1411 - E3
CH 08 - Advanced Theories of Covalent Bonding

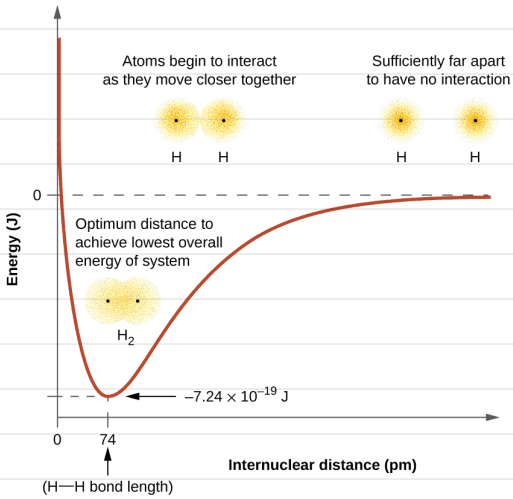
8

Chapter 08: ADVANCED THEORIES OF COVALENT BONDING

Valence Bond Theory [8.1]

Valence bond energy — covalent bond = atomic orbital overlaps

ENERGY & DISTANCE ⟹



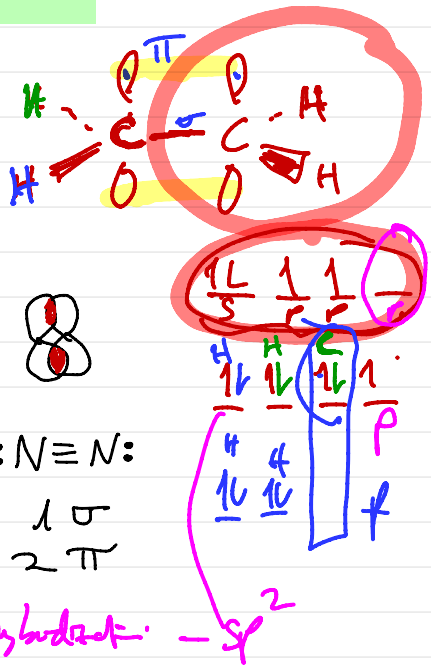
Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)	Bond	Length (pm)	Energy (kJ/mol)
H–H	74	436	C–O	140.1	358
H–C	106.8	413	C = O	119.7	745
H–N	101.5	391	C ≡ O	113.7	1072
H–O	97.5	467	H–Cl	127.5	431
C–C	150.6	347	H–Br	141.4	366
C = C	133.5	614	H–I	160.9	298
C ≡ C	120.8	839	O–O	148	146
C–N	142.1	305	O = O	120.8	498
C = N	130.0	615	F–F	141.2	159
C ≡ N	116.1	891	Cl–Cl	198.8	243

Table 8.1

Sigma and Pi bonds

(σ) Sigma bond – bond along INTERNUCLEAR AXIS
(π) pi bond – bond outside INTERNUCLEAR AXIS
└ side-by-side p-orbital overlap



(σ) 

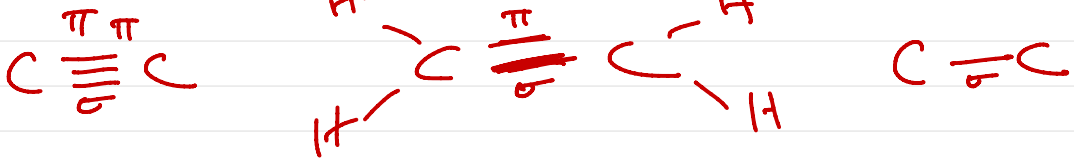
(π)

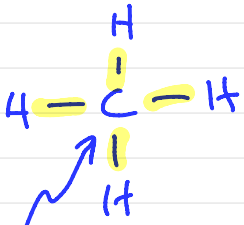
H – Cl:
1 σ
× π

O=O
1 σ
1 π

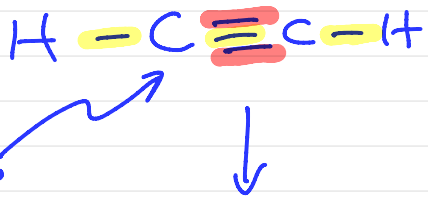
:N≡N:
1 σ
2 π

hybridized – sp^2

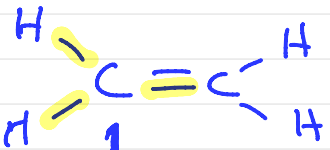




sp^3 tetrahedral

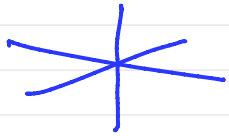


sp linear

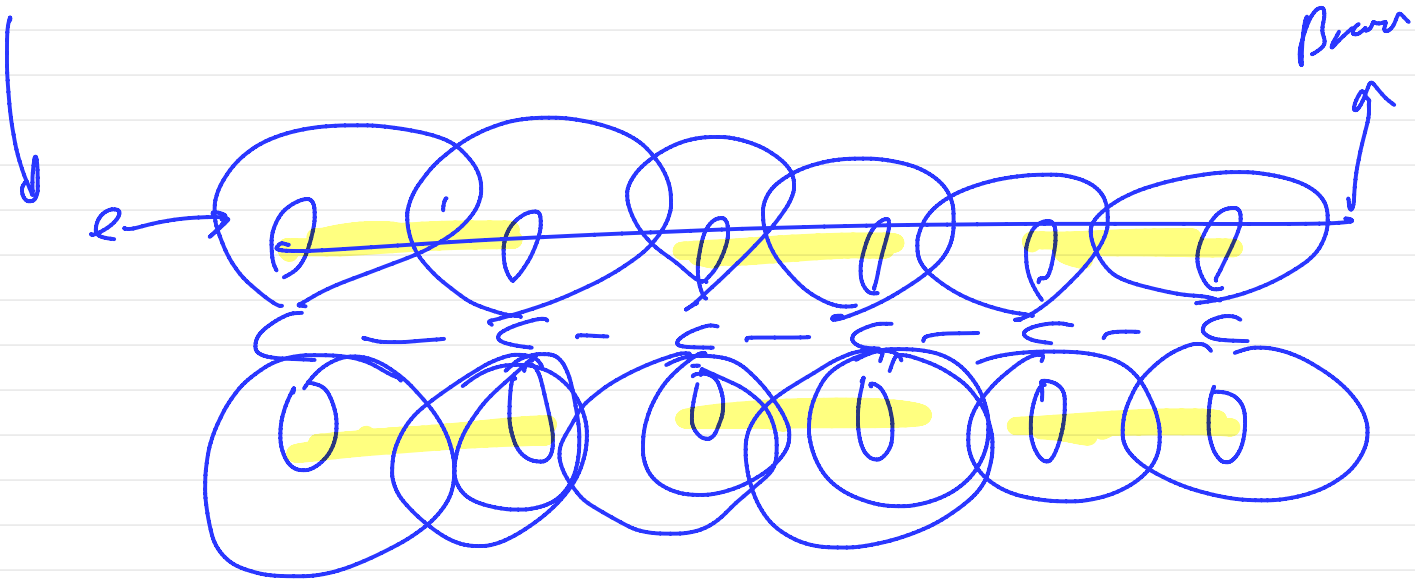


sp^2 trig planar

sp^3d trig bipyramidal



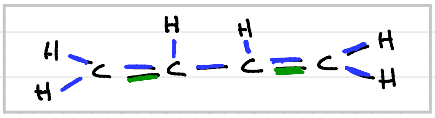
sp^3d^2 octahedral


Bravo

EX: Count σ and π Bonds [EX: 8.1]

i Butadiene, C_4H_6, is a component of synthetic rubber.

ID the number of σ & π bonds.



7 σ bonds from single bonds
2 σ bonds from double bonds
} 9 σ bond total

2 π bonds " " "

Hybrid Atomic Orbitals [8.2]

AO's —"Morph"→ MO's

"Morph" = combine AO's

process = LCAO (Linear Combination of Atomic Orbitals)

hybridization (new shapes of combined AO's)

sp Hybridization

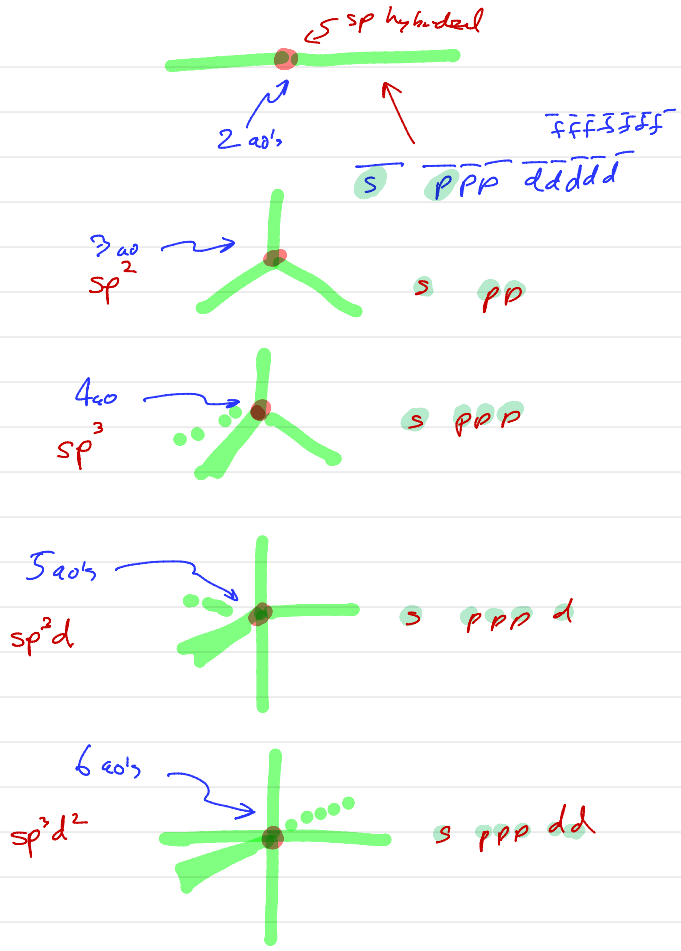
Consider Be in $BeCl_2$

Cl – Be – Cl → Be: 1↓ (2s) 0 (2p) 0 (2p) 0 (2p) → 1↓ (sp) 1↓ (sp) 0 (2p) 0 (2p)

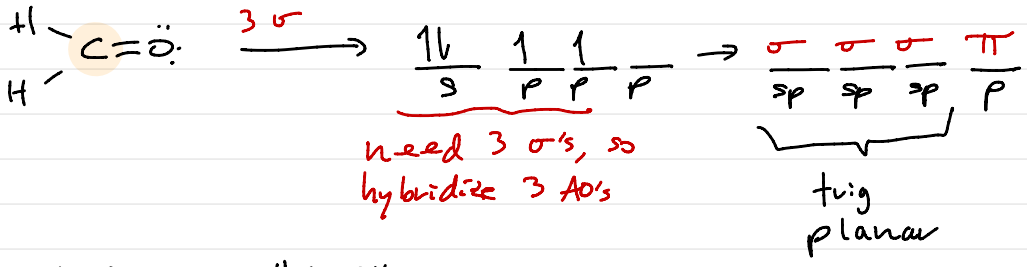
hybridize 2 AO's to produce 2 MO's (σ bonds)

↓

(sp) Be (sp)

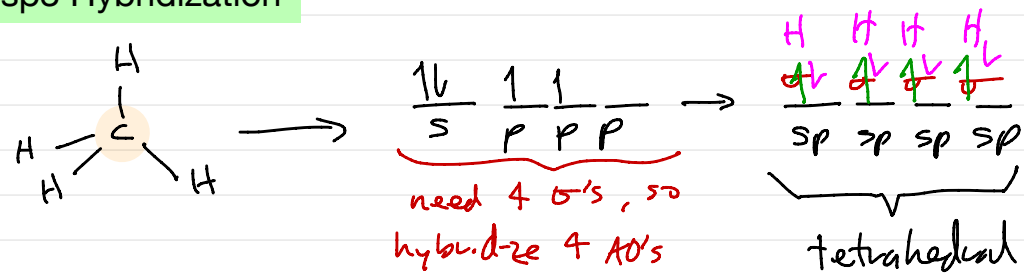

sp hybrided
2 ao's
s p p p d d d d d
3 ao
sp²
s p p
4 ao
sp³
s p p p
5 ao's
sp²d
s p p p d
6 ao's
sp³d²
s p p p d d

sp2 Hybridization

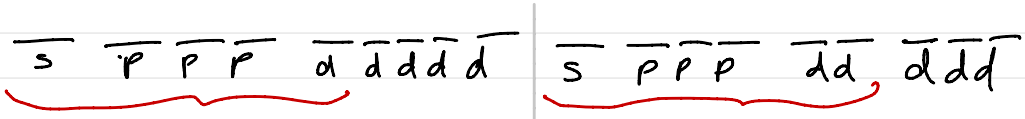


ex: CH_2O $H_2C=CH_2$

sp3 Hybridization



sp3d and sp3d2 Hybridization



hybridize 5 AO's to produce 5 σ's

ex: PCl_5, SF_4

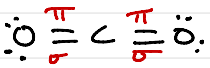
hybridize 6 AO's to produce 6 σ's

ex: PCl_6^-, XeF_4

Assignment of Hybrid Orbitals to Central Atoms

↳ essentially: treat each atom as central atom:
① determine LDS, ② determine AttND, and 1D bonding using VSEPR,
③ assign hybridization

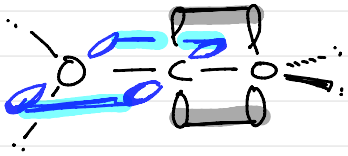
Multiple Bonds [8.3]



C: 2s 2p 2p 2p ⟹ sp sp p p

hybridize: need 2 σ MO's, so hybridize 2 AO's

linear: as far apart as can get ↔ bonds



EX: $HC{\equiv}CH$, $HgCl_2$, $BeCl_2$

$2\sigma \leftarrow 2$ AO's $\leftarrow 1s + 1p = sp$ (×2)

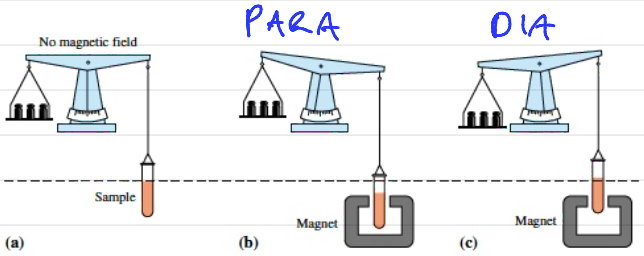
$2\pi \leftarrow$ 4 p-orbitals, overlap in pairs

End of Chapter (skip section 8.4)

Molecular Orbital Theory [8.4]

[P 421 / 429]

	Magnetic Field	Apparent Weight	All electrons paired or not?
Paramagnetic	attracts	appears heavier	unpaired electrons
Diamagnetic	repels	" lighter	paired electrons



Comparison of Bonding Theories

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Table 8.2

molecular orbital (MO) theory - uses quantum mech. ψ

molecular orbital = ψ^2

homonuclear diatomic molecule = ex: H_2, Cl_2

LCAO = Linear Combination of Orbitals = mathematical combinations of atomic orbital wave functions

Bonding (σ) vs. Antibonding (σ^*)

Figure 8.28 (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

S-Orbital Combination : σ_s

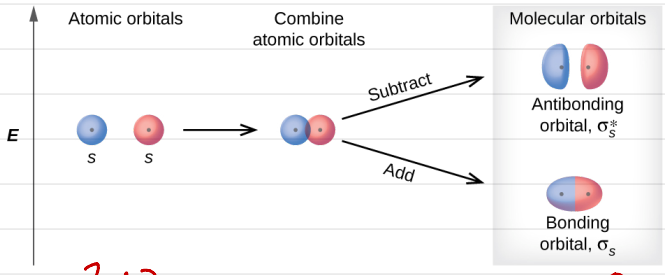


FIG 9.29

2 AO ⟶ 2 MO

P-Orbital Combination : Head-to-Head

σ_{px}

σ_{px}^*

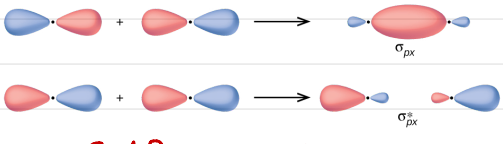


FIG 8.30

2 AO ⟶ 2 MO

P-Orbital Combination : Side-by-Side

π_p^+

π_p

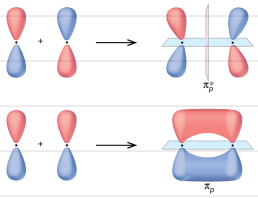
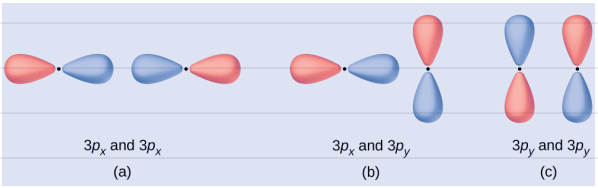


FIG 8.31

2AO ⟶ 2MO

↳ **Degenerate orbitals** — π_{py} and π_{pz} have same energy, but are "orthogonal"

EX: PREDICT AO COMBINATION → MO [EX 8.5]



(a) head-to-head ∴ σ
in phase ∴ σ (bonding)
3p × 3p orbitals ∴ σ_{3p}

(b) head-to-side ∴ incorrect alignment
both in-phase and out-of-phase overlap
↳ ∴ cancels out
no bonding

(c) side-to-side ∴ π
out-of-phase ∴ π^* (antibonding)
3p + 3p ∴ π^*_{3p}

EX: DESCRIBE GIVEN MO [EX 8.55]

i Label as σ, π, bond, antibond*

(i) head-to-head ∴ σ
(ii) out-of phase ∴ σ^*

Molecular Orbital Energy Diagrams

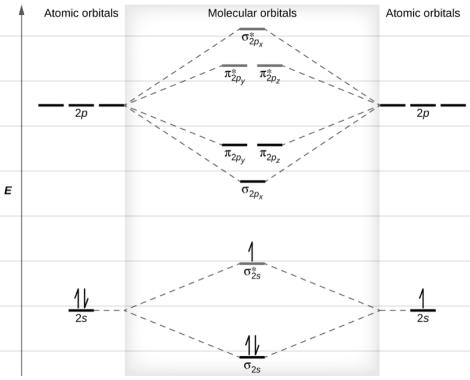


Figure 8.34 This is the molecular orbital diagram for the homonuclear diatomic Be2+ , showing the molecular orbitals of the valence shell only.

The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Bond Order

BOND ORDER – net ("" & *) contribution of electrons to bond strgth.

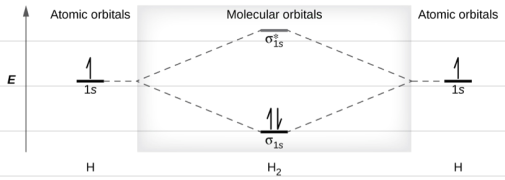
$$\text{bond order} = \frac{(\#\text{ bonding e's}) - (\#\text{ NON-bonding e's})}{2}$$

Bonding in Diatomic Molecules

[P 430/ 438]

ex: H_2

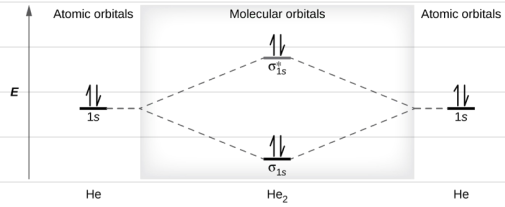
FIG 8.35



↳ BO = (2-0)/2 = 1 bond

ex: He_2

FIG 8.36



↳ BO = (2-2)/2 = 0/2 = ∅ bonds found

S-p Mixing

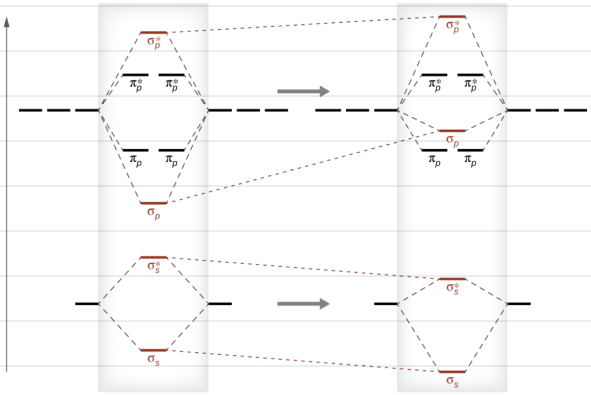


Figure 8.38 Without mixing, the MO pattern occurs as expected, with the σ p orbital lower in energy than the σ p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ p orbital higher in energy than the π p orbitals.

Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{2s})^2(\sigma_{2s}^*)^2$	0
B_2	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py},\ \pi_{2pz})^2$	1
C_2	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py},\ \pi_{2pz})^4$	2
N_2	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$	3
O_2	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi_{2py}^*,\ \pi_{2pz}^*)^2$	2
F_2	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi_{2py}^*,\ \pi_{2pz}^*)^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi_{2py}^*,\ \pi_{2pz}^*)^4(\sigma_{2px}^*)^2$	0

Table 8.3

Li–Li

B–B

C=C

N≡N

O=O

F–F

LDS vs. MO Representations : O_2

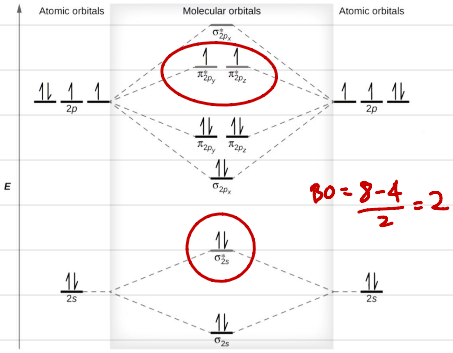
Redux : Para-, Dia-Magnetism

☒ LDS predicts DIA- (all e's paired)

☑ MO " PARA- (2 unpaired e's)

⇓

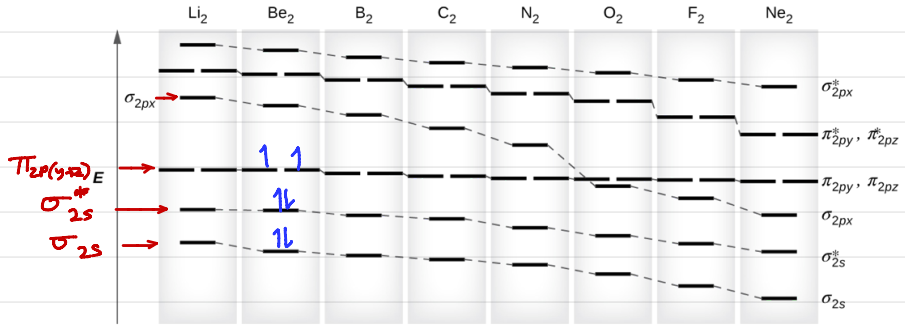
MO is correct !!!



$BO = \frac{8-4}{2} = 2$

EX: PREDICT BOND ORDER (BO) & PARA- or DIA- [EX 8.7b]

¿ How many unpaired electrons would be present on a Be2^2- diamagnetic?



Be^{2-} = 6 valence electrons.

(i) 2 unpaired electrons
(ii) ∴ paramagnetic

ASIDE

Be_2^{2-}

N = 2(4) = 8
A = 2(2) + 2 = 6
S = [1BP] 2
A' = [2BP] 4

∴ Be — Be ∴

BO = (4 bond − 2 *bond)/2 = 2/2 = 1 bond