bonded to the three Cl atoms and has one nonbonding pair; thus, we have four electron domains, meaning tetrahedral electron-domain geometry (Table 9.1) with one vertex occupied

TABLE 9.1 • Electron-Domain Geometries as a Function of Number of Electron Domains

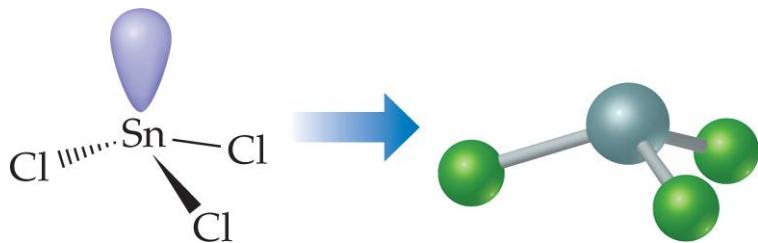
Number of Electron Domains	Arrangement of Electron Domains	Electron-Domain Geometry	Predicted Bond Angles
2		Linear	180°
3		Trigonal planar	120°
4		Tetrahedral	109.5°
5		Trigonal bipyramidal	120° 90°
6		Octahedral	90°

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Sample Exercise 9.1 Using the VSPER Model

Continued

by a nonbonding pair of electrons. Tetrahedral electron domain geometry with three bonding and one nonbonding domains means the molecular geometry is trigonal pyramidal (Table 9.2).



Practice Exercise

Predict the electron-domain and molecular geometries for (a) SeCl_2 , (b) CO_3^{2-} .

Answers: (a) tetrahedral, bent; (b) trigonal planar, trigonal planar

TABLE 9.2 • Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	$\ddot{\text{O}}=\text{C}=\ddot{\text{O}}$
3	Trigonal planar	3	0	Trigonal planar	BF_3
		2	1	Bent	NO_2^-
4	Tetrahedral	4	0	Tetrahedral	CH_4
		3	1	Trigonal pyramidal	NH_3
		2	2	Bent	H_2O

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Sample Exercise 9.2 Molecular Geometries of Molecules with Expanded Valence Shells

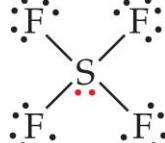
Use the VSEPR model to predict the molecular geometry of (a) SF₄, (b) IF₅.

Solution

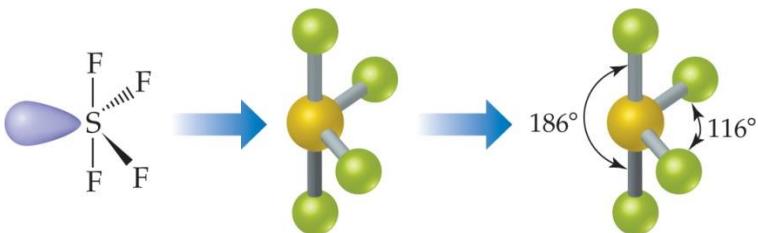
Analyze The molecules are of the AB_n type with a central p-block atom.

Plan We first draw Lewis structures and then use the VSEPR model to determine the electron-domain geometry and molecular geometry.

Solve (a) The Lewis structure for SF₄ is



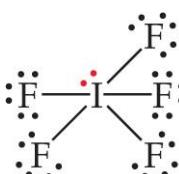
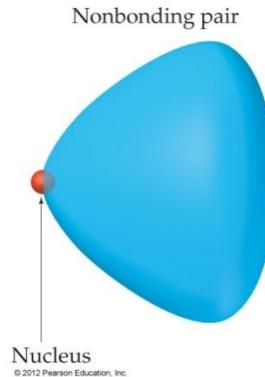
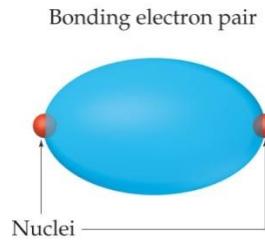
The sulfur has five electron domains around it: four from the S—F bonds and one from the nonbonding pair. Each domain points toward a vertex of a trigonal bipyramidal. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions, resulting in a molecular geometry that is described as see-saw shaped:



Sample Exercise 9.2 Molecular Geometries of Molecules with Expanded Valence Shells

Use the VSEPR model to predict the molecular geometry of (a) SF₄, (b) IF₅.

Comment The experimentally observed structure is shown on the right. We can infer that the nonbonding electron domain occupies an equatorial position, as predicted. The axial and equatorial S—F bonds are slightly bent away from the nonbonding domain, suggesting that the bonding domains are “pushed” by the nonbonding domain, which exerts a greater repulsion (Figure 9.7).

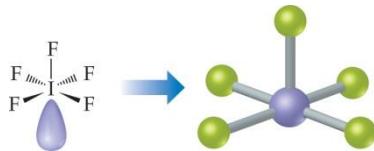


(b) The Lewis structure of IF₅ is

Sample Exercise 9.2 Molecular Geometries of Molecules with Expanded Valence Shells

Continued

The iodine has six electron domains around it, one of which is nonbonding. The electron-domain geometry is therefore octahedral, with one position occupied by the nonbonding pair, and the molecular geometry is square pyramidal (Table 9.3):



Comment Because the nonbonding domain is larger than the bonding domains, we predict that the four F atoms in the base of the pyramid will be tipped up slightly toward the top F atom. Experimentally, we find that the angle between the base atoms and top F atom is 82° , smaller than the ideal 90° angle of an octahedron.

Practice Exercise

Predict the electron-domain and molecular geometries of (a) BrF_3 , (b) ICl_4^- .

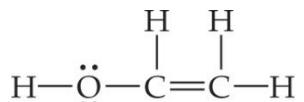
Answers: (a) trigonal bipyramidal, T-shaped; (b) octahedral, square planar

TABLE 9.3 • Electron-Domain and Molecular Geometries for Five and Six Electron Domains around a Central Atom

Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
4		1		Seesaw	SF_4
3		2		T-shaped	ClF_3
2		3		Linear	XeF_2
6	Octahedral	6	0	Octahedral	SF_6
5		1		Square pyramidal	BrF_5
4		2		Square planar	XeF_4

Sample Exercise 9.3 Predicting Bond Angles

Eyedrops for dry eyes usually contain a water-soluble polymer called *poly(vinyl alcohol)*, which is based on the unstable organic molecule *vinyl alcohol*:



Predict the approximate values for the H—O—C and O—C—C bond angles in vinyl alcohol.

Solution

Analyze We are given a Lewis structure and asked to determine two bond angles.

Plan To predict a bond angle, we determine the number of electron domains surrounding the middle atom in the bond. The ideal angle corresponds to the electron-domain geometry around the atom. The angle will be compressed somewhat by nonbonding electrons or multiple bonds.

Solve In H—O—C, the O atom has four electron domains (two bonding, two nonbonding). The electron-domain geometry around O is therefore tetrahedral, which gives an ideal angle of 109.5° . The H—O—C angle is compressed somewhat by the nonbonding pairs, so we expect this angle to be slightly less than 109.5° .

To predict the O—C—C bond angle, we examine the middle atom in the angle. In the molecule, there are three atoms bonded to this C atom and no nonbonding pairs, and so it has three electron domains about it. The predicted electron-domain geometry is trigonal planar, resulting in an ideal bond angle of 120° . Because of the larger size of the C=C domain, the bond angle should be slightly greater than 120° .

Sample Exercise 9.4 Polarity of Molecules

Predict whether these molecules are polar or nonpolar: (a) BrCl, (b) SO₂, (c) SF₆.

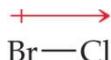
Solution

Analyze We are given three molecular formulas and asked to predict whether the molecules are polar.

Plan A molecule containing only two atoms is polar if the atoms differ in electronegativity. The polarity of a molecule containing three or more atoms depends on both the molecular geometry and the individual bond polarities. Thus, we must draw a Lewis structure for each molecule containing three or more atoms and determine its molecular geometry. We then use electronegativity values to determine the direction of the bond dipoles. Finally, we see whether the bond dipoles cancel to give a nonpolar molecule or reinforce each other to give a polar one.

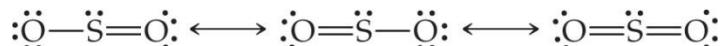
Solve

- (a) Chlorine is more electronegative than bromine. All diatomic molecules with polar bonds are polar molecules. Consequently, BrCl is polar, with chlorine carrying the partial negative charge:



The measured dipole moment of BrCl is $\mu = 0.57 \text{ D}$.

- (b) Because oxygen is more electronegative than sulfur, SO₂ has polar bonds. Three resonance forms can be written:



For each of these, the VSEPR model predicts a bent molecular geometry. Because the molecule is bent, the bond dipoles do not cancel, and the molecule is polar:

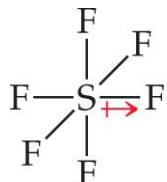


Sample Exercise 9.4 Polarity of Molecules

Continued

Experimentally, the dipole moment of SO_2 is $\mu = 1.63 \text{ D}$.

(c) Fluorine is more electronegative than sulfur, so the bond dipoles point toward fluorine. For clarity, only one $\text{S} - \text{F}$ dipole is shown. The six $\text{S} - \text{F}$ bonds are arranged octahedrally around the central sulfur:



Because the octahedral molecular geometry is symmetrical, the bond dipoles cancel, and the molecule is nonpolar, meaning that $\mu = 0$.

Practice Exercise

Determine whether the following molecules are polar or nonpolar: (a) NF_3 , (b) BCl_3 .

Answers: (a) polar because polar bonds are arranged in a trigonal-pyramidal geometry, (b) nonpolar because polar bonds are arranged in a trigonal-planar geometry

➤ Overlap and Bonding

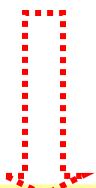
□ VSEPR theory

- Can predict molecular geometries well
- CANNOT explain why bonds exist between atoms

Lewis's electron-pair bonds (bond formation by sharing e^-)

+

atomic orbitals (using quantum mechanics)



□ Valence Bond theory(价键理论)

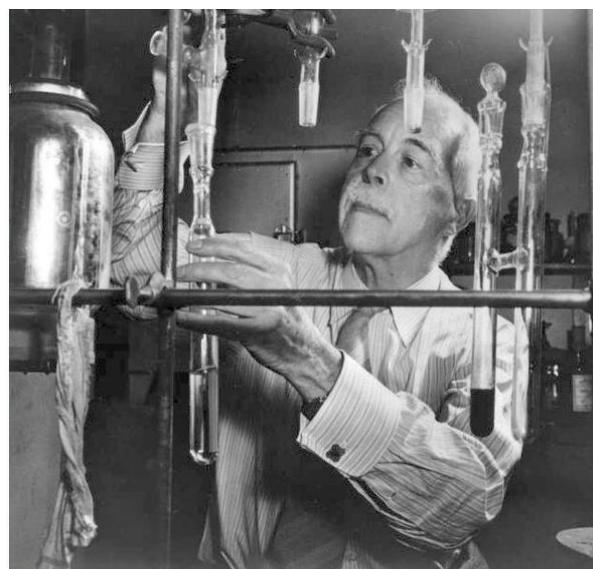
- Bonding electron pairs are concentrated between atoms
- Orbital overlap → buildup of e^- density between nuclei → covalent bond formation

➤ Valence Bond (VB) Theory

- Hybridization(杂化) is a major player in this approach to bonding.
- There are two ways orbitals can overlap to form bonds between atoms.



Fritz Wolfgang London
(1900–1954)



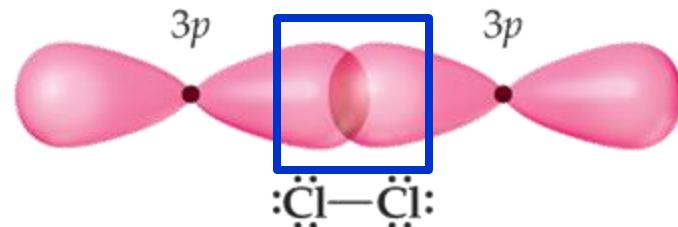
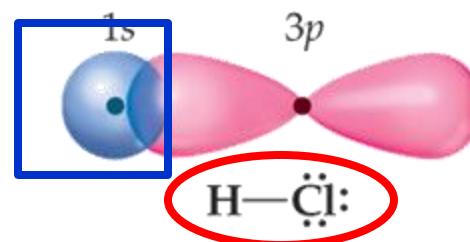
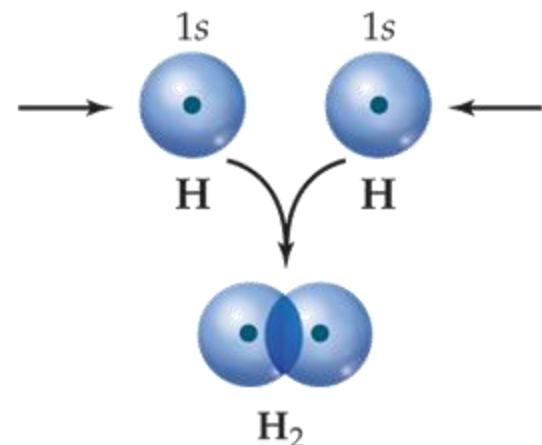
Gilbert Newton Lewis
(1875–1946)



Linus Carl Pauling
(1901–1994)

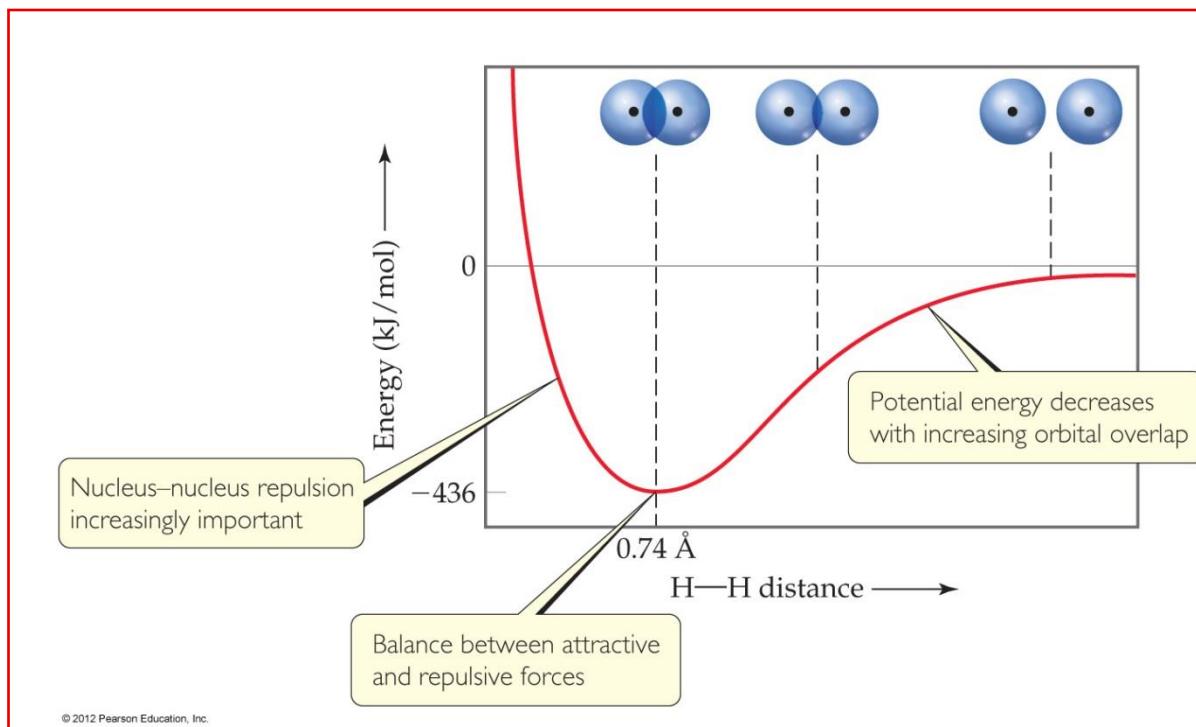
➤ Overlap and Bonding

- Lewis theory: We think of covalent bonds forming through the sharing of electrons by adjacent atoms.
- In valence bond theory: this can only occur when orbitals on the two atoms overlap.



➤ Overlap and Bonding

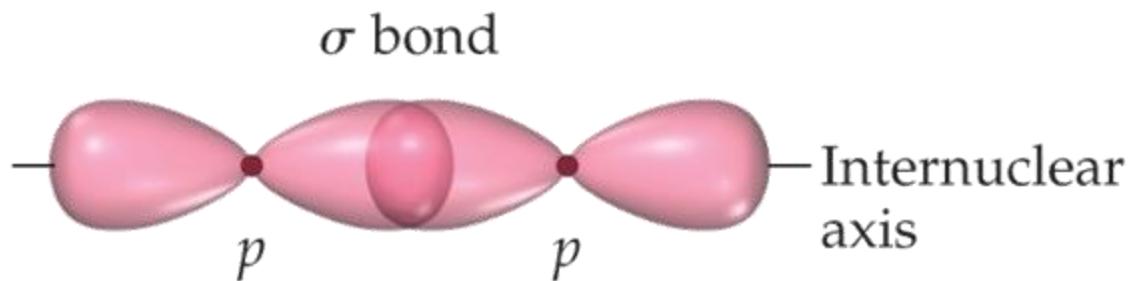
- Increased overlap brings the electrons and nuclei closer together while simultaneously(同时) decreasing electron-electron repulsion.
- However, if atoms get too close, the internuclear repulsion greatly raises the energy.

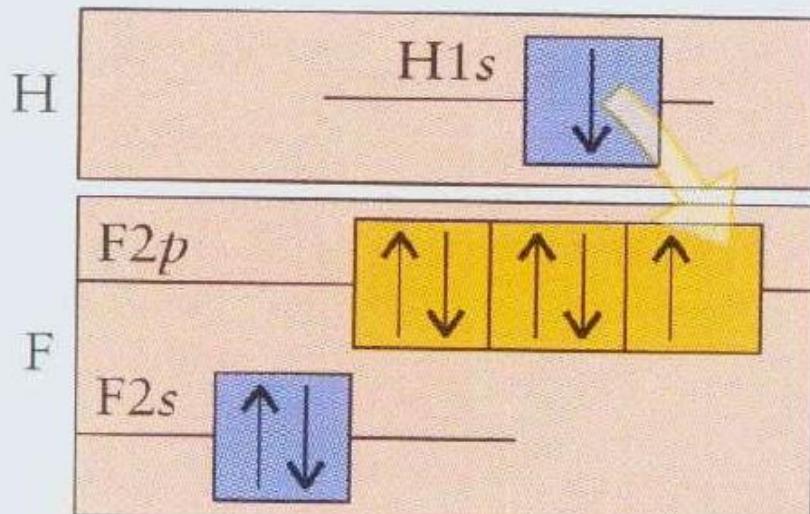


➤ Sigma (σ) Bonds

□ Sigma bonds are characterized by

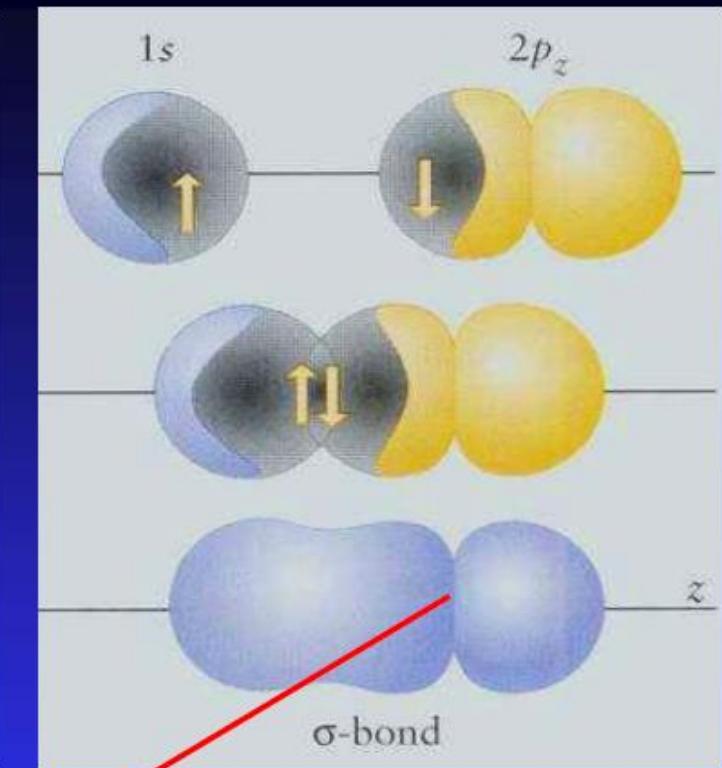
- Head-to-head overlap.
- Cylindrical symmetry of electron density about the internuclear axis.





Hydrogen fluoride, HF

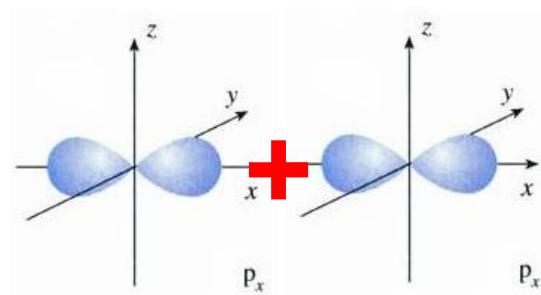
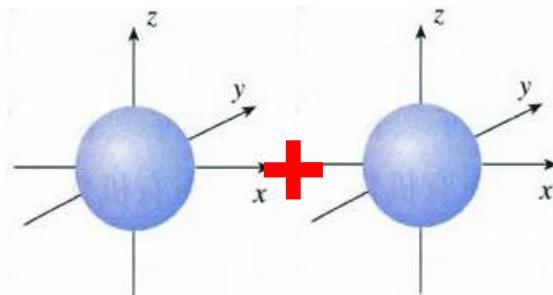
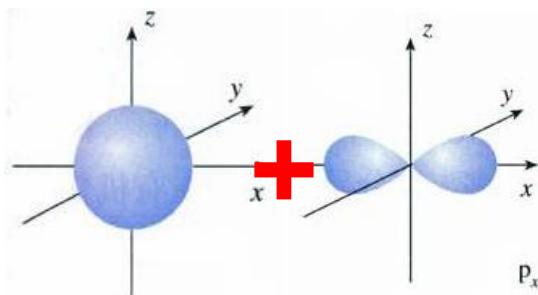
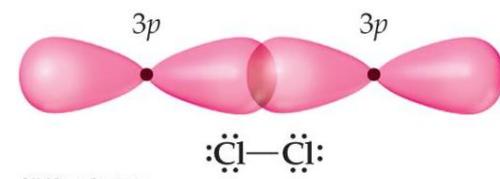
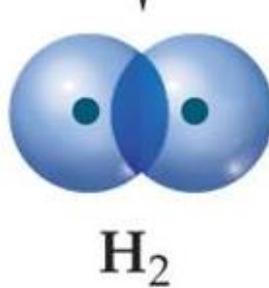
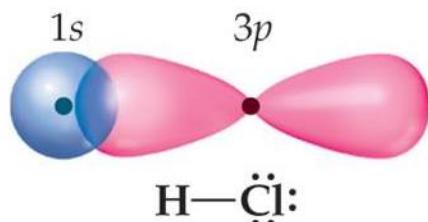
A σ -bond can be formed when electrons in 1s- and 2p_z-orbitals pair (where z is the direction along the internuclear axis). The two electrons in the bond are spread over the entire region of space enclosed by the boundary surface.



σ 键：成键时两原子沿键轴(两个原子核的连线)方向，以“头碰头”的方式发生轨道重叠，轨道重叠的部分呈圆柱形对称。

➤ Sigma (σ) Bonds

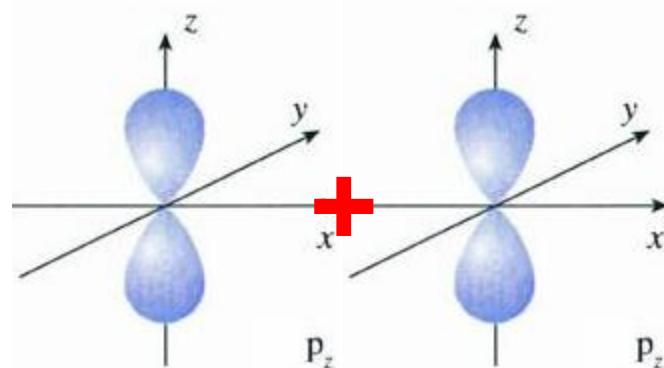
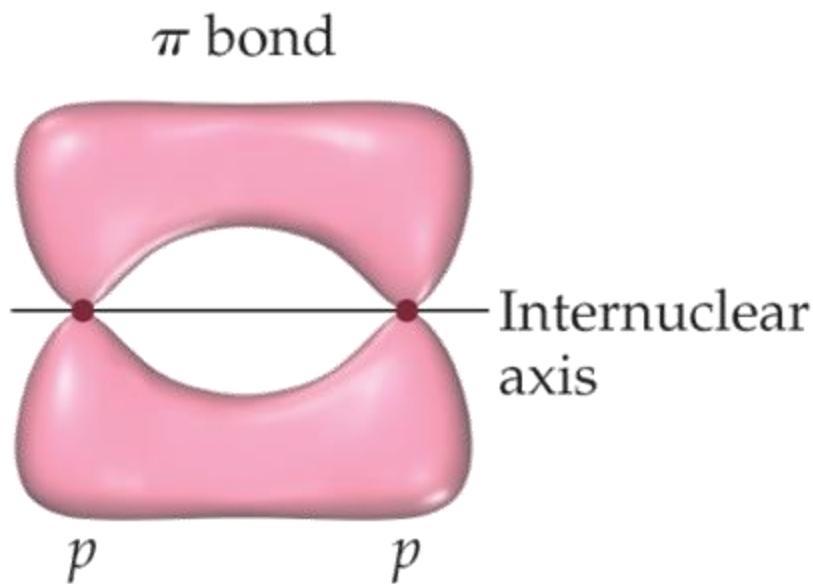
- The overlap of two s orbitals in H_2 , an s and a p orbital in HCl , and two p orbitals in Cl_2 .



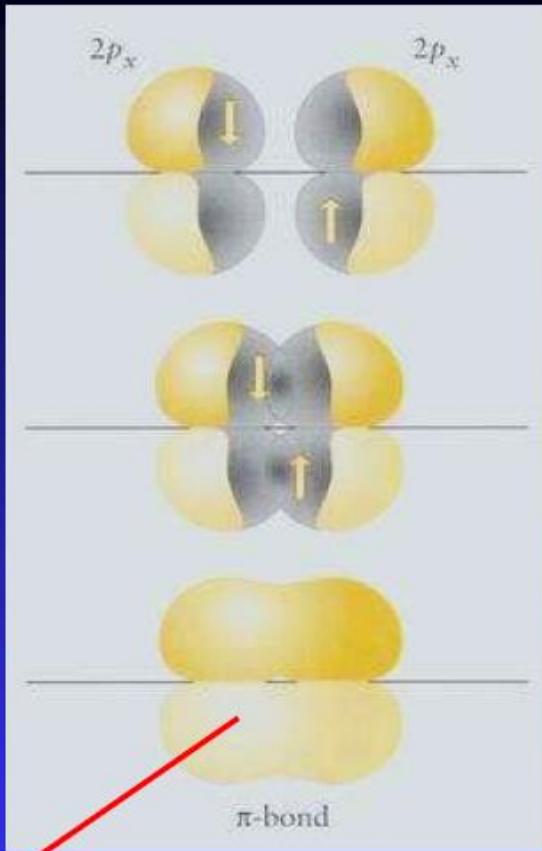
➤ Pi (π) Bonds

□ Pi bonds are characterized by

- Overlap between two p orbitals oriented perpendicularly to the internuclear axis.
- Electron density above and below the internuclear axis.
- π bonds are weaker than σ bonds

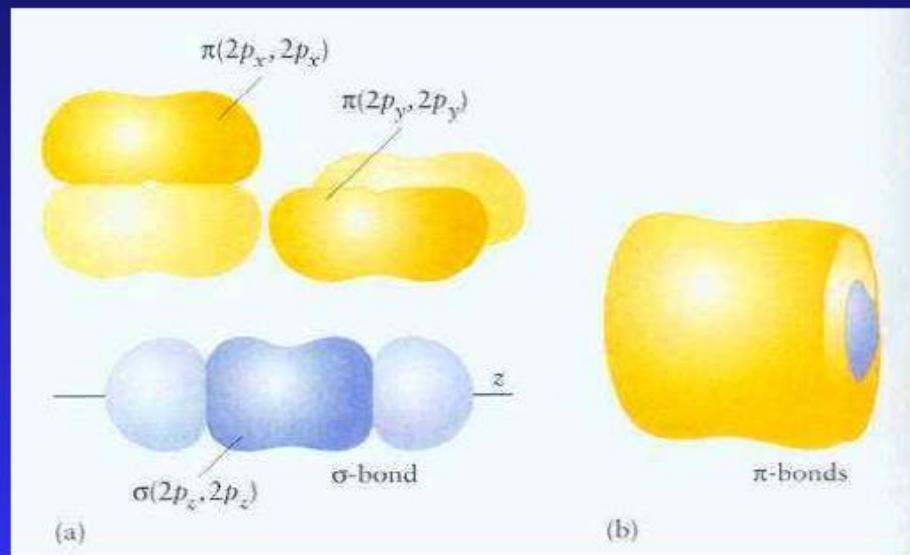


N₂分子中π键的形成



π键——成键时由两原子的 *p* 轨道以“肩并肩”方式，平行重叠而成，其特点是电子云对一个通过键轴、密度为零的平面呈对称分布。

A π -bond is formed when electron in two $2p$ -orbitals pair and overlap side by side. The middle diagram shows the density of the resulting electron cloud, and the bottom diagram shows the corresponding boundary surface. Even though the bond has a complicated shape, with two lobes, it is occupied by one pair of electrons and counts as one bond,



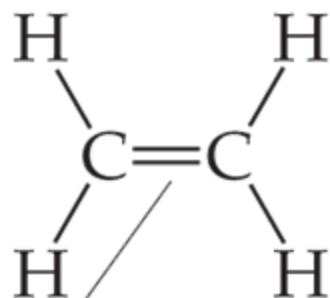
The bonding pattern in a nitrogen molecule, N₂. (a) The two atoms are bonded together by one σ-bond (blue) and two perpendicular π-bonds (yellow). (b) When the three π-bonds are put together, it turns out that the two π-bonds result in a long doughnut-shaped cloud surrounding the σ-bond cloud, so the overall structure resembles a cylindrical hot dog.

➤ Single Bonds

- Single bonds are always σ bonds, because σ overlap is greater, resulting in a stronger bond and more energy lowering (more stable).



One σ bond



One σ bond plus
one π bond



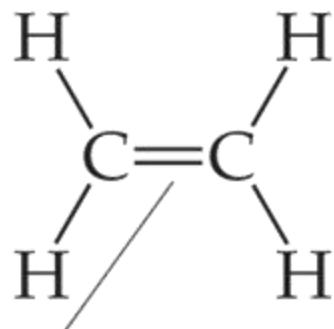
One σ bond plus
two π bonds

➤ Multiple Bonds

- In a multiple bond, one of the bonds is a σ bond and the rest are π bonds.



One σ bond

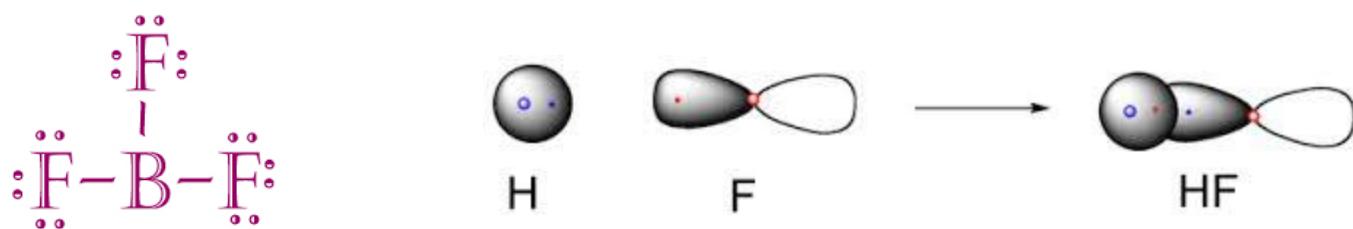


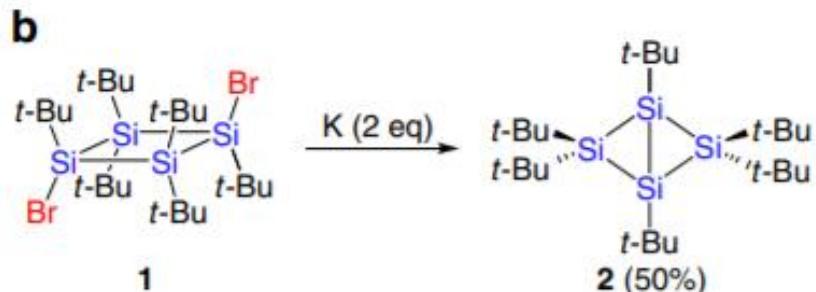
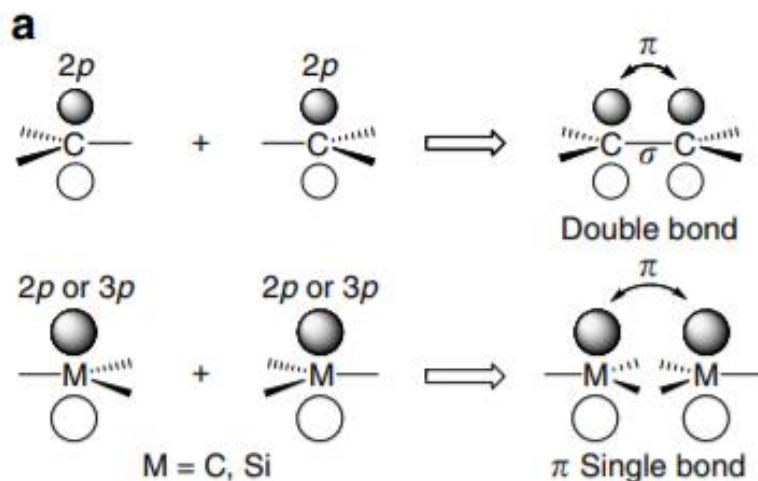
One σ bond plus
one π bond



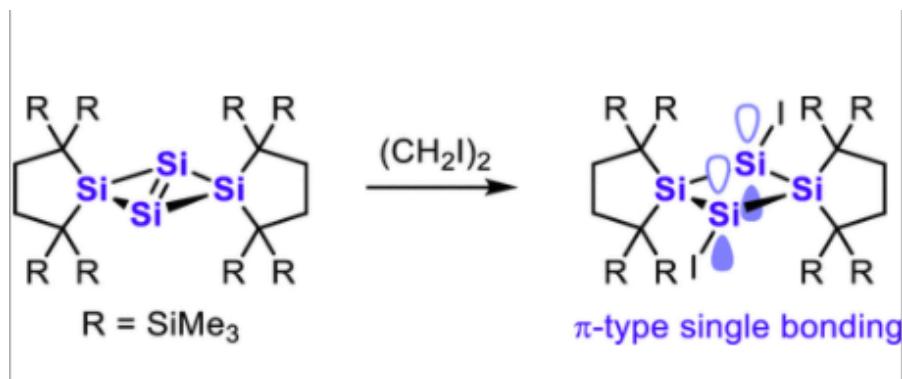
One σ bond plus
two π bonds

- The valence-bond model we have developed for period 2 elements works well. For compounds of periods 3 elements so long as we have no more than an octet of electrons in the valence-shell orbitals.
- Models in science are not reality but rather are our attempts to describe aspects of reality that we have been able to measure, such as bond distances, bond energies, molecular geometries, and so on.
- **A model may work well up to a certain point.**





Nat. Commun. **2020**, *11*, 4009.



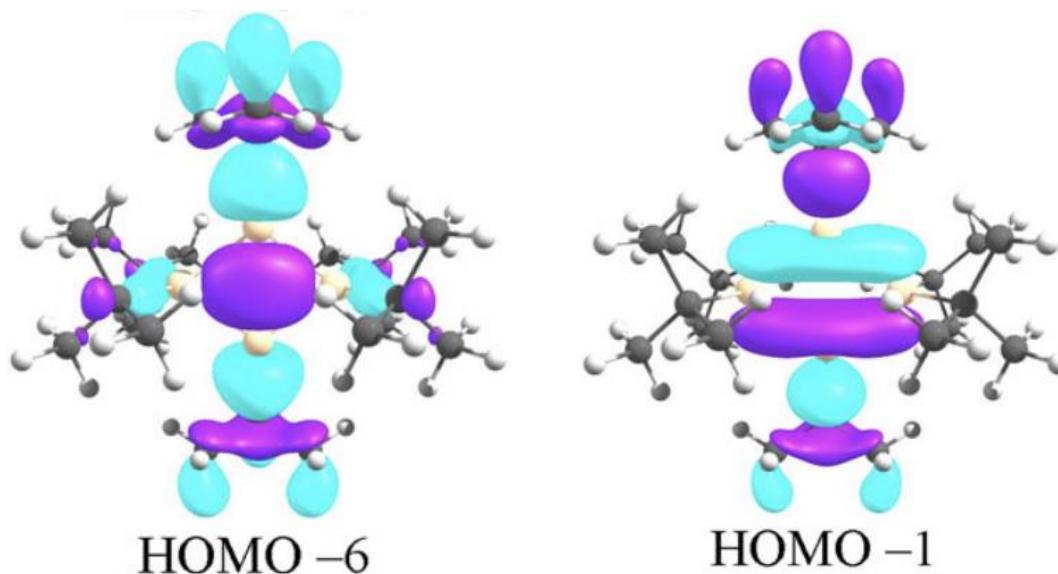
J. Am. Chem. Soc. **2020**, *142*, 9920.

A double bond with weak σ - and strong π -interactions is still a double bond

[Cina Foroutan-Nejad](#) 

[Nature Communications](#) **12**, Article number: 4037 (2021) | [Cite this article](#)

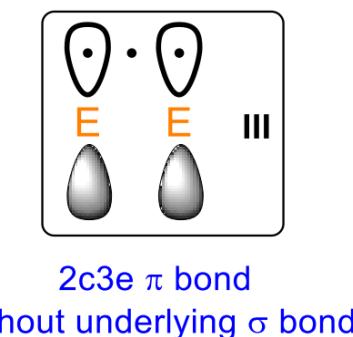
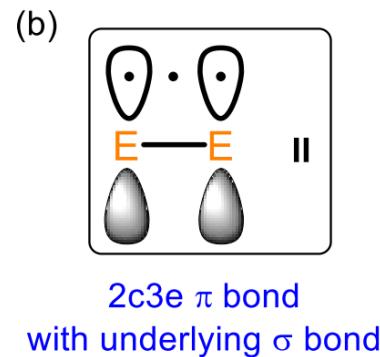
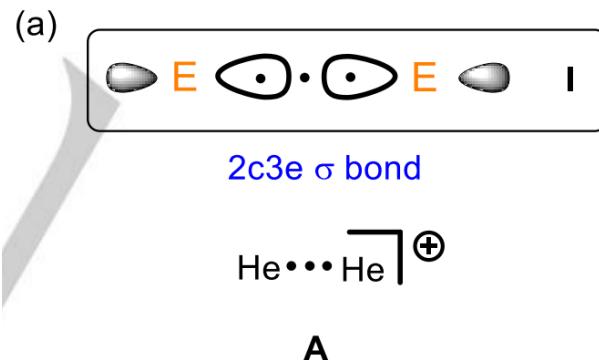
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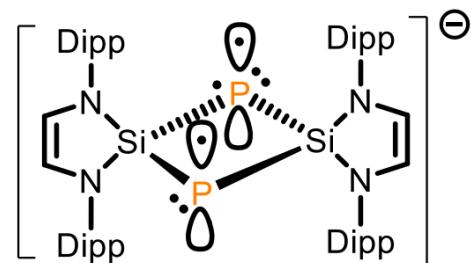
An Isolable Radical Anion Featuring a 2-Center-3-Electron π -Bond without a Clearly Defined σ -Bond

Yanbo Mei^{[a],[c]}, Xiaodan Chen^[d], Rui Wei^[a], Xiao-Yong Chang^[a], Lizhi Tao^[a], Liu Leo Liu^{*[a],[b]}

In memory of Professor Wei Jiang



This work

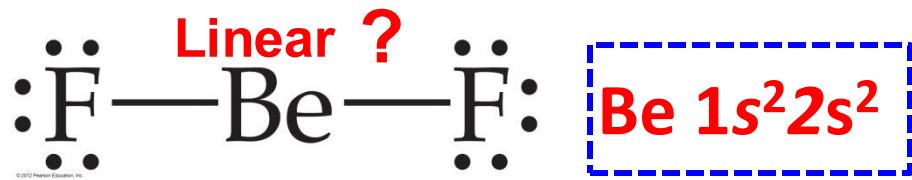
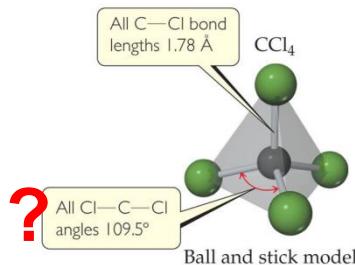


2c3e P-P π bond
without P-P σ bond

Dipp = 2,6-diisopropylphenyl

➤ Hybrid Orbitals(杂化轨道)

- The VSEPR model has no obvious relationship to the filling and shapes of atomic orbitals.



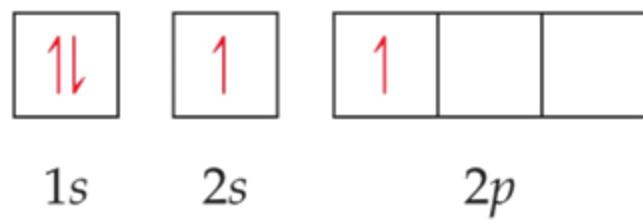
- **Hybrid orbitals:** Atomic orbitals on an atom mix to form the shapes of the original atomic orbitals. The process of mixing atomic orbitals is a **mathematical operation** called **hybridization**. The number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

➤ ***sp* Hybrid Orbitals**

- Consider beryllium, in its ground electronic state, beryllium would not be able to form bonds, because it has no singly occupied orbitals.



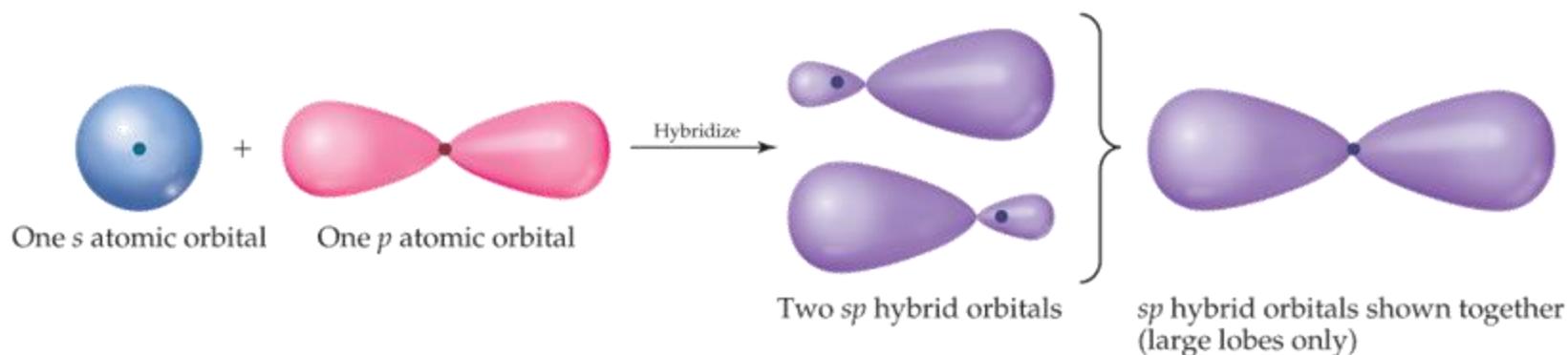
- But if it absorbs the small amount of energy needed to promote an electron from the 2s to the 2p orbital, it can form two bonds. BUT still cannot explain the geometry



➤ *sp* Hybrid Orbitals

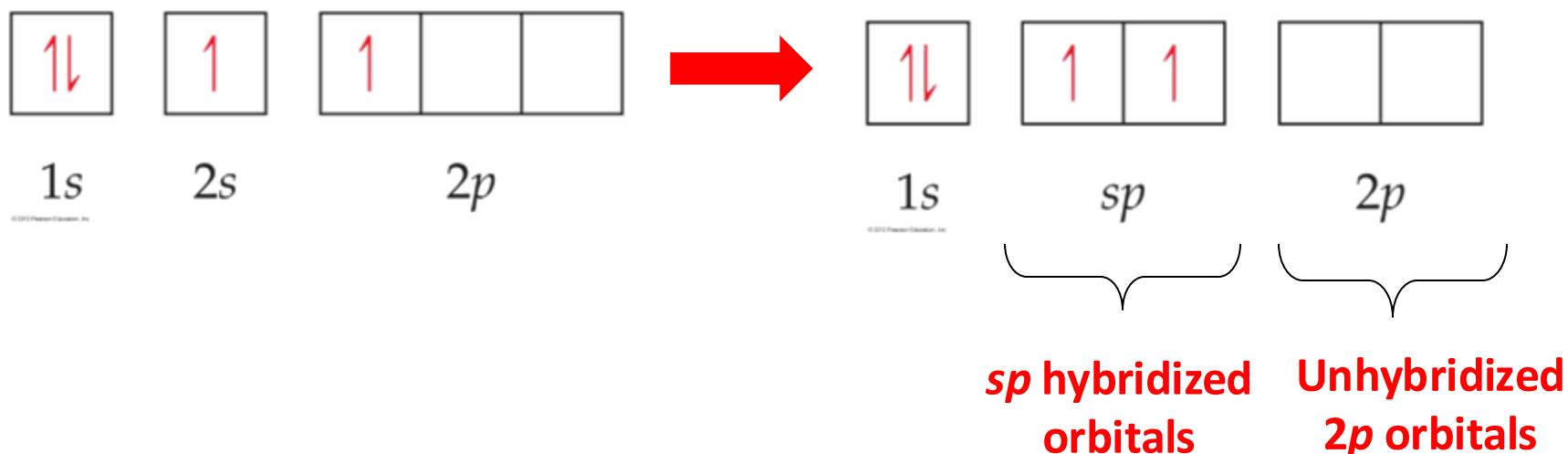
□ Mixing the *s* and *p* orbitals yields two **degenerate** orbitals that are hybrids of the two orbitals.

- These *sp* hybrid orbitals have two lobes like a *p* orbital.
- One of the lobes (瓣) is larger and more rounded, as is the *s* orbital.
- Each *sp* hybrid orbital contains 50% *s* orbital and 50% *p* orbital characters (**one *s* + one *p* → two *sp* hybrid orbital**)



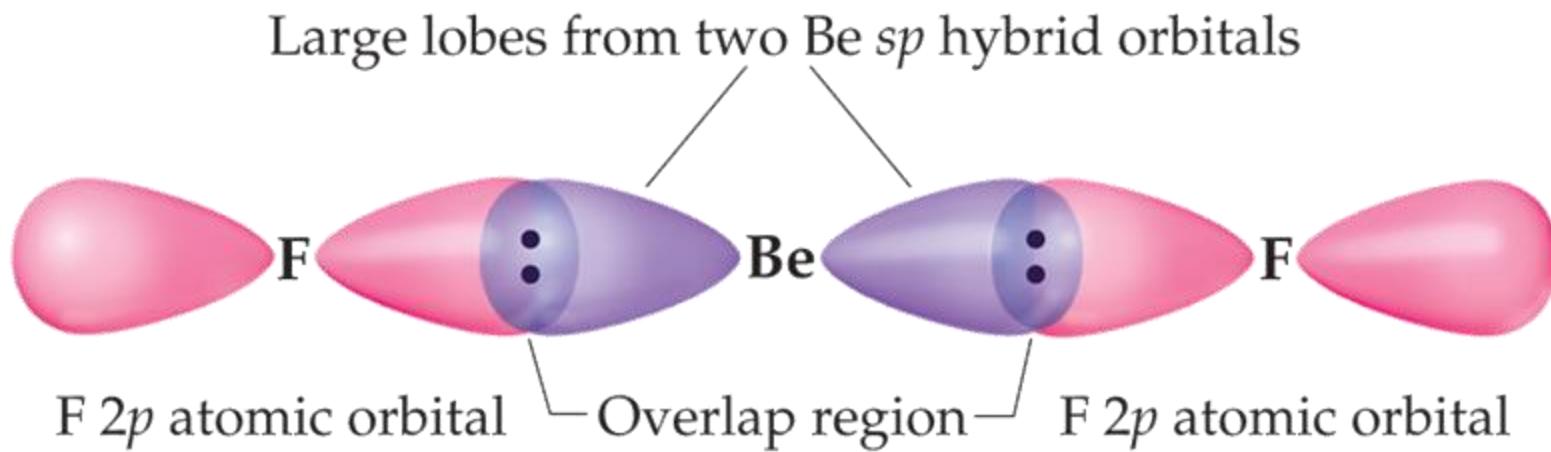
➤ *sp* Hybrid Orbitals

- With hybrid orbitals, the orbital diagram for beryllium would look like this .
- The *sp* orbitals are higher in energy than the 1s orbital, but lower than the 2*p*.



➤ *sp* Hybrid Orbitals

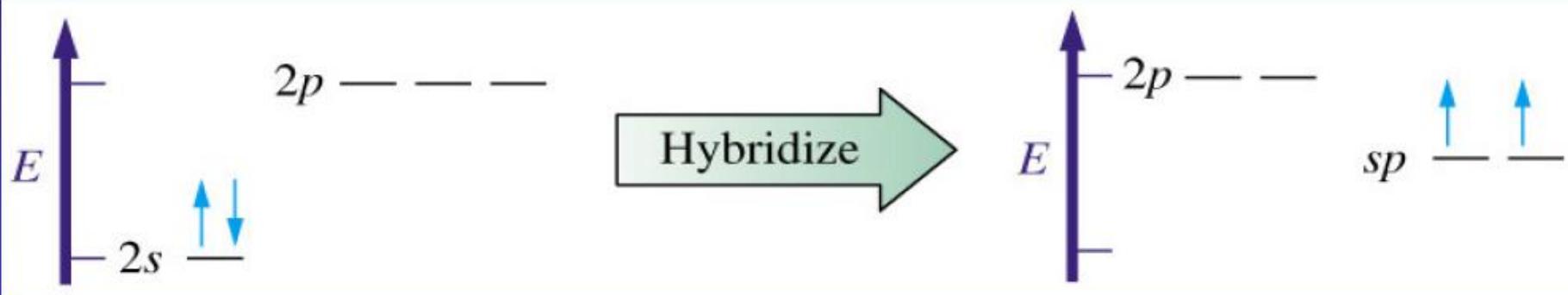
- These two degenerate orbitals would align themselves 180° from each other.
- This is consistent with the observed geometry of beryllium compounds: linear.



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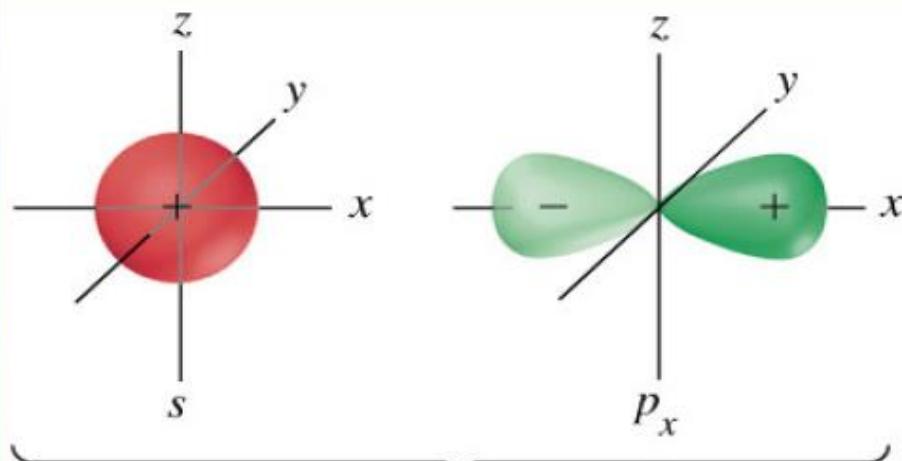
3) sp 杂化轨道

由1个s轨道和1个p轨道组合，产生2个等同的 sp 杂化轨道，每一个 sp 杂化轨道中含有1/2个s轨道和1/2个p轨道的成分。因为2个 sp 杂化轨道间的夹角是 180° ，所以分子具有直线形的空间结构。

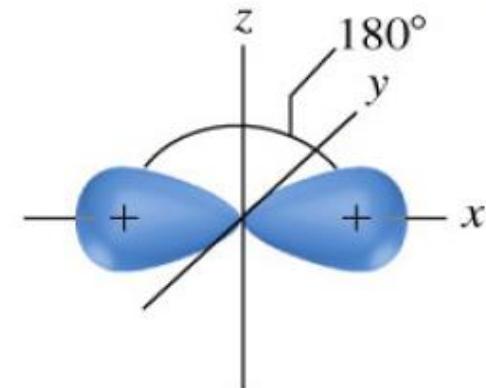
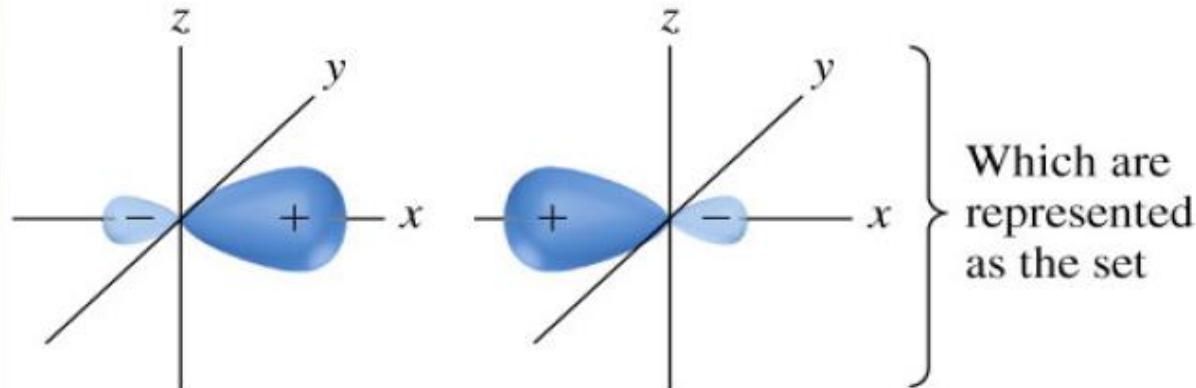


BeCl₂中Be原子的sp杂化轨道的形成

Be原子sp杂化轨道的形成

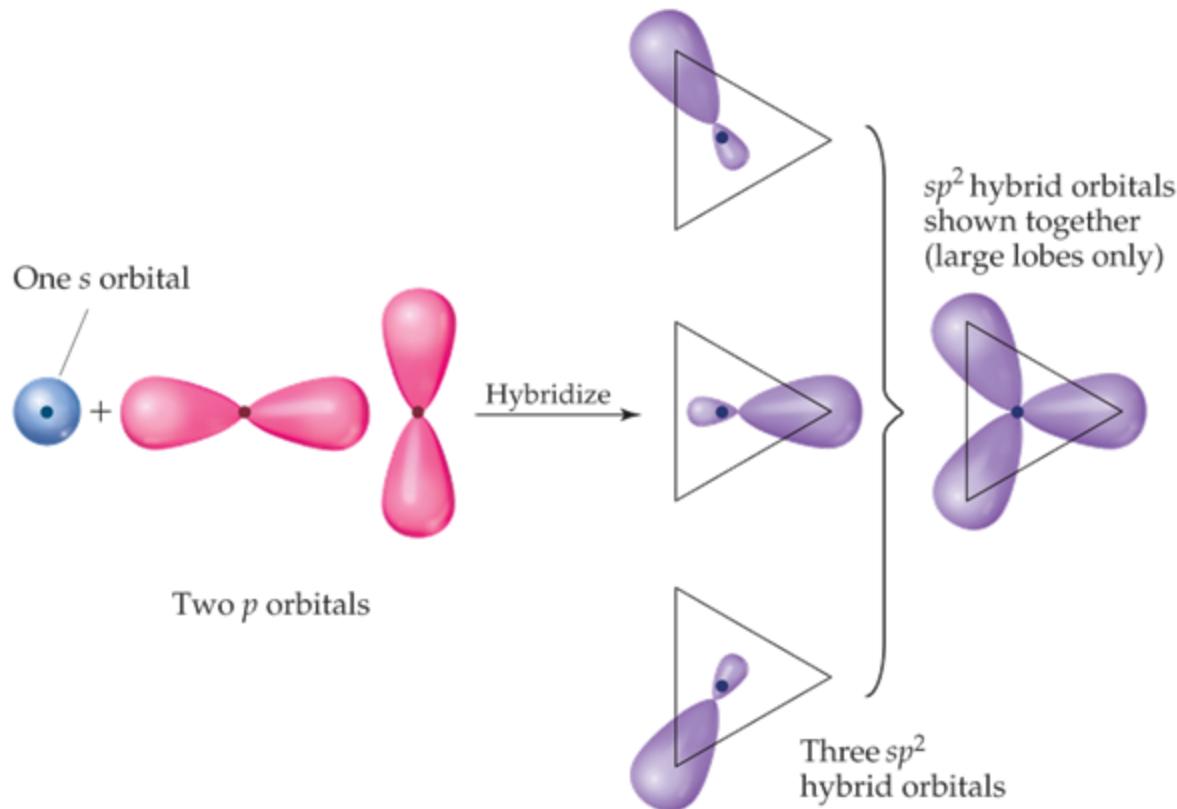


Combine to generate
two sp orbitals



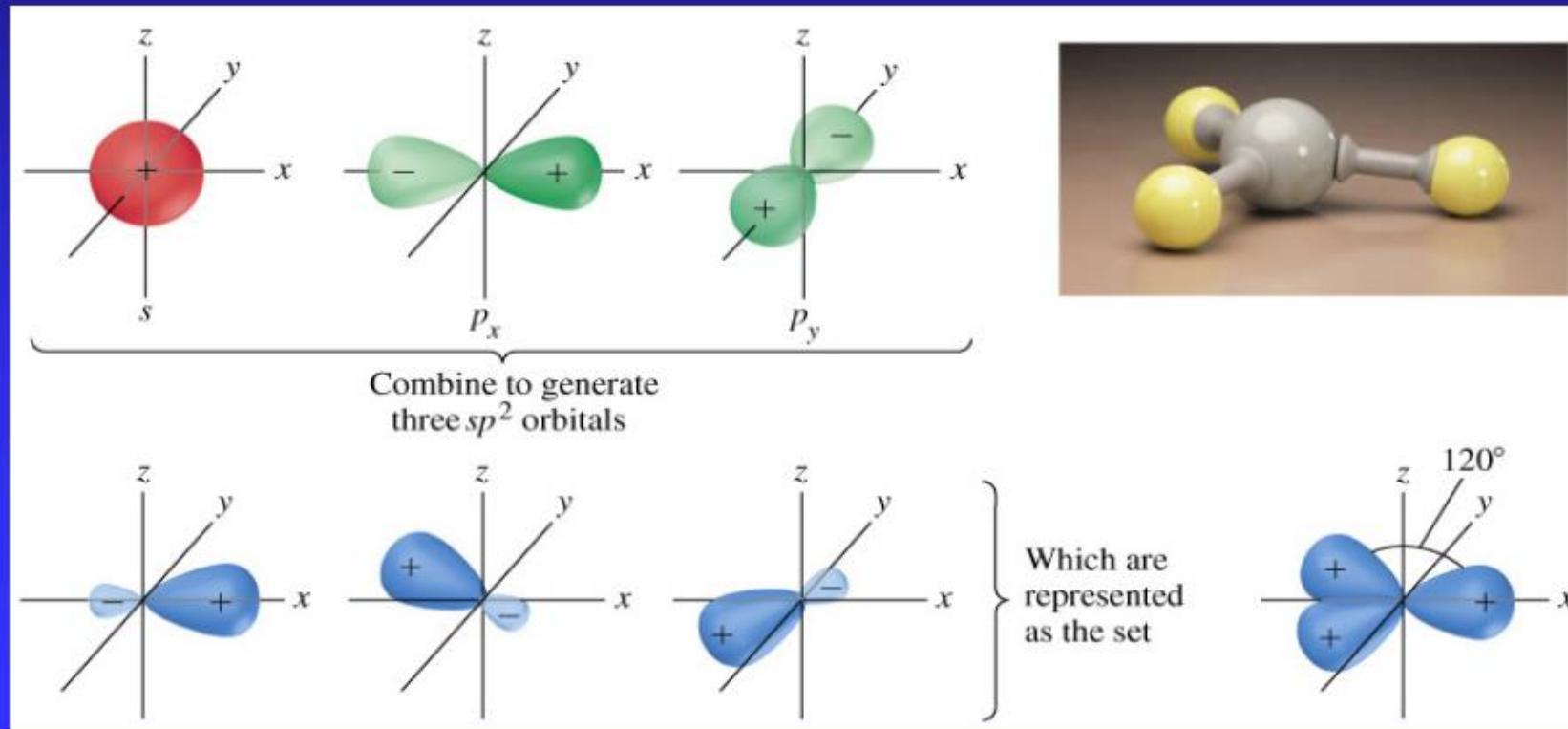
➤ sp^2 Hybrid Orbitals

- Using a similar model for boron leads to three degenerate sp^2 orbitals.



2) sp^2 杂化轨道

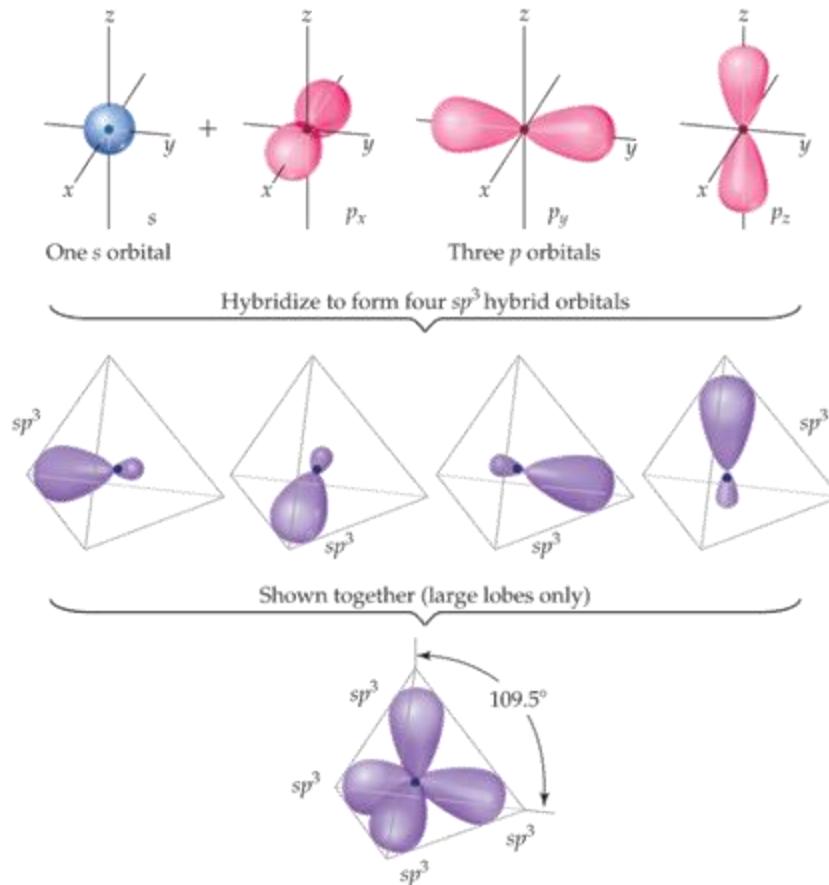
由1个s轨道和2个p轨道组合产生3个等同的 sp^2 杂化轨道，每个 sp^2 杂化轨道含有1/3个s轨道和2/3个p轨道的成分。由于3个 sp^2 杂化轨道间的夹角为120°，所以呈平面三角形结构。



BCl_3
中
B
原
子
的
 sp^2
杂
化
轨
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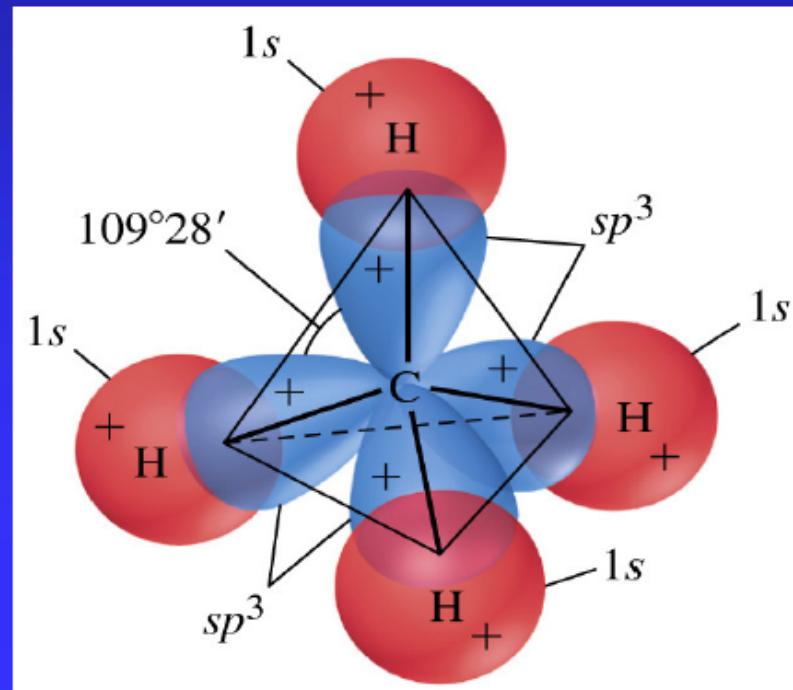
➤ *sp*³ Hybrid Orbitals

- With carbon, we get four degenerate *sp*³ orbitals.

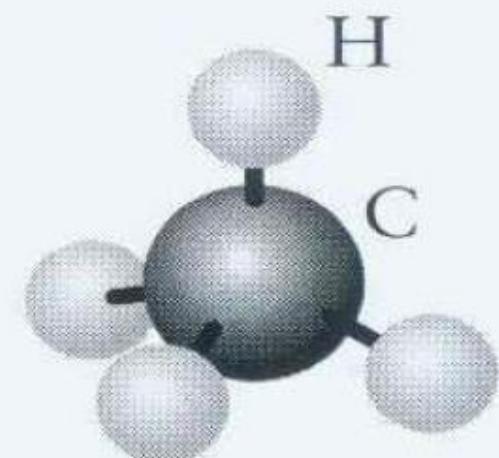
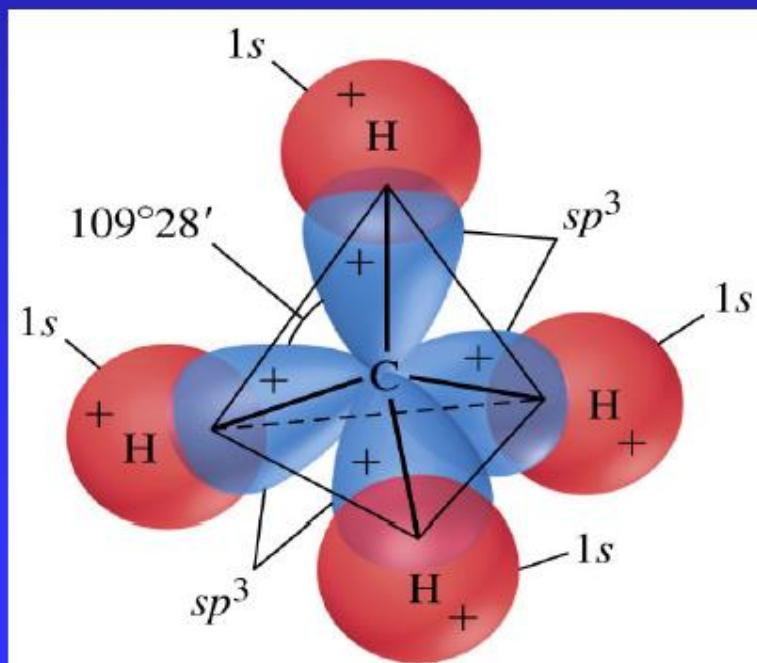
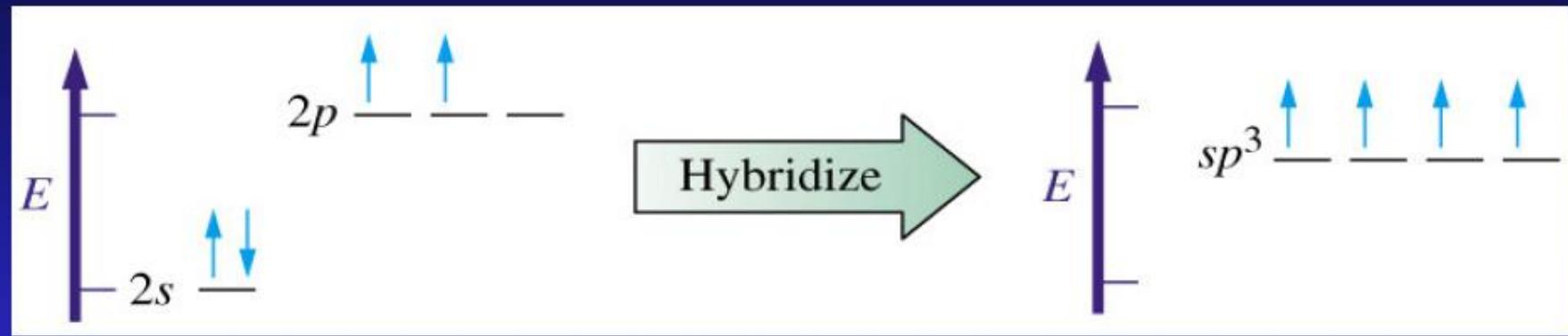


1) sp^3 杂化轨道

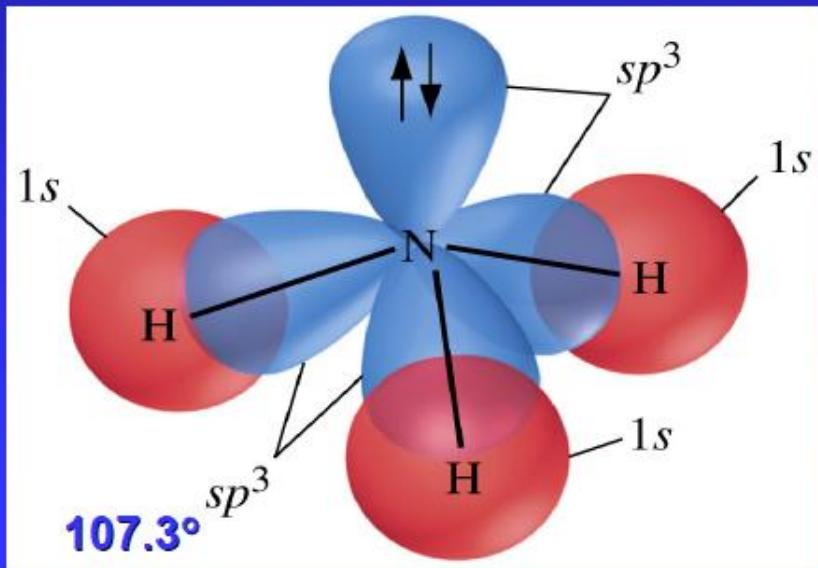
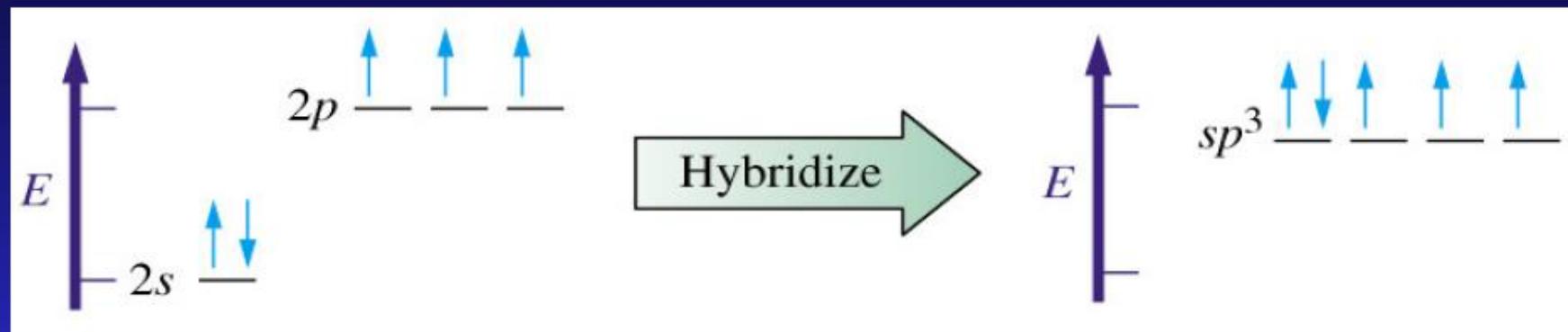
由1个 ns 轨道和3个 np 轨道组合产生4个等同的 sp^3 杂化轨道，每一个 sp^3 杂化轨道含有1/4个s轨道和3/4个 p 轨道的成分。 CH_4 分子就是C原子通过4个 sp^3 杂化轨道与4个氢原子的1s轨道重叠成键而生成。由于4个 sp^3 杂化轨道间的夹角是 109.5° ，所以呈四面体空间结构。



CH₄分子中的sp³杂化轨道

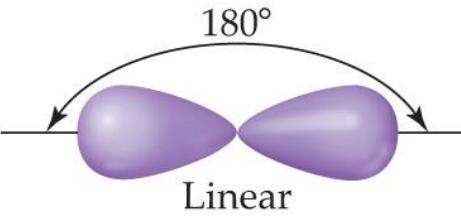
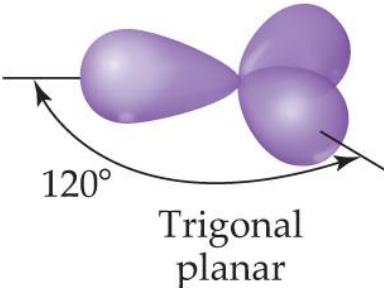
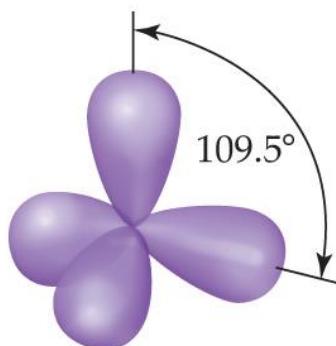


NH₃分子中N原子的sp³杂化



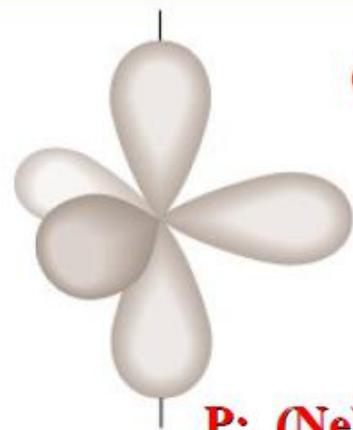
不等性杂化轨道: H₂O和NH₃中的O原子和N原子也是通过2s轨道与3个2p轨道杂化，但由于N和O原子分别比C原子多1个与2个电子，它们各自形成的sp³杂化轨道中分别含有未成键的一对与两对孤对电子，使得其杂化轨道略有差异。化学上称为不等性杂化轨道。

TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets

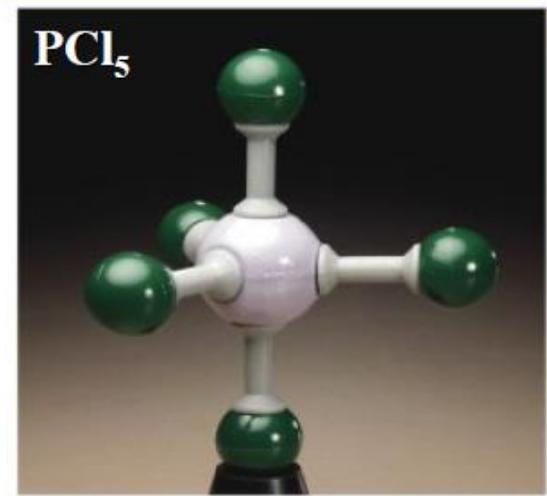
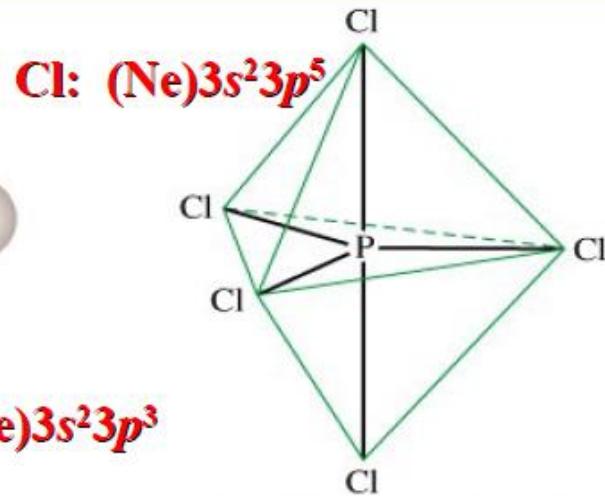
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two sp	 Linear 180°	$\text{BeF}_2, \text{HgCl}_2$
s,p,p	Three sp^2	 Trigonal planar 120°	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral 109.5°	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$

4) sp^3d , sp^3d^2 杂化轨道

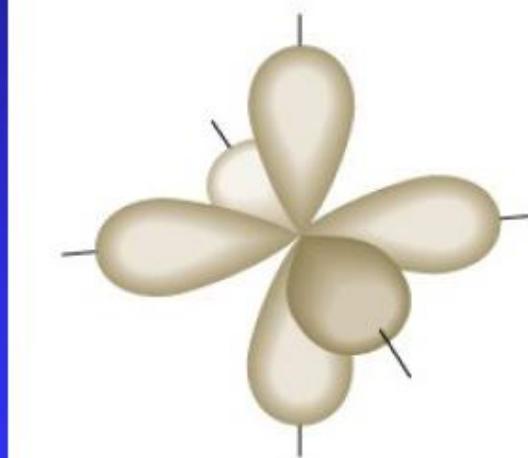
第三周期元素的原子由于d轨道能参与成键，所以还能生成由s轨道、p轨道和d轨道组合的 sp^3d , sp^3d^2 等杂化轨道。 PCl_5 、 SF_6 等分子中的P、S原子就是这方面的例子。在 PCl_5 分子中，3个 sp^3d 杂化轨道互成120°位于一个平面上，另外2个 sp^3d 杂化轨道垂直于这个平面，所以该分子的空间构型为三角双锥形。



sp^3d orbitals

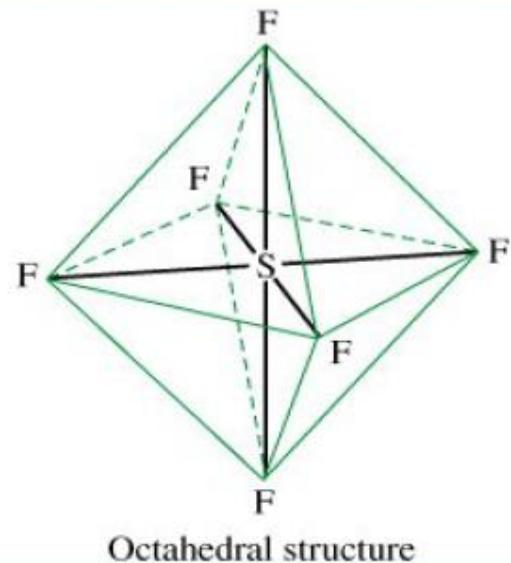


SF₆分子中6个杂化轨道指向八面体的6个顶点，4个杂化轨道在同一平面上夹角互成90°，另外2个垂直于平面，所以该分子的空间构型为正八面体。



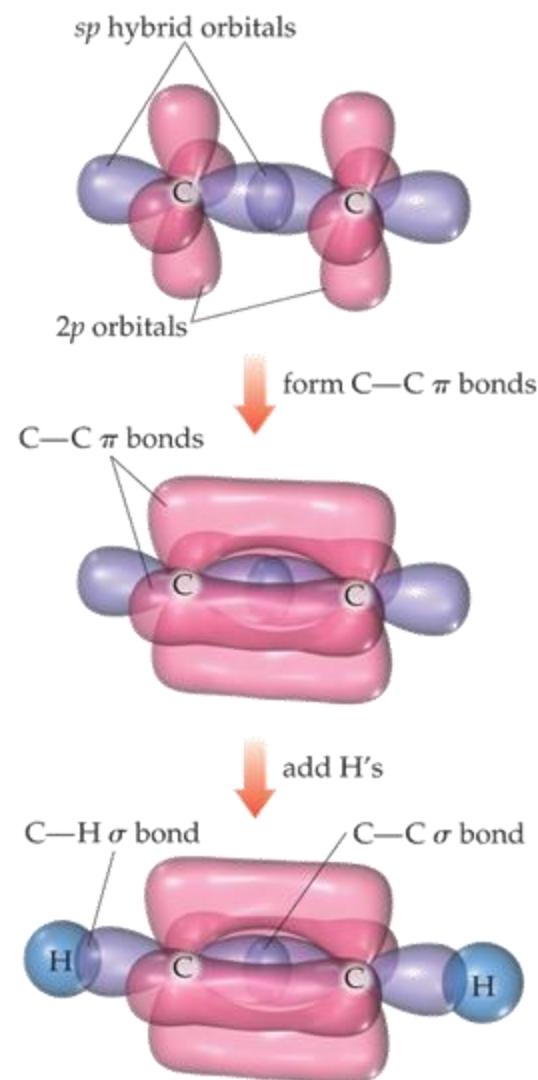
(b)

sp^3d^2 orbitals



➤ Multiple Bonds

- In triple bonds, as in acetylene, two *sp* orbitals form a σ bond between the carbons, and two pairs of *p* orbitals overlap in π fashion to form the two π bonds.



sp Hybridization of a Carbon Atom

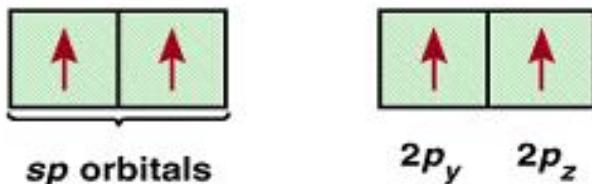
Ground state



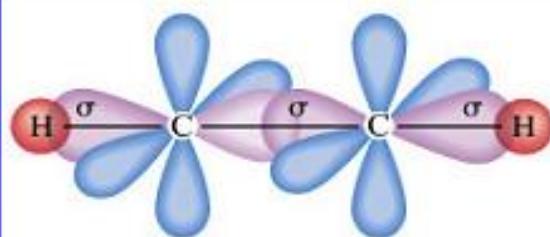
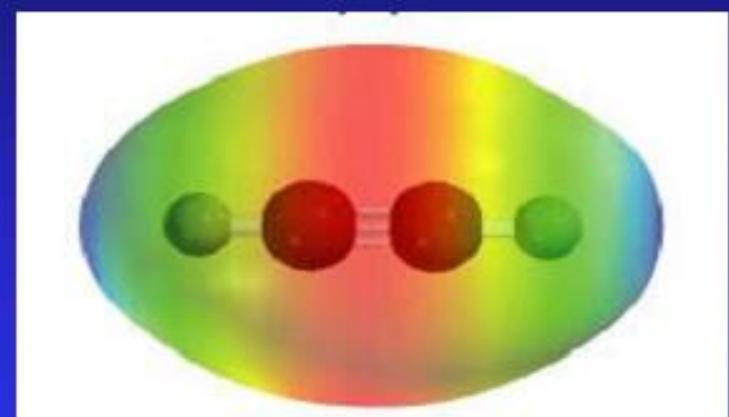
Promotion of electron



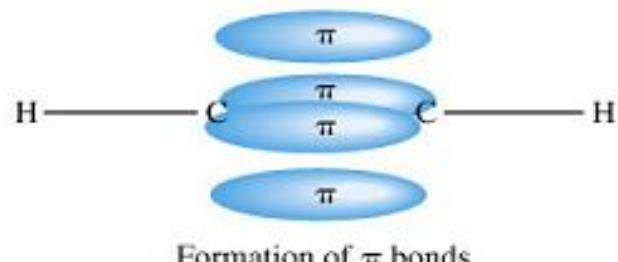
sp-Hybridized state



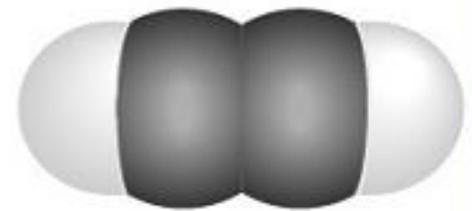
乙炔分子C₂H₂中C原子的sp杂化及成键结构



Formation of σ bonds



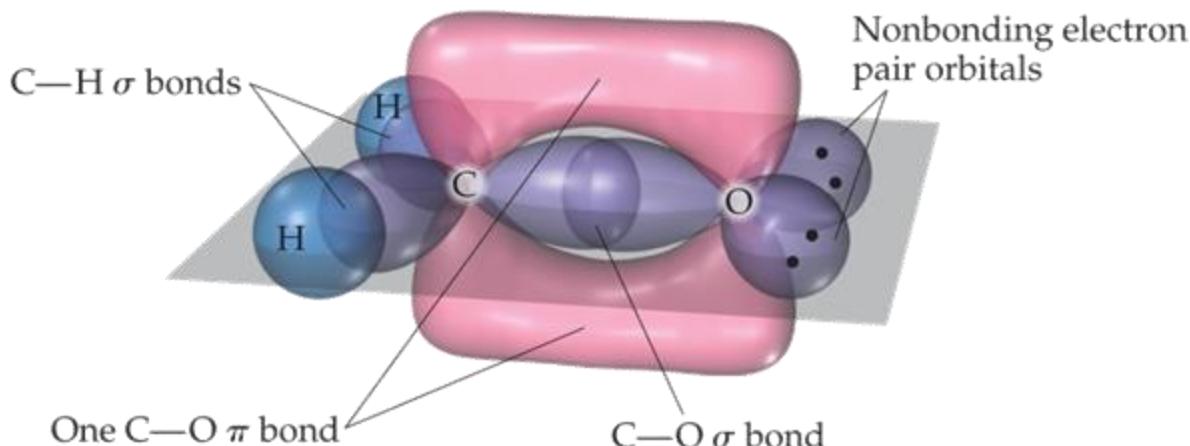
Formation of π bonds



Space-filling model

➤ Multiple Bonds

- In a molecule like formaldehyde (shown at left), an sp^2 orbital on carbon overlaps in σ fashion with the corresponding orbital on the oxygen.
- The unhybridized p orbitals overlap in π fashion.



$\text{H}_2\text{C}=\text{O}$

3 electron domains

Trigonal planar geometry

Sp^2 hybridization

sp^2 Hybridization of a Carbon Atom

Ground state



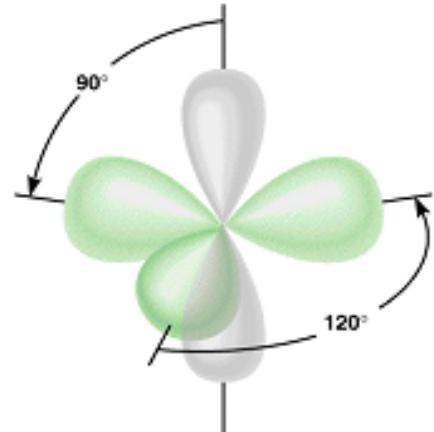
Promotion of electron



sp^2 -Hybridized state

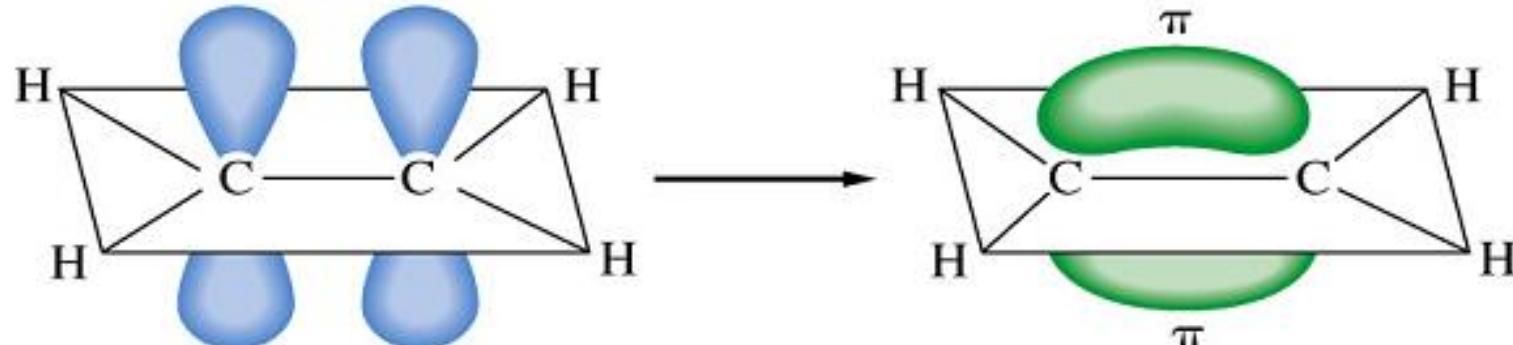
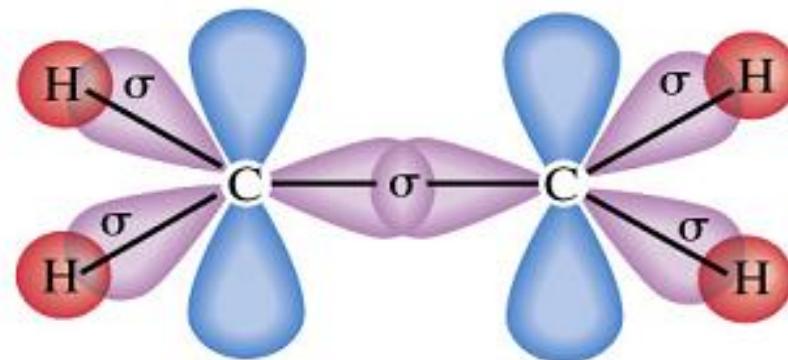
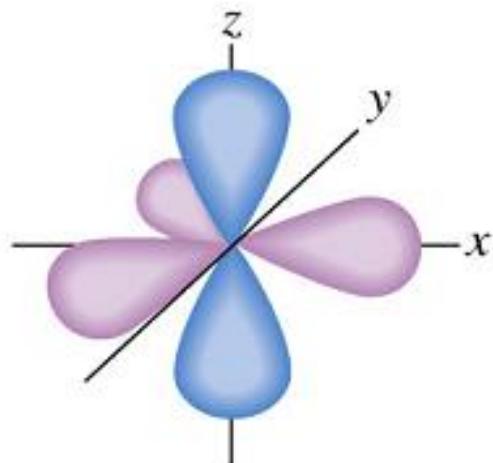


$2p_z$ Orbital Is Perpendicular to the Plane of the Hybrid Orbitals

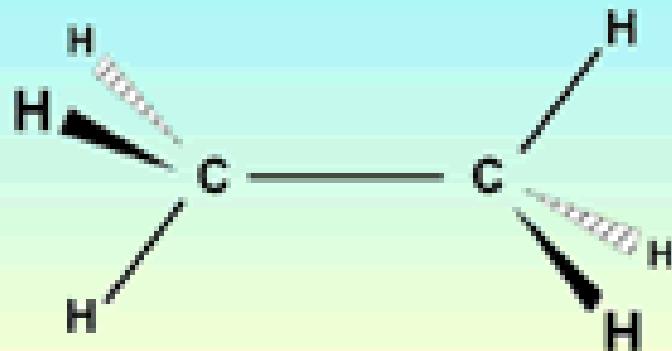


乙烯分子 C_2H_4 中 C 原子的 sp^2 杂化

乙烯分子的成键结构

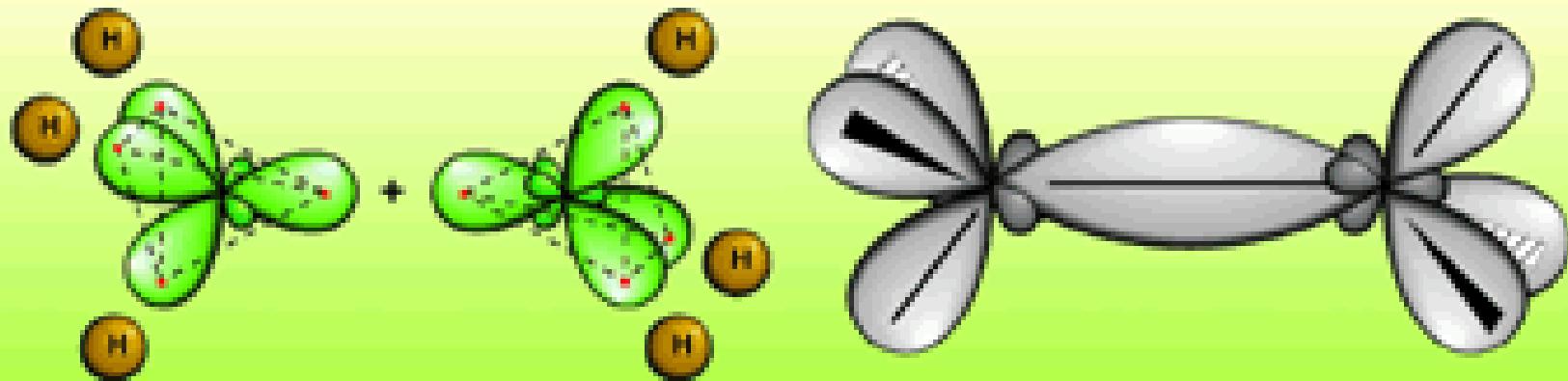


sp^3



1111
4 x sp^3

σ :
C—C
C—H
C—H
C—H



- We can not experimentally observe a π bond directly, the structure of the compounds provides strong support for its presence.

乙烷、乙烯乙炔分子的键级、键长和键能的比较

分 子	C ₂ H ₆	C ₂ H ₄	C ₂ H ₂
C-C键级	1	2	3
C-C键长/pm	154	135	121
碳碳间键能/(kJ·mol ⁻¹)	376	720	962

1、价键理论发展小结

1927年德国物理学家海特勒(W. Heitler, 1904–1981)和伦敦(F. W. London, 1900–1954)首先把量子力学应用到分子结构中，建立和求解了氢分子的薛定谔方程，揭示了氢分子中每个原子共用一对电子形成化学键的本质，指出只有自旋相反的未成对电子才能形成共价键。

1930年，美国化学家鲍林(L. Pauling, 1901–1994)和德国物理学家斯莱特(J. C. Slater, 1900–1976)把海特勒和伦敦的电子对成键理论推广到多种单质和化合物中，从而形成了现代价键理论，简称**VB**理论或电子配对理论，亦称**HLSP**理论。

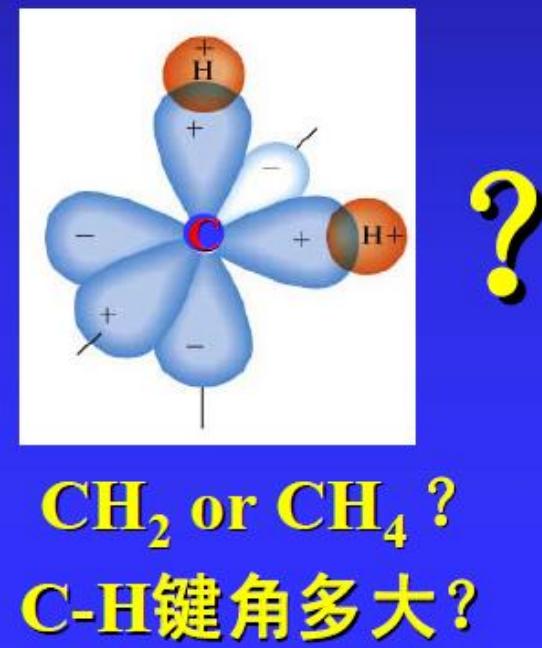
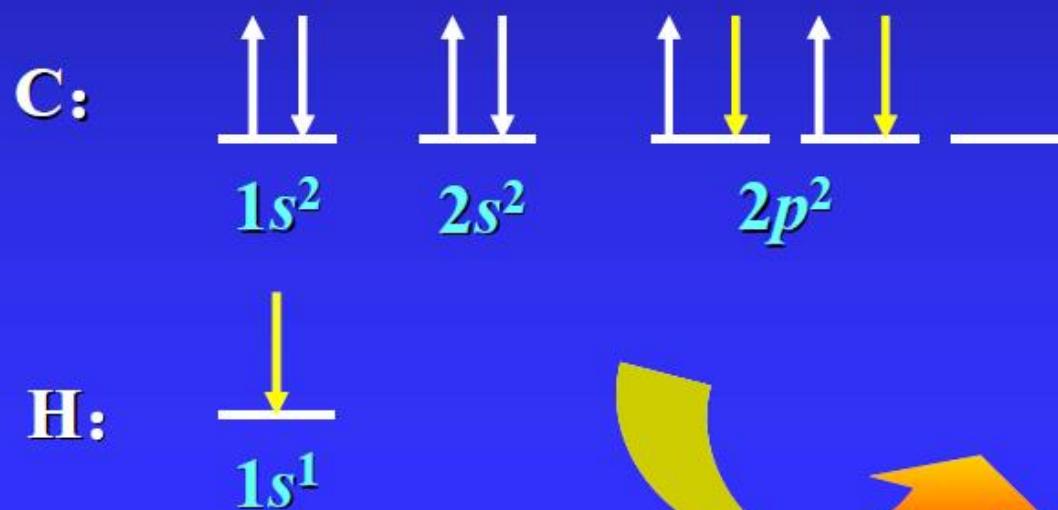
1931年，为解释甲烷分子的空间构型，鲍林和斯莱特又根据波函数叠加原理，提出了杂化轨道理论。作为价键理论的重要补充，较满意地解释了共价多原子分子的空间构型。

1931–1933年，为了合理处理用路易斯结构难以描述的分子，鲍林又提出了共振概念。

价键理论将量子力学的原理和化学的直观经验紧密结合，在经典化学中引入了量子力学理论和一系列的新概念，如杂化、共振、 σ 键、 π 键、电负性、电子配对等，阐明了共价键的本质，阐明了共价键的方向性和饱和性，对化学键理论的发展起了重要作用。

4、杂化轨道的概念

为了解释分子的空间结构(键长、键角), Pauling提出了杂化轨道(hybridization)的概念,丰富和发展了价键理论。从电子具有波动性、波可以叠加的量子力学观点出发,他认为: 在同一个原子中能量相近的不同类型(s, p, d, \dots)的几个原子轨道波函数可以互叠加而组成同等数目的能量完全相同的杂化原子轨道。

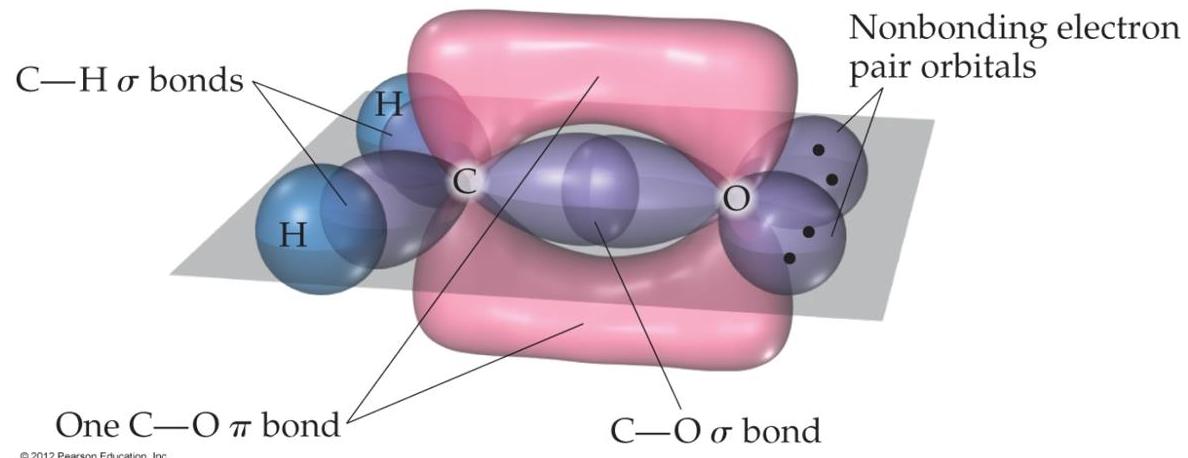


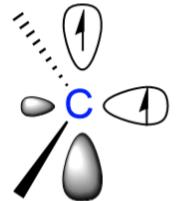
思考：

卡宾(Carbene), $\text{H}_2\text{C}\colon$, 碳可以怎么杂化？外层电子是否全部成对？

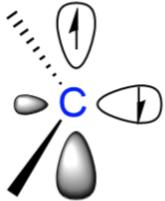
如果假设卡宾碳采用sp²杂化，并且外层电子全部成对，请画出两种类似于下图的两种 $\text{H}_2\text{C}\colon$ 。

这两种中，哪一种更稳定？

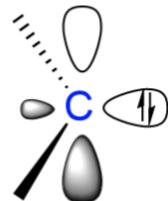




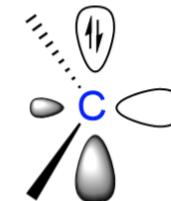
$\sigma^1\pi^1$ triplet



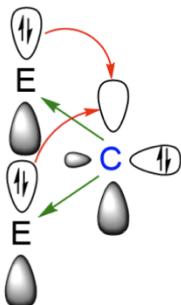
$\sigma^1\pi^1$ singlet



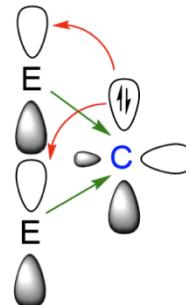
$\sigma^2\pi^0$ singlet



$\sigma^0\pi^2$ singlet



push/push mesomeric and
pull/pull inductive effect



pull/pull mesomeric and
push/push inductive effect



反电子态双亲性碳

The hybridization of the oxygen atom in a water molecule is

- a. sp.
- b. sp^2 .
- c. sp^3 .
- d. sp^3d .

The central atom of which molecule below is sp^3d -hybridized?

- a. CH_4
- b. SO_3
- c. SeBr_4
- d. XeOF_4

A molecule of acetonitrile (CH_3CN) contains _____ sigma bonds.

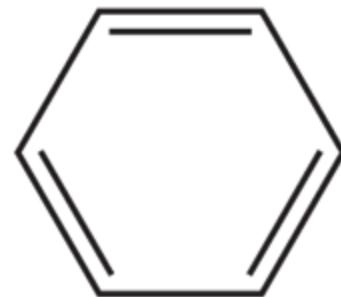
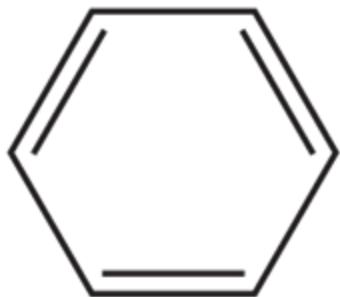
- a. 2
- b. 3
- c. 4
- d. 5

A molecule of crotonaldehyde
 $(CH_3CH=CH-CH=O)$ contains
_____ pi bonds.

- a. 1
- b. 2
- c. 3
- d. 4

➤ Resonance

- In reality the π electrons in benzene are not localized, but delocalized.
- The even distribution of the π electrons in benzene makes the molecule unusually stable.



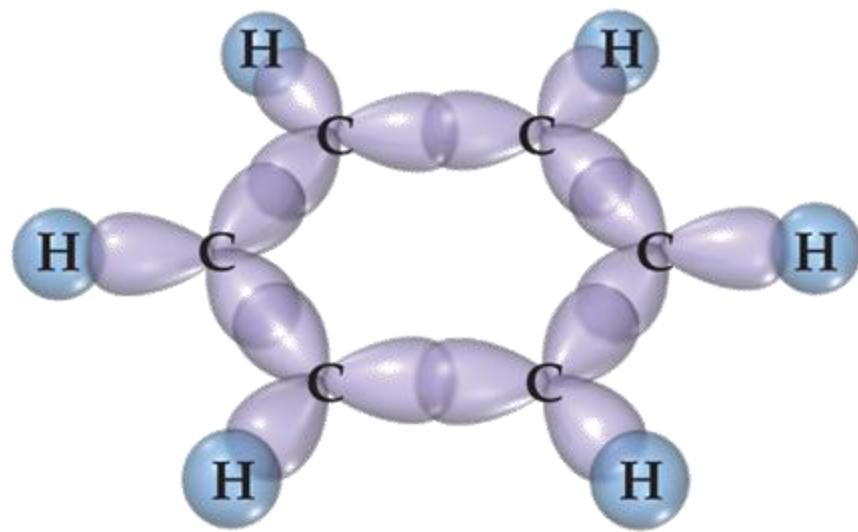
or



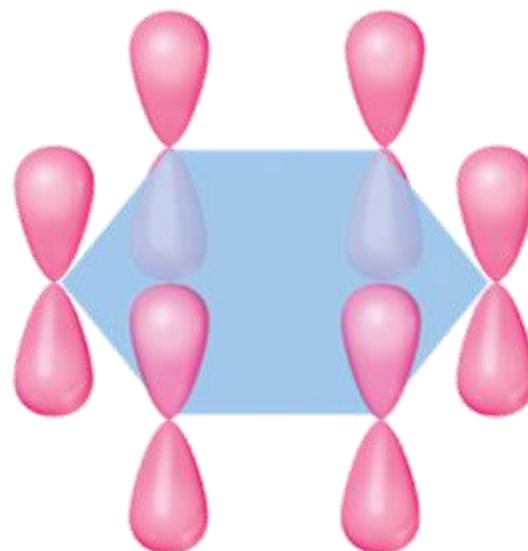
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➤ Resonance

- The organic molecule benzene has 3 σ bonds and a p orbital on each carbon atom, sp^2 hybridization.



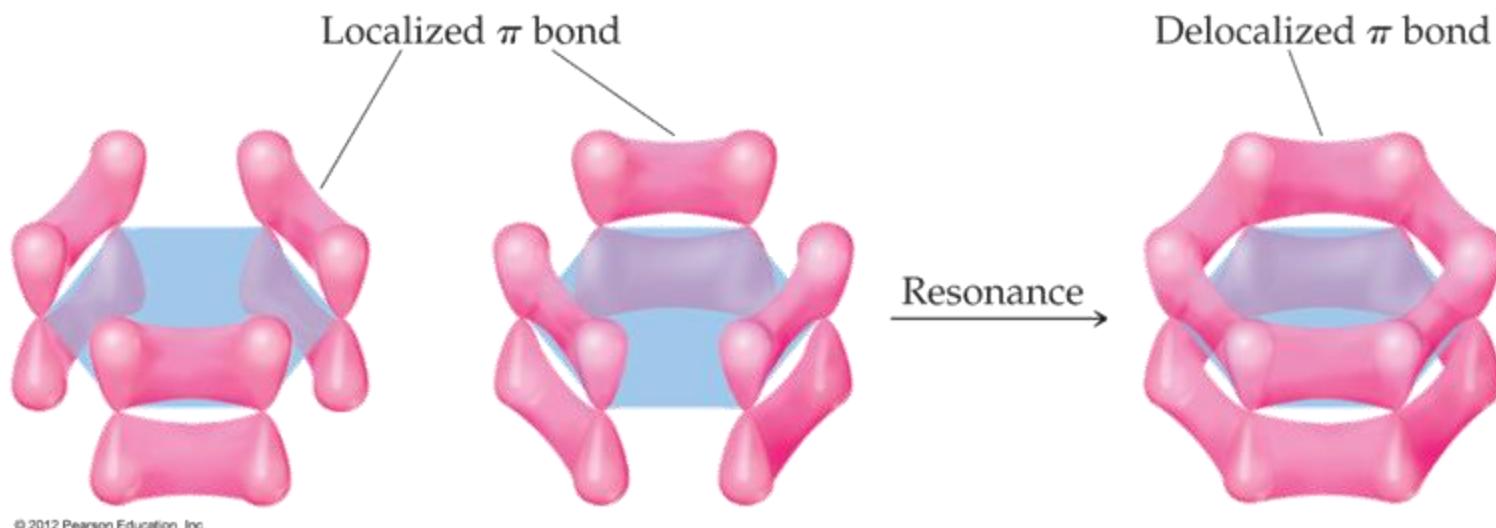
(a) σ bonds



(b) 2p atomic orbitals

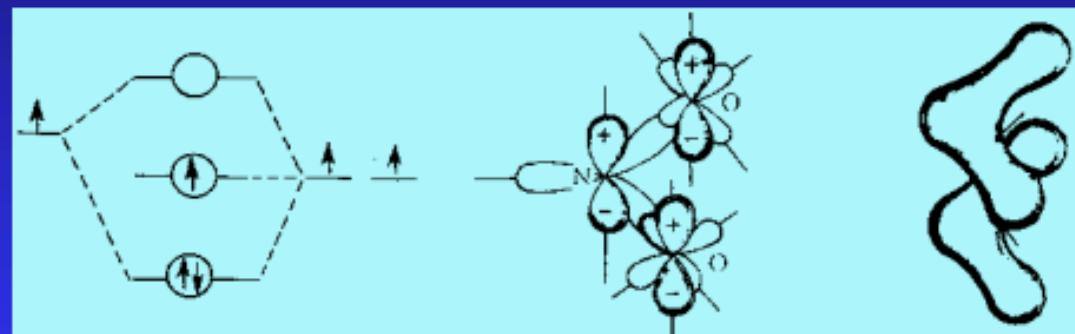
➤ Resonance

- In reality the π electrons in benzene are not localized, but delocalized.
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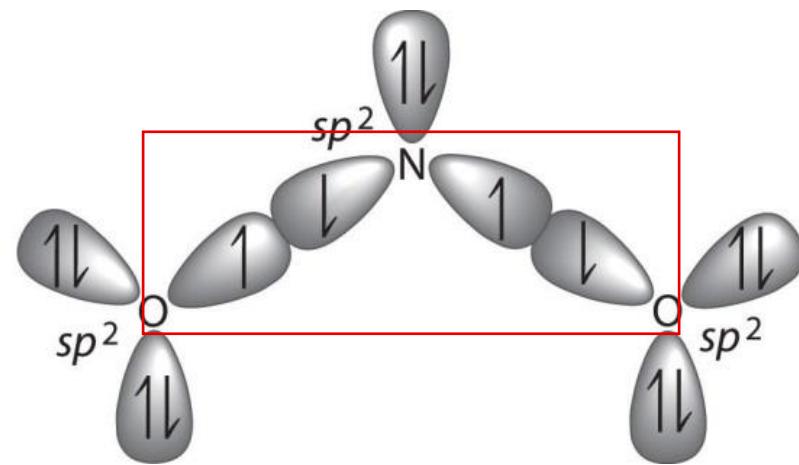
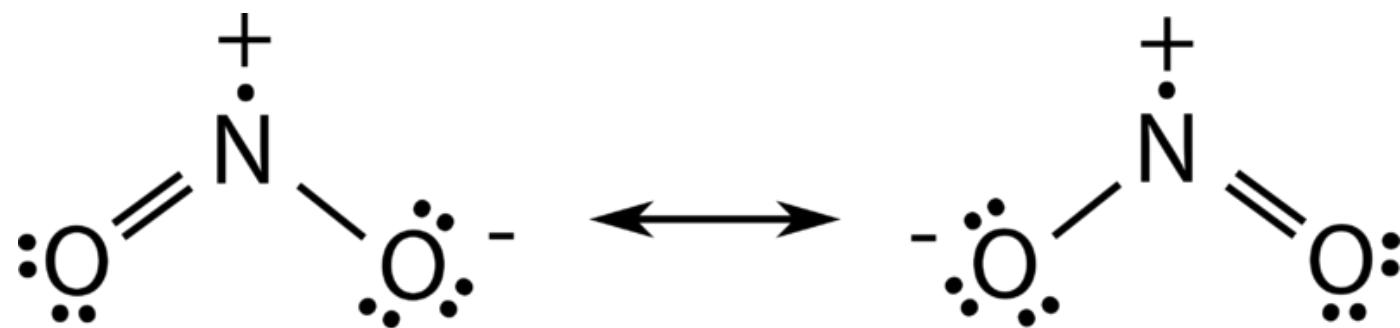


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NO₂分子的结构 —— π_3^3 离域π键

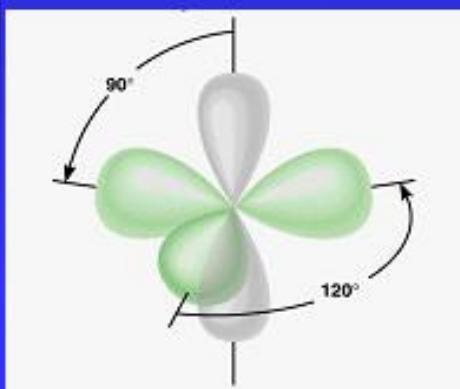
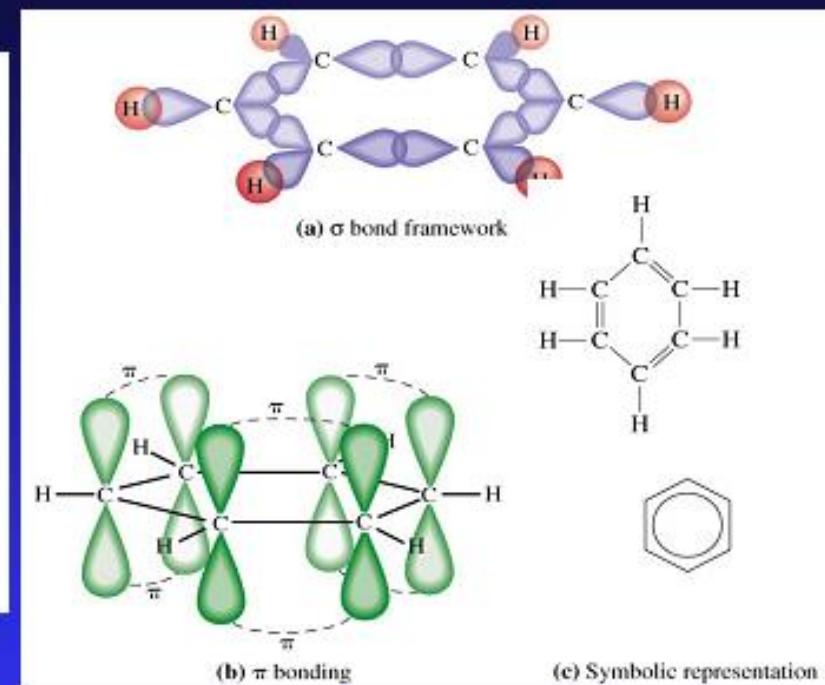
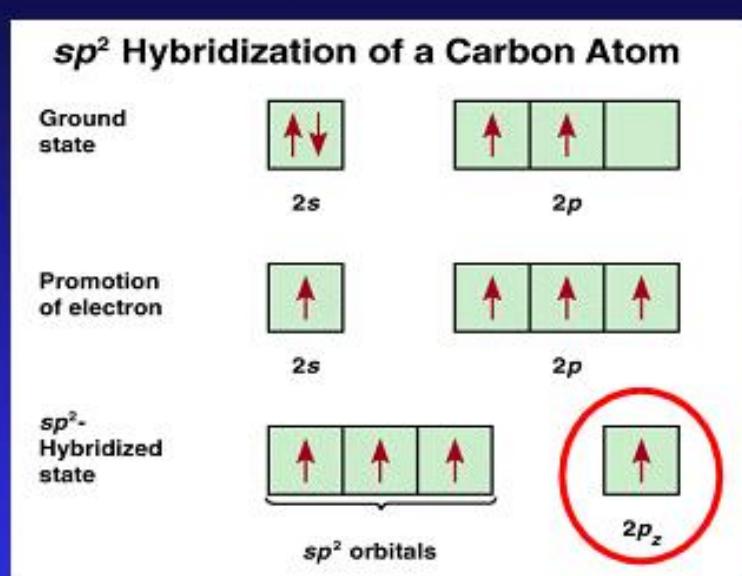


NO₂分子的中心N原子用sp²杂化轨道与2个O原子组成2个σ键，但N原子的另一个p轨道与2个O原子的p轨道都垂直于NO₂分子的平面。3个相互平行的p原子轨道组成3个π键分子轨道，包括成键、反键和非键轨道。每一个分子轨道上的π子都不再局限于2个原子之间，而为3个原子所共有，形成离域大π键。右侧图最低能级的(π)²分子轨道。

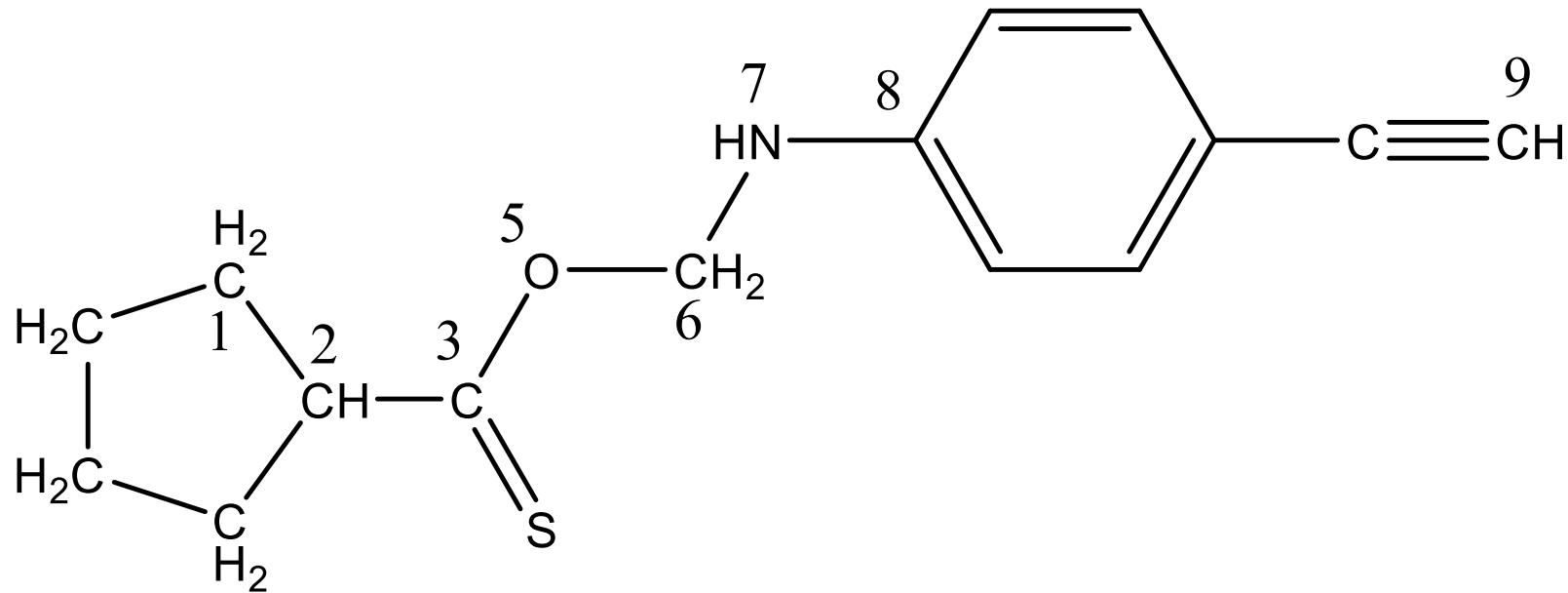


$\text{O}_3?$?

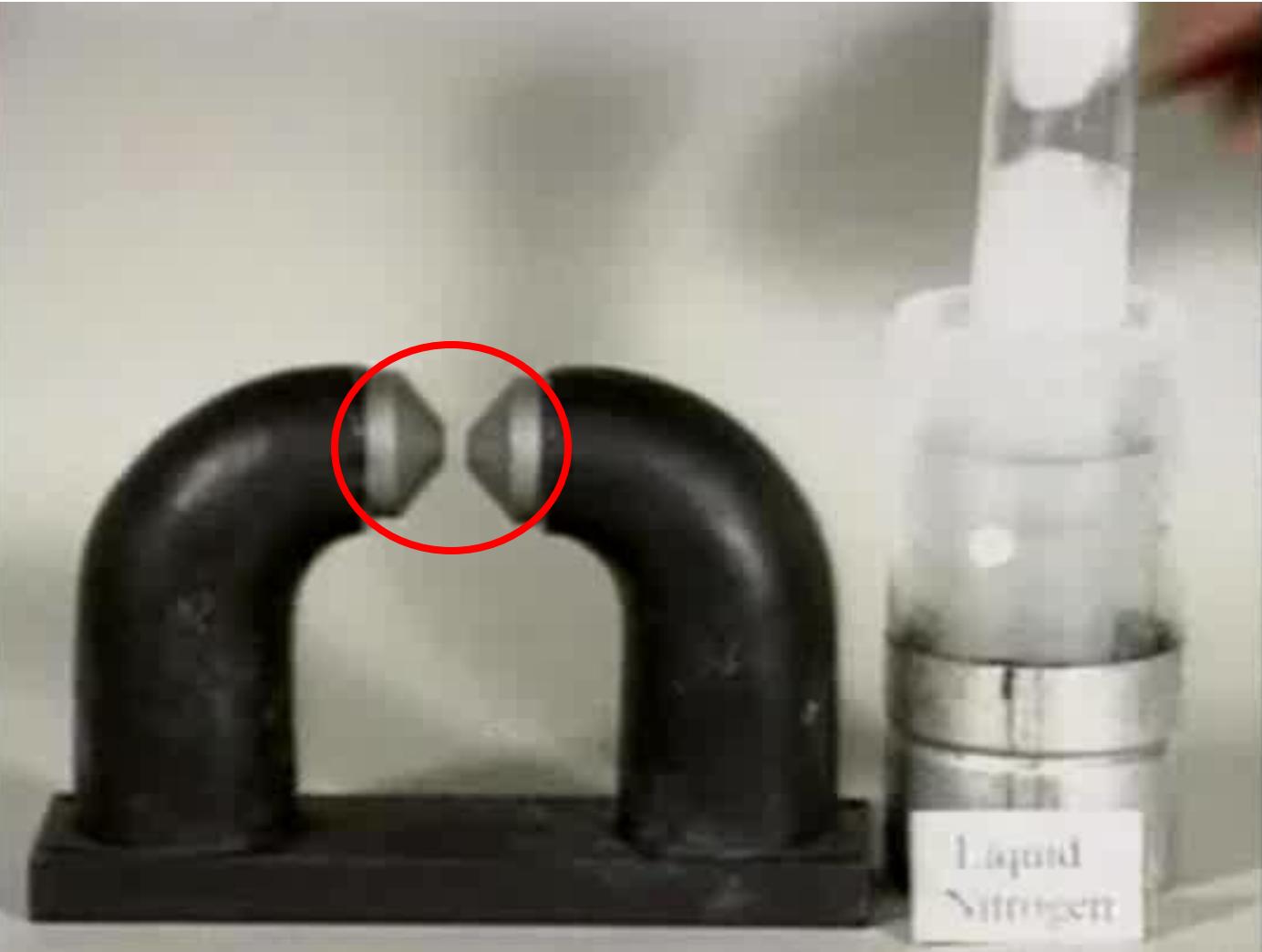
价键理论对苯分子结构的解释



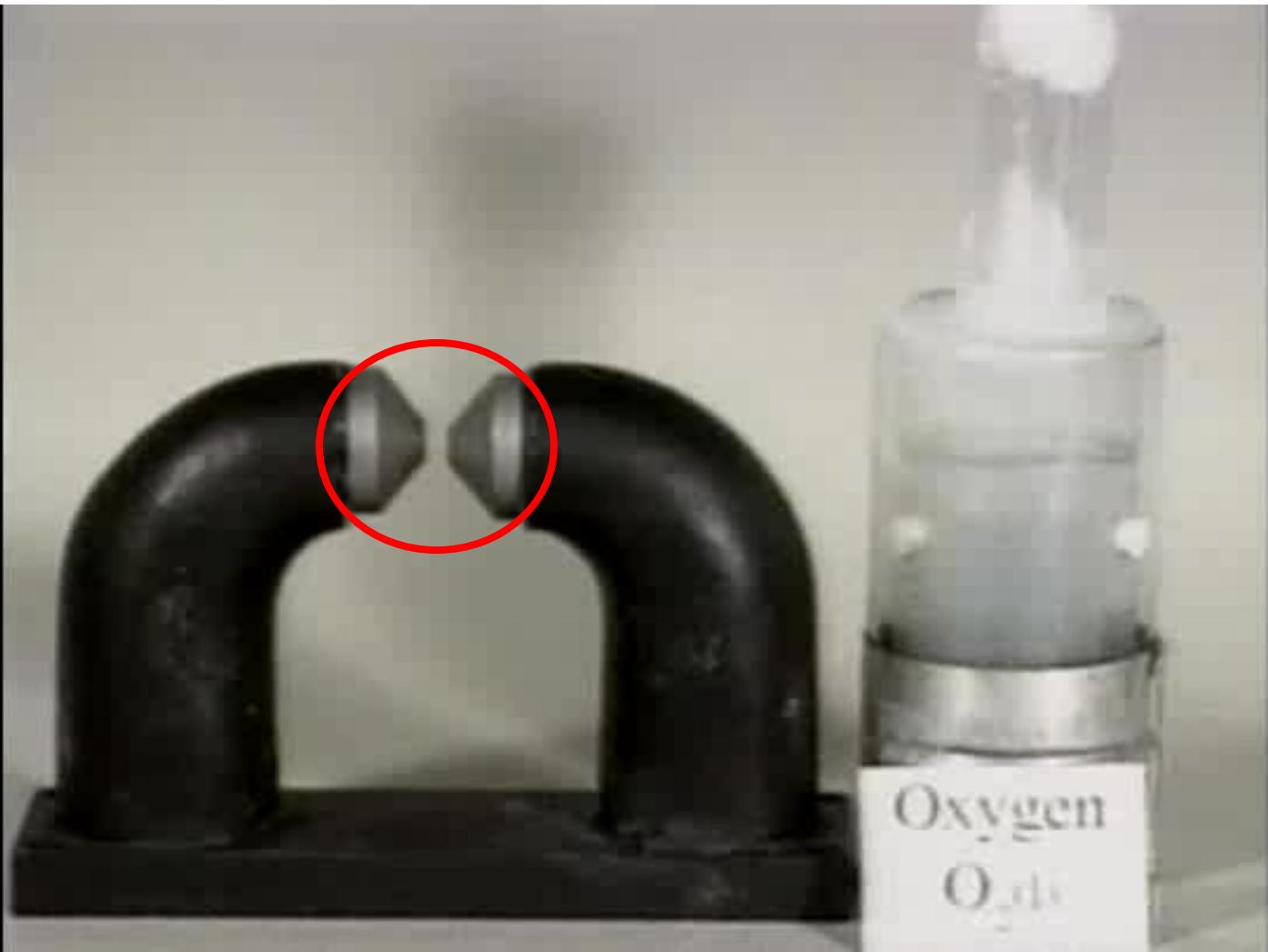
考虑到苯分子中各键角都等于 120° ，所以C原子采用*sp²*化轨道。每个C原子形成3个 σ 键，其中2个与相邻的C原子，第三个是与H原子。剩余的1个与*sp²*轨道垂直的2p_z道和相邻的C原子以肩并肩形式构成3个 π 键。显然，须助于共振概念才能解释C-C键长均相等的实验事实。



For above molecule, (a) describe the hybridization of all atoms except H.
 (b) What are bond angles of C1-C2-C3, C2-C3-O5, C3-O5-C6, C6-N7-C8?
 (c) How many sigma bonds and pi bonds? (d) Is N7 in the same plane of C9? Why?



Liquid Nitrogen



Liquid Oxygen

- **Electron configurations and molecular properties**
- **Paramagnetism (顺磁性):** Molecules with one or more **unpaired electrons** are attracted to a magnetic field. 顺磁性是一种弱磁性。当分子轨道或原子轨道上有落单的电子时，就会产生顺磁性。
- **Diamagnetism(反磁性):** Substance with **no unpaired electrons** are weakly repelled by magnetic field.
 - Lewis structure for O₂ shows a double bond and complete pairing of electrons;
 - Together with valence bond theory, both can not explain the **Paramagnetism** of O₂.

➤ Molecular Orbitals

- Valence-bond theory and hybrid orbitals allow us to move in a straightforward way from Lewis structures to rationalizing molecular geometries in terms of atomic orbitals.
- Does not explain all aspects of bonding: the excited state of molecules to understand how molecules absorb light, giving them color.





Molecular-Orbital (MO) Theory



Robert Sanderson Mulliken
(1896–1986)

Friedrich Hermann Hund
(1896–1997)

MO理论：应用于分子体系的量子化学研究方法。

MO理论与VB理论几乎同时期发展起来，二者在化学键描述上采取了不同的理论路径。

需要注意的是，MO理论是一套独立于VB理论的理论体系。尽管两者在发展过程中存在深刻的联系与呼应，但并无派生关系，而是各自形成完整框架。

VB理论的优点在于其直观性强，与化学家的经验认知较为契合；

而MO理论的优势则体现在其易于程序化实现，能够高效地应用于大规模量子化学计算。

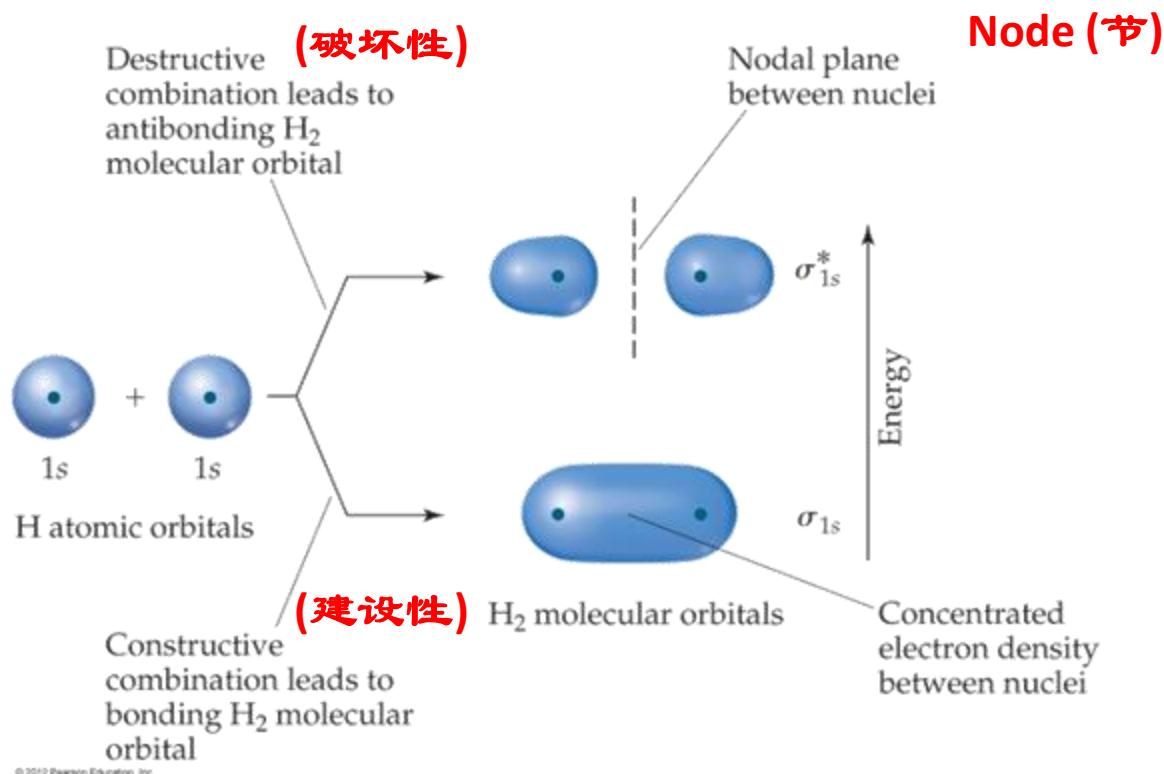
分子轨道理论的出发点是分子的整体性，重视分子中电子的运动状况，以分子轨道的概念来克服价键理论中强调电子配对所造成的分子电子波函数难于进行数学运算的缺点。

莫利肯把原子轨道线性组合成分子轨道，可用数学计算并程序化。

分子轨道法处理分子结构的结果与分子光谱数据吻合，因此20世纪50年代开始，价键理论逐渐被分子轨道理论所替代。

➤ Molecular-Orbital (MO) Theory

- Though valence bond theory effectively conveys most observed properties of ions and molecules, there are some concepts better represented by molecular orbitals.



组合前后，轨道总数不变（俩AO得到两个MO）

组合前后，轨道总能量不变，相比于AO，能量下降的MO称为成键（分子）轨道，能量上升的MO称为反键（分子）轨道，能量几乎不变的称为非键（分子）轨道。

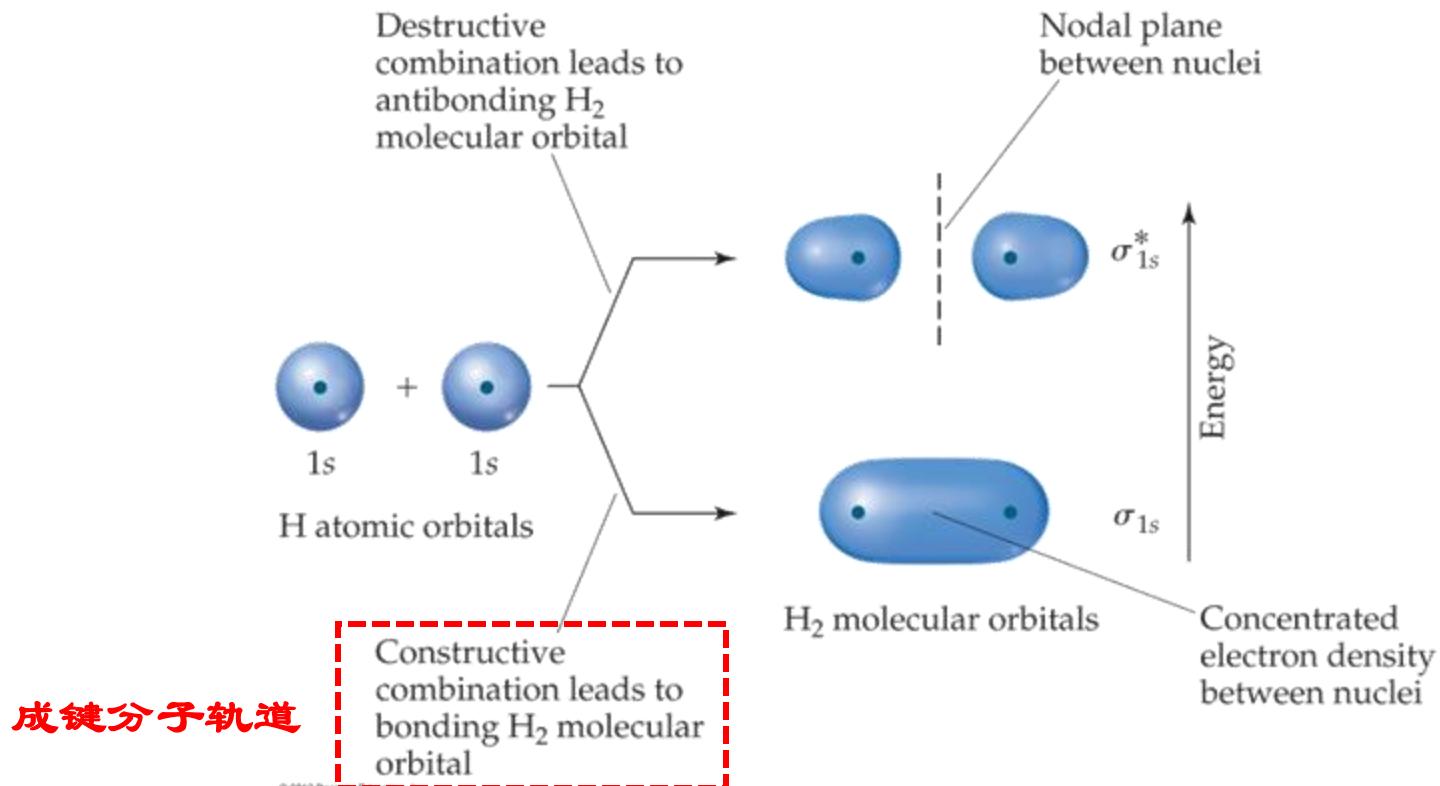
成键轨道的电子云在原子之间有较大概率分布。

反键轨道的电子云在原子之间出现节面。

非键轨道的电子云和原子轨道基本相同。

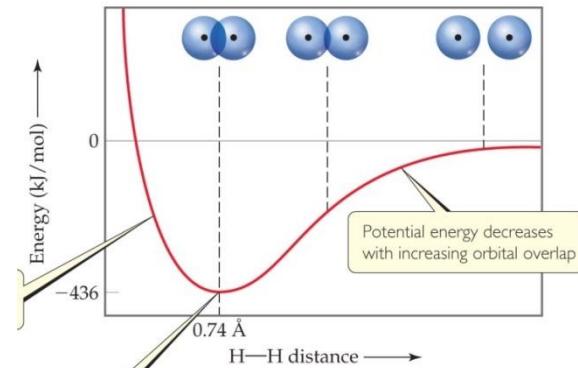
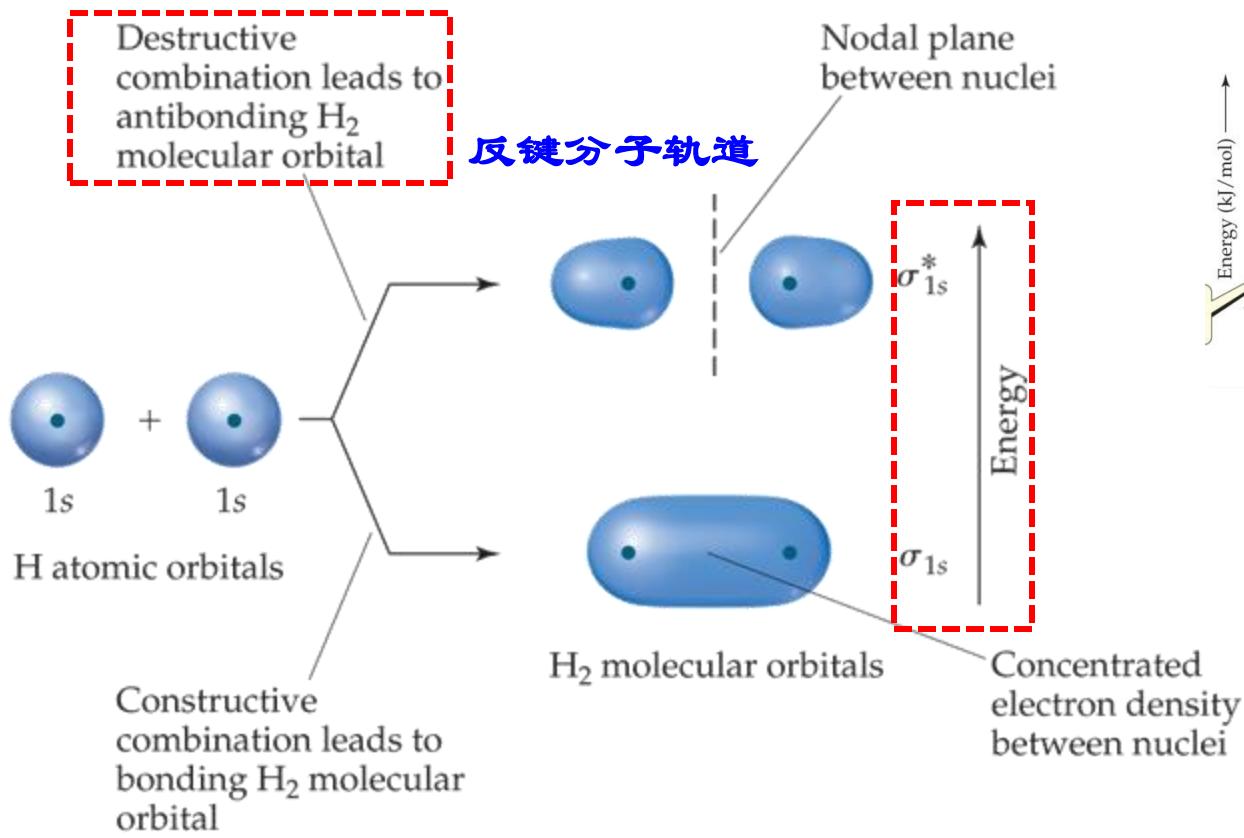
➤ Molecular-Orbital (MO) Theory

- In MO theory, we consider the wave nature of electrons.
- If waves interact constructively, the resulting orbital is lower in energy: a bonding molecular orbital.

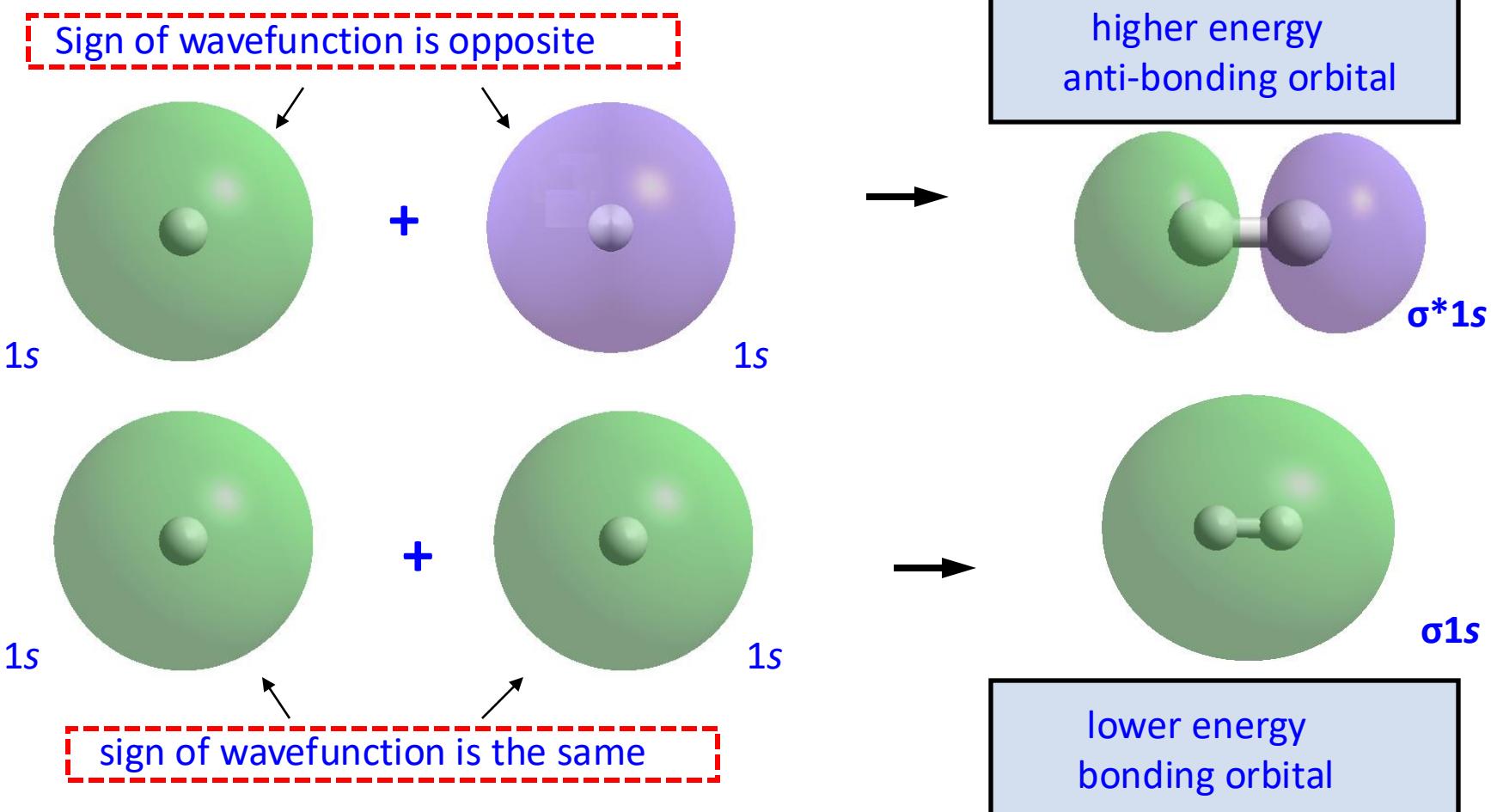


➤ Molecular-Orbital (MO) Theory

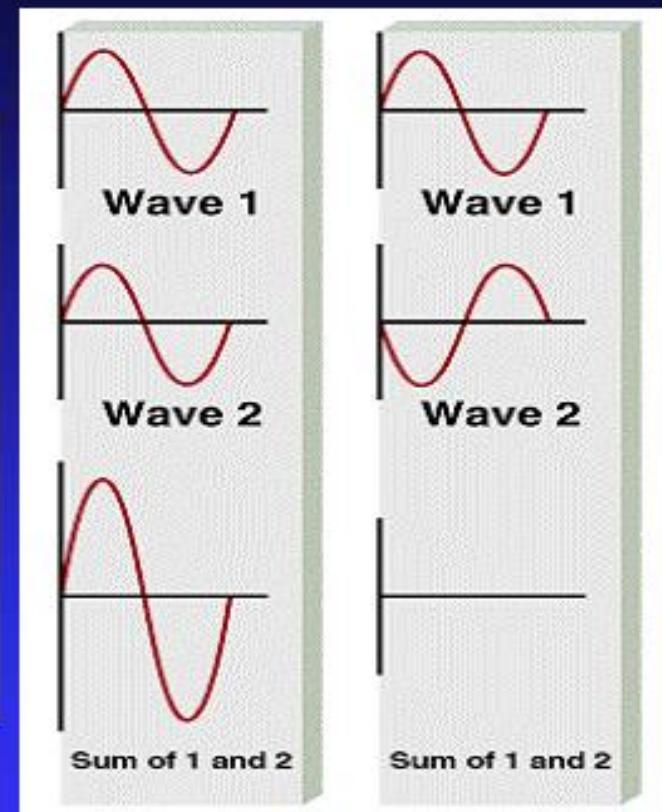
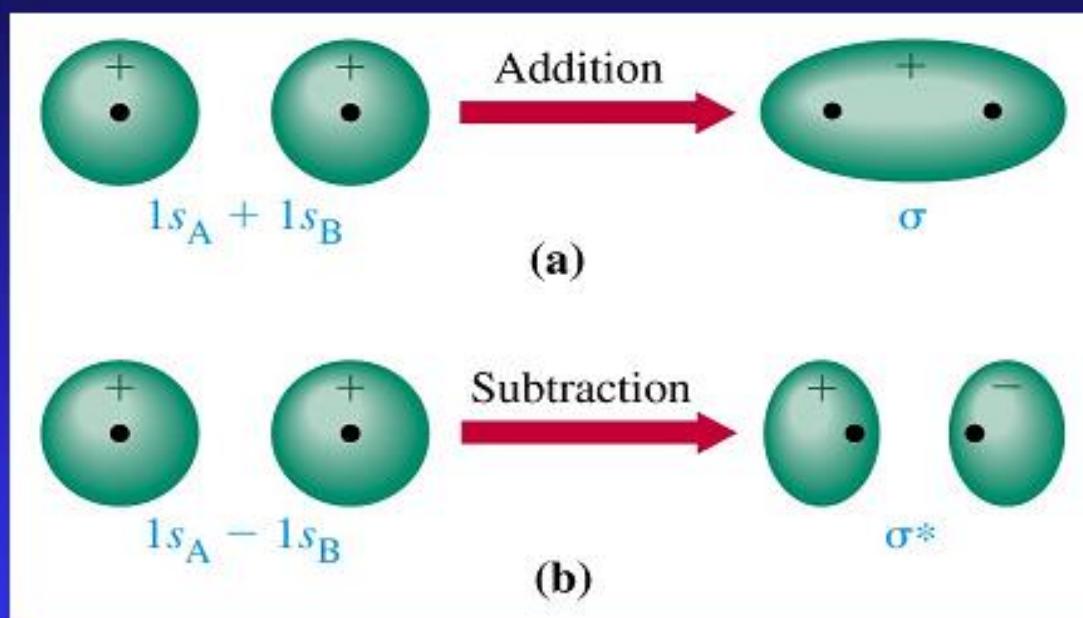
- If waves interact destructively, the resulting orbital is higher in energy: an antibonding molecular orbital.



- The essence of MO theory is that overlap of two orbitals always occurs in two ways. In one (bottom), the two 1s orbitals shown here overlapping have the same sign of the wavefunction, and so a net overlap occurs. This produces a lower energy bonding orbital. In the upper case, the two orbitals are of opposite sign, and so no net overlap occurs. This produces a higher energy anti-bonding orbital.



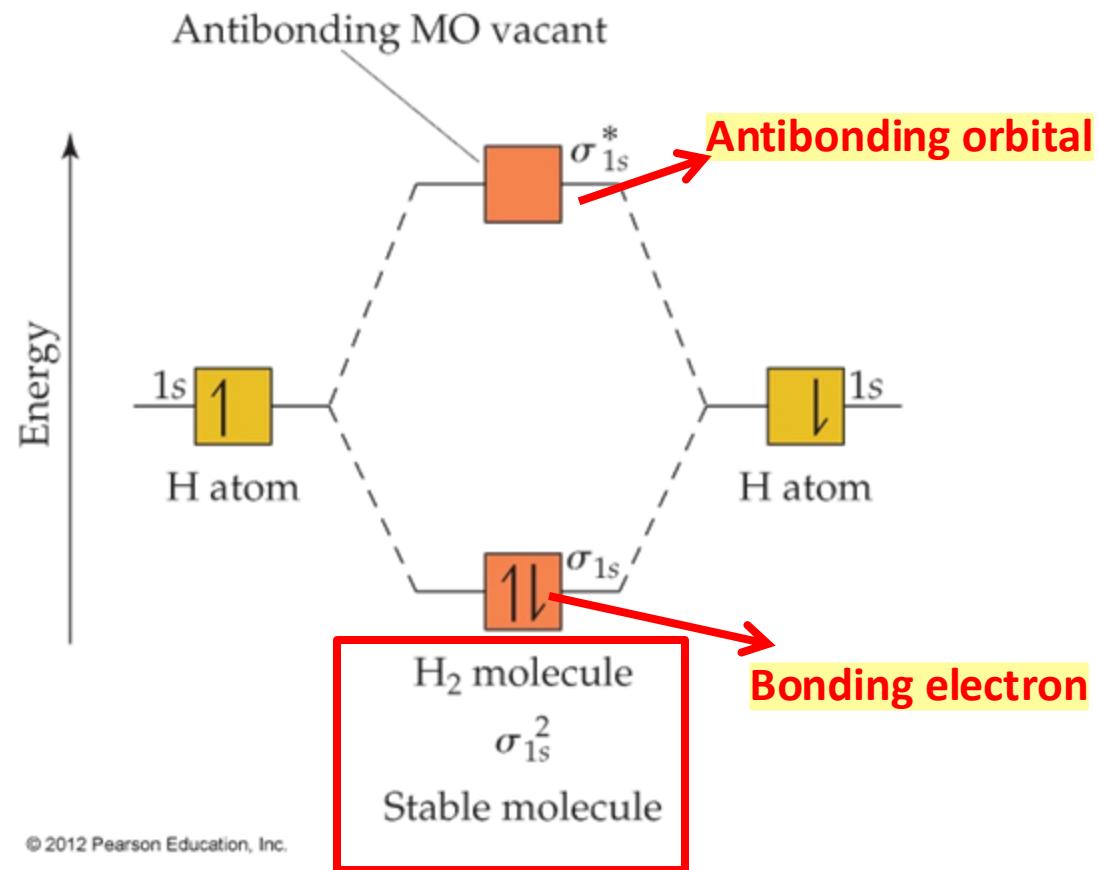
Combining Atomic Orbitals



轨道线性叠加，相位相同时波增强，能量降低，形成成键轨道；
相位相反时波减弱，能量升高，形成反键轨道。

- In molecules, atomic orbitals combine to form molecular orbitals which surround the molecule. Similar to atomic orbitals, molecular orbitals are **wave functions** giving the probability of finding an electron in certain regions of a molecule. Each molecular orbital can only have 2 electrons, each with an opposite spin.

Energy-level diagram Molecular orbital diagram



Principle

Details/Examples

	Principle	Details/Examples
1	Total number of molecular orbitals is equal to the total number of atomic orbitals from combining atoms.	The molecule H ₂ is composed of two H atoms. Both H atoms have a 1s orbital, so when bonded together, there are therefore two molecular orbitals.
2	Bonding molecular orbitals have less energy than the constituent atomic orbitals before bonding. Antibonding molecular orbitals have more energy than the constituent atomic orbitals before bonding.	Bonding molecular orbitals help stabilize a system of atoms since less energy is associated with bonded atoms as opposed to a system of unbound atoms. Likewise, antibonding molecular orbitals cause a system to be destabilized since more energy is associated with bonded atoms than that of a system of unbound atoms.
3	Following both the Pauli exclusion principle and Hund's rule, electrons fill in orbitals of increasing energy.	Electrons fill orbitals with the lowest energy first. No more than 2 electrons can occupy 1 molecular orbital at a time. Furthermore, all orbitals at an energy level must be filled with one electron before they can be paired. (see second diagram below)
4	Molecular orbitals are best formed when composed of Atomic orbitals of like energies.	Molecular Orbital Configuration of Li ₂ : $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2$ The bonding (σ_{1s}) ² and antibonding (σ^*_{1s}) ² cancel each other out, leaving (σ_{2s}) ² as the valence electrons involved in the atoms' bonding.

2) 原子轨道有效组合成分子轨道必须满足以下3条原则：

对称性匹配原则：原子轨道波函数相互叠加组分子轨道时，要像波叠加一样须考虑位相的正负号。 σ 和 π 成键分子轨道都是由两个子轨道波函数同号区域相重叠而成($\psi = \psi_1 + \psi_2$)，而 σ^* 和 π^* 反键分子轨道则是由波函数异号区域相重叠而成($\psi = \psi_1 - \psi_2$)。这就是所谓对称性匹配原则。

能量近似原则：只有能量相似的原子轨道才能组合成有效的分子轨道。例如，同核双原子分子中，2个原子能量等同的1s(或2s, 2p)轨道组合成分子轨道，而内层的1s轨道不可能和能量相差很大的2s, 2p轨道组合成分子轨道。至于2s和2p轨道之间能否进行组合，取决于二者之间能量差多少，而这个能量差则随原子不同而异。

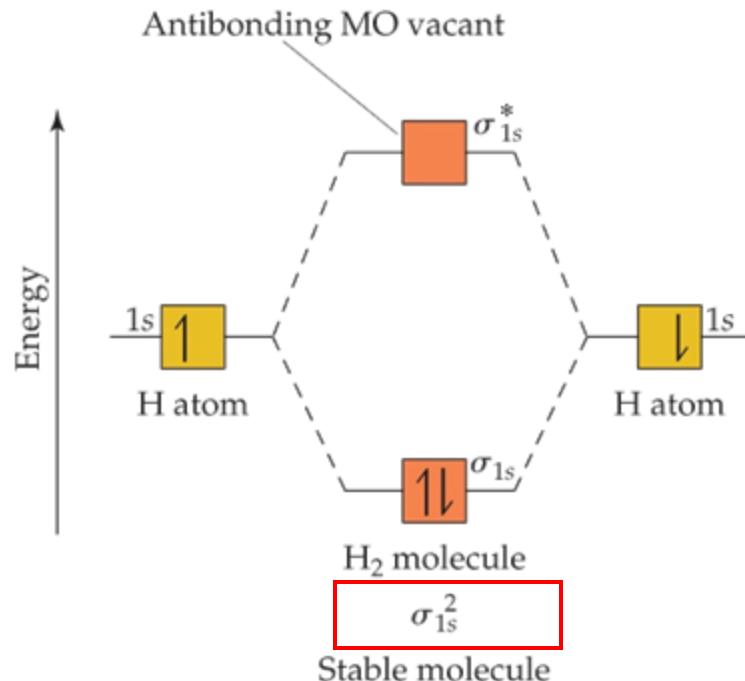
最大重叠原则：两个原子轨道要有效组成分子轨道，必须尽可能多重叠，以使成键分子轨道的能量尽可能降低。

3) 电子在分子轨道上的排布也遵从原子轨道电子排布的同样原则，即：

- 每个分子轨道最多能容纳2个自旋相反的电子(Pauli原理)；
- 电子总是尽量先占据能量最低的轨道，只有当能量较低的轨道填满以后，才开始填入能量较高的轨道(能量最低原理)；
- 当电子填入2个或多个等能量的轨道(又称简并分子轨道)时，电子总是先以自旋相同的方式分占这些轨道直到半充满(Hund规则)。

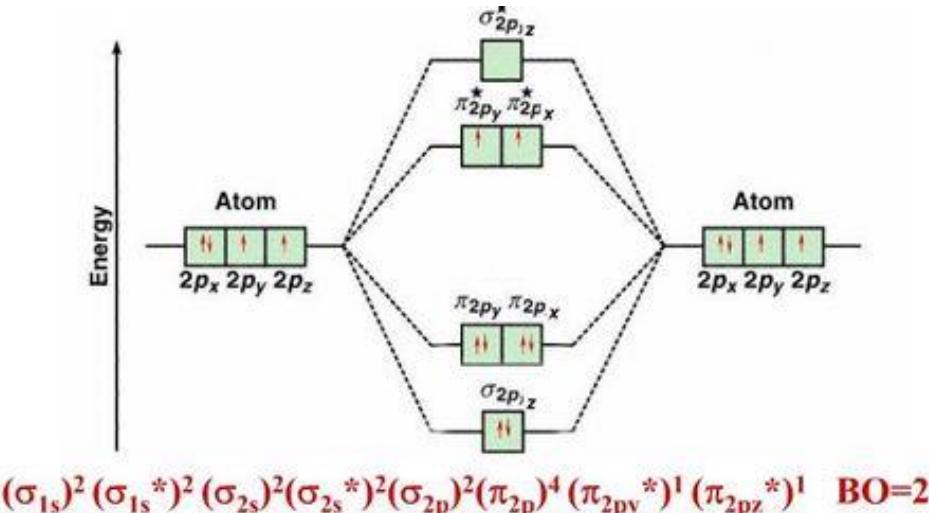
➤ MO Theory

- In H_2 the two electrons go into the bonding molecular orbital.
- The **bond order** is one half the difference between the number of bonding and antibonding electrons.



➤ Bond Order

- In molecular orbital theory, the **stability of a covalent bond** is related to its bond order.
bond order = $\frac{1}{2}(\text{bonding electrons} - \text{antibonding electrons})$
- Bond order of 1- single bond, 2-double bond, 3-triple bond; bond order of $\frac{1}{2}$, $\frac{3}{2}$ or $\frac{5}{2}$ are possible; bond order of 0 means that no bond exists.

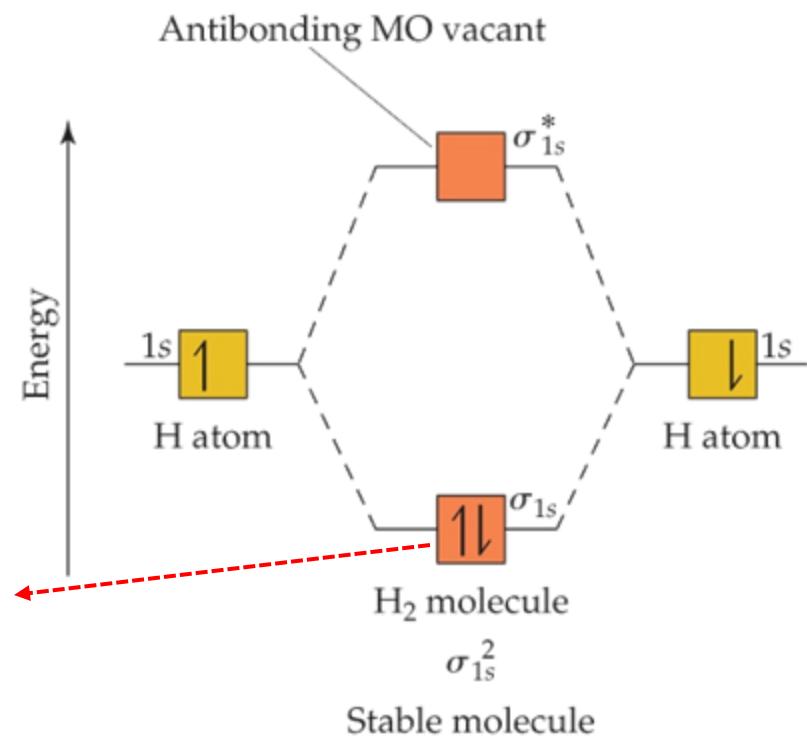


➤ MO Theory

- For hydrogen, with two electrons in the bonding MO and none in the antibonding MO,
the bond order is

$$\frac{1}{2} (2 - 0) = 1$$

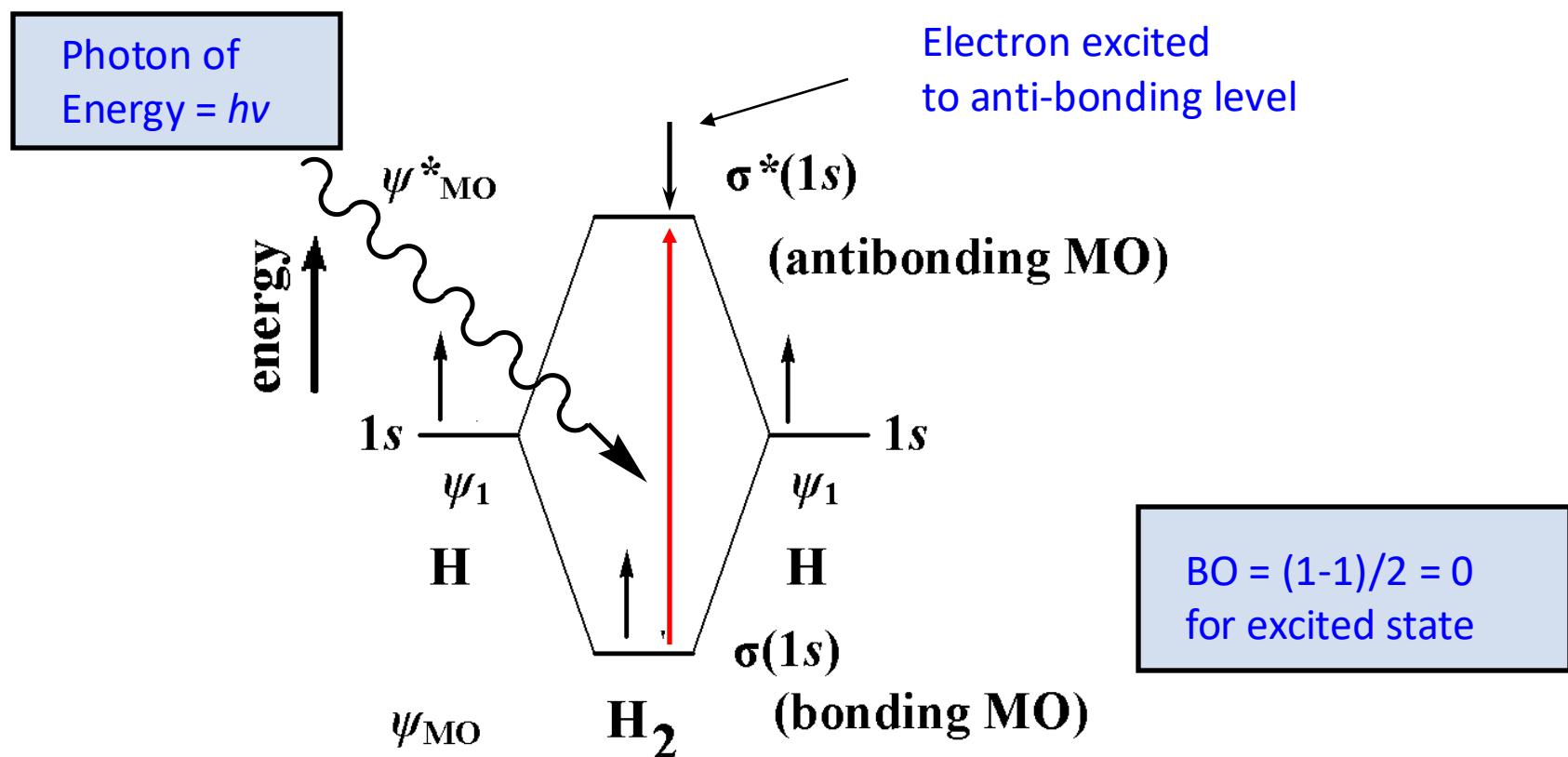
the two arrows are
opposite in direction
indicating a pair of spin-paired
electrons of opposite spin



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➤ Even More Observations on MO Diagrams

- MO diagrams show how a photon of energy = $h\nu$ = the difference in energy between two MO's, can cause an electron to be excited to the higher energy level MO. In this excited state the bond order = zero and so the H_2 molecule can **photo-dissociate**.



➤ MO Theory

- In the case of He_2 , the bond order would be

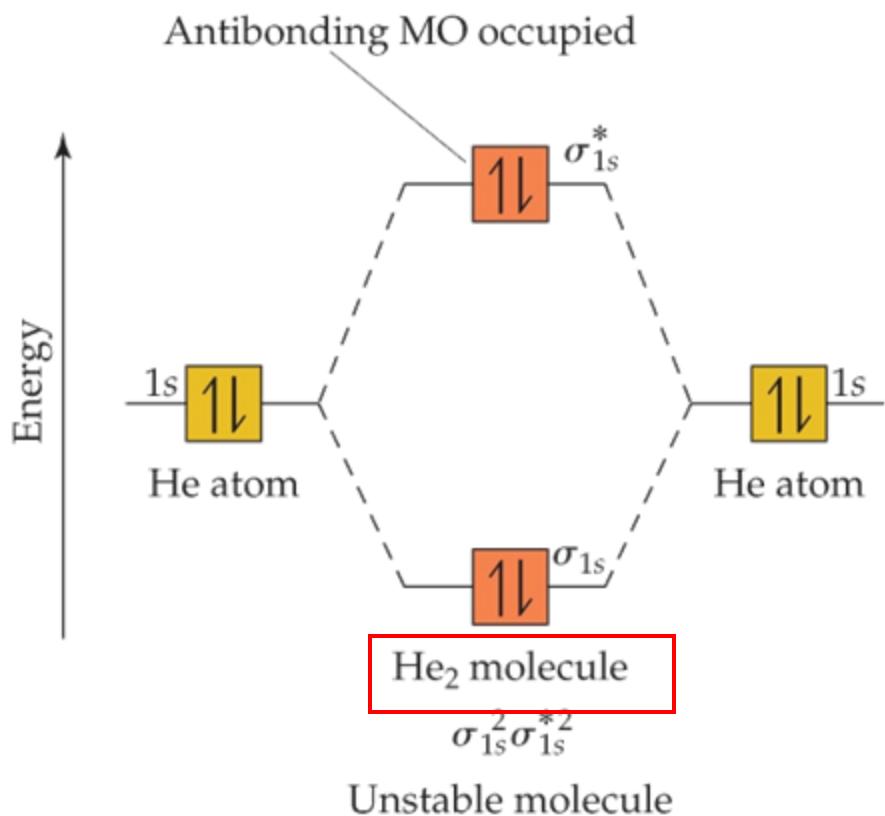
$$\frac{1}{2} (2 - 2) = 0$$

- Therefore, He_2 does not exist.

根据分子轨道 (MO) 理论，这是因为一个 He_2 (二氦) 分子总共有 4 个价电子需要填充。

具体步骤如下：

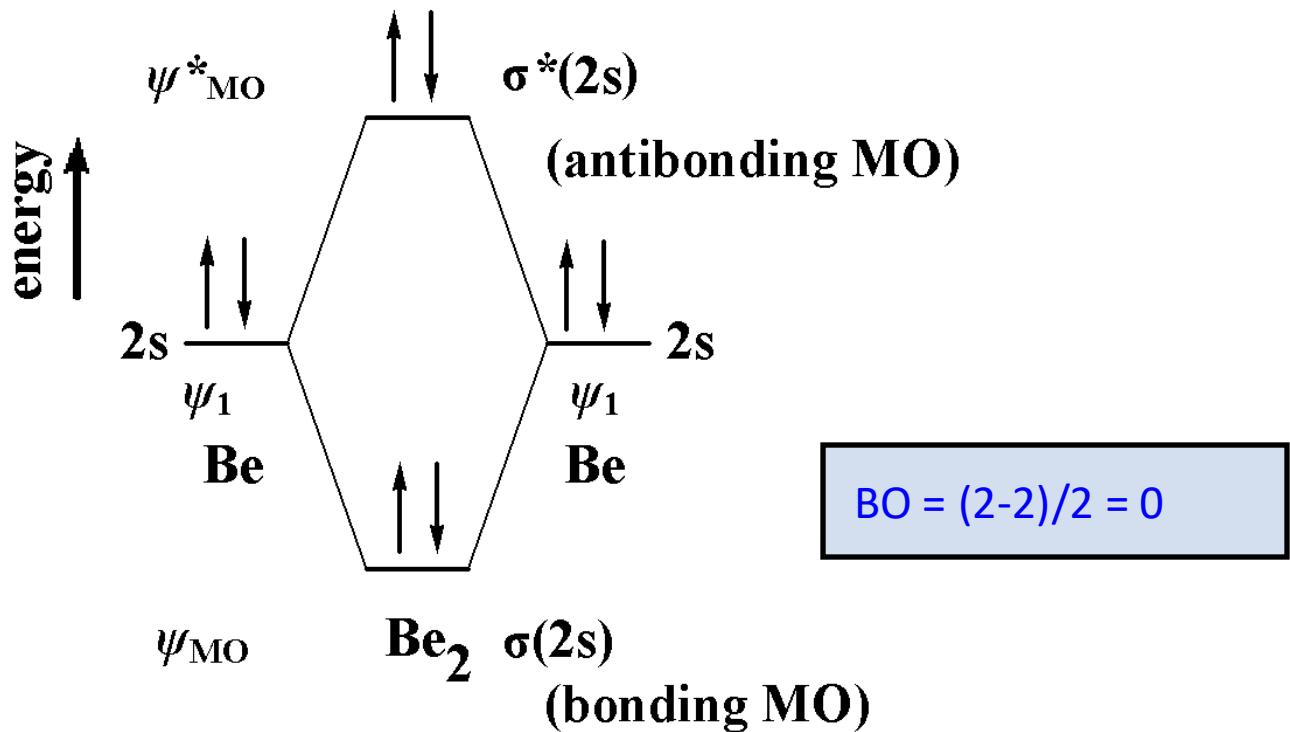
- 原子的电子：一个 He (氦) 原子有 2 个电子，其电子构型为 $1s^2$ 。
- 分子的总电子：当两个 He 原子尝试结合形成 He_2 分子时，总共就有 $2 + 2 = 4$ 个电子需要填入 He_2 的分子轨道中。
- 轨道的形成与填充：
 - 两个 He 原子的 $1s$ 原子轨道 (Atomic Orbitals) 会组合形成两个分子轨道 (Molecular Orbitals):
 - 一个能量较低的 σ_{1s} 成键轨道 (Bonding MO)
 - 一个能量较高的 σ_{1s}^* 反键轨道 (Antibonding MO)
 - 根据电子填充的构造原理 (Aufbau principle)，电子会从能量最低的轨道开始填充。
 - 总共有 4 个电子：
 - 前 2 个电子会填入能量较低的 σ_{1s} 成键轨道，使其填满。
 - 剩下的 2 个电子没有其他地方可去，只能被迫填入能量较高的 σ_{1s}^* 反键轨道。

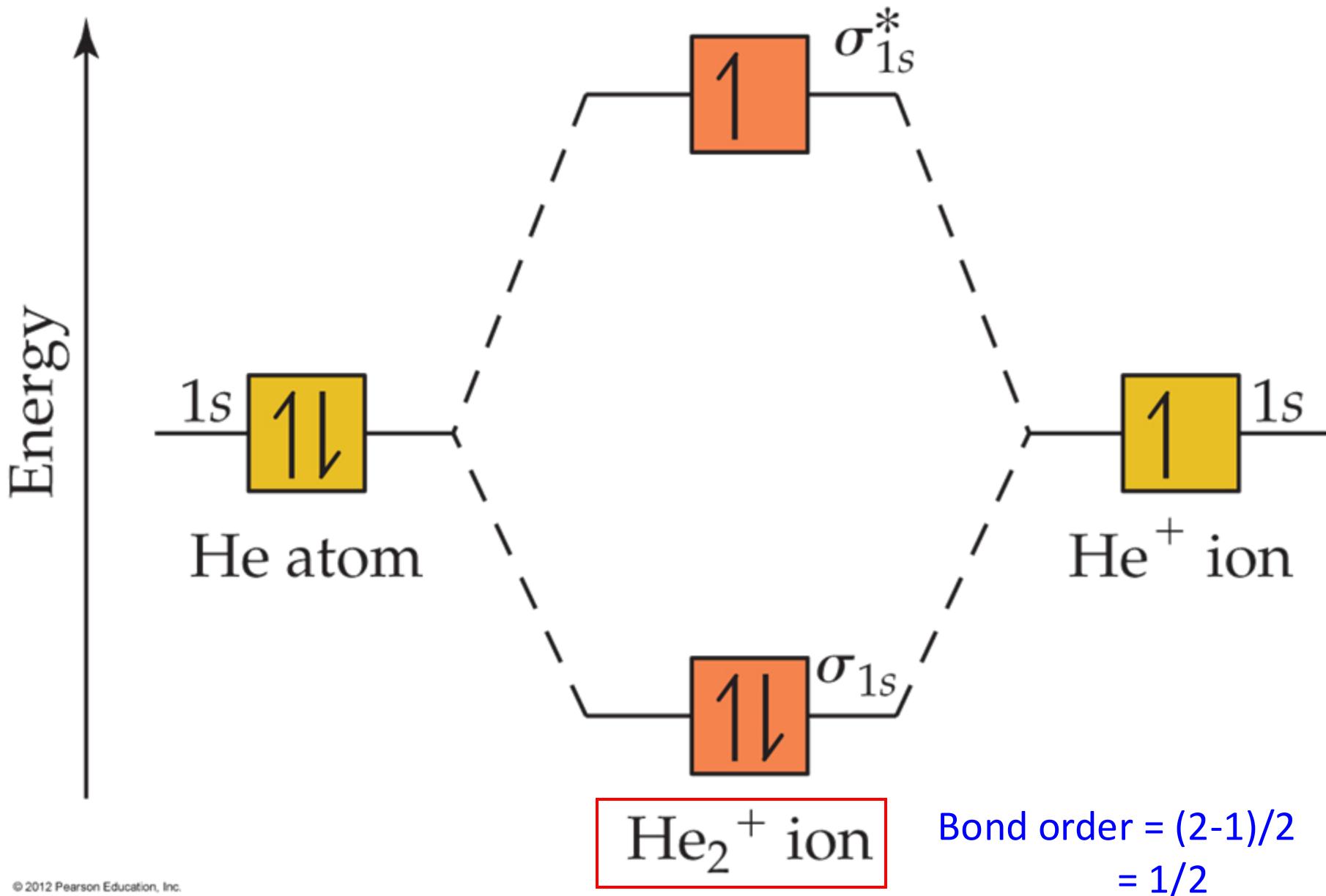


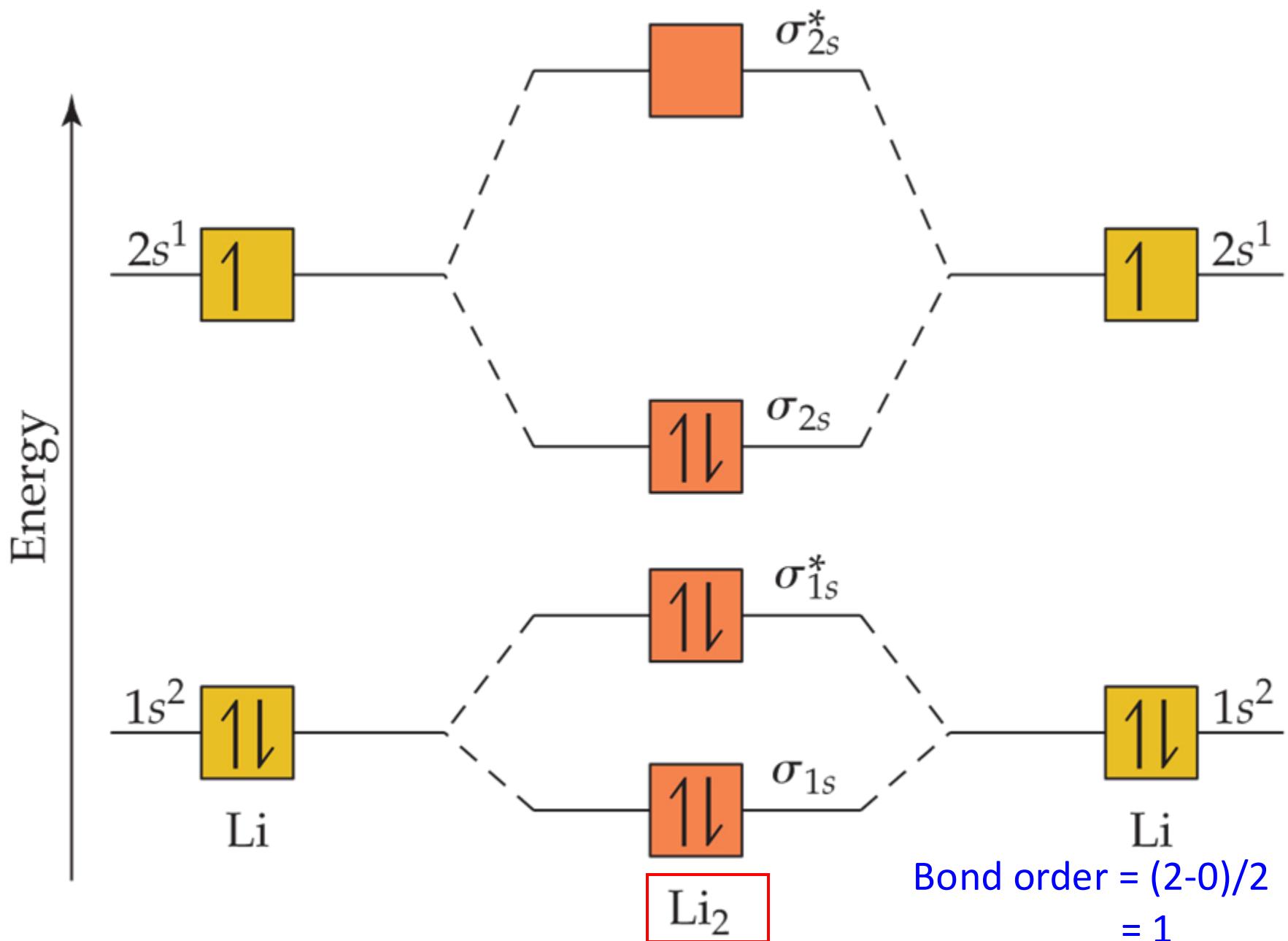
➤ The Non-Existent Be₂ Molecule

(Bond Order = 0)

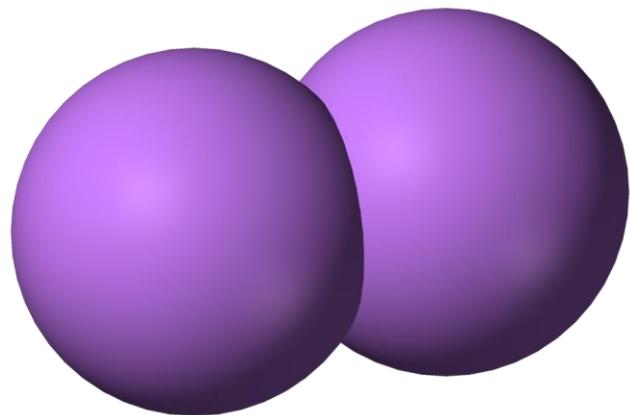
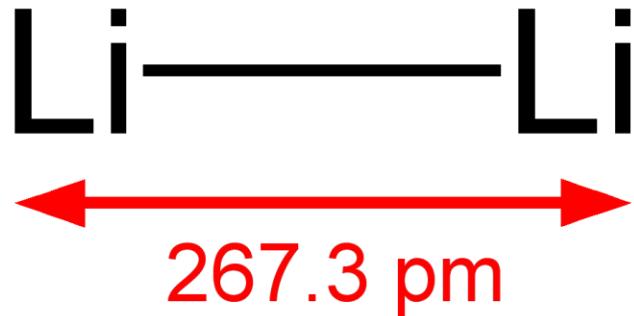
- Here again, MO theory predicts that Be₂ does not exist, which Lewis dot diagrams do not predict.



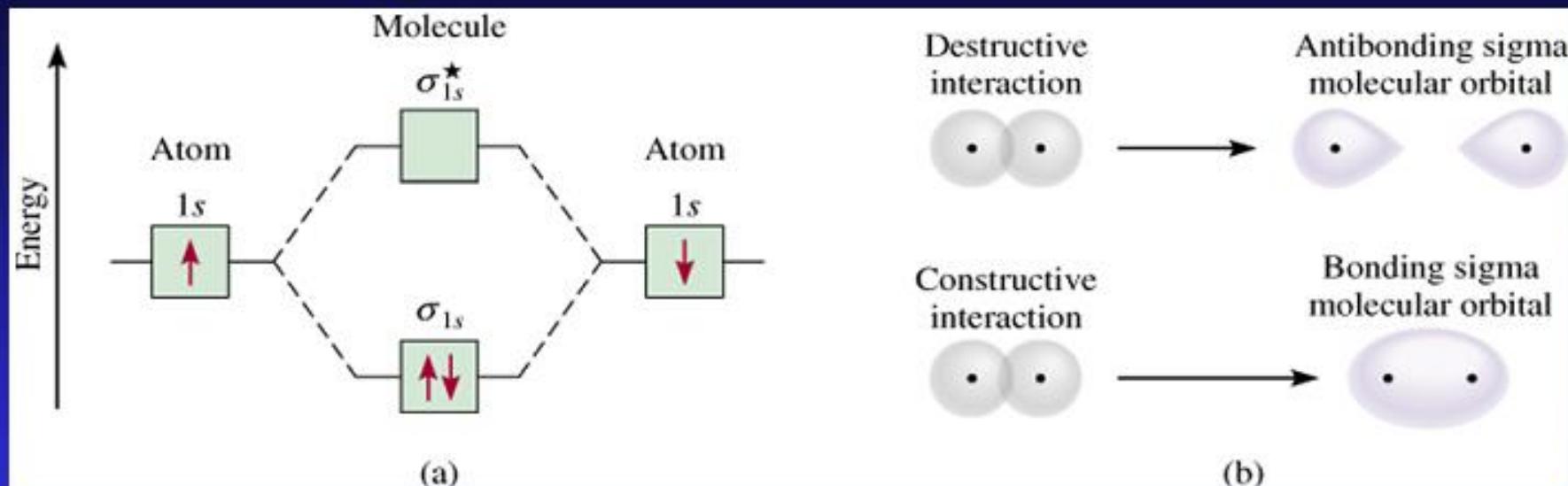




- **Dilithium, Li₂,**
- A strongly electrophilic(亲电子的), diatomic molecule comprising two lithium atoms covalently bonded together. Li₂ is known in the gas phase. It has a bond order of 1, an internuclear separation of 267.3 pm and a bond energy of 101 kJ mol⁻¹. It has been observed that 1% (by mass) of lithium in the vapor phase is in the form of dilithium.



H₂分子的成键和反键分子轨道



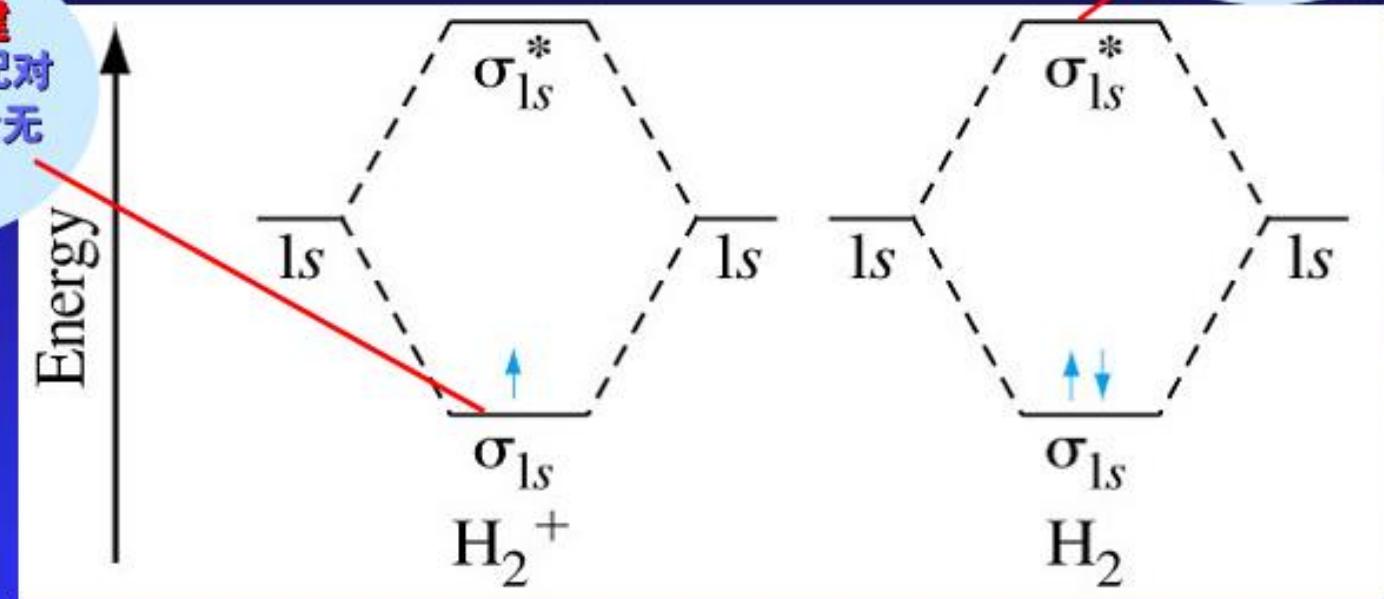
σ_{1s} : 成键分子轨道，电子在两核间出现的几率较大，电子同时受两核吸引，故其能量低于原子轨道能量。

σ_{1s}^* : 反键分子轨道，电子在两核的左右两侧出现几率较大，核间节面处电子云密度等于零，因此两核共同吸引电子的能力减弱，故其能量总是比相应原子轨道能量高。

H₂ 分子与H₂⁺离子

激发态
即是二个自旋平行的电子分占成键和反键轨道。

单电子键
Lewis电子配对
和价键理论无法解释



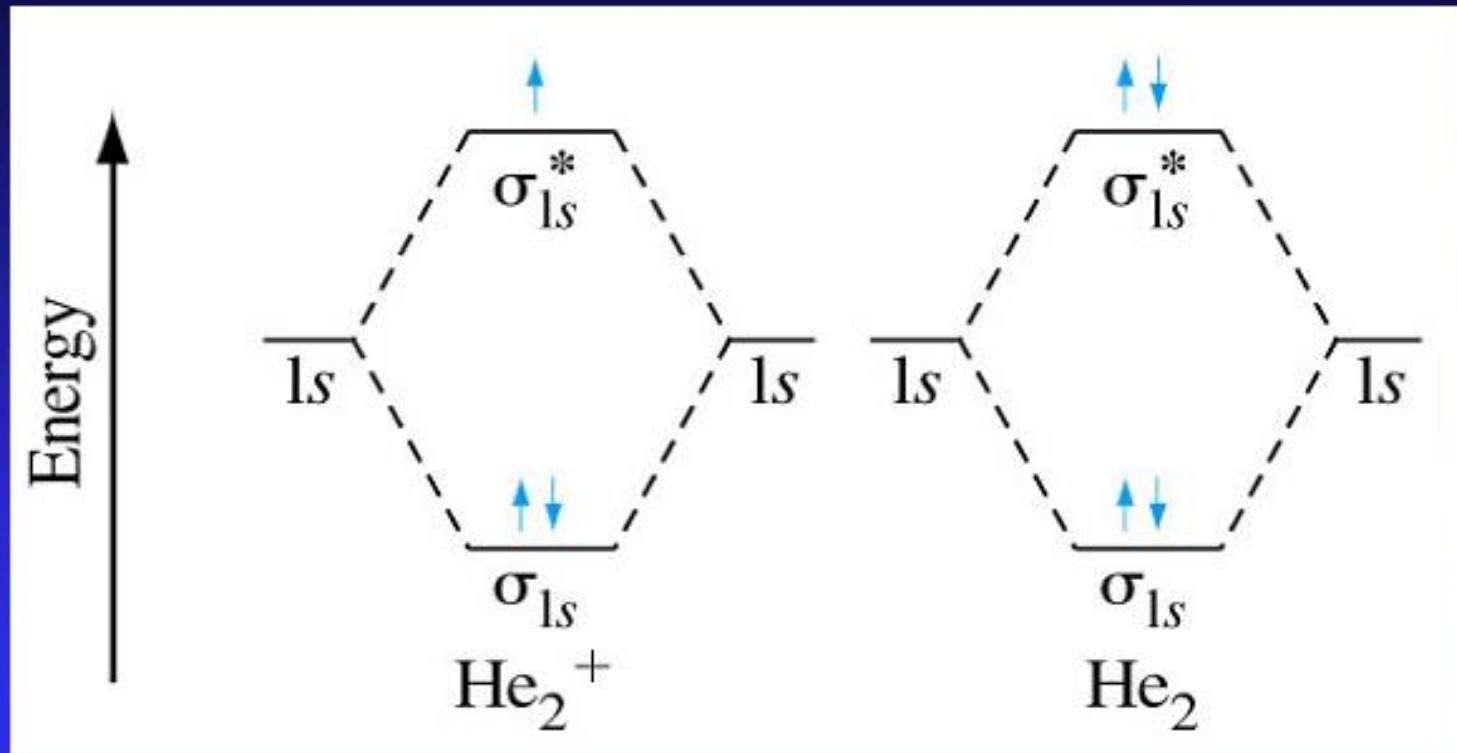
$$BO = (e_{bond} - e_{antibond})/2$$

键级 (Bond Order)

$$BO_{H_2^+} = (1 - 0)/2 = \frac{1}{2}$$

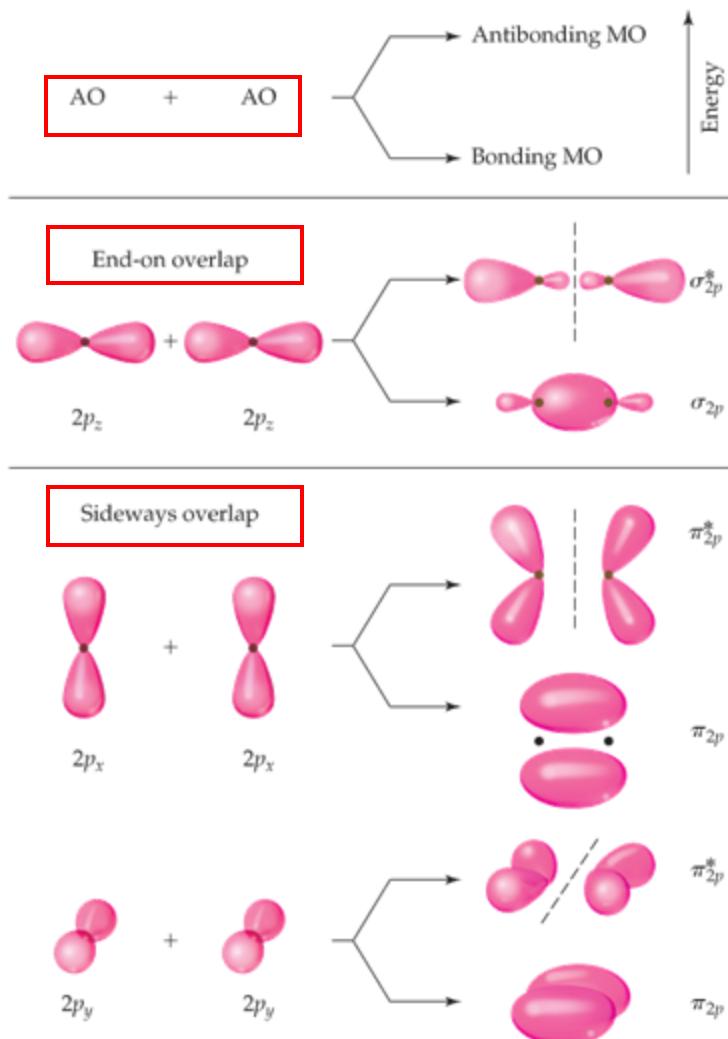
$$BO_{H_2} = (2 - 0)/2 = 1$$

He₂分子与He₂⁺离子



成键和反键能量相互抵消，不能成键。因此He₂分子实际上不存在。

➤ MO Orbital from 2p Atomic Orbital



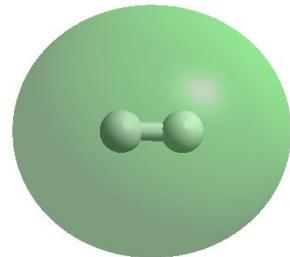
□ For atoms with both *s* and *p* orbitals, there are two types of interactions between *p* orbitals:

- The *p* and the *p* orbitals that face each other overlap in σ fashion.
- The other two sets of *p* orbitals overlap in π fashion (sideway).

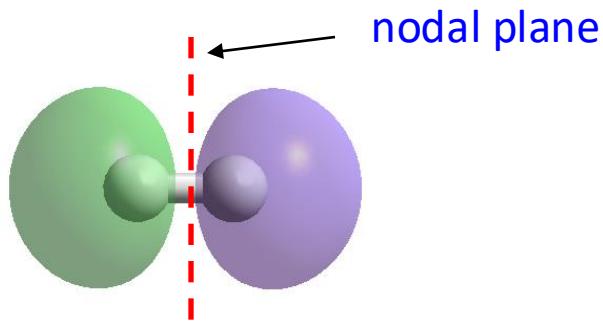
Two degenerate orbital

➤ Bonding and Anti-Bonding Molecular Orbitals

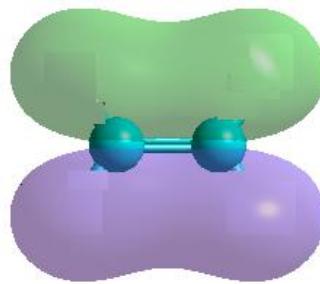
- A bonding MO has no nodal plane between the two atoms forming the bond, i.e. the electron density does not go to zero at a node. An anti-bonding MO has a nodal plane where electron-density = zero:



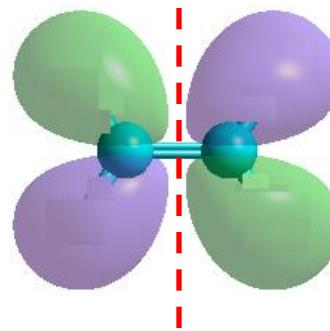
$\sigma(1s)$ bonding orbital



$\sigma^*(1s)$ anti-bonding orbital



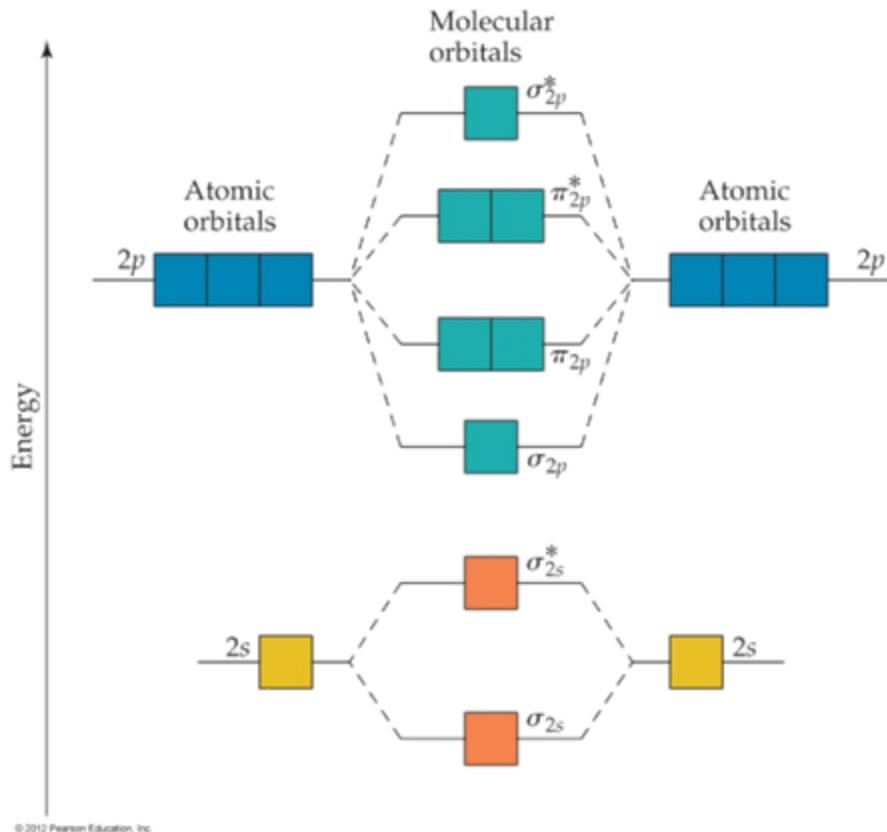
$\pi(2p)$ bonding orbital



$\pi^*(2p)$ anti-bonding orbital

➤ MO Theory

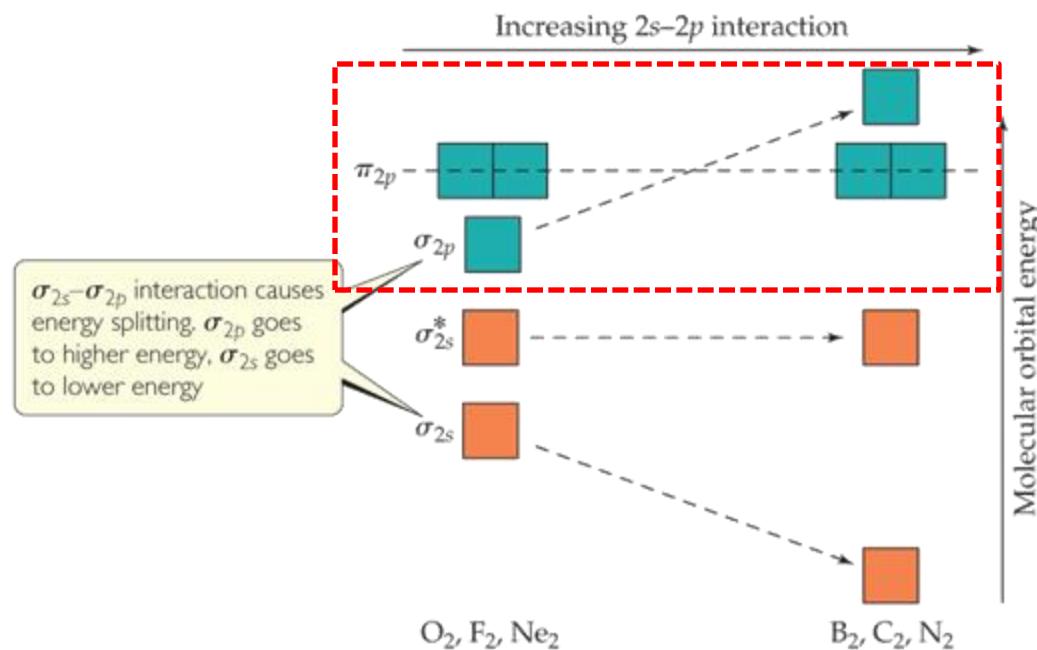
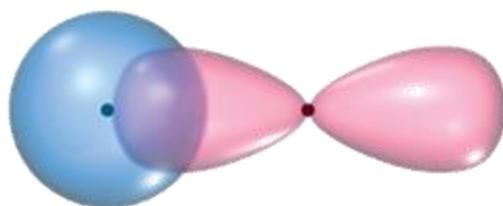
- The resulting MO diagram looks like this.
- There are both σ and π bonding molecular orbitals and σ^* and π^* antibonding molecular orbitals.



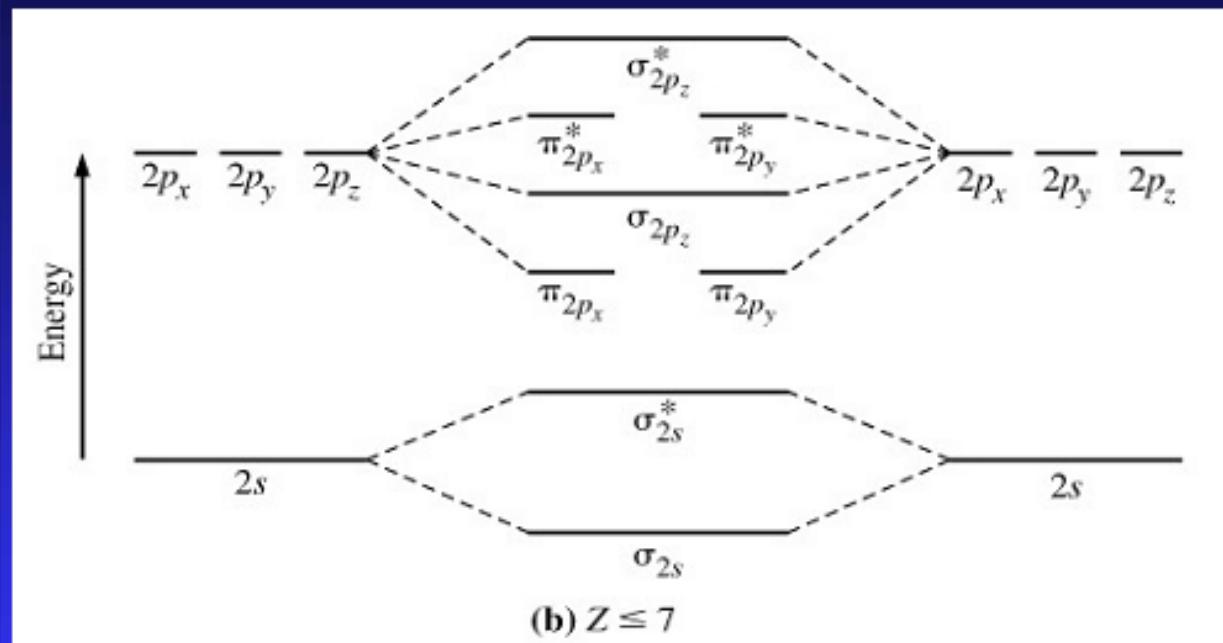
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➤ MO Theory

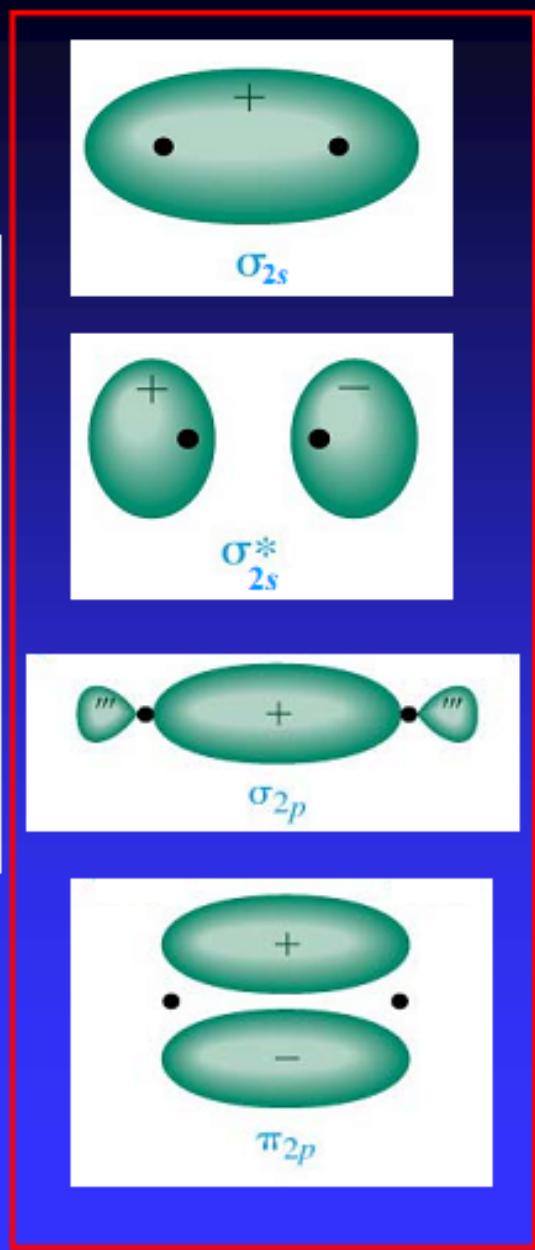
- The smaller *p*-block elements in the second period have a sizable interaction between the *s* and *p* orbitals.
- This flips(倒裝) the order of the σ and π molecular orbitals in these elements.



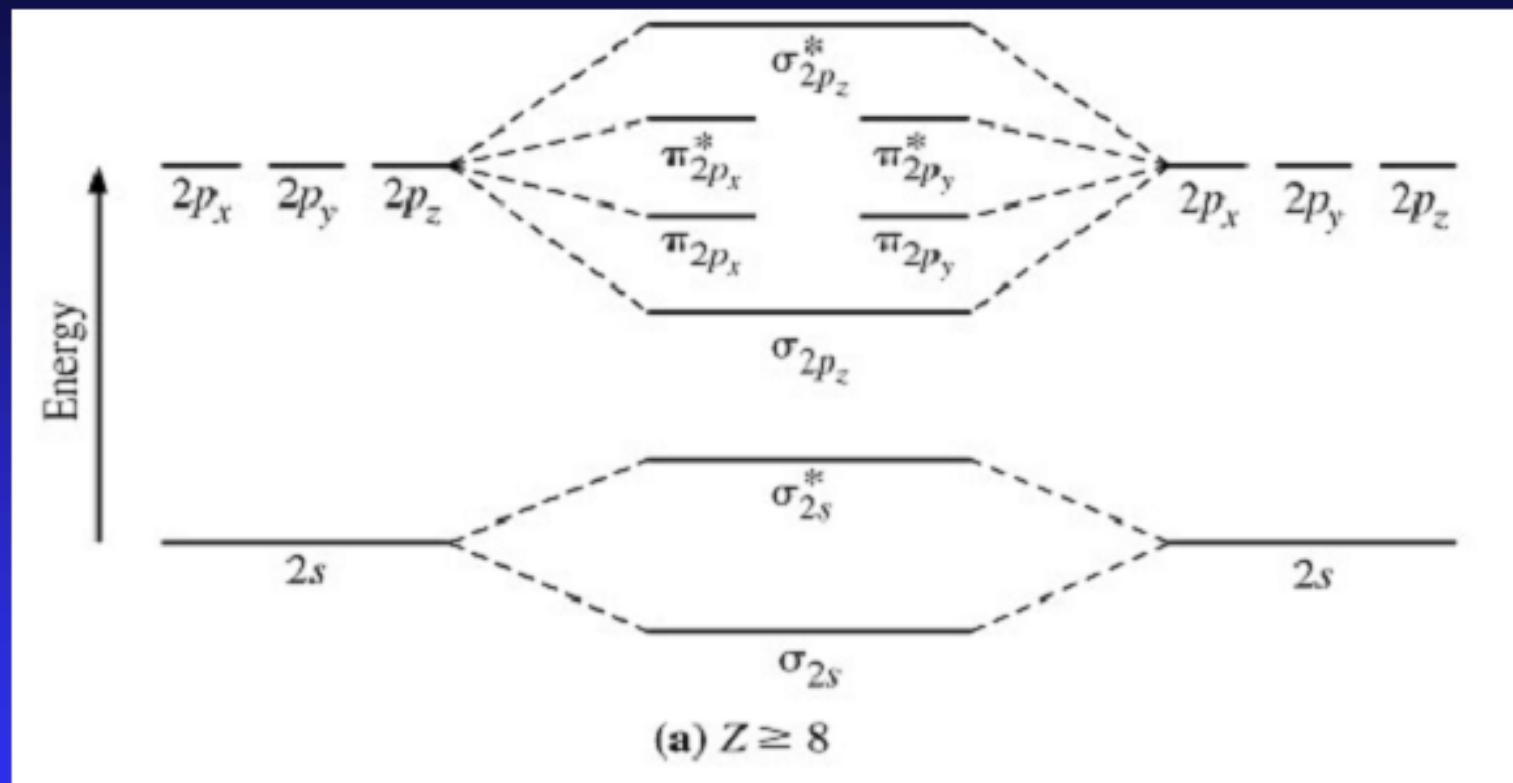
同核双原子分子Li₂/Be₂/B₂/C₂/N₂的分子轨道能级排列顺序



第二周期从左至右随着各元素原子核电荷递增，内层原子轨道离核越近，2s-2p能级差也越大。对于Li, B, C, N等原子，2s-2p能量相差较小。当形成分子时，2s₁-2p_{z1}和2s₂-2p_{z1}相互作用使 σ_{2s}^* 和 σ_{2p_z} 兼有s和p_z的性质，所以 σ_{2p_z} 能量升高位于 π_{2p_x} 和 π_{2p_y} 之上。

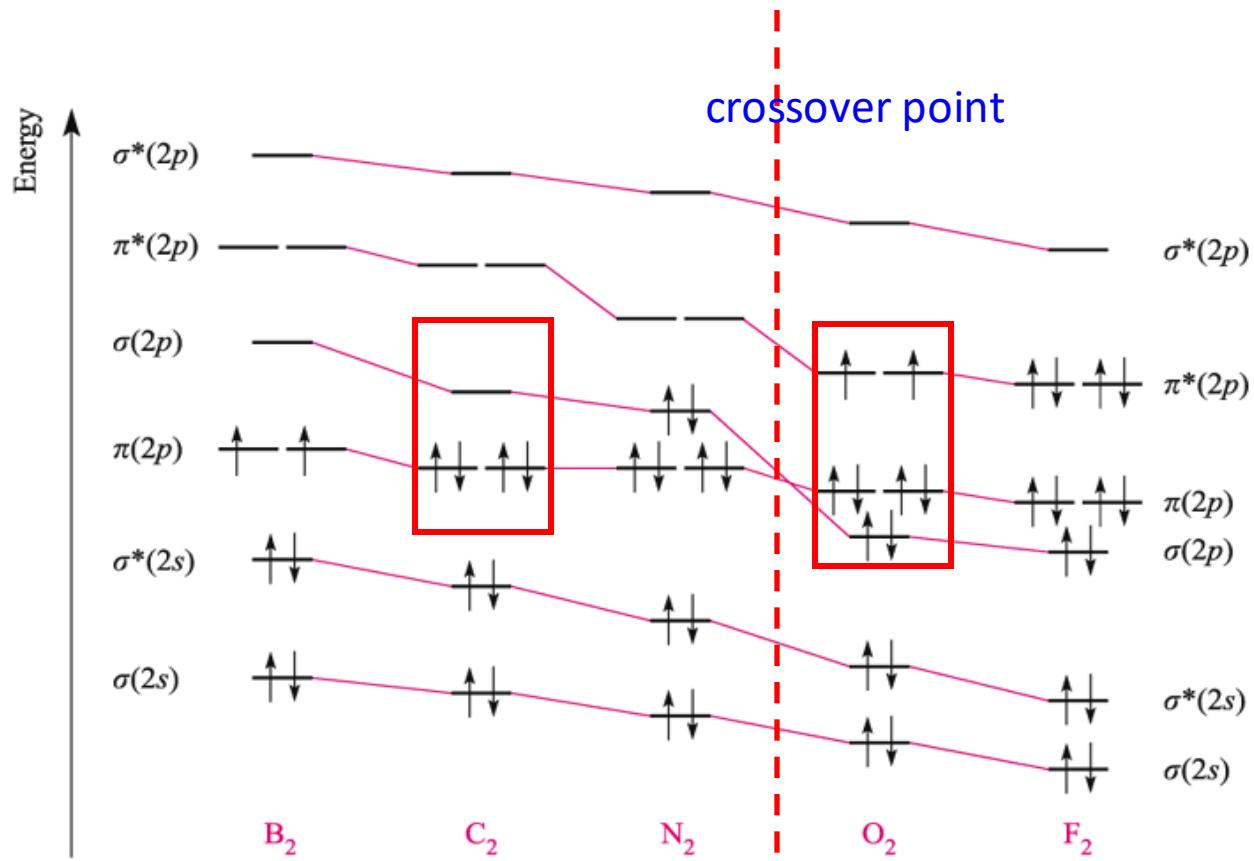


原子序数Z≥8的同核双原子分子的分子轨道能级排列顺序



对于O₂(F₂)双原子分子来说，由于2s-2p能级差越来越大，一个原子的2s电子和另一个原子的2p电子相互作用的可能性完全可以不考虑。

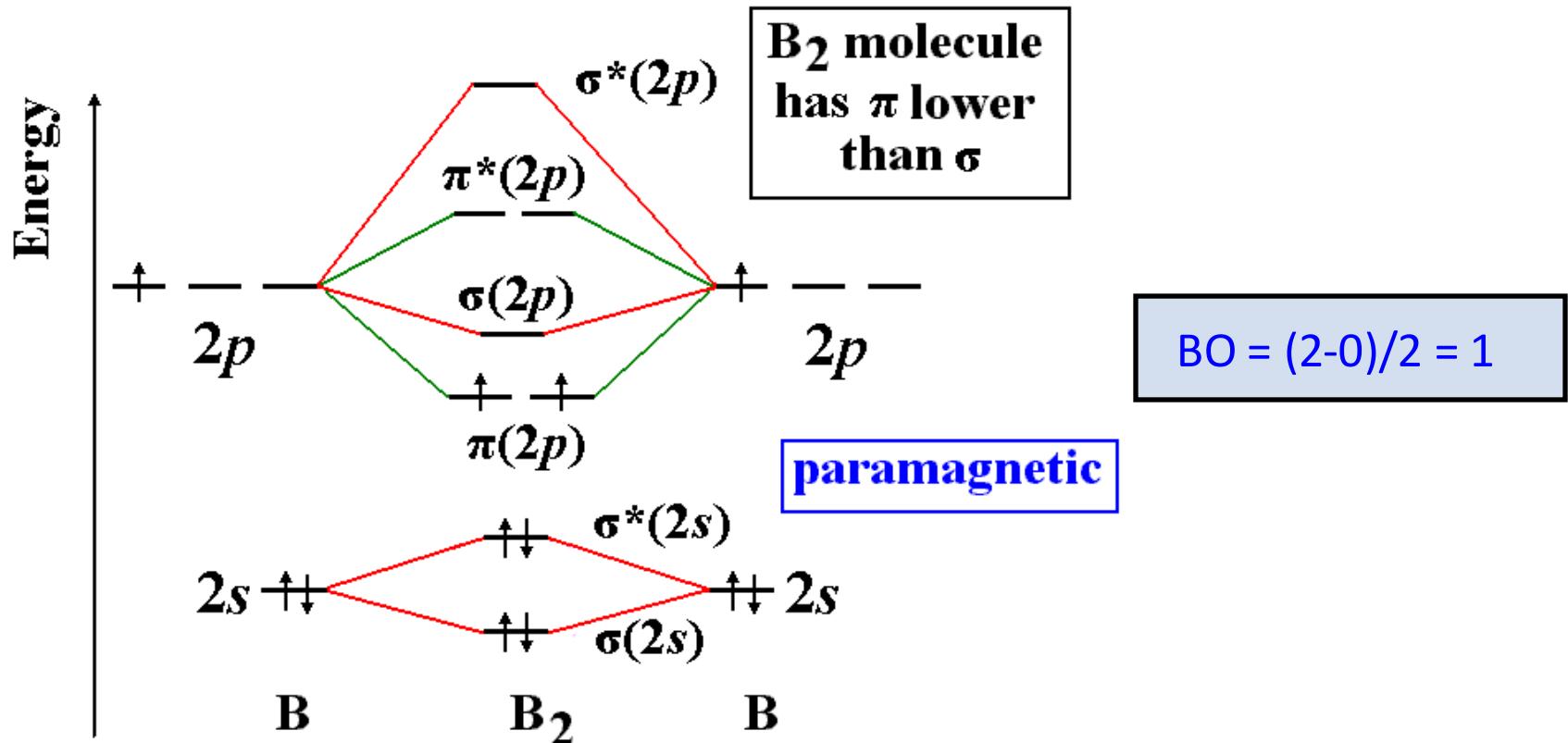
➤ Energy Levels of First-Row Homonuclear Diatomic Molecules



Molecules Li_2 , Be_2 , B_2 , C_2 and N_2 have $\pi(2p)$ lower in energy than $\sigma(2p)$

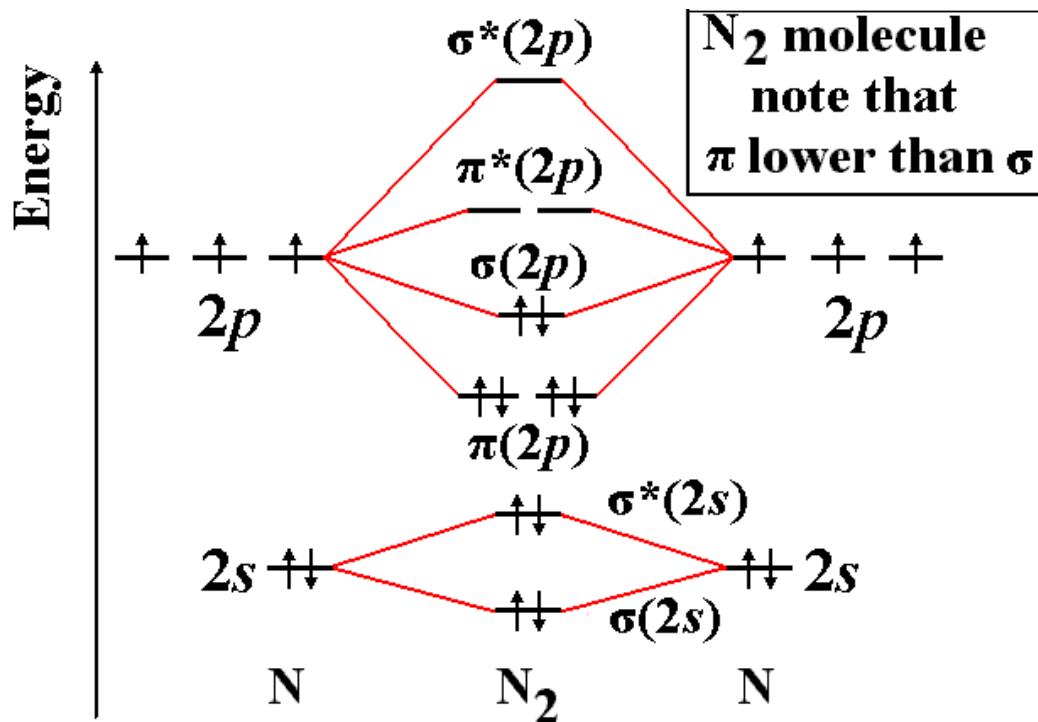
Molecules O_2 , and F_2 have $\pi(2p)$ higher in energy than $\sigma(2p)$

➤ The B_2 Molecule (Bond Order = 1)



MO diagram for B_2 molecule, bond order = 1.

➤ The N₂ Molecule (Bond Order = 3)



MO diagram for dinitrogen (N₂) molecule

N≡N 941 kJ/mol

N–N 193

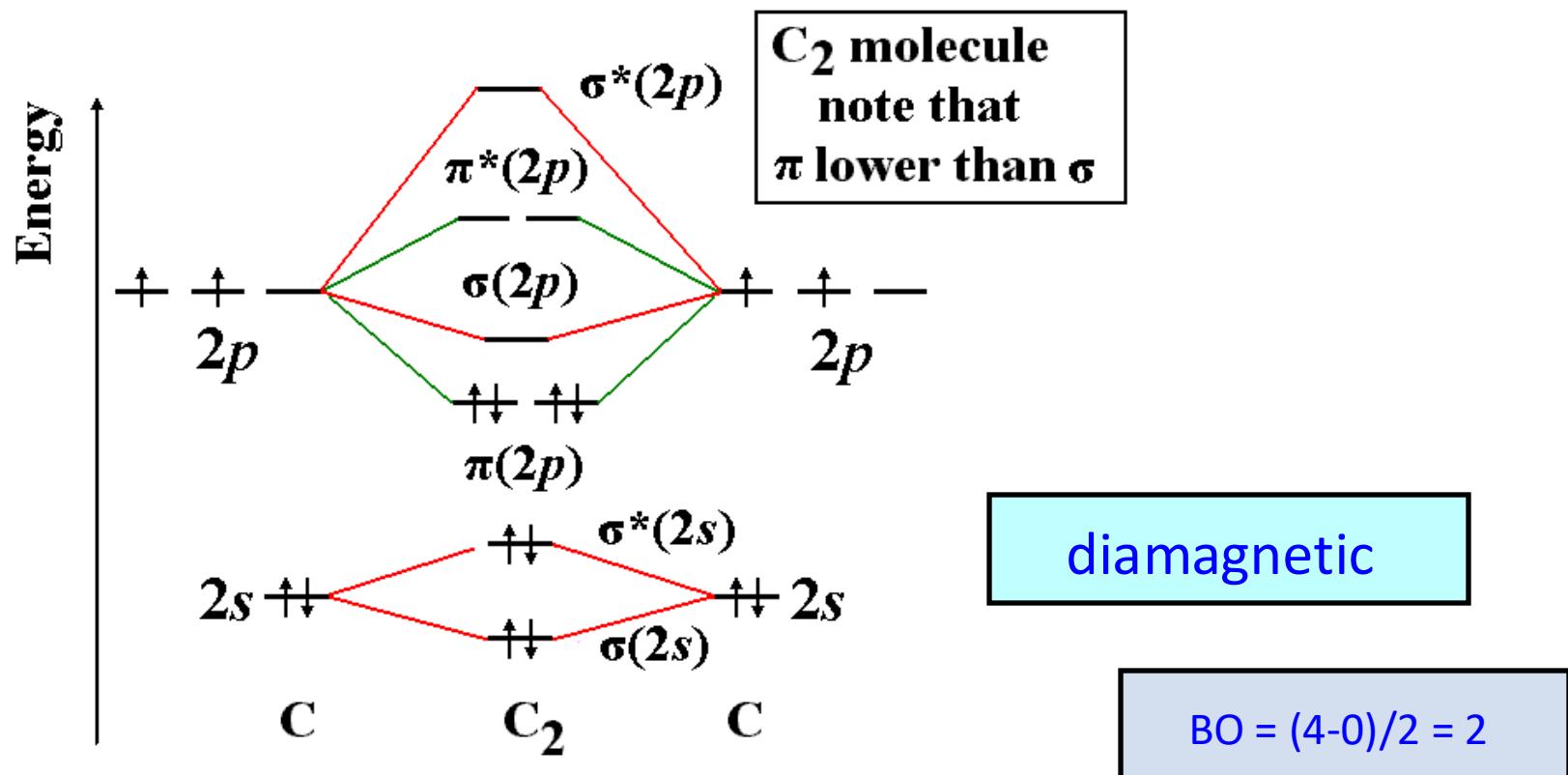
N=N 418



diamagnetic

$$BO = (6-0)/2 = 3$$

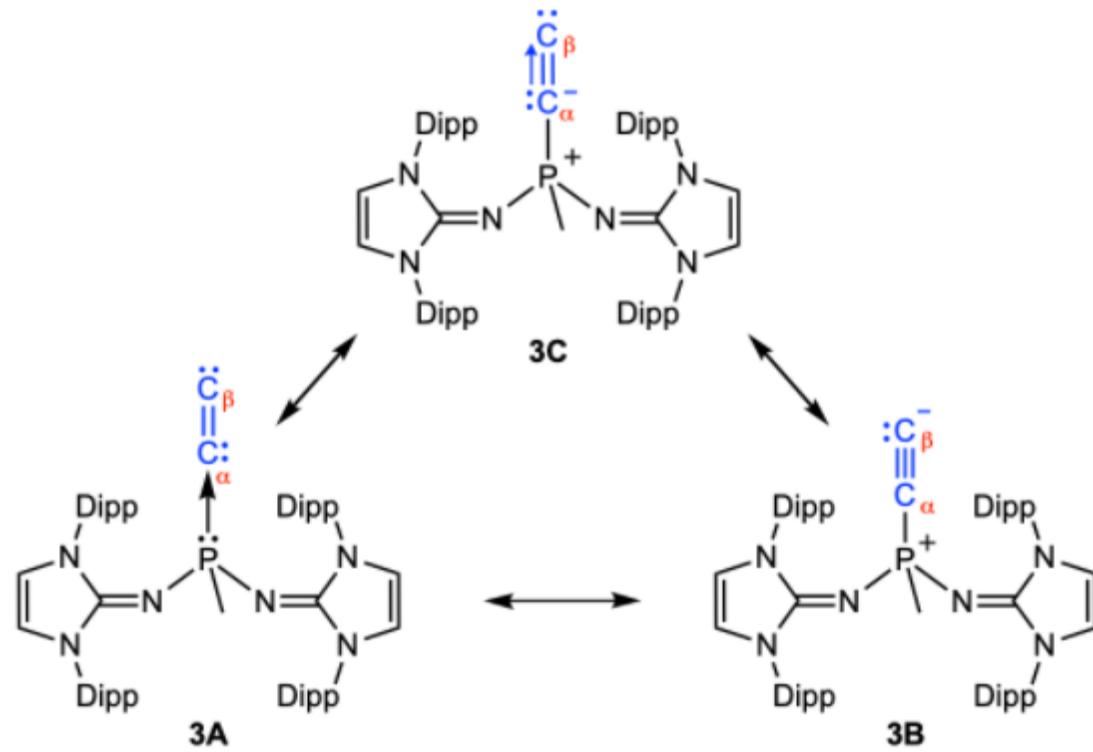
➤ The C₂ Molecule (Bond Order = 2)



MO diagram for C₂ molecule, bond order = 2.

➤ Diatomic carbon – C₂

- Diatomic carbon (systematically named **ethynylidene** and **dicarbon(C—C)**), is an inorganic chemical with the chemical formula C≡C (also written [C2] or C2). It is a gas that only exists above 3,642 °C), below which it aggregates into graphit or other fullerenes. It occurs in carbon vapor, for example in electric arcs; in comets, stellar atmosphere and the interstellar medium; and in blue hydrocarbon flames. Valence bond theory predicts a quadruple(四重) bond as the only way to satisfy the octet rule for carbon. However, molecular orbital theory shows that there are two sets of paired electrons in a degenerate pi bonding set of orbitals. This gives a bond order of 2, meaning that there should exist a double bond between the two carbons in a C₂ molecule.



Nat. Chem. **2021**, *13*, 89

➤ Second-Row MO Diagrams

	Large 2s-2p interaction			Small 2s-2p interaction		
	B ₂	C ₂	N ₂	O ₂	F ₂	Ne ₂
σ_{2p}^*	□	□	□	□	□	1↓
π_{2p}^*	1↑ 1↓	1↑ 1↓	1↑ 1↓	1↑ 1↓	1↓ 1↑	1↓ 1↑
σ_{2p}	□	□	1↓	1↓ 1↑	1↓ 1↑	1↓ 1↑
π_{2p}	1↑ 1↓	1↓ 1↑	1↓ 1↑	1↓ 1↑	1↓ 1↑	1↓ 1↑
σ_{2s}^*	1↓	1↓	1↓	1↓	1↓	1↓
σ_{2s}	1↓	1↓	1↓	1↓	1↓	1↓
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	—

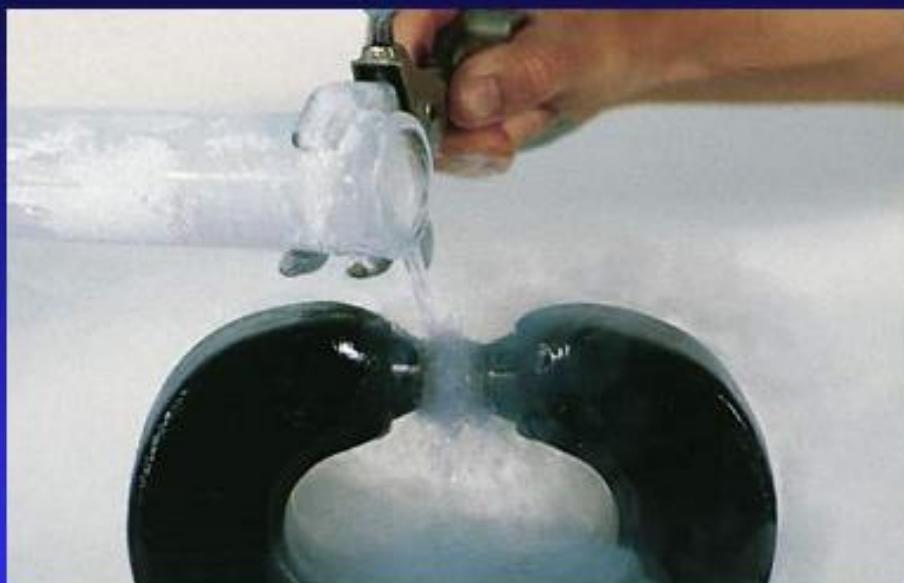
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O_2 分子的Lewis结构式为：



按价键理论，所有电子都已配对，不存在自旋平行的电子，因此应该表现为抗磁性。但事实上 O_2 分子表现为顺磁性。分子轨道理论可以很好的解释这一点，对键长和键能的解释也是成功的。

O_2 分子的顺磁性实

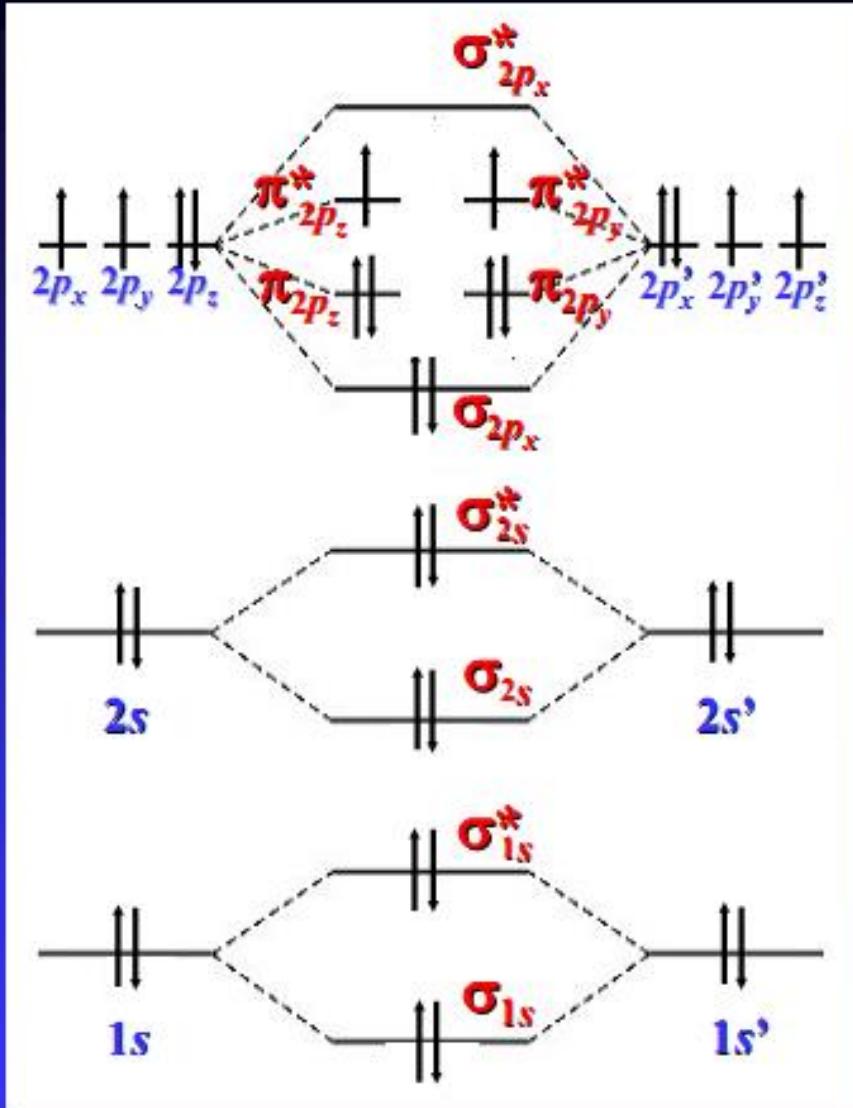


The paramagnetic properties of oxygen are evident when liquid oxygen is poured between the poles of a magnet. The liquid sticks to the magnet instead of flowing past it.

1. **组合轨道**: 两个氧原子(O)靠近形成 O_2 分子时, 它们的原子轨道(AO)会组合成分子轨道(MO)。我们主要关心 $2p$ 轨道的组合。
2. **电子填充**: 一个O原子有4个 $2p$ 电子, 所以 O_2 分子总共有8个 $2p$ 电子需要填充到 p 轨道形成的分子轨道中。
3. **能级顺序**: O_2 分子的 p 轨道能级顺序为:
 - σ_{2p} (成键)
 - π_{2p} (成键, 有两个等能量的轨道)
 - π_{2p}^* (反键, 有两个等能量的轨道) ← **关键所在**
 - σ_{2p}^* (反键)
4. **填充电子(共8个)**:
 - 2个电子填入 σ_{2p}
 - 4个电子填入 π_{2p} (两个轨道各2个)
 - 还剩2个电子
5. **洪德规则(Hund's Rule)**: 当这最后2个电子要填入 π_{2p}^* 这两个能量相等的反键轨道时, 根据洪德规则, 它们会优先分占两个不同的轨道, 且自旋方向相同。

最终结果: O_2 分子在能量最高的 π_{2p}^* 反键轨道上, 存在两个未成对的电子 (一个在 $\pi_{2p_x}^*$, 一个在 $\pi_{2p_y}^*$)。

正是这两个未成对的电子, 使得 O_2 分子整体表现出强烈的顺磁性, 完美地解释了实验中液氧被磁铁吸引的现象。

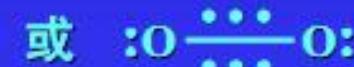


$$(\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_x})^2 \\ (\pi_{2p_z})^2 (\pi_{2p_y})^2 (\pi_{2p_z}^*)^1 (\pi_{2p_y}^*)^1$$

或

$$KK (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_x})^2 (\pi_{2p_z})^2 \\ (\pi_{2p_y})^2 (\pi_{2p_z}^*)^1 (\pi_{2p_y}^*)^1$$

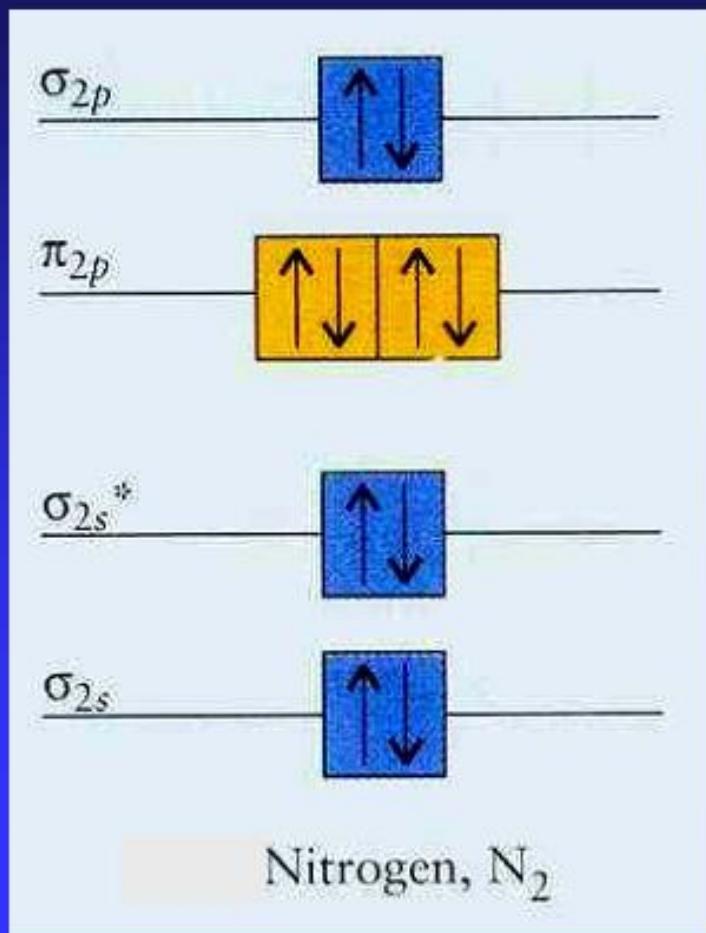
由于 $(\pi_{2p_z})^2 (\pi_{2p_z}^*)^1$ 和 $(\pi_{2p_y})^2 (\pi_{2p_y}^*)^1$ 各有 3 个电子，通常称为 2 个三电子 π 键，可写成：



$$BO_{O_2} = (6 - 2)/2 = 2$$

O₂分子轨道和原子轨道能量关

$$KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_z})^2(\pi_{2p_y})^2(\sigma_{2p_x})^2$$



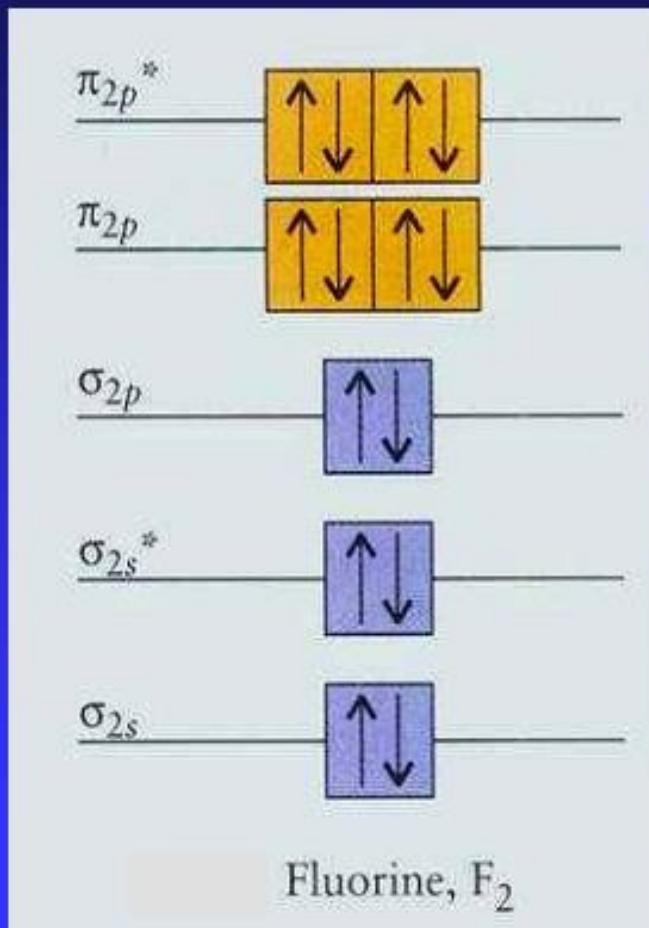
$$N: \quad 1s^2 2s^2 2p^3$$

$$BO_{N_2} = (6 - 0)/2 = 3$$

其中对成键有贡献的是一个 σ 键、2个 π 键。与价键结构式完全一致。



$$KK(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_z})^2(\pi_{2p_y}^*)^2(\pi_{2p_z}^*)^2$$



$$F: \quad 1s^2 2s^2 2p^5$$

$$BO_{F_2} = (6 - 4)/2 = 1$$

其中对成键有贡献的是一个 σ 与价键结构式完全一致。



➤ VB vs. MO

- Valence bond (VB) theory focuses on how the atomic orbitals of the atoms combine to give individual chemical bonds when a molecule is formed.
- In contrast, molecular orbital (MO) theory has orbitals that cover the whole molecule.
- Molecular orbital theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule.
- Molecular orbital theory was seen as a competitor to valence bond theory in the 1930s, before it was realized that the two methods are closely related and that when extended they become equivalent.

2、分子轨道理论的基本要点

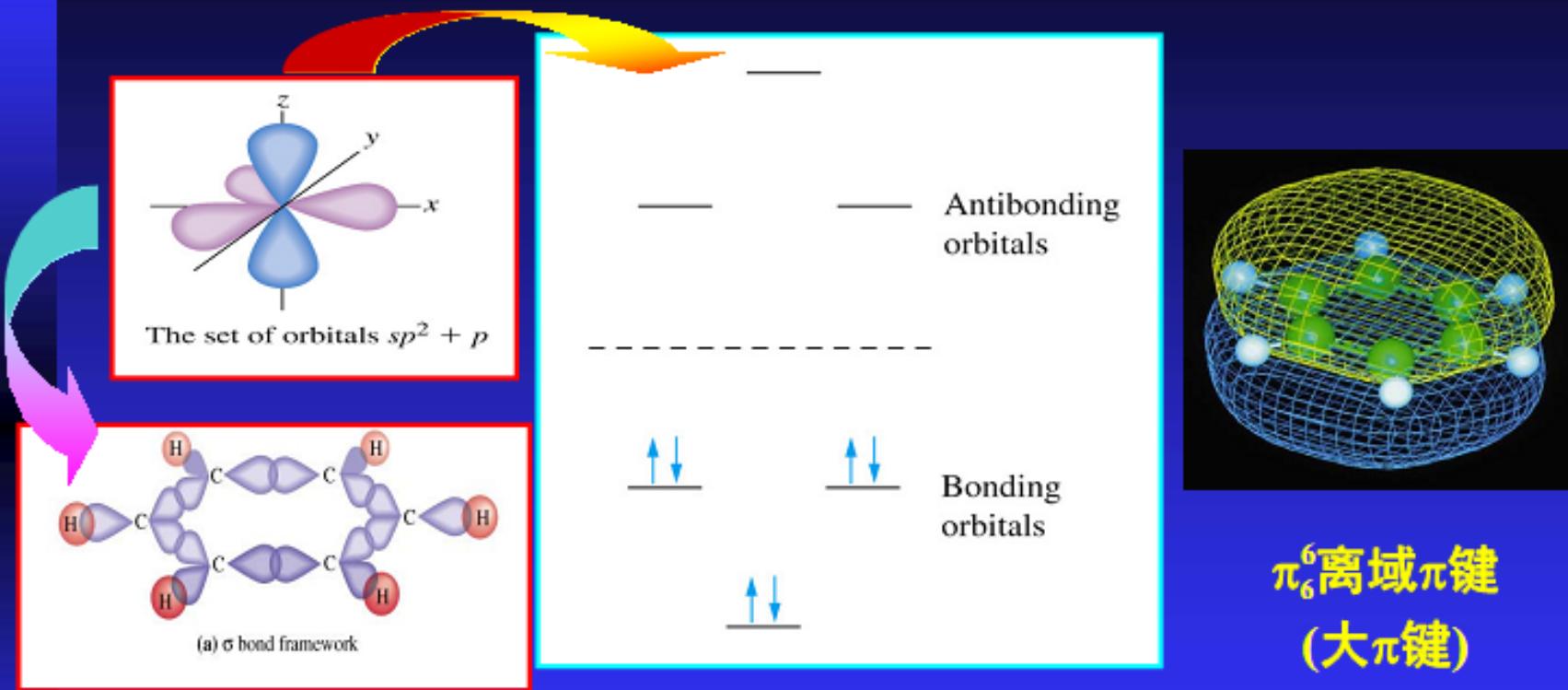
1) 把分子看作一个整体，其中电子不再从属于某一个原子而是整个分子势场范围内运动。因此，分子中的电子运动状态用分子轨道波函数(简称分子轨道)来描述。

各个分子轨道可近似地用组成它的电子的原子轨道波函数 ψ_1, \dots, ψ_n 线性组合得到。如双原子分子的分子轨道波函数 ψ 可表达为原子轨道波函数 ψ_1 和 ψ_2 的线性组合，即

$$\psi = \psi_1 \pm \psi_2$$

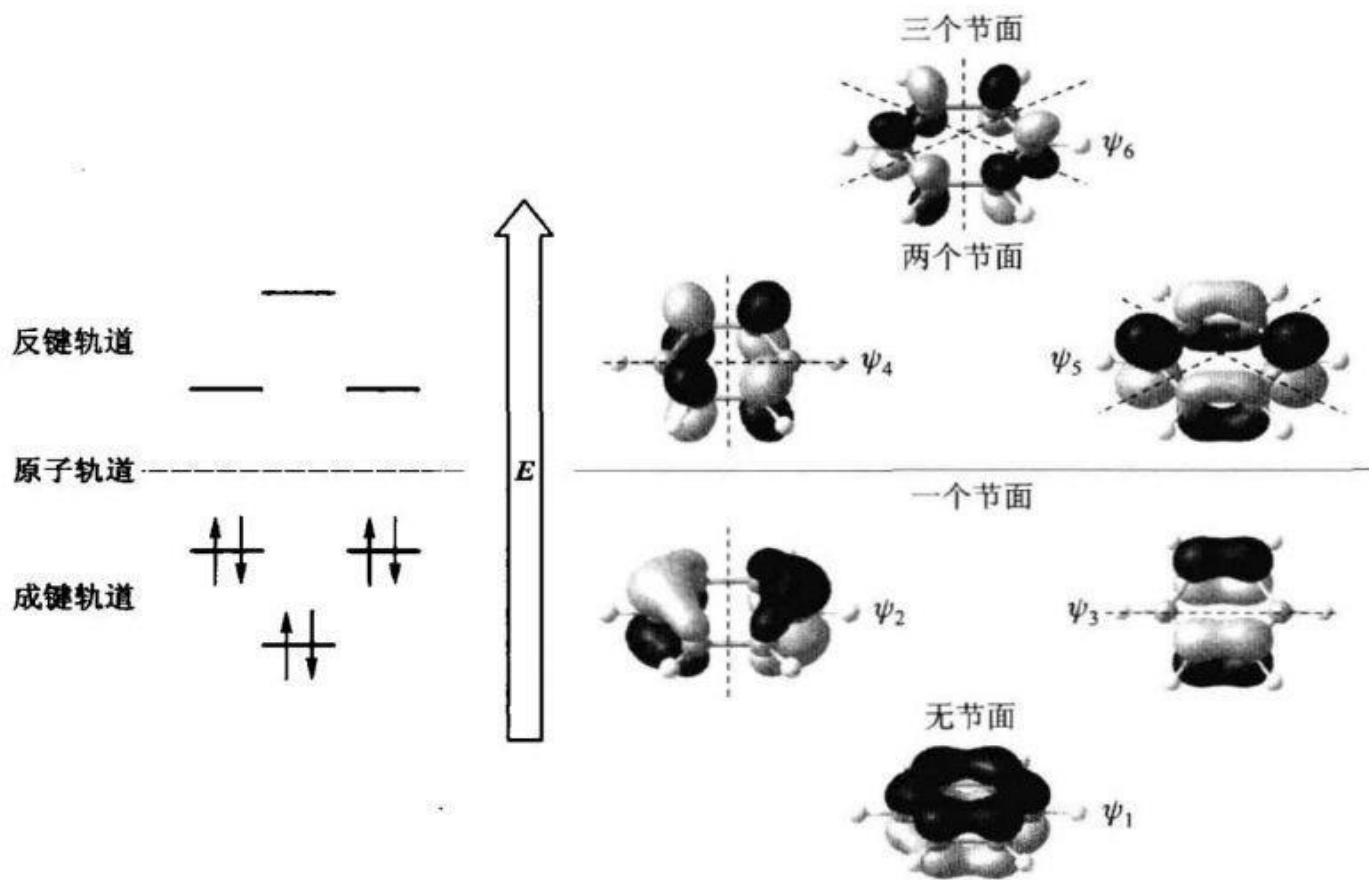
在一个分子中，分子轨道的数目等于组分分子的各原子轨道数目之和。

分子轨道理论对苯分子结构的解释



π_6^6 离域 π 键
(大 π 键)

按分子轨道理论，C原子仍采用 sp^2 杂化轨道，但6个C原子剩余的6个p轨道形成6条分子轨道，其中3条是成键轨道，3条是反键轨道。剩余的6个p电子放在3条成键轨道上，由此形成苯分子的 π_6^6 离域大 π 键。其中6个电子由6个C原子共有，所以每个C-C间的键长都相等，并介于单键和双键之间。



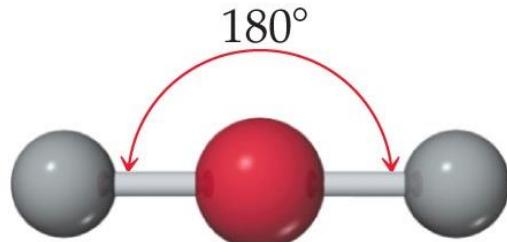
➤ 价键理论和分子轨道理论的比较：

- (1) 价键理论将共价键看作两个原子之间的定域键，反映了原间直接的相互作用，形象直观而易于与分子的几何构型相联系。
- (2) 分子轨道理论着眼于分子的整体性，可对那些价键理论不说明的问题给以比较合理的解释。虽然这种理论不如价键模型直观，但在量子力学的数学处理方面远比价键理论方便，因此分子轨道路理论目前发展较快，应用较广。

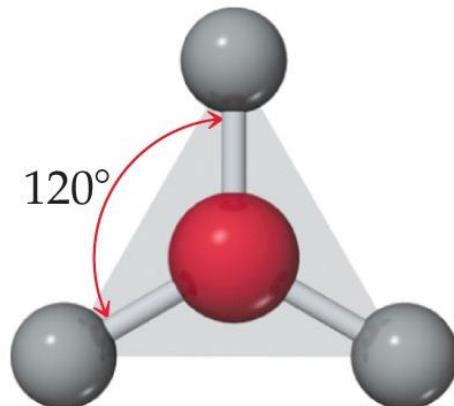
GIVE IT SOME THOUGHT

In addition to tetrahedral, another common shape for AB_4 molecules is *square planar*. All five atoms lie in the same plane, with the B atoms at the corners of a square and the A atom at the center of the square. Which shape in Figure 9.3 could lead to a square-planar shape upon removal of one or more atoms?

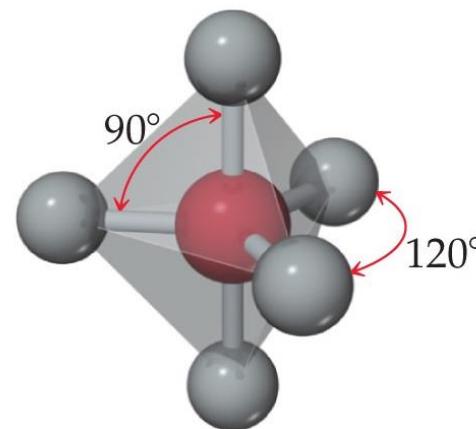
- A. trigonal planar
- B. tetrahedral
- C. trigonal bipyramidal
- D. octahedral



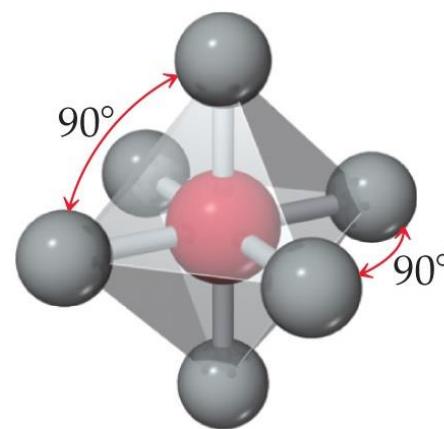
AB_2 linear



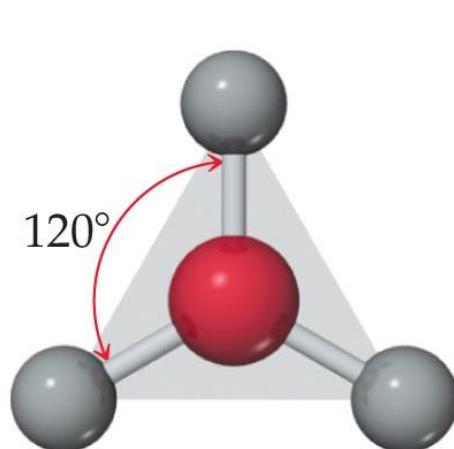
AB_3 trigonal planar



AB_5 trigonal bipyramidal



AB_6 octahedral

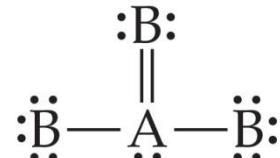


AB_4 tetrahedral



GIVE IT SOME THOUGHT

Suppose a particular AB₃ molecule has the resonance structure

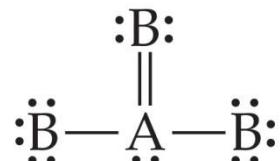


Does this structure follow the octet rule? How many electron domains are there around the A atom?

- A. No, there are 10 electrons around A.
- B. Yes, there are 8 electrons around A.
- C. Yes, there are three bonds and one electron pair about A.
- D. Yes, there are four bonds about A

 GIVE IT SOME THOUGHT

Suppose a particular AB₃ molecule has the resonance structure



Does this structure follow the octet rule? How many electron domains are there around the A atom?

- A. One electron domain
- B. Two electron domains
- C. Three electron domains
- D. Four electron domains



GIVE IT SOME THOUGHT

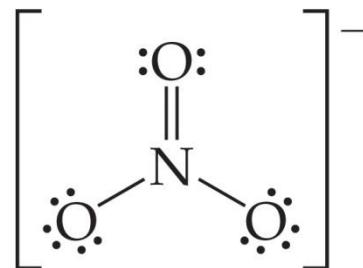
From the standpoint of the VSEPR model, what do nonbonding electron pairs, single bonds, and multiple bonds have in common?

- A. There are no common features.
- B. Each occurs about the central atom only.
- C. Each represents a single electron domain.
- D. All exist when a particular Lewis structure is drawn.



GIVE IT SOME THOUGHT

One resonance structure of the nitrate ion is



The bond angles in this ion are 120° . Is this observation consistent with the preceding discussion of the effect of multiple bonds on bond angles?

- A. No, the domain with the double bond should “push” the other two electron domains resulting in the bond angle between single bonds to less than 120° .
- B. Yes, the existence of resonance with three resonance structures equalizes repulsions between electron domains resulting in all bond angles equaling 120° .



GIVE IT SOME THOUGHT

The molecule $\text{O}=\text{C}=\text{S}$ is linear and has a Lewis structure analogous to that of CO_2 . Would you expect this molecule to have a dipole moment?

- A. Yes, because COS has different elements than in CO_2 .
- B. No, because COS is linear.
- C. Yes, because O and S have different electronegativities, and CO and CS bond dipoles do not cancel each other.
- D. No, because O and S have similar electronegativities, and CO and CS bond dipoles cancel each other.



GIVE IT SOME THOUGHT

What is the orientation of the two unhybridized *p* orbitals on Be with respect to the two Be—F bonds?

- A. Both *p* orbitals are parallel to the Be-F bonds.
- B. Both *p* orbitals intersect the Be-F bonds.
- C. Both *p* orbitals are at an angle of 120° to the Be-F bonds.
- D. Both *p* orbitals are perpendicular to the Be-F bonds.



GIVE IT SOME THOUGHT

In an sp^2 hybridized atom, what is the orientation of the unhybridized p atomic orbital relative to the three sp^2 hybrid orbitals?

- A. The unhybridized p -orbital is 180° from the plane of the sp^2 orbitals.
- B. The unhybridized p -orbital is coplanar with the plane of the sp^2 orbitals.
- C. The unhybridized p -orbital is 109.5° from the plane of the sp^2 orbitals.
- D. The unhybridized p -orbital is perpendicular to the plane of the sp^2 orbitals.



GIVE IT SOME THOUGHT

The molecule called *diazine* has the formula N₂H₂ and the Lewis structure



Do you expect diazine to be a linear molecule (all four atoms on the same line)? If not, do you expect the molecule to be planar (all four atoms in the same plane)?

- A. The molecule is both linear and planar.
- B. The molecule is not linear, but is planar.
- C. The molecule is linear, but not planar.
- D. The molecule is neither linear nor planar.



GIVE IT SOME THOUGHT

When two atoms are bonded by a triple bond, what is the hybridization of the orbitals that make up the σ -bond component of the bond?

- A. sp hybrid atomic orbitals
- B. sp^2 hybrid atomic orbitals
- C. sp^3 hybrid atomic orbitals
- D. sp^3d hybrid atomic orbitals



GIVE IT SOME THOUGHT

Would you expect Be_2^+ to be a stable ion?

- A. No, because the bond order is 0.
- B. Yes, because the bond order is 0.5.
- C. Yes, because the bond order is 1.
- D. Yes, because the bond order is 1.5.

Sample Exercise 9.5 Hybridization

Indicate the orbital hybridization around the central atom in NH_2^- .

Solution

Analyze We are given the chemical formula for a polyatomic anion and asked to describe the type of hybrid orbitals surrounding the central atom.

Plan To determine the central atom hybrid orbitals, we must know the electron-domain geometry around the atom. Thus, we draw the Lewis structure to determine the number of electron domains around the central atom. The hybridization conforms to the number and geometry of electron domains around the central atom as predicted by the VSEPR model.

Solve The Lewis structure is

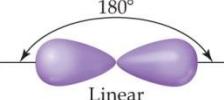
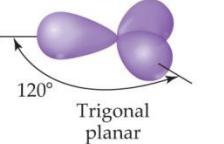
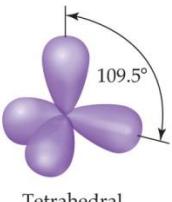


Sample Exercise 9.5 Hybridization

Indicate the orbital hybridization around the central atom in NH_2^- .

Because there are four electron domains around N, the electron-domain geometry is tetrahedral. The hybridization that gives a tetrahedral electron-domain geometry is sp^3 (Table 9.4). Two of the sp^3 hybrid orbitals contain nonbonding pairs of electrons, and the other two are used to make bonds with the hydrogen atoms.

TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets

Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two sp	 Linear 180°	$\text{BeF}_2, \text{HgCl}_2$
s,p,p	Three sp^2	 Trigonal planar 120°	BF_3, SO_3
s,p,p,p	Four sp^3	 Tetrahedral 109.5°	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$

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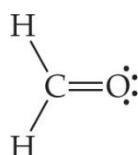
Practice Exercise

Predict the electron-domain geometry and hybridization of the central atom in SO_3^{2-} .

Answer: tetrahedral, sp^3

Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Formaldehyde has the Lewis structure



Describe how the bonds in formaldehyde are formed in terms of overlaps of hybrid and unhybridized orbitals.

Solution

Analyze We are asked to describe the bonding in formaldehyde in terms of hybrid orbitals.

Plan Single bonds σ are bonds, and double bonds consist of one π bond and one π bond. The ways in which these bonds form can be deduced from the molecular geometry, which we predict using the VSEPR model.

Solve The C atom has three electron domains around it, which suggests a trigonal-planar geometry with bond angles of about 120° . This geometry implies sp^2 hybrid orbitals on C (Table 9.4). These hybrids are used to make the two C — H and one C — O bonds to C. There remains an unhybridized $2p$ orbital on carbon, perpendicular to the plane of the three sp^2 hybrids.

TABLE 9.4 • Geometric Arrangements Characteristic of Hybrid Orbital Sets

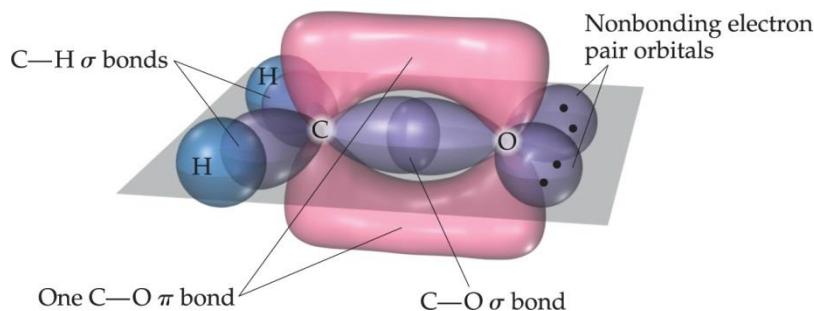
Atomic Orbital Set	Hybrid Orbital Set	Geometry	Examples
s,p	Two sp	Linear 180°	$\text{BeF}_2, \text{HgCl}_2$
s,p,p	Three sp^2	Trigonal planar 120°	BF_3, SO_3
s,p,p,p	Four sp^3	Tetrahedral 109.5°	$\text{CH}_4, \text{NH}_3, \text{H}_2\text{O}, \text{NH}_4^+$

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Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Continued

The O atom also has three electron domains around it, and so we assume it has sp^2 hybridization as well. One of these hybrid orbitals participates in the C—O σ bond, while the other two hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized $2p$ orbital that is perpendicular to the plane of the molecule. These two orbitals overlap to form a C—O π bond (Figure 9.25)

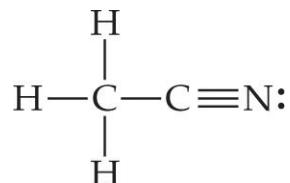


Sample Exercise 9.6 Describing σ and π Bonds in a Molecule

Continued

Practice Exercise

- (a) Predict the bond angles around each carbon atom in acetonitrile:



- (b) Describe the hybridization at each carbon atom, and (c) determine the number of σ and π bonds in the molecule.

Answers: (a) approximately 109° around the left C and 180° around the right C; (b) sp^3 , sp ; (c) five σ bonds and two π bonds

Sample Exercise 9.7 Delocalized Bonding

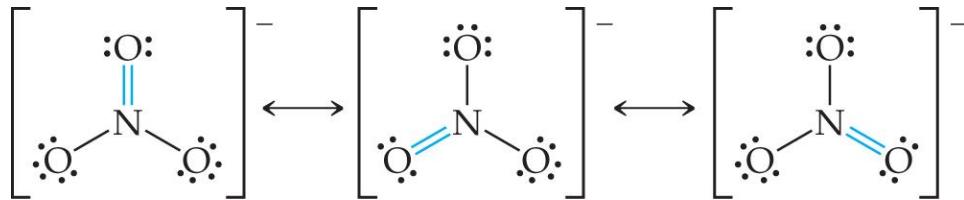
Describe the bonding in the nitrate ion, NO_3^- . Does this ion have delocalized π bonds?

Solution

Analyze Given the chemical formula for a polyatomic anion, we are asked to describe the bonding and determine whether the ion has delocalized π bonds.

Plan Our first step is to draw Lewis structures. Multiple resonance structures involving the placement of the double bonds in different locations suggest that the π component of the double bonds is delocalized.

Solve In Section 8.6 we saw that NO_3^- has three resonance structures:



In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies sp^2 hybridization of the N atom. The sp^2 hybrid orbitals are used to construct the three N — O σ bonds present in each resonance structure.

Sample Exercise 9.7 Delocalized Bonding

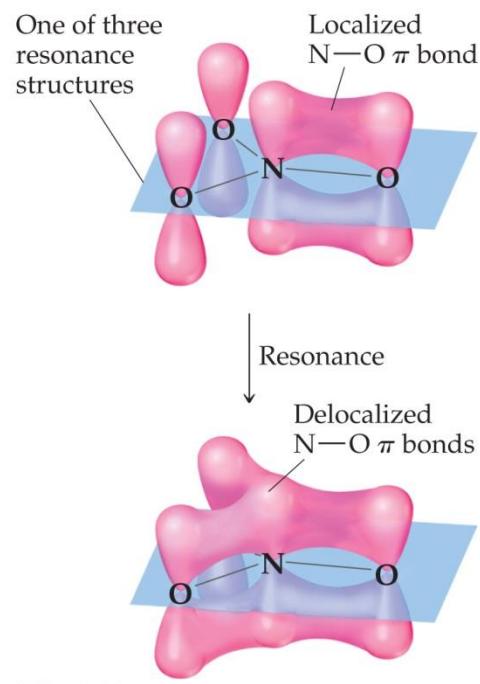
Continued

The unhybridized $2p$ orbital on the N atom can be used to make π bonds. For any one of the three resonance structures shown, we might imagine a single localized N—O π bond formed by the overlap of the unhybridized $2p$ orbital on N and a $2p$ orbital on one of the O atoms, as shown in Figure 9.28. Because each resonance structure contributes equally to the observed structure of NO_3^- , however, we represent the π bonding as delocalized over the N—O three bonds, as shown in the figure.

Practice Exercise

Which of these species have delocalized bonding: SO_3 , SO_3^{2-} , H_2CO , O_3 , NH_4^+ ?

Answer: SO_3 and O_3 , as indicated by the presence of two or more resonance structures involving π bonding for each of these molecules



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Quiz:

For the F_2^- ion, draw the MOs and predict (a) number of unpaired electrons, (b) bond order.

For the B_2^+ ion, draw the MOs and predict (a) number of unpaired electrons, (b) bond order.

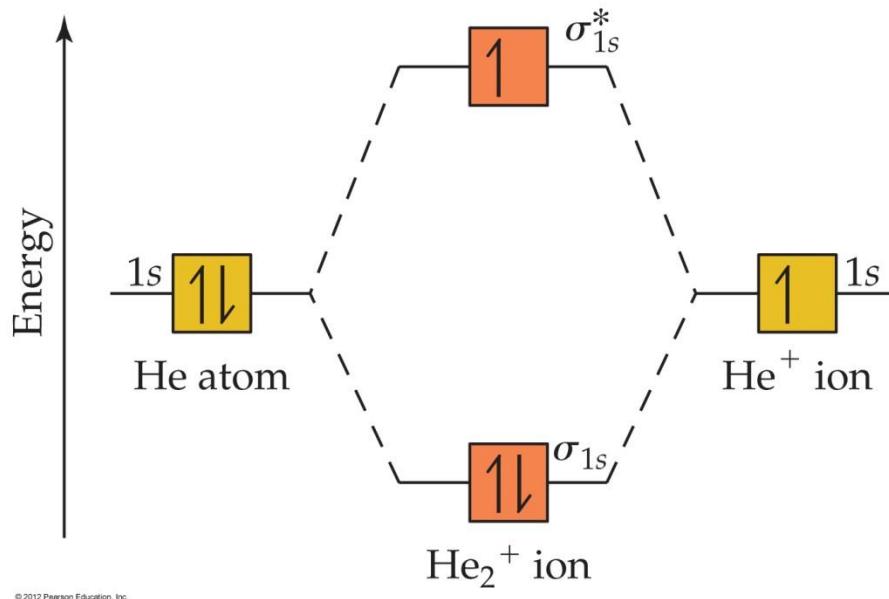
Sample Exercise 9.8 Bond Order

What is the bond order of the He_2^+ ion? Would you expect this ion to be stable relative to the separated He atom and He^+ ion?

Solution

Analyze We will determine the bond order for the He_2^+ ion and use it to predict whether the ion is stable.

Plan To determine the bond order, we must determine the number of electrons in the molecule and how these electrons populate the available MOs. The valence electrons of He are in the 1s orbital, and the 1s orbitals combine to give an MO diagram like that for H_2 or He_2 (Figure 9.33). If the bond order is greater than 0, we expect a bond to exist, and the ion is stable.



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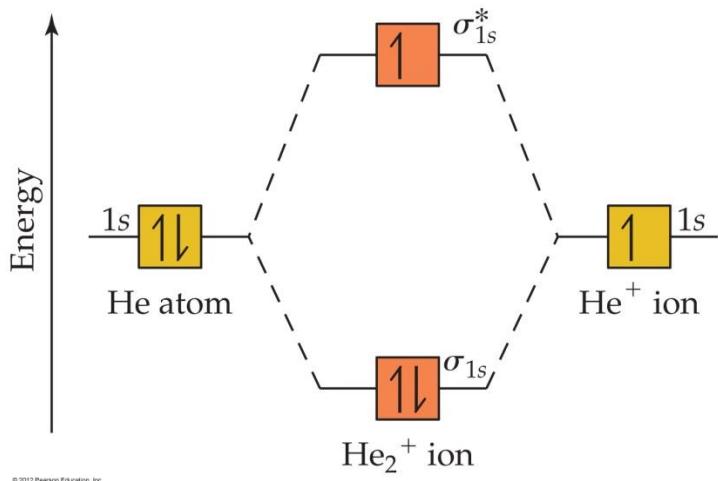
Sample Exercise 9.8 Bond Order

Continued

Solve The energy-level diagram for the He_2^+ ion is shown in Figure 9.34. This ion has three electrons. Two are placed in the bonding orbital and the third in the antibonding orbital. Thus, the bond order is

$$\text{Bond order} = \frac{1}{2}(2 - 1) = \frac{1}{2}$$

Because the bond order is greater than 0, we predict the He_2^+ ion to be stable relative to the separated He and the He^+ . Formation of He_2^+ in the gas phase has been demonstrated in laboratory experiments.



Practice Exercise

Determine the bond order of the H_2^- ion.

Answer: $\frac{1}{2}$

Sample Exercise 9.9 Molecular Orbitals of a Period 2 Diatomic Ion

For the O_2^+ ion, predict (a) number of unpaired electrons, (b) bond order, (c) bond enthalpy and bond length.

Solution

Analyze Our task is to predict several properties of the cation O_2^+ .

Plan We will use the MO description of O_2^+ to determine the desired properties. We must first determine the number of electrons in O_2^+ and then draw its MO energy diagram. The unpaired electrons are those without a partner of opposite spin. The bond order is one-half the difference between the number of bonding and antibonding electrons. After calculating the bond order, we can use Figure 9.43 to estimate the bond enthalpy and bond length.

Solve

(a) The O_2^+ ion has 11 valence electrons, one fewer than O_2 . The electron removed from O_2 to form O_2^+ is one of the two unpaired π_{2p}^* electrons (Figure 9.43). Therefore, O_2^+ has one unpaired electron.

Large 2s–2p interaction			Small 2s–2p interaction		
B_2	C_2	N_2	O_2	F_2	Ne_2
σ_{2p}^*	□	□	□	□	□
π_{2p}^*	□□	□□	□□	1 1	1 1
σ_{2p}	□	□	1 1	1 1	1 1
π_{2p}	1 1	1 1	1 1	1 1	1 1
σ_{2s}^*	1	1	1	1	1
σ_{2s}	1	1	1	1	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

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Sample Exercise 9.9 Molecular Orbitals of a Period 2 Diatomic Ion

Continued

(b) The molecule has eight bonding electrons (the same as O₂) and three antibonding electrons (one fewer than O₂). Thus, its bond order is

$$\frac{1}{2}(8 - 3) = 2\frac{1}{2}$$

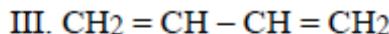
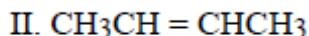
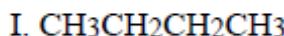
(c) The bond order of O₂⁺ is between that for O₂ (bond order 2) and N₂ (bond order 3). Thus, the bond enthalpy and bond length should be about midway between those for O₂ and N₂, approximately between 495-941 kJ/mol and 1.15 Å. (The experimentally measured values are and 1.123 Å.)

Practice Exercise

Predict the magnetic properties and bond orders of (a) the peroxide ion, O₂²⁻ (b) the acetylide ion, C₂²⁻.

Answers: (a) diamagnetic, 1; (b) diamagnetic, 3

1. In which of the compounds below is there more than one kind of hybridization (sp , sp^2 , sp^3) for carbon?



A) II and III

B) II only

C) III and IV

D) I, II, and III

E) III only

2. Which of the following molecules contains the shortest C–C bond?

A) C_2H_2

B) C_2H_4

C) C_2H_6

D) C_2Cl_4

E) both B and D

3. If a molecule demonstrates paramagnetism, then

I. The substance can have both paired and unpaired electrons.

II. The bond order is not a whole number.

III. It can be determined by drawing a Lewis structure.

IV. It must be an ion.

A) I, II

B) I, II, IV

C) II, III

D) I only

E) All of the above are correct.

4. In the molecule XeF_2 , how many pairs of electrons surround Xe and what is the molecular geometry?
- A) 4, bent
 - B) 4, pyramidal
 - C) 5, linear
 - D) 5, bent
 - E) 6, linear
5. According to VSEPR theory, which of the following species has a square planar molecular structure?
- A) TeBr_4
 - B) BrF_3
 - C) IF_5
 - D) XeF_4
 - E) SCl_2
6. According to MO theory, overlap of two s atomic orbitals produces _____.
A) one bonding molecular orbital and one hybrid orbital
B) two bonding molecular orbitals
C) two bonding molecular orbitals and two antibonding molecular orbitals
D) two bonding molecular orbitals and one antibonding molecular orbital
E) one bonding molecular orbital and one antibonding molecular orbital
7. Of the following species, _____ will have bond angles of 120° .
- A) PH_3
 - B) ClF_3
 - C) NCl_3
 - D) BCl_3
 - E) All of these will have bond angles of 120° .

8. According to valence bond theory, which orbitals overlap in the formation of the bond in HCl?

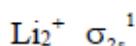
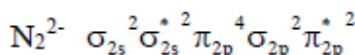
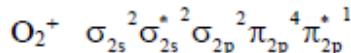
- A) 1s on H and 2p on Cl
- B) 2s on H and 3p on Cl
- C) 1s on H and 3s on Cl
- D) 1s on H and 3p on Cl
- E) 1s on H and 4p on Cl

9. Draw molecular orbital electron configurations of the following ions: O_2^+ , N_2^{2-} ,

Li_2^+ . (b) Predict the magnetic properties and bond orders of them.

Answer:

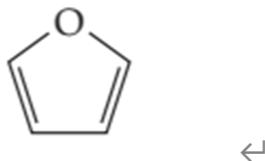
(a)



(b)

Ions	Magnetic property	Bond order
O_2^+	paramagnetic	2.5
N_2^{2-}	paramagnetic	2
Li_2^+	paramagnetic	0.5

1. The molecule shown below is called furan. It is represented in typical shorthand way for organic molecules, with hydrogen atoms not shown. ↵



(a) What is the molecular formula for furan? (b) How many valence electrons are there in the molecule? (c) What is the hybridization at each of the carbon atoms? (d) How many electrons are in the π system of the molecule? (e) The C – C – C bond angles in furan are much smaller than those in benzene. The likely reason is which of the following: (i) The hybridization of the carbon atoms in furan is different from that in benzene, (ii) Furan does not have another resonance structure equivalent to the one above, or (iii) The atoms in a five-membered ring are forced to adopt smaller angles than in a six-membered ring. ↵

(a) C_4H_4O ↵

(b) 26 ↵

(c) sp^2 ↵

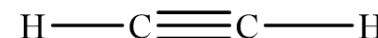
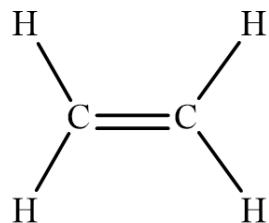
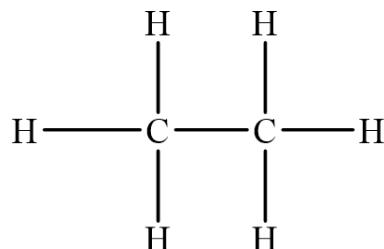
(d) 4 electrons

(e) (iii) ↵

2. Use the VSEPR model to predict the electron-domain and molecular geometries for
 (a) SeCl_2 , (b) CO_3^{2-} , (c) BrF_3 , (d) SF_5^+ .

\square	electron-domain \square	Molecular geometry \square
(a) SeCl_2 \square	Tetrahedral \square	Bent \square
(b) $\text{CO}_3^{2-}\square$	Trigonal planar \square	Trigonal planar \square
(c) BrF_3 \square	Trigonal bipyramidal \square	T-shaped \square
(d) $\text{SF}_5^+\square$	Trigonal bipyramidal \square	Trigonal bipyramidal \square

3. (a) Draw Lewis structures for ethane (C_2H_6), ethylene (C_2H_4), and acetylene (C_2H_2).
 (b) What is the hybridization of the carbon atoms in each molecule? (c) Predict which molecules, if any, are planar. (d) How many σ and π bonds are there in each molecule?



\square

- (b) sp^3
 (c) nonplanar
 (d) $7\sigma, 0\pi$

- sp^2
 planar
 $5\sigma, 1\pi$

- sp \square
 planar \square
 $3\sigma, 2\pi$ \square