Chapter 8
Advanced Theories of Covalent Bonding

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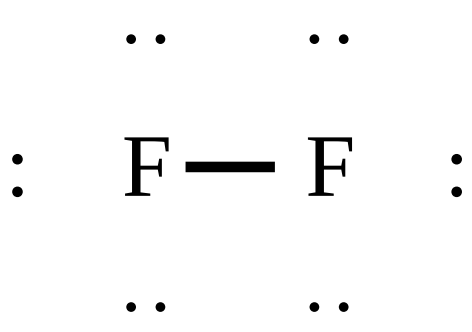
Two Quantum Mechanical Theories for Chemical Bonding

Lewis VSEPR model can predict molecular geometry but cannot explain the difference between the two bonds



150.6 kJ/mol and 142 pm

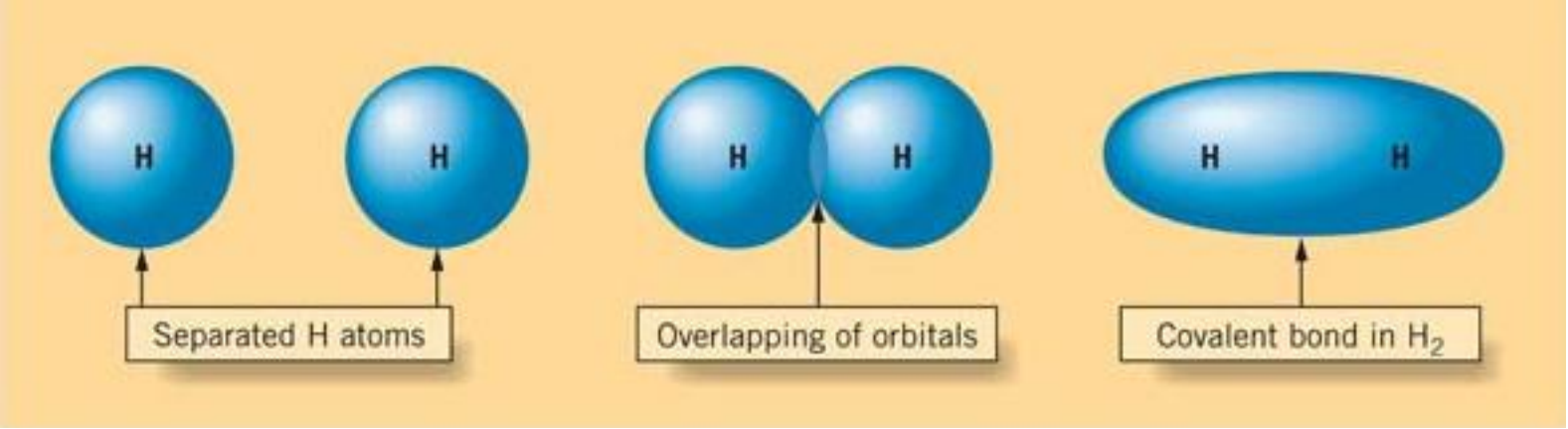
436.4 kJ/mol and 74 pm

Valence Bond (VB) Theory and Molecular Orbital (MO) Theory can explain!

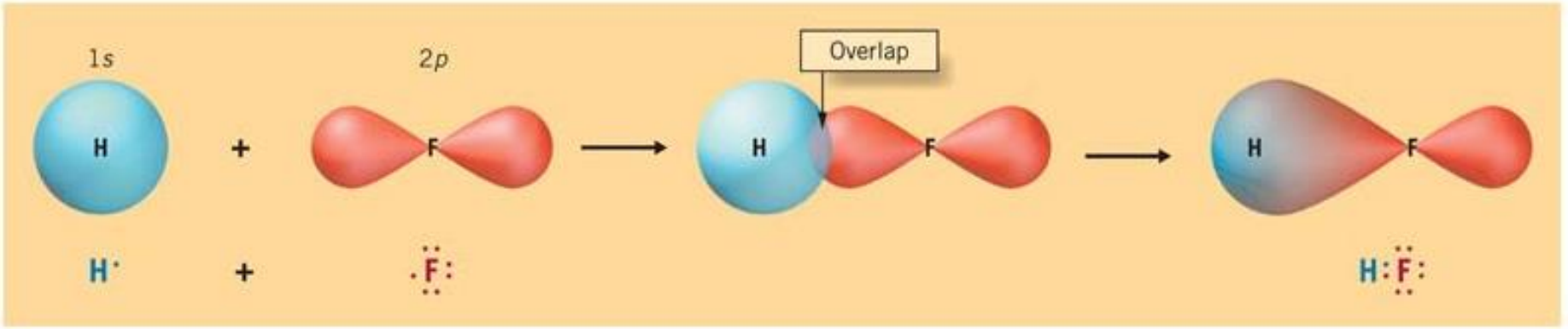
Valence Bond Theory

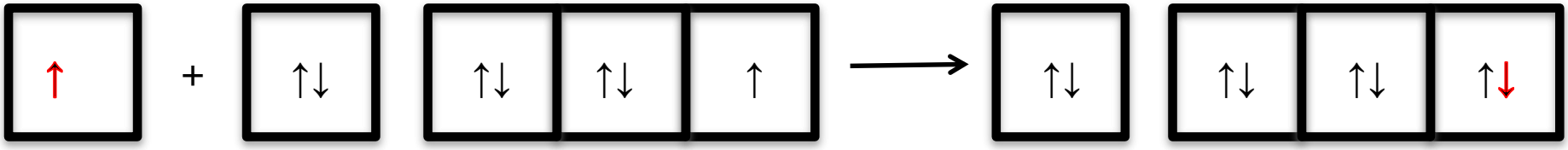
Covalent bond is formed when **two atomic orbitals from each of the atoms are overlapped**.

Only one pair of electrons should be shared by two overlapping orbitals and their spins should be opposite.



Valence Bond Theory



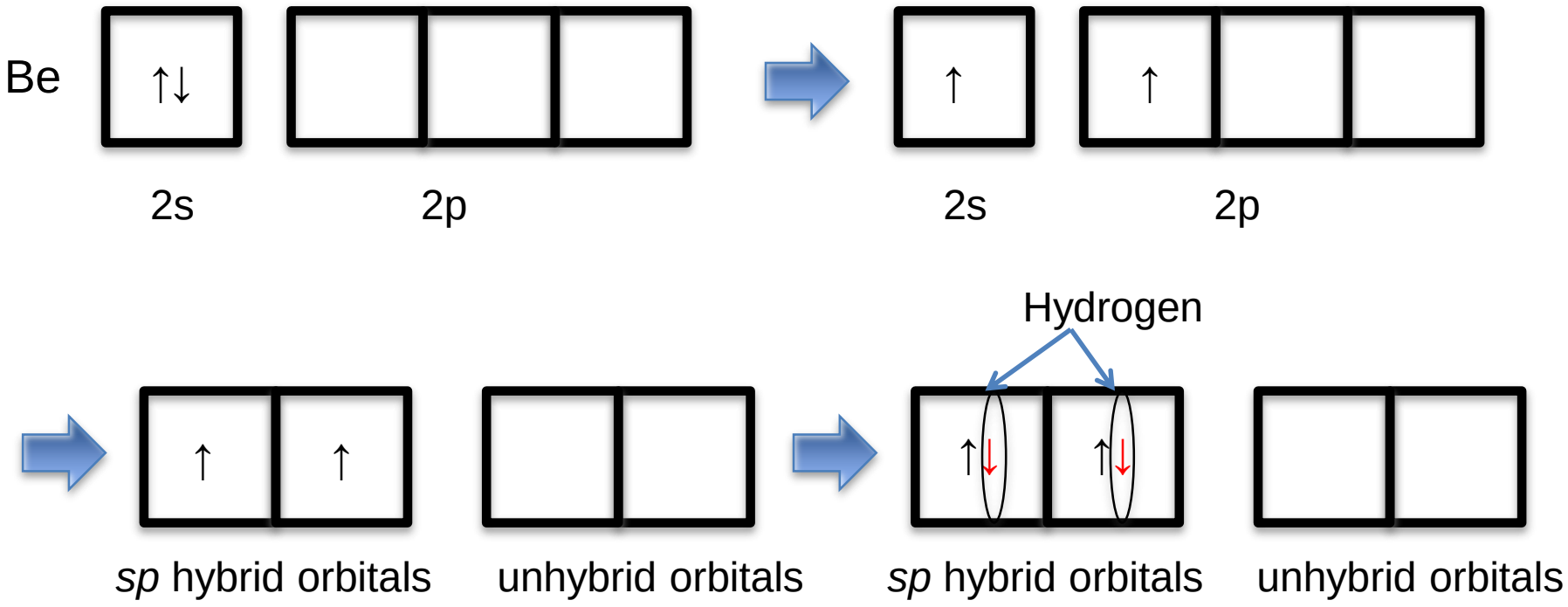


Now, let's consider polyatomic molecules.

Hybridization of Atomic Orbitals

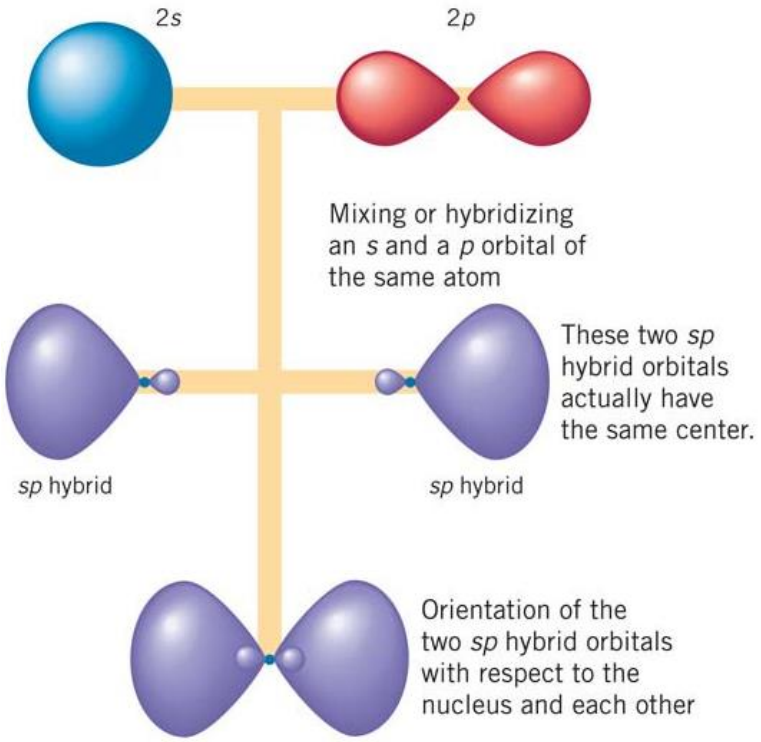
To explain the variety of molecular shapes, we often must **mix** **two or more atomic orbitals** in an atom to produce a set of hybrid orbitals

BeH_2

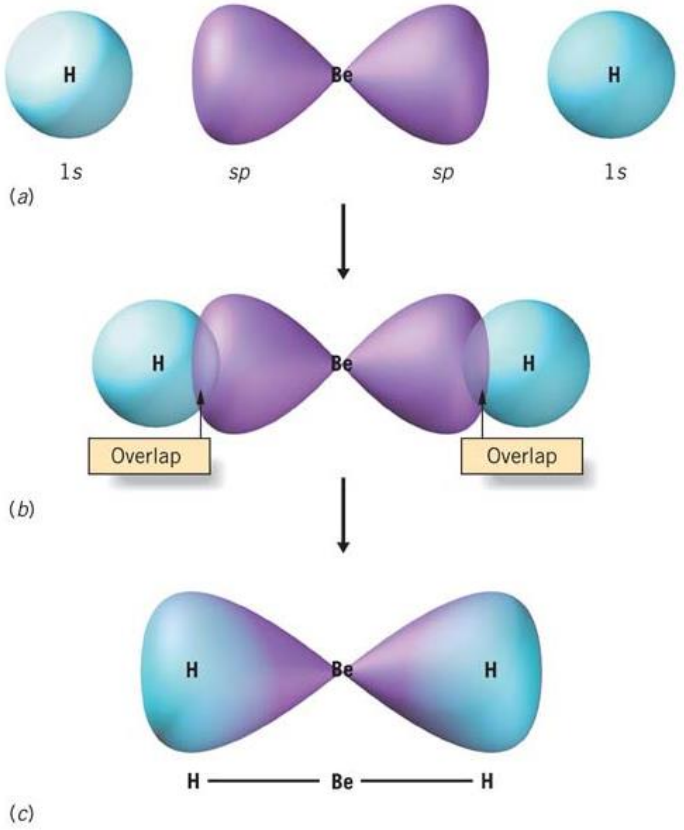


Hybridization of Atomic Orbitals: *sp:* Linear Structure

Formation of *sp* hybrid orbitals

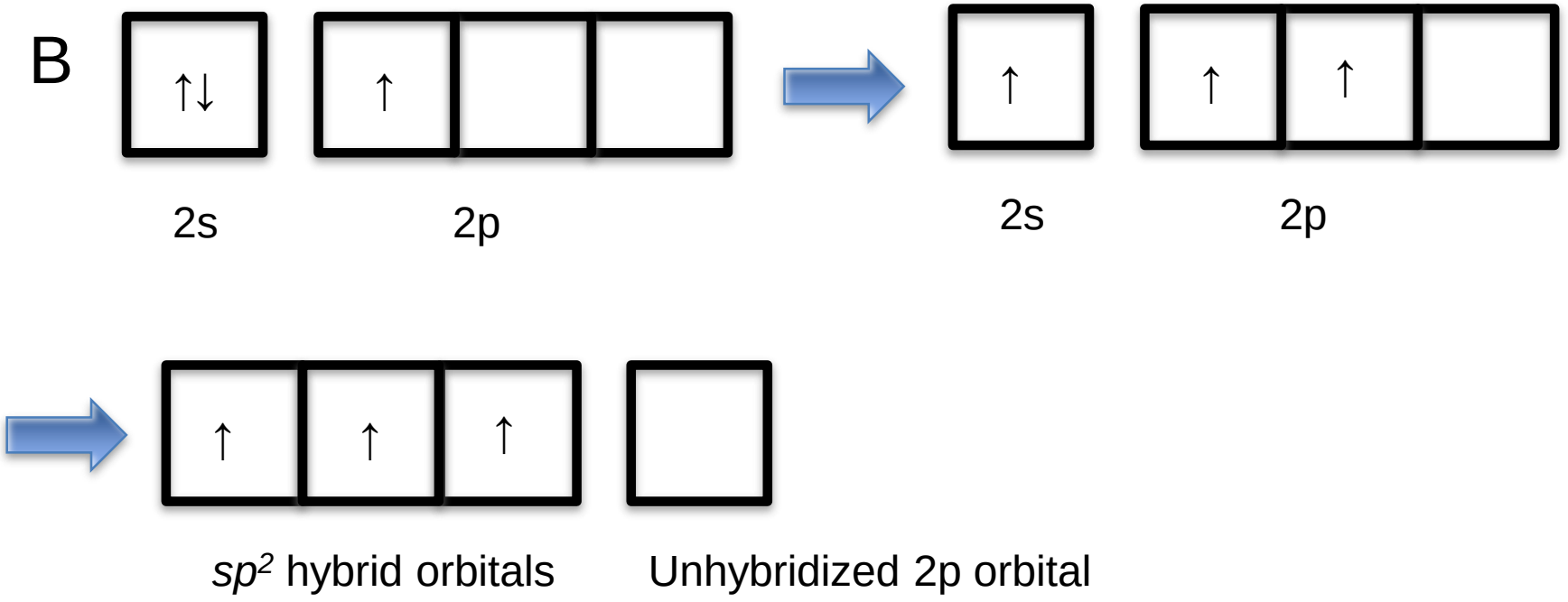


Bonding in BeH_2



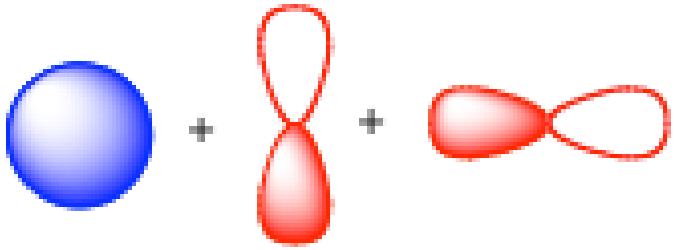
Hybridization of Atomic Orbitals: sp^2 Trigonal Planar

BCl_3

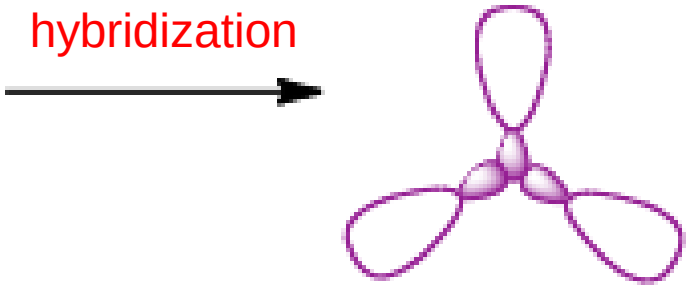


sp^2 Hybrid Orbitals

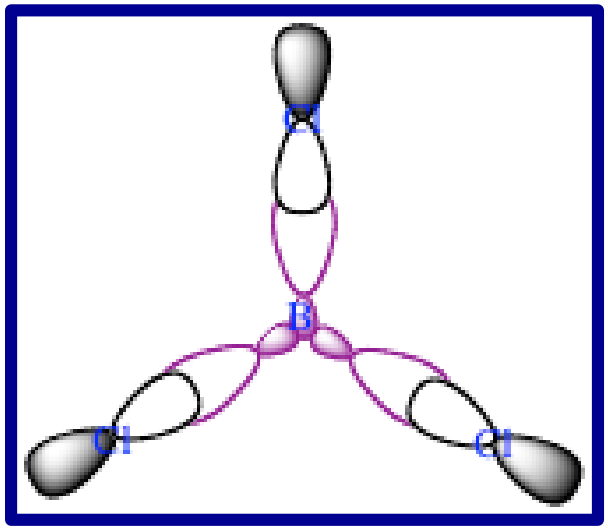
s orbital Two perpendicular *p* orbitals



hybridization



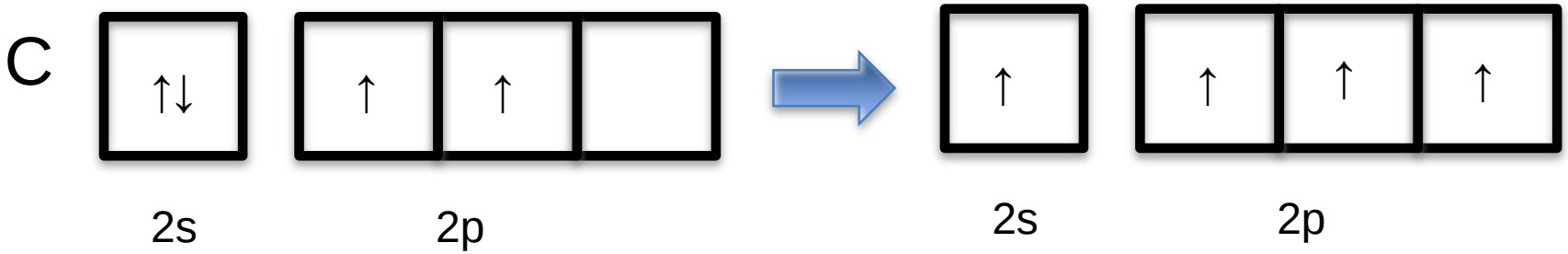
Three sp^2 hybrid orbitals in central atom B

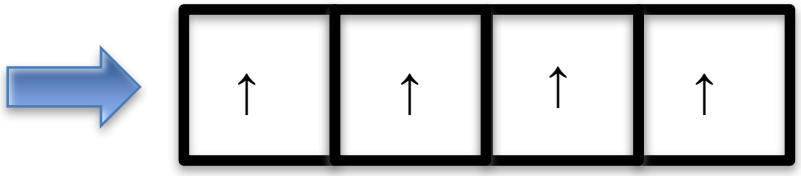


Three *p*-orbitals of Cl are overlapped with three sp^2 hybrid orbitals

sp^3 Hybrid Orbitals

CH_4

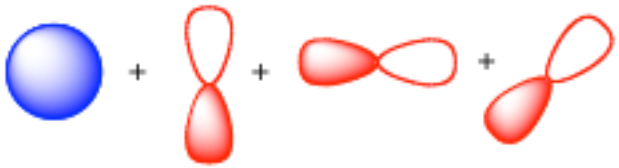


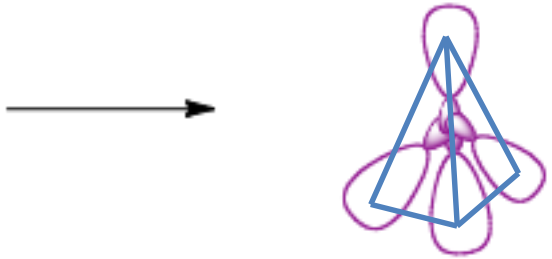


sp^3 hybrid orbitals

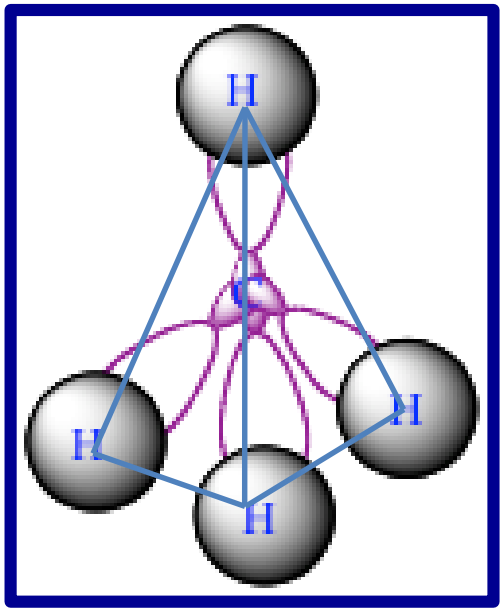
sp^3 Hybrid Orbitals: Tetrahedral

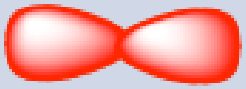
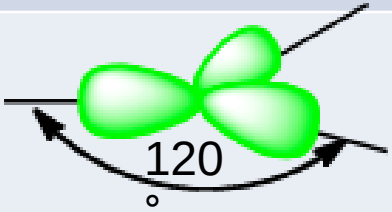
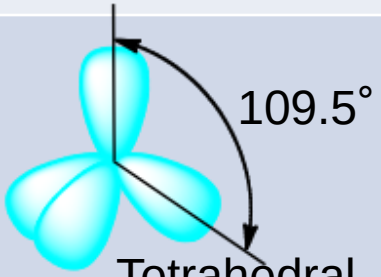
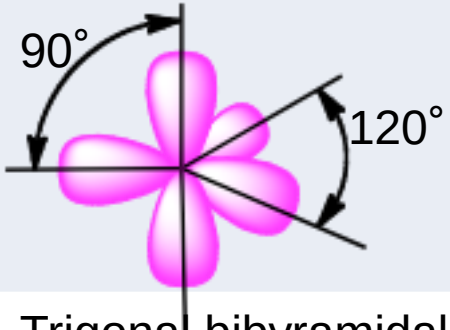
s orbital Three perpendicular *p*-orbitals

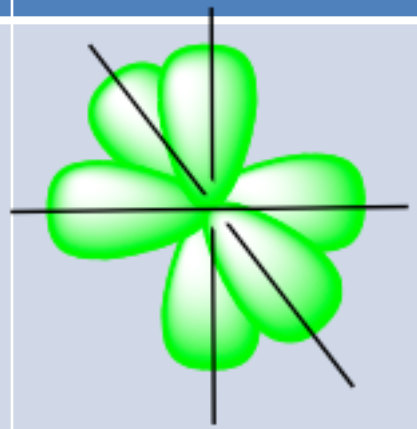




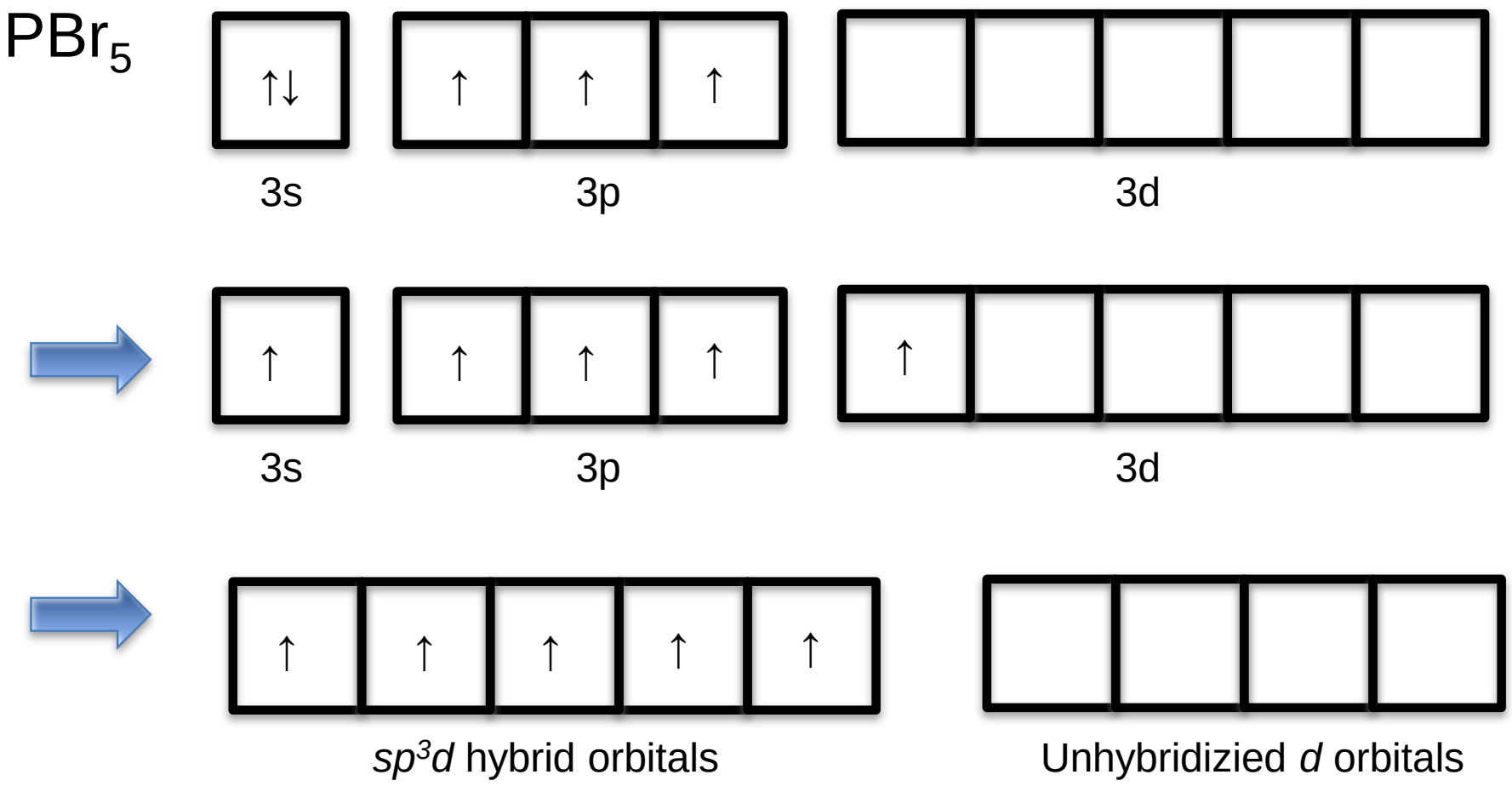
Four sp^3 hybrid orbitals



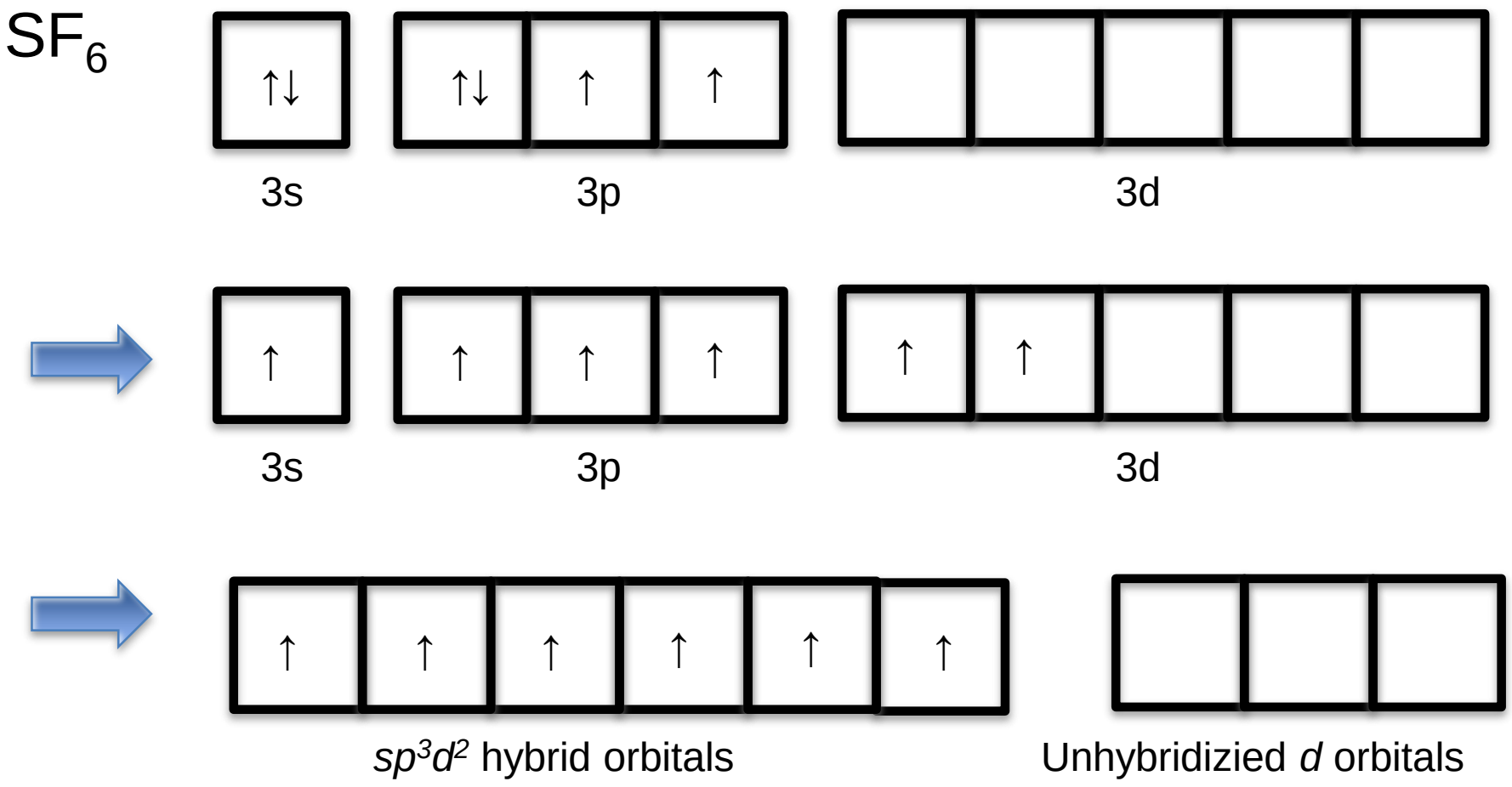
Hybridization of central atom	Number of hybrid orbtials	Shape of hybrid orbitals	Examples
sp	2	 linear	$BeCl_2$
sp^2	3	 Trigonal planar	BF_3
sp^3	4	 Tetrahedral	CH_4
sp^3d	5	 Trigonal bibyramidal	PCl_5

Hybridization of central atom	Number of hybrid orbtials	Shape of hybrid orbitals	Examples
sp^3d^2	6	 Octahedral	SF_6

sp^3d Hybrid Orbitals: Trigonal Bipyramid



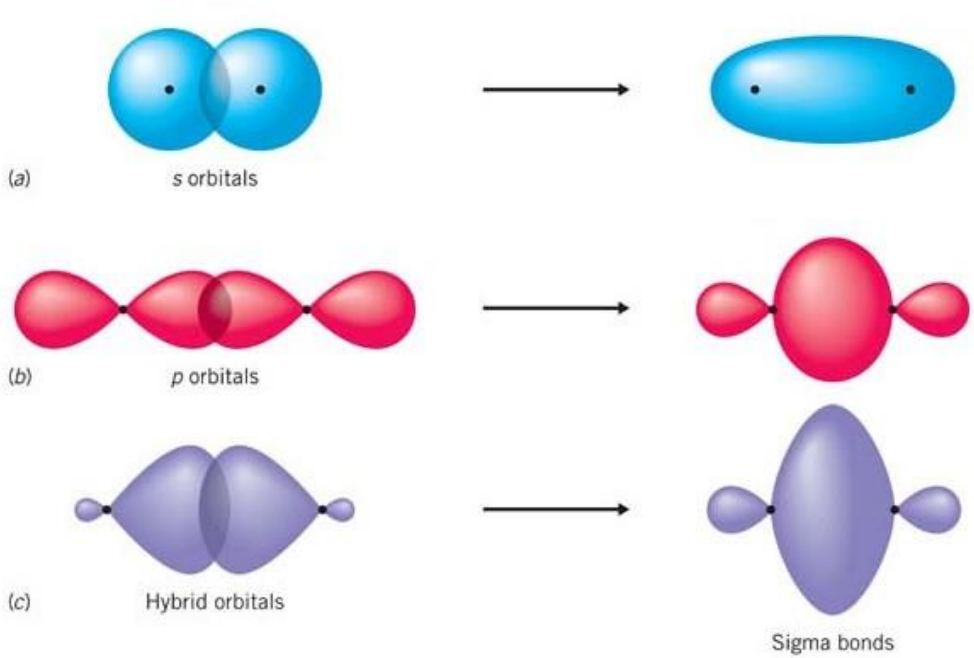
sp^3d^2 Hybridization Orbital: Octahedral

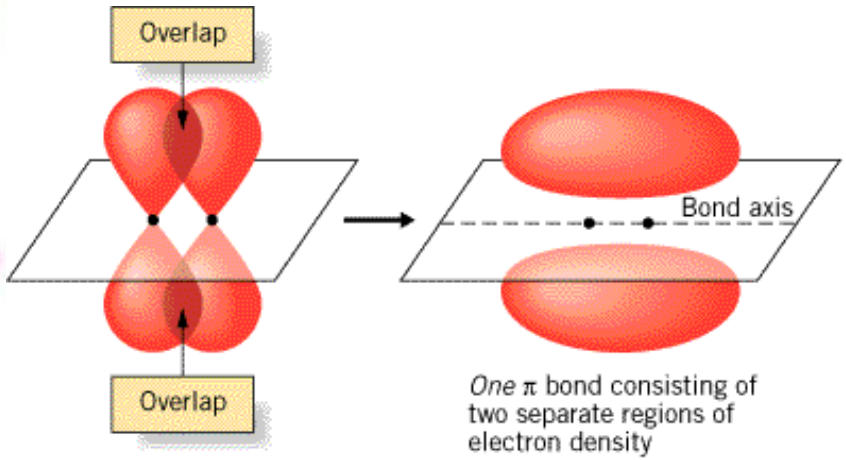


Hybridization in Molecules Containing Double and Triple Bonds

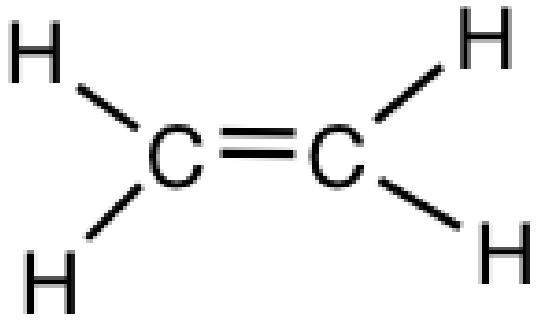
σ bonding

π bonding

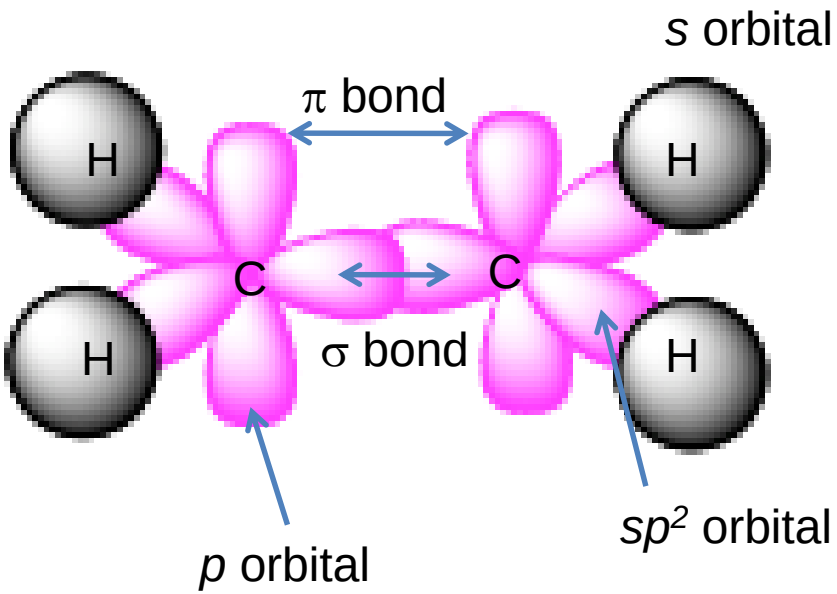


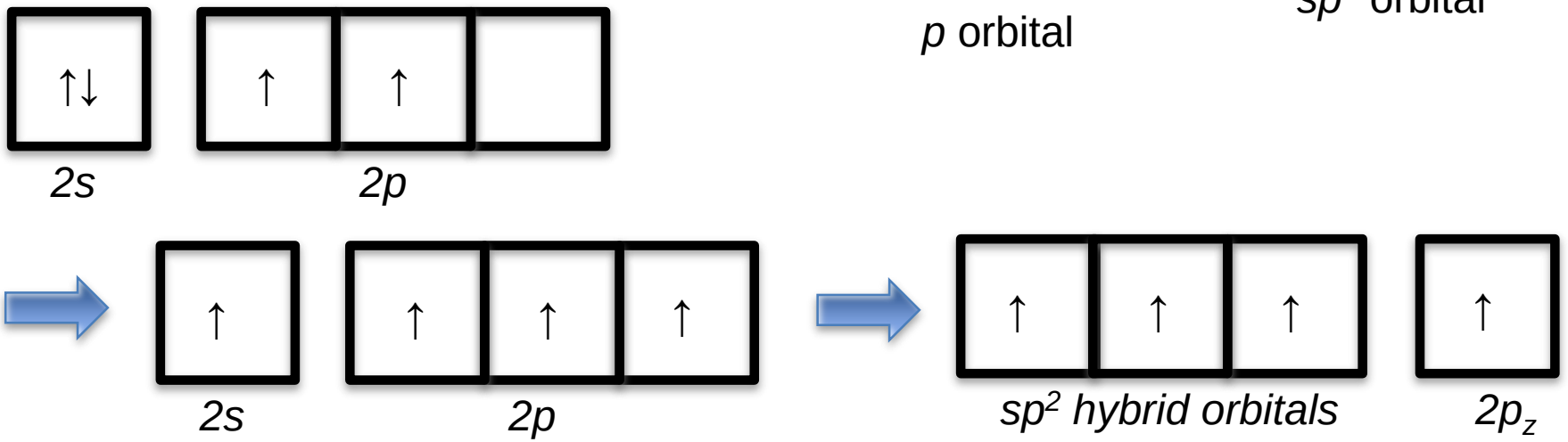


Hybridization in Molecules Containing Double Bond

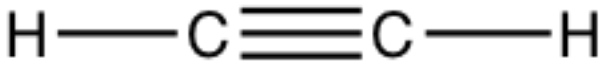


Double bond consists of one σ bond and one π bond



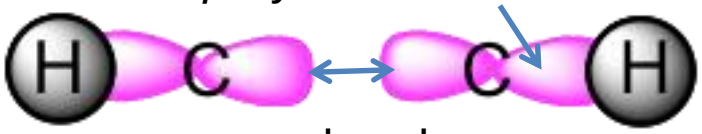


Hybridization in Molecules Containing Triple Bond

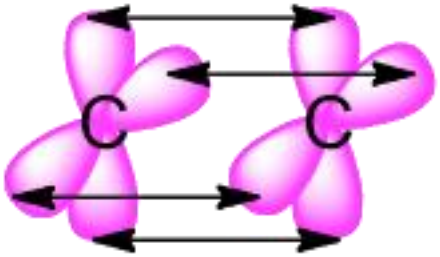


Triple bond consists of one σ bond and two π bonds

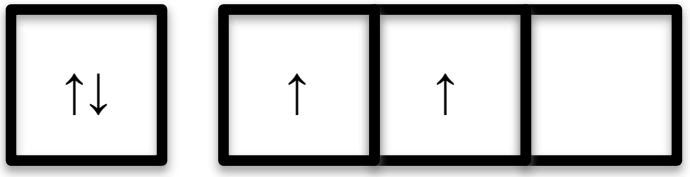
sp hybrid orbital

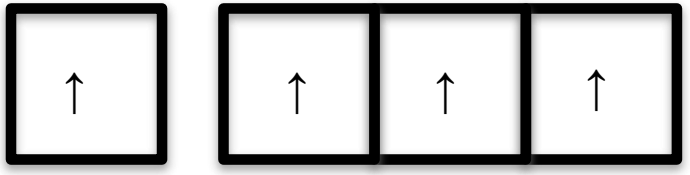


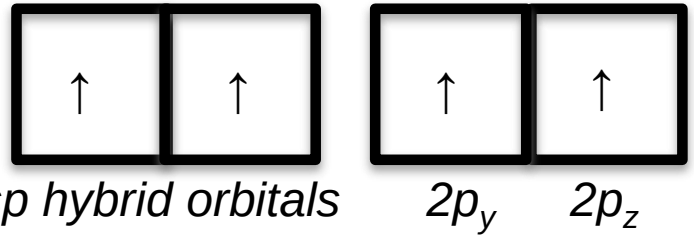
σ bond



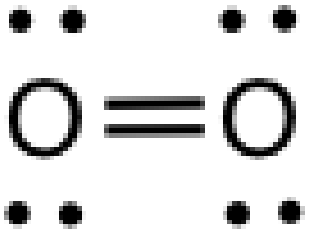
π bond







Molecular Orbital (MO) Theory



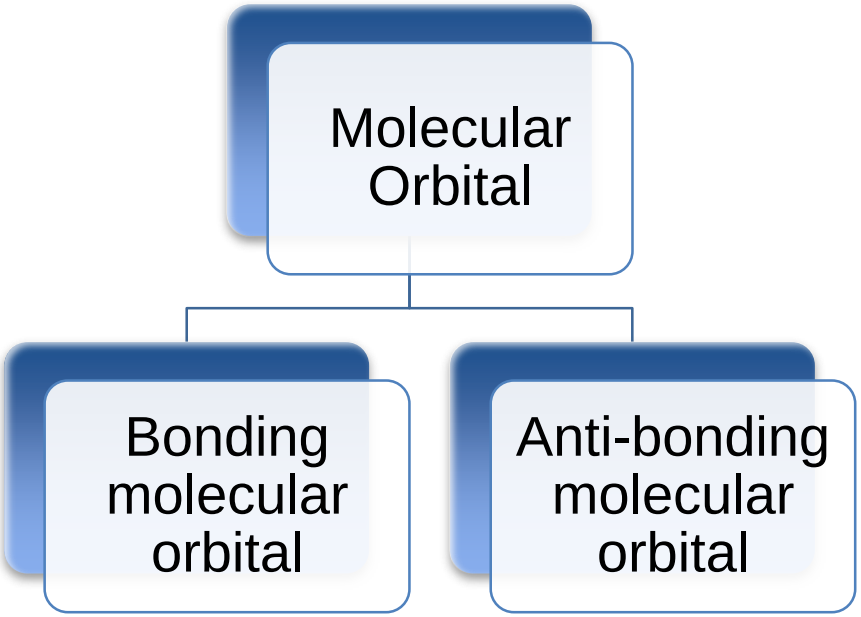
O_2 molecules should be **diamagnetic**, because there is no unpaired electron in O_2.
Note that O atom alone is paramagnetic

Valence bond theory cannot explain why O_2 molecules are paramagnetic.

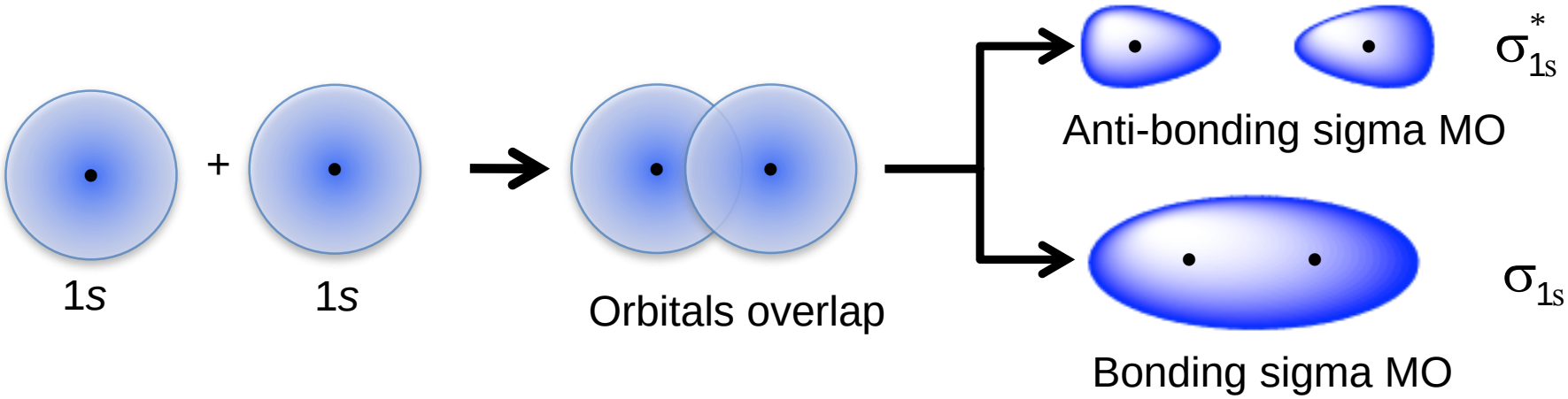
Diamagnetic: all electrons are paired (↑↓)
Paramagnetic: some electrons are unpaired (↑)

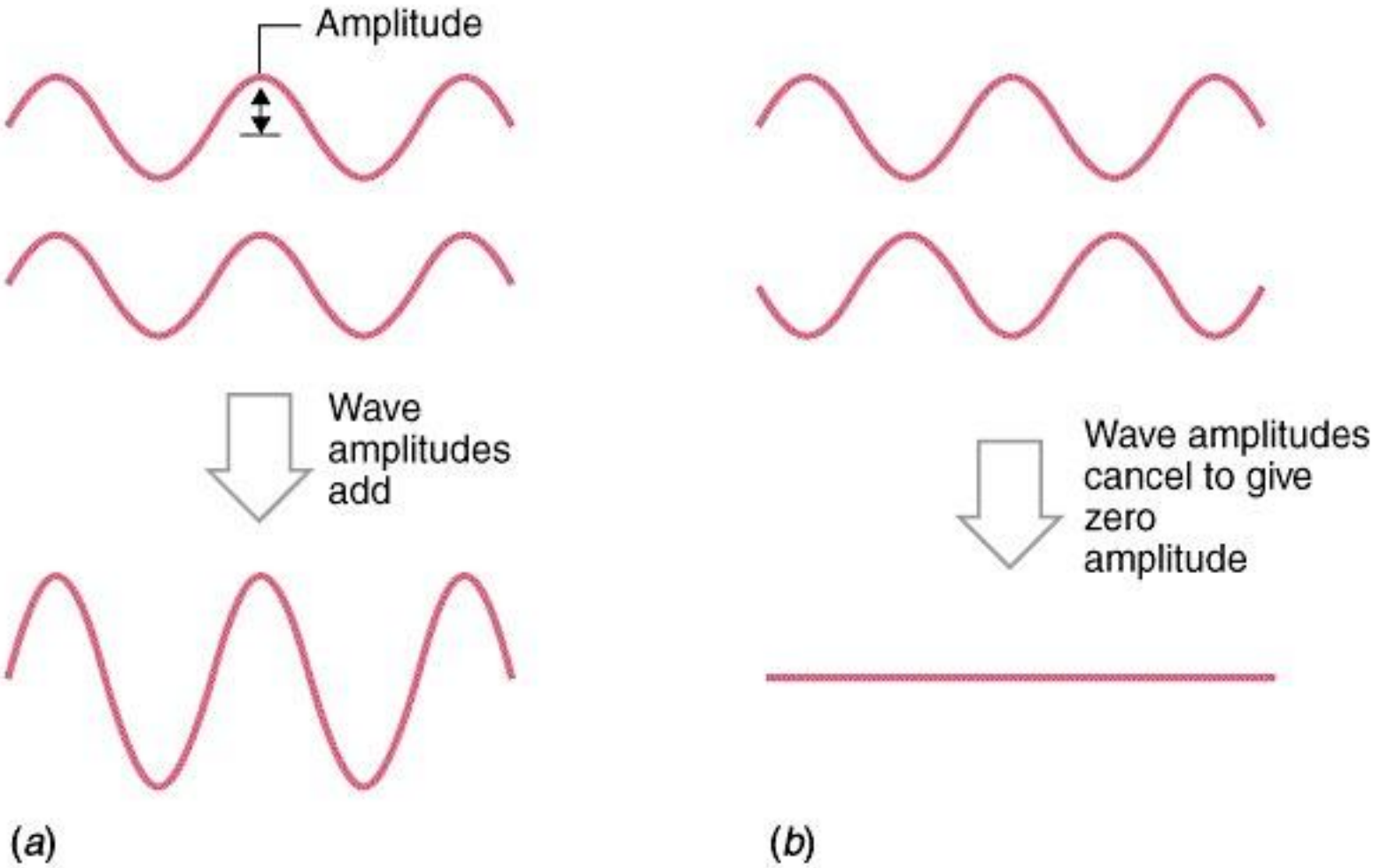
Molecular Orbital (MO) theory

Explains covalent bonds in terms of **molecular orbitals**, which result from interaction of the atomic orbitals of the bonding atoms and are associated with the entire molecule.

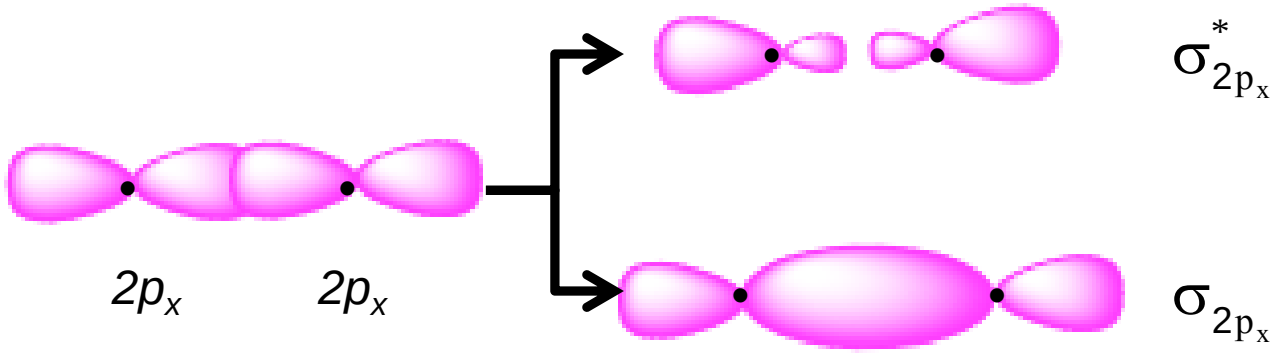


Bonding and Anti-bonding Molecular Orbitals



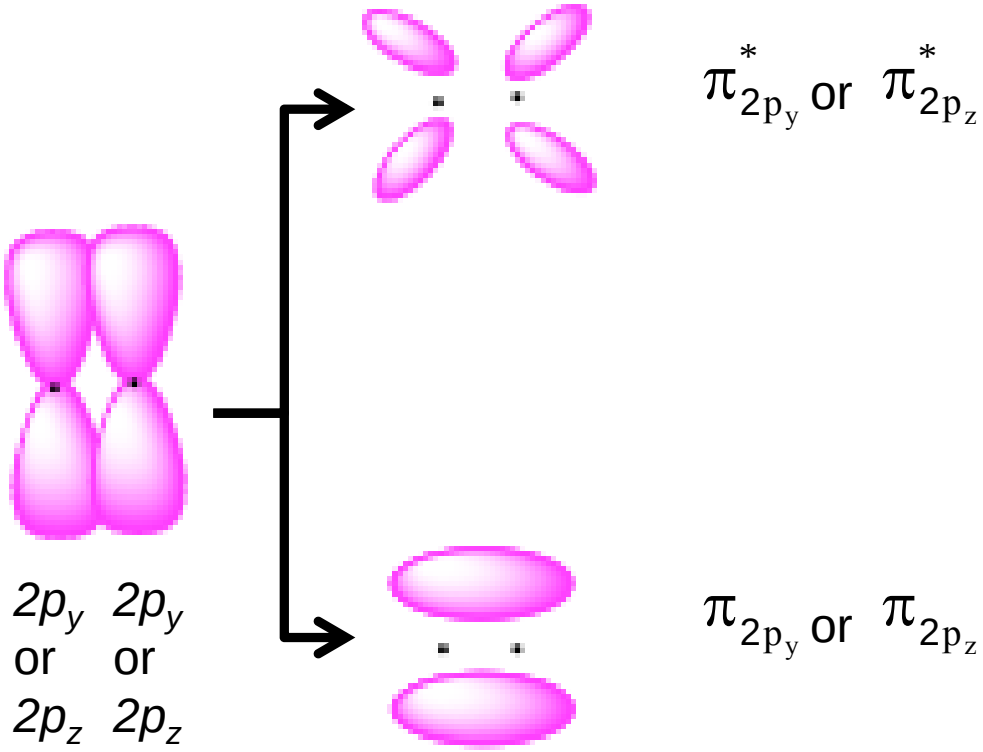


Bonding and Anti-bonding Molecular Orbitals

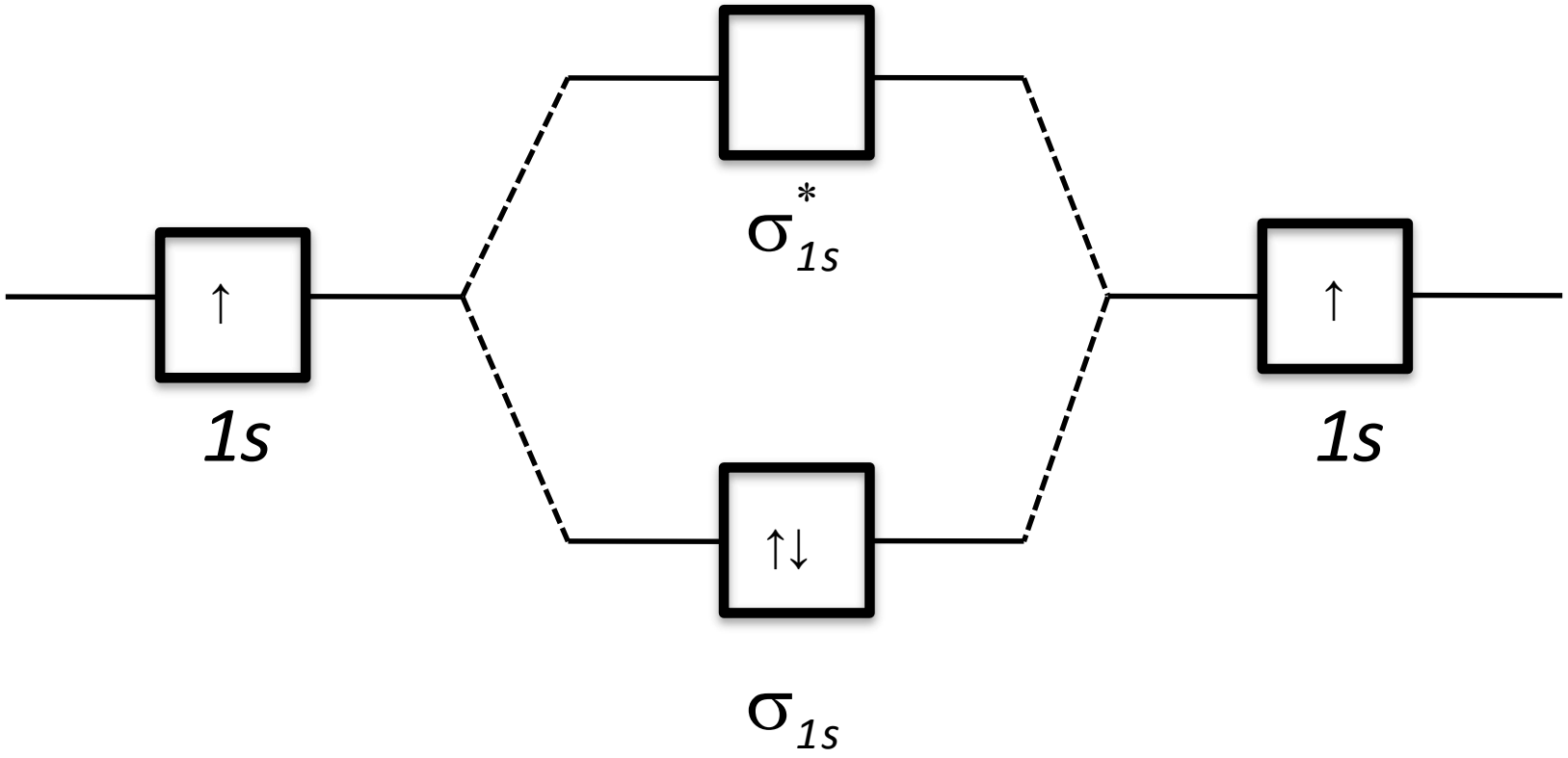


Note that x, y, and z directions of *p* orbitals are arbitrary.

Bonding and Anti-bonding Molecular Orbitals



Molecular Orbital Energy Diagram: H_2



Rules for Molecular Orbital Energy Diagram

The number of molecular orbitals will always be **the same as the number of atomic orbitals** used to construct them.

Electrons fill the lowest energy orbitals that are available.

Each molecular orbital can hold **two electrons**, but the spins must be opposite.

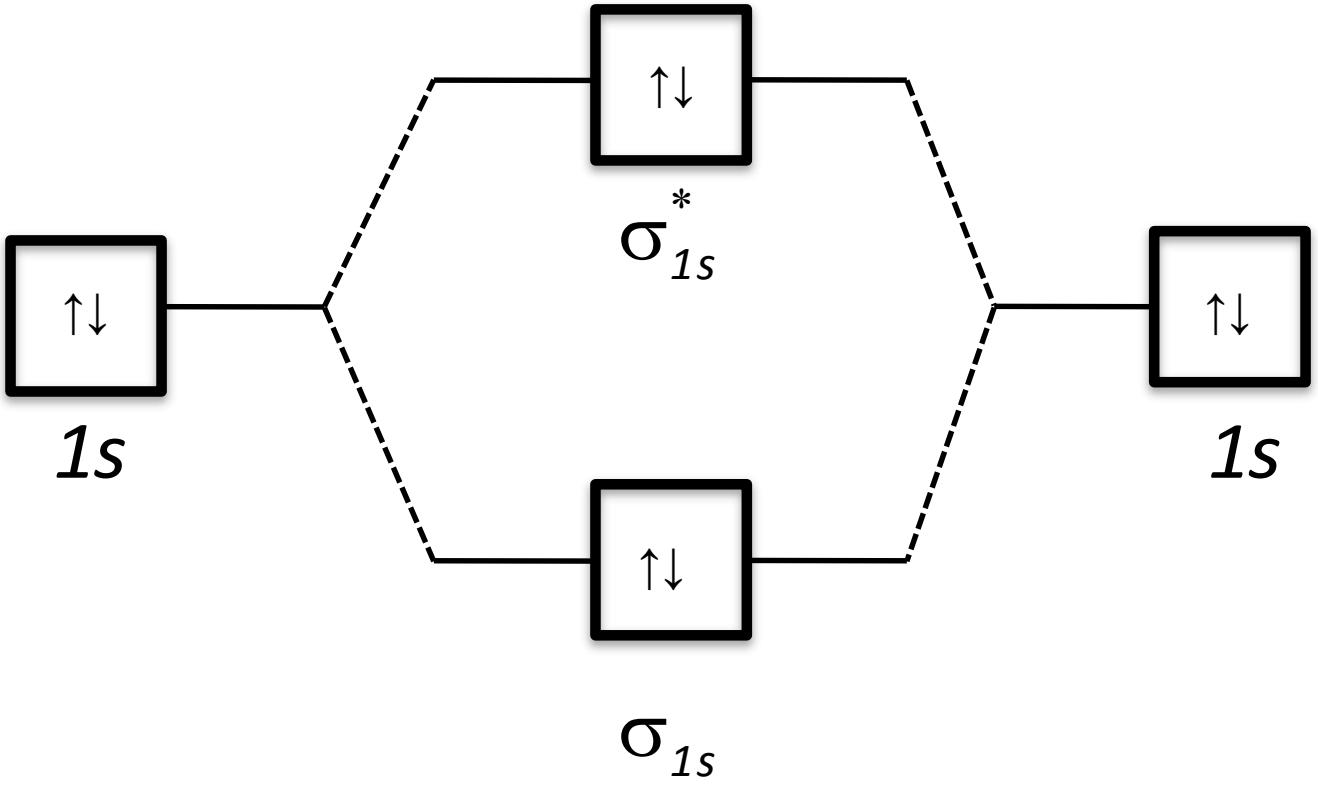
As in the atomic orbtals, **Hund's rule** should be considered.

Bond Order

$$\frac{(\#\ \text{of bonding electrons} - \#\ \text{of antibonding electrons})}{2}$$

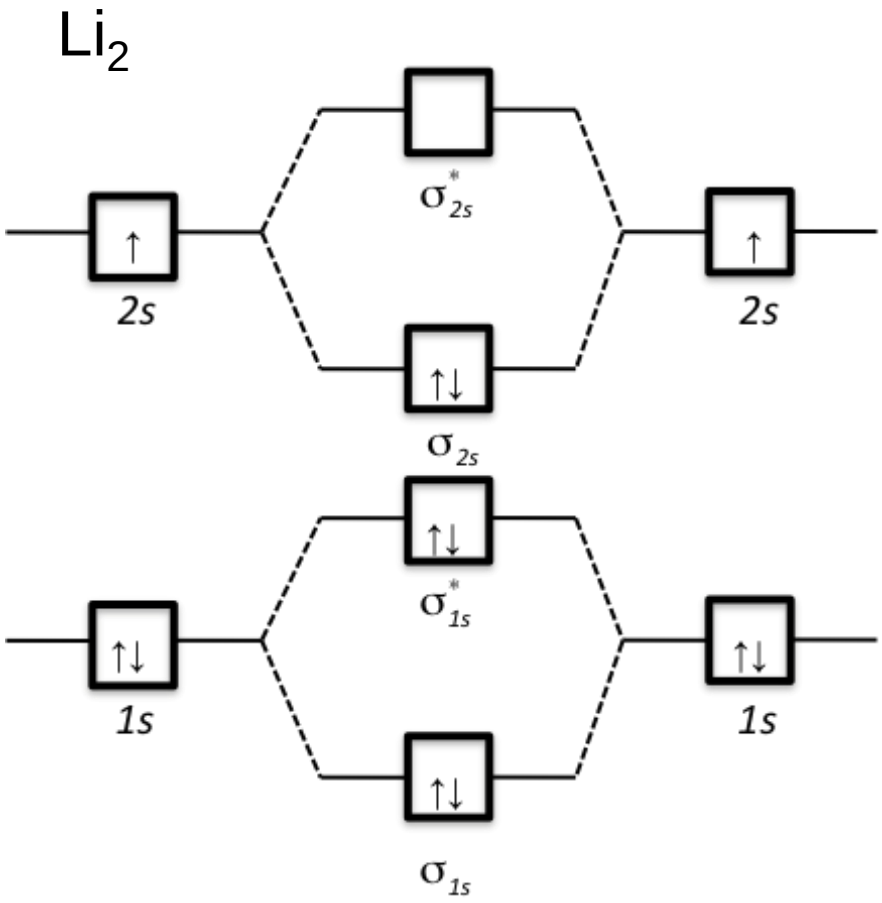
What are the bond orders of H_2, H_2^-, and H_2^+?

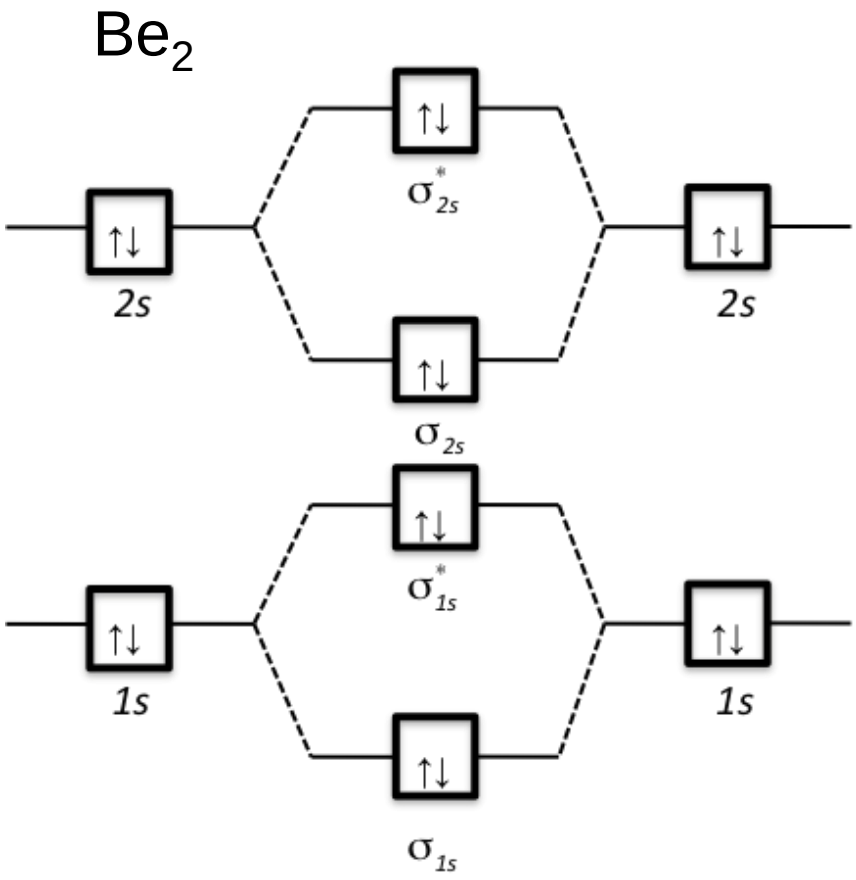
Molecular Orbital Energy Diagram: He_2



What is the bond order?

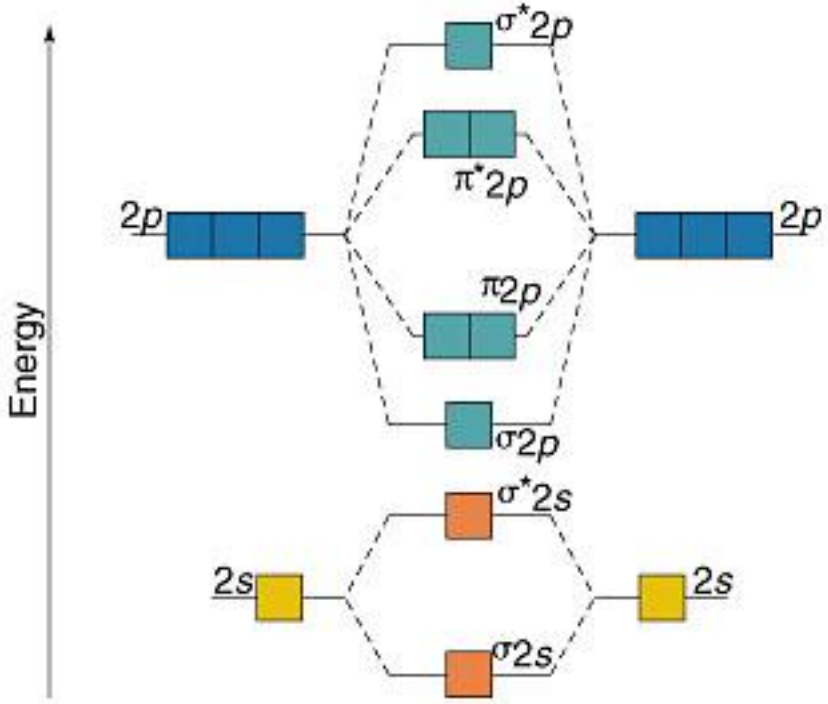
Molecular Orbital Energy Diagram

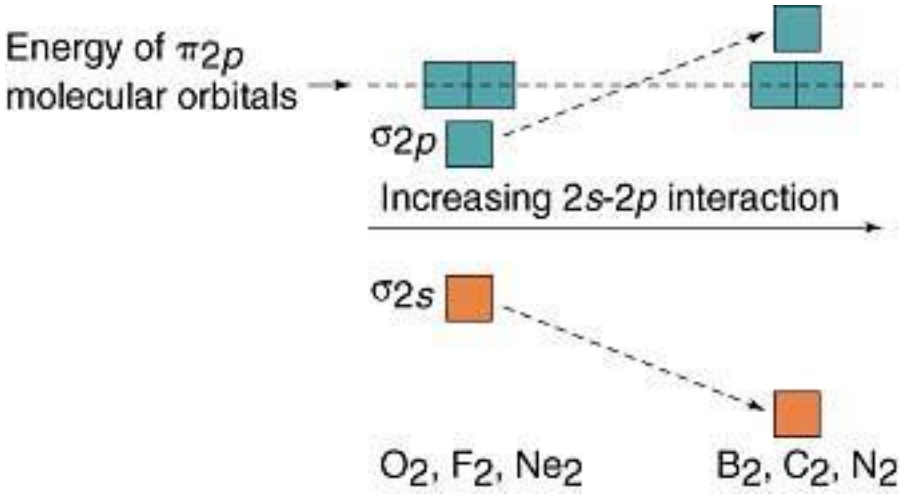




What are the bond orders of Li_2 and Be_2?

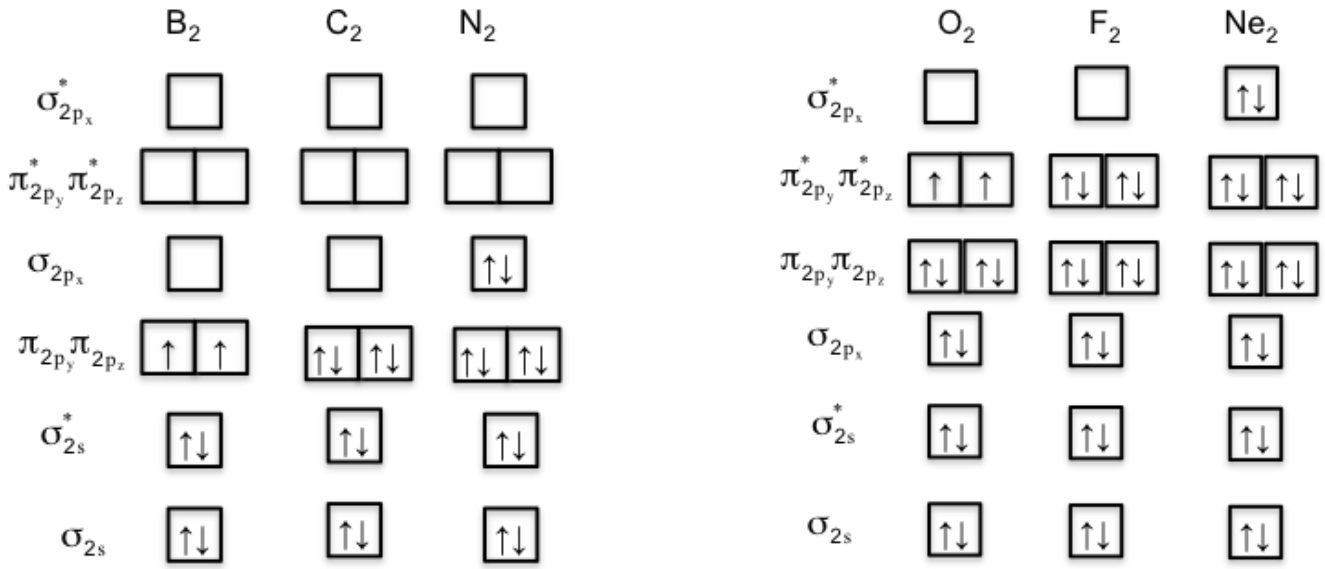
Molecular Orbital Energy Diagram in Second Periodic Diatomic Molecules





Note that the energetic ordering of the molecular orbitals can be altered because of 2s-2p orbital interaction. In B_2, C_2, and N_2 molecules, π_{2p} orbitals are lower in energy than σ_{2p} orbital.

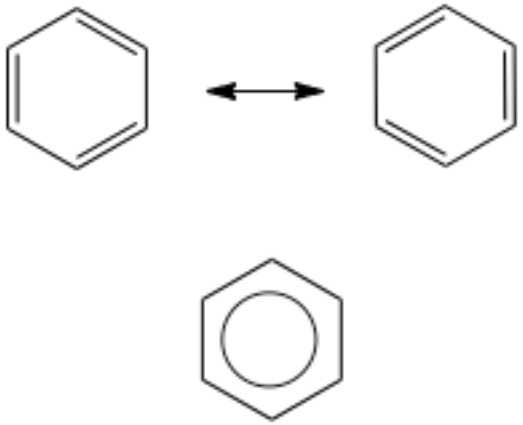
Molecular Orbital Energy Diagram in Second Periodic Diatomic Molecules

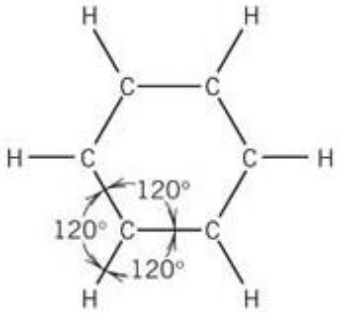


	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond length (pm)	159	131	110	121	142	-
Bond energy (kJ/mol)	288.7	627.6	941.4	498.7	156.9	-
Magnetic properties	Para-	Dia-	Dia-	Para-	Dia-	Dia-

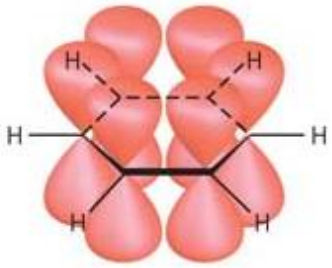
Delocalized Molecular Orbitals

- Lewis structures use **resonance** to explain that the actual molecule appears to have several equivalent bonds, rather than different possible structures
- MO theory shows the electrons being **delocalized** in the structure

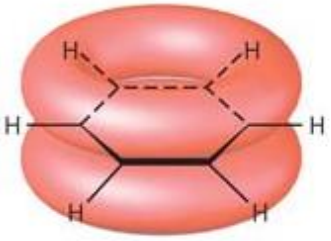




σ-bond network in benzene (*a*)



p orbitals ready to overlap (*b*)



Delocalized π electrons (*c*)

Homework

TBA