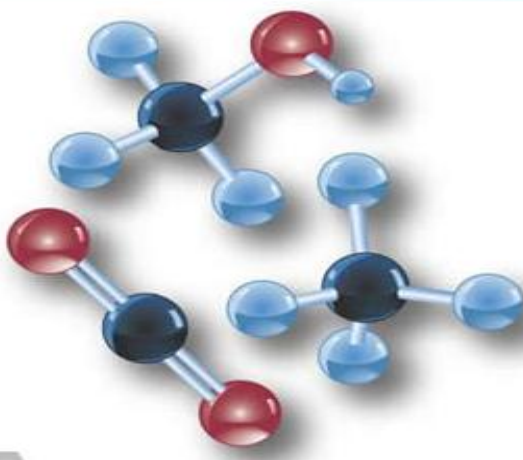


Organic Chemistry





价层电子对互斥理论 (Valence Shell Electron Pair Repulsion, 简称 **VSEPR**) :

通过中心原子的**价层电子对**之间的静电排斥作用, 来**预测和解释共价分子 / 离子的空间几何构型**。

◆ 核心依据: 分子的空间构型, 只由中心原子的价层电子对的排斥作用决定。

◆ 价层电子对包括两类: **成键电子对 (σ 键)** 和**孤电子对**

所有 π 键都是依附在 σ 键之上的, σ 键决定了原子之间的空间取向

◆ 排斥大小规律 (核心中的核心)

孤电子对-孤电子对 > 孤电子对-成键对 > 成键对-成键对

VSEPR = 价层电子对互相排斥 → 尽量远离 → 形成稳定空间构型。



$$VP = \sigma \text{ 键电子对数} + \text{孤电子对数}$$

1. 数 σ 键 (只数 σ , π 键一律不算)

- 单键: 1 个 σ
- 双键: 1 个 σ + 1 个 π $\rightarrow$ 只算 1
- 三键: 1 个 σ + 2 个 π $\rightarrow$ 只算 1

2. 算中心原子的孤电子对数

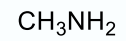
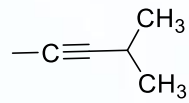
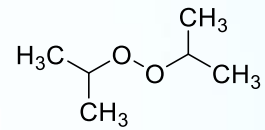
通用公式: $1/2$ (价电子数 - 成键电子数)

3. 加起来 $VP = \sigma \text{ 键数} + \text{孤电子对数}$

分子式 $\rightarrow$ 路易斯结构式 $\rightarrow$ 数 σ $\rightarrow$ 数孤对 $\rightarrow$ 算 VP



确定下来分子的形状





Chapter 4

Basic Theory (3)

—Theories of Covalent Bonding

有机化学结构理论知识:

1.1 How do we describe the electronic structure of atoms?

1.2 What is the Lewis model of bonding?

1.3 How do we predict bond angles and the shapes of molecules?

1.4 How do we predict if a molecule is polar or nonpolar?

1.5 What is resonance?

1.6 What is the orbital overlap model of covalent bonding?

Outline:

1. Valence bond (VB) theory and orbital hybridization

Central themes of VB theory

Types of hybrid orbitals

2. Modes of orbital overlap and the types of covalent bonds

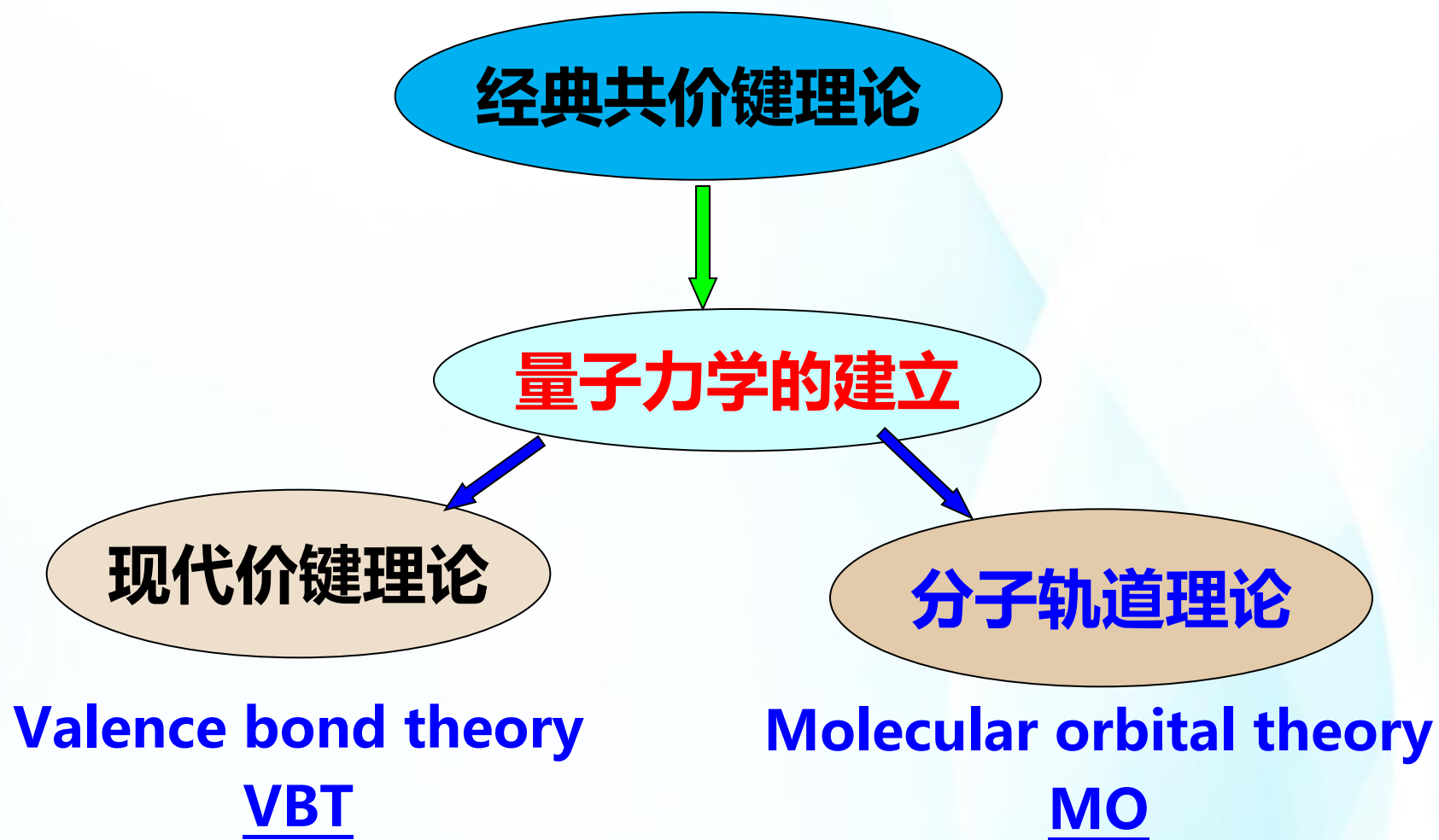
Orbital overlap in single and multiple bonds

Orbital overlap and molecular rotation

3. Molecular orbital (MO) theory and electron delocalization

Central themes of MO theory

Typical organic compounds



经典共价键理论:1916年由 *G.N.Lewis* (美) 提出。 **理论**

要点: 共价键是由成键原子双方通过**共用电子对**来形成8电子稳定结构的一种化学键。

优点: 初步揭示了共价键与离子键的区别。

局限性:

- 1) 一些共价分子的中心原子最外层电子数虽少于8或多于8 (如 BF_3 、 PCl_5) , 为什么仍相当稳定?
- 2) 为什么两个带负电荷的电子不相互排斥反而能够相互配对?
- 3) 共价键为什么具有方向性和饱和性?

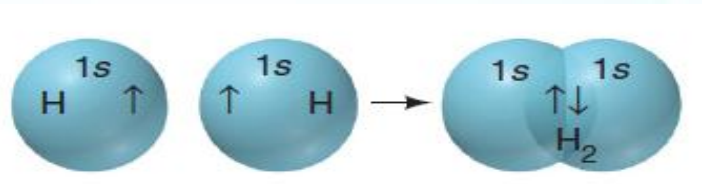
1. Valence bond theory and orbital hybridization

1927年德国化学家W. Heitler和F. London应用量子力学处理氢分子结构：共价键的形成是两个成键原子的原子轨道相互重叠的结果。

其后由美国化学家Pauling和Slater将量子力学对氢分子研究结果推广到其他分子，进一步形成了现代价键理论（VB法）。

The central themes of VB

The basic principle of VB theory is that a covalent bond forms when orbitals of two atoms overlap and a pair of electrons occupy the overlap region.



1) Opposing spins of the electron pair.

As the exclusion principle requires, the space formed by the overlapping orbitals has a maximum capacity for two electrons that have opposite spins.

只有自旋相反的未成对电子可以相互配对，形成稳定的共价键。

2) Maximum overlap of bonding orbitals.

成键电子的原子轨道尽可能达到最大重叠。轨道重叠程度越大，两核之间电子的概率密度越大，系统能量降低越多，形成的共价键越稳定。这称作最大重叠原理。

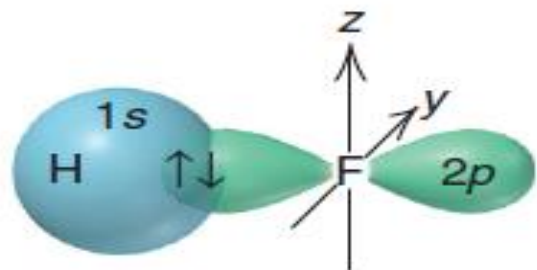
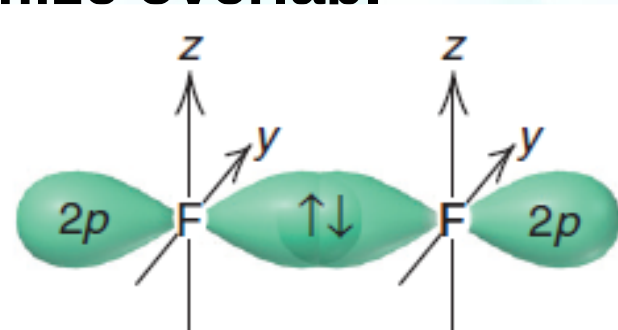
Bond strength depends on the attraction between nuclei and shared electrons, so the greater the orbital overlap, the stronger the bond.



根据最大重叠原理，具有一定形状和取向的原子轨道必须沿着一定的方向进行重叠，这就是共价键的方向性。

Extent of overlap depends on orbital shape and direction.

An s orbital is spherical, so its orientation is the same in any direction, but p and d orbitals have specified directions. Thus, a p or d orbital involved in a bond is oriented to maximize overlap.



The two half-filled 2p orbitals interact end to end, that is, along the long axes of the orbitals.



每个原子所形成共价键的数目取决于该原子中的单电子数目, 即一个原子含有几个单电子, 就能与几个自旋方向相反的单电子形成共价键, 这就是共价键的饱和性。

Methane has the formula CH₄, not CH₂, and its bond angles are 109.5°

1931 年鲍林在价键理论的基础上, 提出了**杂化轨道理论**: 原子在形成分子时, 由于原子间的相互影响, 同一个原子内的不同类型、**能量相近**的原子轨道可以**重新组合**成能量、形状和空间方向与原来轨道完全不同的新的原子轨道。这种重新组合过程称为**杂化**, 所形成的新的原子轨道称为**杂化轨道**。



(2) Hybridization of atomic orbitals.

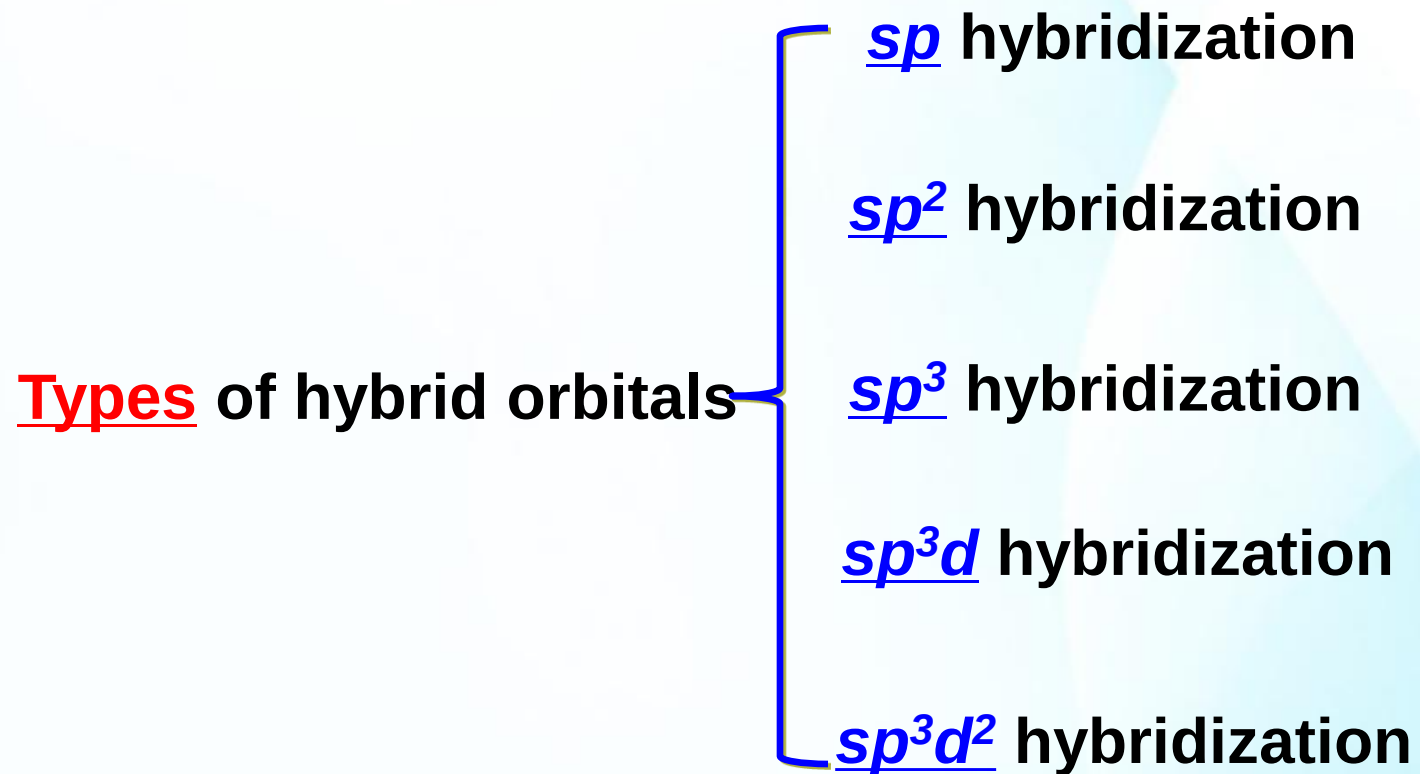
Linus Pauling proposed that, during bonding, the valence atomic orbitals in the isolated atoms become different when they are in the molecule.

Quantum-mechanical calculations show that if we mathematically “mix” certain combinations of orbitals, we form new ones whose spatial orientations do match the observed molecular shapes. The process of orbital mixing is called hybridization, and the new atomic orbitals are called hybrid orbitals.

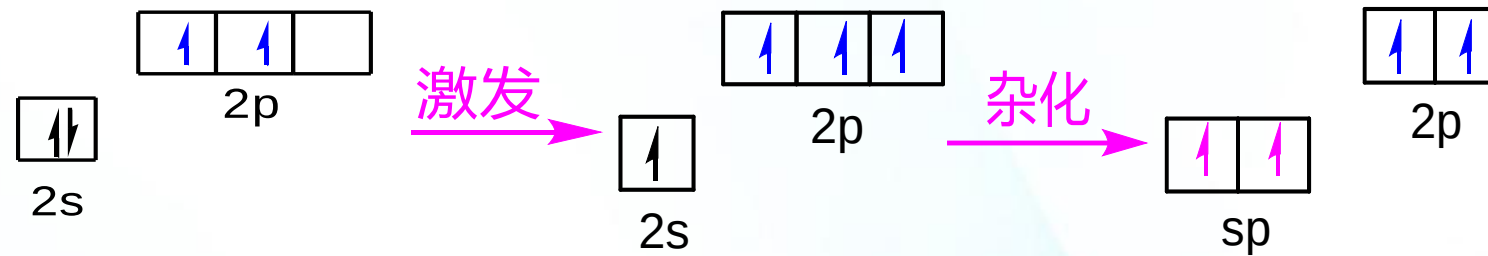
In truth, hybridization is a concept that helps us explain the molecular shapes we observe.

The number of hybrid orbitals formed equals the number of atomic orbitals mixed.

The type of hybrid orbitals formed varies with the types of atomic orbitals mixed.

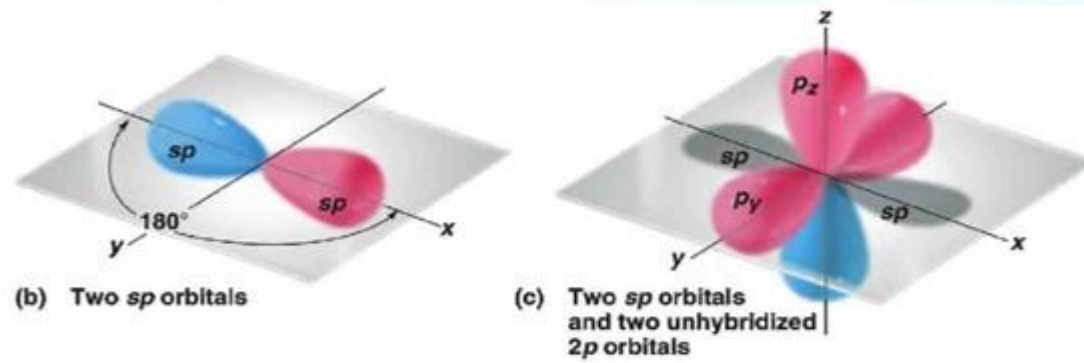


1) sp hybridization



(a) An sp orbital

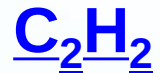
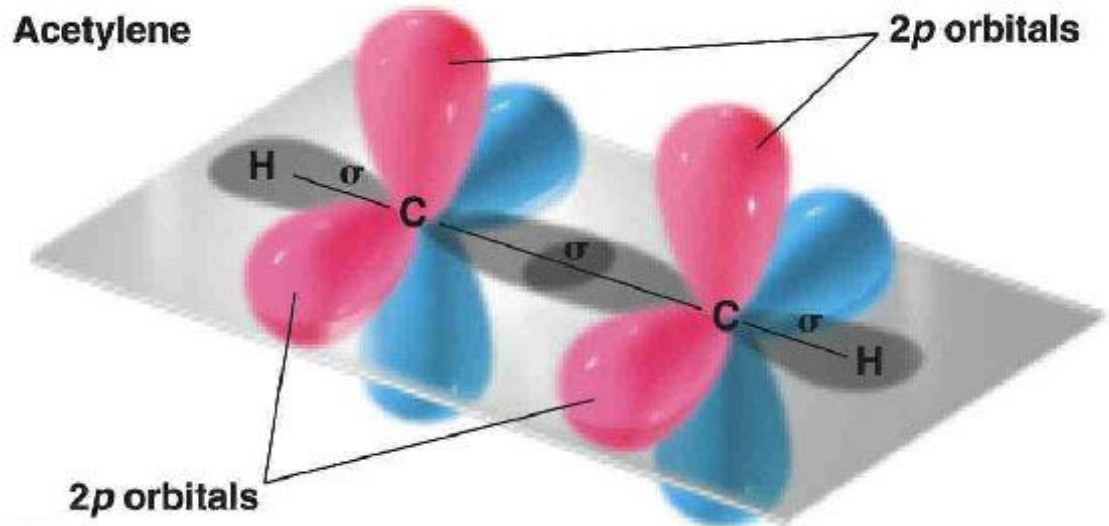
The shape of these hybrid orbitals, with one large and one small lobe, differs markedly from the shapes of the atomic orbitals that were mixed.



1) sp hybridization

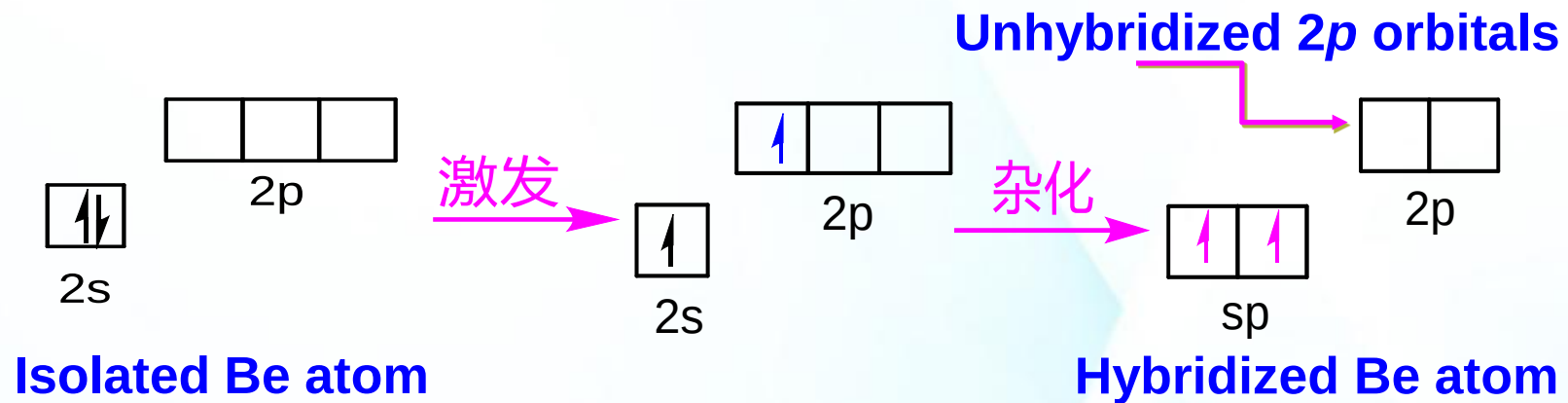
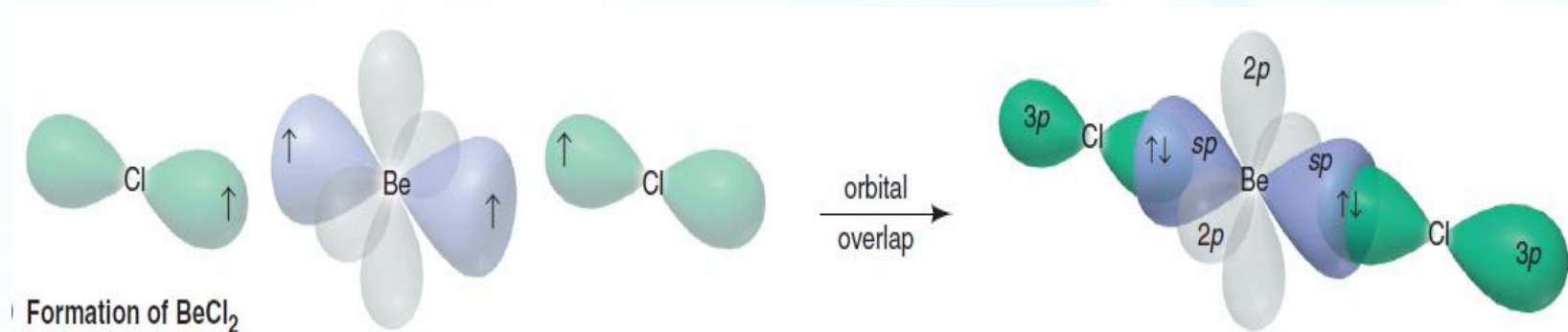
The orbital orientations increase electron density in the bonding direction and minimize repulsions between electrons that occupy them.

Thus, both shape and orientation maximize overlap with the orbital of the other atom in the bond.

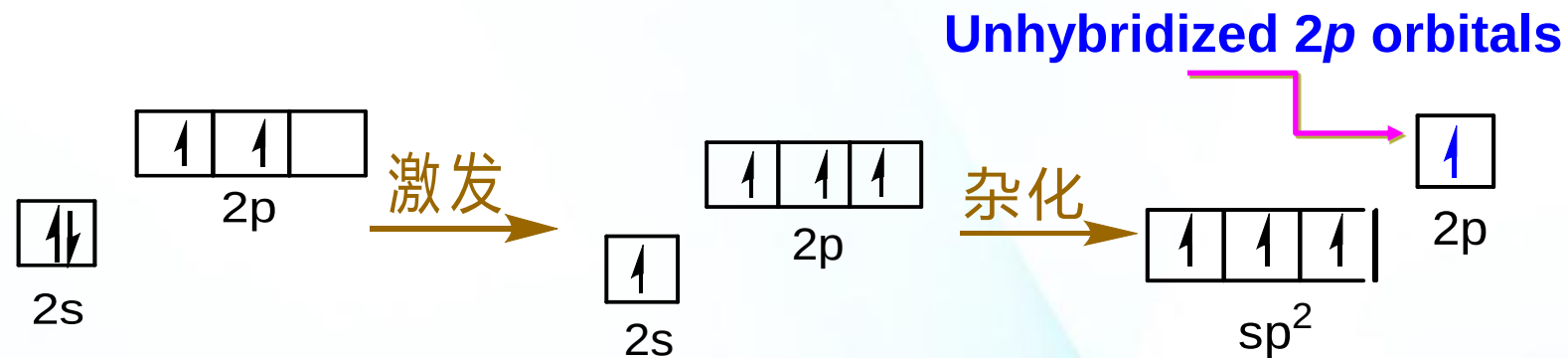


1) sp hybridization

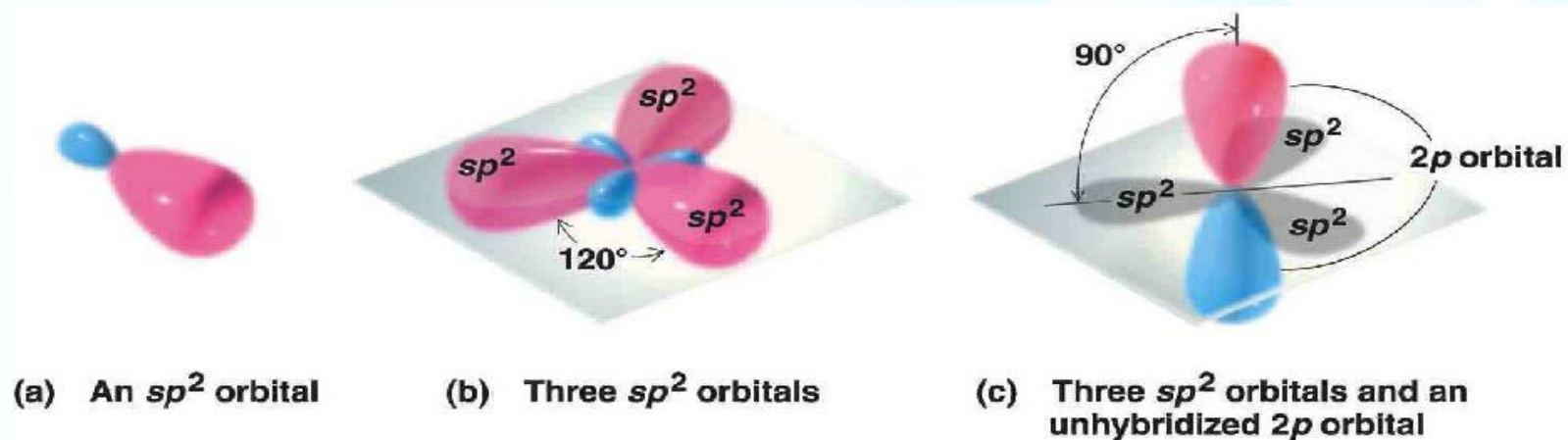
BeCl₂

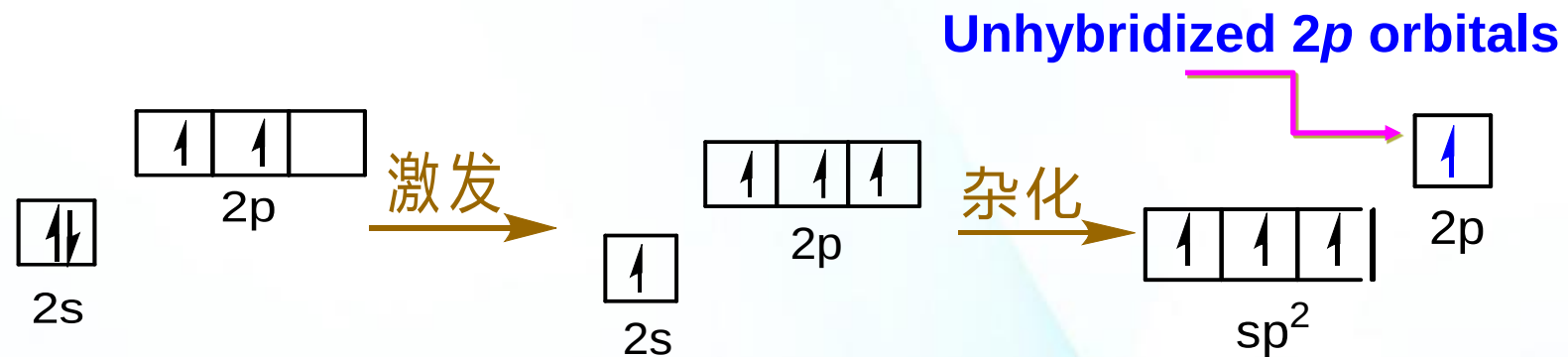


The hybrid orbitals overlap the half-filled 3p orbital in each of two Cl atoms.

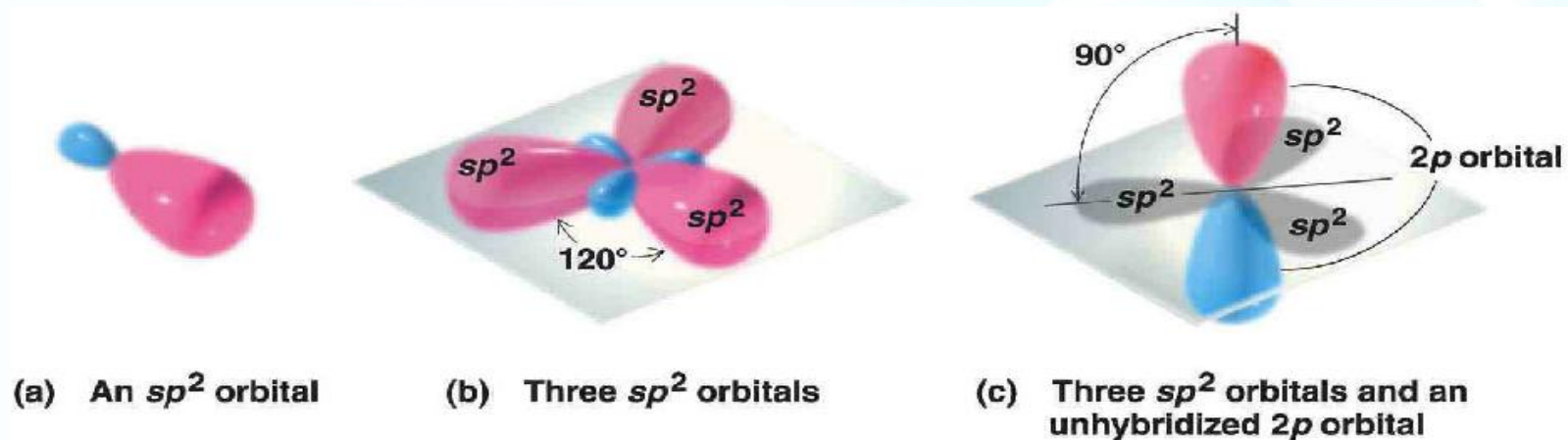


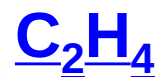
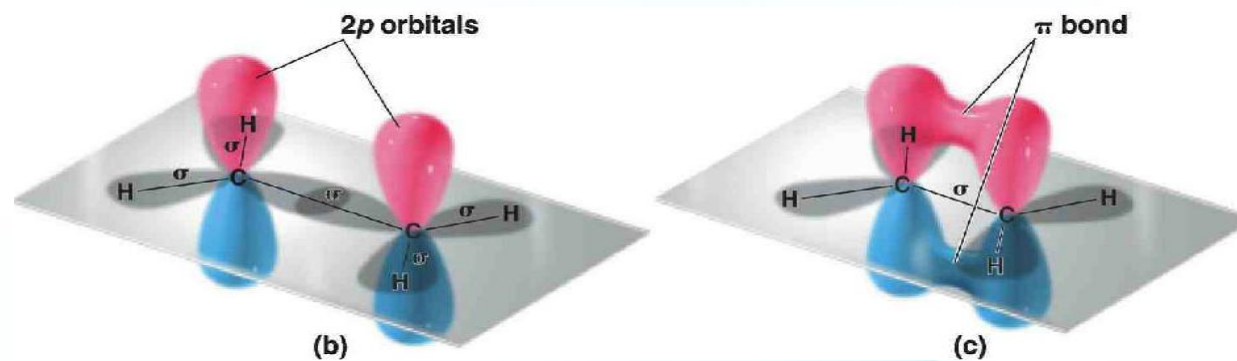
Mixing one s and two p orbitals gives three sp^2 hybrid orbitals that point to the corners of an equilateral triangle, their axes 120° apart.



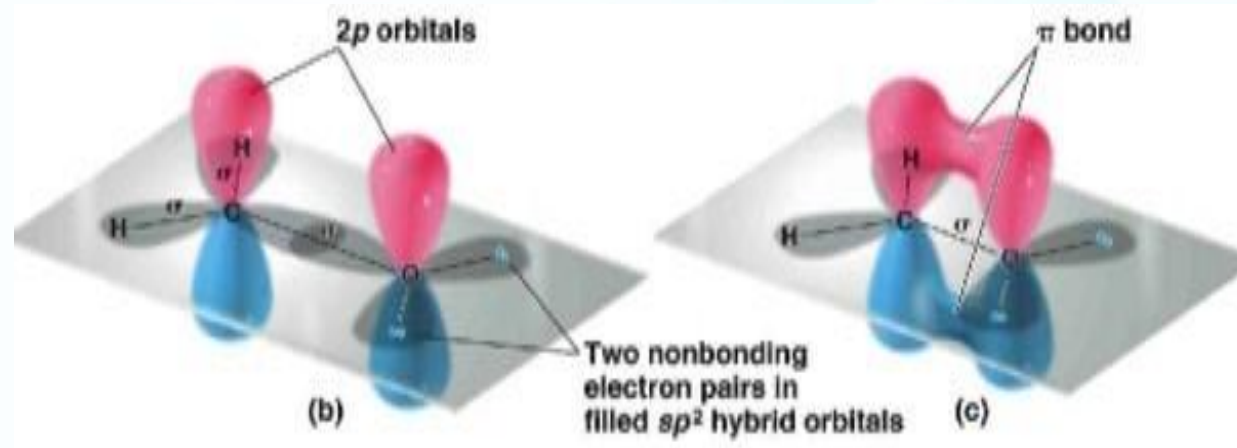


Mixing one s and two p orbitals gives three sp^2 hybrid orbitals that point to the corners of an equilateral triangle, their axes 120° apart.





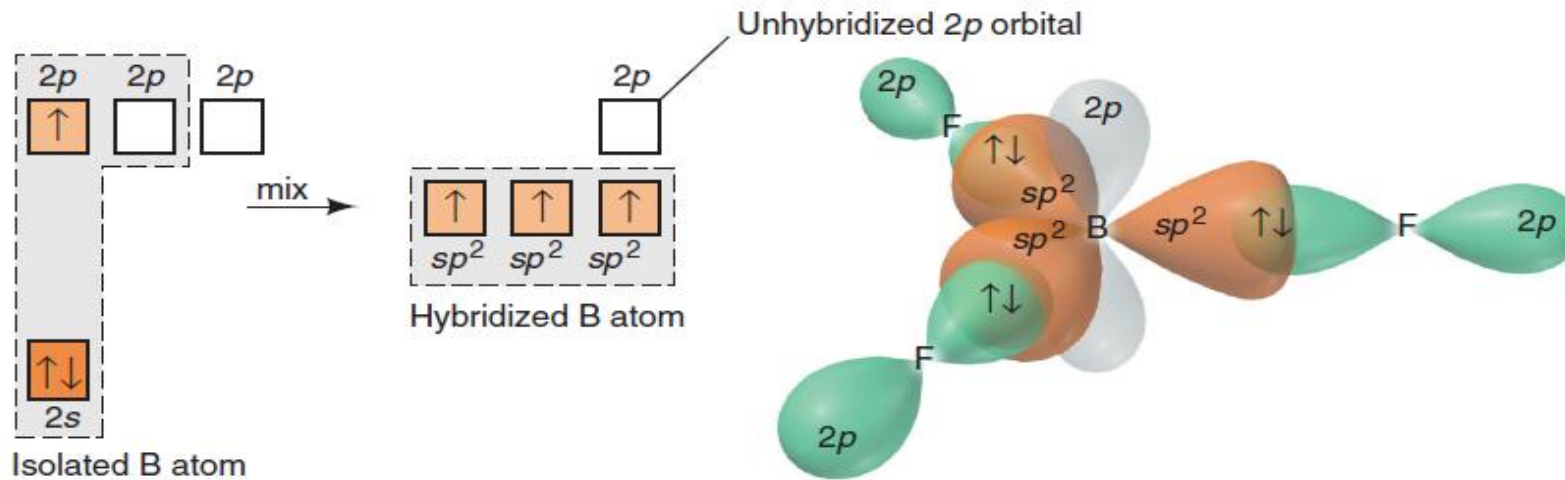
π 键特点：电子云分布在平面的上下，以平面为对称，流动性大，反应性强，必须与 σ 键共存，不能自由旋转。



2) sp^2 hybridization

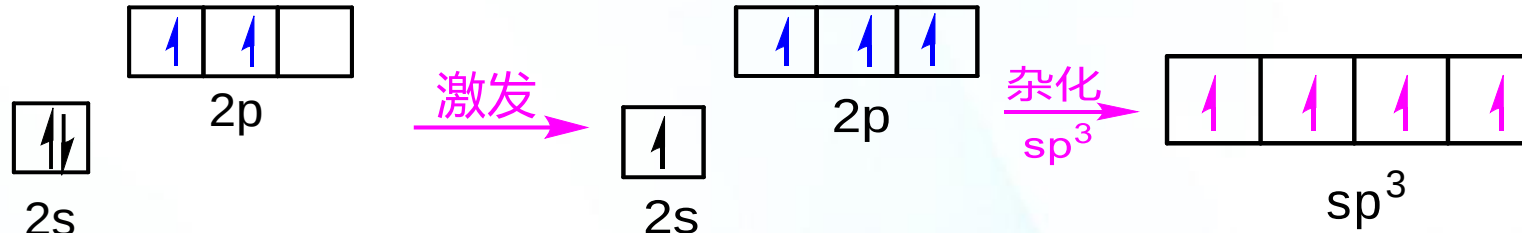
$$\underline{\underline{\text{BF}_3}}$$

The central **B atom** in BF_3 is **sp^2 hybridized**, with the three sp^2 orbitals in a trigonal plane and the third 2p orbital unhybridized and perpendicular to this plane.

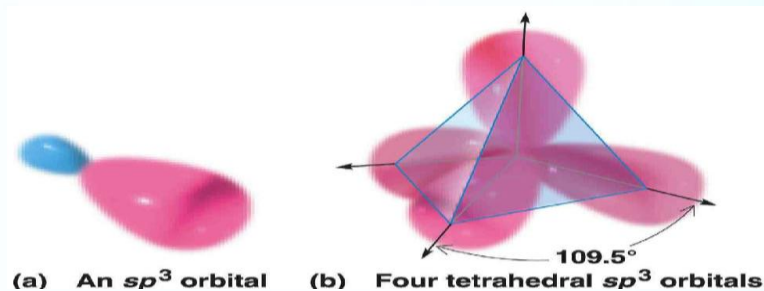
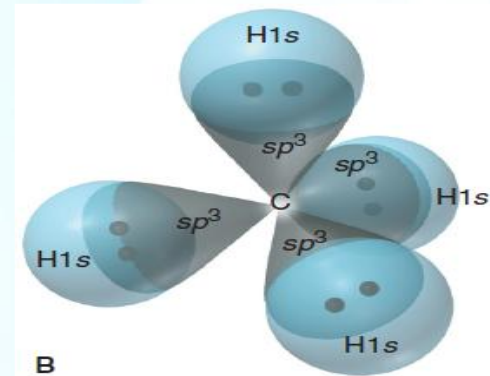


Each half-filled sp^2 orbital overlaps the half-filled 2p orbital of an F atom.

3) sp^3 hybridization



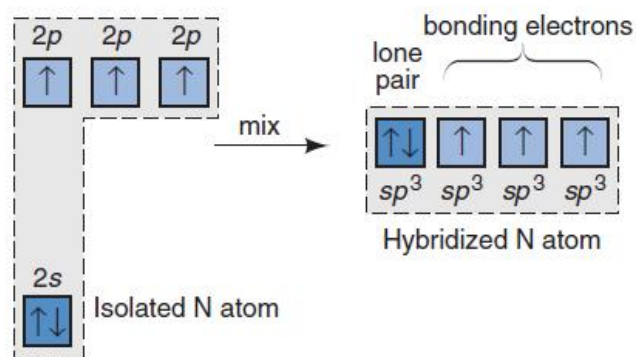
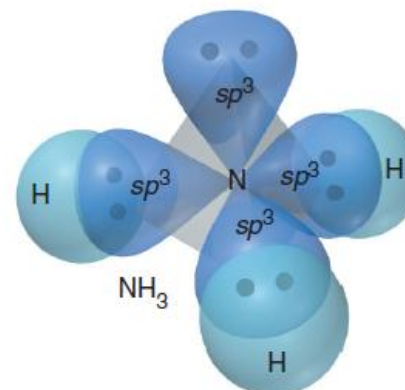
Mixing one s and three p orbitals gives four sp^3 hybrid orbitals that point to the corners of a tetrahedron.



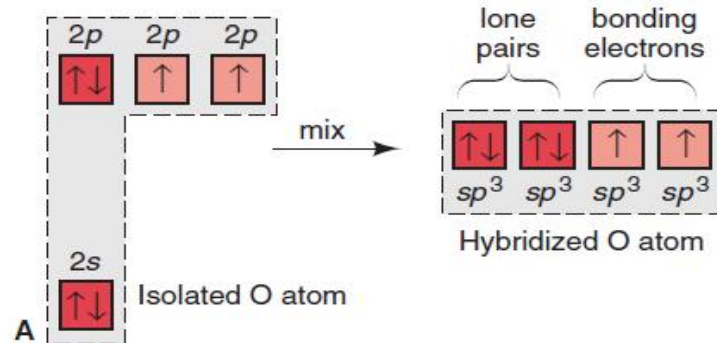
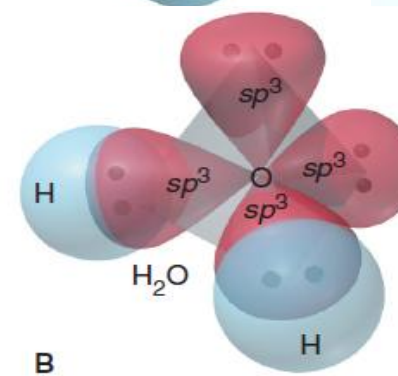
- ① sp^3 轨道具有更强的成键能力和更大的方向性;
- ② 四个 sp^3 杂化轨道完全相同, 取最大的空间距离为**正四面体构型**, 轨道夹角为 109.5° 。

The trigonal pyramidal shape of NH_3 arises when a lone pair fills any one of the four sp^3 orbitals of N, and the bent shape of H_2O arises when lone pairs fill any two of the sp^3 orbitals of O.

NH_3



H_2O

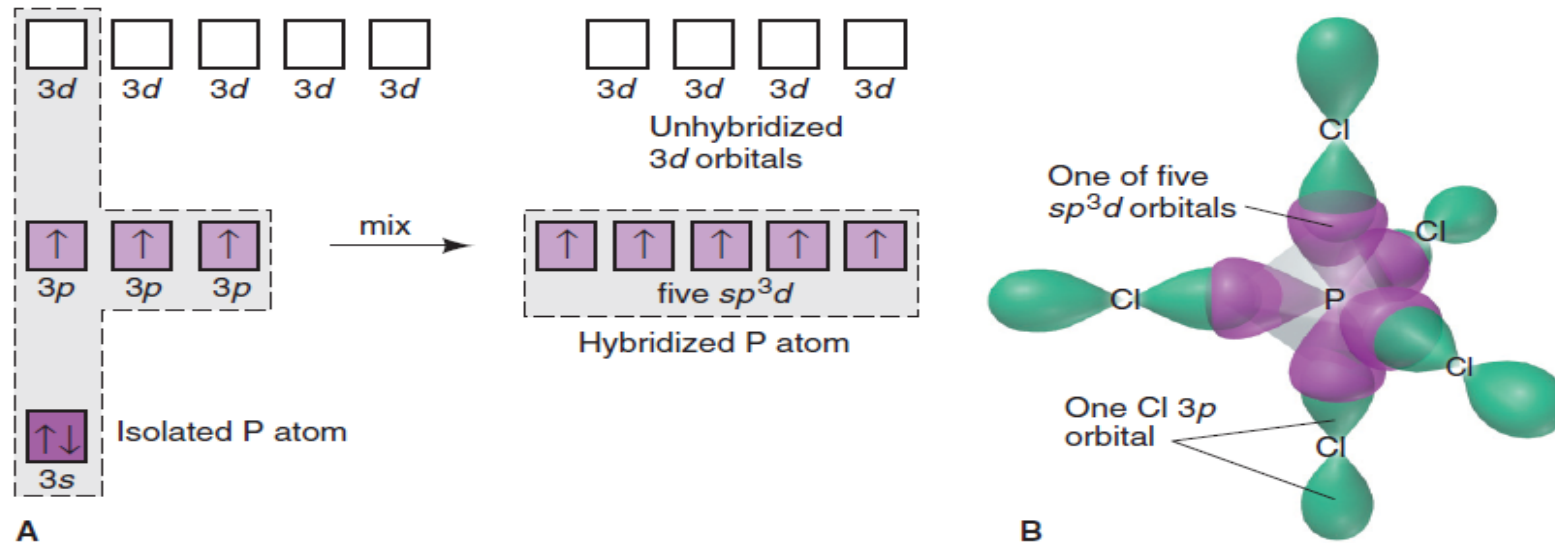




- 杂化轨道可形成σ键，如C-H、C-C、C-X、C-O、C-N等。σ键是有机分子构成碳链或碳环的基础。
- 未参与杂化的p轨道可形成π键，如C=C、C=O、C≡C、C≡N等。
- 不同杂化态碳原子的电负性不同，导致其与氢原子或其它原子形成的σ键的性质不同。

杂化状态	sp^3	sp^2	sp
S 成分	$\frac{1}{4} S$	$\frac{1}{3} S$	$\frac{1}{2} S$
电负性	最小	中间	最大

Mixing one 3s, the three 3p, and one of the five 3d orbitals gives five sp^3d hybrid orbitals, which point to the corners of a trigonal bipyramid.

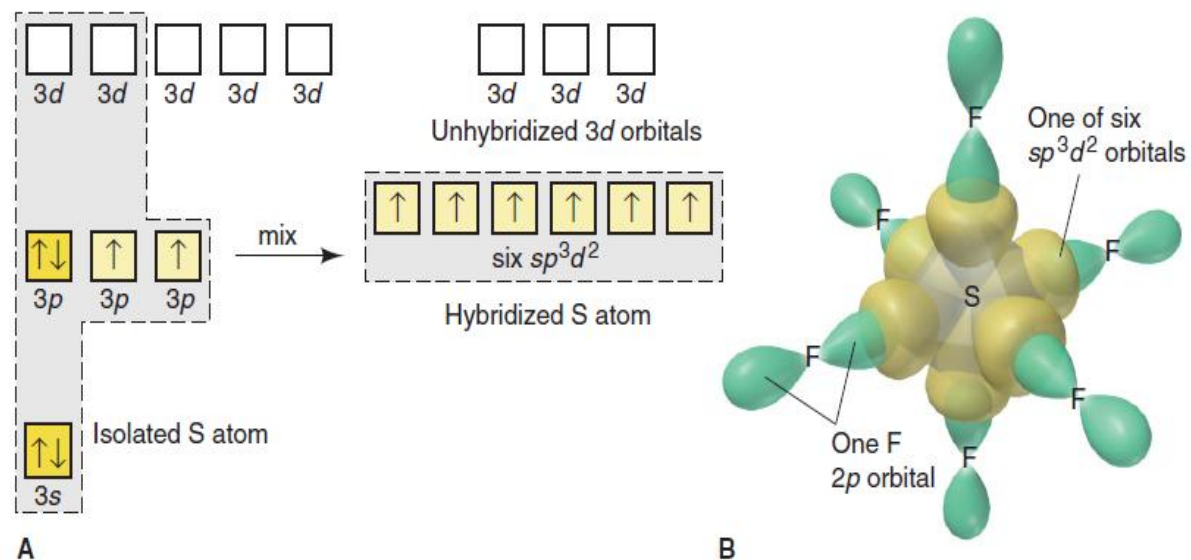


The P atom in PCl₅ is sp^3d hybridized. Each hybrid orbital overlaps a 3p orbital of a Cl atom.

5) sp^3d^2 hybridization

Mixing one 3s, the three 3p, and two 3d orbitals gives six sp^3d^2 hybrid orbitals, which point to the corners of an octahedron.

SF₆

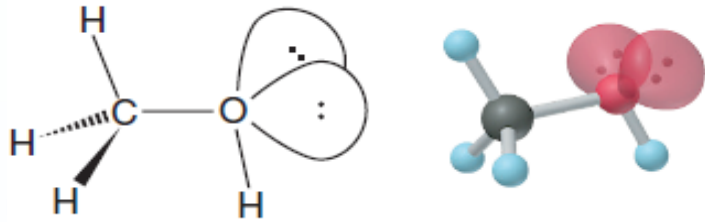


The S atom in SF₆ is sp³d² hybridized. Each half-filled hybrid orbital overlaps a half-filled 2p orbital of an F atom.

CH₃OH

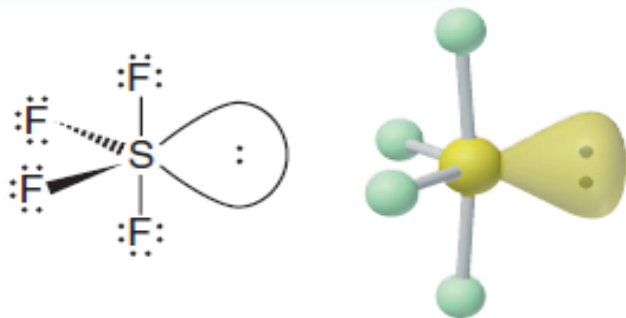
The C atom has four half-filled sp³ orbitals.

The O atom has two half-filled sp³ orbitals and two filled with lone pairs.



SF₄

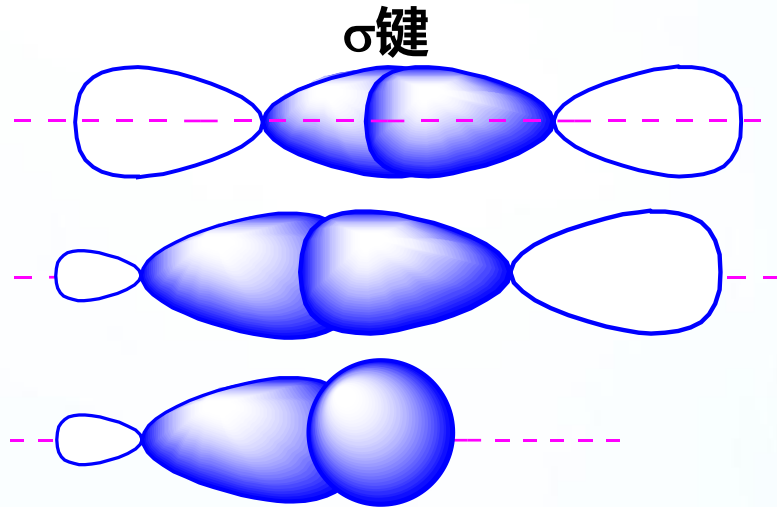
The electron-group arrangement is trigonal bipyramidal, so the central S atom is sp³d hybridized.



One hybrid orbital is filled with a lone pair, and four are half-filled. Four unhybridized 3d orbitals remain empty.

2. Modes of orbital overlap and the types of bonds

(1) Sigma (σ) 键—原子轨道沿对称轴方向重叠 (头对头)

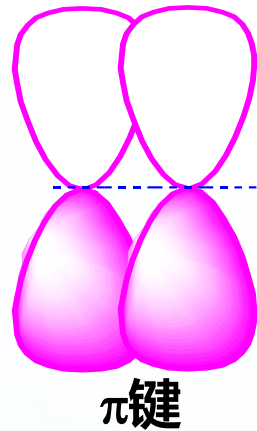


A σ bond allows free rotation because the extent of overlap is not affected.

σ 键特点—可以沿键轴自由旋转；牢固。

End-to-end overlap forms a sigma bond, which has its highest electron density along the bond axis and is shaped like an ellipse rotated about its long axis. All single bonds are σ bonds, including the six C-H bonds in ethane.

(2) Pi (π) 键—p轨道平行重叠 (肩并肩)



键轴：原子核间的连线

A π bond restricts rotation because p orbitals must be parallel to each other to overlap most effectively.

π 键特点—不能自由旋转；易断裂。

It has two regions of electron density, one above and one below the σ -bond axis. The two electrons in one π bond occupy both lobes.

Orbitals overlap less side to side than end to end, a π bond is weaker than a σ bond.



3. Molecular orbital (MO) theory

The MO model is a quantum-mechanical treatment for molecules similar to the one for atoms.

A molecular orbitals (MOs) of given energies and shapes that are occupied by the molecule's electrons.

VB theory pictures a molecule as a group of atoms bonded through localized overlapping of valence-shell atomic and/or hybrid orbitals occupied by electrons.

MO theory pictures a molecule as a collection of nuclei with orbitals delocalized over the whole molecule and occupied by electrons.

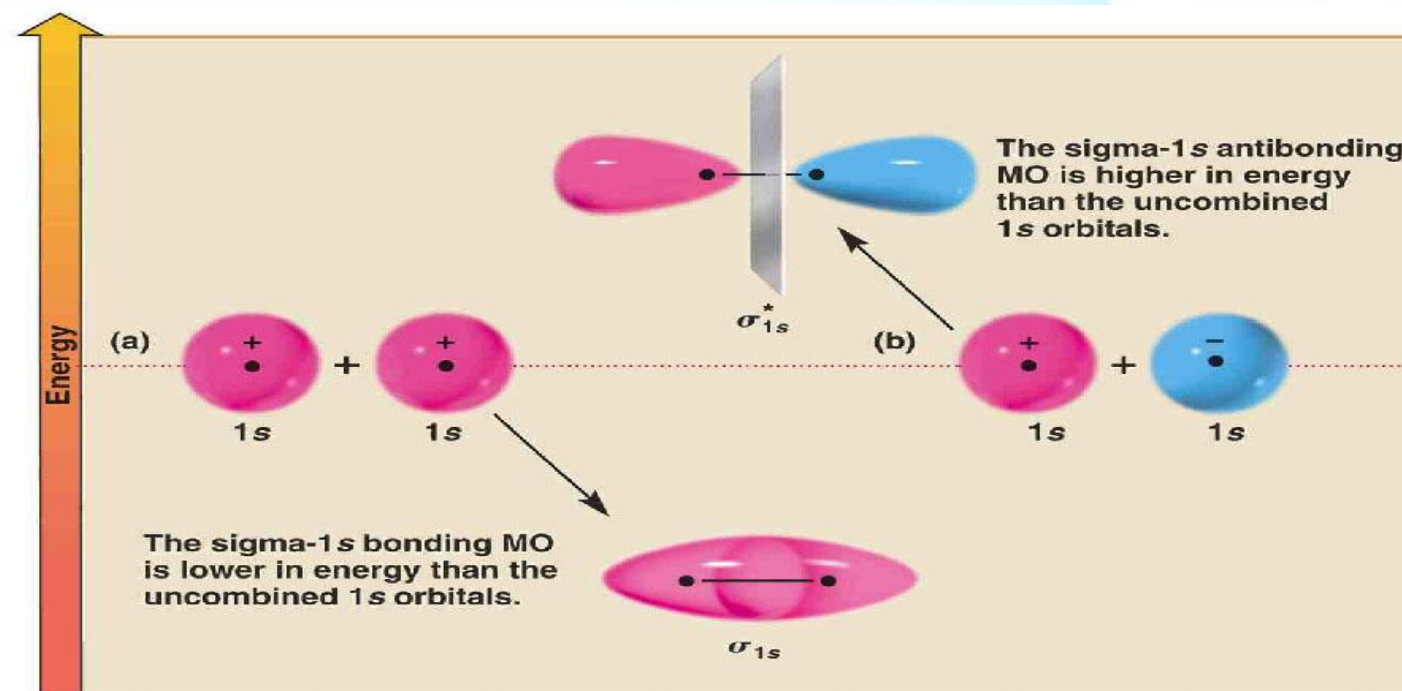
- 1) 分子中的电子在遍及整个分子的范围内运动，每一个电子的运动状态都可以用一个分子波函数来描述。
- 2) 分子轨道可以通过相应的原子轨道线性组合而成。有几个原子轨道进行线性组合，就可形成几个分子轨道。在组合产生的分子轨道中，成键轨道的能量降低，反键轨道的能量升高，但系统总能量守恒。
- 3) 为有效地组成分子轨道，原子轨道必须满足下述三个原则：
 - ✓ 对称性匹配原则
 - ✓ 能量近似原则
 - ✓ 轨道最大重叠原则

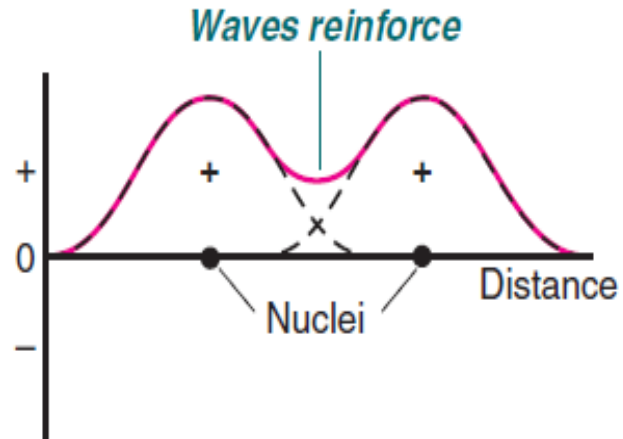


(1) The central themes of MO theory

Formation of molecular orbitals

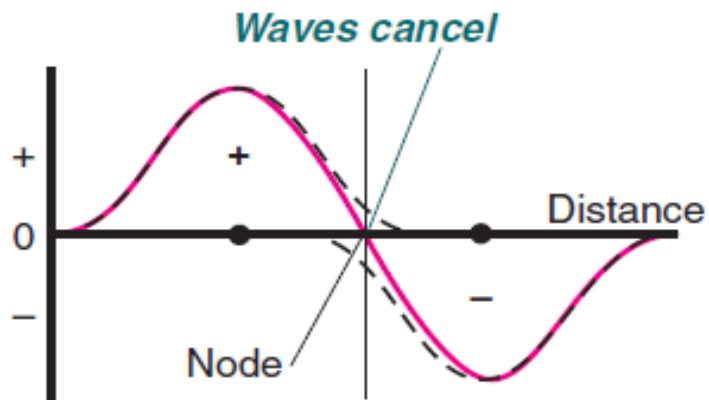
The approximation is to mathematically combine (add or subtract) AOs (atomic wave functions) of nearby atoms to form MOs(molecular wave functions).





A Amplitudes of wave functions added

This combination forms a bonding MO, which has a region of high electron density between the nuclei.



B Amplitudes of wave functions subtracted

This combination forms an antibonding MO, which has a node, a region of zero electron density, between the nuclei.

(2) Electrons in molecular orbitals

1) Filling MOs with electrons. Electrons enter Mos just as they do AOs:

- ✓ MOs are filled in order of increasing energy (Aufbau principle).
- ✓ An MO can hold a maximum of two electrons with opposite spins (exclusion principle).
- ✓ Orbitals of equal energy are half-filled, with spins parallel, before any of them are filled (Hund's rule).

2) MO energy-level diagrams.

A molecular orbital (MO) diagram shows the relative energy and number of electrons for each MO.

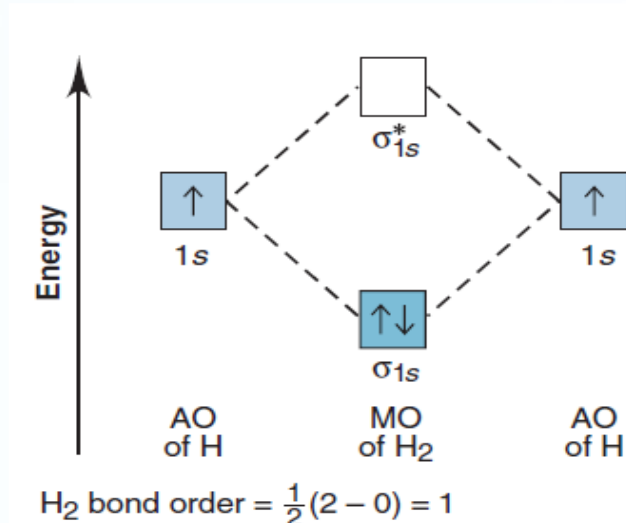
3) Electron configuration.

The electron configuration of H_2 is $(\sigma_{1s})^2$

4) Bond order

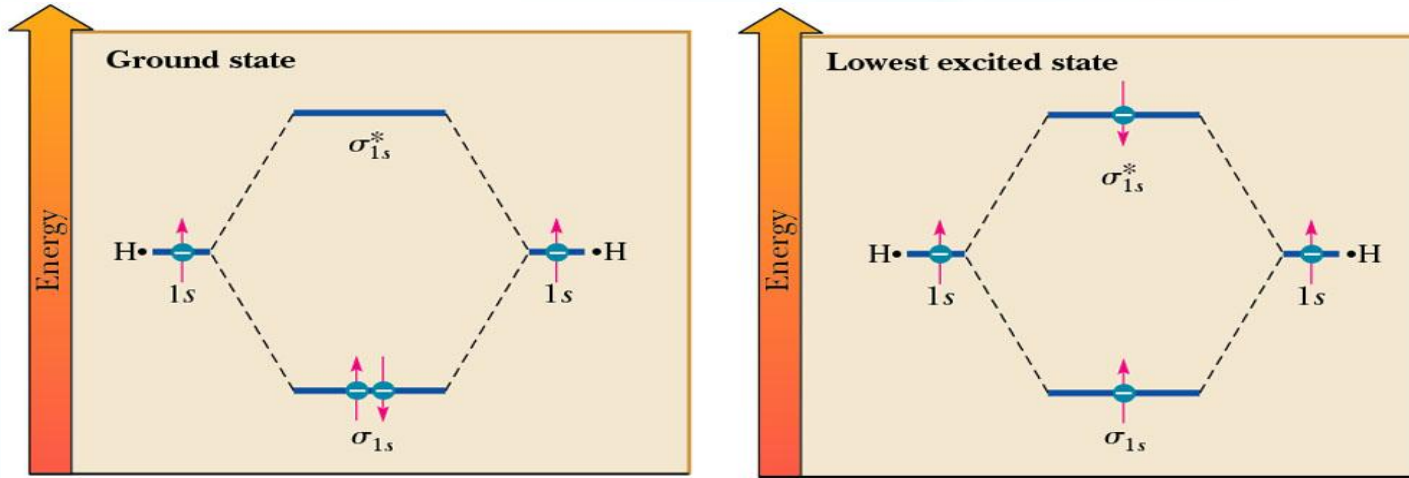
In a Lewis structure, bond order is the number of electron pairs per atom-to-atom linkage. 对双原子分子来说，把成键电子数与反键电子数的差值的一半，称为键级

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



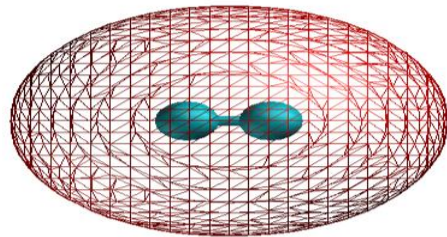
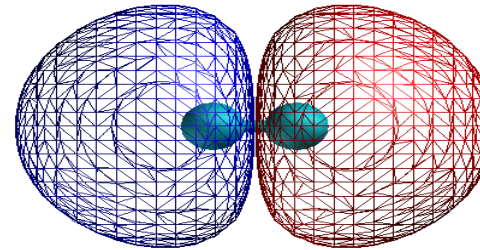
$$H_2 \text{ bond order} = \frac{1}{2}(2 - 0) = 1$$

- MO energy diagram for H_2 : (a) ground state and (b) lowest excited state



© 2006 Brooks/Cole - Thomson

- computed sigma bonding and antibonding MOs for H_2



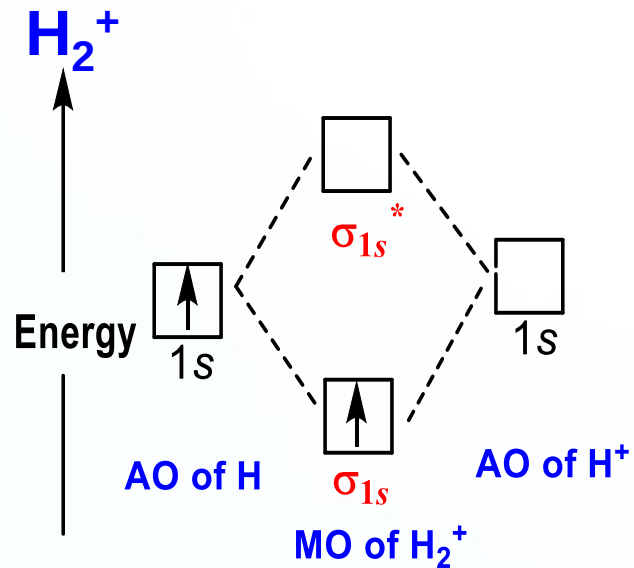
Here are key points about MO bond order:

- ✓ Bond order > 0, the molecule is more stable than the separate atoms, so it will form. For H_2 , the bond order is $\frac{1}{2} (2-0) = 1$.
- ✓ Bond order = 0, the molecule is as stable as the separate atoms, so it will not form.

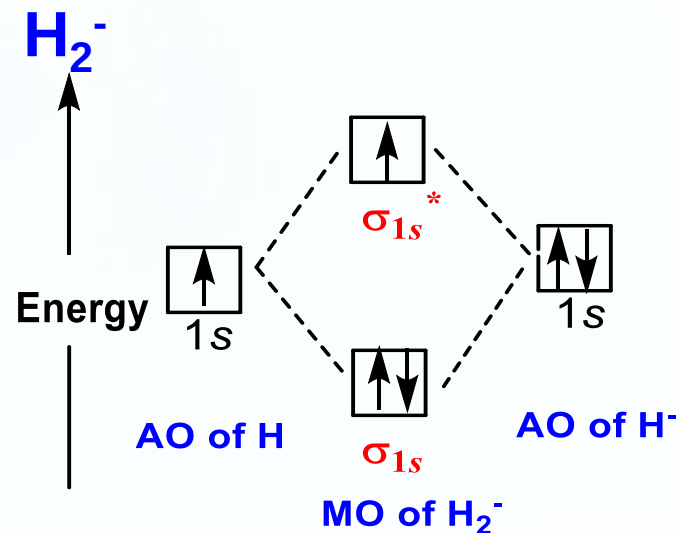
In general, the higher the bond order, the stronger the bond is.

Do H_2^+ and H_2^- exist ?

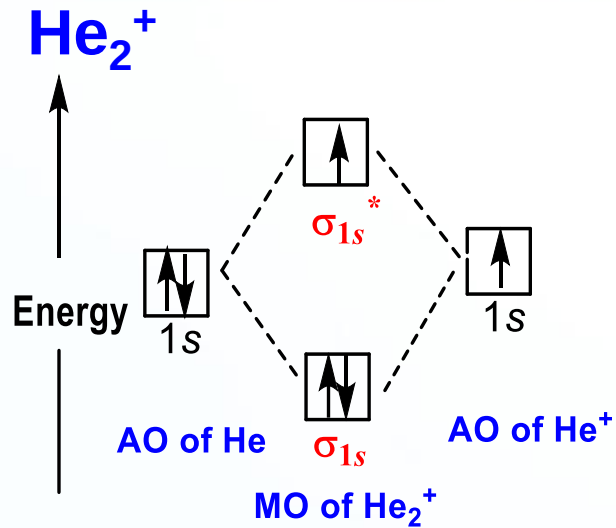
Do He_2^+ and He_2 exist ?



For H_2^+ , H_2 has two e⁻, so H_2^+ has only one, which enters the bonding MO. The bond order is $\frac{1}{2}(1-0)=1/2$, so we predict that H_2^+ exists. The electron configuration is $(\sigma_{1s})^1$.

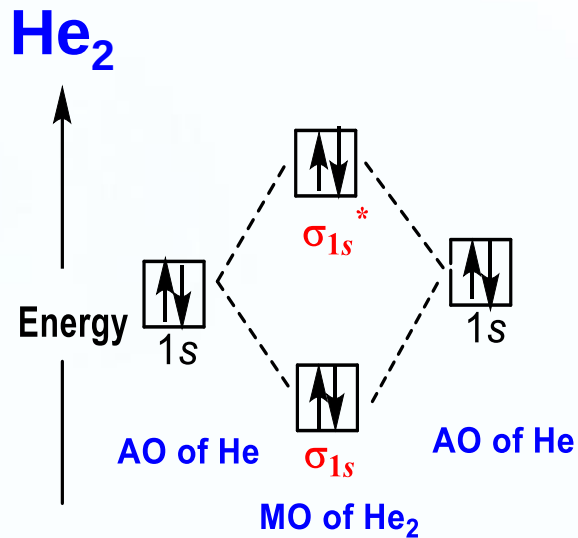


For H_2^- , H_2 has two e⁻, so H_2^- has three. The bond order is $\frac{1}{2}(2-1)=1/2$, so we predict that H_2^- exists. The electron configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^1$.



A He₂⁺ bond order = 1/2

He₂⁺ has a relatively weak bond, but it should exist. Its electron configuration is $(\sigma_{1s})^2(\sigma_{1s}^*)^1$

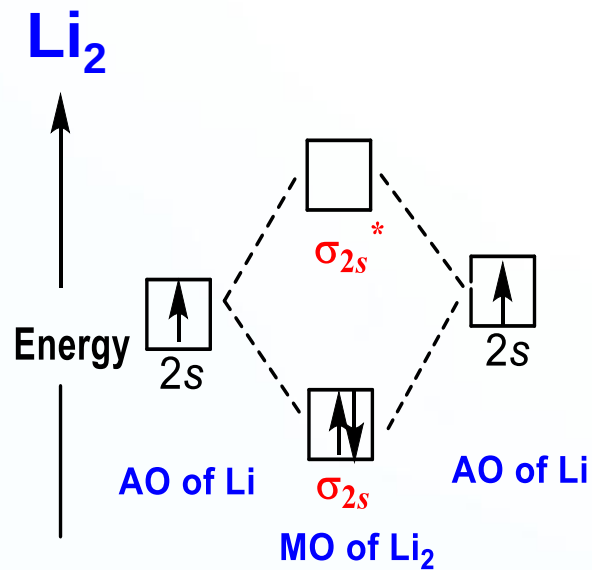


A He₂ bond order = 0

In He₂, with four electrons in the σ_{1s} and σ_{1s}^* MOs, both the bonding and antibonding orbitals are filled. A covalent He₂ molecule does not exist.

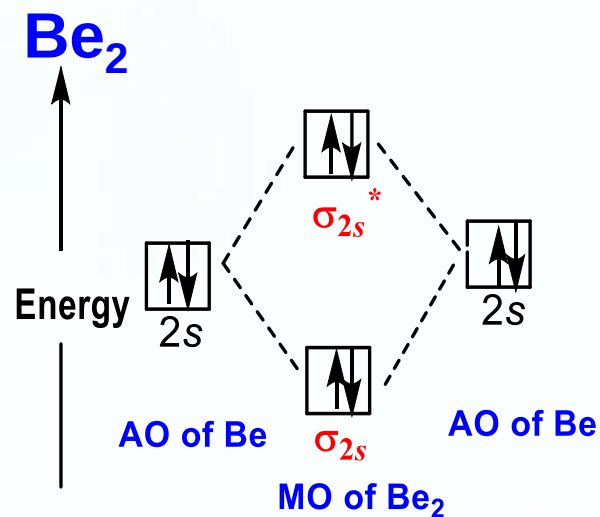


(3) Homonuclear diatomic molecules



A Li₂ bond order = 1

Li₂ has been observed, the electron configuration is $(\sigma_{2s})^2$

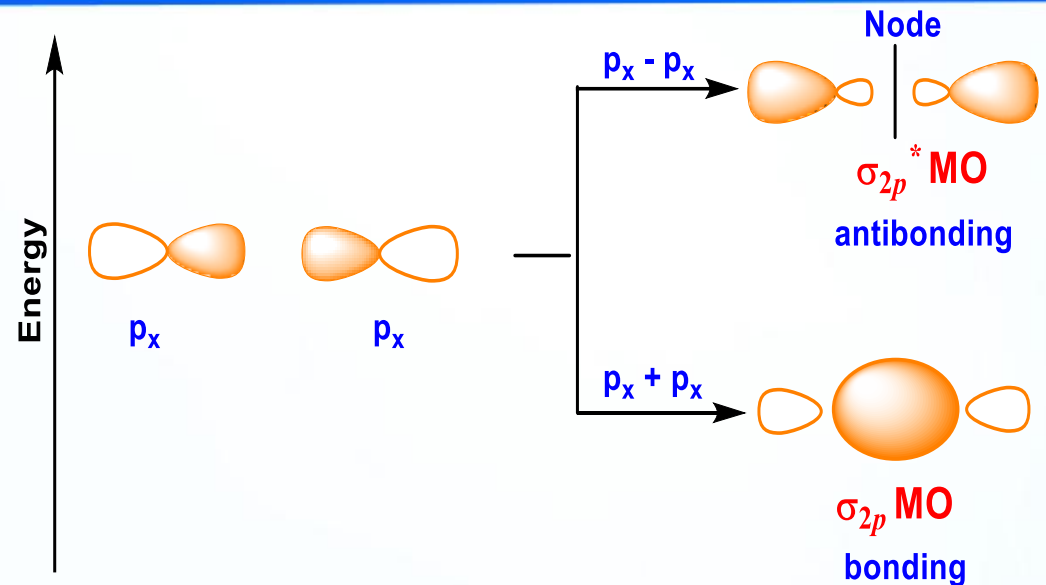


A Be₂ bond order = 0

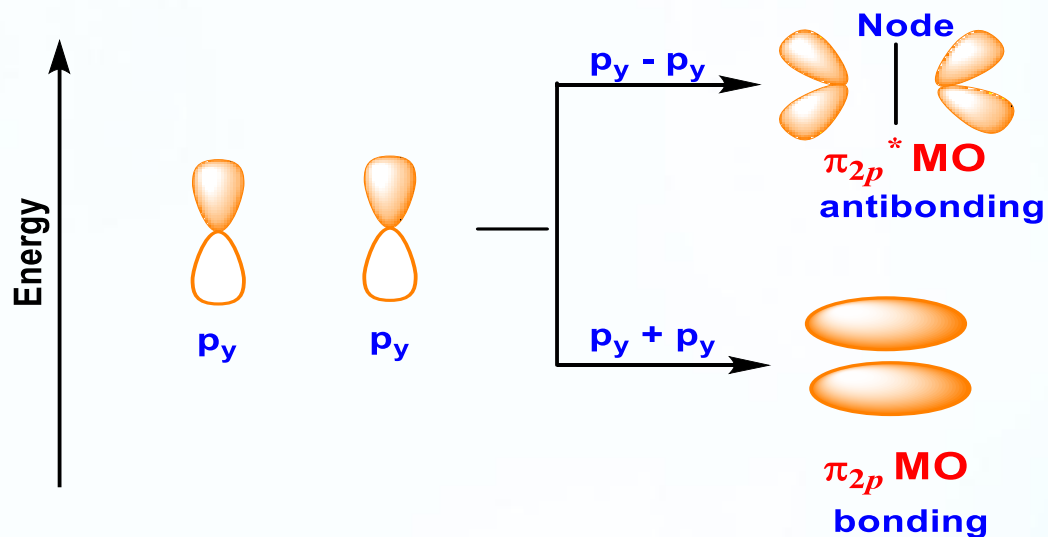
The ground state of Be₂ has never been observed.



Shape of MOs from atomic p-orbital combinations

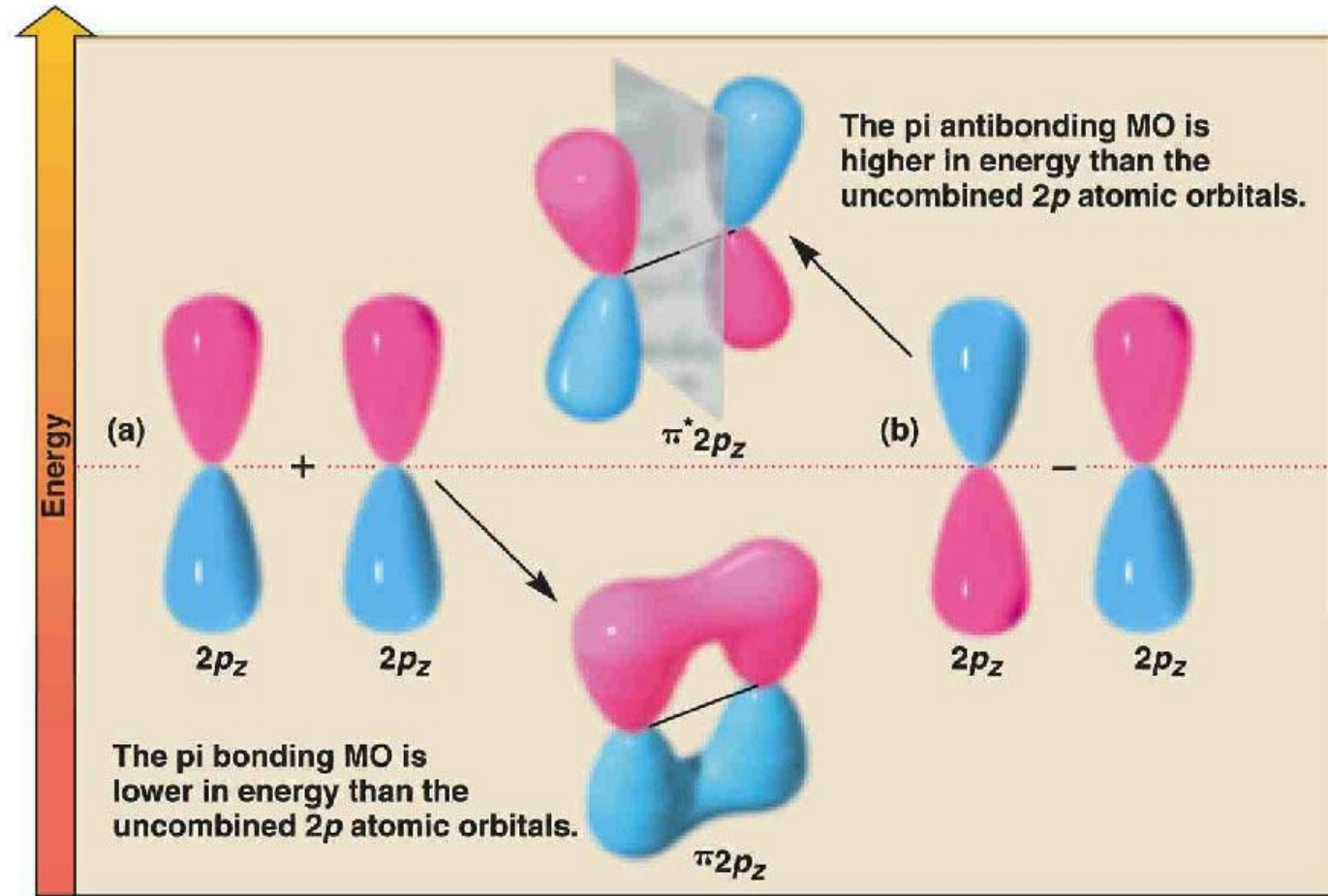


End-to-end combination gives a pair of σ MOs, the σ_{2p} and σ_{2p}^* .



Side-to-side combination gives a pair of Pi (π) MOs, the π_{2p} and π_{2p}^* .

■ pi bonding and antibonding MOs



The order of energy levels for MOs, whether bonding or antibonding, is based on the order of AO energy levels and on the mode of the p-orbital overlap:

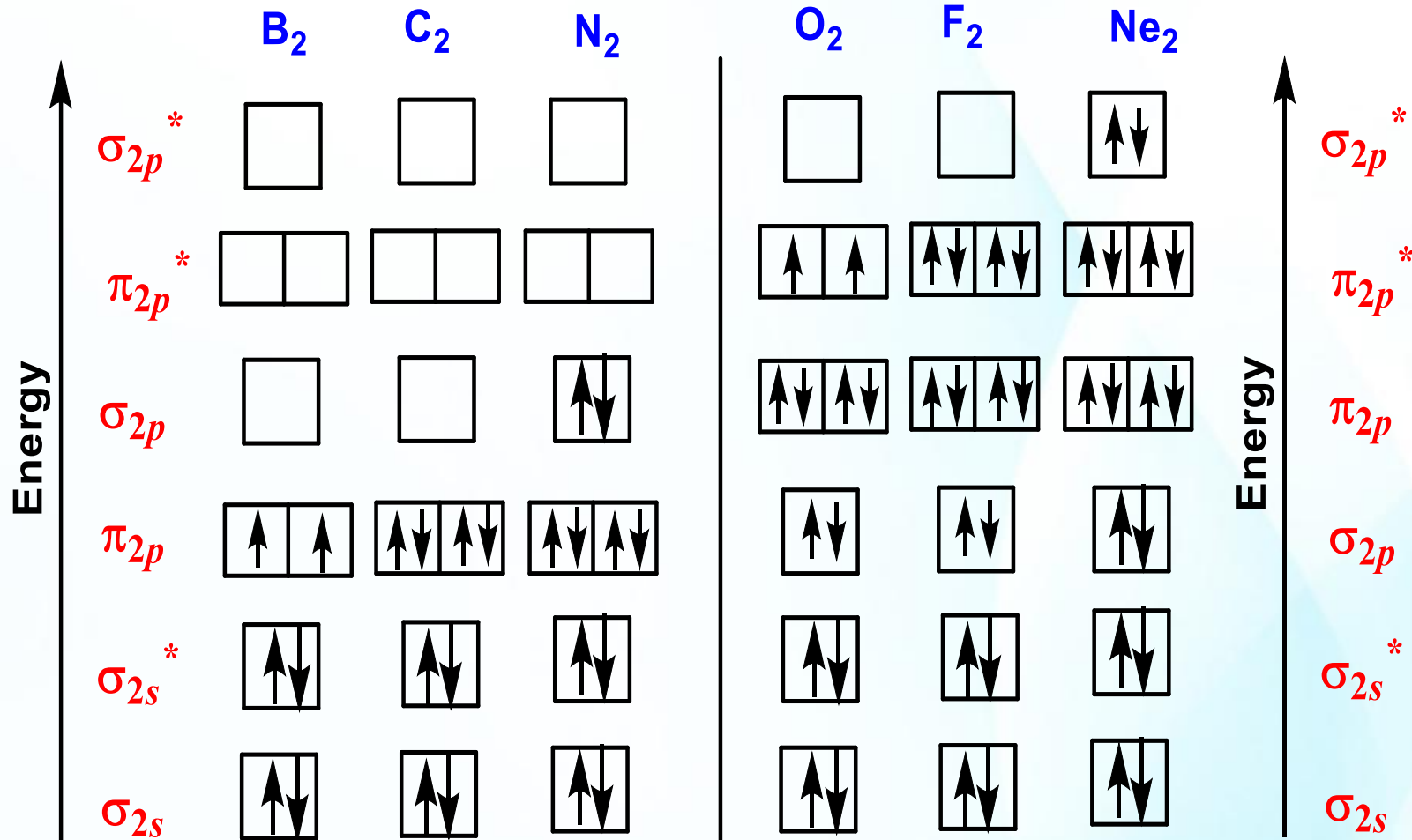
- ✓ MOs formed from 2s orbitals are lower in energy than MOs formed from 2p orbitals because 2s AOs are lower in energy than 2p AOs.
- ✓ Bonding MOs are lower in energy than antibonding MOs: σ_{2p} is lower in energy than σ_{2p}^* and π_{2p} is lower than π_{2p}^* .
- ✓ Atomic p orbitals overlap more extensively end to end than side to side.

Thus, the σ_{2p} MO is usually lower in energy than the π_{2p} MO.

- ✓ 同核双原子分子的分子轨道能级次序: $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2px} < \pi_{2py} =$

$$\pi_{2pz} < \pi_{2py}^* = \pi_{2py}^* < \sigma_{2px}^*$$

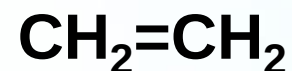
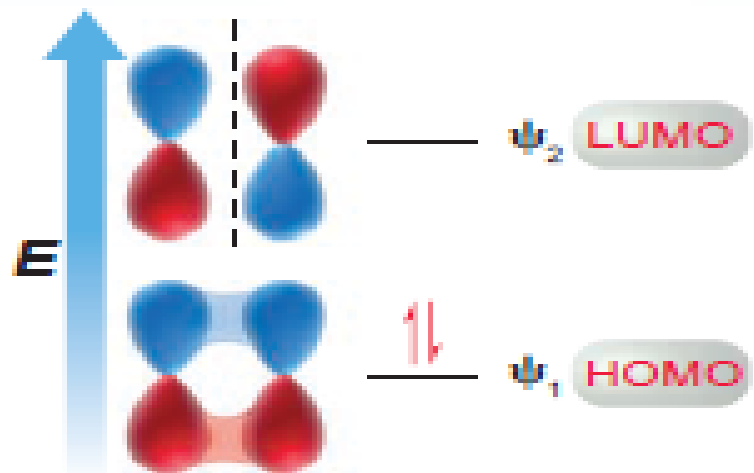
Homonuclear Diatomic Molecules (p-block)





◆ 乙烯

- 分子轨道理论主要用来处理p电子或 π 电子。



乙烯分子中有两个未参加杂化的p轨道，这两个p轨道可通过线性组合而形成两个分子轨道(π 轨道)。

能量最高已占轨道
(HOMO)

Highest Occupied
Molecular Orbital

核对这些电子的
束缚最松弛

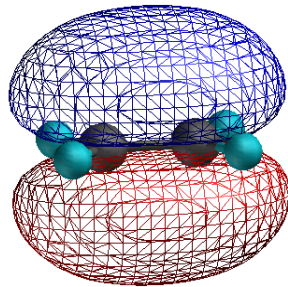
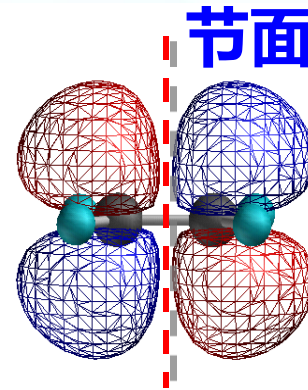
能量最低空轨道
(LUMO)

Lowest Unoccupied
Molecular Orbital

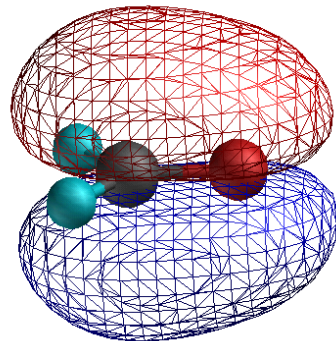
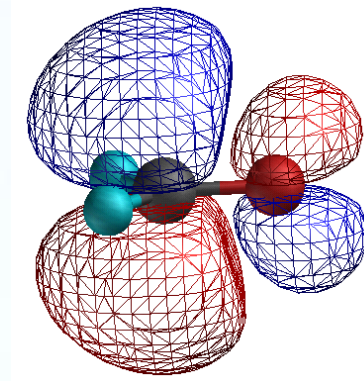
前线轨道

FMO (Frontier Molecular Orbital)

- computed pi bonding and antibonding MOs for ethylene.

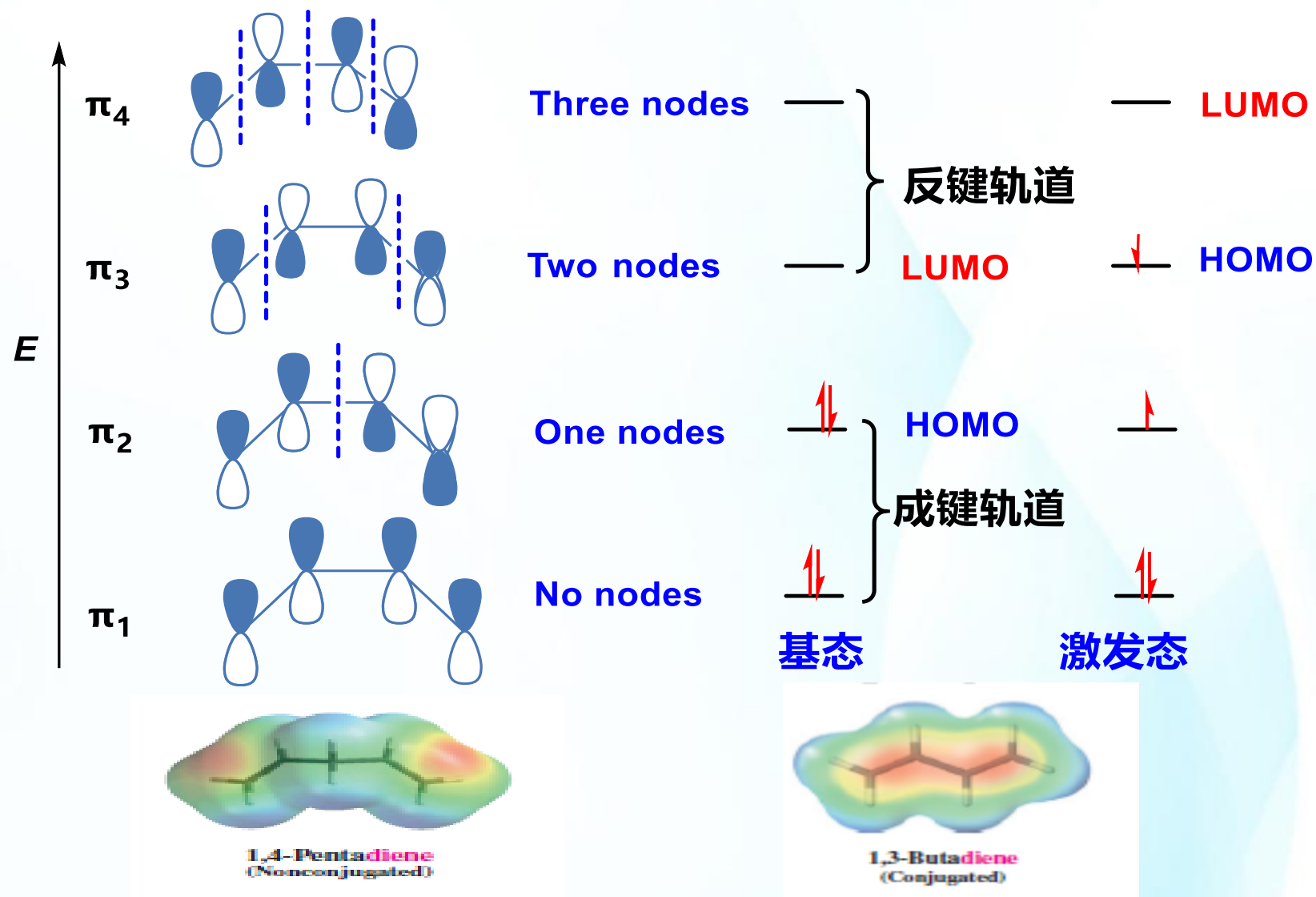


- computed pi bonding and antibonding orbitals for formaldehyde



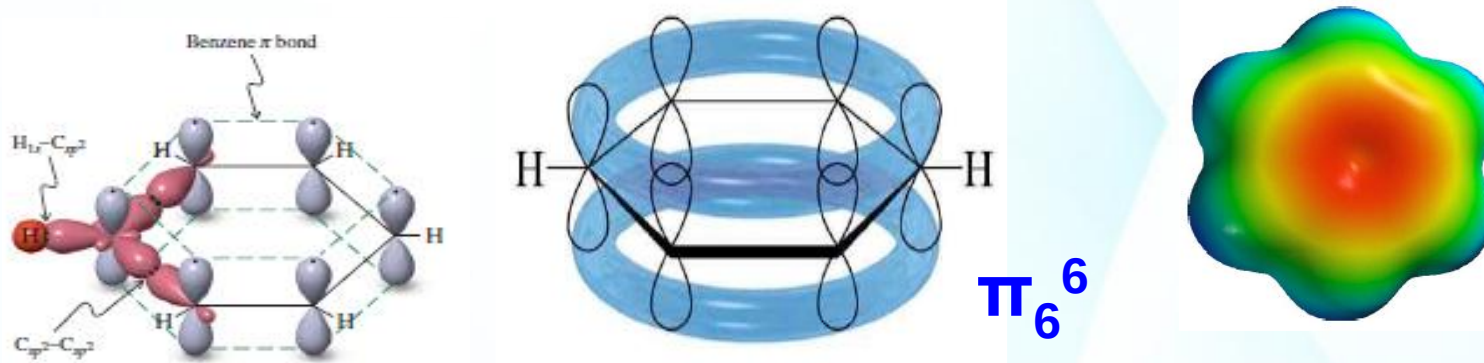
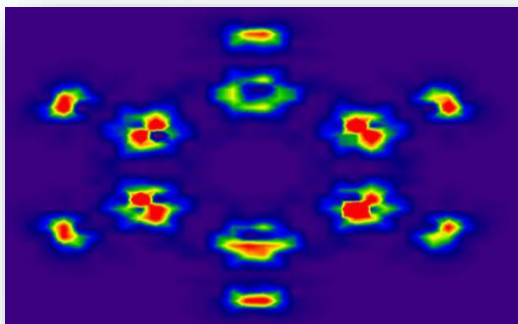


◆ 丁二烯



Each sp^2 hybridized C in the ring has an unhybridized p orbital perpendicular to the ring which overlaps around the ring

Benzene (C_6H_6) is not “cyclohexatriene!”



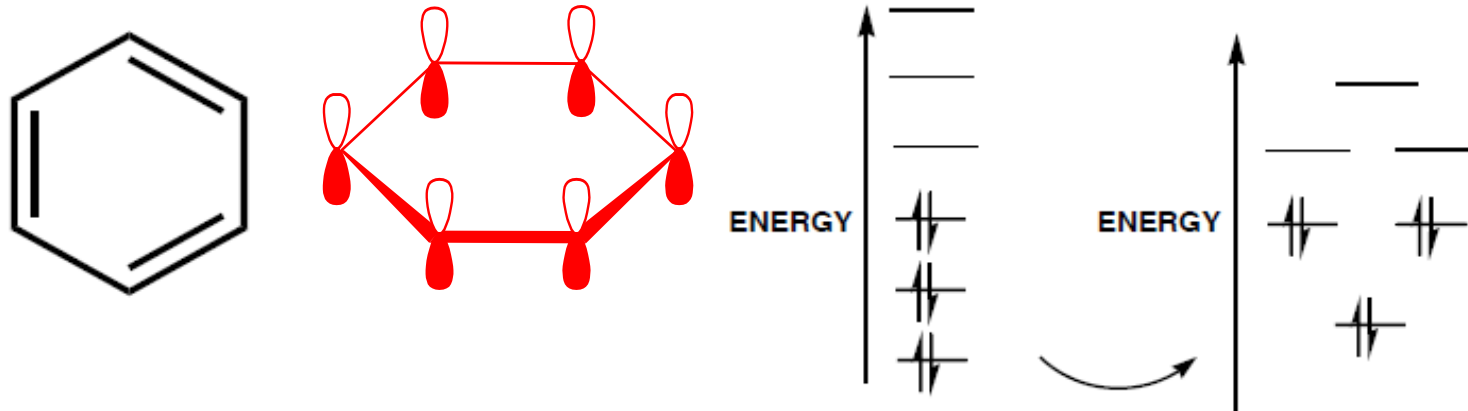
苯分子的扫描隧道显微镜照片

苯分子结构中，形成闭合的 π - π 共轭体系， π 电子高度离域，电子云密度完全平均化，环上没有单、双键的区别，形成非常稳定的体系。

◆ 分子轨道理论对苯分子结构的解释

MO Rules for Benzene □

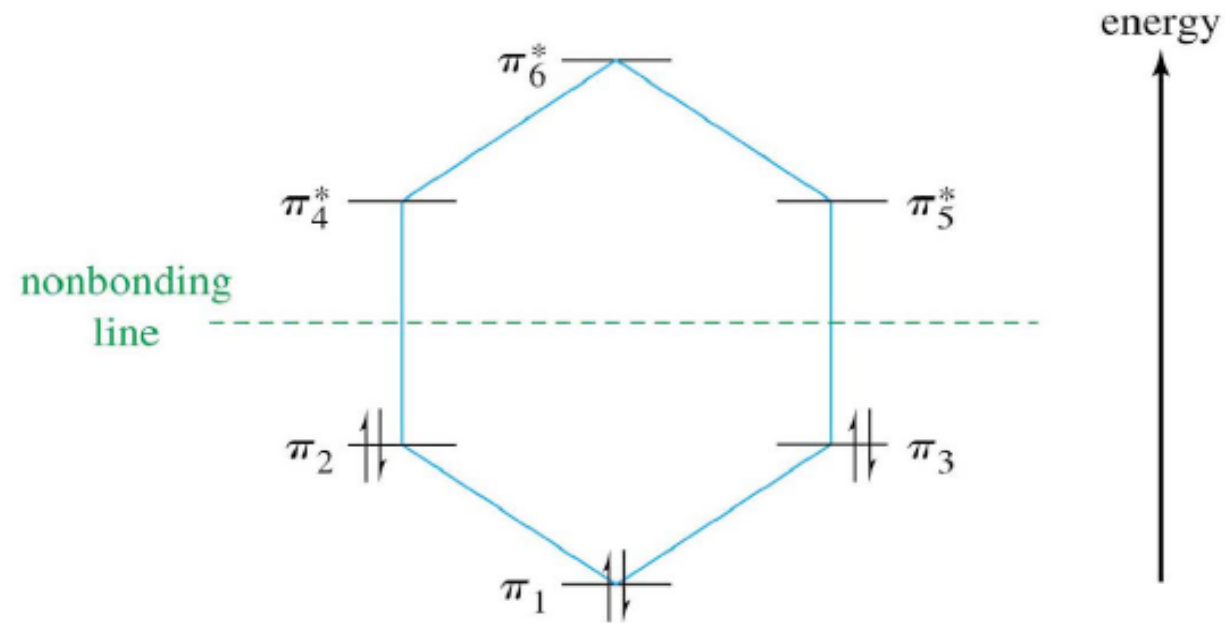
- Six overlapping p orbitals must form six molecular orbitals
- Three will be bonding, three antibonding
- Lowest energy MO will have all bonding interactions, no nodes
- As energy of MO increases, the number of nodes increases
- System symmetric so 2 pairs of degenerate orbitals



Energy Diagram for Benzene $\square$

6 atomic orbitals - 6 molecular orbitals

System symmetric so 2 pairs of degenerate orbitals



The six electrons fill three bonding pi orbitals.

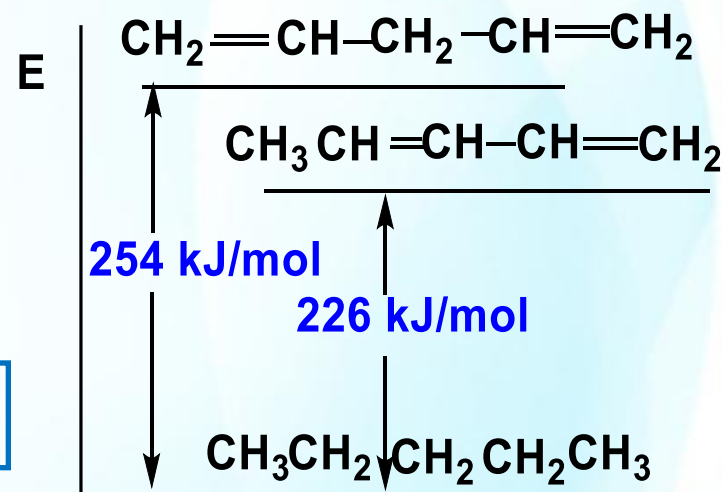
All bonding orbitals are filled ("closed shell"), an extremely stable arrangement (AROMATIC STABILIZATION).



- **共轭效应**：在能形成共轭 π 键的体系中（**共轭体系**中）由于相邻 p 轨道的重叠而产生的电子间的相互流动，致使**体系能量降低**，**键长平均化**，**分子趋于稳定的电子效应**。
- **共轭体系**：三个或三个以上**互相平行的 p 轨道**形成的大 π 键。
- **电子离域**：共轭体系中，成键电子运动范围扩大的现象。
电子离域使共轭体系能量降低。

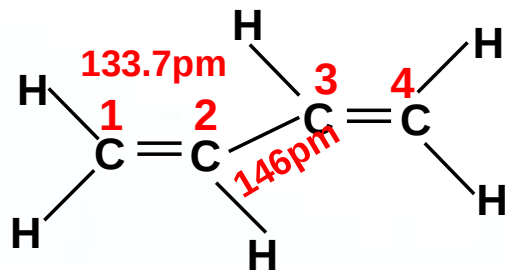
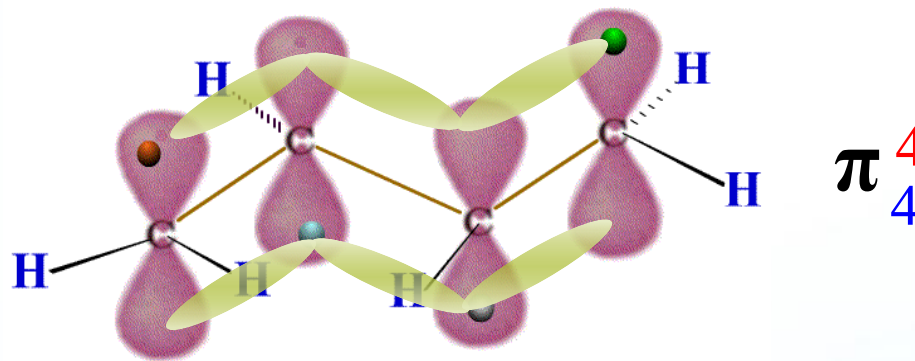
离域能-键的离域而导致分子更稳定的能量（ **$254 - 226 = 28\text{kJ/mol}$** ）。

离域能**越大**,表明此共轭体系**越稳定**。

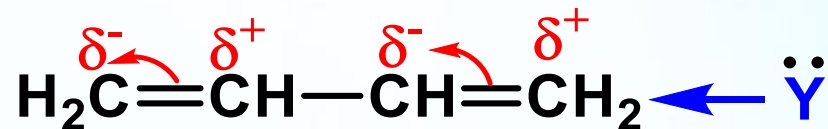




• π - π 共轭



- π - π 共轭体系的结构特征是单双键交替。

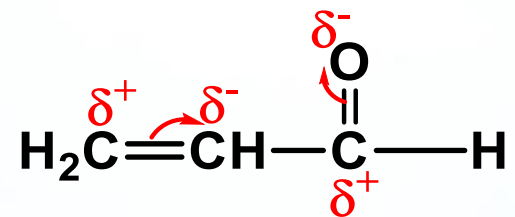
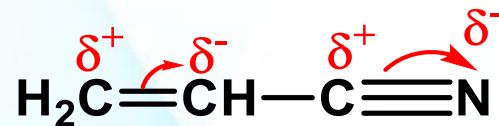


共轭体系的表示及其特点:

- ①用弯箭头表示由共轭效应引起的电子流动方向;
- ②共轭碳链可产生极性 (正负电荷) 交替现象;
- ③共轭效应不随共轭链增长而减弱。



- ✓ 形成 π - π 共轭体系的重键不限于双键，**叁键**亦可；组成共轭体系的原子亦不限于碳原子，**氧、氮原子**均可。



- ✓ **吸电子共轭效应 (-C)**：凡共轭体系上的取代基能**降低体系的电子云密度**，称吸电子共轭效应。

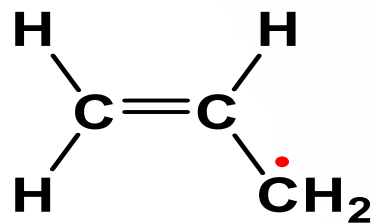
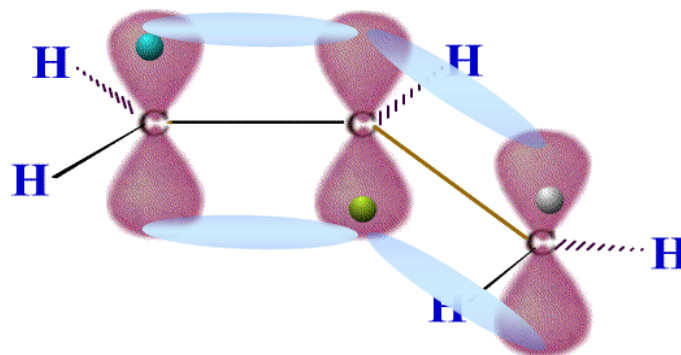
如：-NO₂, -COOH, -CHO等。

- ✓ **给电子共轭效应 (+C)**：凡共轭体系上的取代基能**增加体系的电子云密度**，称给电子共轭效应。

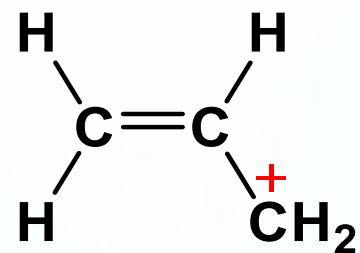
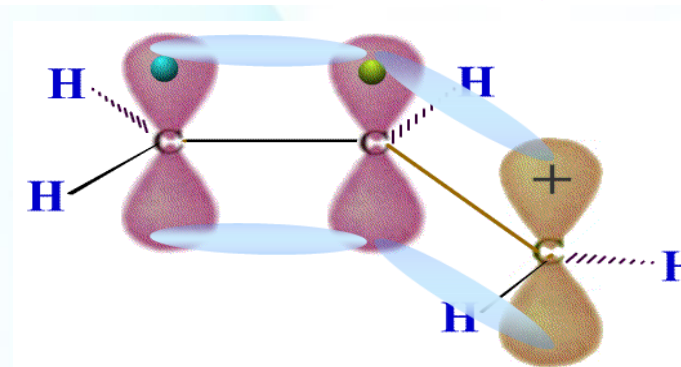
如：-NH₂, -OH等。



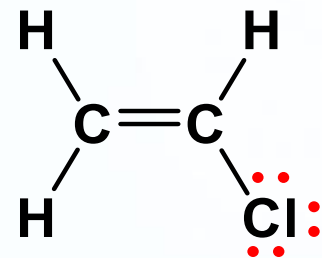
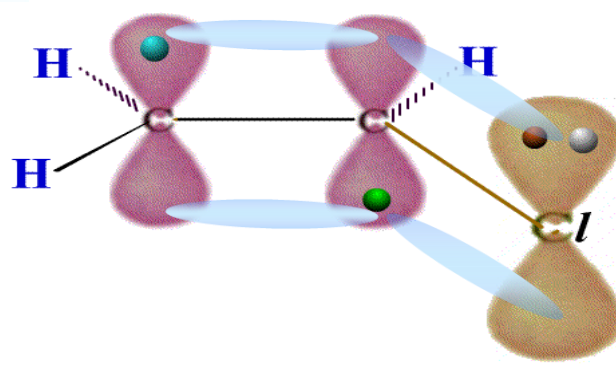
π_3^3



π_3^2



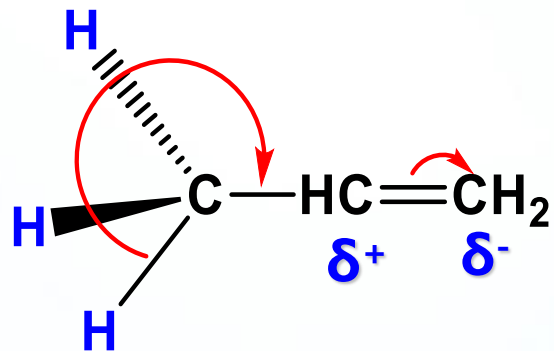
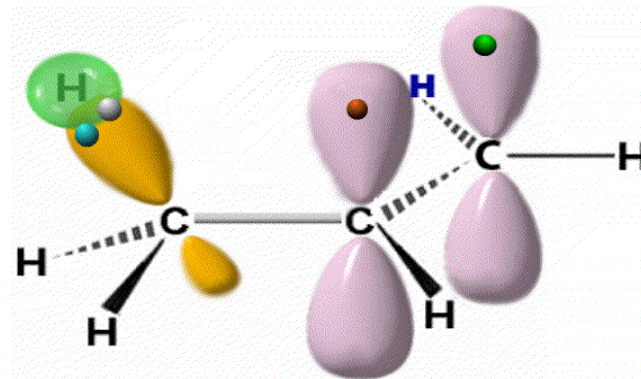
π_3^4



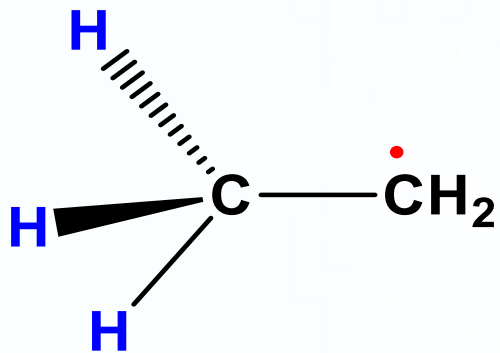
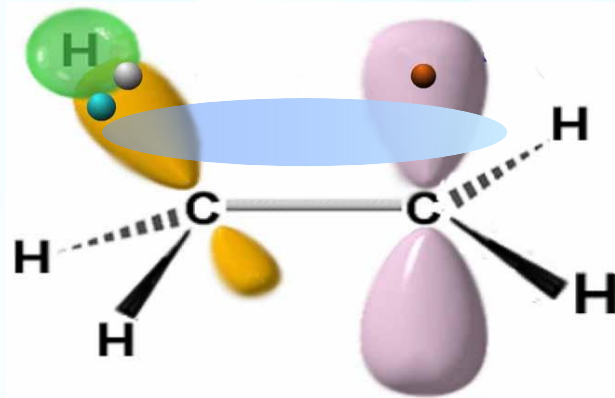


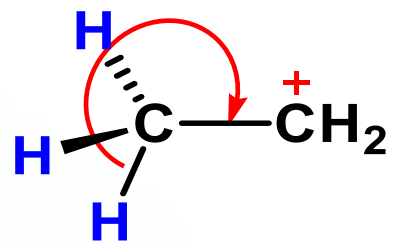
• σ - π 超共轲

起因于 π 键与相邻 C-H σ 键的重叠。

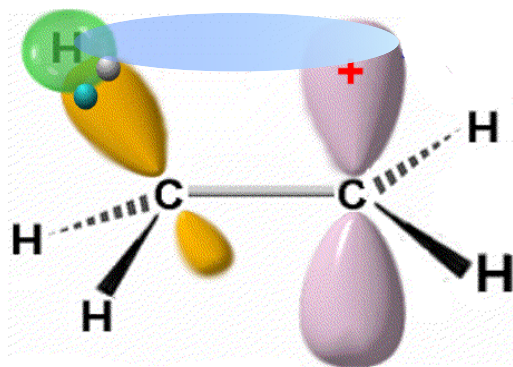
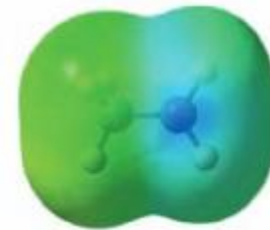


• σ - p 超共轲

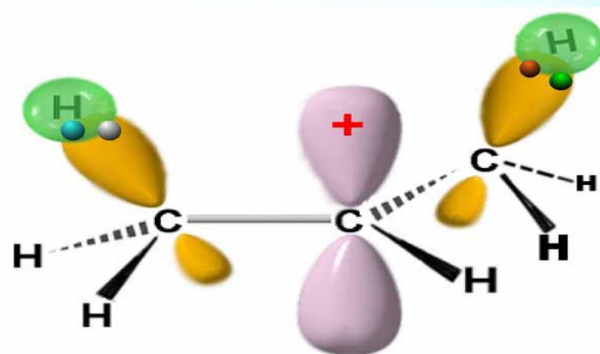
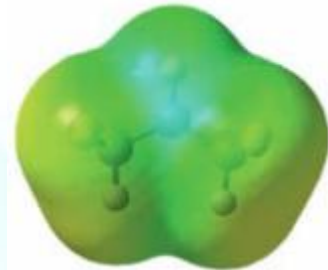
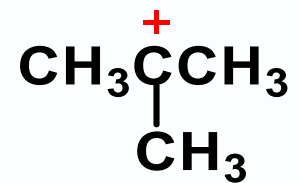




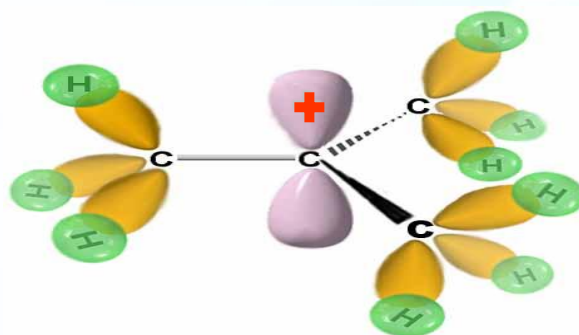
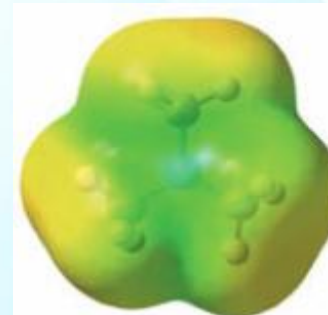
3 (σ - p)



6 (σ - p)



9 (σ - p)



Summary

1. VBT基本要点;
2. 杂化轨道和类型;
3. 共价键类型;
4. MOT基本要点;
5. 同核双原子（第二周期）的分子轨道与乙烯、丁二烯、苯的分子轨道;
6. 共轭效应。



也许有一天, 不知不觉, 你将渐渐活出写满答案的人生!