

CHEM103

General Chemistry

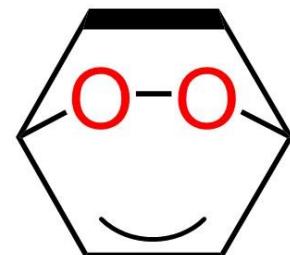
Chapter 9: Molecular Geometries and Bonding Theories



Dr. ($O_6S_4C_4Ar$) Lung Wa CHUNG(钟龙华)
oscarchung@sustech.edu.cn

luation, Inc.

Department of Chemistry
SUSTech



Assignments 8-9 & Mid-term EXAM

Homework 8

Due date: 7th Nov. (Mon)

Homework 9

Due date: 9th Nov. (Wed)

Q&A + Course Review

Due date: 9th Nov. (Wed)

Mid-term exam (Chapters 1-9)

Bring your calculator & student ID card

10:00AM-12:00 PM, 13th Nov. (Sun).

Review on Chapter 8

Lewis Symbol, Octet Rule

1. Ionic Bond: Lattice Energy
2. Covalent Bond: Polar, Dipole Moment, Formal Charge, Bond Strength/Enthalpy
 3. Metallic Bond

Electronegativity, Lewis Structure,
Resonance, Localized and Delocalized
Electrons

Outline of Chapter 9

Valence-Shell Electron-Pair Repulsion Theory (VSEPR): (Non)Bonding Electron Pairs, Electron Domains, Molecular Geometry

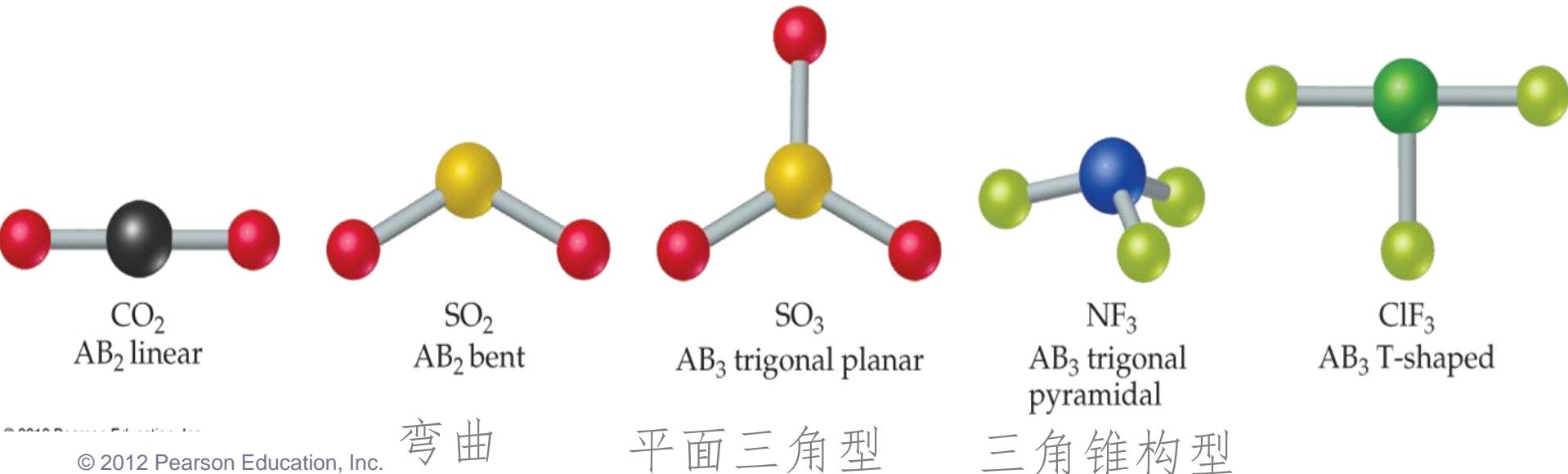
Valence Bond (VB) Theory: Orbital Overlap, Hybrid Orbital, Hybridization

Molecular Orbital (MO) Theory: Orbital Overlap (linear combinations), Bonding Molecular Orbital, Anti-bonding Molecular Orbital, Bond Order, Energy-Level Diagram

(σ) Sigma-Bond, (π) Pi-Bond, Paramagnetism & Diamagnetism

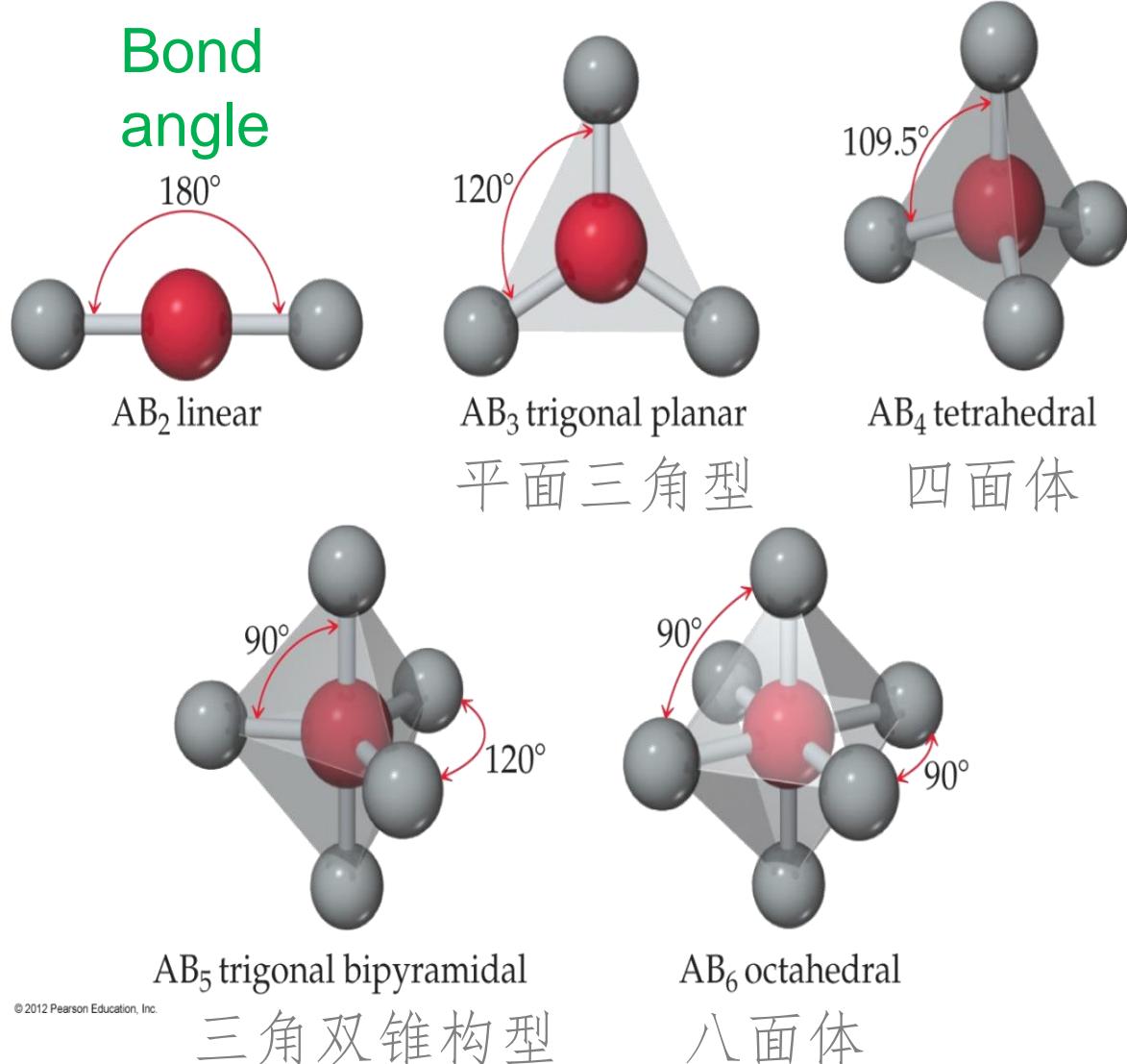
Molecular Shapes

- The **shape** of a molecule plays an important role in its **reactivity and properties**.
- By counting the **number of bonding & non-bonding electron pairs**, we can easily **predict the shape** of the molecule.



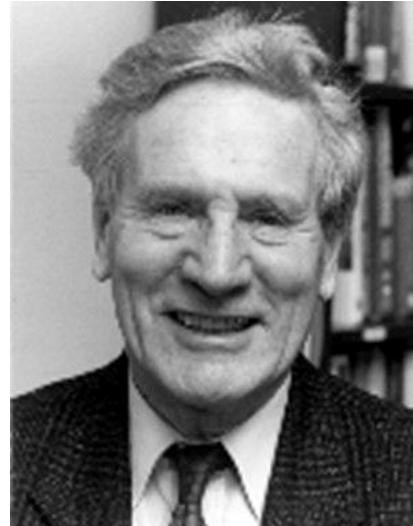
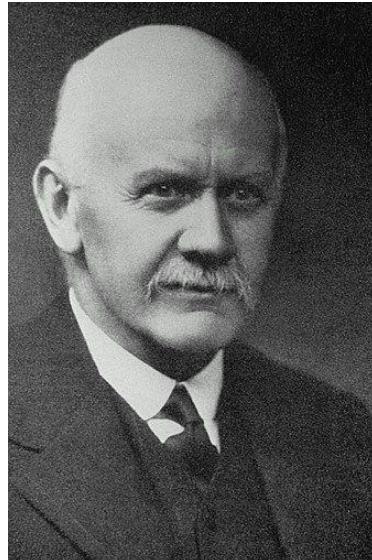
What Determines the Shape of a Molecule?

- (bonding or non-bonding) **Electron pairs repel** each other.



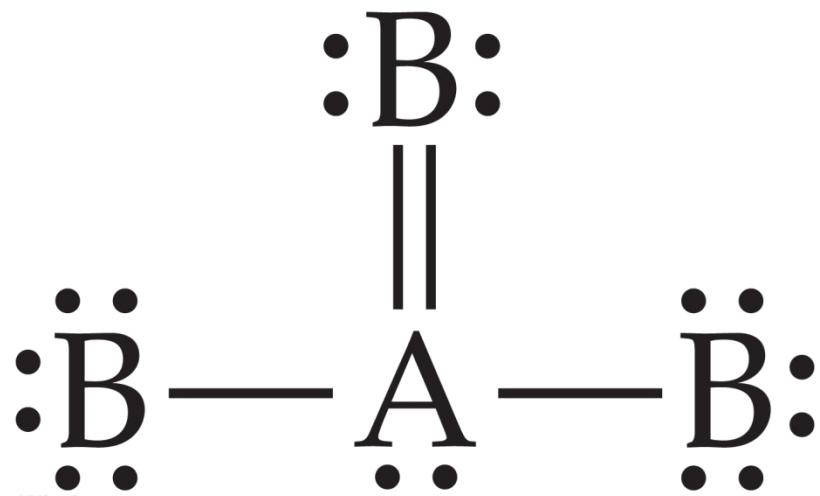
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Valence-Shell Electron-Pair Repulsion Theory (VSEPR) (价层电子对排斥理论)



Nevil Vincent Sidgwick Ronald James Gillespie

Electron Domains



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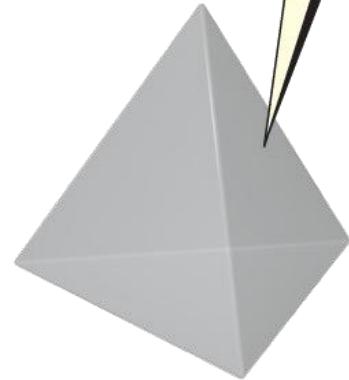
- The central atom (A) has **four** electron domains.
- The left & right **B** atoms have **four** electron domains.
- The top **B** atom has **three** electron domains.

- **Electron domains** (域): a region where electrons stay most likely: **Electron pairs** (bonding pairs and/or non-bonding pairs).

- Each electron pairs can contribute one domain.
- For a **double or triple bond**, all electrons shared between those two atoms are only counted as **one electron domain** in total.

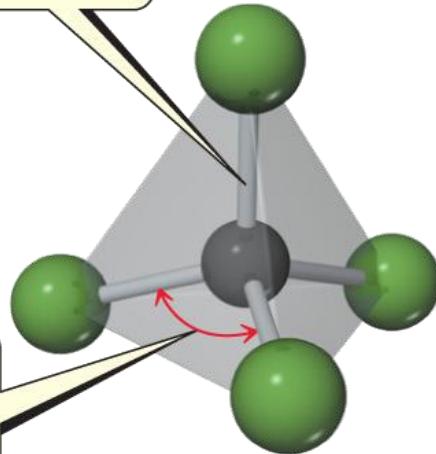
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Four equivalent faces

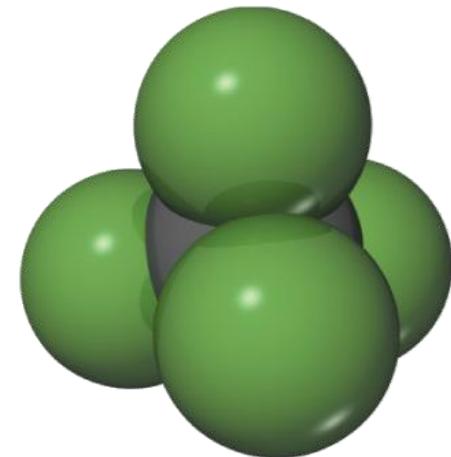


Tetrahedron

All C—Cl bond lengths 1.78 Å



Ball and stick model

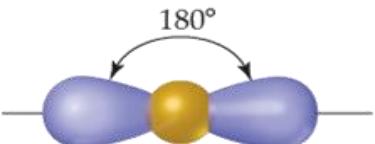
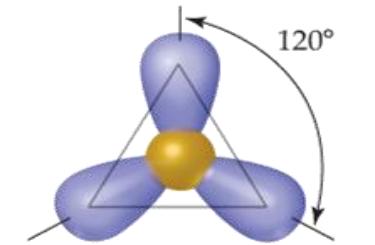
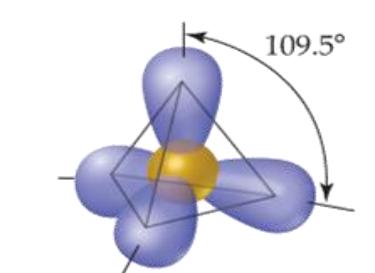
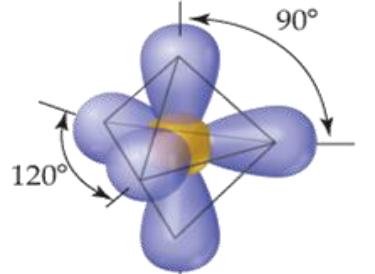
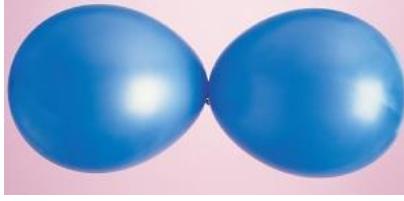
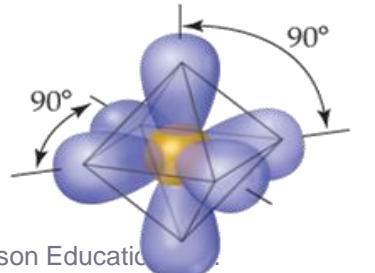


Space-filling model

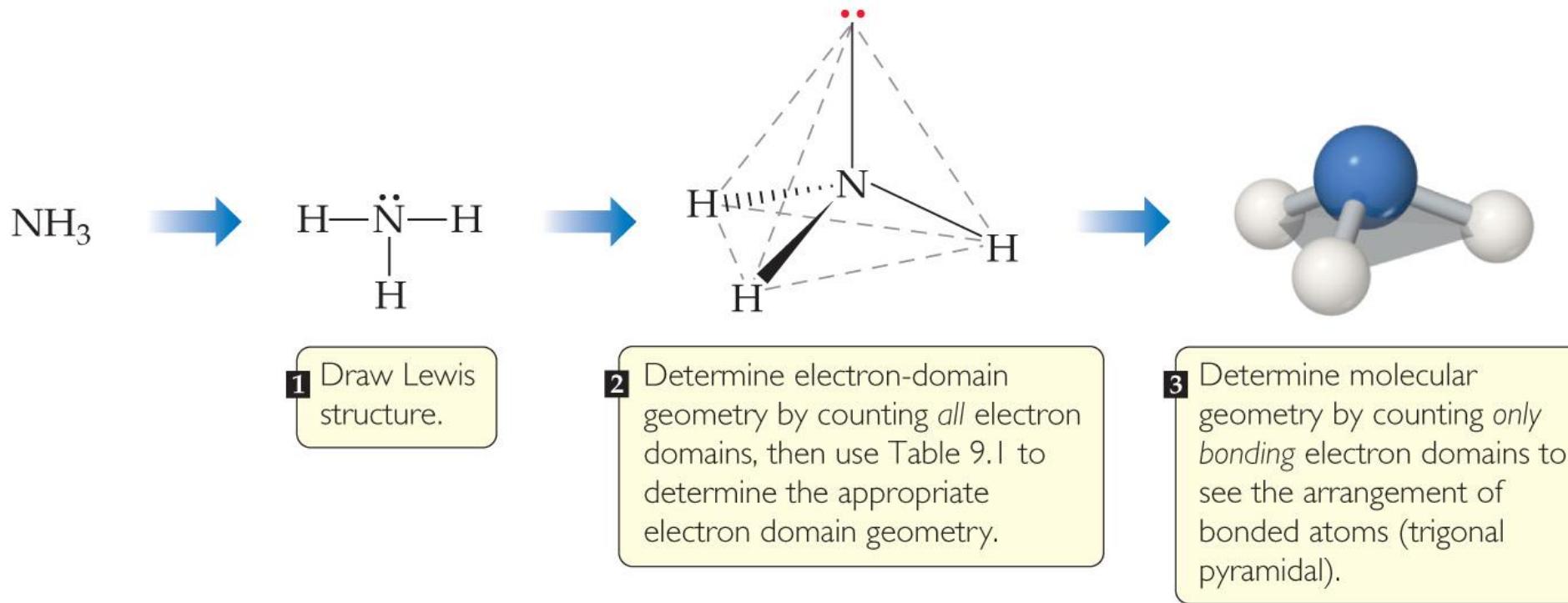
The **best arrangement** of a given number of electron domains: the one **minimizes the repulsions among the electron domains**.



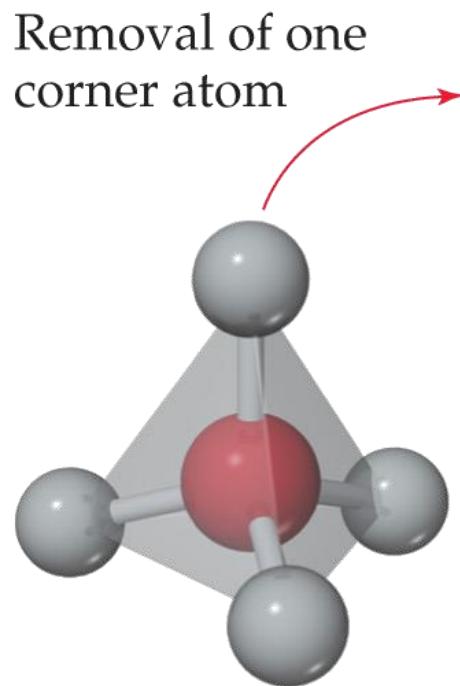
- Draw a Lewis structure.
- **Count the number of electron domains** in the Lewis structure.
- The **electron-domain geometry** is determined by the number of electron domains (see the next slide).

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

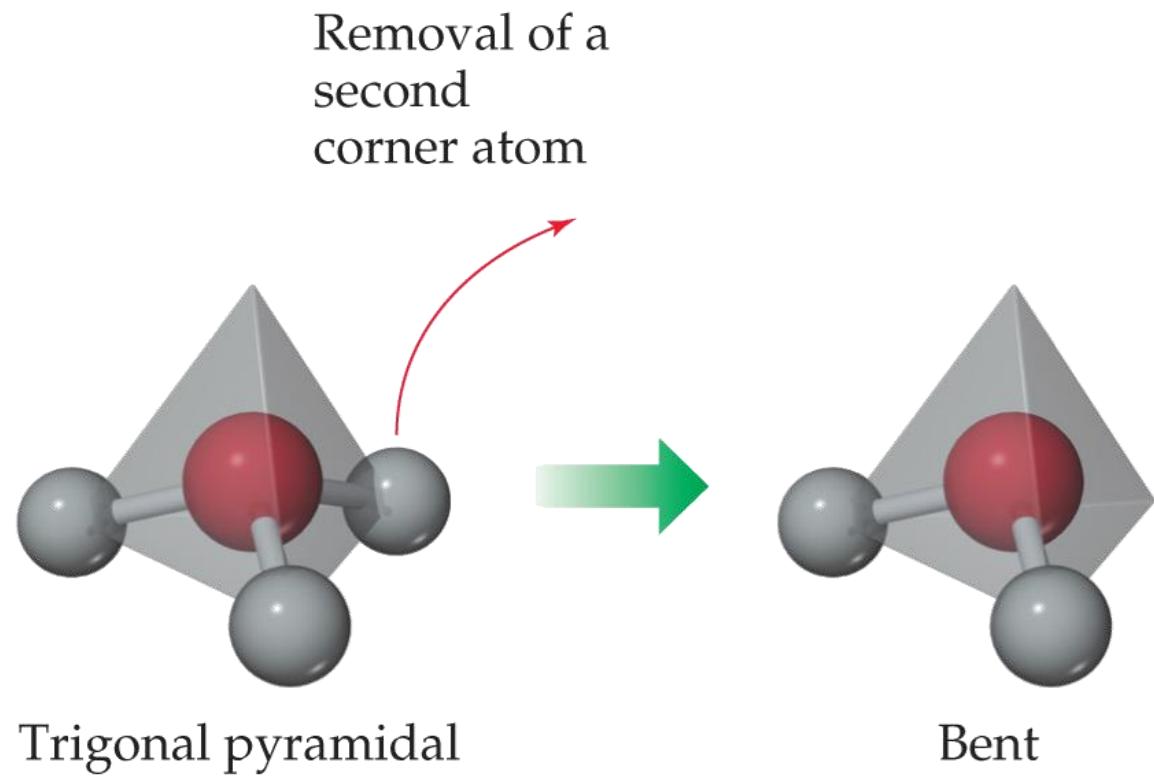
Molecular Geometries



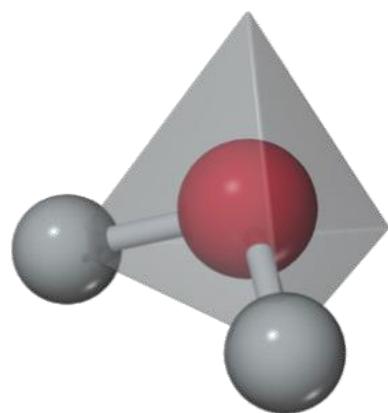
- The **electron-domain geometry** is often **NOT** the **shape of the molecule**.
- The **molecular geometry** is defined by the arrangement of **only the bonded atoms** in the molecules, **NOT the non-bonding pairs**.



Tetrahedral



Trigonal pyramidal



Bent

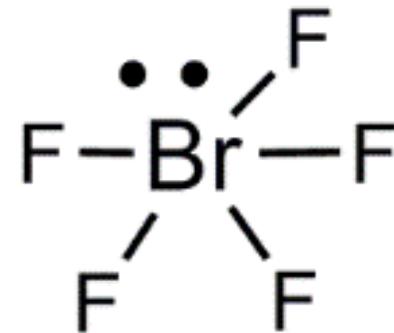
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Within each electron domain, there could be **more than one** molecular geometry.

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How to use VSEPR

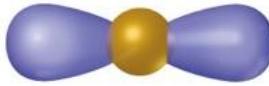
- 1) **Draw** a Lewis structure for the molecule or ion.
(I skip lone-pairs on F for simplicity)



- 2) **Count** the number of **electron domains** for the **central atom** (n): For BrF_5 , $n = 6$.
- 3) **Relate n to the type of structure.** E.g. $n = 6$, → **octahedral (electron-domain geometry)**.
- 4) Place lone pairs in expected positions, **maximizing separation of lone pairs**. For **molecular geometry** of BrF_5 , ignore one lone pair → **square pyramidal**.

Linear Electron Domain

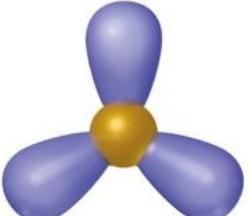
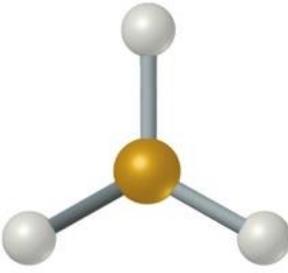
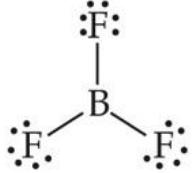
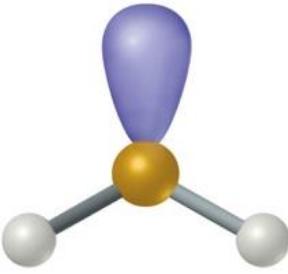
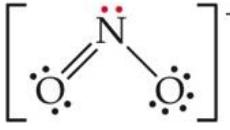
Table 9.2 Electron-Domain and Molecular Geometries for Two, Three, and Four Electron Domains around a Central Atom

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

- In the **linear domain**, there is **only one molecular geometry**: **linear**.
- If there are **only two atoms** in the molecule (EX), the molecule is linear no matter what the electron domain is.

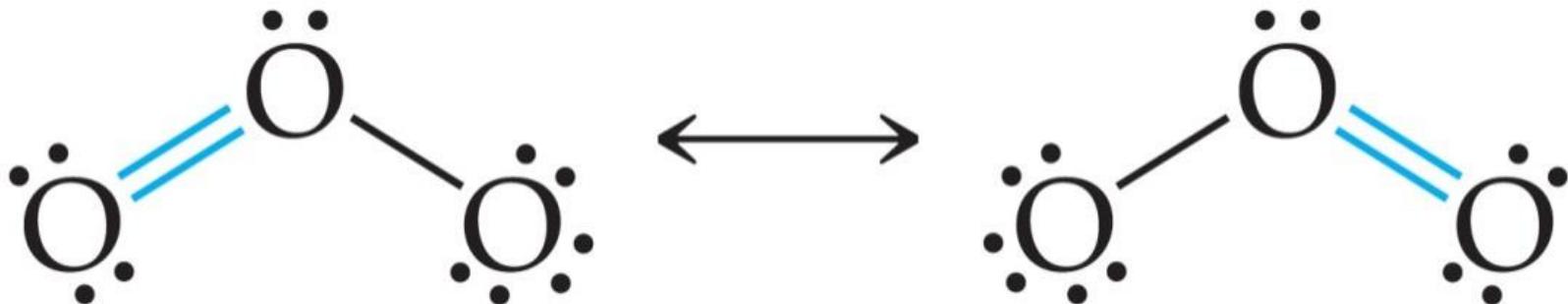
3 Electron Domains: Trigonal Planar

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
3		3	0		
	Trigonal planar				

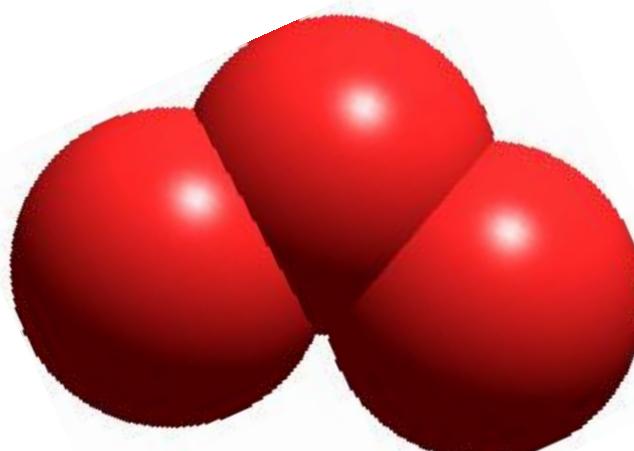
- 2 possible molecular geometries: **Trigonal planar**, if all the electron domains are bonding;
- **Bent**, if **one** of the domains is a **non-bonding pair**.

Ozone

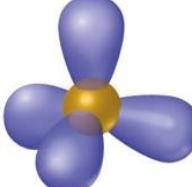
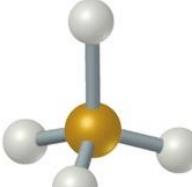
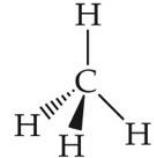
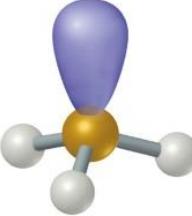
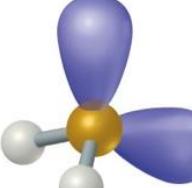


Double bond is still counted as **only one electron domain**.

$n = 3 \rightarrow$ Electron-domain geometry: Trigonal planar;
Molecular geometry: **Bent**

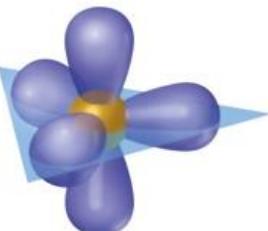
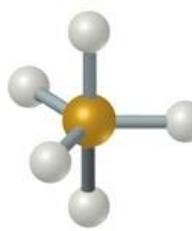
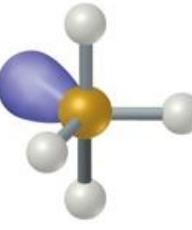
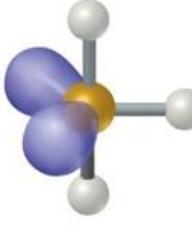
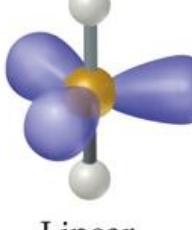


4 Electron Domains: Tetrahedral

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

- 3 possible molecular geometries:
Tetrahedral, if all are bonding pairs;
Trigonal pyramidal, if **one** is a **non-bonding pair**;
Bent, if there are **two non-bonding pairs**.

5 Electron Domains: Trigonal Bipyramidal

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

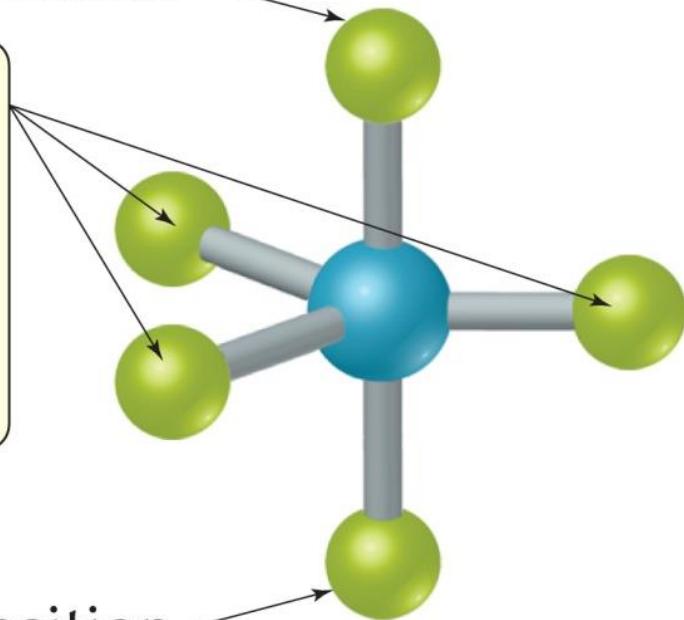
- 4 possible molecular geometries:

**Trigonal bipyramidal (TBP);
Seesaw;
T-shaped;
Linear.**

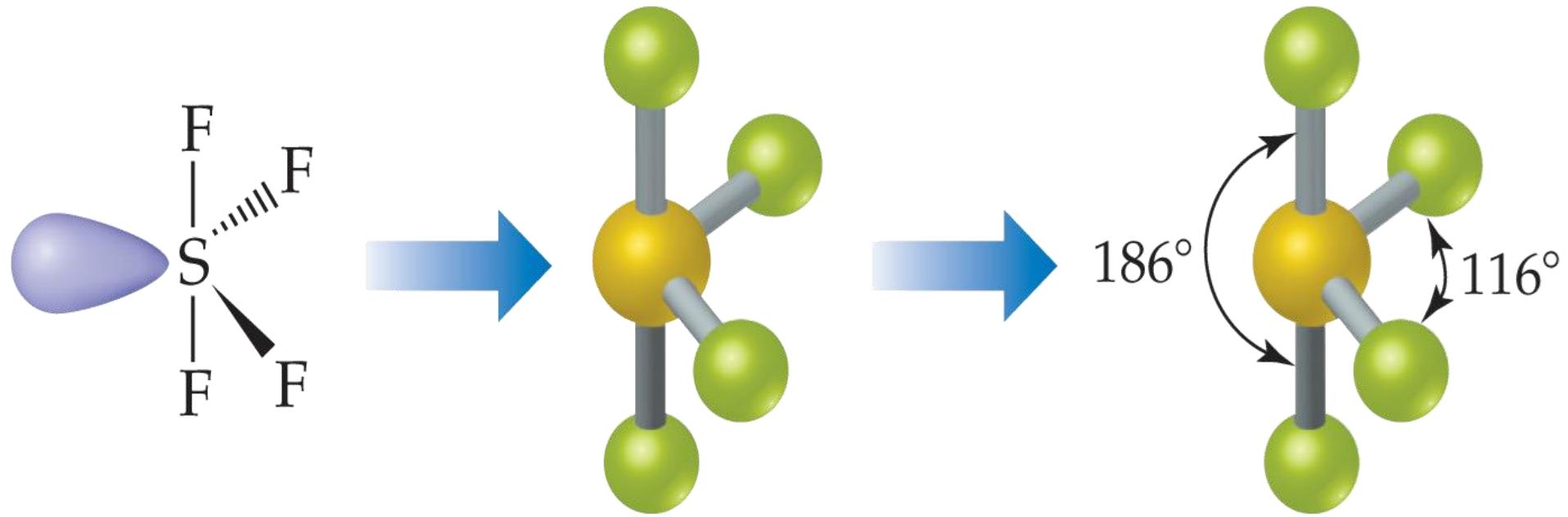
Axial position

Three equatorial positions form an equilateral triangle

Axial position



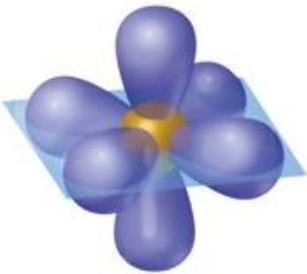
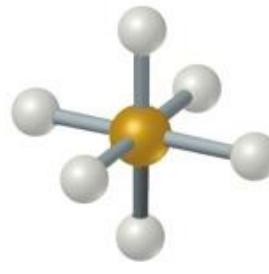
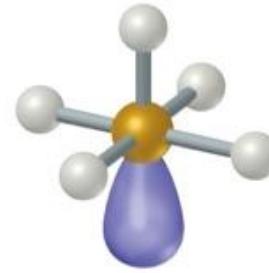
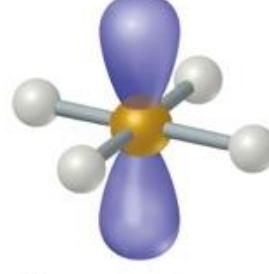
- There are 2 distinct positions in this TBP geometry:
Axial (轴向位) & **Equatorial** (赤道位)



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Lower-energy conformations result from having non-bonding electron pairs in equatorial, rather than axial, positions in this geometry.

6 Electron Domains: Octahedral

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

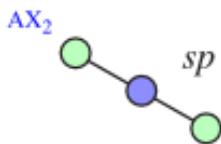
- All positions are same;
- 3 possible molecular geometries at least:

Octahedral;

Square pyramidal;

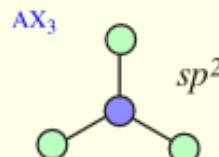
Square planar.

2 electron regions



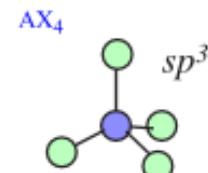
linear

3 electron regions



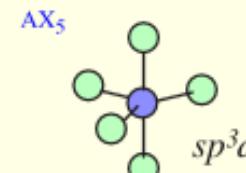
trigonal planar

4 electron regions



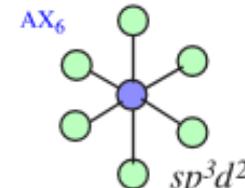
tetrahedral

5 electron regions



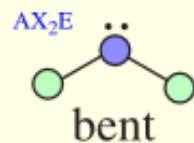
trigonal bipyramidal

6 electron regions

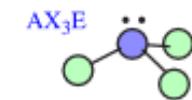


octahedral

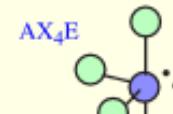
1 position occupied by a lone pair



bent



trigonal pyramidal

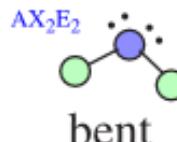


see-saw

note that the lone pairs all go in the equatorial positions

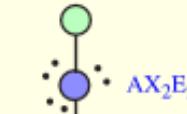


T-shaped



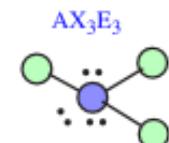
bent

2 positions occupied by a lone pair



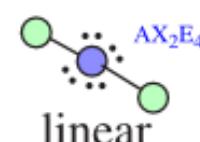
linear

3 positions occupied by a lone pair



T-shaped

4 positions occupied by a lone pair



linear

Molecular Geometries

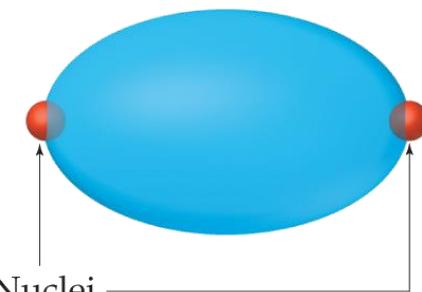
can be any of the shapes on the whole page. The electronic geometries are only those in the box (and orbital hybridizations). The molecular geometry will be different from the electronic when there is at least one or more lone pairs on the central atom. Look at the top of the table and go DOWN a column. As you change from bonding electrons to lone pair electrons, the molecular shape is now different from the electronic because some of the positions are missing atoms. The new shape is then renamed based on the shape of the atoms.

Remember, once you have established the correct electronic geometry, the molecular geometry MUST be either the same as the electronic or one of the shapes listed directly under the electronic geometry. In other words, each shape in a given column here has the same electronic geometry given at the top of the column.

Nonbonding Pairs and Bond Angle

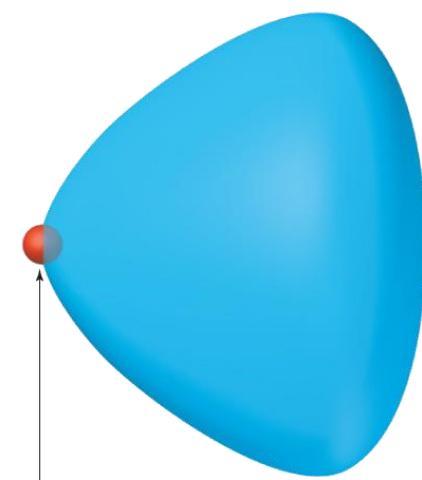
- **Non-bonding pairs (lone pairs LP)** are physically **larger** (more diffuse & occupy more space) than **bonding pairs (BP)**.

Bonding electron pair

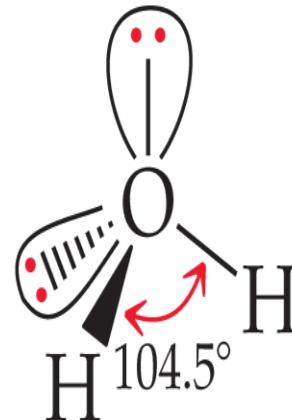
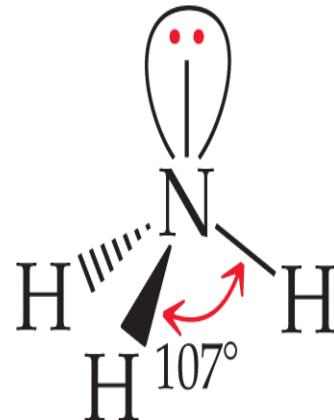
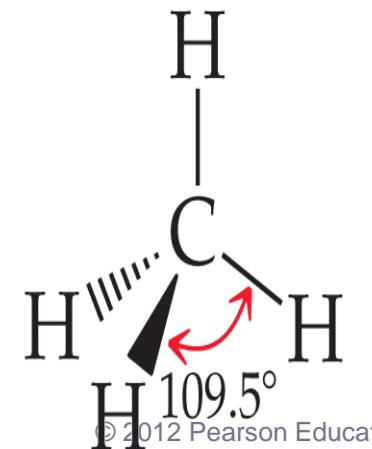


- **Repulsions** with **non-bonding pairs** are **greater** and bond angles are compressed away from the lone pairs → **decrease bond angles** in a molecule:
Repulsions: LP-LP > LP-BP > BP-BP

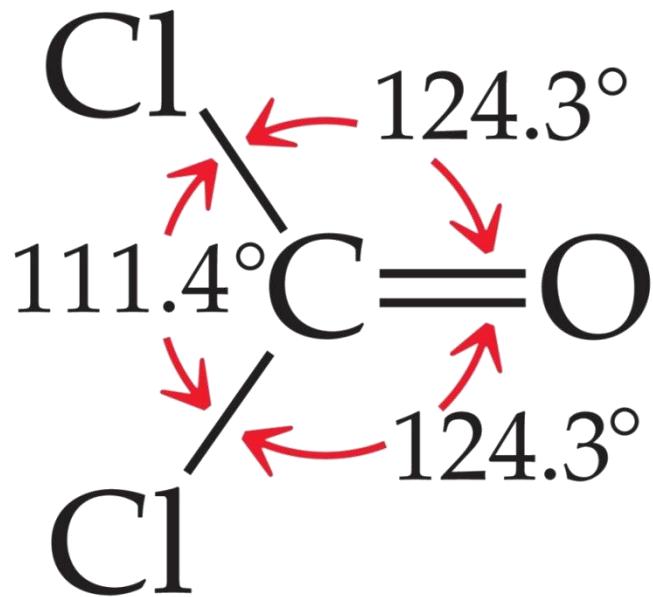
Nonbonding pair



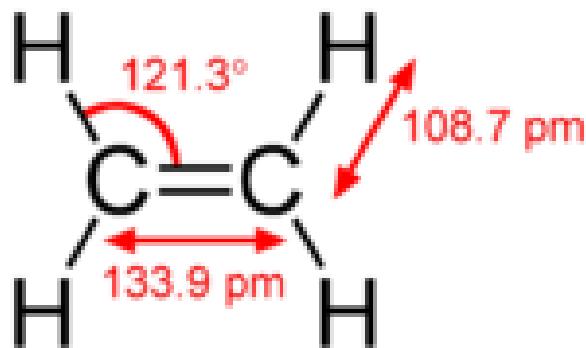
Nucleus
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Multiple Bonds and Bond Angles



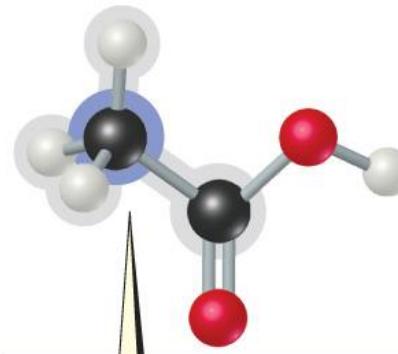
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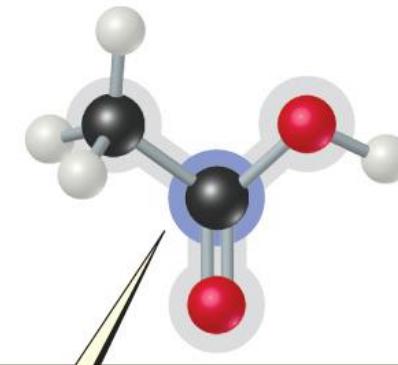
- Double and triple bonds have **greater electron density** on one side of the central atom than do single bonds.
- Therefore, they also **affect bond angles** (longer C-Cl bonds can affect as well: NH₃, 107°; PH₃, 93.5°).

Larger Molecules

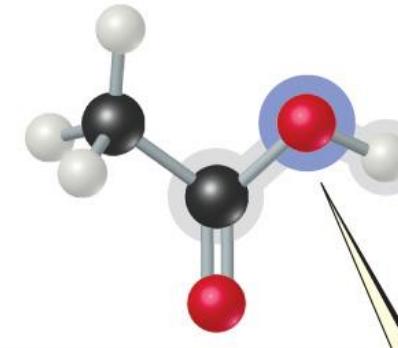
In larger molecules, it makes more sense to talk about the **geometry about a particular atom** rather than the geometry of the molecule as a whole.



Electron-domain geometry tetrahedral,
molecular geometry tetrahedral



Electron-domain geometry trigonal planar,
molecular geometry trigonal planar

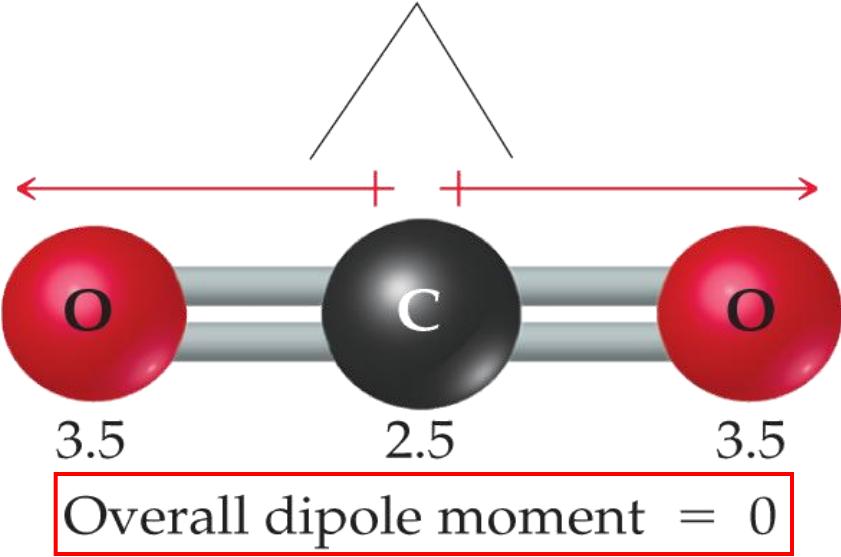


Electron-domain geometry tetrahedral,
molecular geometry bent

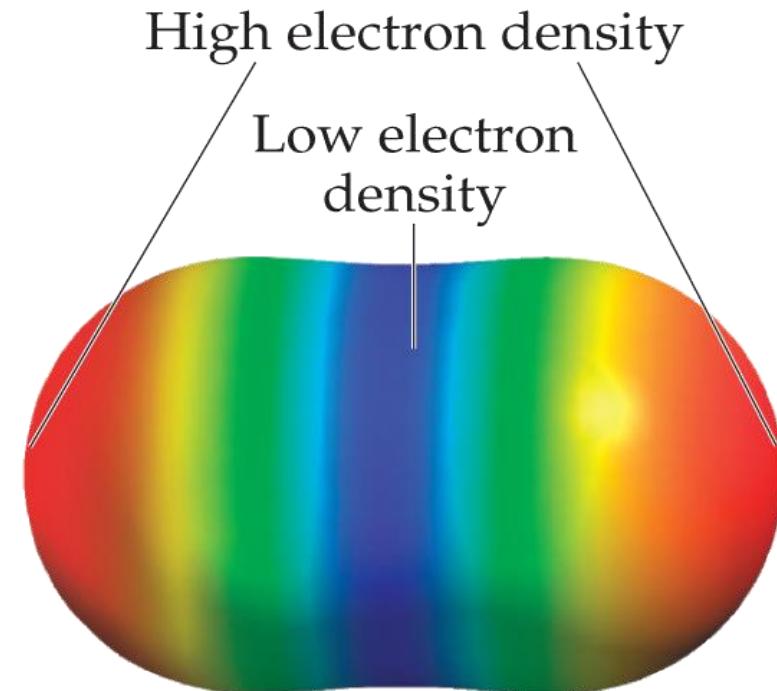
Polarity

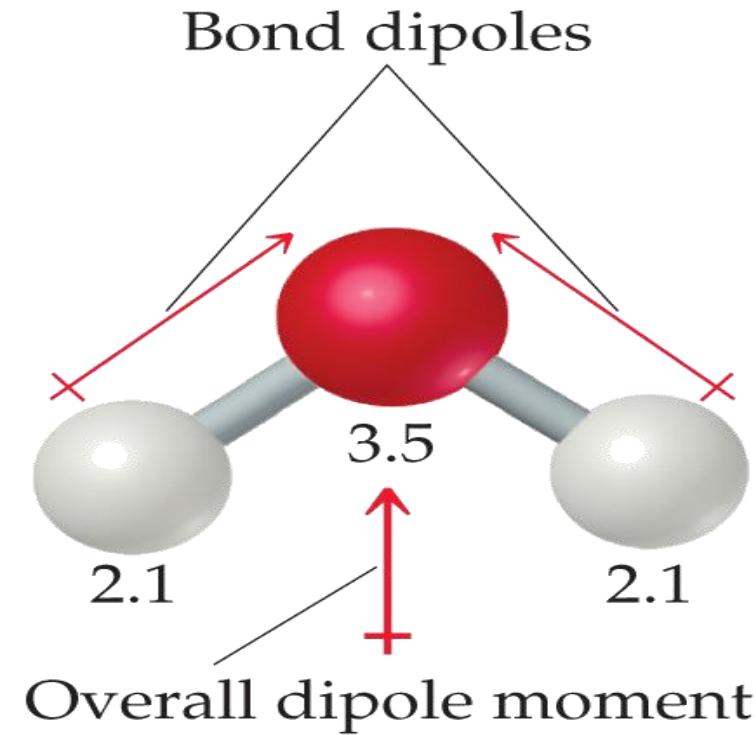
A **molecule** which possesses **polar bonds** does **NOT always** mean that the **molecule** as a *whole* is **polar!**

Equal and oppositely directed bond dipoles



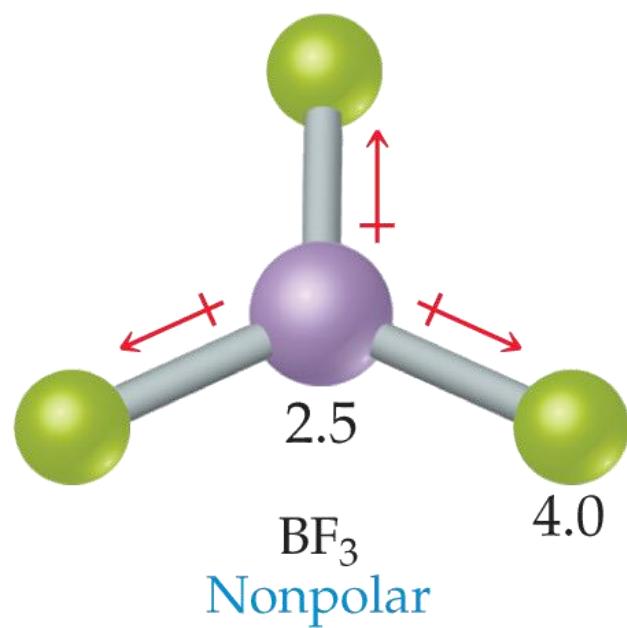
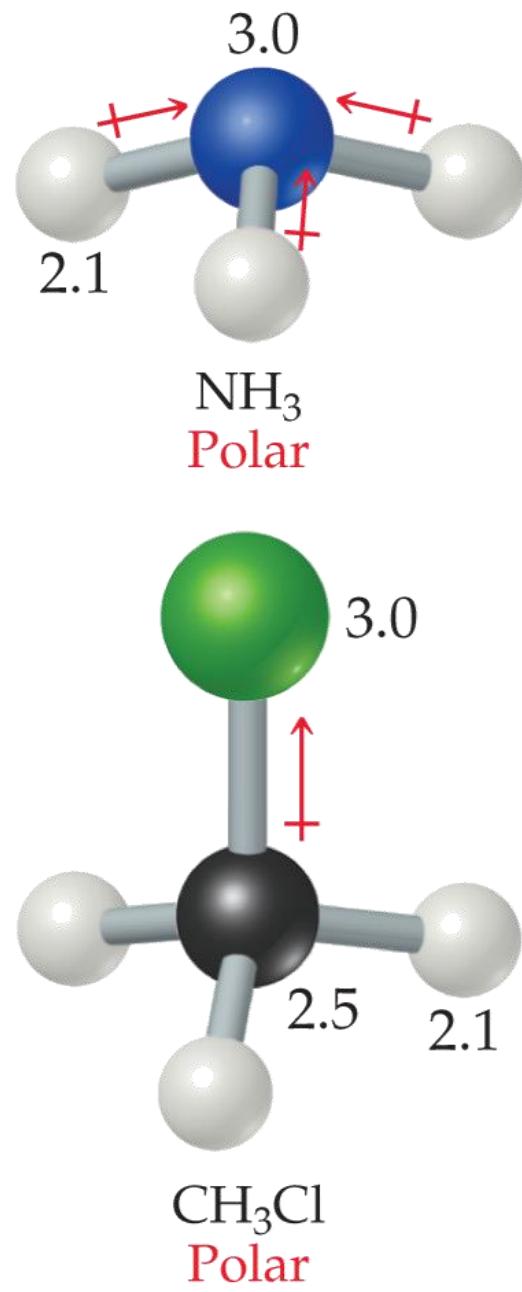
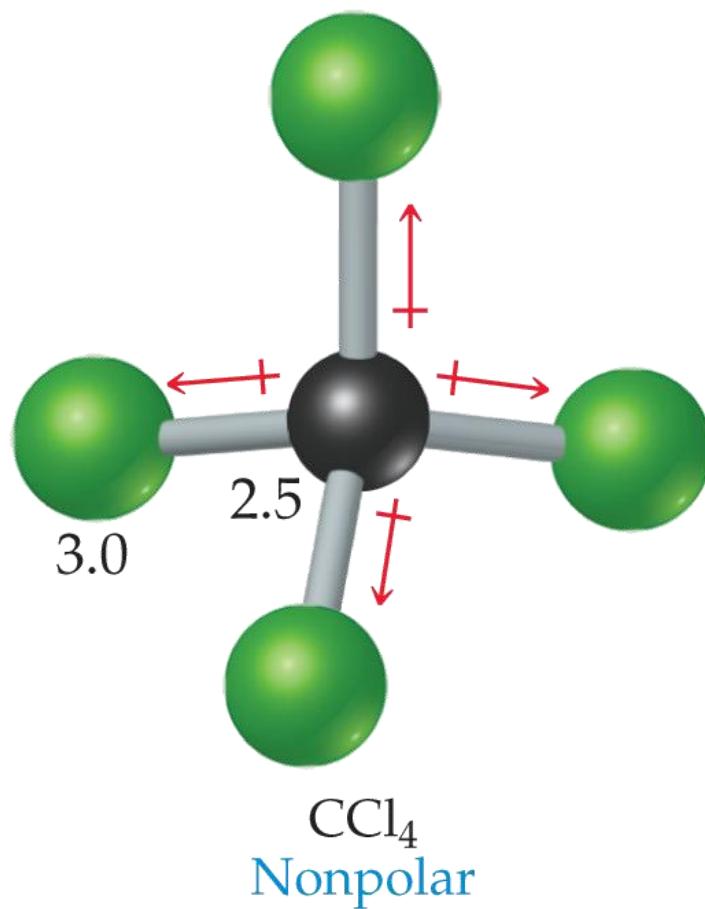
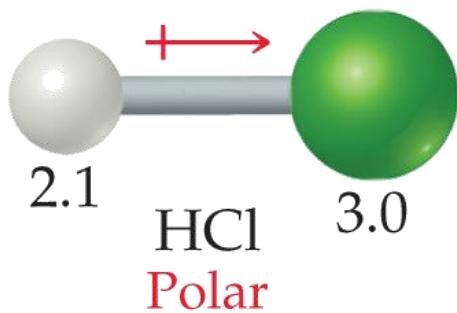
Non-polar
molecule

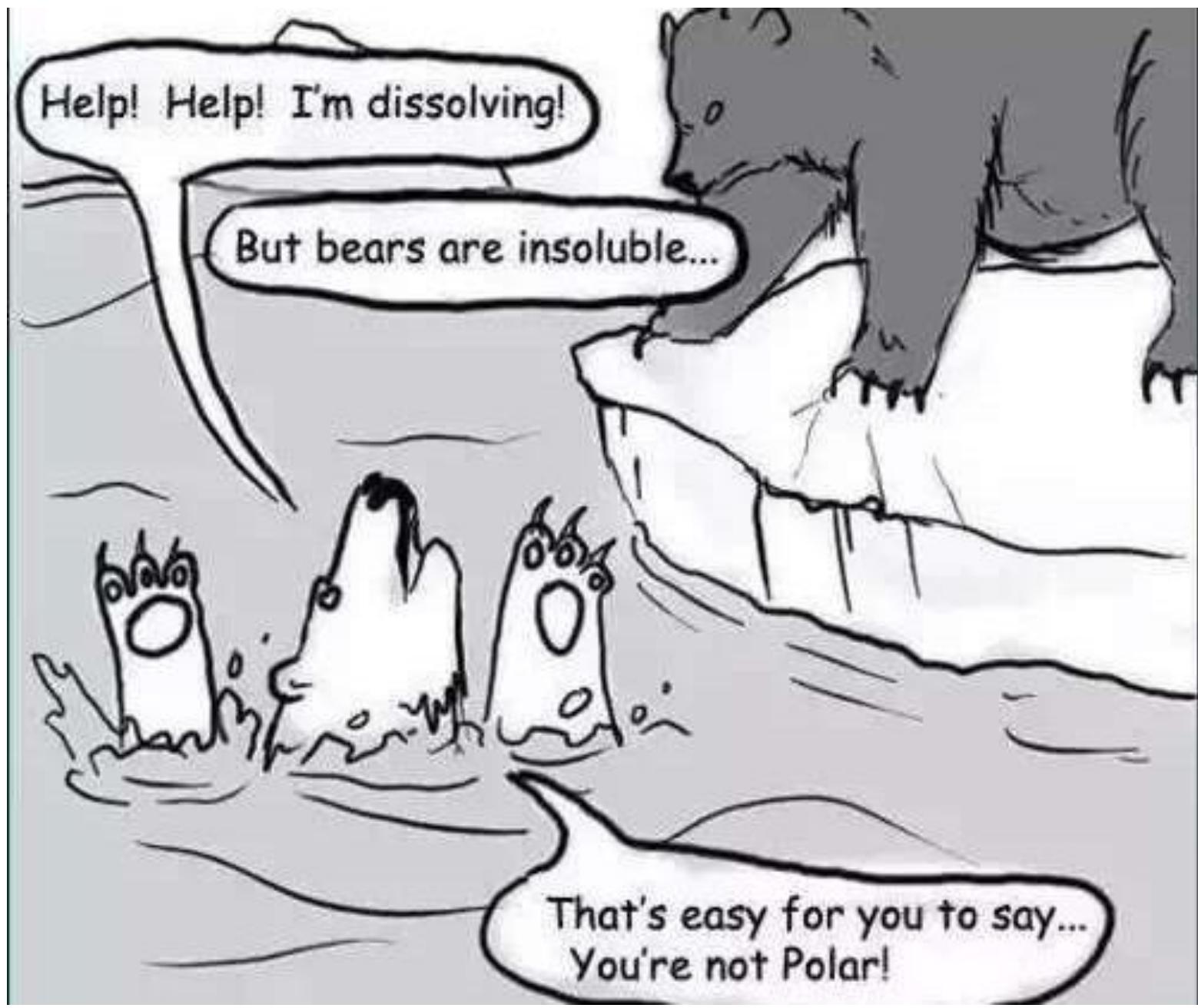




By **summing** the individual **bond dipoles** (like sum of vectors), one can determine the **overall dipole moment** for the molecule.

Polar molecule





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 phosphorus trichloride (PCl_3) molecule is

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

The geometry of the methane (CH_4) molecule is

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

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

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.

Which molecule is polar?

- a. CH₄
- b. BBr₃
- c. SF₆
- d. NH₃

Which molecule is nonpolar?

- a. CO₂
- b. SO₂
- c. IF₃
- d. IF₅

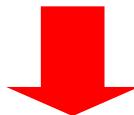
Valence Bond (VB) Theory

Valence Bond (VB) Theory

VSEPR theory

- Can predict molecular geometries well.
- Cannot explain why/how **bonds form** between atoms.

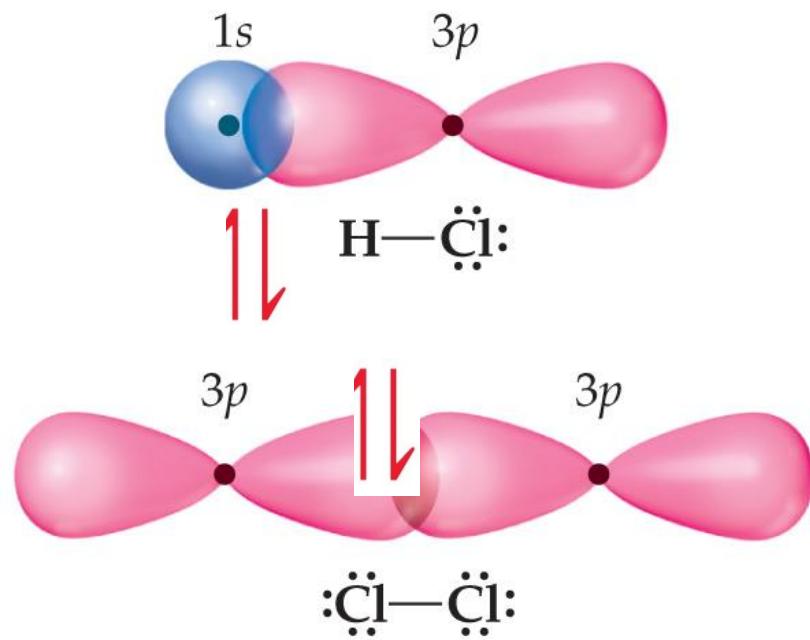
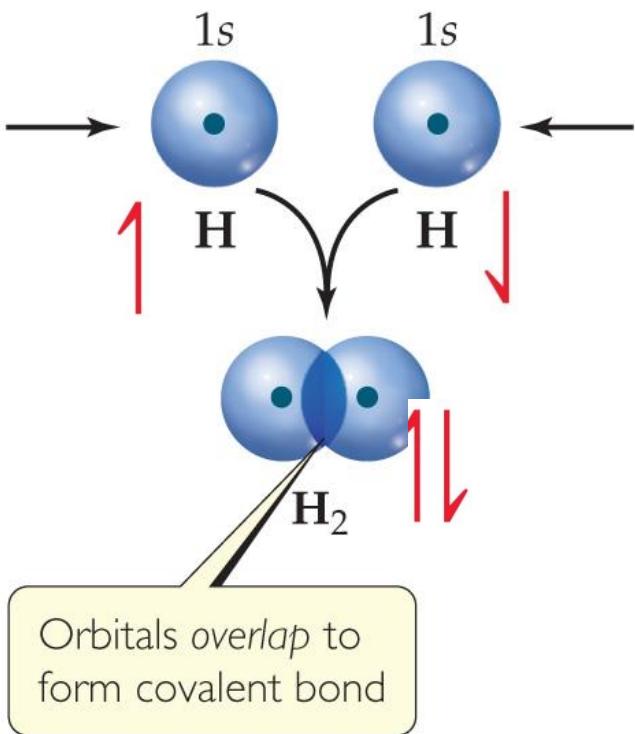
Lewis's **electron-pair bonds** (bond formation by sharing e^-) + **atomic orbitals** (using quantum mechanics).



Valence Bond theory

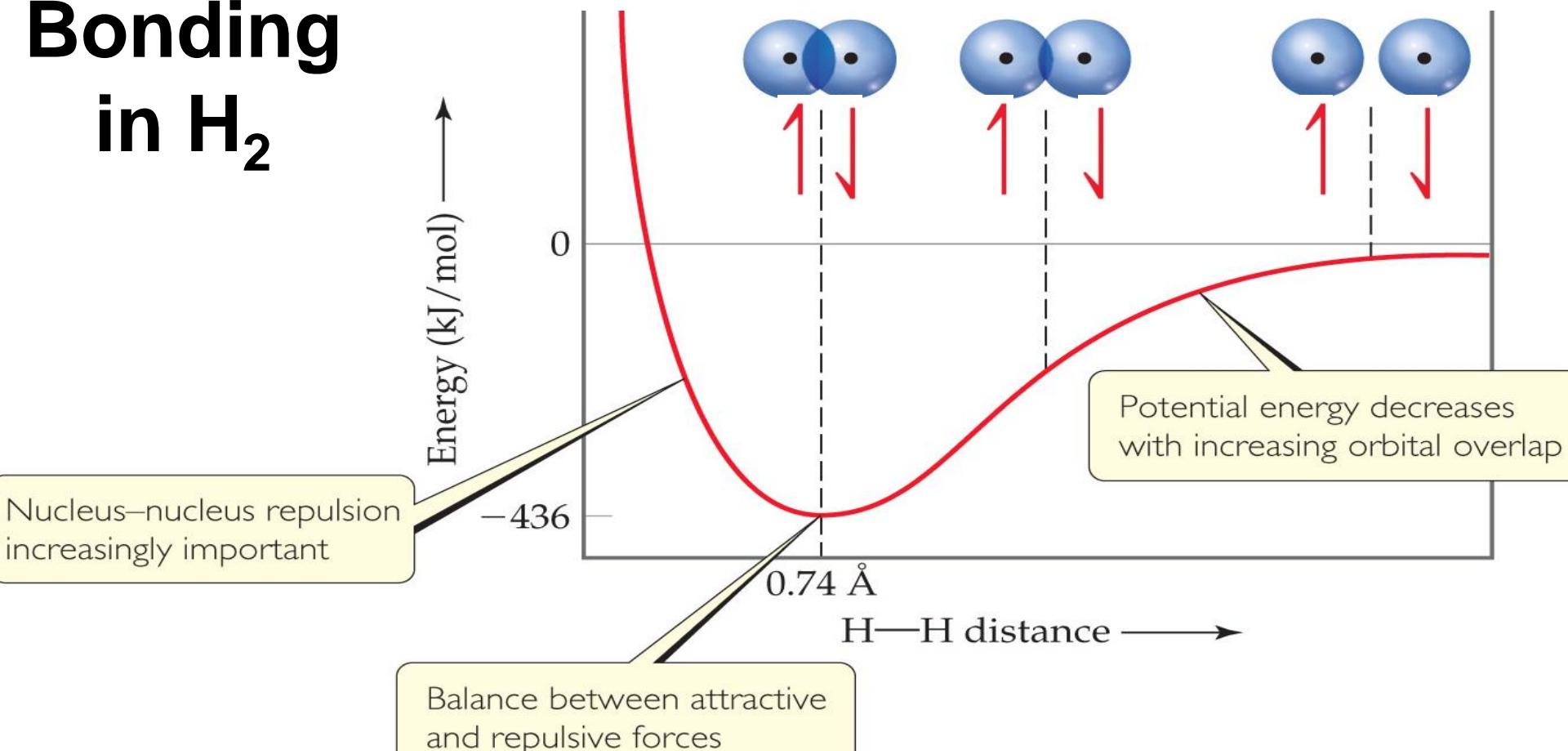
- Bonding electron pairs are concentrated between atoms.
- **Orbital overlap** → buildup of **e^- density** between nuclei → **covalent bond** formation.

Overlap (重叠) & Bonding



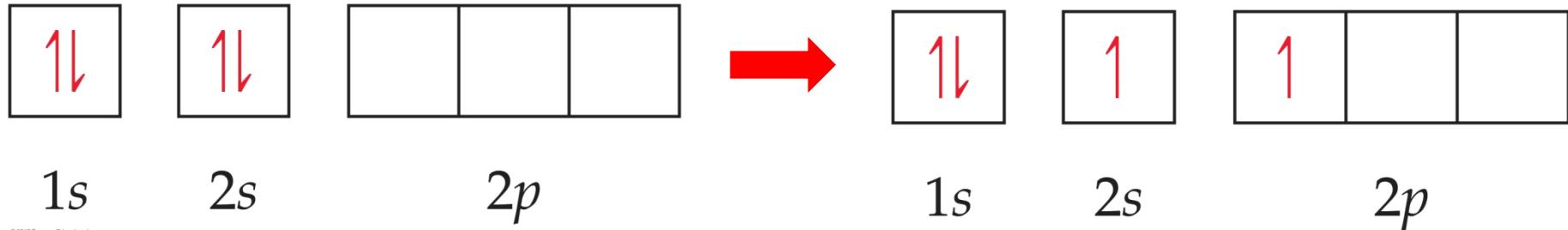
- **Covalent bonds forming** through the sharing of electrons by adjacent atoms.
- In such an approach, this can only occur when **half-filled orbitals** (with **opposite spin**) on the two atoms **overlap** (region the electrons are shared).

Bonding in H₂



- **Shorten the bond distance** (electrons and nuclei become closer), **increases overlap** of the two atomic orbitals (**more sharing** electrons) and **energy decreases**.
- If the atoms get too close, the **internuclear repulsion (nuclei–nuclei repulsion)** greatly raises the energy.

Hybrid Orbitals



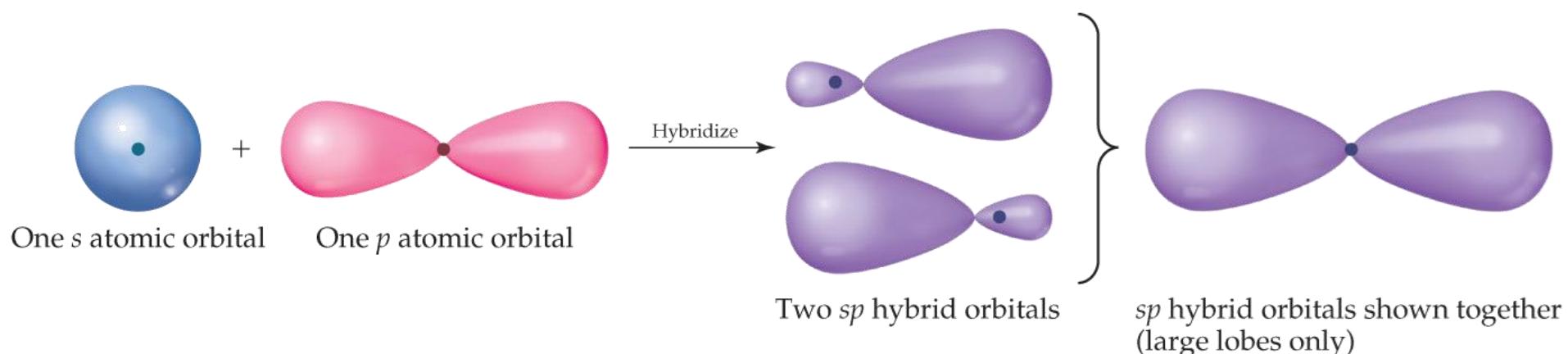
Consider **beryllium**:

In its electronic ground state ($1s^22s^2$), beryllium would **not** be able to **form bonds**, because it has **no singly occupied orbitals**.

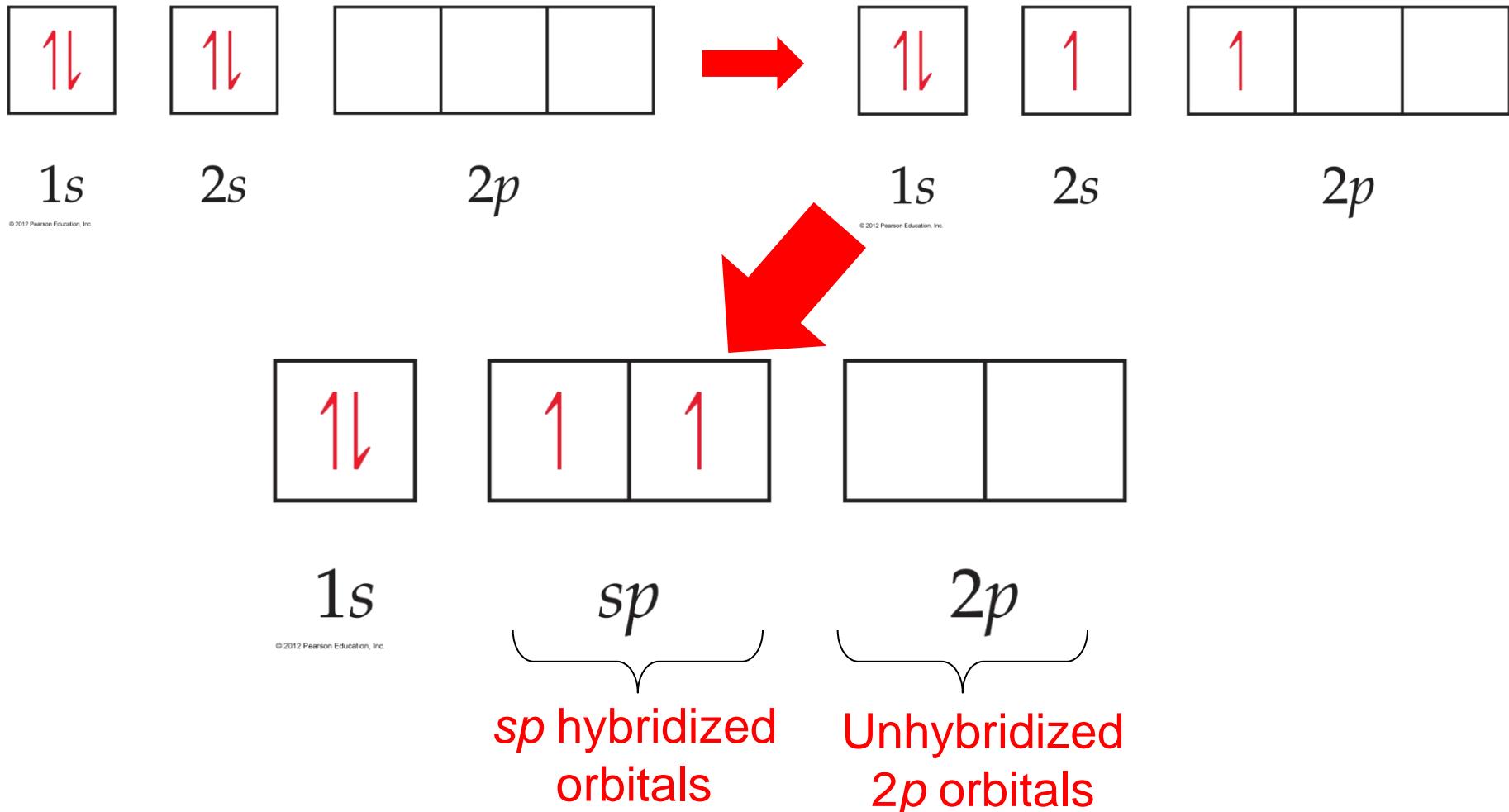
If it absorbs the **small amount of energy** needed to **promote one electron** from the **2s** to the **2p** orbital, it can **form two bonds**. However, it still **cannot explain** the **linear geometry** by using one 2s & one 2p.

Mixing one s orbital and one p orbital yields **two degenerate** orbitals: hybrids of the two orbitals.

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

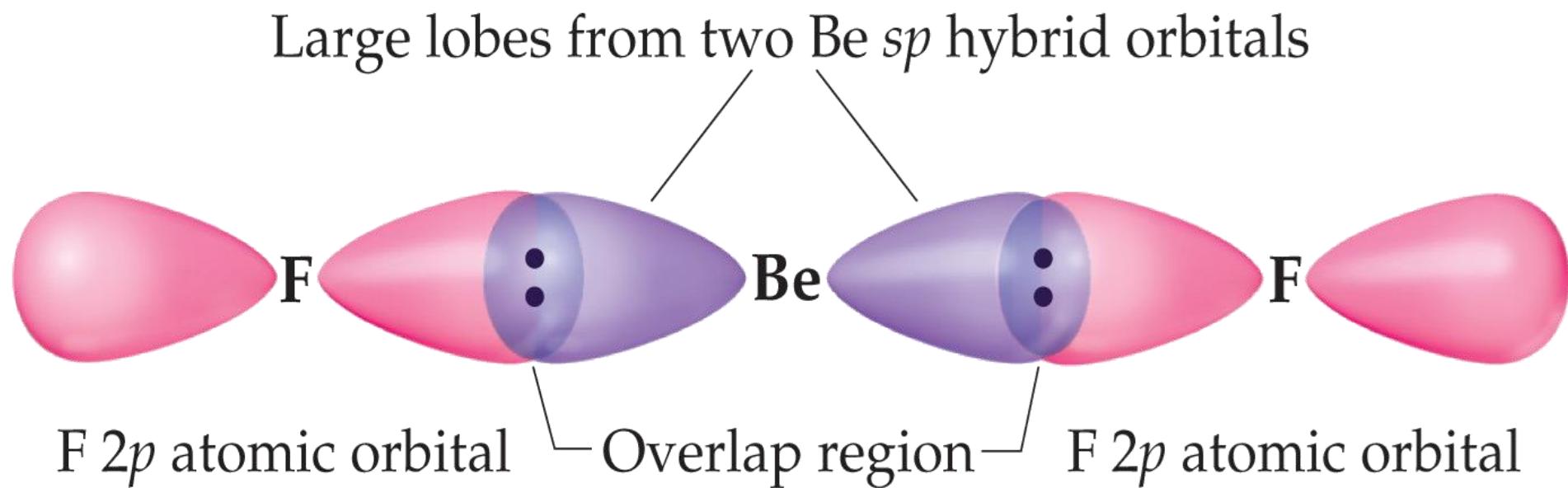


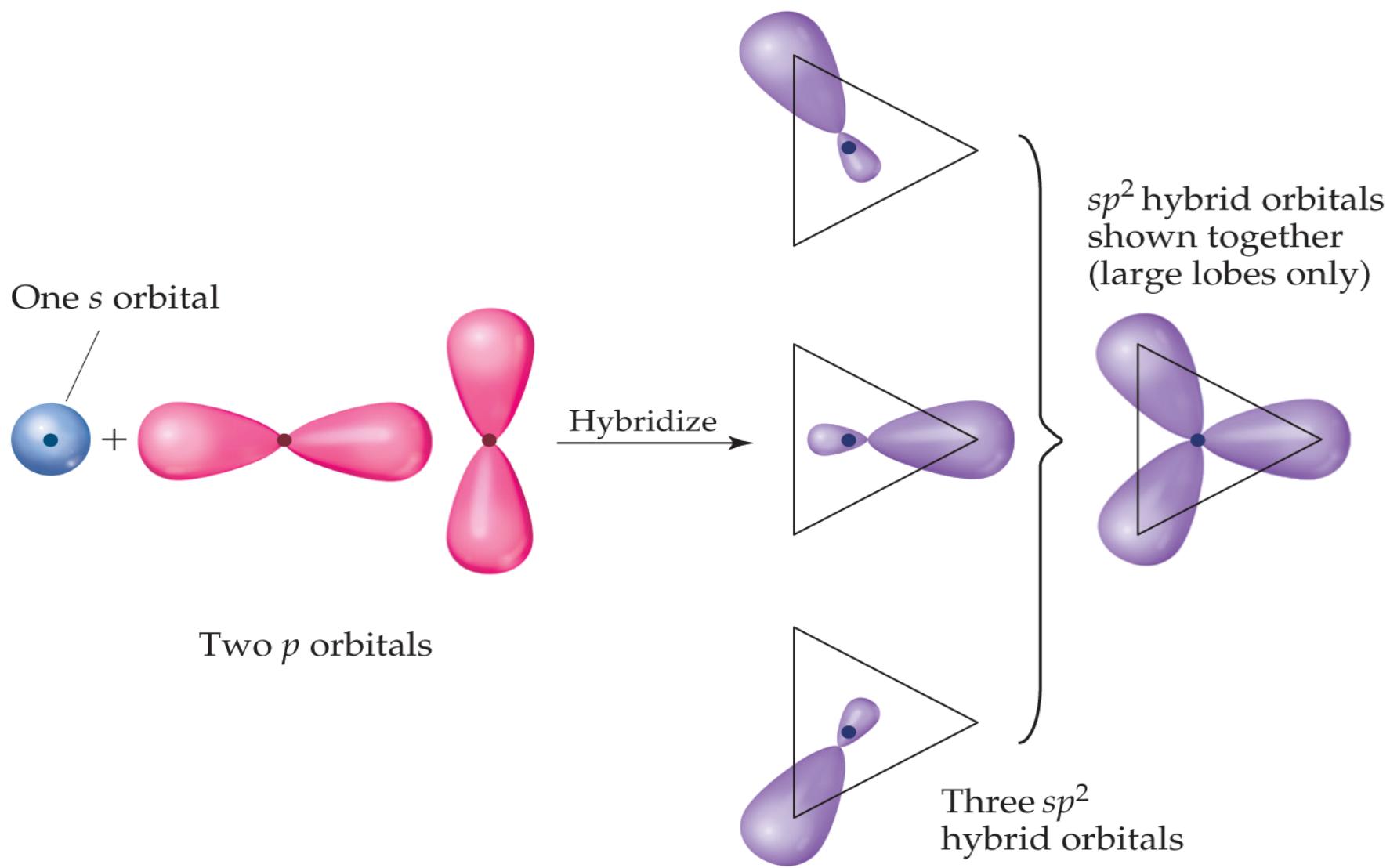
- With hybrid orbitals, the orbital diagram for beryllium would look like this:



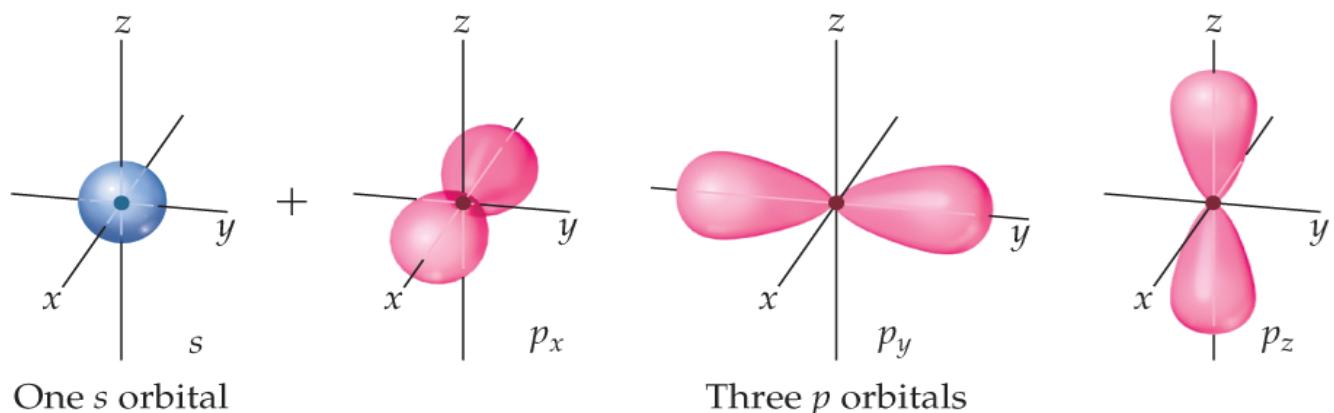
- The sp orbitals are higher in energy than the 1s & 2s orbitals, but lower than the 2p orbitals.

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





Using a similar model for **boron** leads to **three degenerate *sp*² orbitals** (**one s + two p → three *sp*² hybrid orbital: 33% s & 67% p orbital characters**).



One *s* orbital

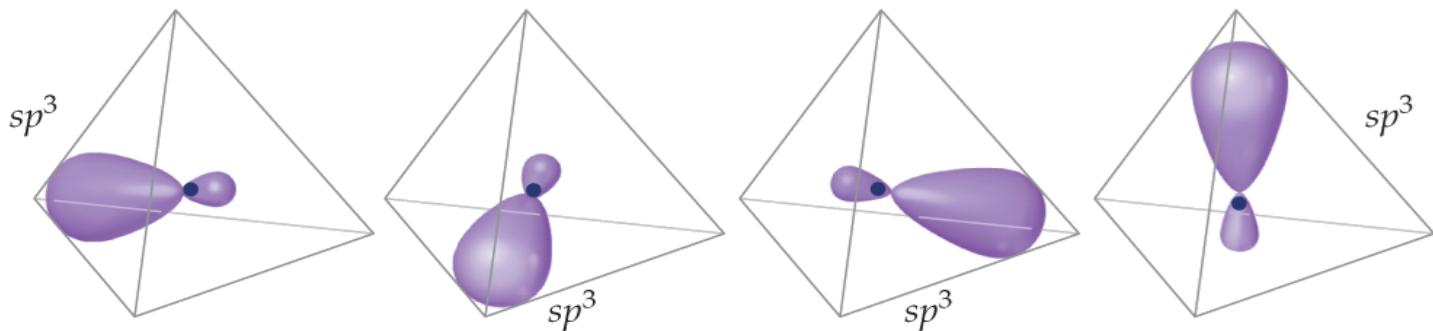
p_x

p_y

p_z

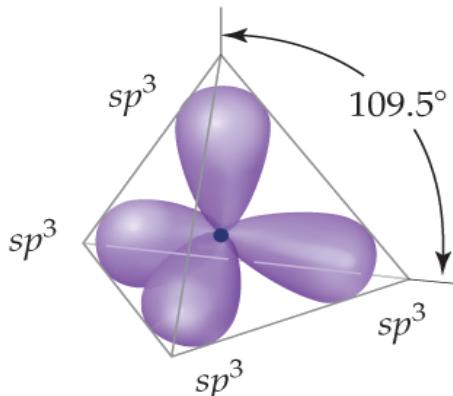
Three *p* orbitals

Hybridize to form four *sp*³ hybrid orbitals



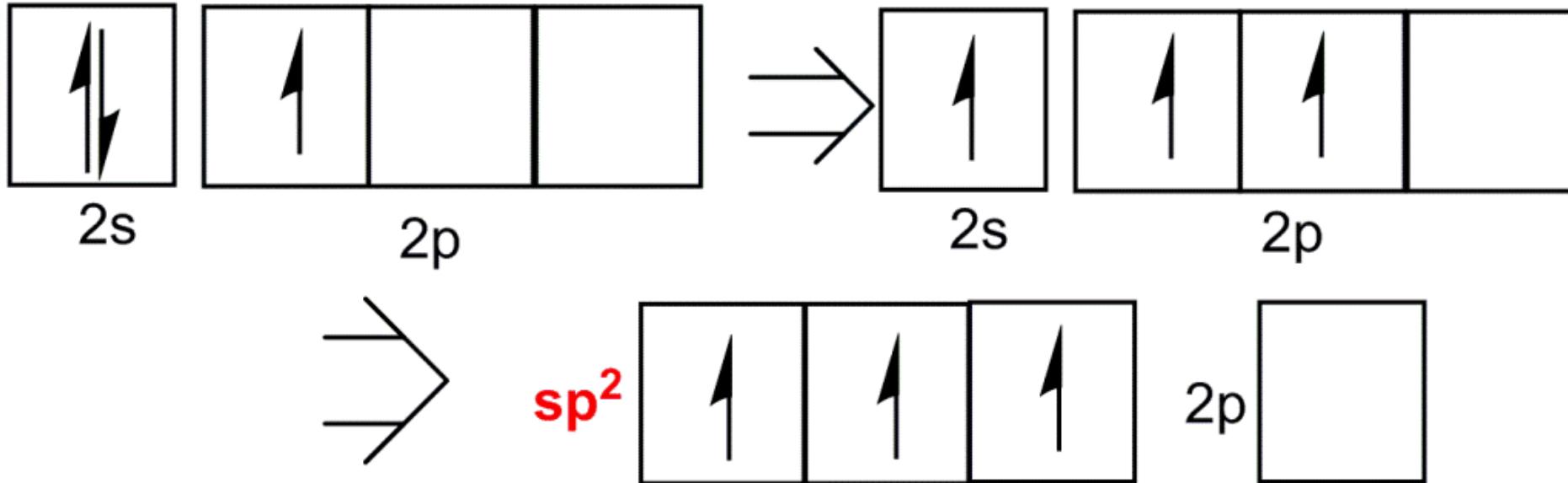
Shown together (large lobes only)

- **Carbon:**
- **four degenerate *sp*³ orbitals (one *s* + three *p*).**
- Energy order of *s*, *p*, *sp*, *sp*² & *sp*³?

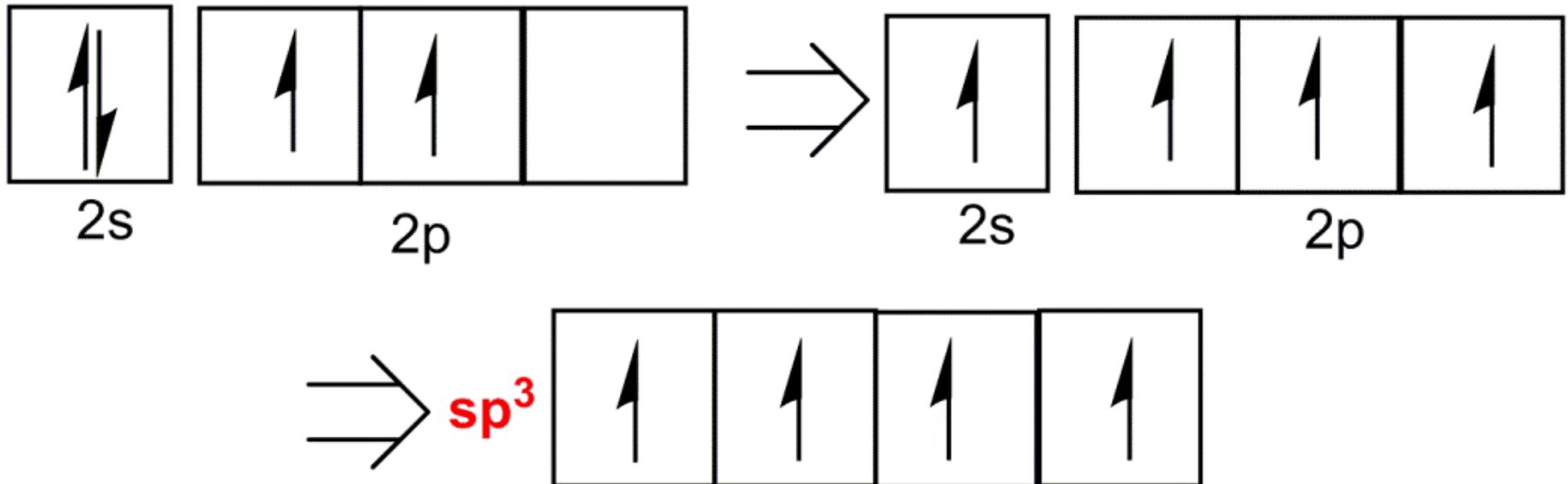


25% *s* & 75% *p* orbital characters

- **Boron** ($1s^2 2s^2 2p^1$):



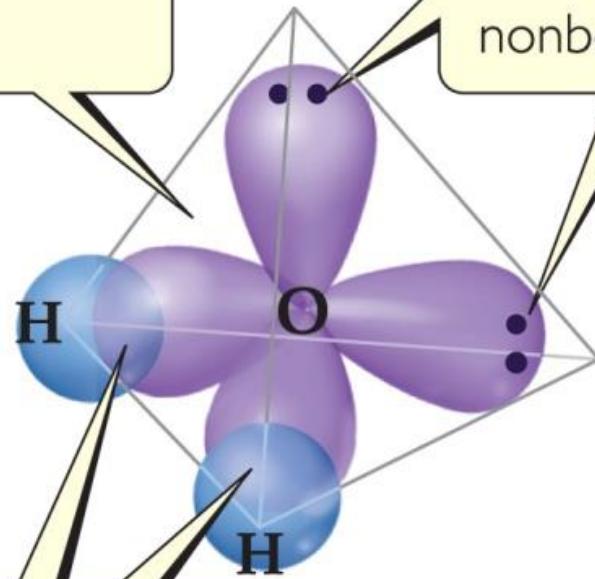
- **Carbon** ($1s^2 2s^2 2p^2$):



Water (H_2O)

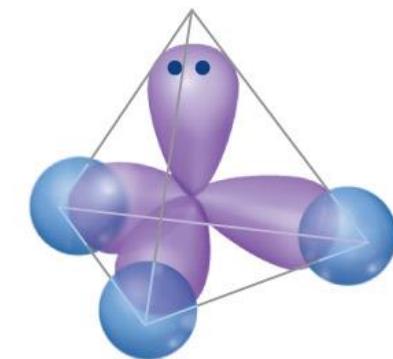
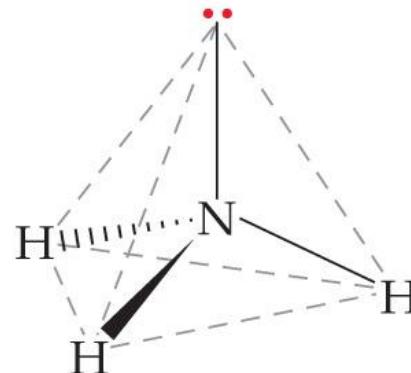
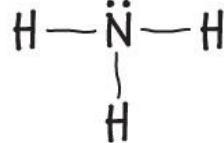
Tetrahedral arrangement
of four sp^3 hybrid orbitals
about oxygen

Two O sp^3 orbitals contain
nonbonding electron pairs



- Why is it 104.5° instead of 90° ?
- Oxygen has **4 electron domains** & requires **4 hybrid orbitals**.
→ sp^3 hybridization.

Hybrid Orbital Summary



sp^3 hybridization

1. Draw Lewis structure

2. Determine electron-domain geometry about central atom from VSEPR model and Table 9.1

3. Using Table 9.4, select sp^3 hybrid orbital set

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1. Draw the **Lewis structure** for the molecule or ion.
2. Determine the **electron-domain geometry** by VSEPR theory.
3. Specify the **hybrid orbitals** needed to accommodate **ALL electron domains** (electron pairs) based on their geometric arrangement. How's about 5 or 6 domains?

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- **Hybridization** is a **major** player in **valence bond** bonding theory.



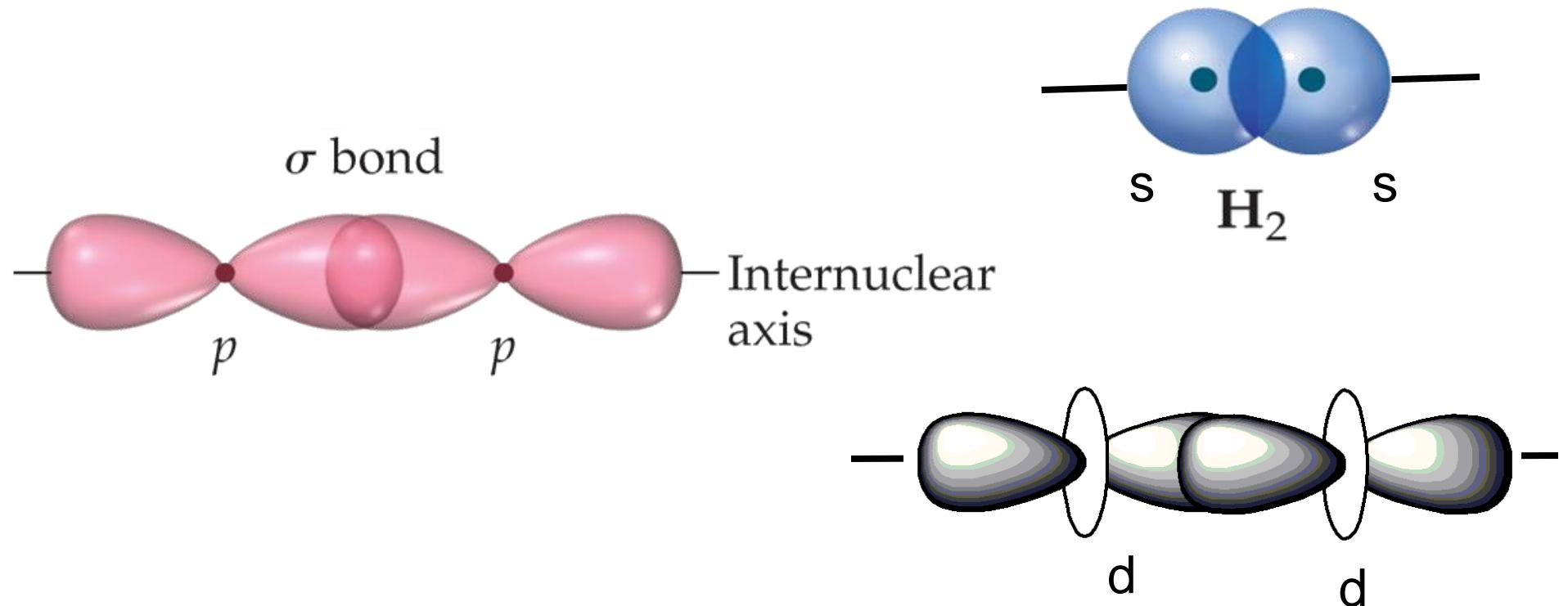
Fritz Wolfgang London

Gilbert Newton Lewis

Linus Carl Pauling

There are **two basic and common ways** orbitals can **overlap to form bonds** between atoms.

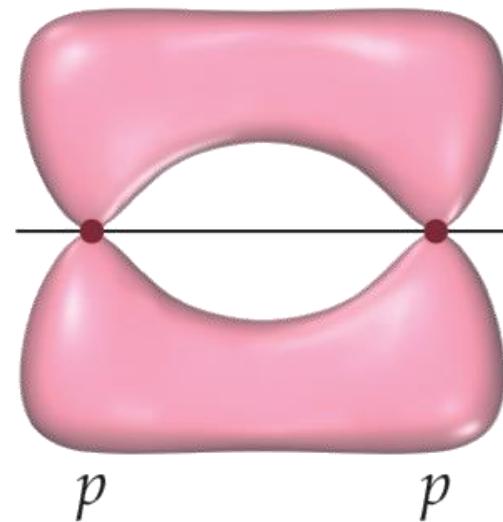
Sigma (σ) Bonds



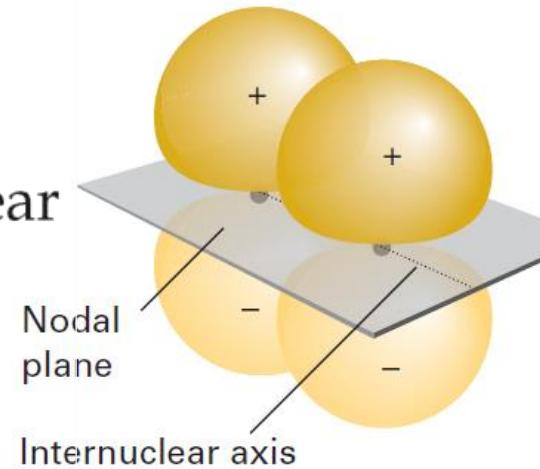
- Sigma bonds are characterized by **head-to-head overlap** except for s orbitals.
- Cylindrical symmetry of **increased electron density along the internuclear axis**.

π bond

Pi (π) Bonds

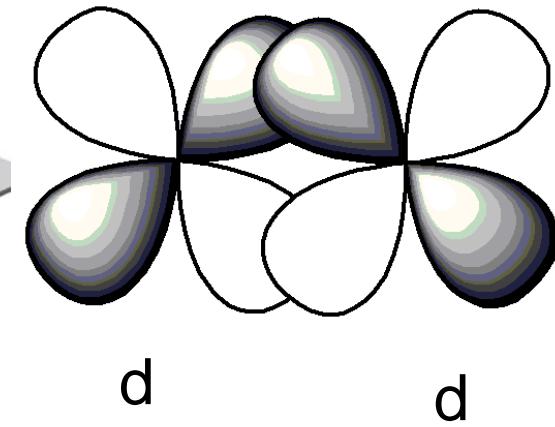


Internuclear
axis



Nodal
plane

Internuclear axis



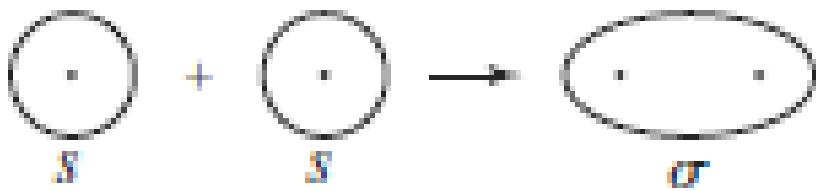
d

d

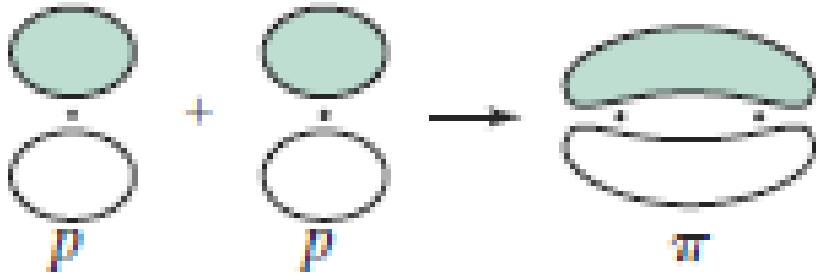
- Pi bonds are characterized by **side-to-side overlap** with **1 nodal plane**.
- **Increased electron density above and below** the internuclear axis.
- **Less** (effective) overlap: **weaker** than sigma bond. (**extra info.**: even less effective overlap for the third-row or below elements.)

Extra Info. Delta (δ) Bonds

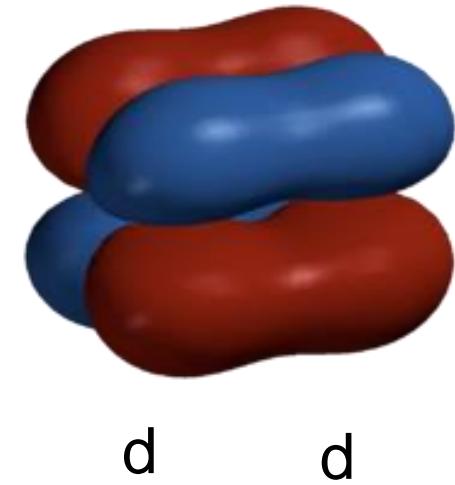
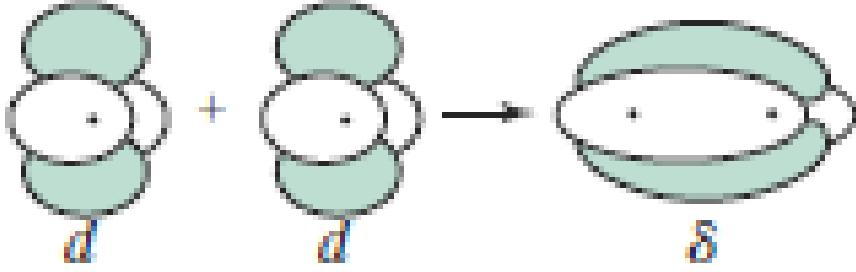
Sigma



Pi



Delta



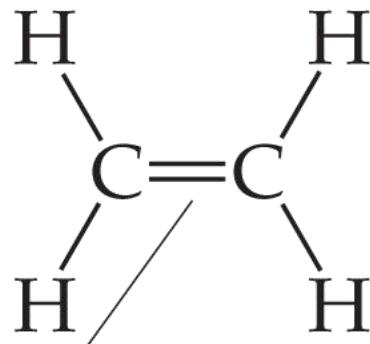
- Delta bonds are characterized by **side-to-side** overlap (e.g. with 2 d orbitals) with **2 nodal** plane.
- Even less (effective) overlap: weaker than pi bond.

Single Bonds & Multiple 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

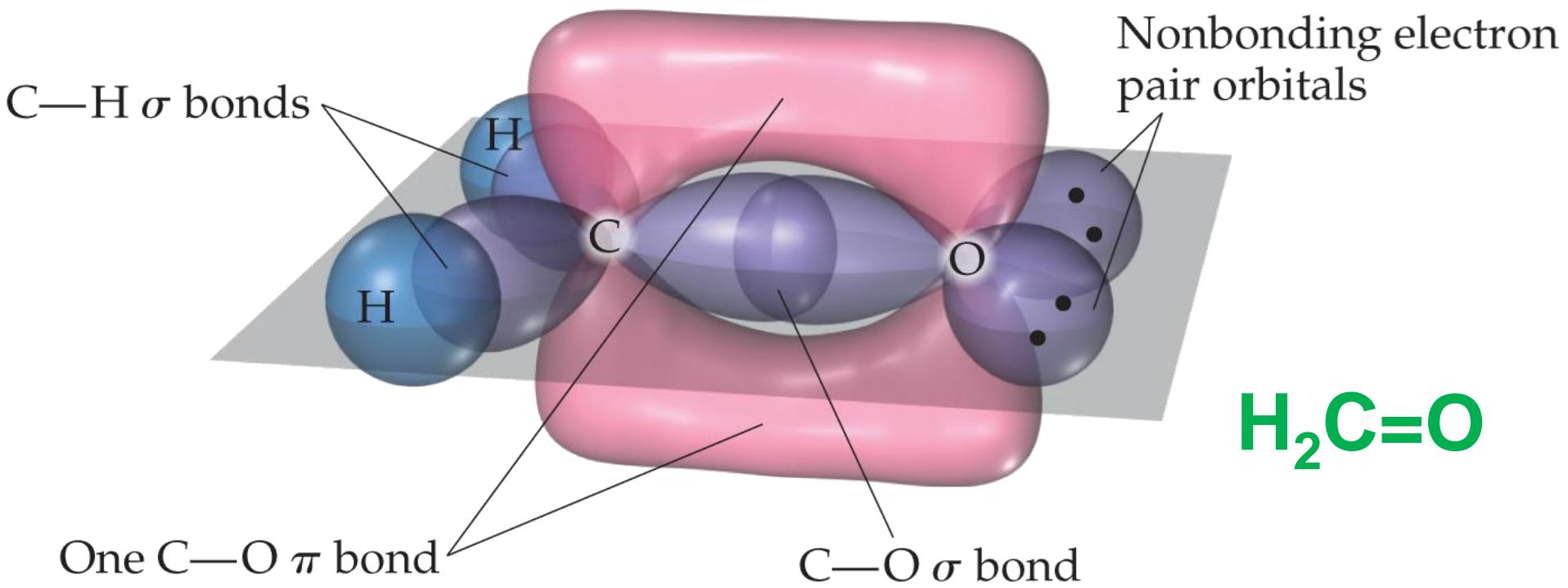


One σ bond plus
two π bonds

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In a multiple bond, **one** of the bonds is a **σ bond** and the **rest** are **π bonds** (and sometimes δ bonds for transition metals).

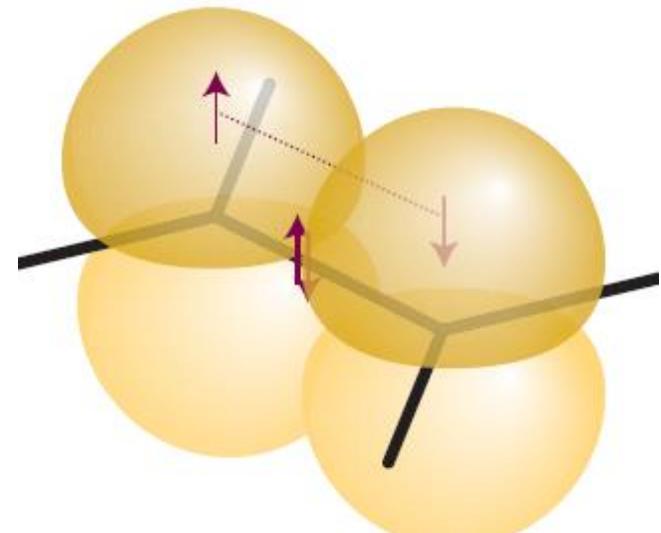
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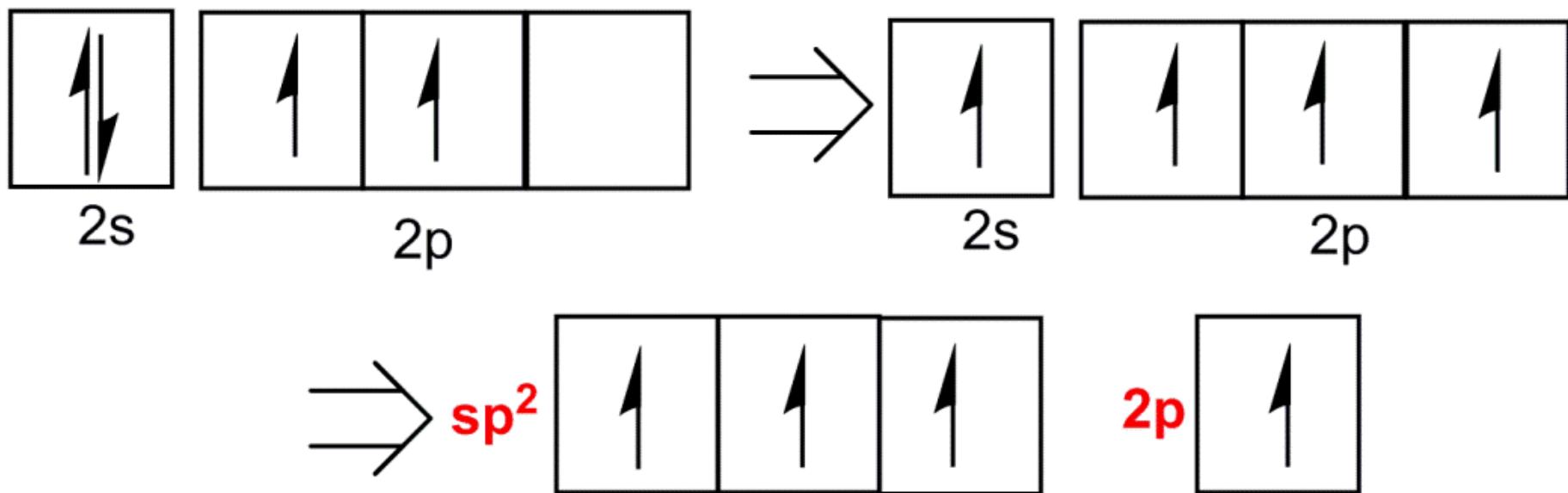
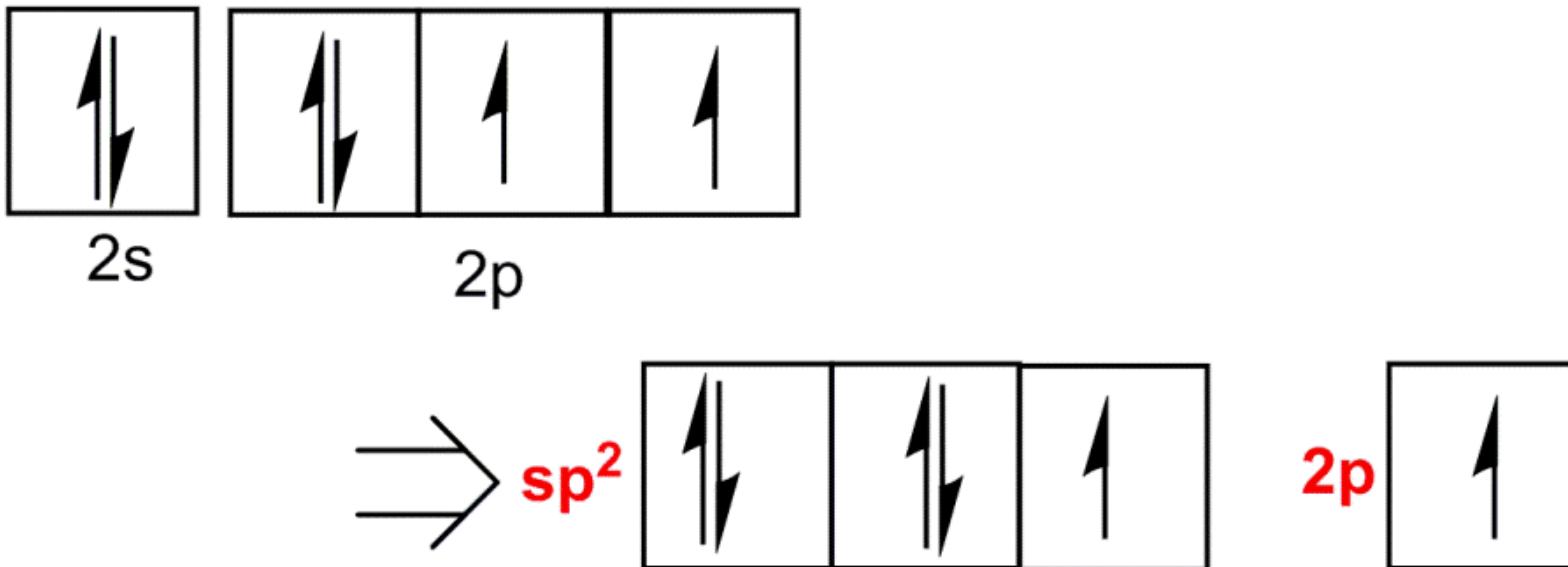


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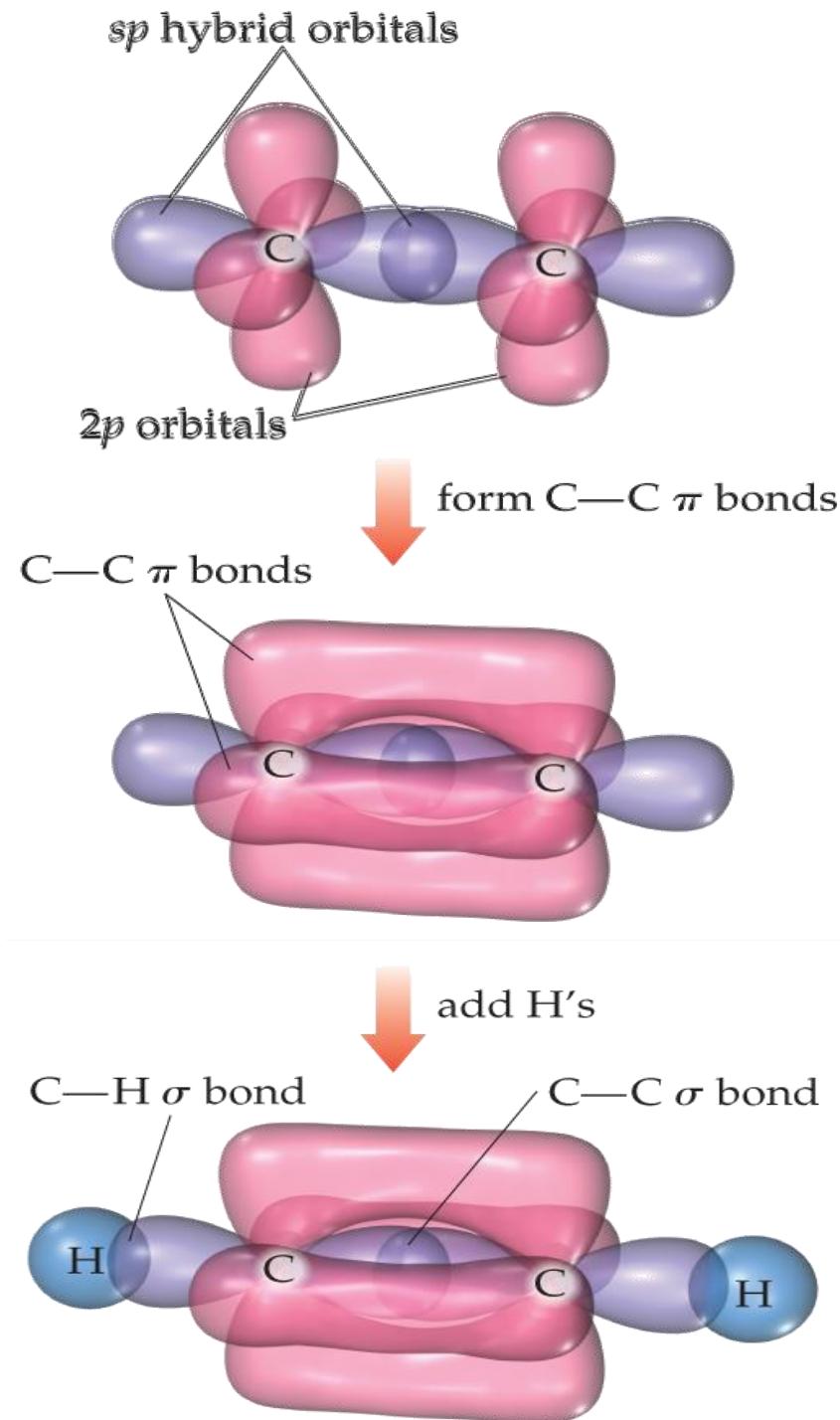
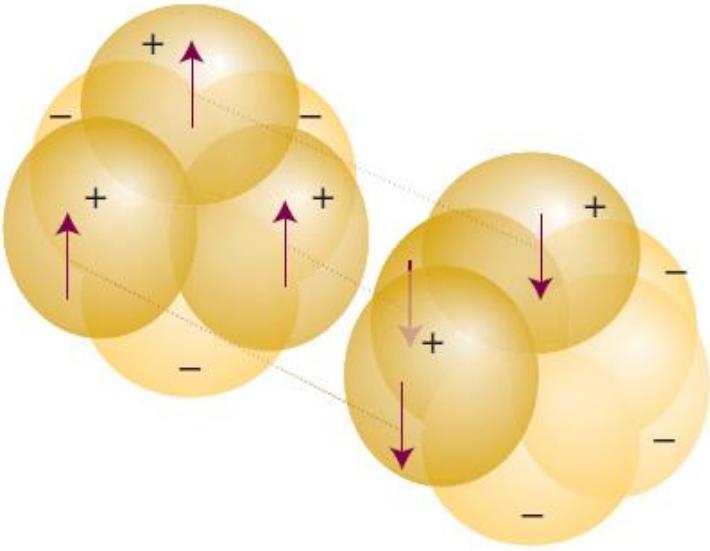
- In a molecule like formaldehyde, an **sp^2 orbital** on carbon **overlaps** with the corresponding orbital on the oxygen in **σ** fashion.
- The **unhybridized p** orbitals **overlap** in **π** fashion.

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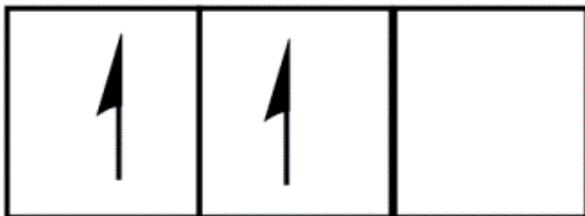
C**O**

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**.

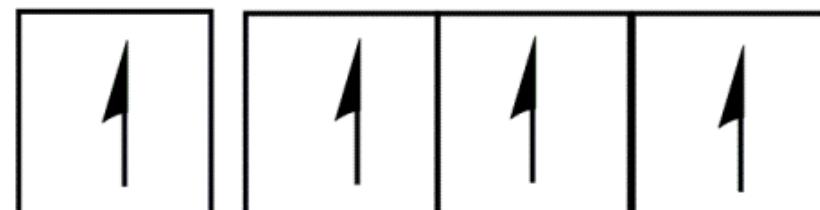
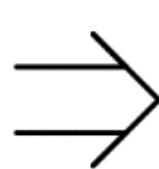


C

2s



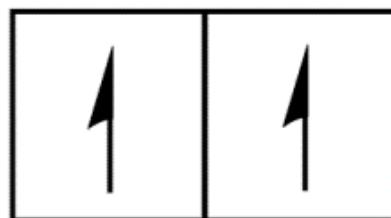
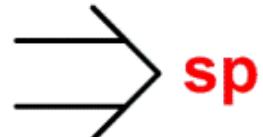
2p



2s



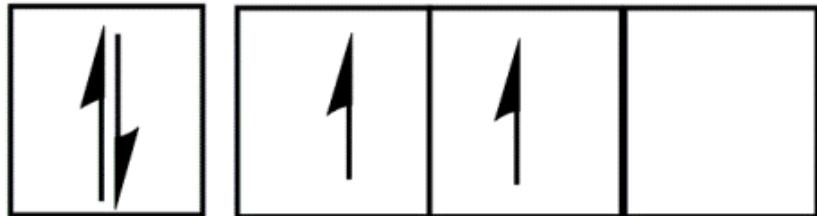
2p



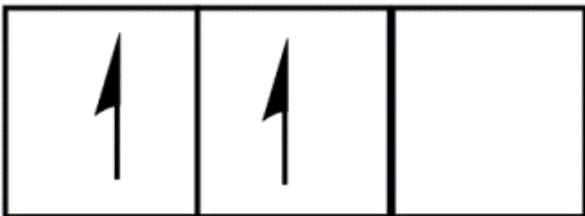
sp



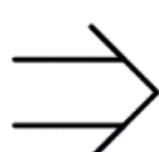
2p

C

2s



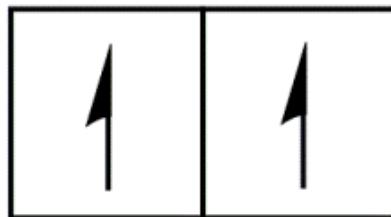
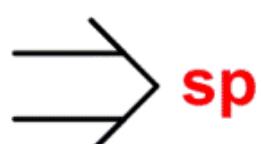
2p



2s



2p



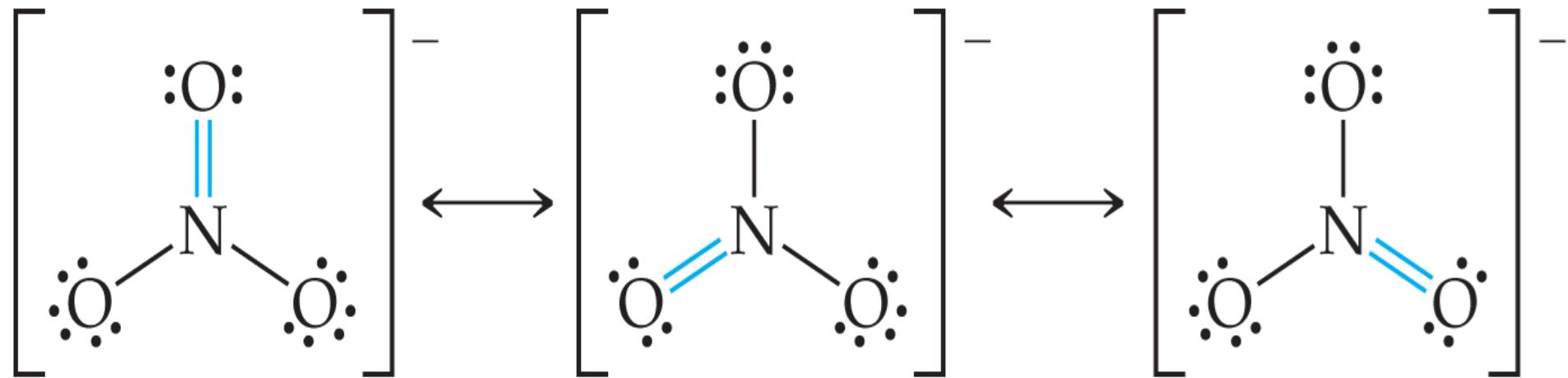
sp



2p

Delocalized Electrons: Resonance

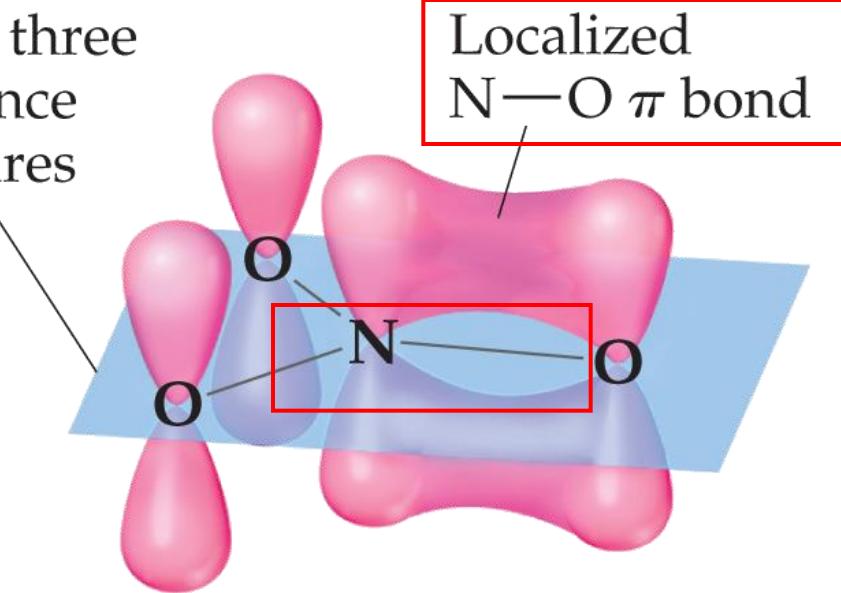
When writing Lewis structures for species like the nitrate ion, we draw **resonance structures (more Lewis structures)** to more accurately reflect the structure of the molecule or ion.



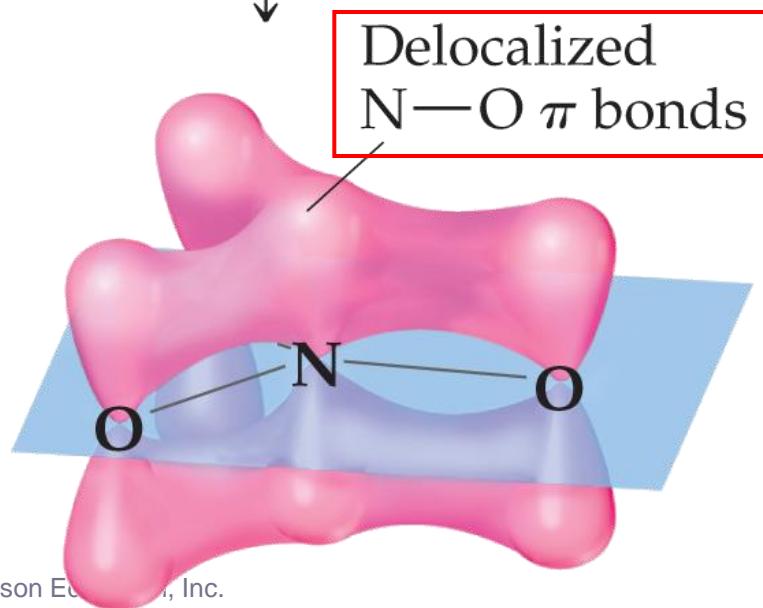
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One of three resonance structures



Resonance

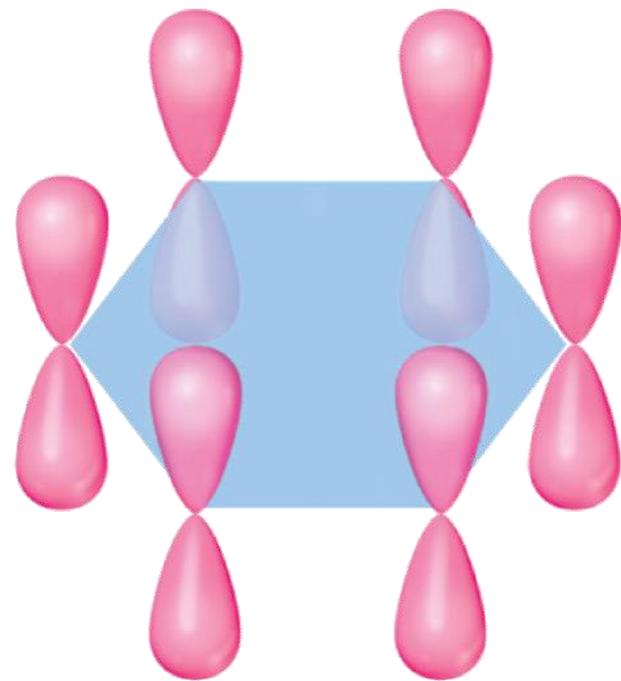
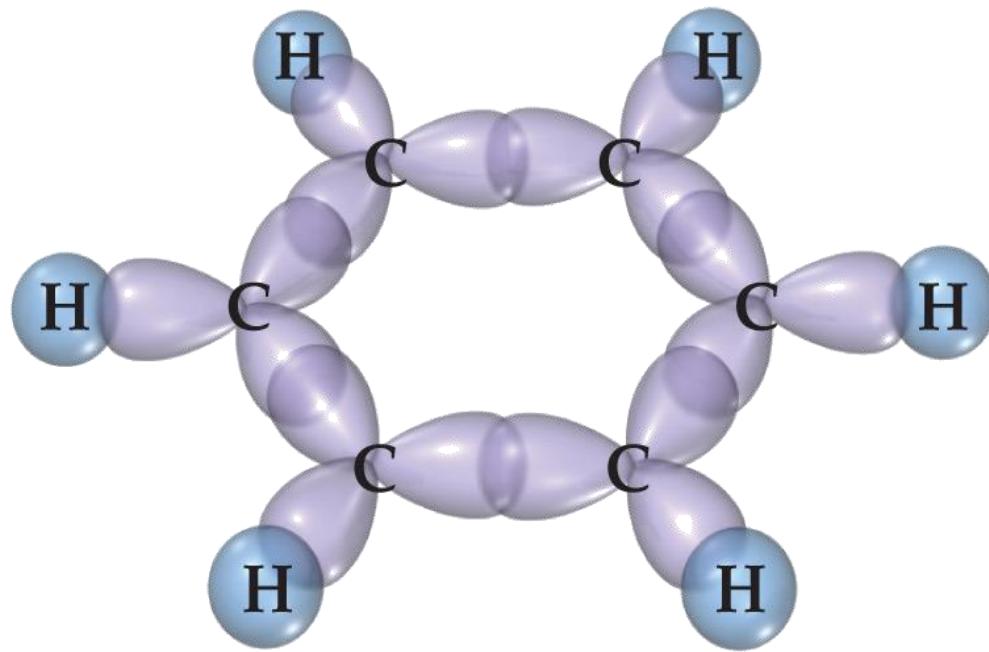


- In reality, each of the four atoms in the nitrate ion has a p orbital.
 - The **p orbitals** on all **three oxygens** overlap with the **p orbital** on the **central nitrogen**.

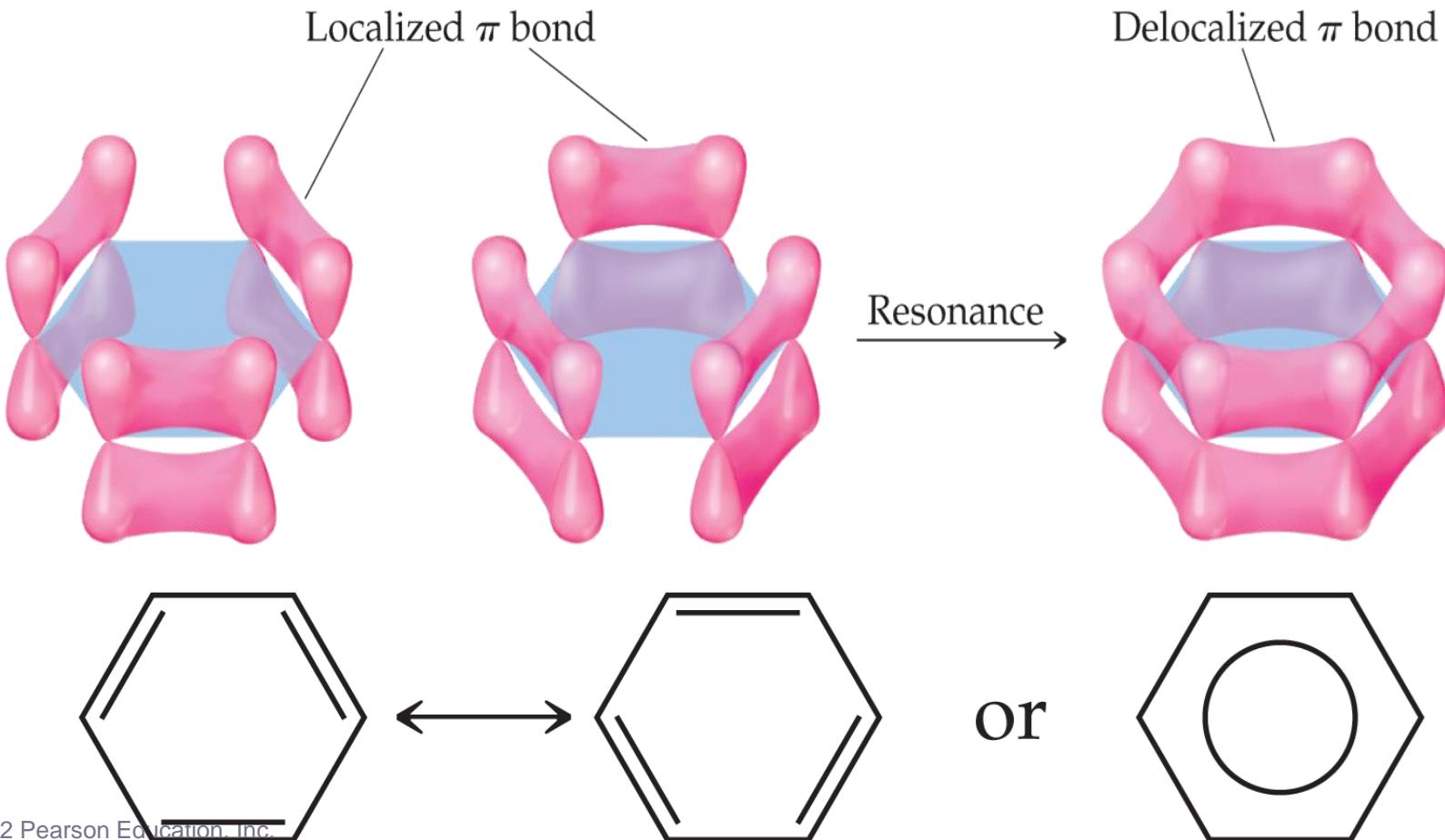
- This means the **π electrons** are **not localized** between the nitrogen and one of the oxygens, but rather are **delocalized throughout the ion**.

Resonance

The organic molecule benzene has **six σ C-C bonds** and **a p orbital on each carbon atom**.

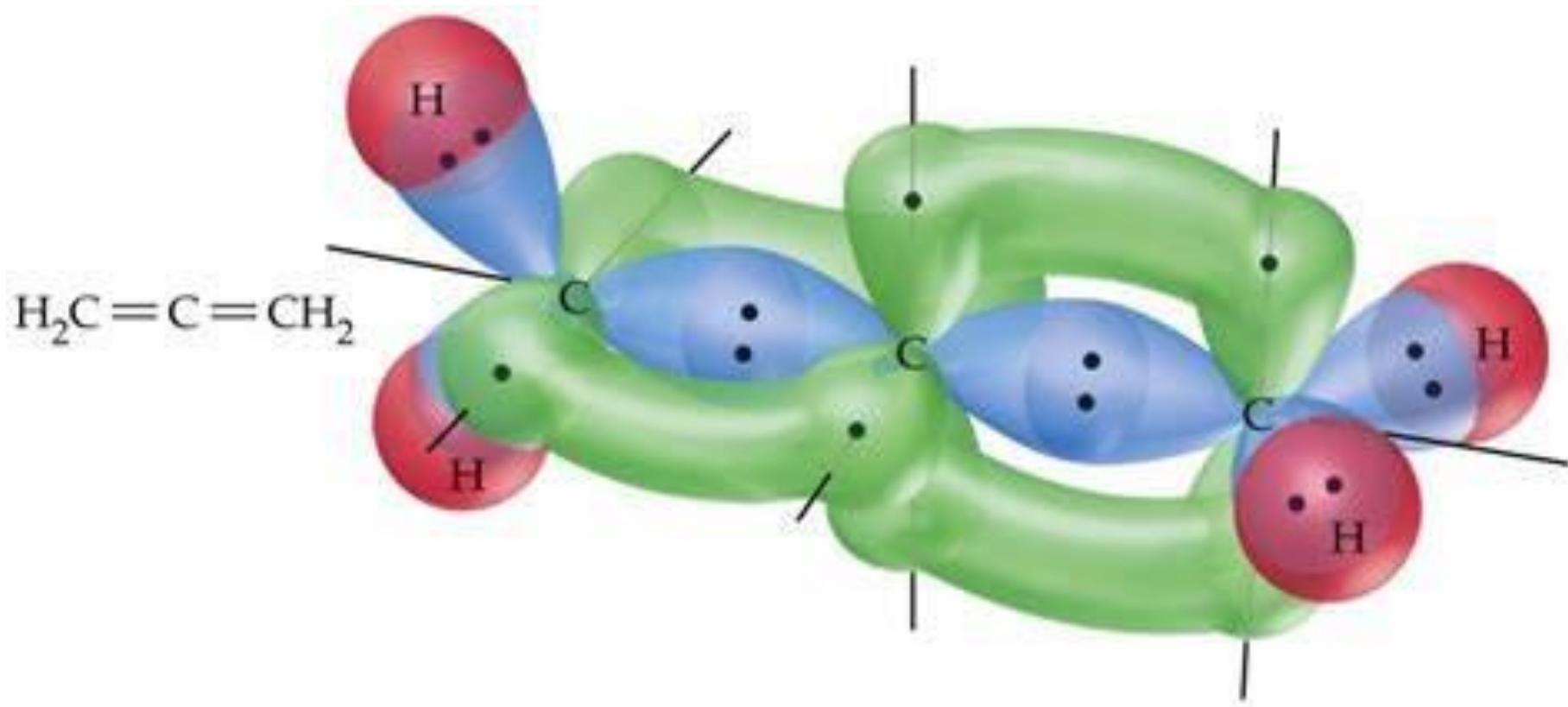


- In reality, **All π electrons** in benzene are **not localized**, but **delocalized** (C-C(benzene): 1.40 Å; typical C-C: 1.54 Å; typical C=C: 1.34 Å).
- The **even distribution** of the π electrons in benzene makes the molecule **unusually stable**.



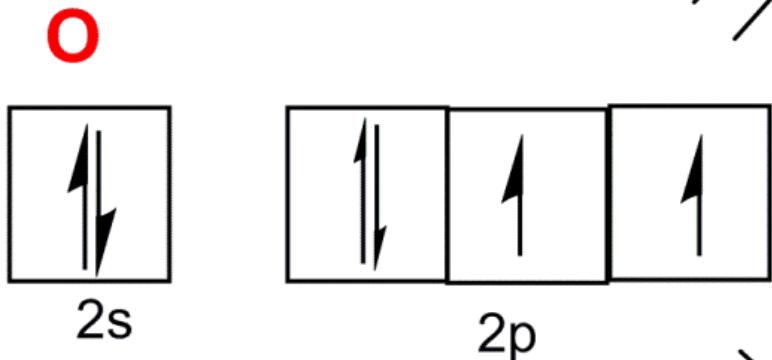
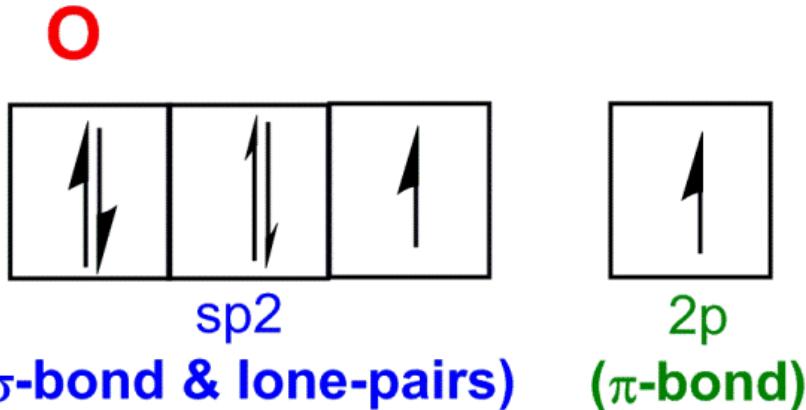
Extra Info.

Allene ($\text{CH}_2=\text{C}=\text{CH}_2$)

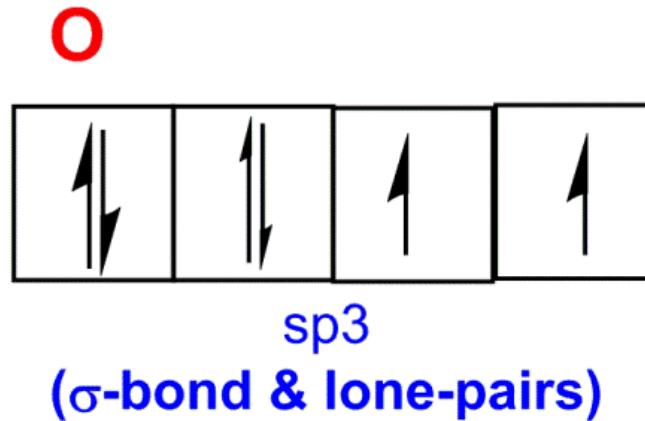


Number of electron domains? Hybridization?

For 3 electron-domains
e.g. H₂CO

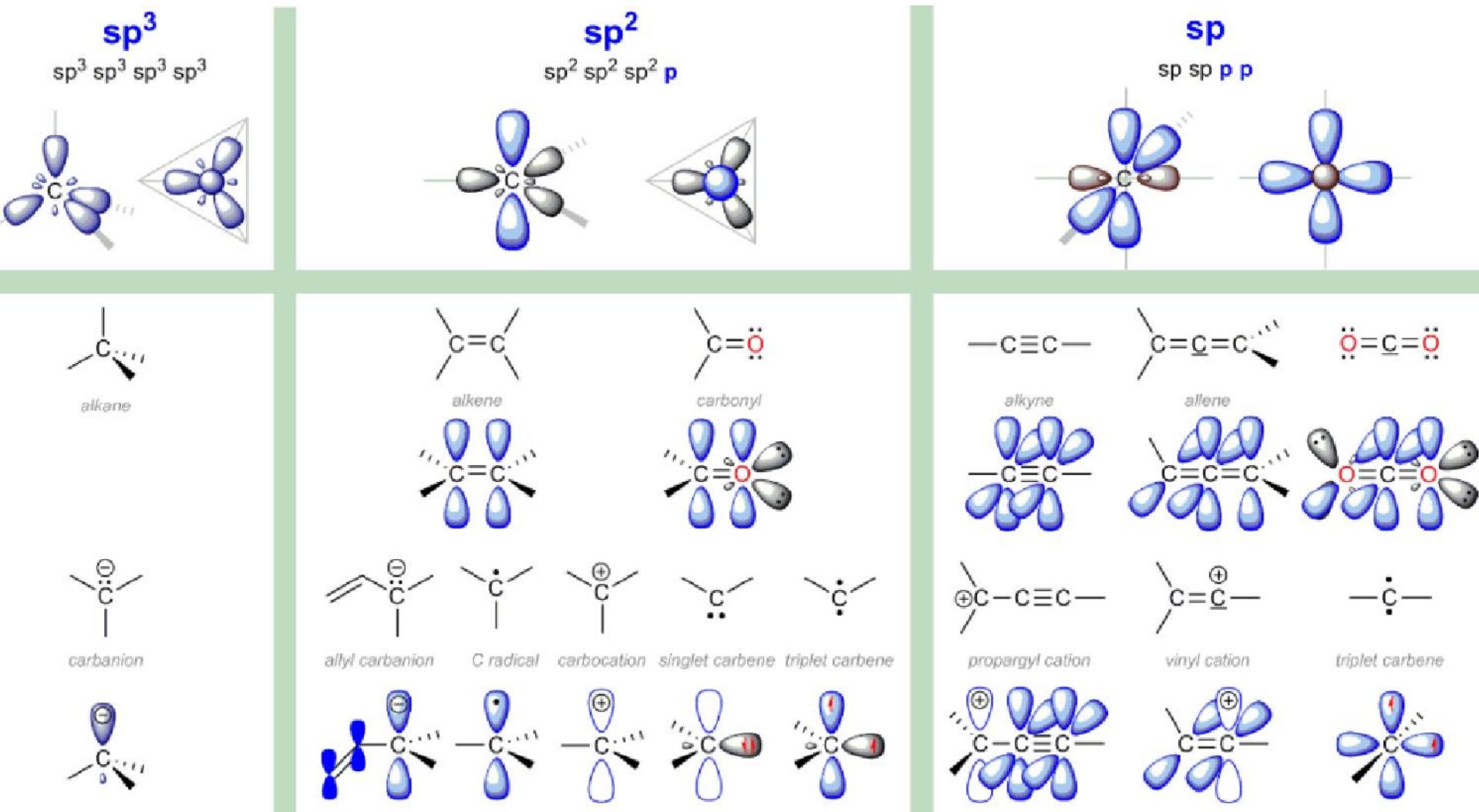


For 4 electron-domains
e.g. H₂O.



Number of **σ-bonds + lone-pairs** (**== electron domains**) = number of **hybrid orbitals** required. Then, **unhybridized 2p orbitals** are used for **π-bonds** (octet).

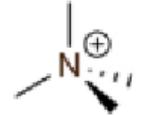
Extra Info.



Extra Info.

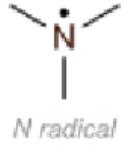
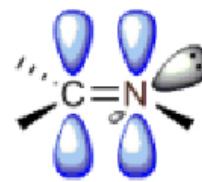
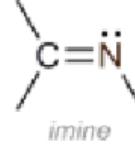
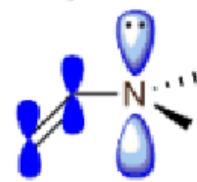
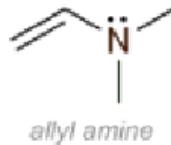
sp³

sp³ sp³ sp³ sp³

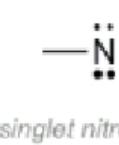


sp²

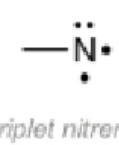
sp² sp² sp² p



N radical



singlet nitrene



triplet nitrene

sp

sp sp p p

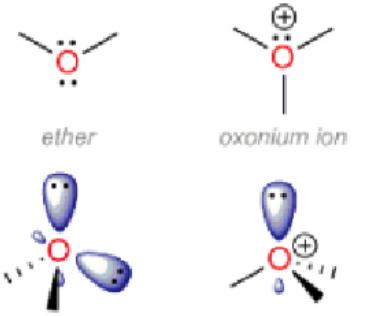


triplet nitrene

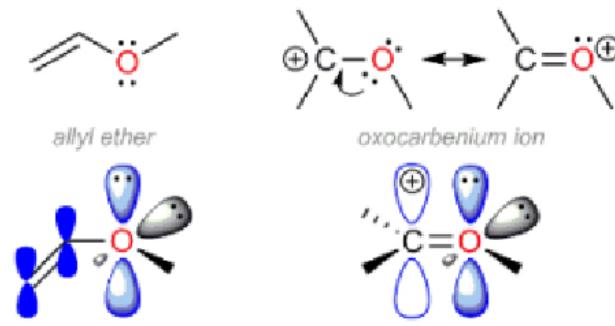


Extra Info.

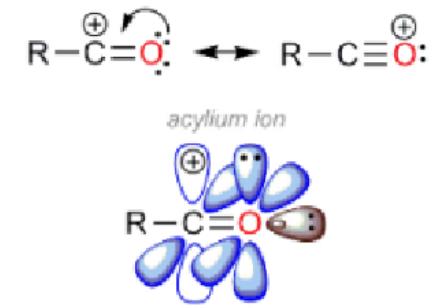
sp³
sp³ sp³ sp³ sp³



sp²
sp² sp² sp² p



sp
sp sp p p



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 ($\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{O}$) contains _____ pi bonds.

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

Molecular-Orbital (MO) Theory

Molecular-Orbital (MO) Theory

Valence Bond theory (+ Hybridization)

- Can predict molecular geometries & explain why/how bonds form between atoms.
- **CANNOT** predict **magnetic & excited states** easily.

Molecular-Orbital Theory

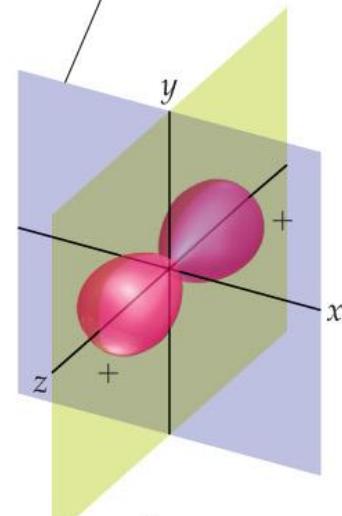
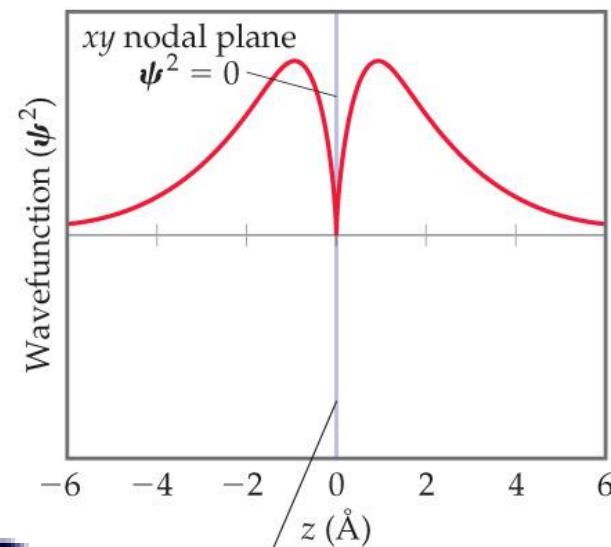
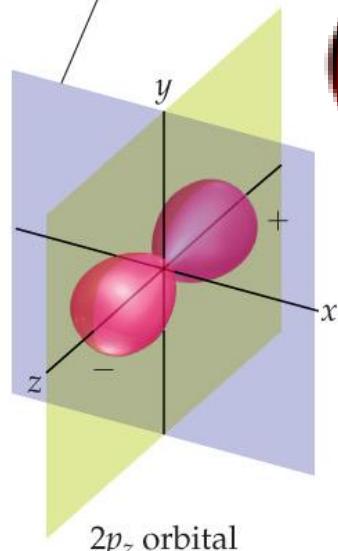
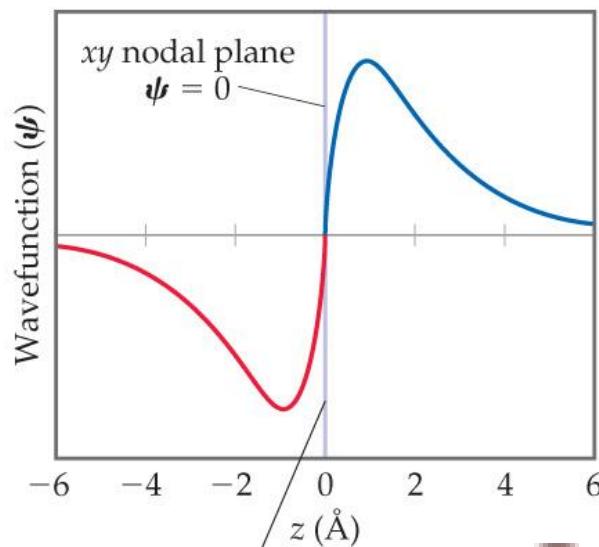
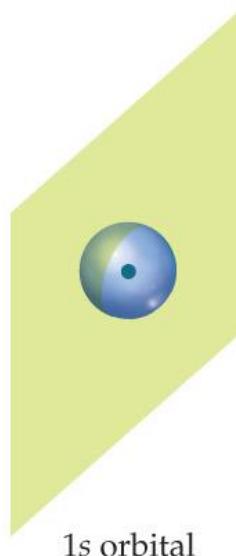
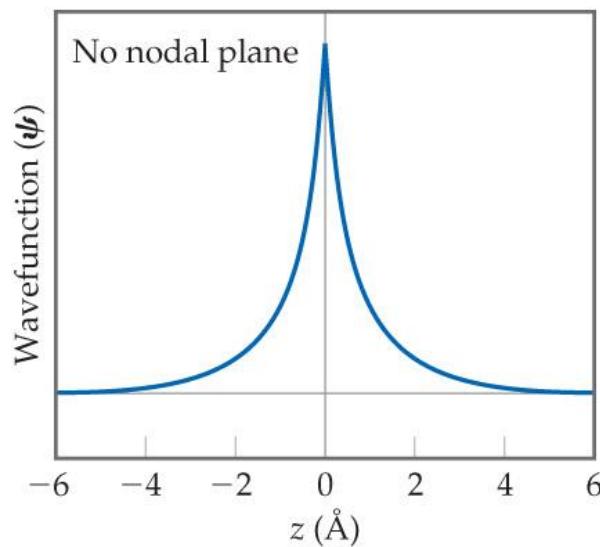
- **Wave nature of electrons** (quantum mechanics).
- **Linear combination** (线性组合) of **wave functions** (or **atomic orbitals**) of **all atoms** → **electrons** are found in orbitals of the **whole molecule**.



Robert Sanderson Mulliken

Friedrich Hermann Hund

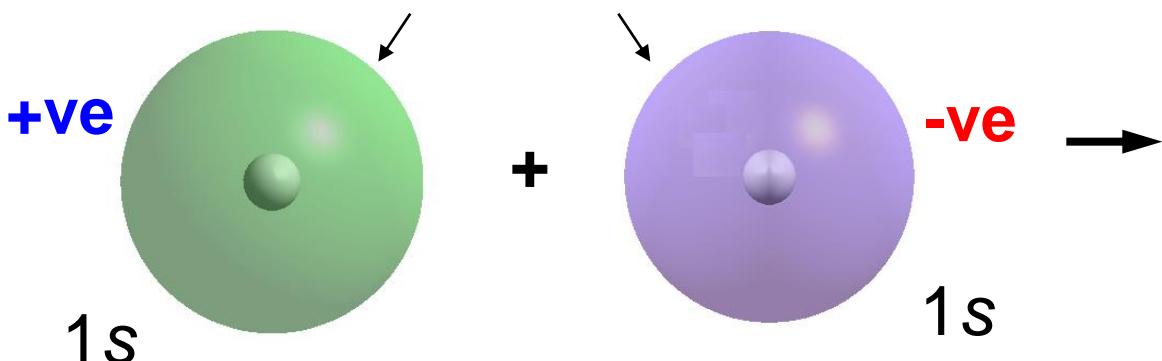
Wave Nature of Electrons



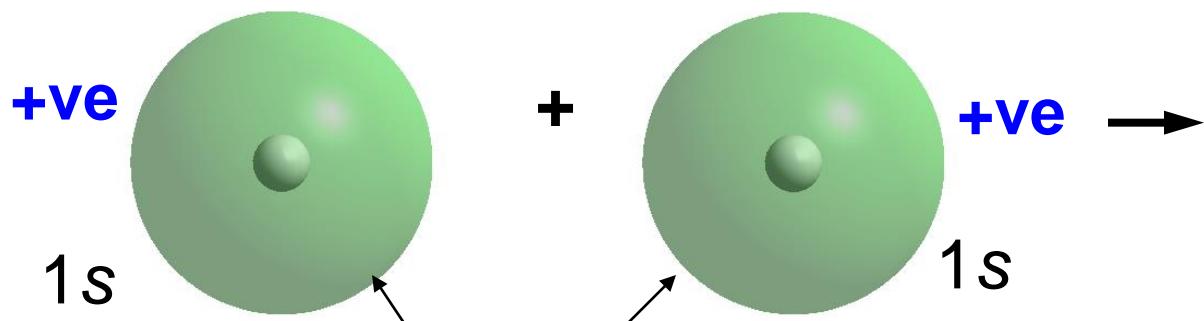
+ & -: Different phases (相)

Two ways for overlapping two atomic orbitals: (1) 1s orbitals overlapping have the **same sign** (phase 相) of the wavefunction (**net overlap**); (2) the two orbitals are of **opposite sign** (**no net overlap**).

Opposite sign of wavefunction



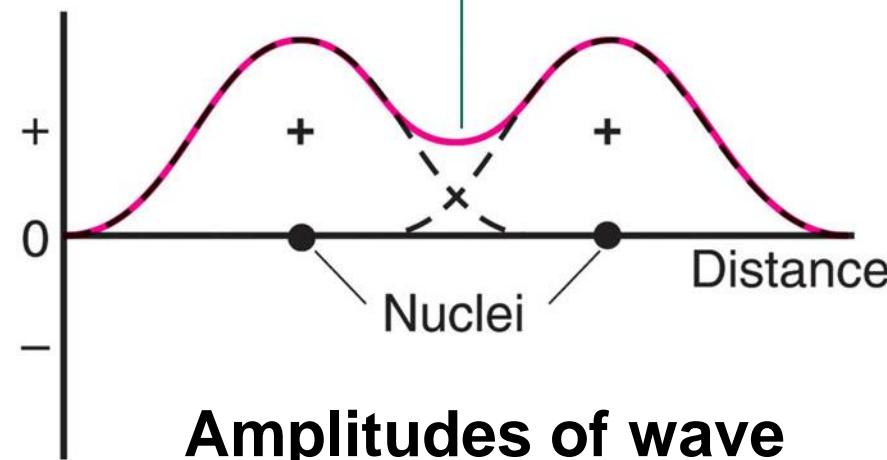
Higher energy anti-bonding orbital



Same sign of wavefunction

Lower energy bonding orbital

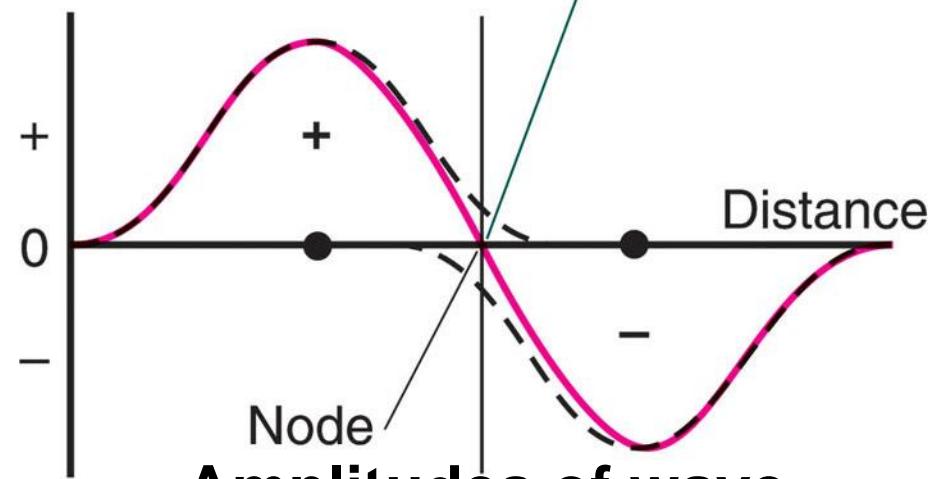
Waves reinforce



Amplitudes of wave functions added

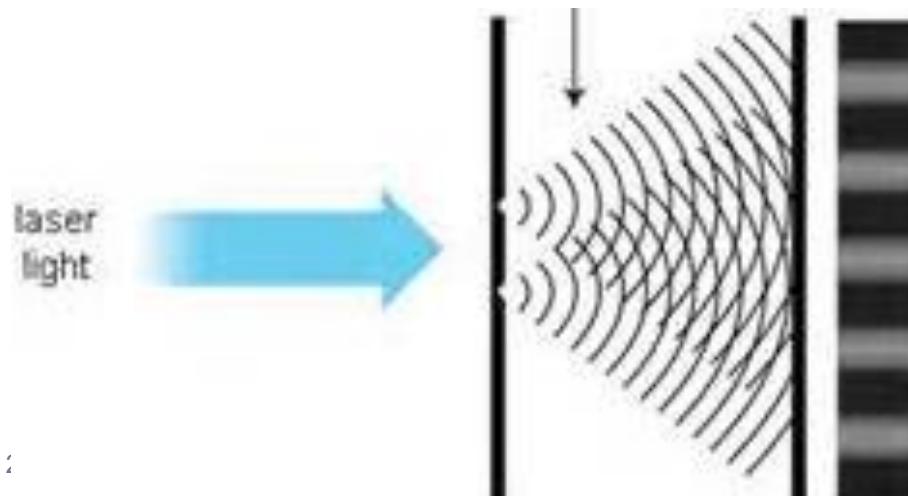
$$\psi_1 + \psi_2$$

Waves cancel



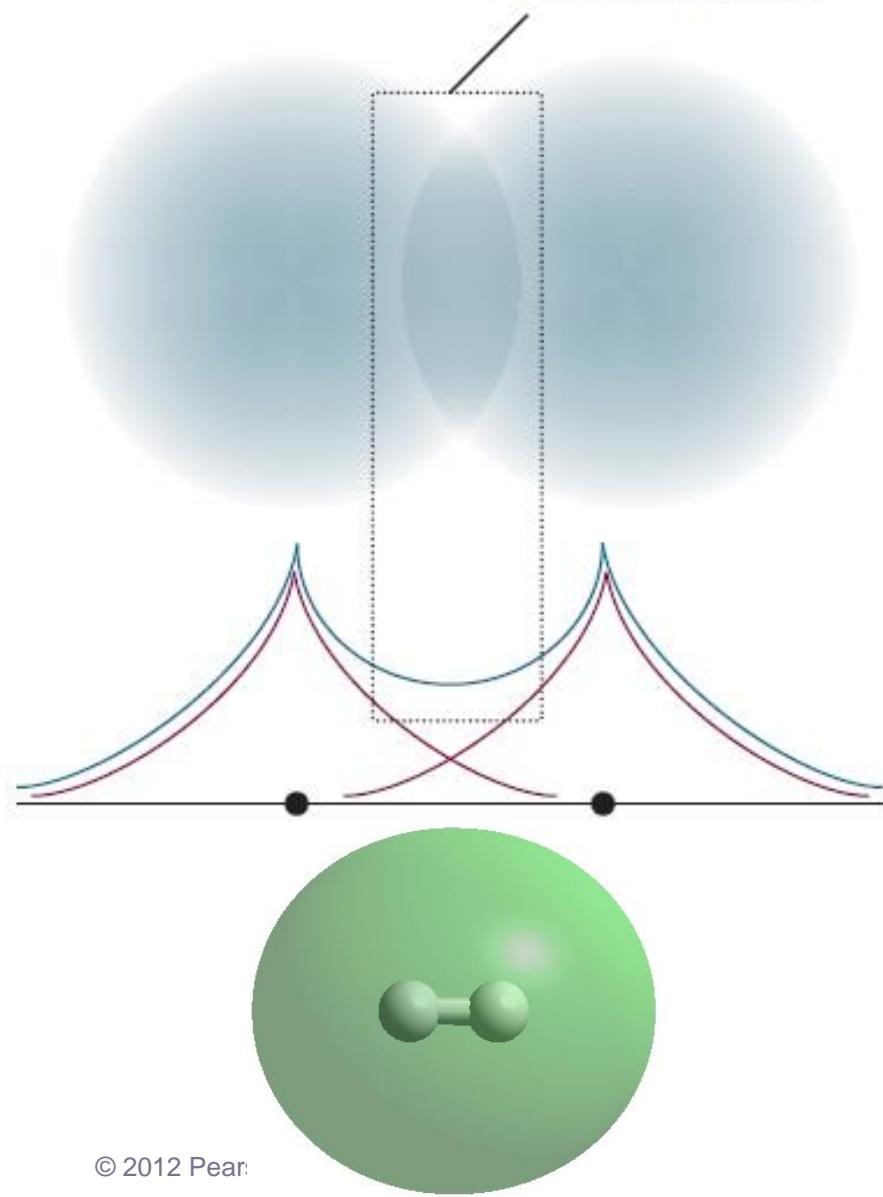
Amplitudes of wave functions subtracted

$$\psi_1 - \psi_2$$

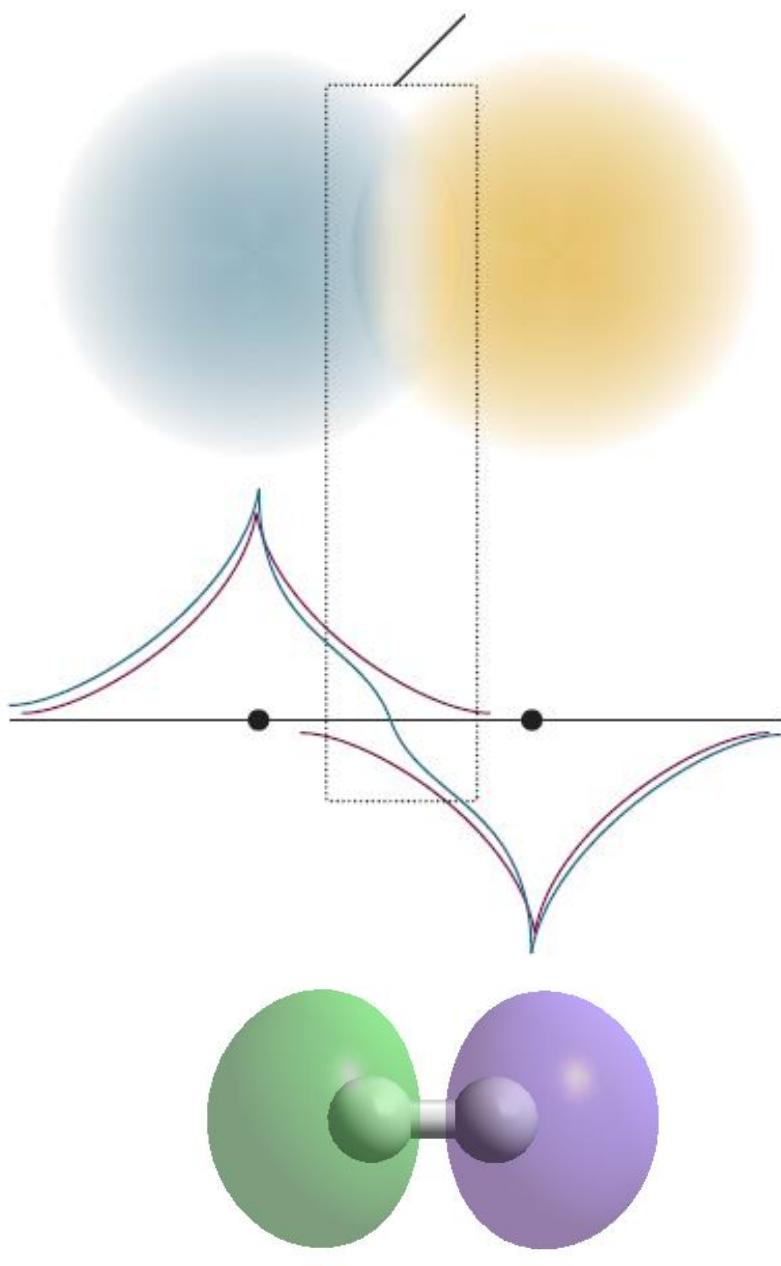


Interference
(干涉)

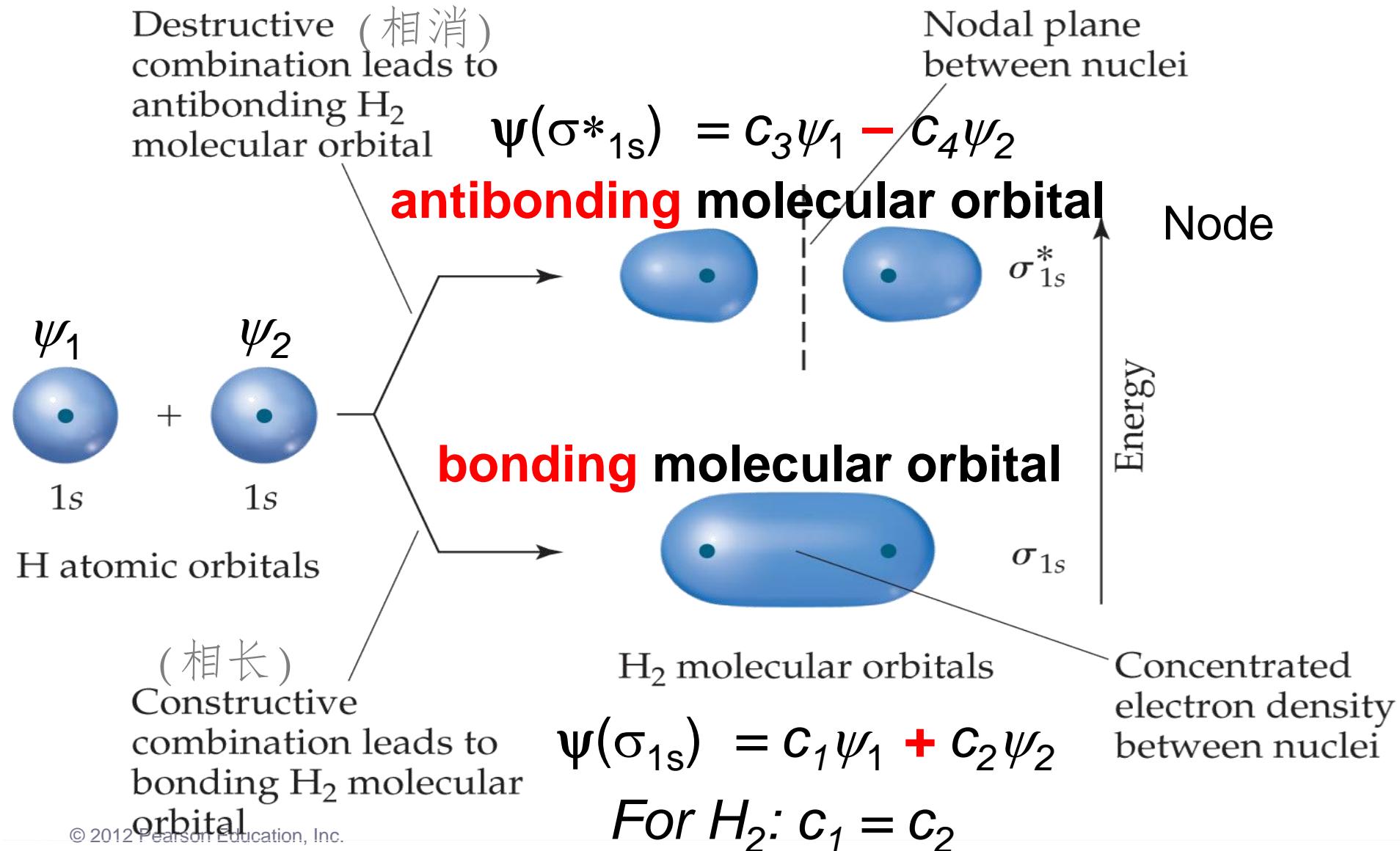
Region of
constructive
interference



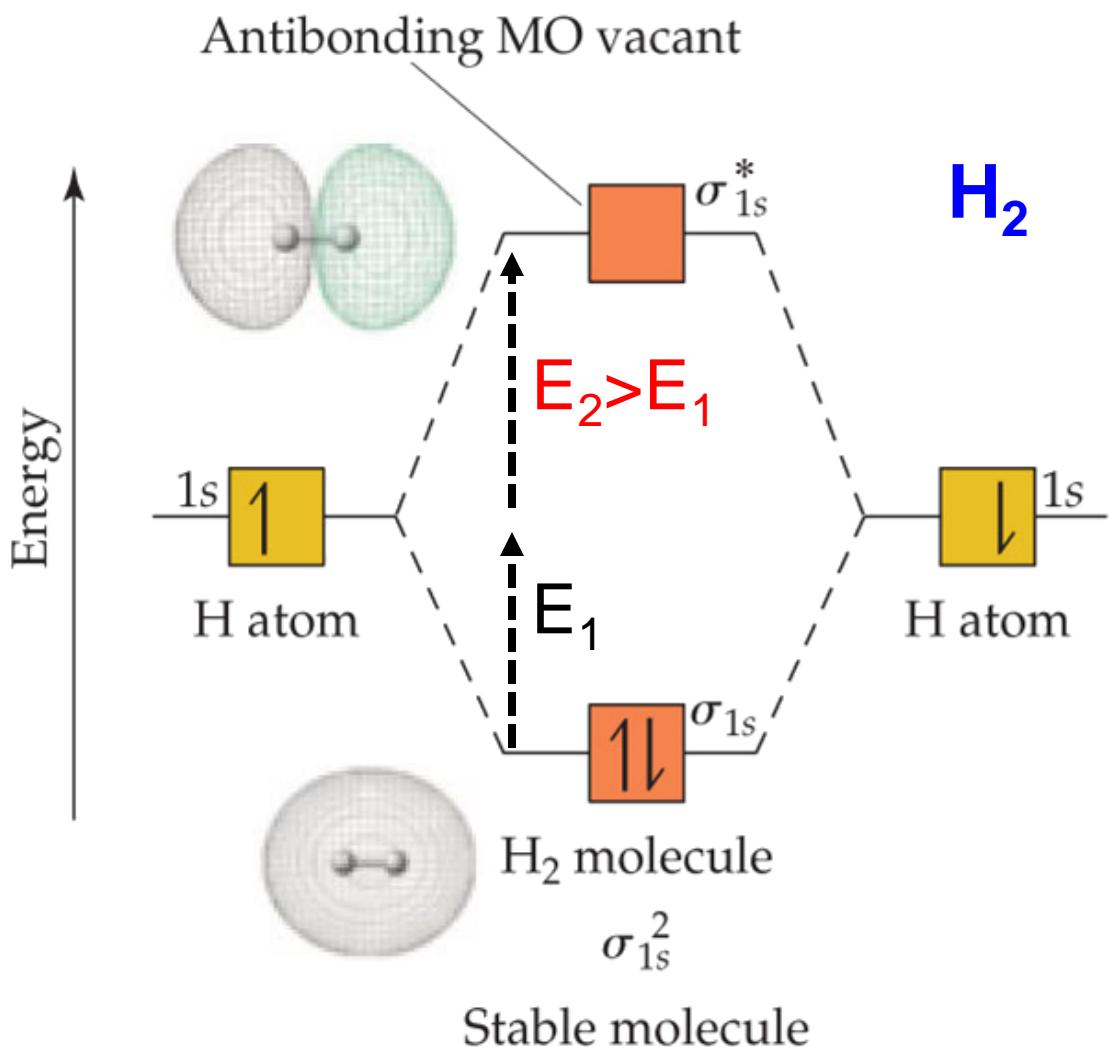
Region of
destructive
interference



MO theory consider the **wave** nature of electrons:
linear combination of wave functions (c^2 : weighting).



Energy-level (MO) Diagram



- In H_2 the two electrons go into the bonding molecular orbital: σ_{1s}^2

- Bond order:** one half the difference between the number of bonding and antibonding electrons.

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

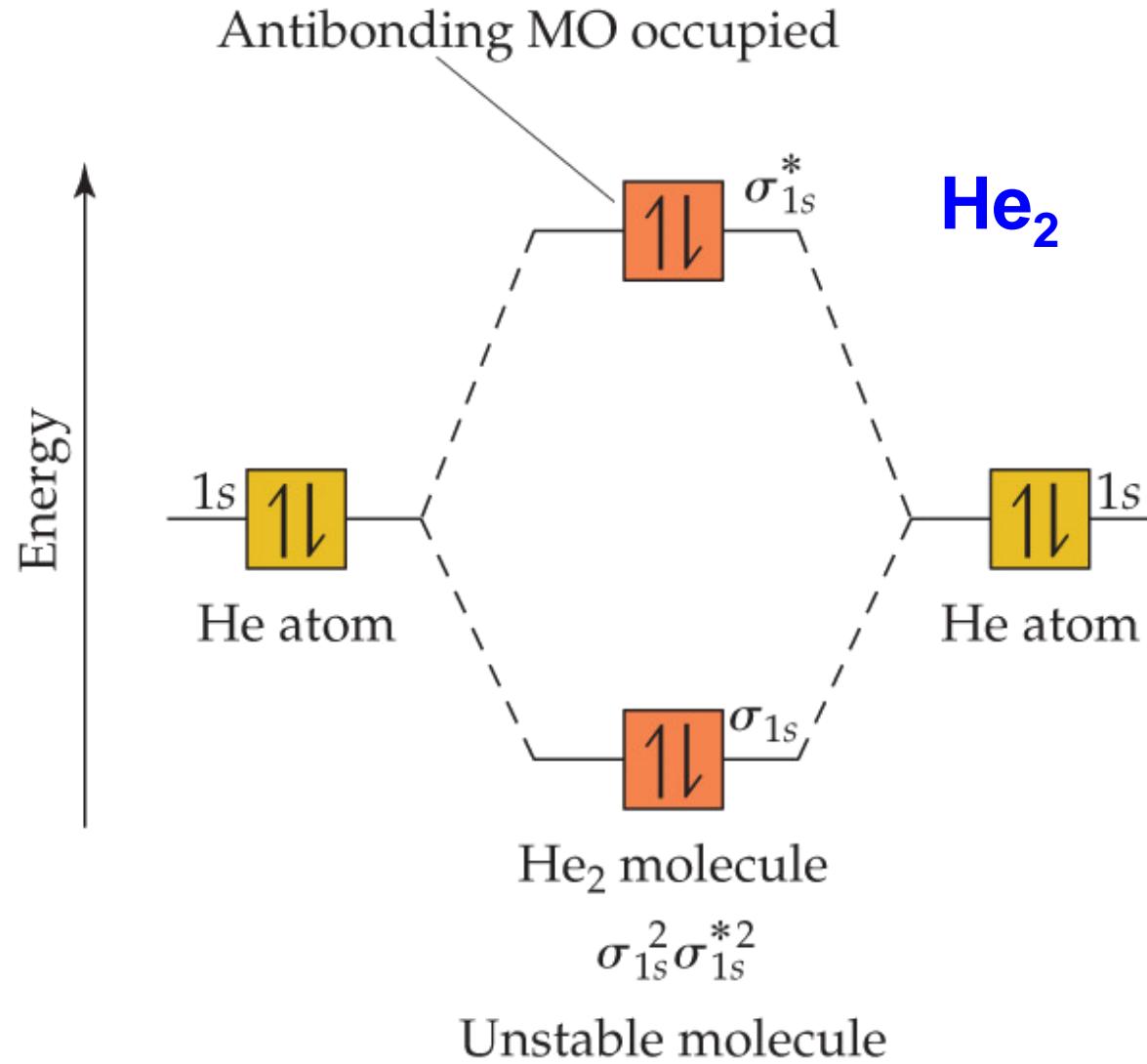
bond order : $\frac{1}{2}(\text{bonding electrons} - \text{antibonding electrons})$

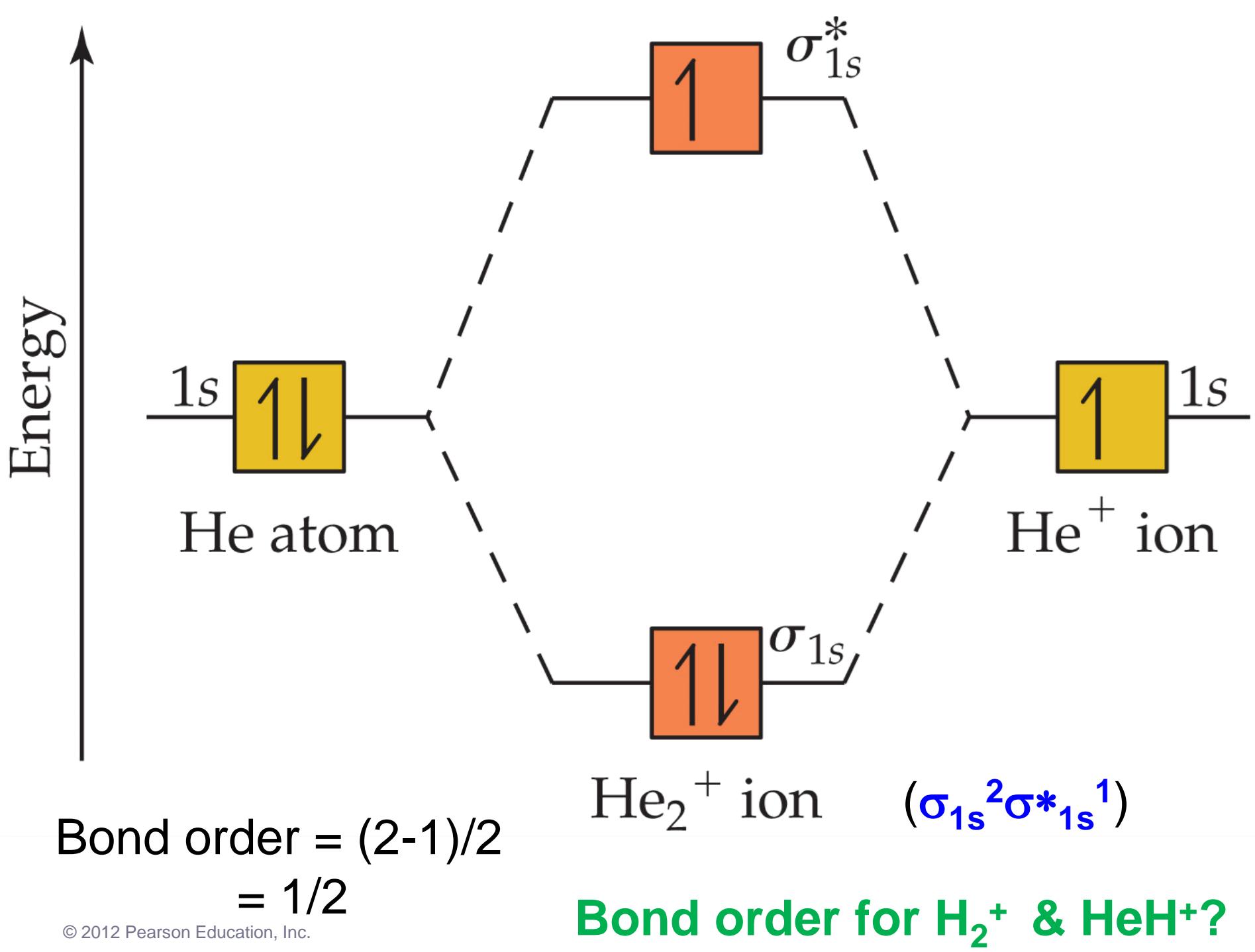
He_2 Molecule

- In the case of He_2 ($\sigma_{1s}^2 \sigma_{1s}^* {}^2$), the bond order would be

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

- Therefore, He_2 does not exist.





Extra Info. The proposed HeH⁺ as the first molecule (the 1st chemical reaction) in the early Universe?

Astrophysical detection of the helium hydride ion HeH⁺

18 APRIL 2019 | VOL 568 | NATURE | 357

Rolf Güsten^{1*}, Helmut Wiesemeyer¹, David Neufeld², Karl M. Menten¹, Urs U. Graf³, Karl Jacobs³, Bernd Klein^{1,4}, Oliver Ricken¹, Christophe Risacher^{1,5} & Jürgen Stutzki³

in the planetary nebula (行星状星云) NGC 7027

During the dawn of chemistry^{1,2}, when the temperature of the young Universe had fallen below some 4,000 kelvin, the ions of the light elements produced in Big Bang nucleosynthesis recombined in reverse order of their ionization potential. With their higher ionization

reaction networks^{19,20} in local plasmas, and might ultimately invalidate present models of the early Universe.

The deployment of the German Receiver for Astronomy at Terahertz Frequencies (GREAT)⁹ heterodyne spectrometer on board the

ASTROCHEMISTRY

Quantum-state-selective electron recombination studies suggest enhanced abundance of primordial HeH⁺

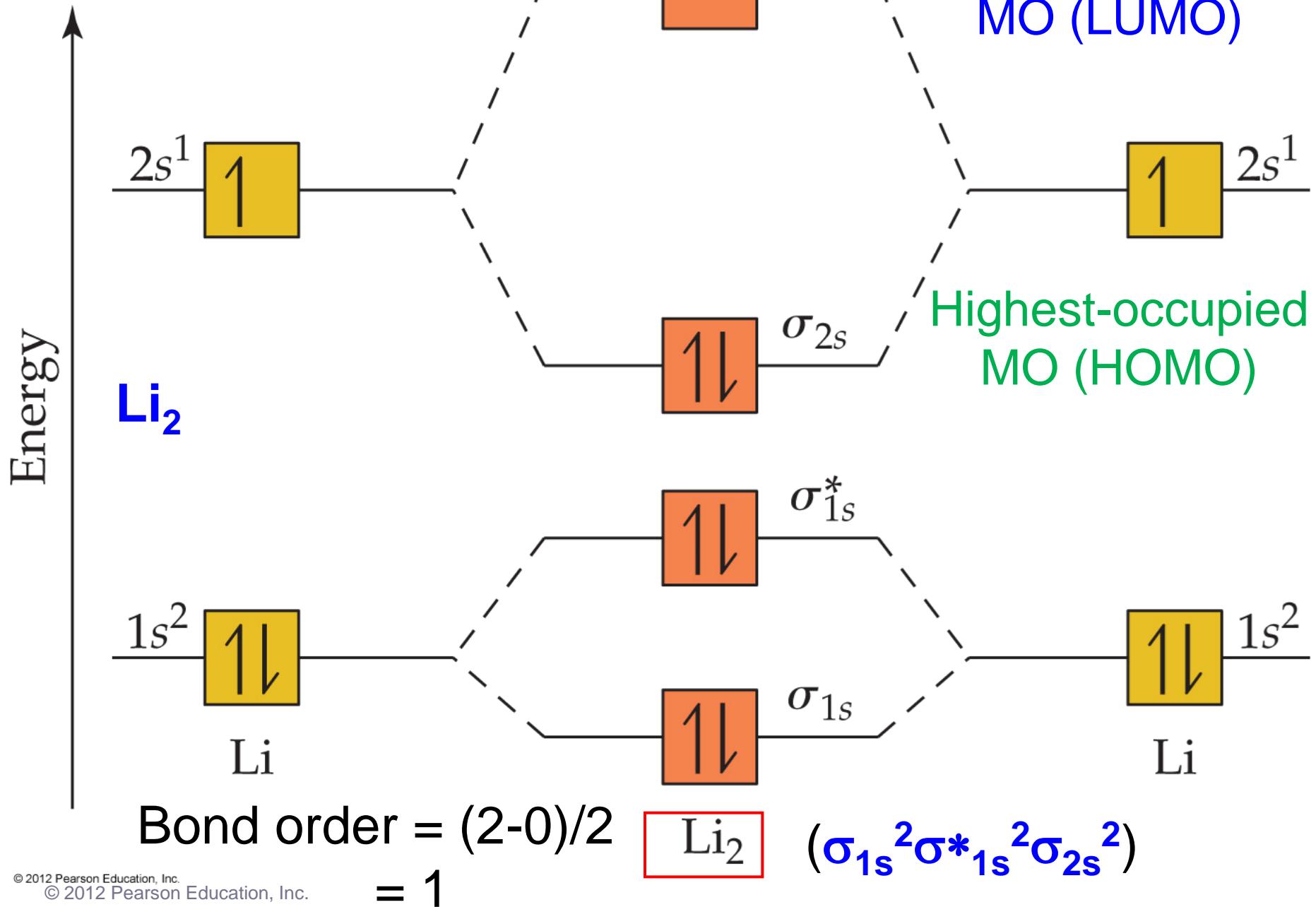
Maybe the strongest (Lewis) acid

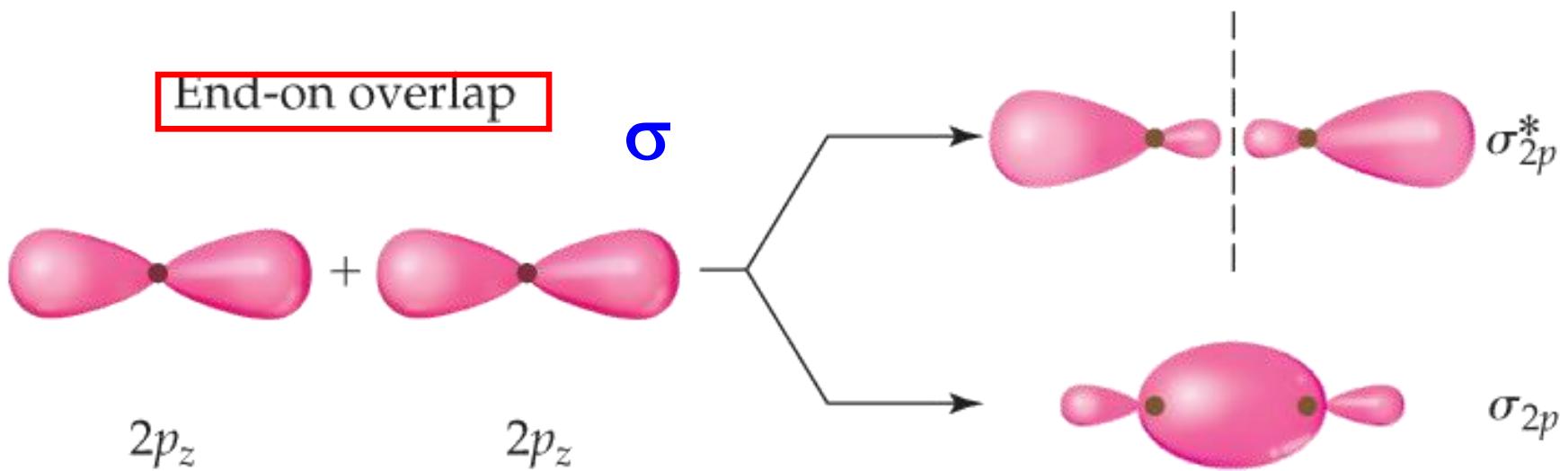
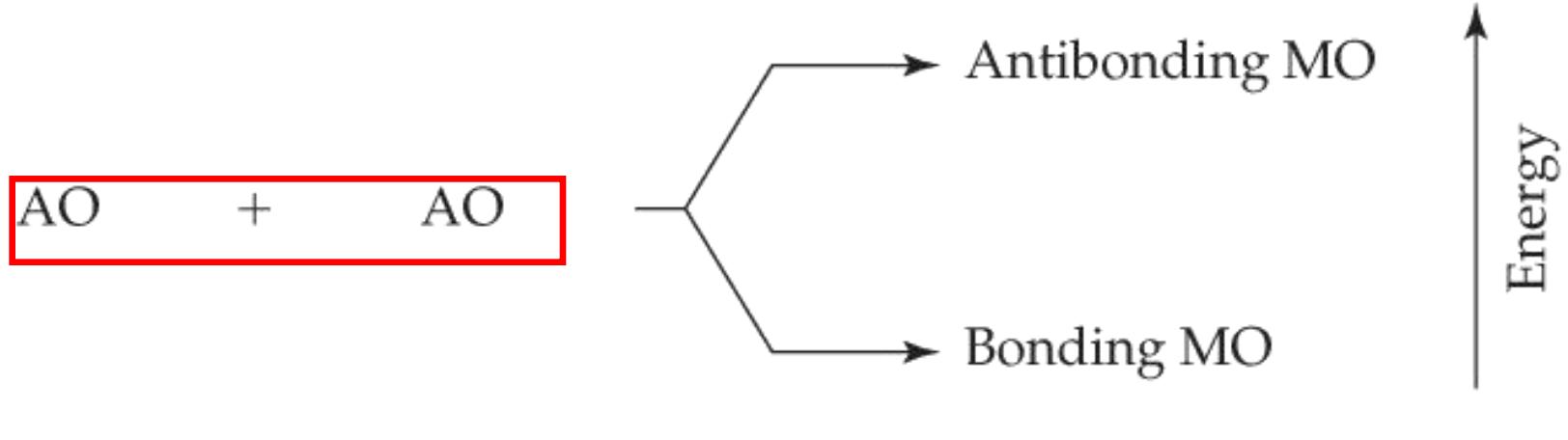
Oldřich Novotný^{1*}, Patrick Wilhelm¹, Daniel Paul¹, Ábel Kálosi^{1,2}, Sunny Saurabh¹, Arno Becker¹, Klaus Blaum¹, Sebastian George^{1,3}, Jürgen Göck¹, Manfred Grieser¹, Florian Grussie¹, Robert von Hahn¹, Claude Krantz¹, Holger Kreckel¹, Christian Meyer¹, Preeti M. Mishra¹, Damian Muell¹, Felix Nuesslein¹, Dmitry A. Orlov¹, Marius Rimmler¹, Viviane C. Schmidt¹, Andrey Shornikov¹, Aleksandr S. Terekhov⁴, Stephen Vogel¹, Daniel Zajfman⁵, Andreas Wolf¹

Science 365, 676–679 (2019)

The epoch of first star formation in the early Universe was dominated by simple atomic and molecular species consisting mainly of two elements: hydrogen and helium.

Li_2 Molecule

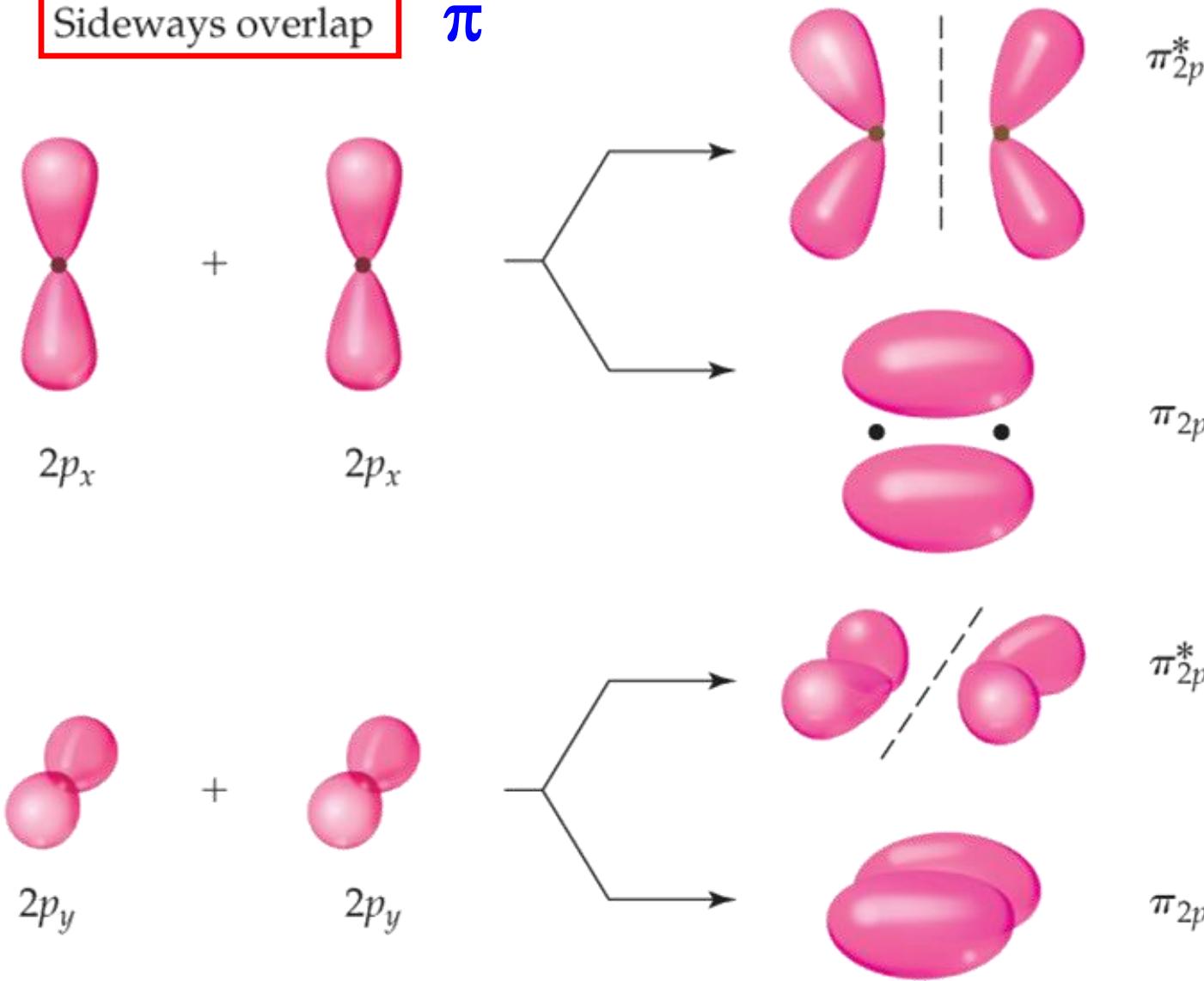




- For atoms with both **s** and **p** **orbitals**, there are **2** types of interactions/**overlap**:
 1. The **s** & **p** orbitals that **face each other** overlap in **σ** fashion: σ_{2s} , σ^*_{2s} , σ_{2p} & σ^*_{2p}

Sideways overlap

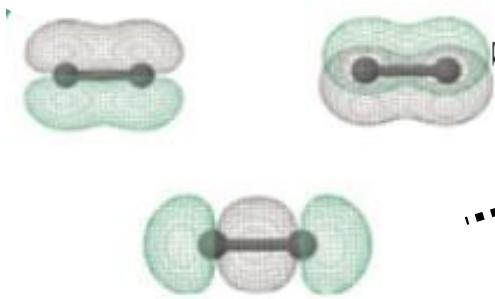
π



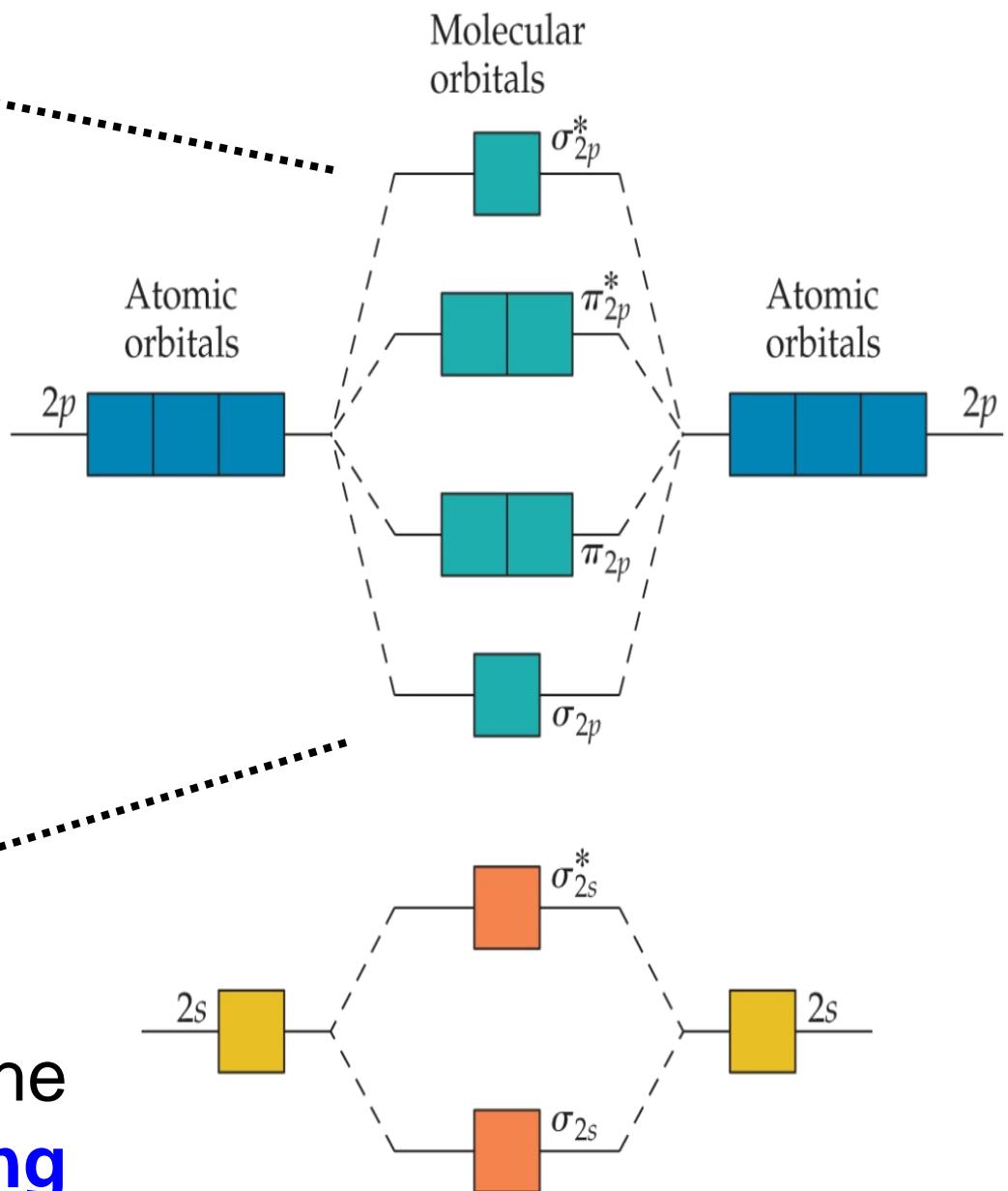
Effects of p Orbitals

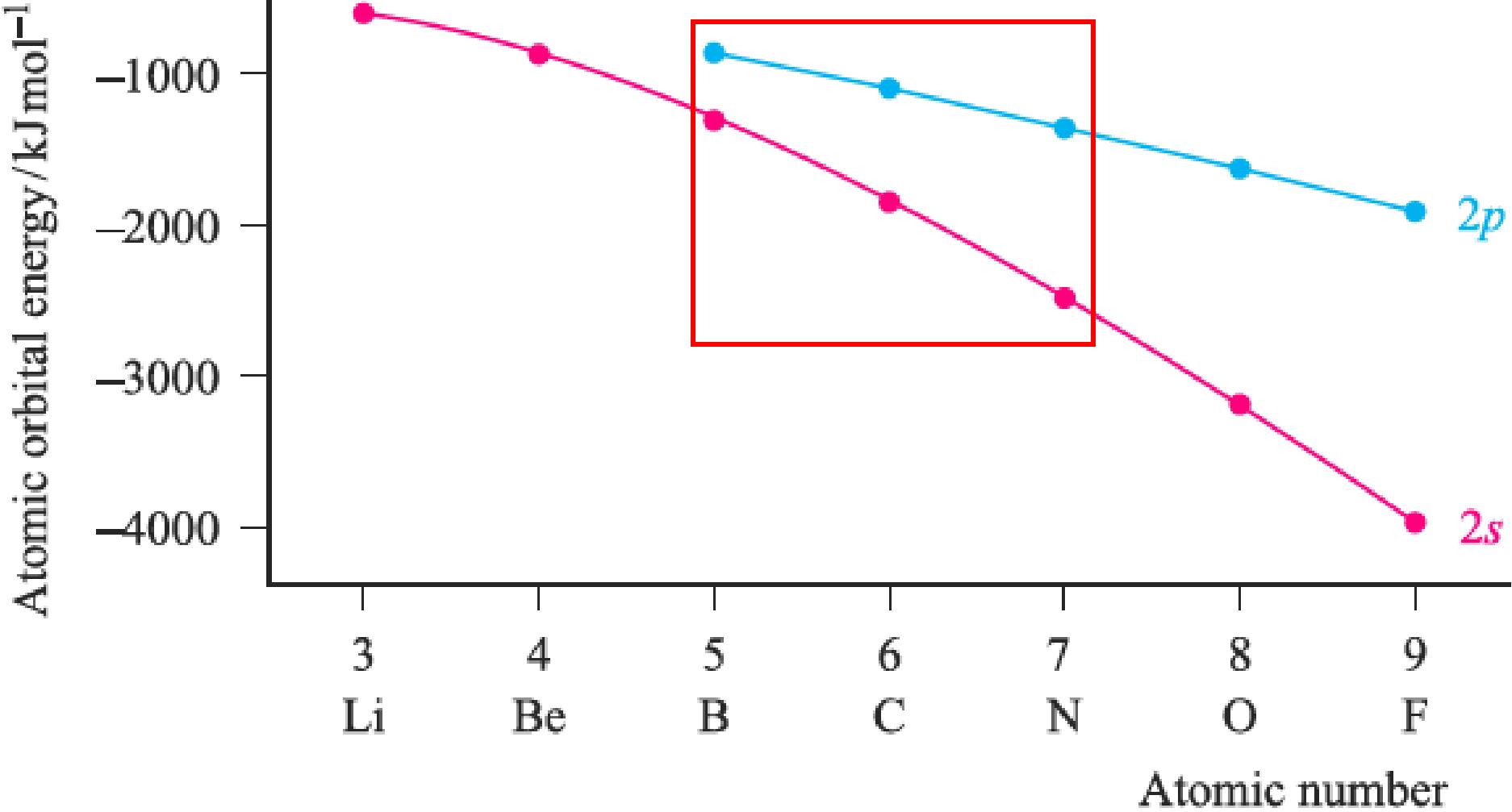
2. The other **two sets of p orbitals** overlap in π fashion (sideway) to four 4 MOs: **2 sets π_{2p}** & **2 sets π_{2p}^***

Both σ & π bonding
MOs & σ^* & π^*
antibonding MOs.

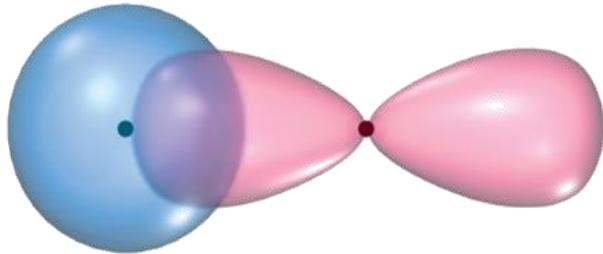


- The **stronger** bond, the **lower energy** the **bonding** MO & **higher energy** **antibonding** MO.

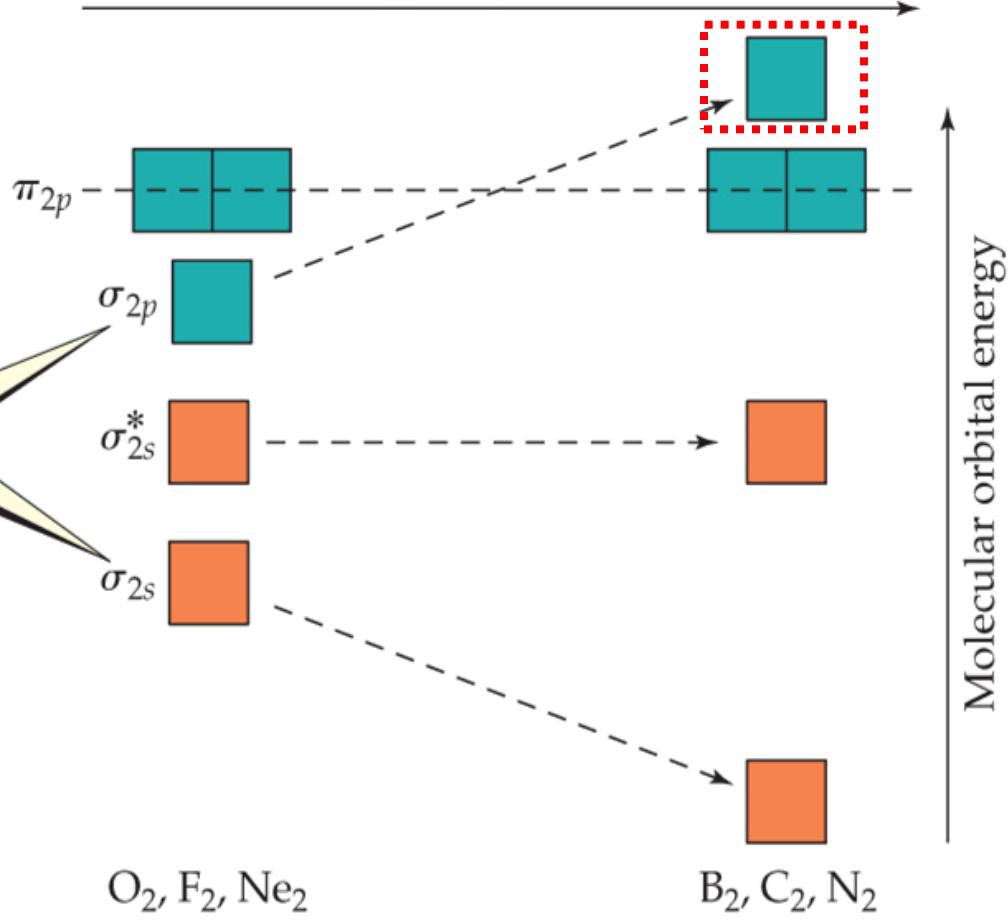




- Orbital energy difference 2s and 2p increases from left to right of the second period of periodic table.
- Atomic orbitals **interact most effectively** with other atomic orbitals of **similar energy**.

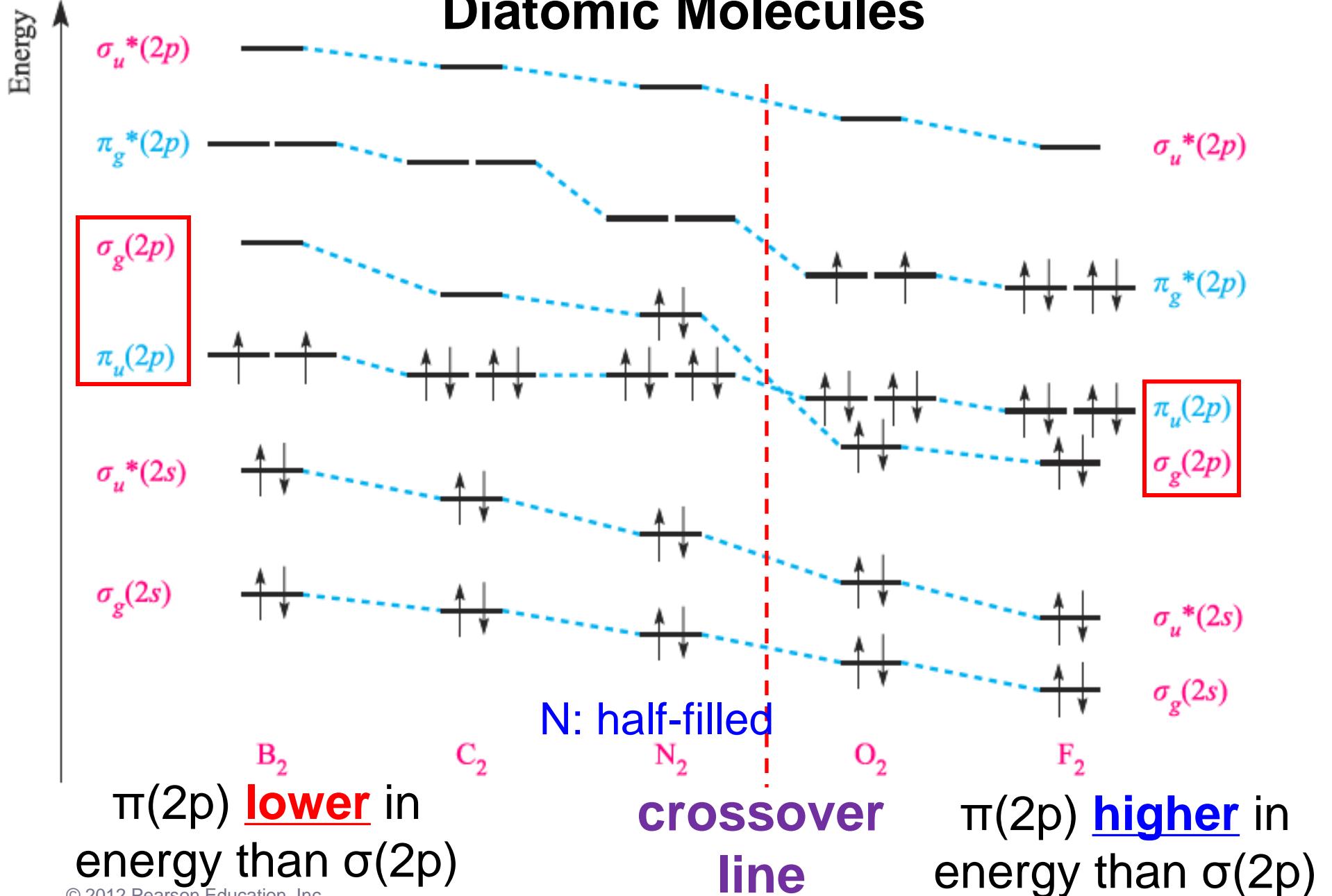


Increasing 2s–2p interaction

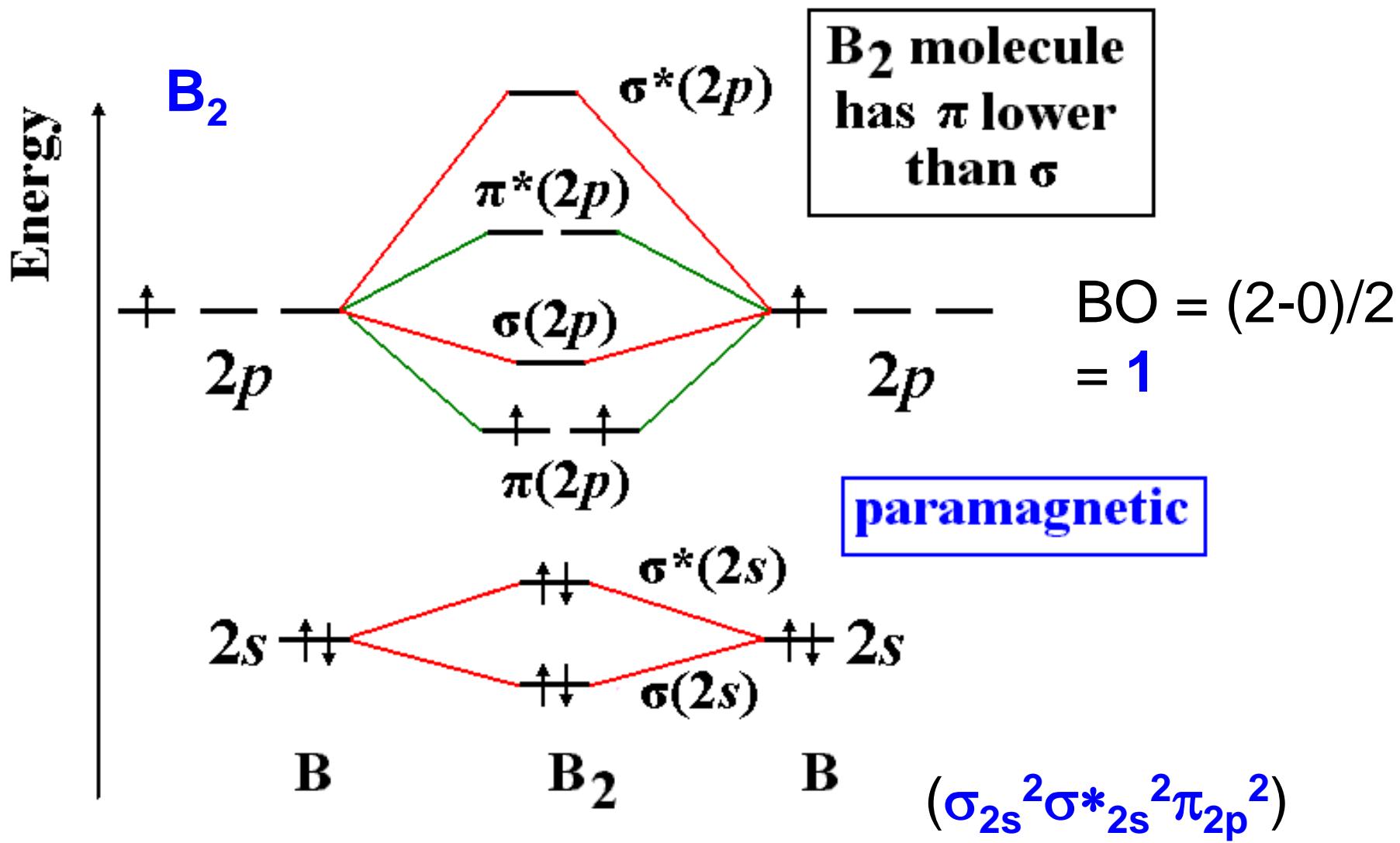


- **2s and 2p_z** orbitals can **further interact/mix** (in a **σ fashion**): the smaller p-block elements in the **second period** have a **sizable interaction** between the s & p.
- σ_{2s} : **decrease** MO energy; σ_{2p} : **increase** MO energy
- **flips order of the σ_{2p} and π_{2p} MO** in B, C & N!

Energy Levels of Second-Row Homonuclear Diatomic Molecules

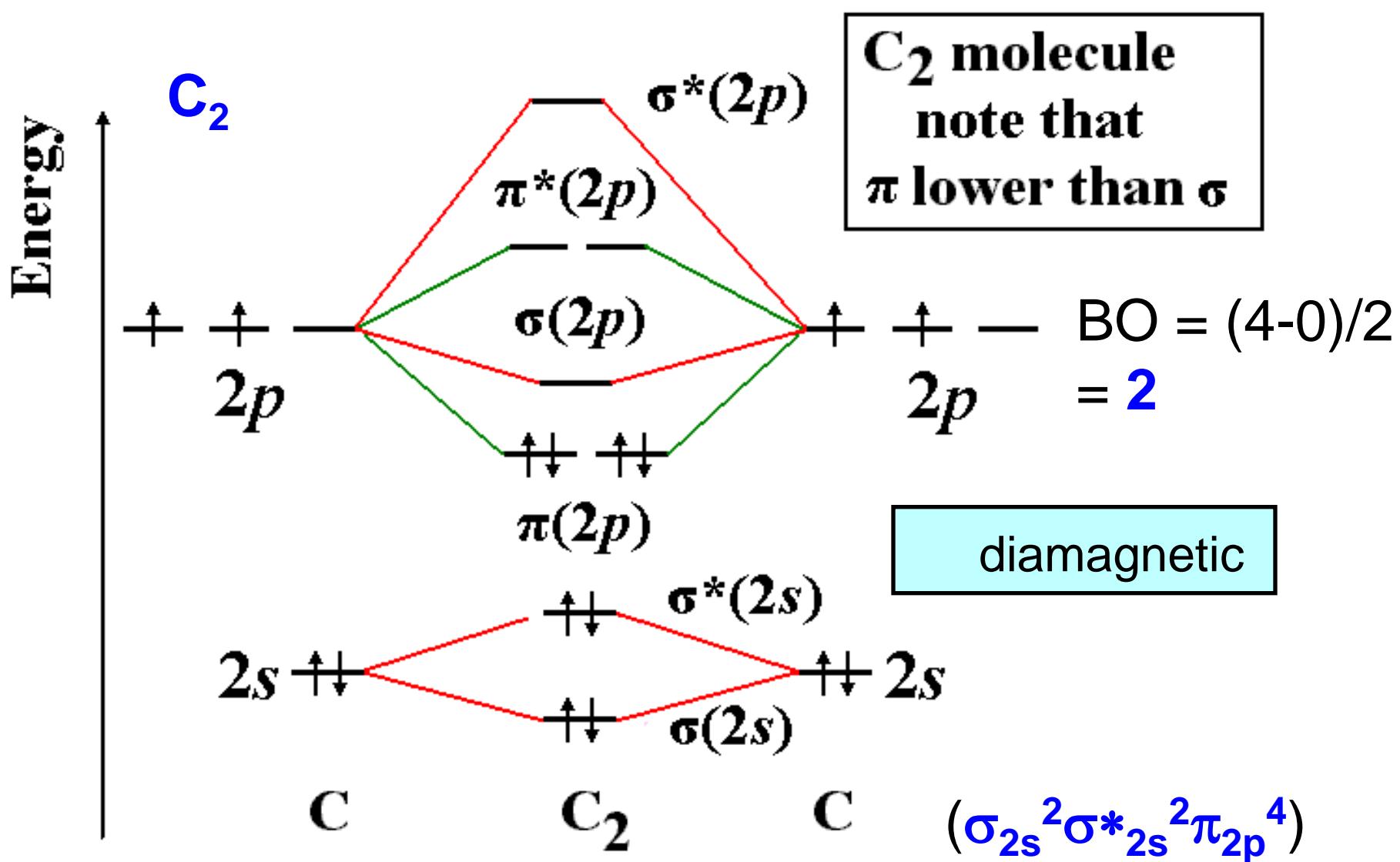


B_2 Molecule



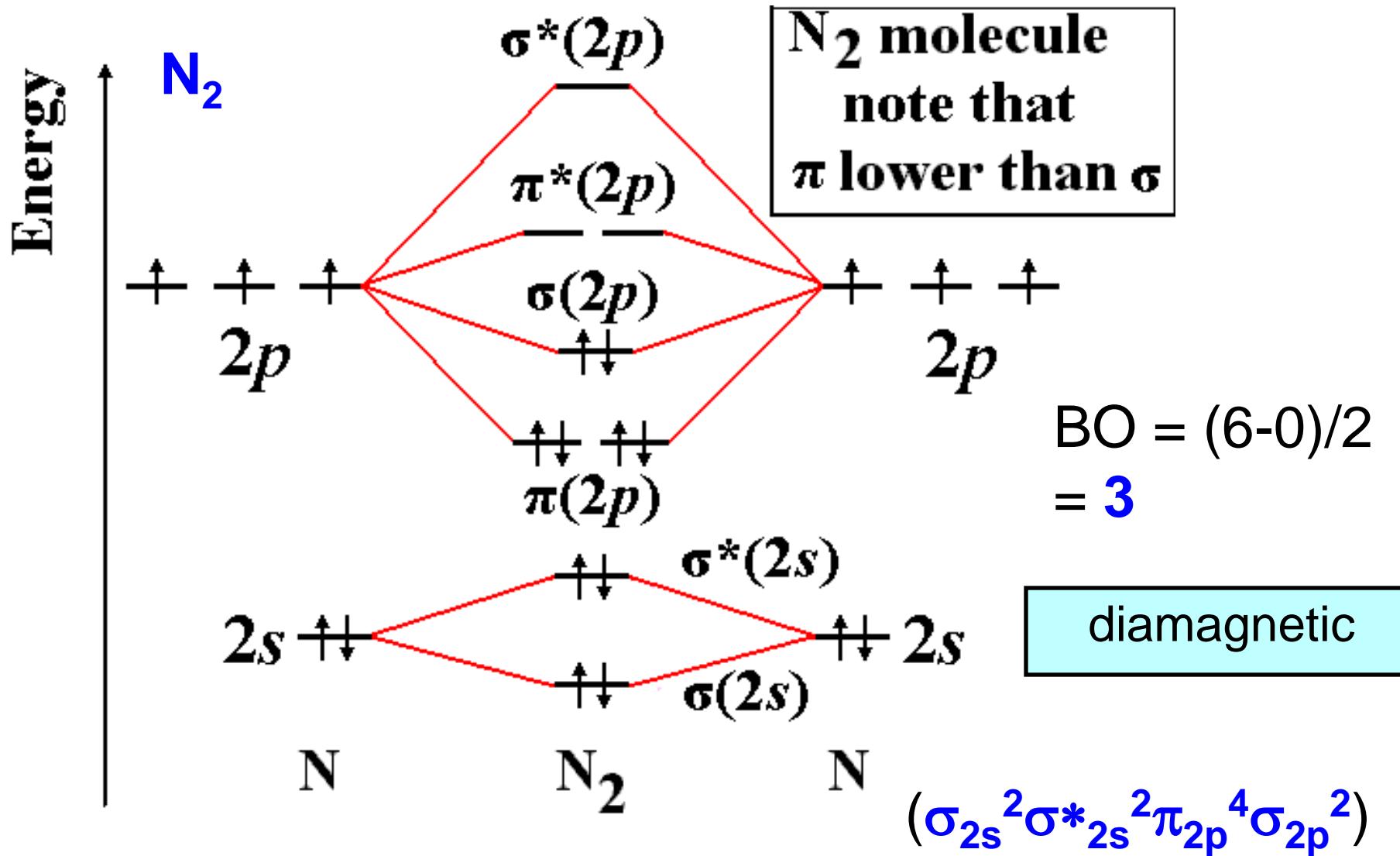
MO diagram for B_2 molecule, bond order = 1.

C₂ Molecule



MO diagram for C₂ molecule, bond order = 2.

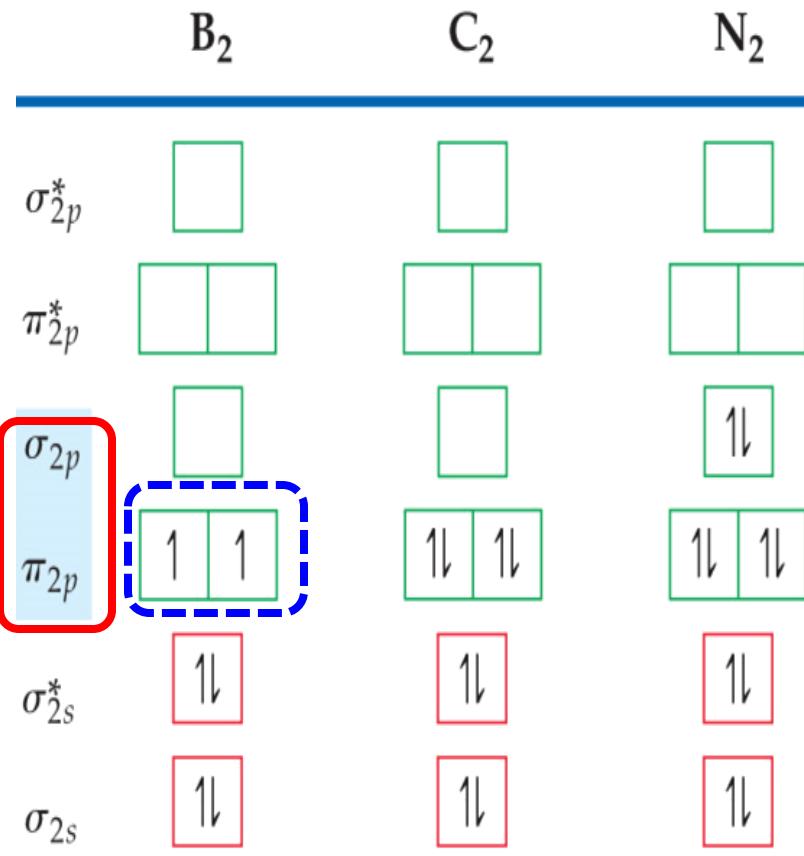
N_2 Molecule



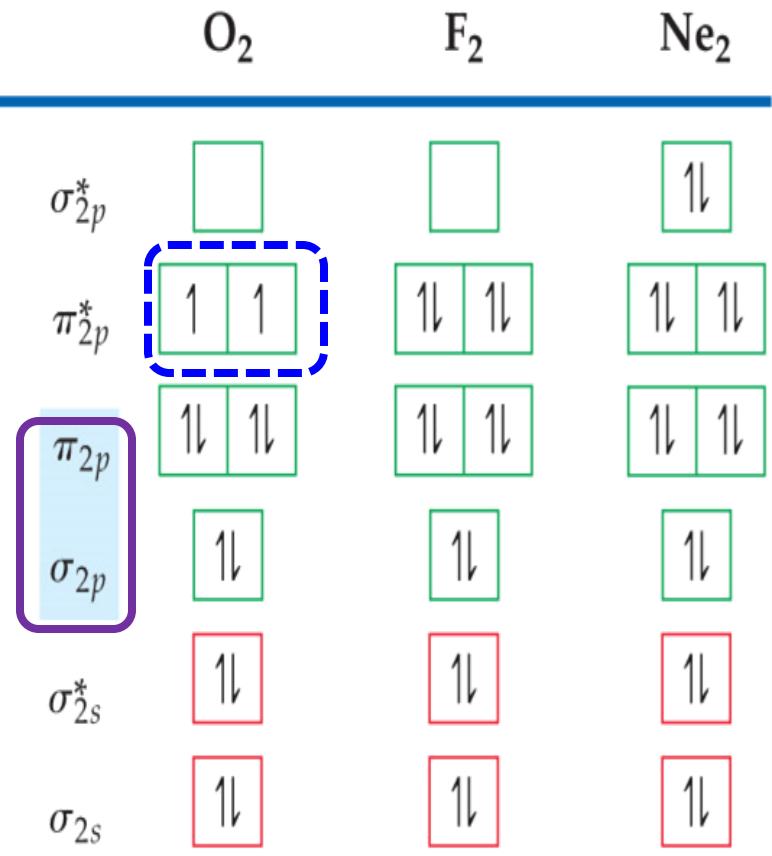
MO diagram for dinitrogen (N_2) molecule

Second-Row MO Diagrams

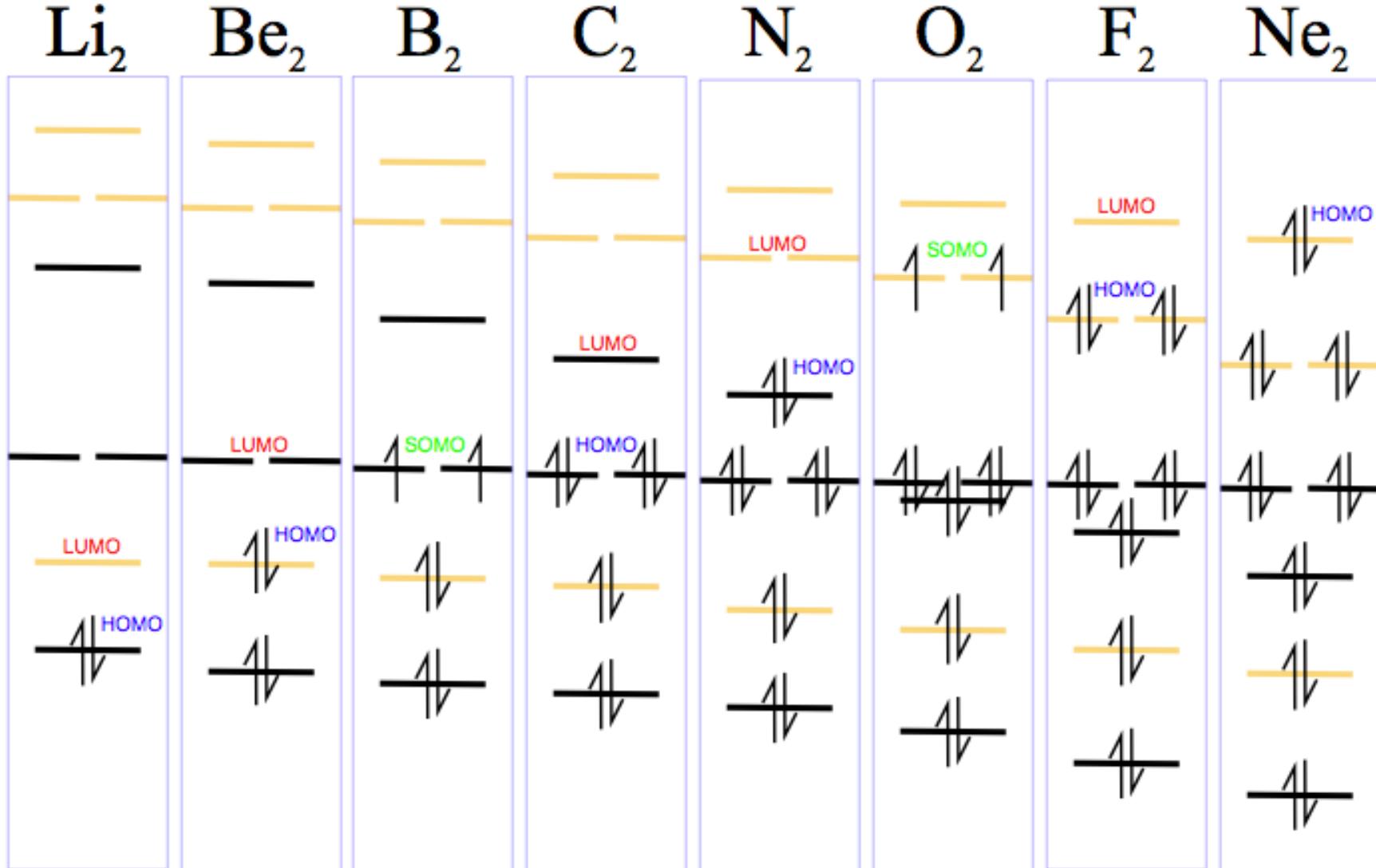
Large 2s–2p interaction



Small 2s–2p interaction

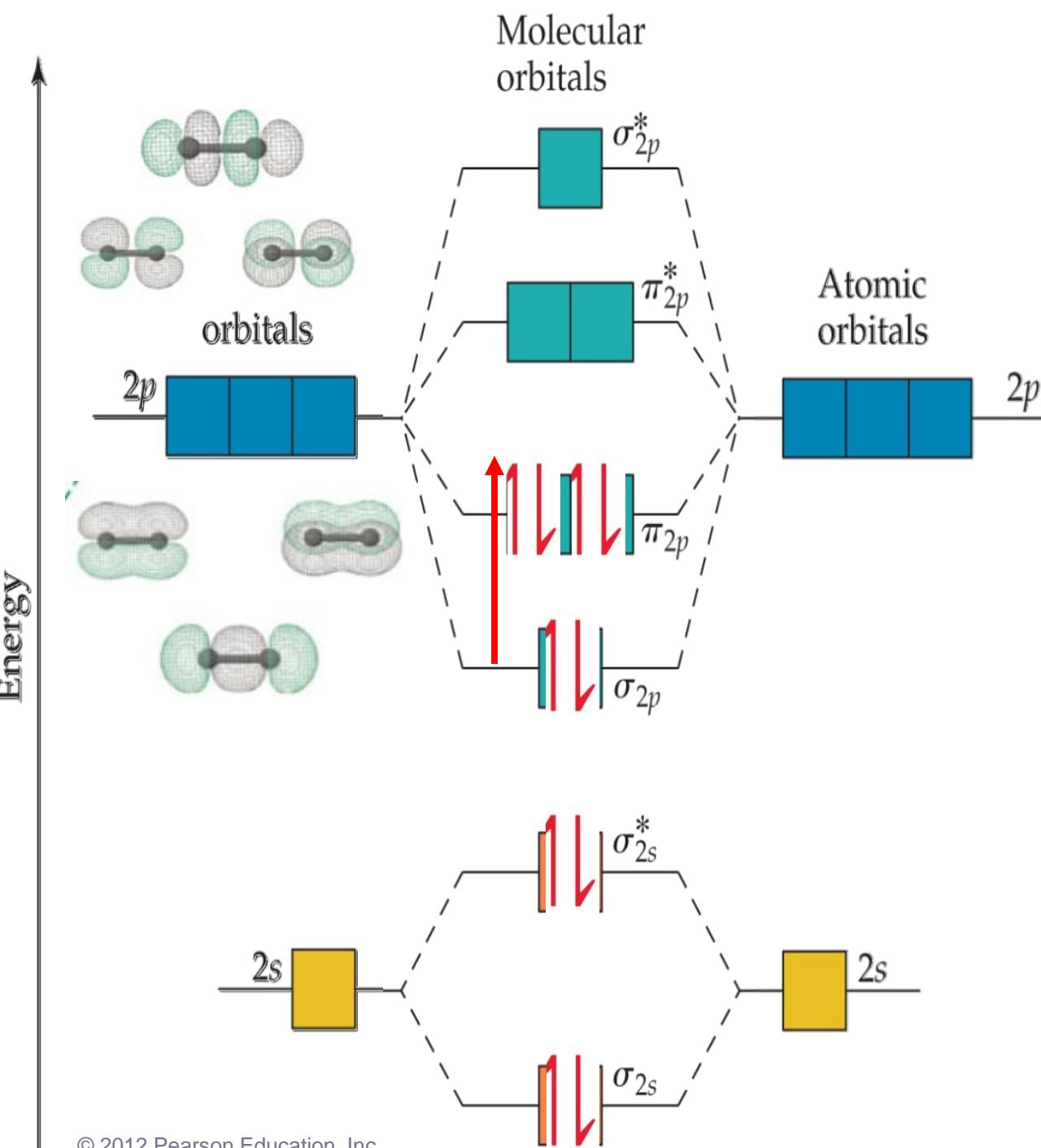


Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	—
Bond length (Å)	1.59	1.31	1.10	1.21	1.43	—
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	—



bond order = (electrons in bonding MOs – electrons in antibonding MOs) / 2

$\text{Li}-\text{Li}$	$\text{Be}-\text{Be}$	$\text{B}-\text{B}$	$\text{C}=\text{C}$	$\text{N}\equiv\text{N}$	$\text{O}=\text{O}$	$\text{F}-\text{F}$	$\text{Ne}-\text{Ne}$
known in the gas phase	dimer unknown	known in the gas phase paramagnetic diradical	known in the gas phase at high temp.	stable gas	stable gas paramagnetic diradical. Singlet & triplet states	stable gas	dimer unknown



- AO + AO → Lower-energy bonding MO + higher-energy antibonding MO.
- Move σ_{2p} higher in energy than π_{2p} **only** for B_2 , C_2 & N_2 (*half-filled p orbitals for N*).
- Put electrons as the atomic cases: **lower-energy orbital first, max. one pair** electrons with **different spin** on **each MO**.





Liquid Nitrogen



Liquid Oxygen

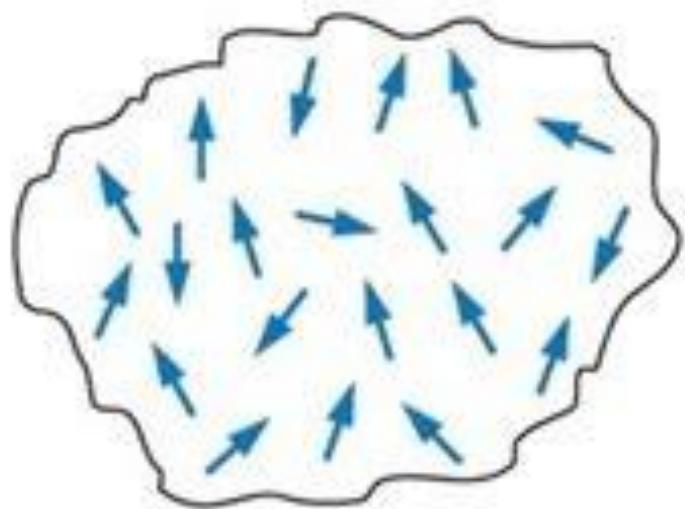
Types of Magnetism

Diamagnetism (反磁性): refers to materials that are not affected by a magnetic field.

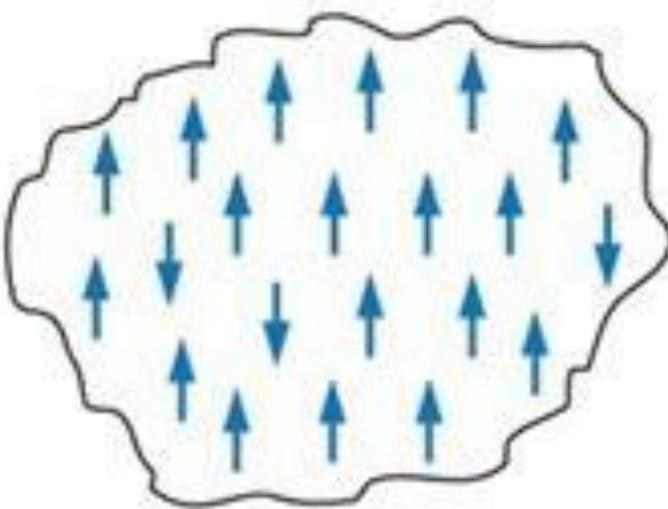
Paramagnetism (顺磁性): refers to materials like aluminum or platinum which become magnetized in a magnetic field but their magnetism disappears when the field is removed.

Ferromagnetism (铁磁性): refers to materials (such as iron and nickel) that can retain their magnetic properties when the magnetic field is removed.

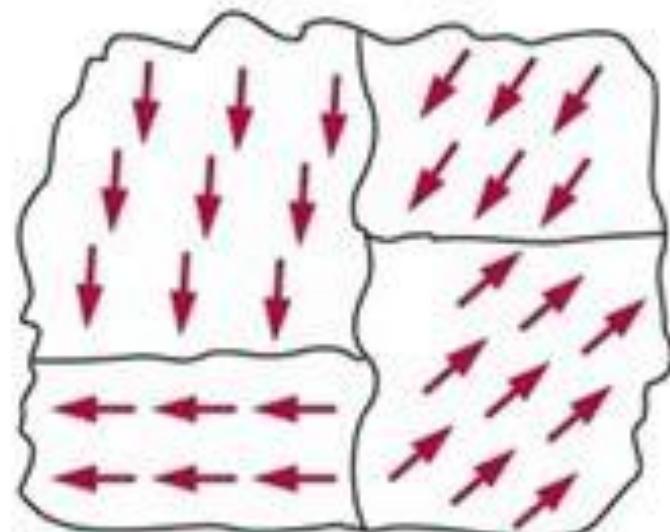
Magnetic field absent



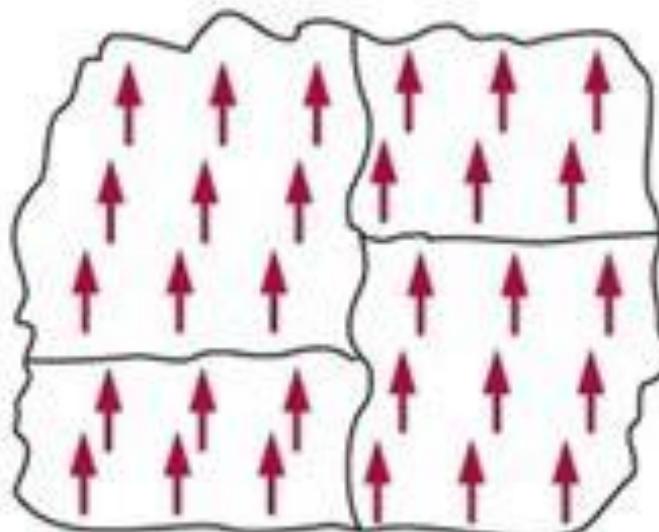
In presence of magnetic field

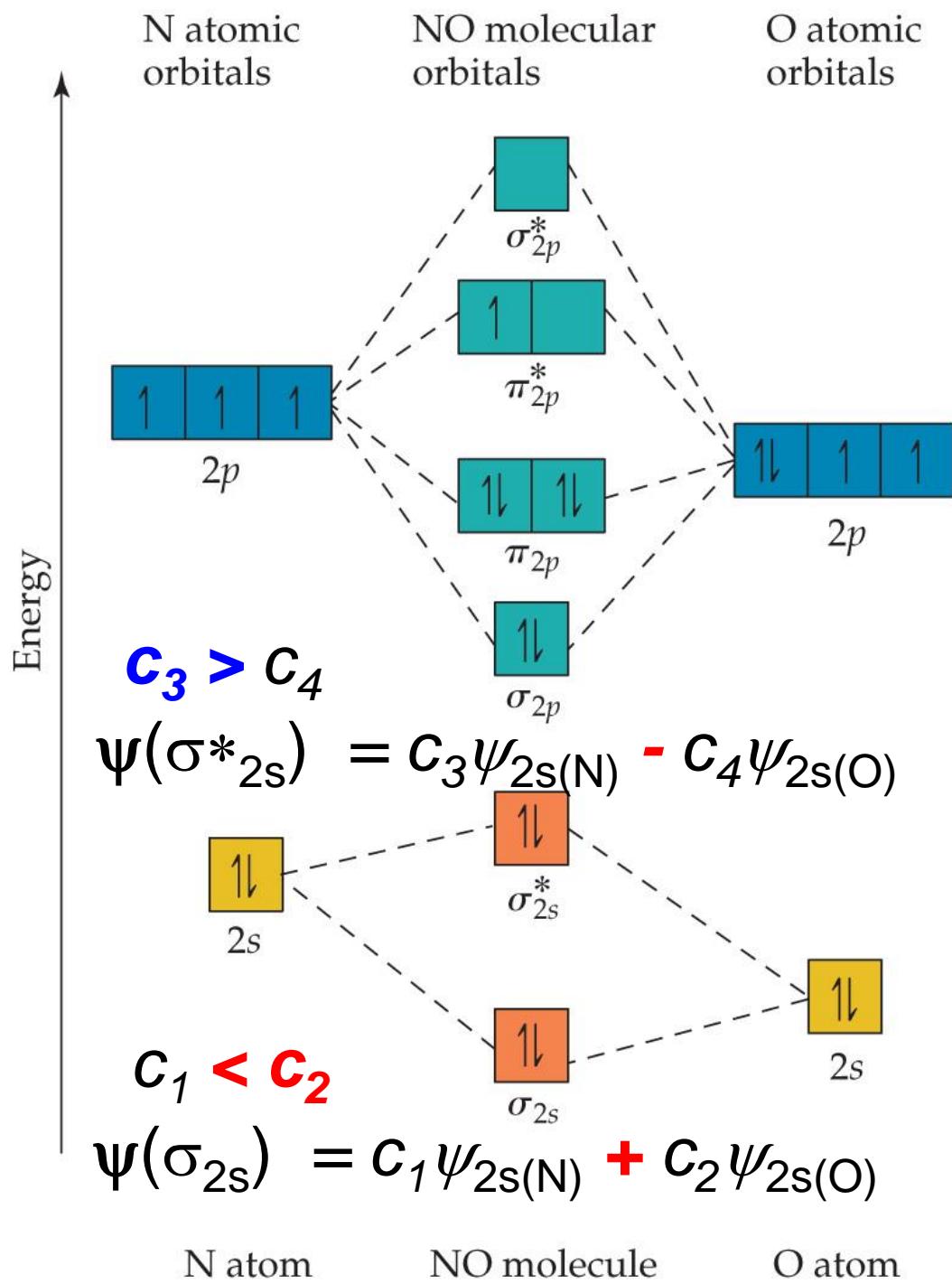


Paramagnetism



Ferromagnetism

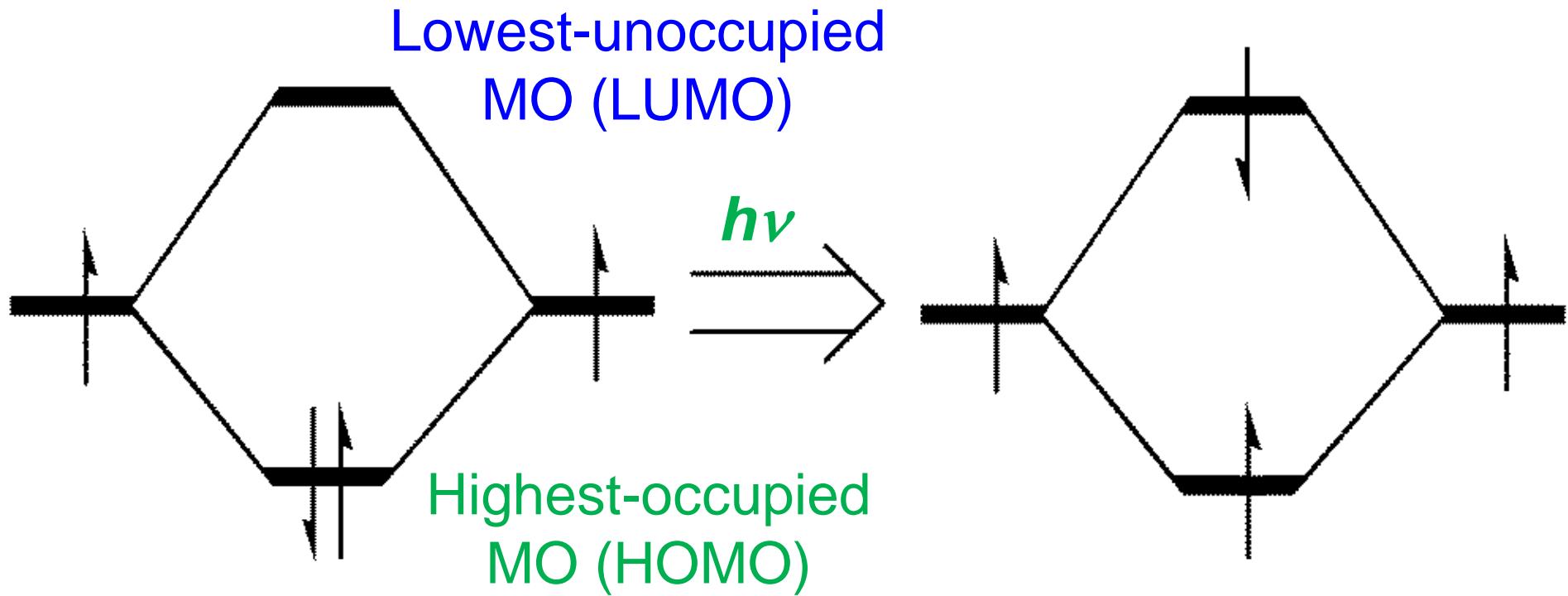




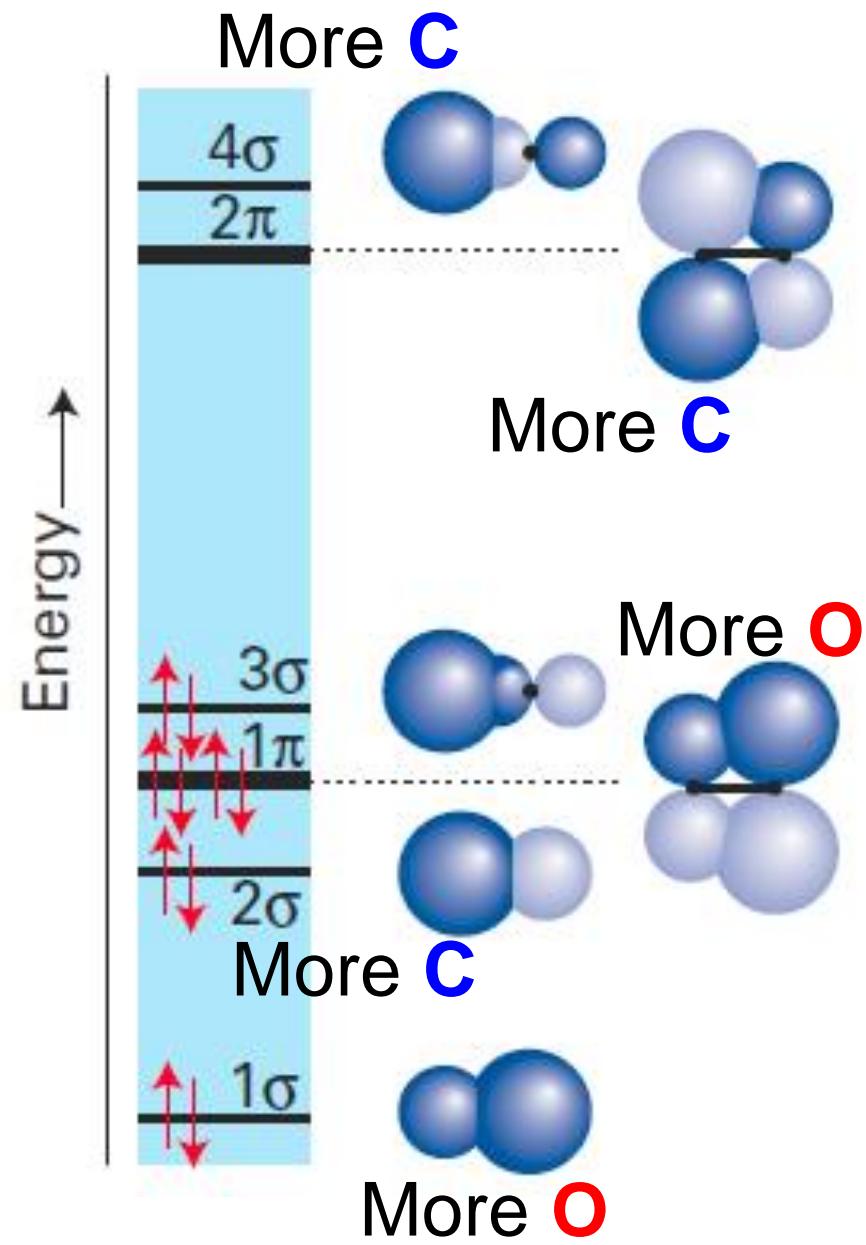
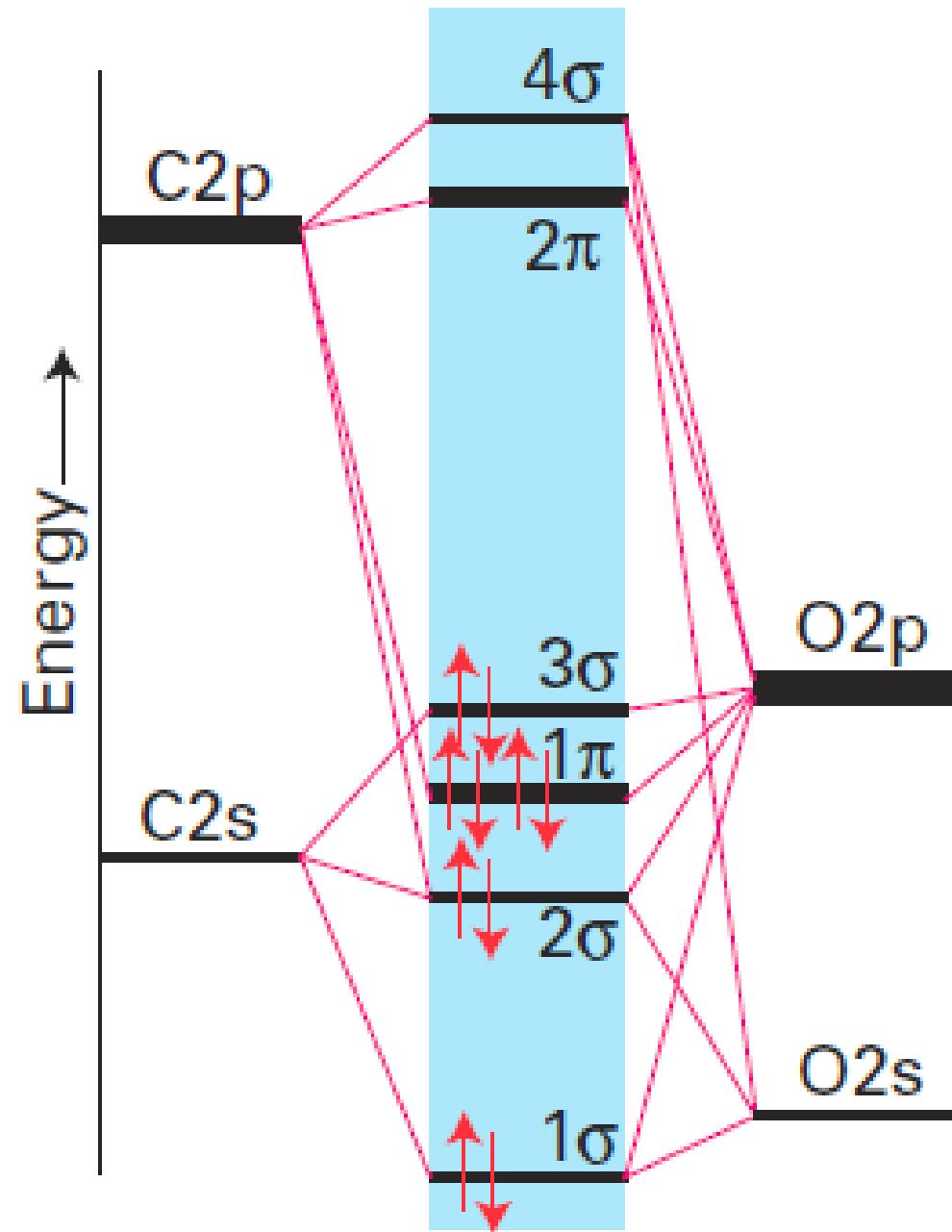
Energy-level diagram for NO (Heteronuclear Diatomic Molecules)

- The **high electronegativity**, the **lower energy** of the atomic orbital (AO).
- An **MO** has a **greater contribution** from the **AO with a closer in energy**. (e.g. 2s orbital of **O** contributes more in **σ_{2s}**, while 2s orbital of **N** contributes more in **σ*_{2s}**).

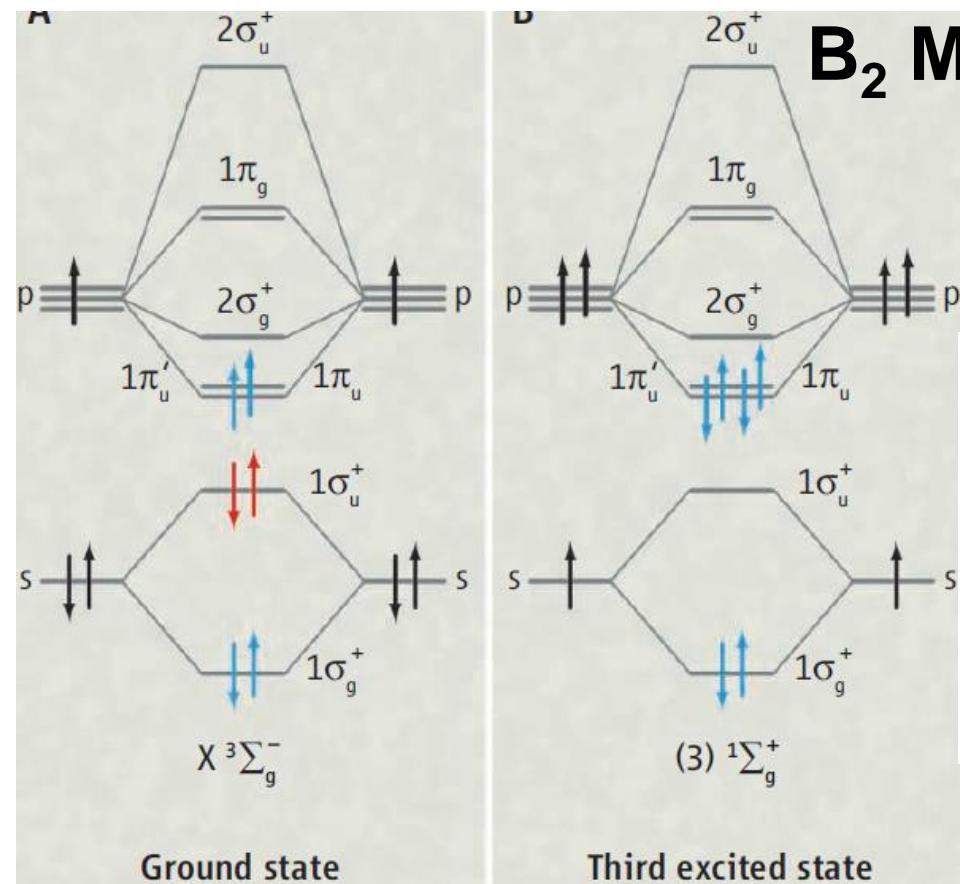
Excitation (Excited State)



Extra Info. MO diagram for CO

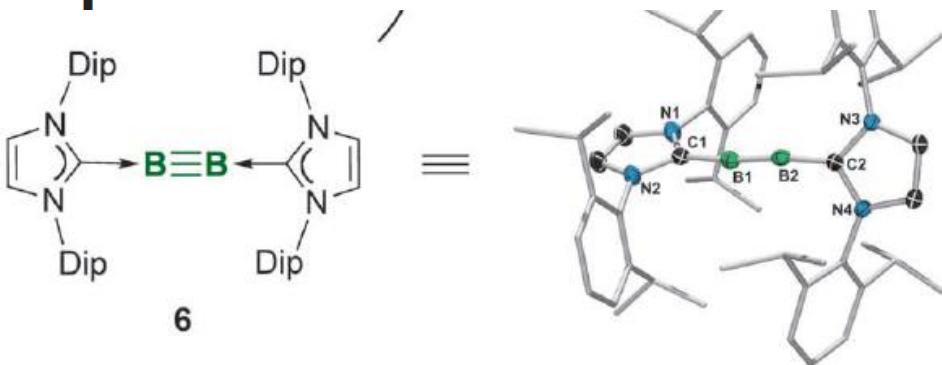


Extra Info. A molecule with a triple-bond is always more stable than with single-bond?



B_2 Molecule

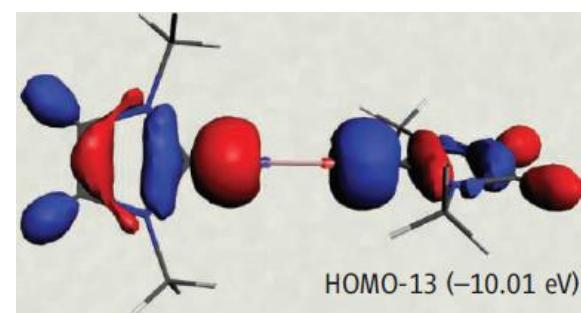
Ambient-Temperature Isolation of a Compound with a Boron-Boron Triple Bond



The first isolated B_2 molecule/structure:

$(L)B-B(L): 1.449 \text{ \AA}$

$(L)BrB=BBr(L): 1.546 \text{ \AA}$

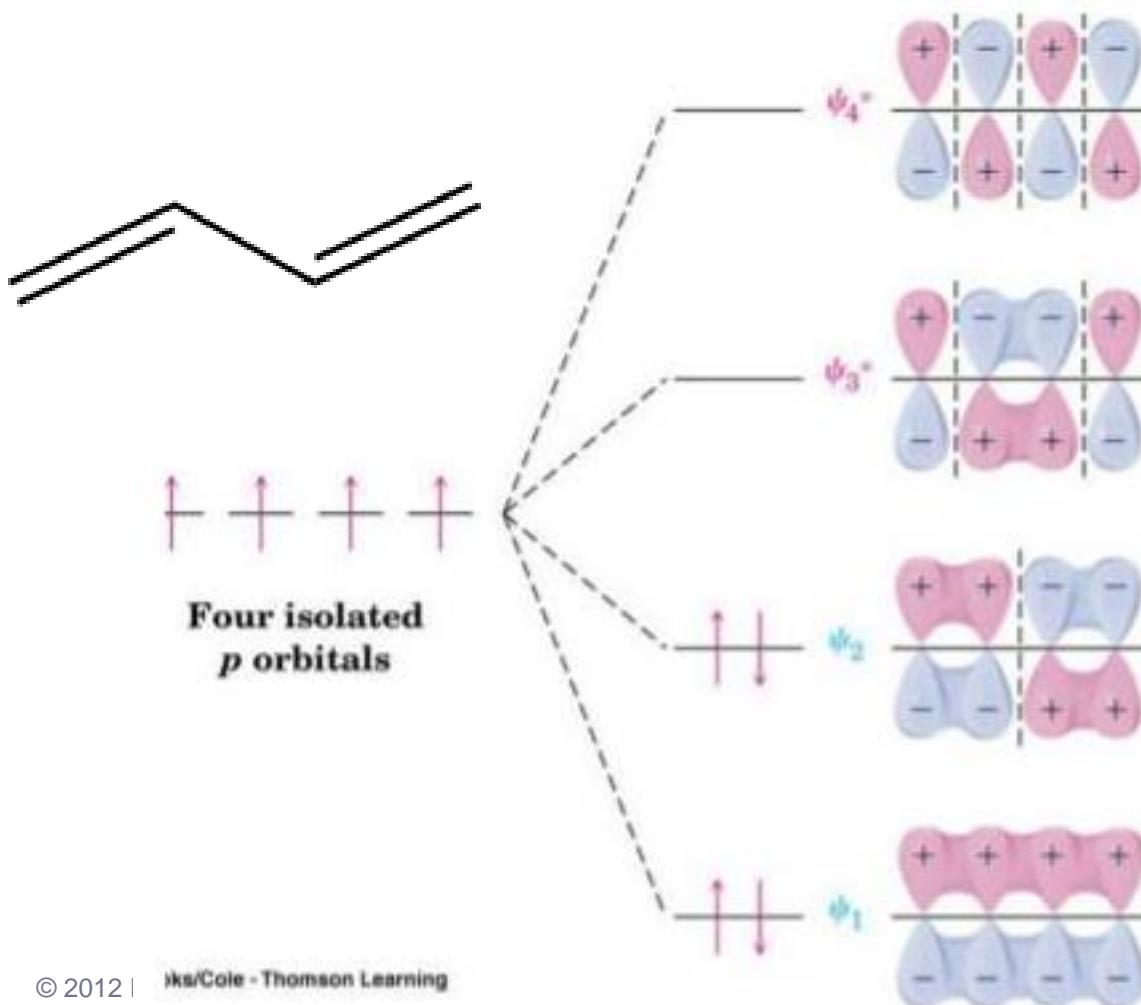


Extra Info. MOs for polyatomic systems

Linear combination of atomic orbitals

$$\Psi = c_1 \Psi_1 + c_2 \Psi_2 + \dots = \sum_k c_k \Psi_k$$

π -molecular orbitals of butadiene



3 Nodes
0 bonding interactions
3 antibonding interactions
ANTIBONDING MO

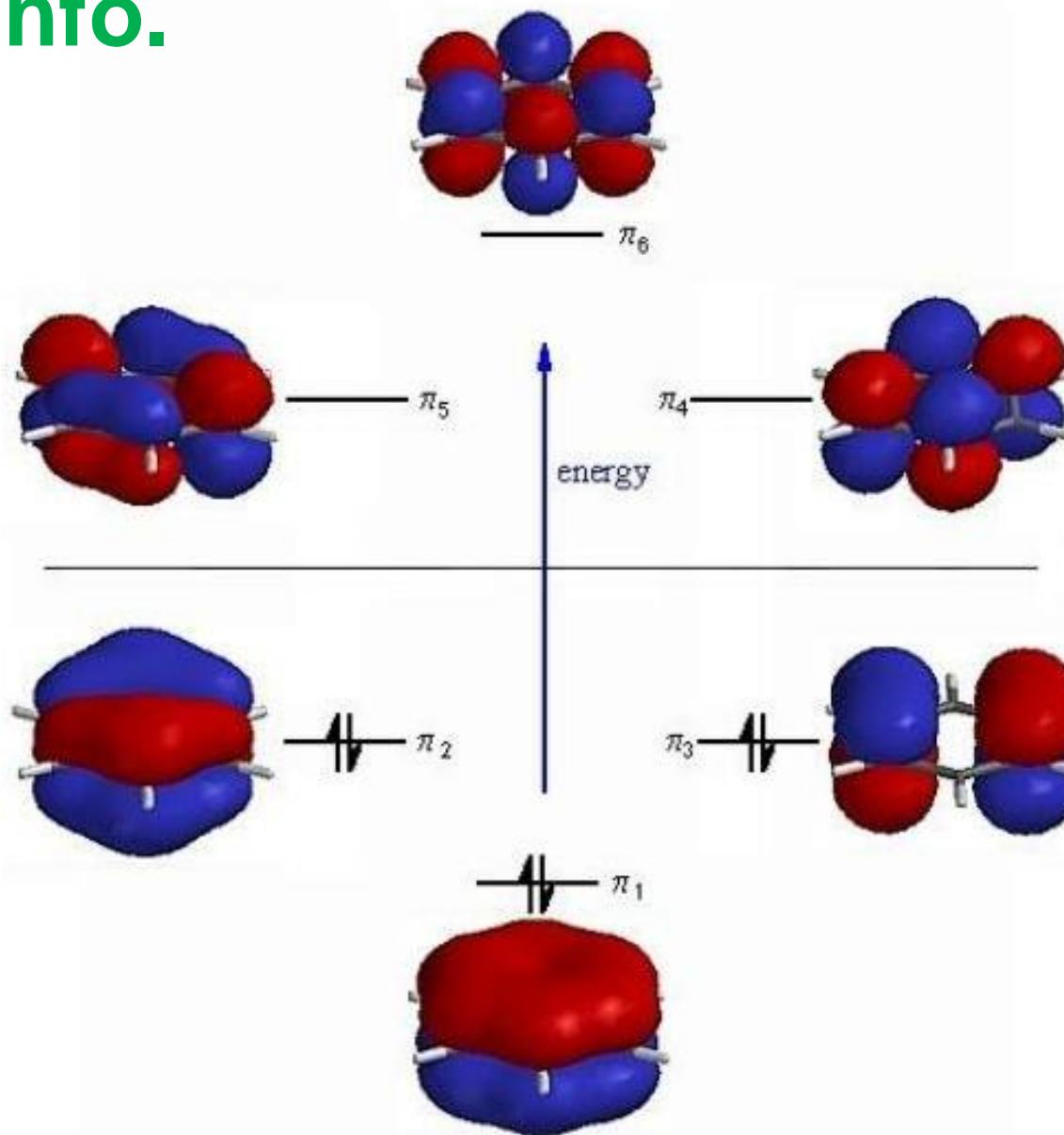
2 Nodes
1 bonding interactions
2 antibonding interactions
ANTIBONDING MO

1 Nodes
2 bonding interactions
1 antibonding interactions
BONDING MO

0 Nodes
3 bonding interactions
0 antibonding interactions
BONDING MO

MOs for benzene

Extra Info.



According to molecular orbital theory, the bond order in the dinitrogen (N_2) molecule is

- a. 0.
- b. 1.
- c. 2.
- d. 3.

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.

Suppose one electron in H_2 is excited from the σ_{1s} MO to the σ_{1s}^* MO. Would you expect the H atoms to remain bonded to each other, or would the molecule fall apart?

- A. Remain bonded, as the bond order remains the same.
- B. Fall apart, as the bond order changes from 1 to 1.5.
- C. Remain bonded, as the bond order changes from 1 to 1.5.
- D. Fall apart, as the bond order changes from 1 to zero.

What difference in electron configuration accounts for most of the difference between the bond enthalpy of N₂ and that of F₂?

- A. F₂ contains more electrons than N₂ and these electrons go into the antibonding π^*2p orbital and the bond order decreases.
- B. The change in the order of π_{2p} and σ_{2p} MOs from N₂ to F₂ reduces the bond order.
- C. The increase in number of occupied MOs in F₂ reduces electron-electron repulsions and decreases bond enthalpy.
- D. The reduction in unoccupied antibonding N₂ and that of F₂ MOs decreases the bond enthalpy.

VB vs. MO

- Valence bond (**VB**) theory focuses on how the atomic orbitals of the atoms combine to give **INDIVIDUAL CHEMICAL BONDS** in a molecule.
- In contrast, molecular orbital (**MO**) theory has **orbitals** that cover the **WHOLE MOLECULE**; 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**.
- **MO theory is more popular** than VB.

VB

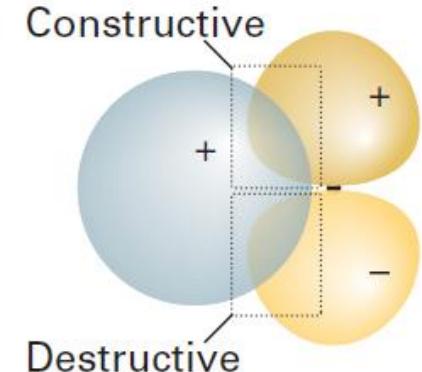
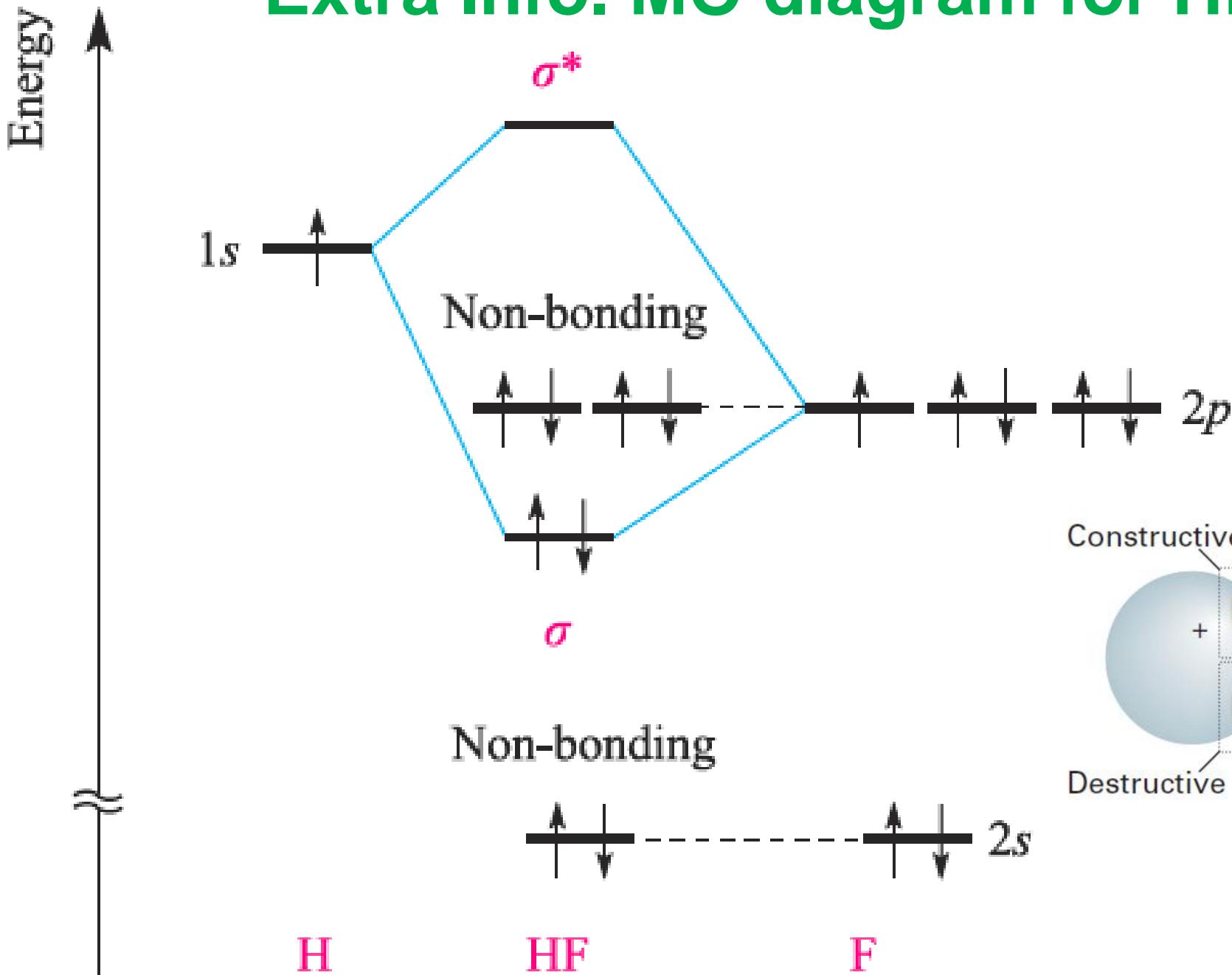
- Overlapping orbitals leads to bonding orbital only (**NO anti-bonding orbital**).
- Mixing **N** atomic orbitals can give **N hybrid** (bonding) orbitals; they have **SAME energy level & shapes**.

MO

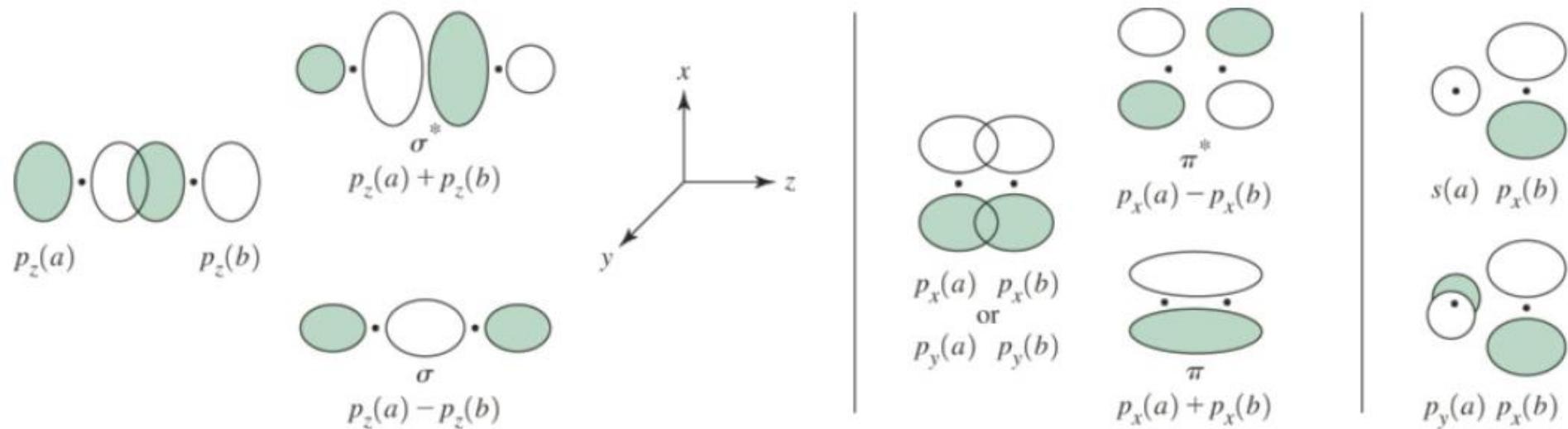
- Overlapping orbitals leads to **bonding & anti-bonding** orbitals.
- Mixing **N** ($=N_1+N_2$) atomic orbitals can give **N_1 bonding MOs + N_2 anti-bonding MOs**; they can have **DIFFERENT energy levels and shapes**.

Both theories: Overlapping orbitals can also form σ & π bonds, depending on the way of the overlapping.

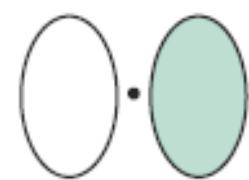
Extra Info. MO diagram for HF



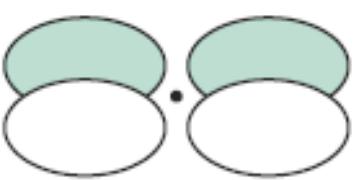
Extra Info. Bonding or non-bonding?



p_z and d_{xz}

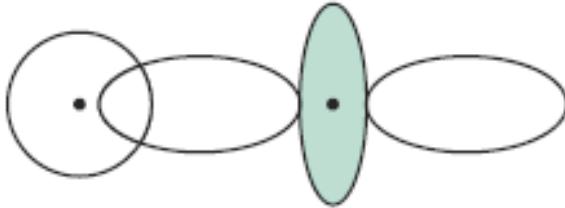


p_z



d_{xz}

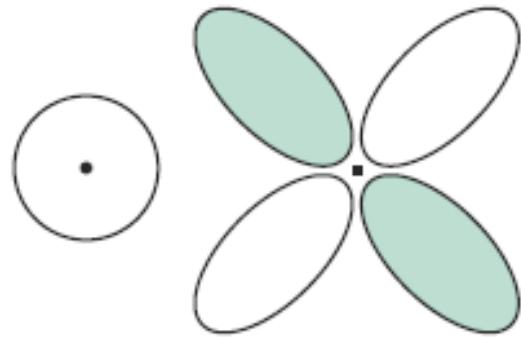
s and d_{z^2}



s

d_{z^2}

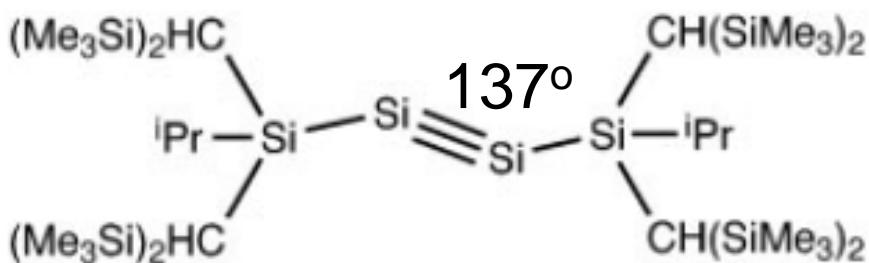
s and d_{yz}



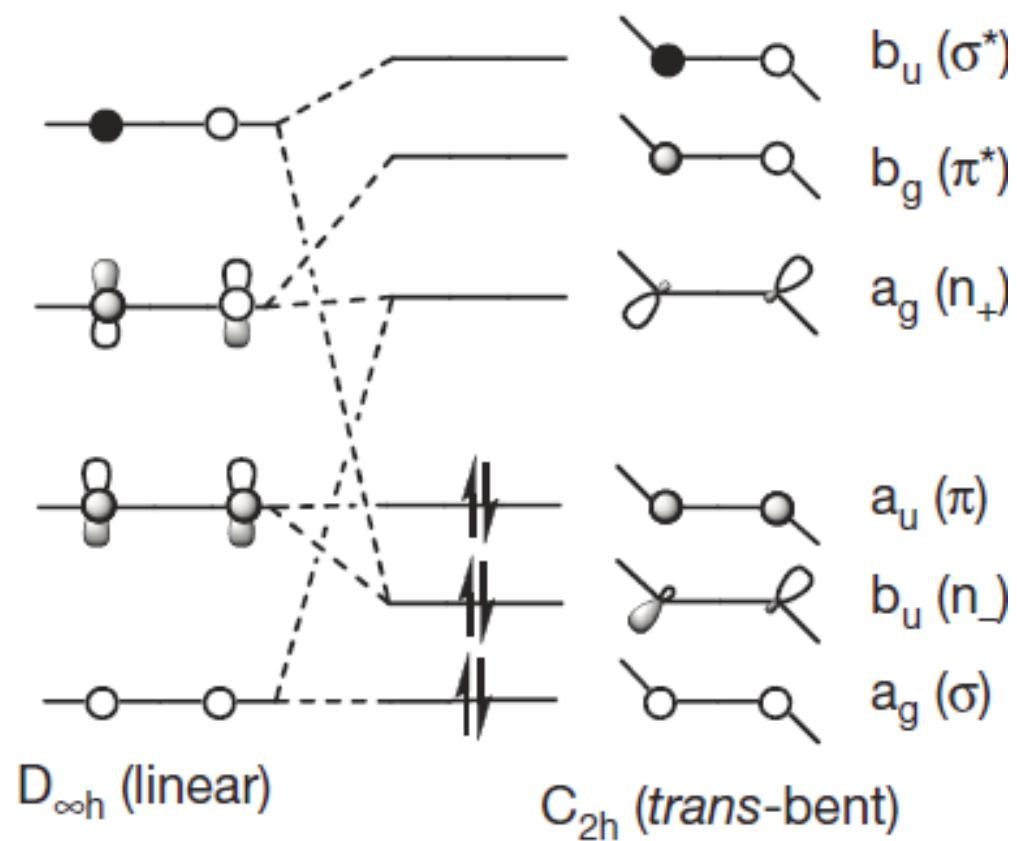
s

d_{yz}

Extra Info. Si-Si Triple Bond

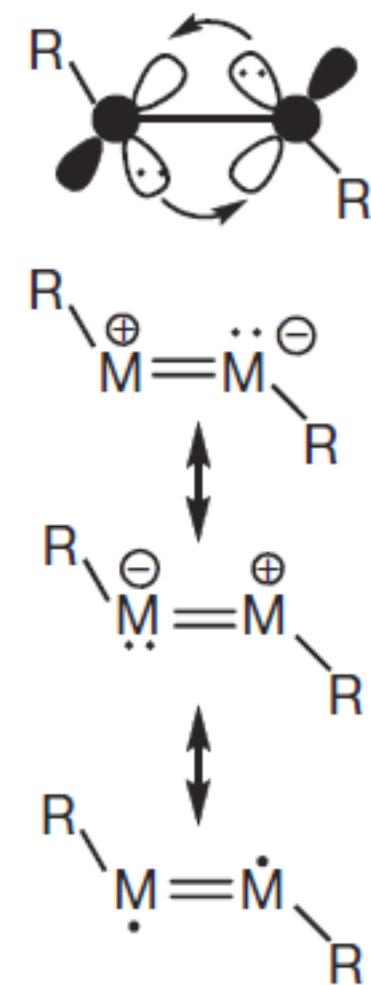


Non linear Si-Si triplet bond
(not effective π bonding for
third row or below): **trans**
bent

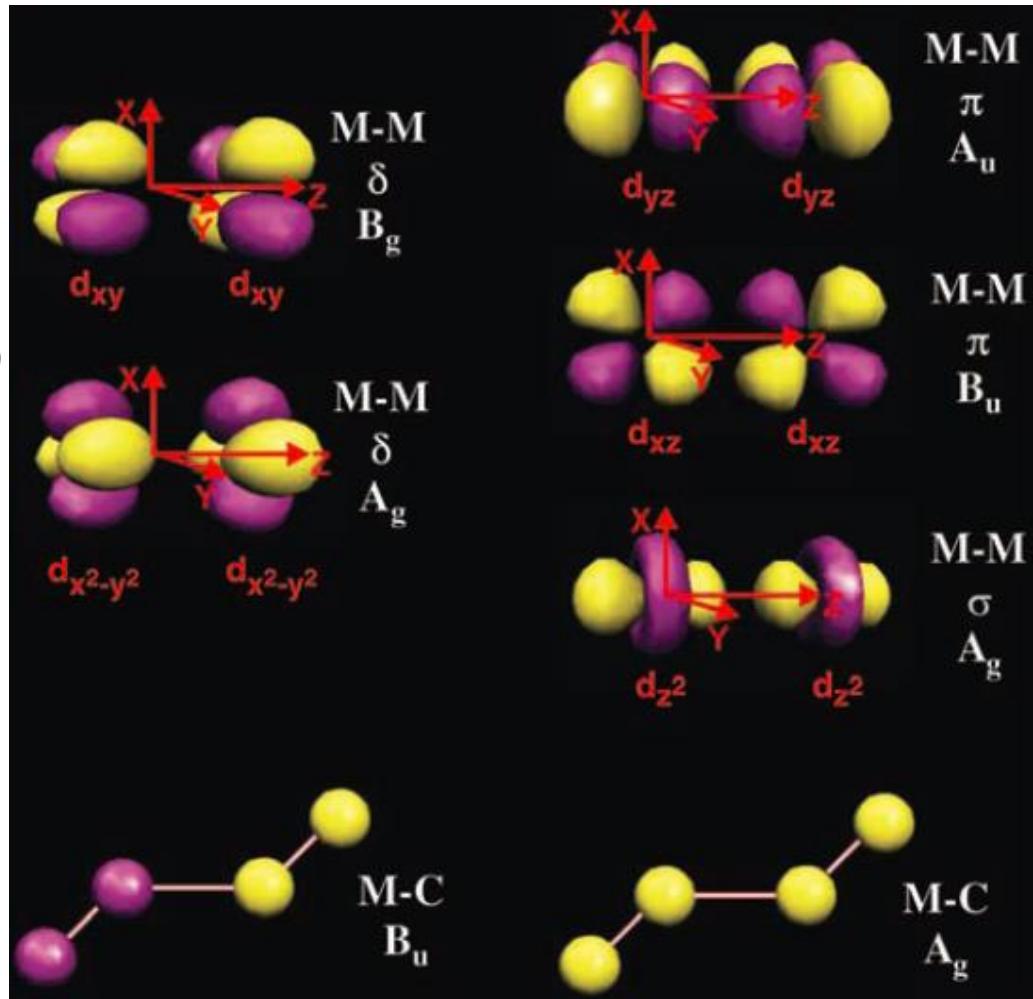
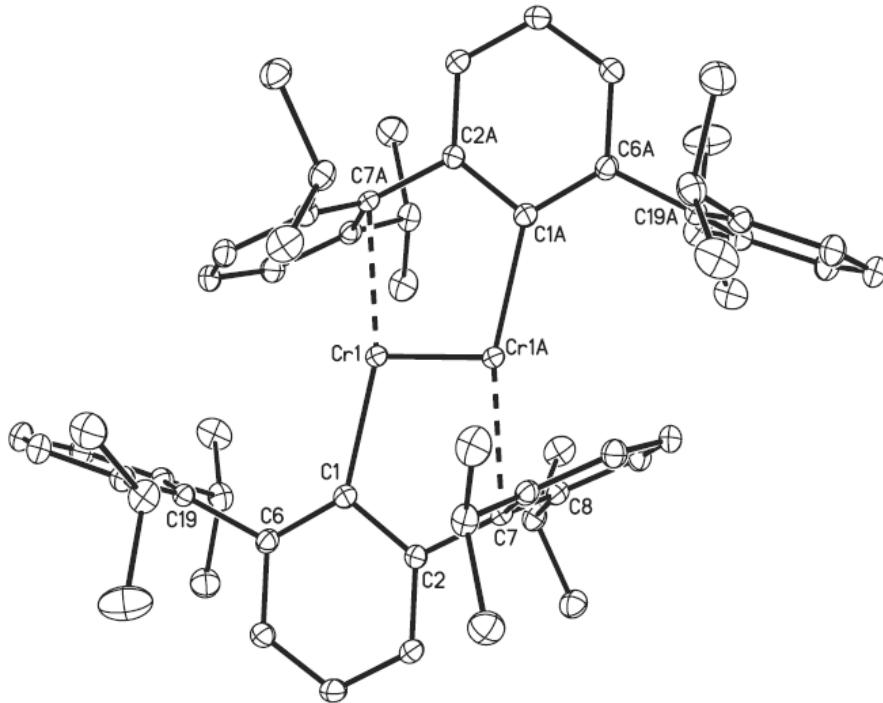


MO (left)
VB (right)

(Science 2004,
305, 1755;
Nature 2010,
463, 171)



Extra Info. Quintuple (δ) Bond



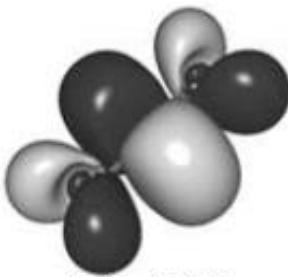
Synthesis of a stable Cr(I)-Cr(I) compound with fivefold bonds.

(Science 2005, 310, 844)

Extra Info. Quintuple (φ) Bond



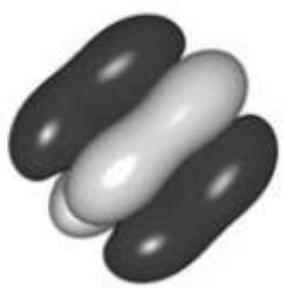
$7s\sigma_g$ (2.00)



$6d\pi_u$ (4.00)



$6d\sigma_g$ (0.97)



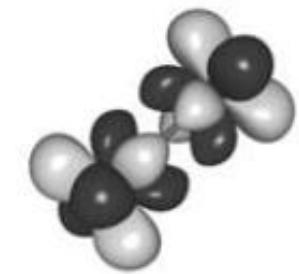
$6d\delta_g$ (0.98)



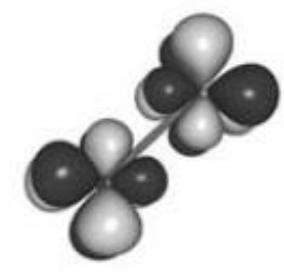
$5f\pi_u$ (0.63)



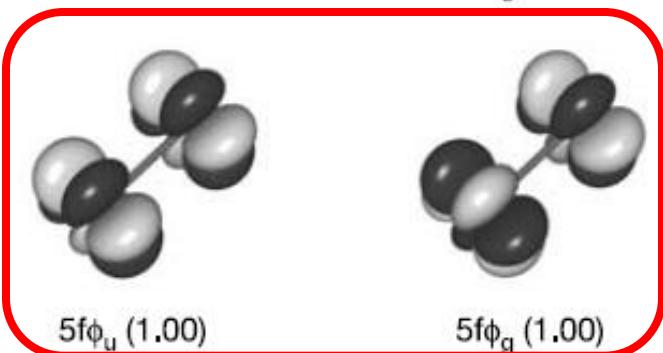
$5f\pi_g$ (0.37)



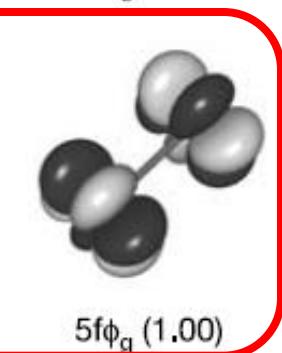
$5f\delta_g$ (0.63)



$5f\delta_u$ (0.37)



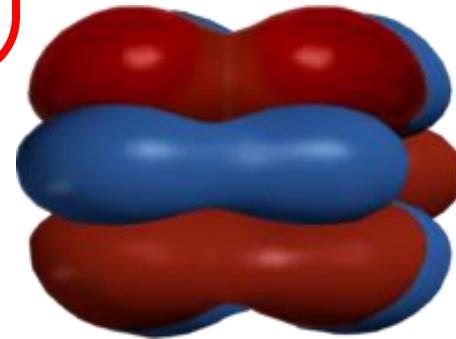
$5f\phi_u$ (1.00)



$5f\phi_g$ (1.00)

Quantum chemistry calculations
on U_2 : φ bond with 2 f orbitals

(Nature 2005, 433, 848)

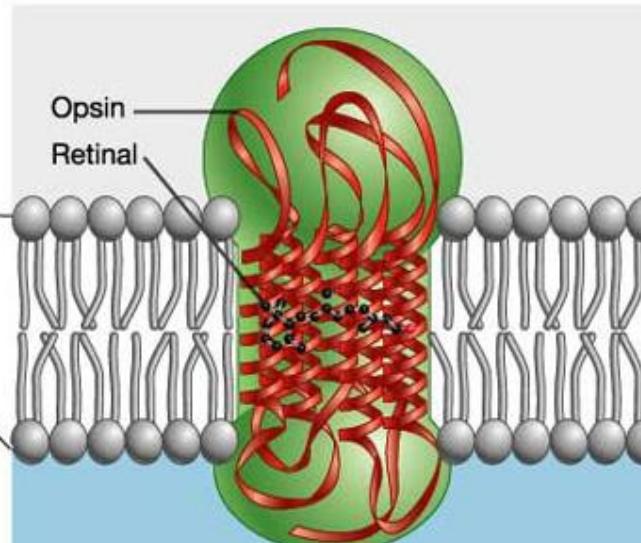


Rhodopsins (GPCR): Visual Pigment

Rods and cones contain stacks of membranes.



Rhodopsin is a transmembrane protein complex.



Extra Info.

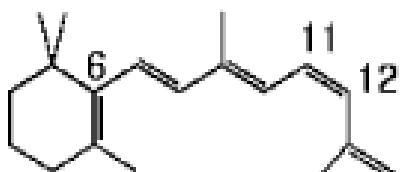


The Nobel Prize in Physiology or Medicine 1967

Ragnar Granit, Haldan K. Hartline, George Wald

Our Vision

11-cis rhodopsin

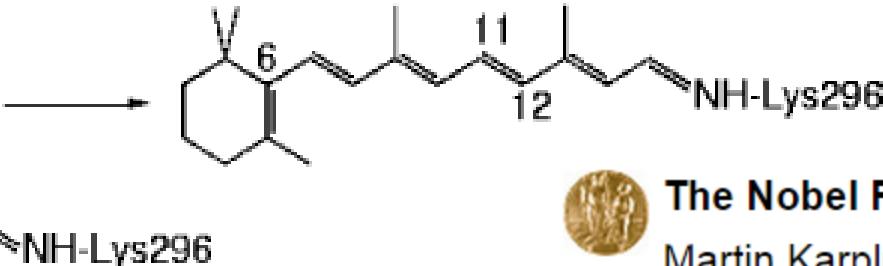


all-trans bathorhod



The Nobel Prize in Chemistry 2012

Robert J. Lefkowitz, Brian K. Kobilka



Retinal



The Nobel Prize in Chemistry 2013

Martin Karplus, Michael Levitt, Arieh Warshel

Photo-isomerization

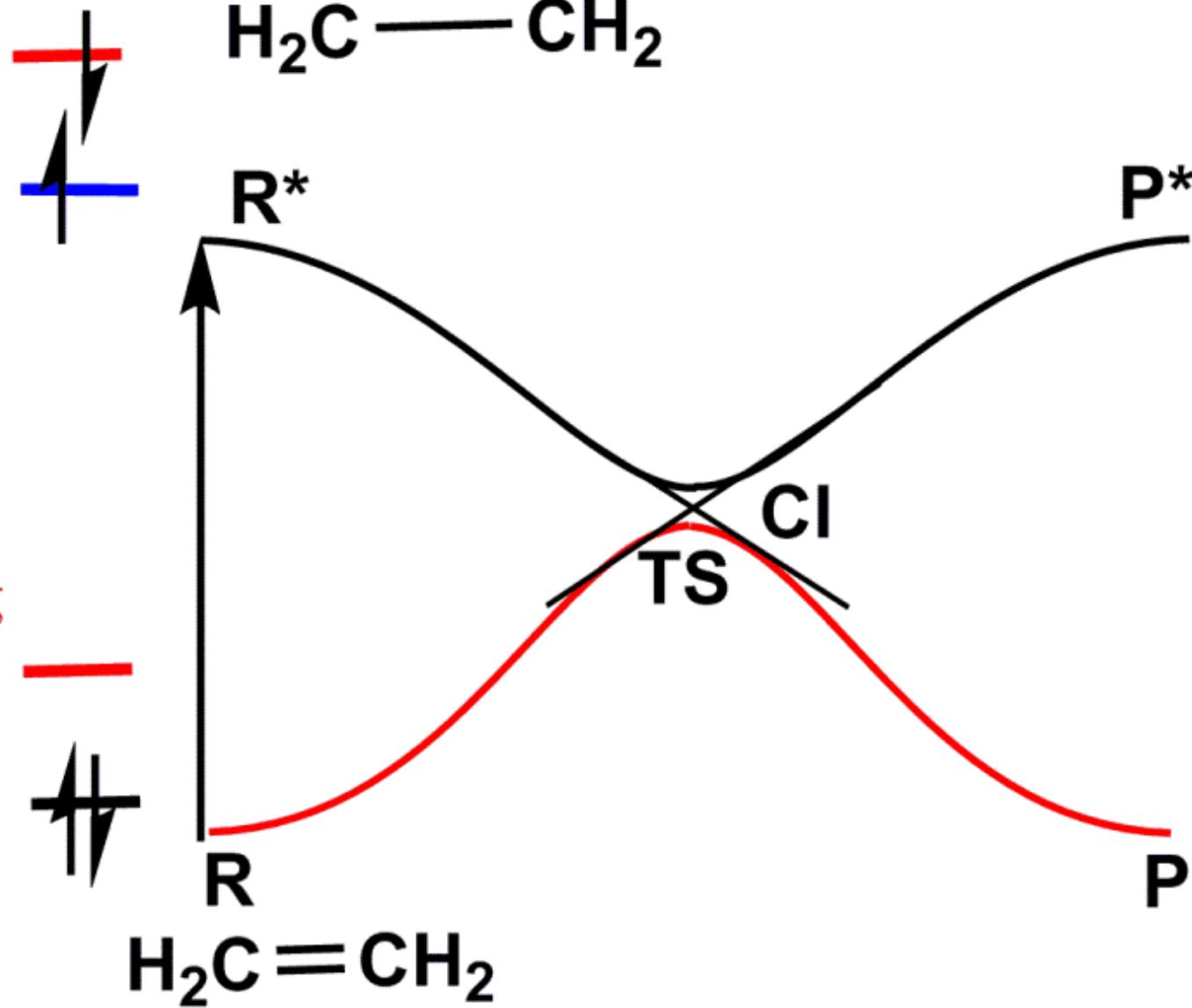
Extra Info.

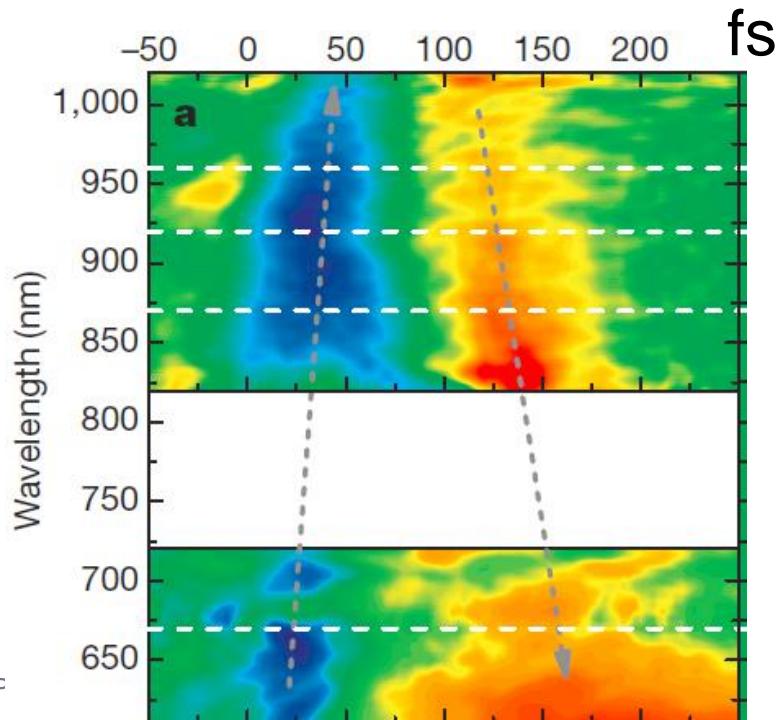
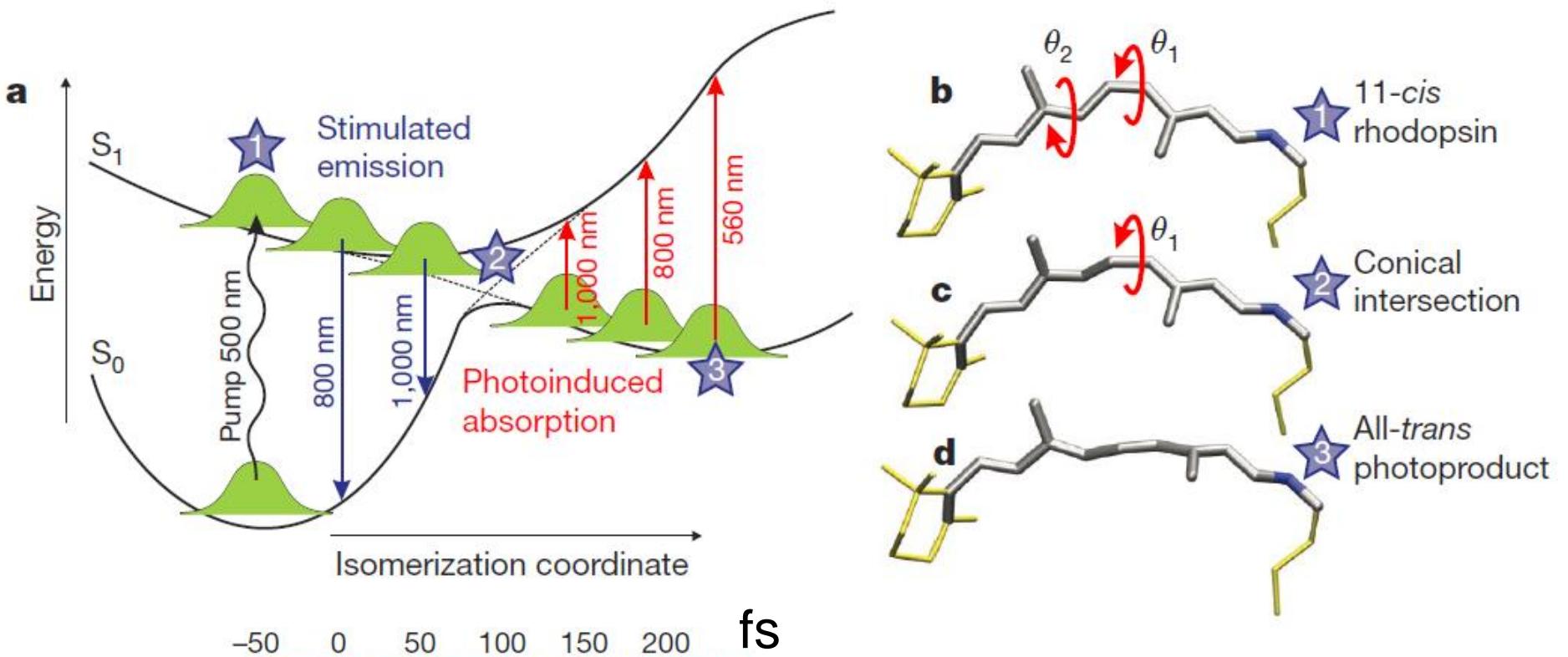
π^* anti-bonding MO

π bonding molecular orbital (MO)

π^* anti-bonding MO

π bonding molecular orbital (MO)





Extra Info.

(Nature 2010, 467, 440)

The Nobel Prize in Chemistry 2016



III: N. Elmehed. ©
Nobel Media 2016
Jean-Pierre Sauvage



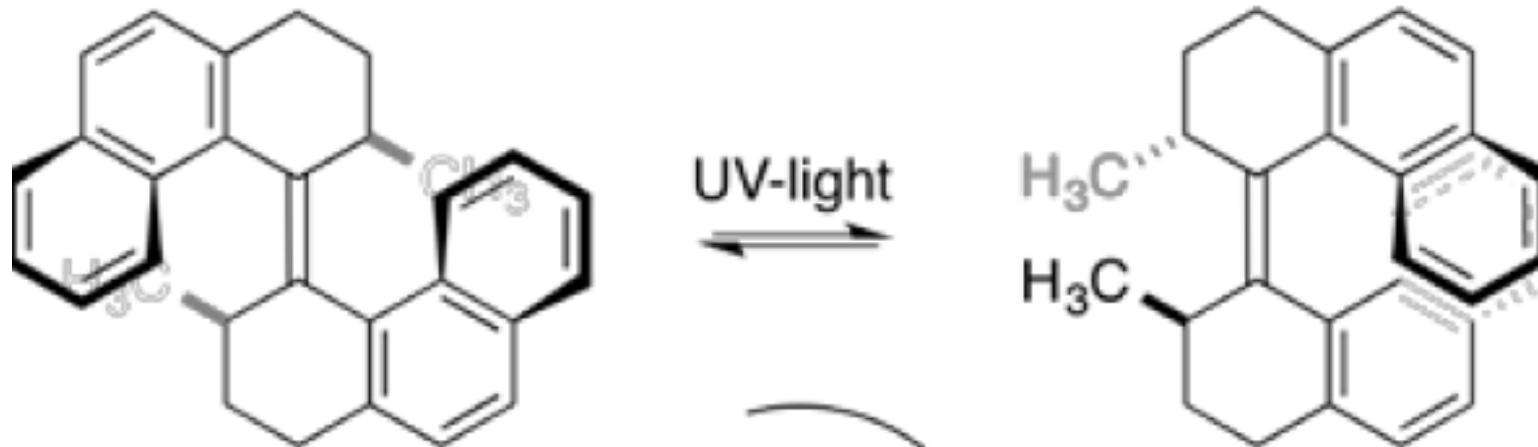
Photo: Northwestern
University
Sir J. Fraser Stoddart



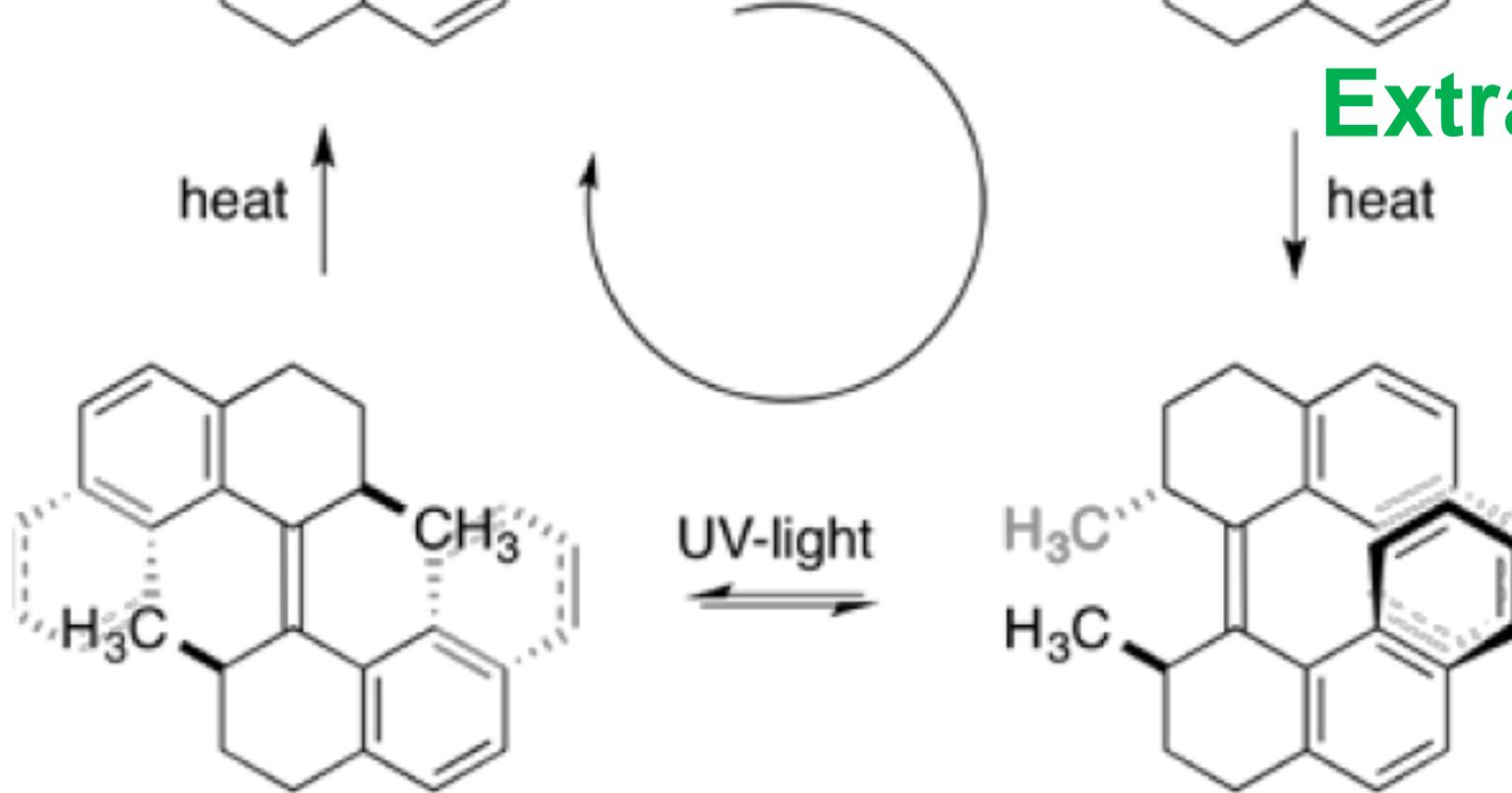
III: N. Elmehed. ©
Nobel Media 2016
Bernard L. Feringa

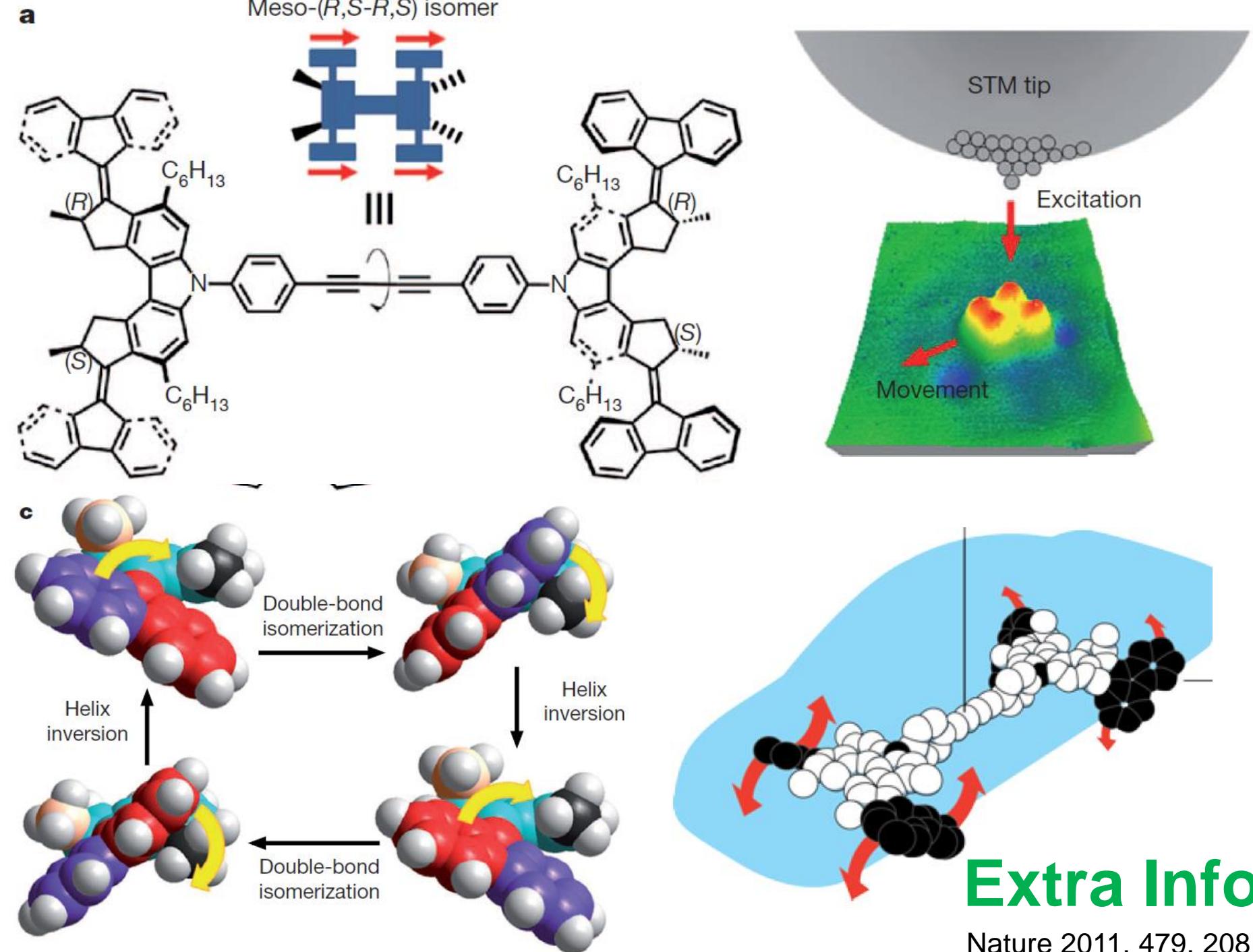
The Nobel Prize in Chemistry 2016 was awarded jointly to Jean-Pierre Sauvage, Sir J. Fraser Stoddart and Bernard L. Feringa *"for the design and synthesis of molecular machines"*.

Unidirectional, light-driven molecular motor (Feringa) Photo-isomerization + thermal-isomerization



Extra Info.





Key Summary

Valence-Shell Electron-Pair Repulsion Theory (VSEPR): (Non)Bonding pairs, Electron Domains, Molecular Geometry

Valence Bond (VB) Theory: Orbital Overlap, Hybrid Orbital, Hybridization

Molecular Orbital (MO) Theory: Orbital Overlap (linear combinations), Bonding Molecular Orbital, Anti-bonding Molecular Orbital, Bond Order, Energy-Level Diagram

(σ) Sigma-Bond, (π) Pi-Bond, Paramagnetism & Diamagnetism

**Thank You for Your
Attention!
Any Questions?**