VC210 Recitation Class

Molecular Theory

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CONTENTS

Chapter 4

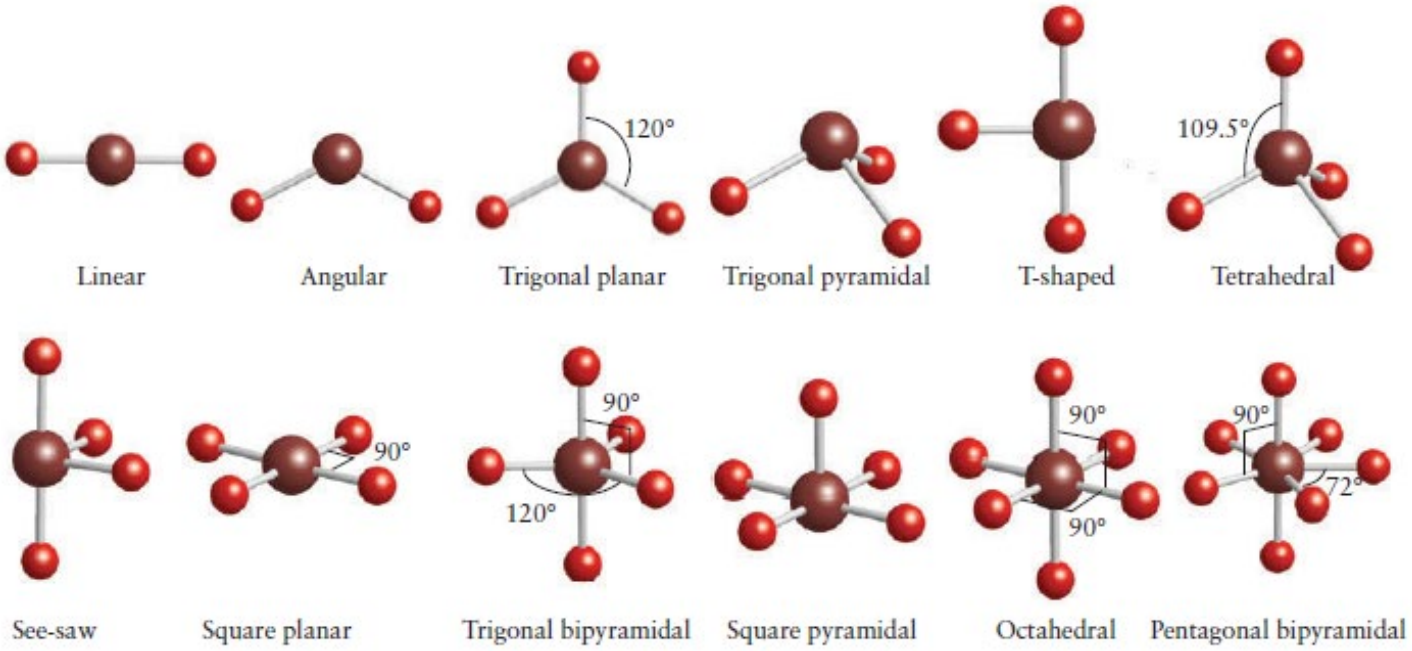
Molecular Theories

/01

Molecular Theories

1.1 VSEPR

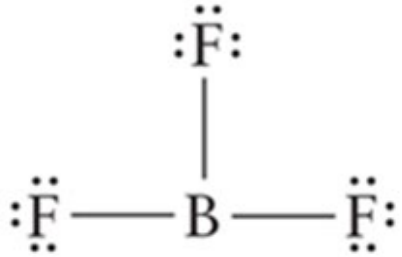
- Extended Lewis theory, only consider electrostatic repulsions.



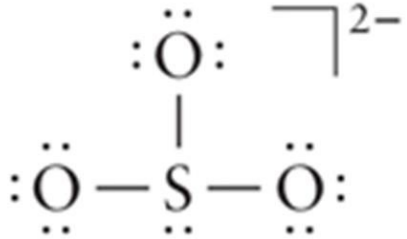
1.1 VSEPR

- Bonding pair & nonbonding pair(lone pair)
- AX_nE_m:
  - "A" represent a central atom
  - "X" represent a bonded electron region
  - "E" represent **a lone pair** electron region
- How to find VSEPR?
  - Draw the Lewis structure.
  - Get AX_nE_m
  - Find the most favorable electron region shape and molecular shape.

1.1 VSEPR

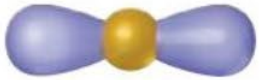
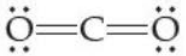
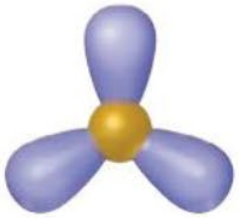
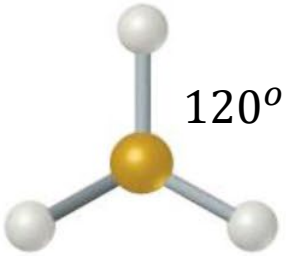
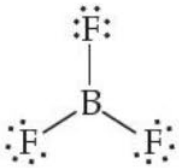
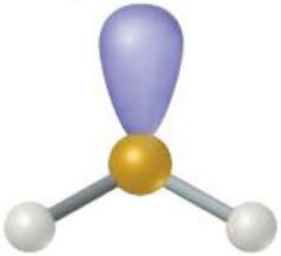
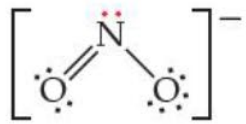


AX_3

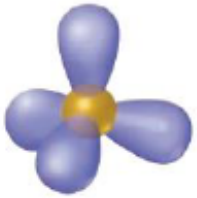
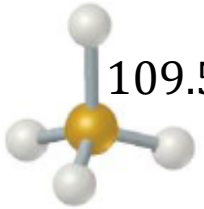
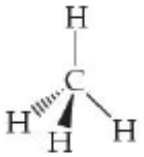
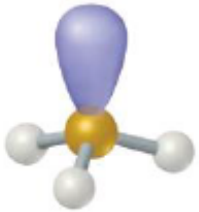
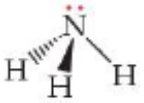
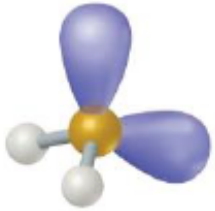


AX_3E

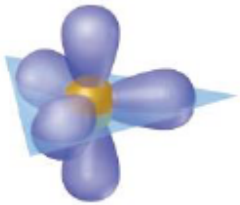
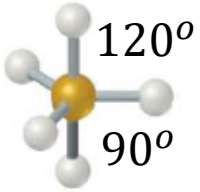
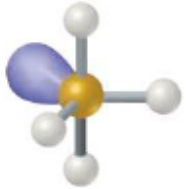
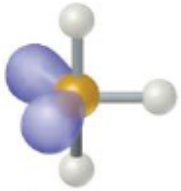
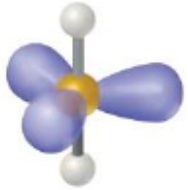
1.1 VSEPR

Number of Electron Domains	Electron-Domain Geometry	X Bonding Domains	E Nonbonding Domains	Molecular Geometry	Example
2	 Linear	2	0	180^o  Linear	
3	 Trigonal planar	3	0	 120^o Trigonal planar	
		2	1	 Bent	

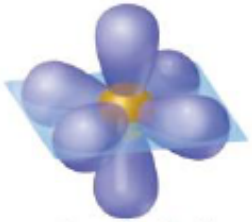
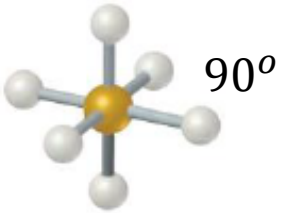
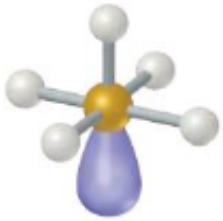
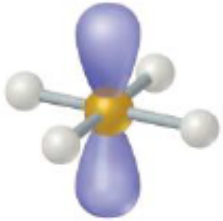
1.1 VSEPR

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	

1.1 VSEPR

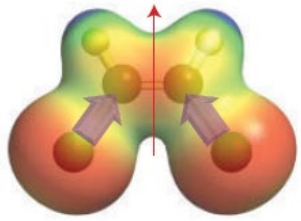
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	 Trigonal bipyramidal	5	0	 Trigonal bipyramidal	PCl_5
		4	1	 Seesaw	SF_4
		3	2	 T-shaped	ClF_3
		2	3	 Linear	XeF_2

1.1 VSEPR

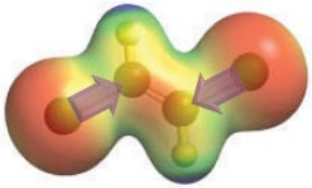
Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
6	 Octahedral	6	0	 Octahedral	SF_6
		5	1	 Square pyramidal	BrF_5
		4	2	 Square planar	XeF_4

1.1 VSEPR

- Chemical bond may be polarized
- Molecules may be polarized
- **Symmetric dipole = Non-polar**
- Asymmetric dipole = Polar
- Two notations of dipole moments



28 *cis*-Dichloroethene, $C_2H_2Cl_2$

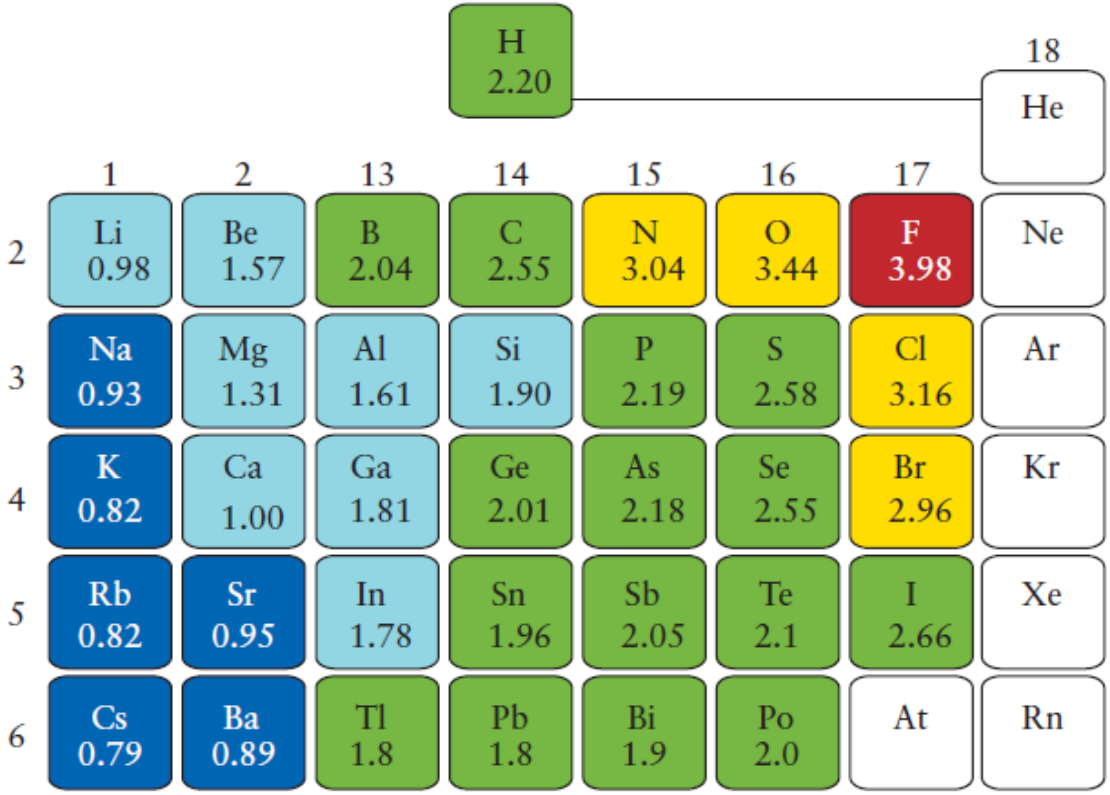


29 *trans*-Dichloroethene, $C_2H_2Cl_2$

Two notations of dipole moments

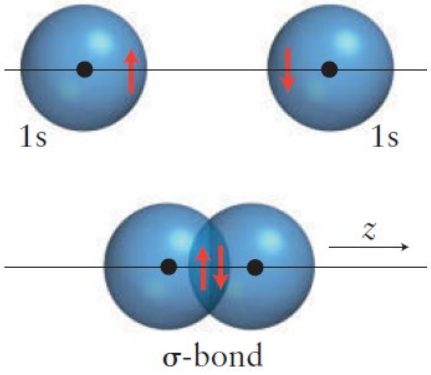
1.1 VSEPR

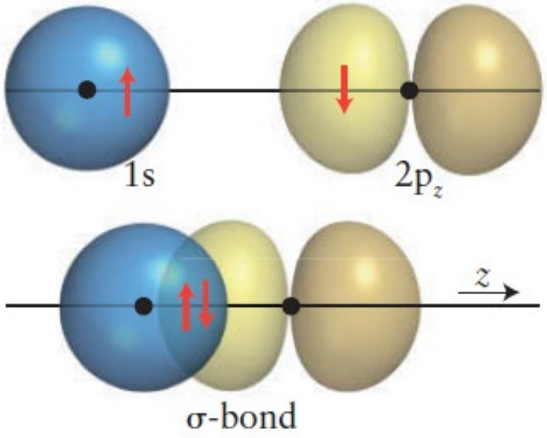
- Elements with higher electronegativity is considered as the negative dipole.

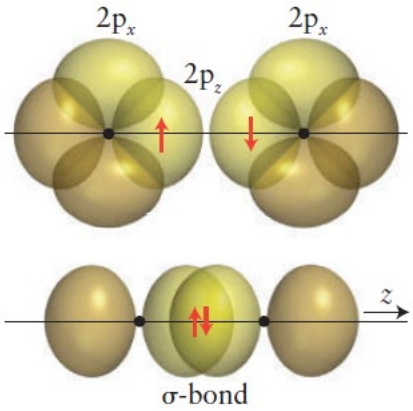


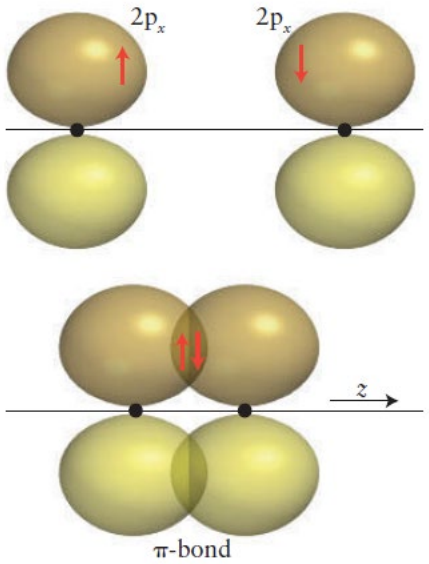
1.2 Valence Bond Theory

- σ-bond and π-bond
- head-to-head overlaps and side-by-side overlaps



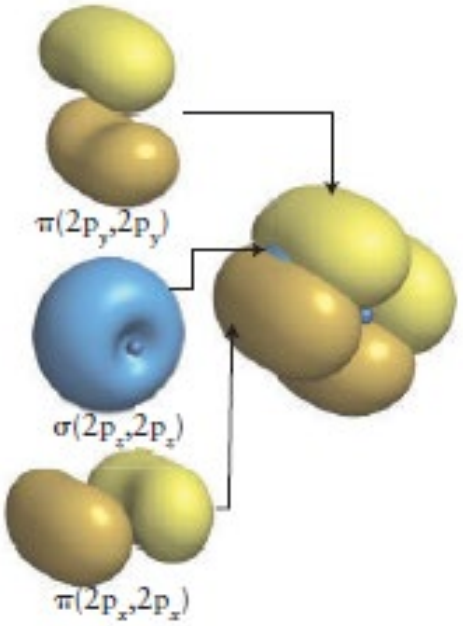






1.2 Valence Bond Theory

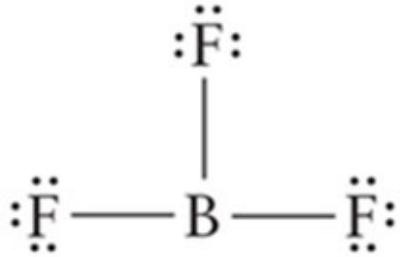
- A single bond is a σ-bond.
- A double bond is a σ-bond plus a π-bond.
- A triple bond is a σ-bond plus two π-bonds.



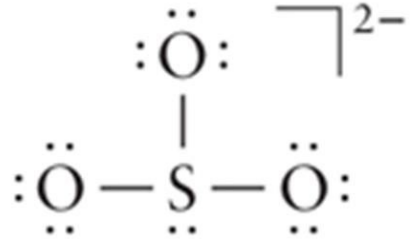
1.2 Valence Bond Theory

- Hybridization: k=m+n
  - $sp: k = 2$
  - $sp^2: k = 3$
  - $sp^3: k = 4$
  - $sp^3d: k = 5$
  - $sp^3d^2: k = 6$
  - m=number of lone pairs of central atom
  - n=number of atoms connected to central atom

1.2 Valence Bond Theory



$m = 0, n = 3$

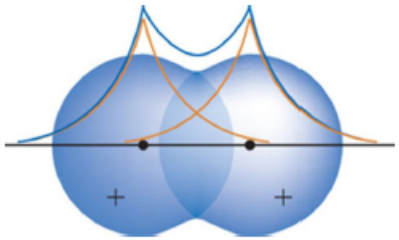


$m = 1, n = 3$

1.3 Molecular Orbital Theory

- The number of MOs equals the number of AOs.
- The MO wave functions can be classified as bonding, nonbonding and anti-bonding.
  - Bonding: $E_{MO} < E_{AO}$
  - Antibonding: $E_{MO} > E_{AO}$
  - Nonbonding: $E_{MO} \approx E_{AO}$

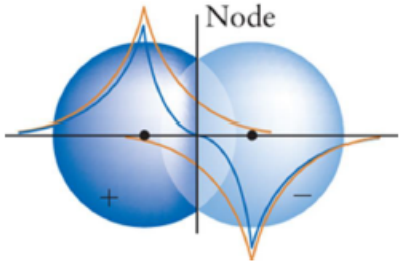
$\psi_1 = \varphi_{1s}(A) + \varphi_{1s}(B)$,



constructive interference

bonding

$\psi_2^* = \varphi_{1s}(A) - \varphi_{1s}(B)$

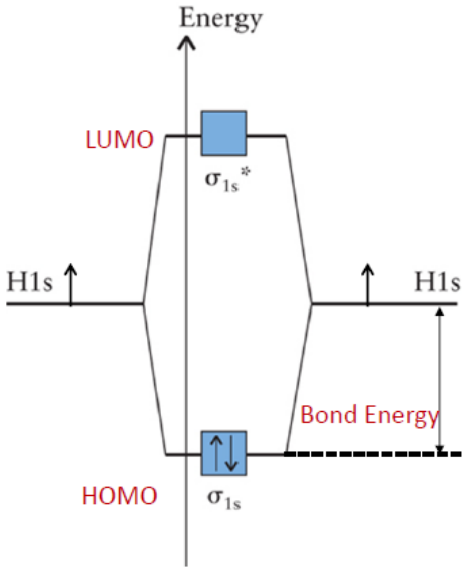


deconstructive interference

antibonding

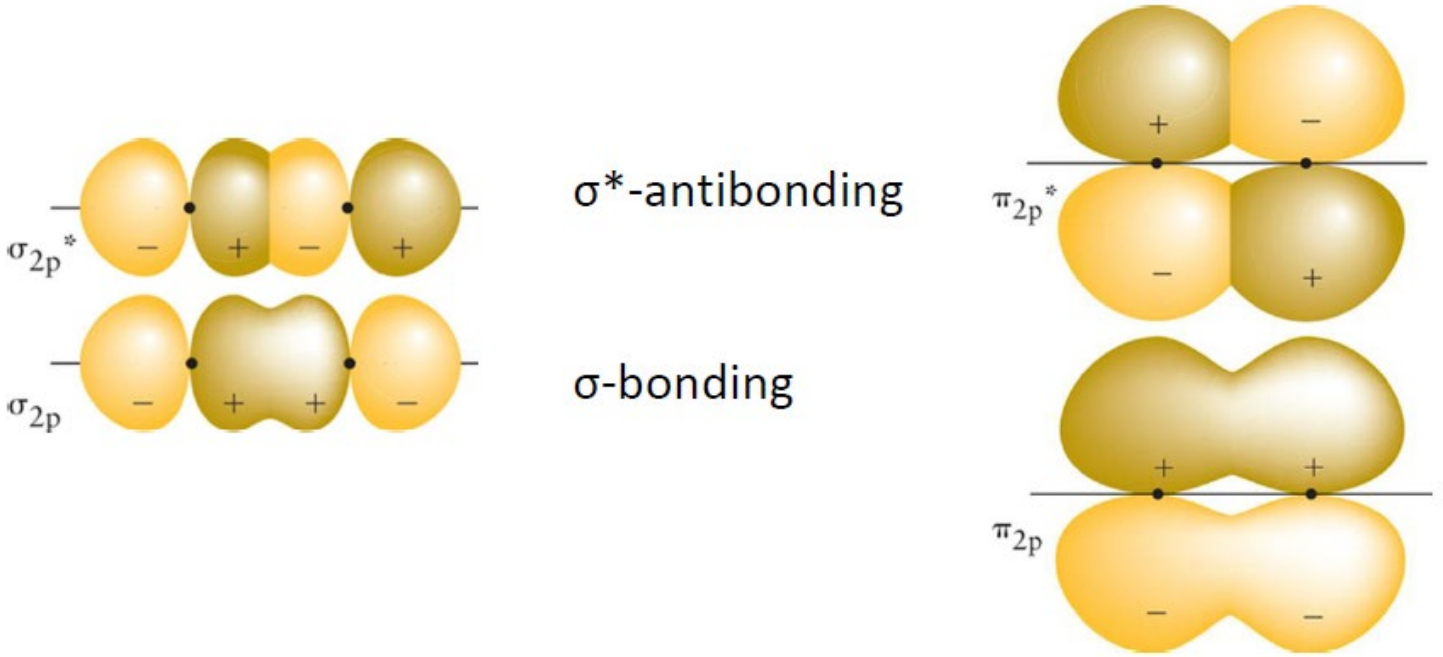
1.3 Molecular Orbital Theory

- $\sigma_{1s}, \sigma_{1s}^{*}$: bonding MO and antibonding MO.
- $E(\sigma_{1s}) < E(\sigma_{1s}^{*})$
- Number of electrons is unchanged.
- HOMO & LUMO
- Elements with higher electronegativity have lower energy of AOs.



1.3 Molecular Orbital Theory

- For s-orbitals, σ-bond is always formed.
- For p-orbitals, we usually form 1 σ-bond and 2 π-bonds.

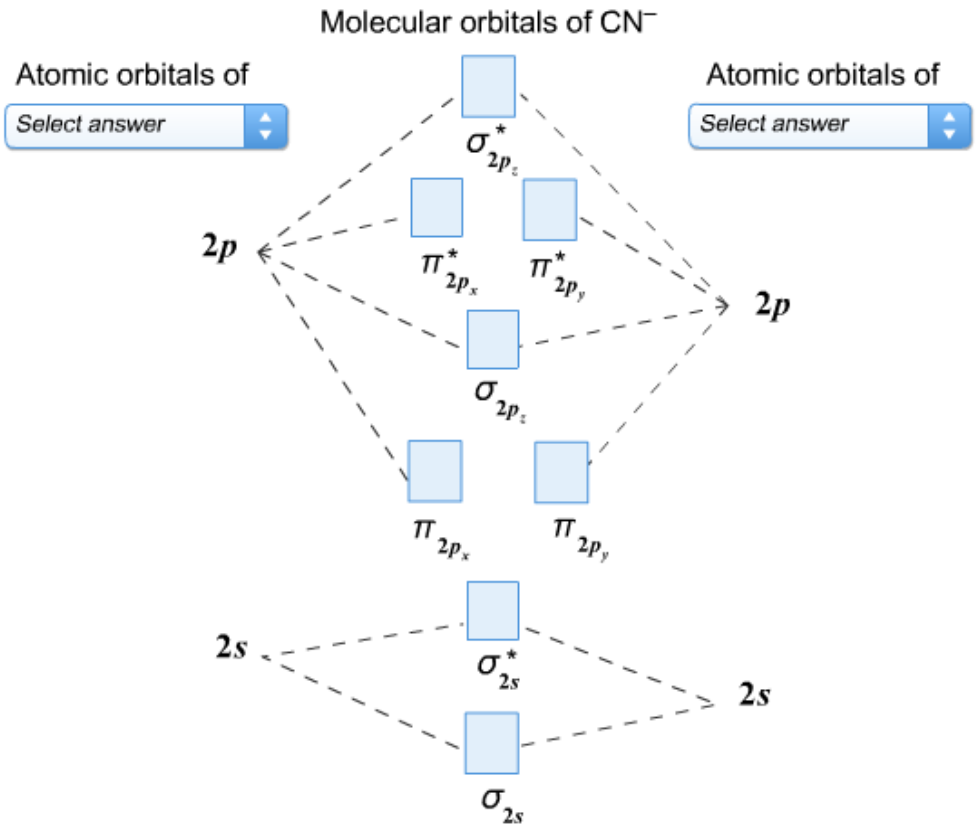


1.3 Molecular Orbital Theory

- Bond order$= \frac{1}{2}(N_b - N_{ab})$
  - N_b -- number of bonding electrons
  - N_{ab} -- number of antibonding electrons
- Bond order and bonds:
  - BO $= 0$, nonbond
  - BO $= 1$, single bond
  - BO $= 2$, double bond
  - BO $= 3$, triple bond

1.3 Molecular Orbital Theory

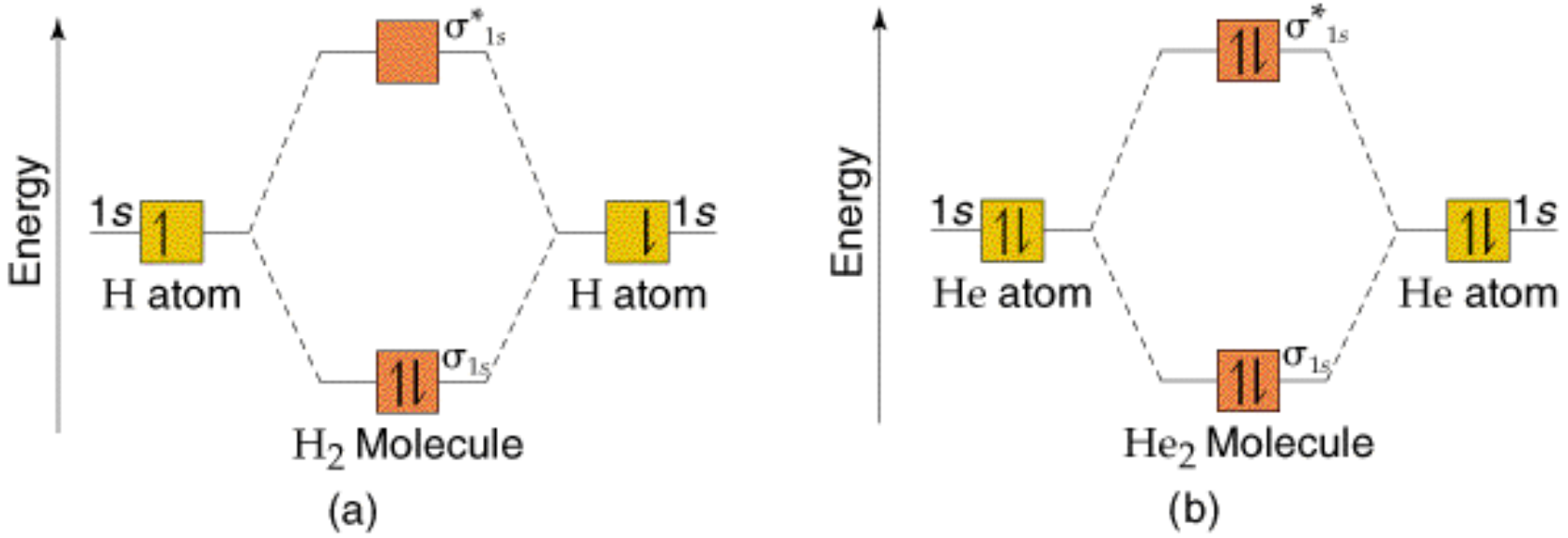
Complete this molecular orbital diagram for CN^- then determine the bond order. Note that the 1*s* orbital is not shown in this problem. To add arrows to the MO diagram, click on the blue boxes.



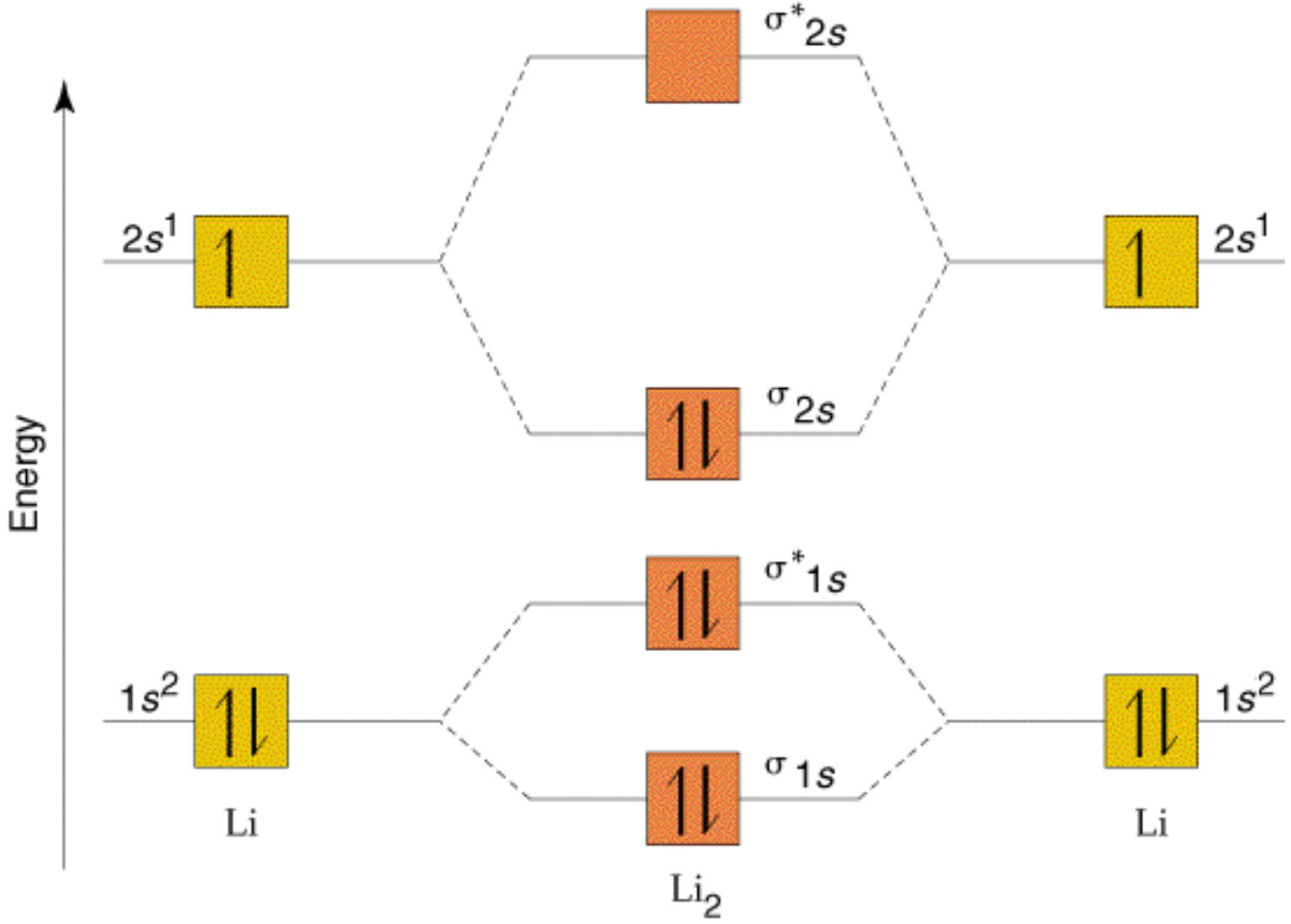
Bond order of CN^-

- 0
- 0.5
- 1
- 1.5
- 2
- 2.5
- 3

1.3 Molecular Orbital Theory

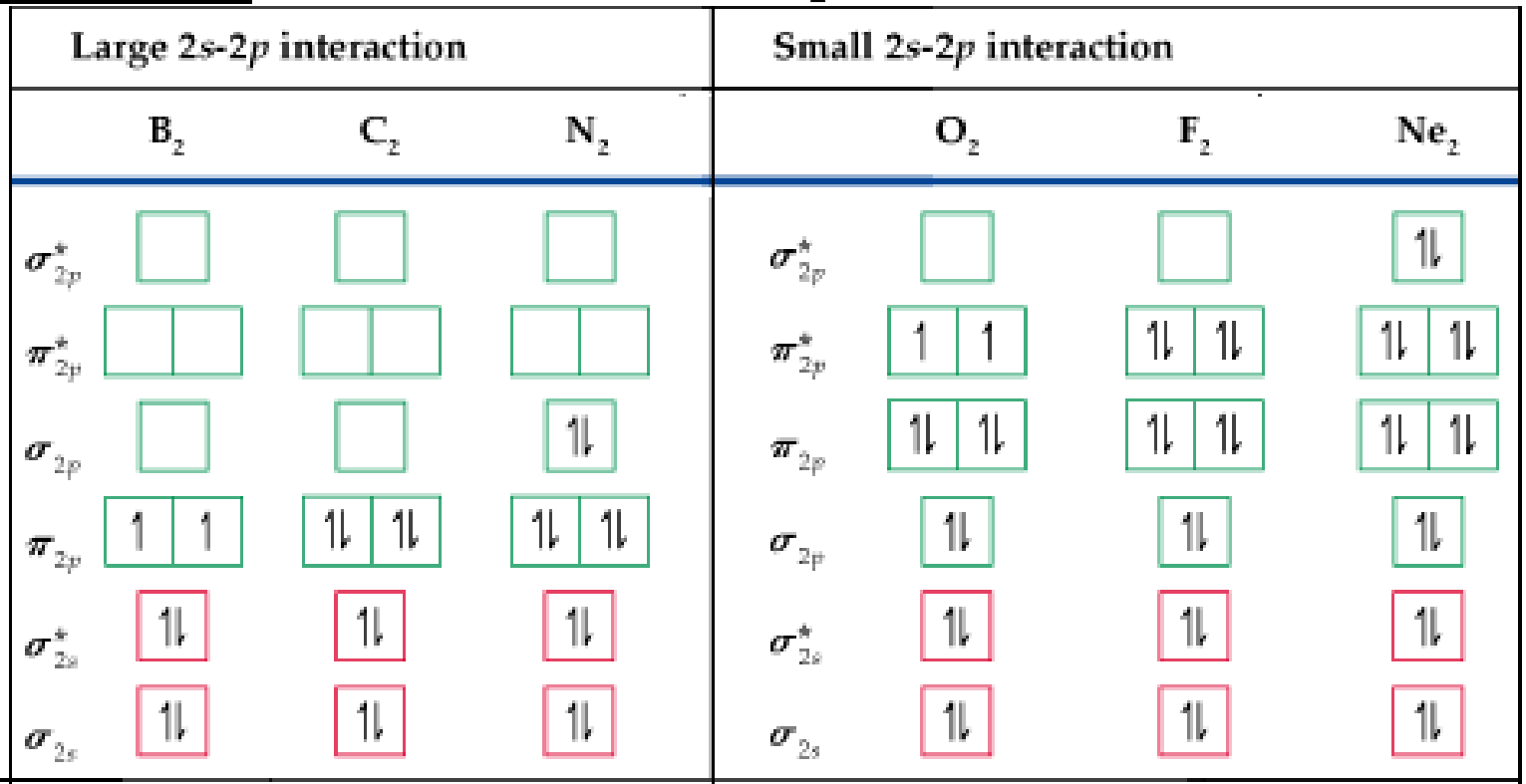


1.3 Molecular Orbital Theory



1.3 Molecular Orbital Theory

- **Paramagnetic**: has unpaired electrons.
- **Diamagnetic**: all electrons are paired.



	B_2	C_2	N_2	O_2	F_2	Ne_2
Bond order	1	2	3	2	1	0
Bond enthalpy (kJ/mol)	290	620	941	495	155	□
Bond length (□)	1.59	1.31	1.10	1.21	1.43	□
Magnetic behavior	Paramagnetic	Diamagnetic	Diamagnetic	Paramagnetic	Diamagnetic	□

1.3 Molecular Orbital Theory

MO diagram

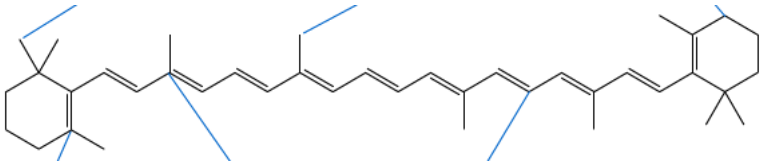
$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p(y) = \pi 2p(z) < \sigma 2p(x) < \pi^* 2p(y) = \pi^* 2p(z) < \sigma^* 2p(x)$

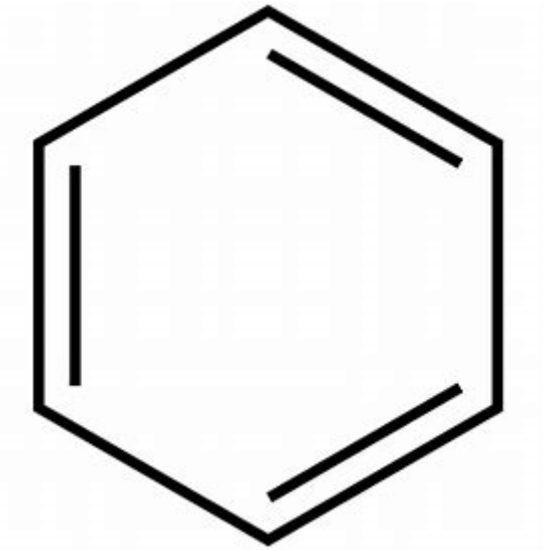
*** O2 & F2 :

$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p(x) < \pi 2p(y) = \pi 2p(z) < \pi^* 2p(y) = \pi^* 2p(z) < \sigma^* 2p(x)$

1.3 Molecular Orbital Theory

- **Orbitals in Polyatomic Molecular**:
  - Conjugated double bonds: Each C atom is sp^2 hybridized, with one electron in each orbital.
  - Each C atom has a p_z-orbital perpendicular to the plane defined by the hybrid orbitals, and it contains one electron.
  - n p_z-orbitals form n $\pi - MOs$.





Thanks.