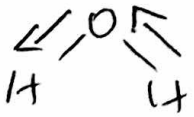
CH431 Lecture 11 10/4/16

Symmetry of IR / Raman stretches:

A_1

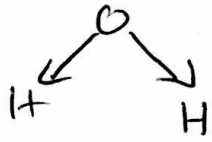


B_1

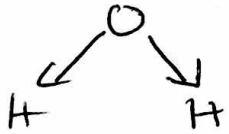
A_1

We can transform these just like orbitals and rotations

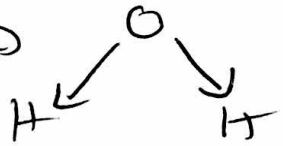
C_{2v}



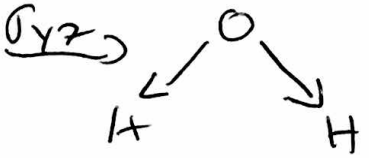
E → character 1



C_2 → character 1

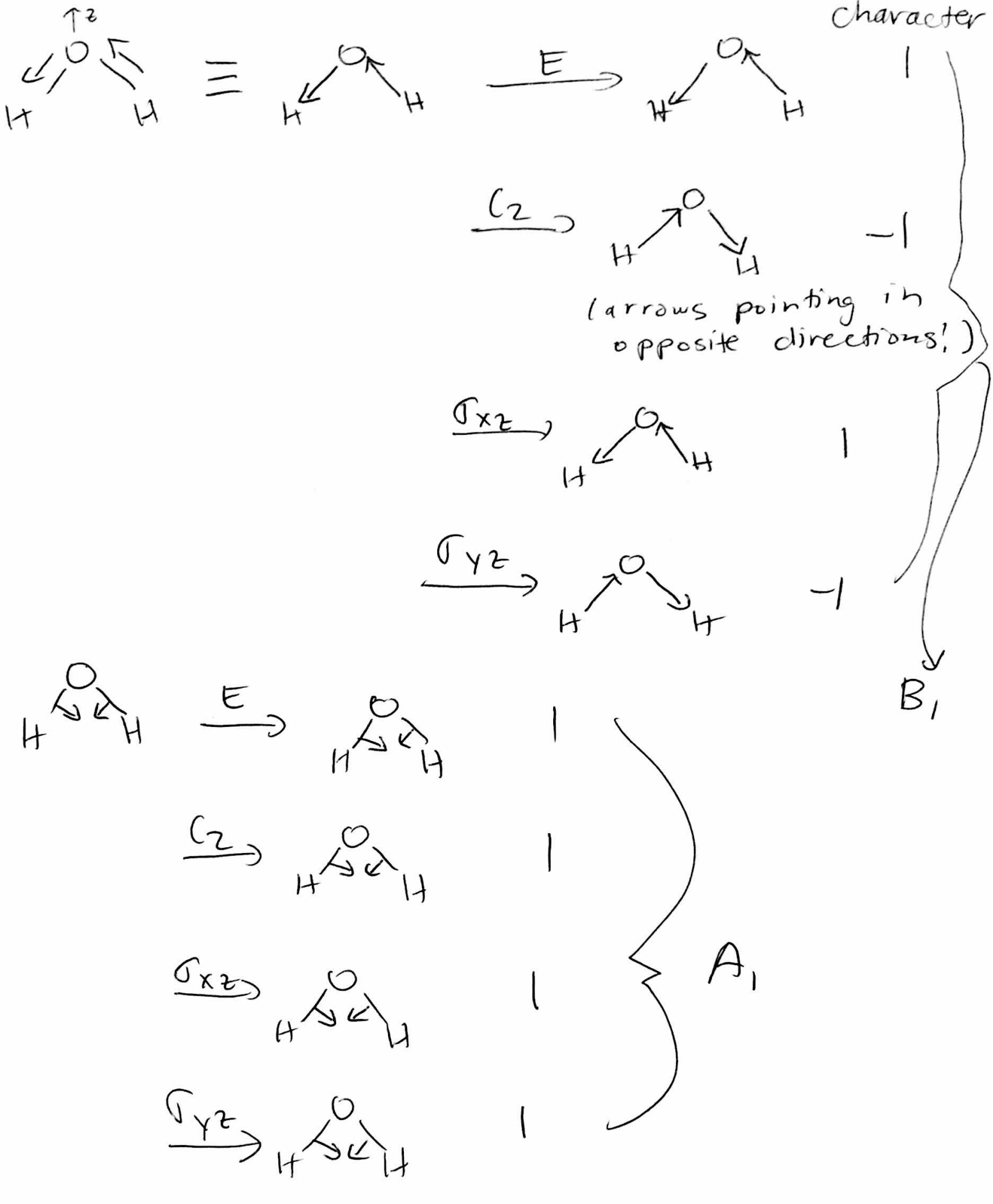


σ_{xz} → character 1



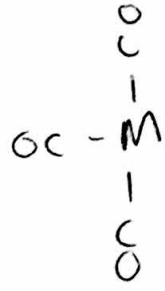
σ_{yz} → character 1

A_1


z
≡
E
C2
σxz
σyz
Character
1
−1
1
−1
(arrows pointing in opposite directions!)
B1
E
C2
σxz
σyz
1
1
1
1
A1

$M(CO)_4$ square planar

$h = 16$



Pyh	E	$2C_4(z)$	$C_2(z)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{CO}	4	0	0	2	0	0	0	4	2	0

↑ reducible representation for all the COs in your molecule

$$n(A_{1g}) = \frac{1}{16}\left(1(4)(1) + 2(0)(1) + 1(0)(1) + 2(2)(1) + 2(0)(1) + 1(0)(1) + 2(0)(1) + 1(4)(1) + 2(2)(1) + 2(0)(1)\right) = 1$$

$$n(A_{2g}) = \frac{1}{16}\left(1(4)(1) + 2(0)(1) + 1(0)(1) + 2(2)(-1) + 2(0)(-1) + 1(0)(1) + 2(0)(1) + 1(4)(1) + 2(2)(-1) + 2(0)(-1)\right) = 0$$

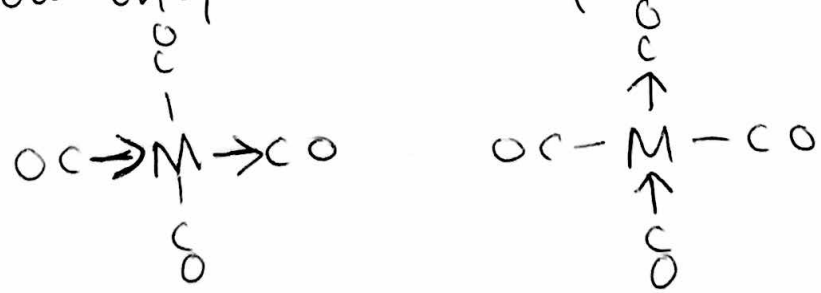
⋮

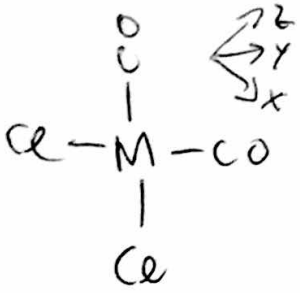
etc.

$$\Gamma_{CO} = \underset{\text{Raman}}{A_{1g}} + \underset{\text{Raman}}{B_{1g}} + \underset{\text{IR}}{E_u}$$

You will see two Raman and one IR stretch.

However E_u is doubly degenerate, there are actually 2 vibrations described by E_u, however they're the same energy, so you only see one peak





C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(xy)$
Γ_{CO}	2	0	2	0

$$\Gamma_{A_1} = \frac{1}{4}(1(2)(1) + 1(0)(1) + 1(2)(1) + 1(0)(1)) = 1$$

$$\Gamma_{A_2} = \frac{1}{4}(1(2)(1) + 1(0)(1) + 1(2)(-1) + 1(0)(-1)) = 0$$

$$\Gamma_{B_1} = \frac{1}{4}(1(2)(1) + 1(0)(-1) + 1(2)(1) + 1(0)(-1)) = 1$$

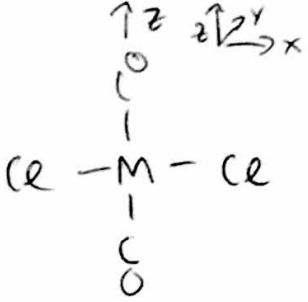
$$\Gamma_{B_2} = \frac{1}{4}(1(2)(1) + 1(0)(-1) + 1(2)(-1) + 1(0)(1)) = 0$$

$$\Gamma_{CO} = A_1 + B_1$$

A_1: IR + Raman

B_1: IR + Raman

$\Rightarrow$ 2 IR and 2 Raman CO peaks



D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	σ_{xy}	σ_{xz}	σ_{yz}
Γ_{CO}	2	2	0	0	0	0	2	2

$$n(A_g) = \frac{1}{8}\left(1(2)(1)+1(2)(1)+1(0)(1)+1(0)(1)+1(0)(1)+1(0)(1)+1(2)(1)+1(2)(1)\right) = 1$$

$$\Gamma_{CO\ trans} = A_g + B_{1u} \Rightarrow$$

A_g: Raman

B_{1u}: IR

one IR and one Raman CO peak

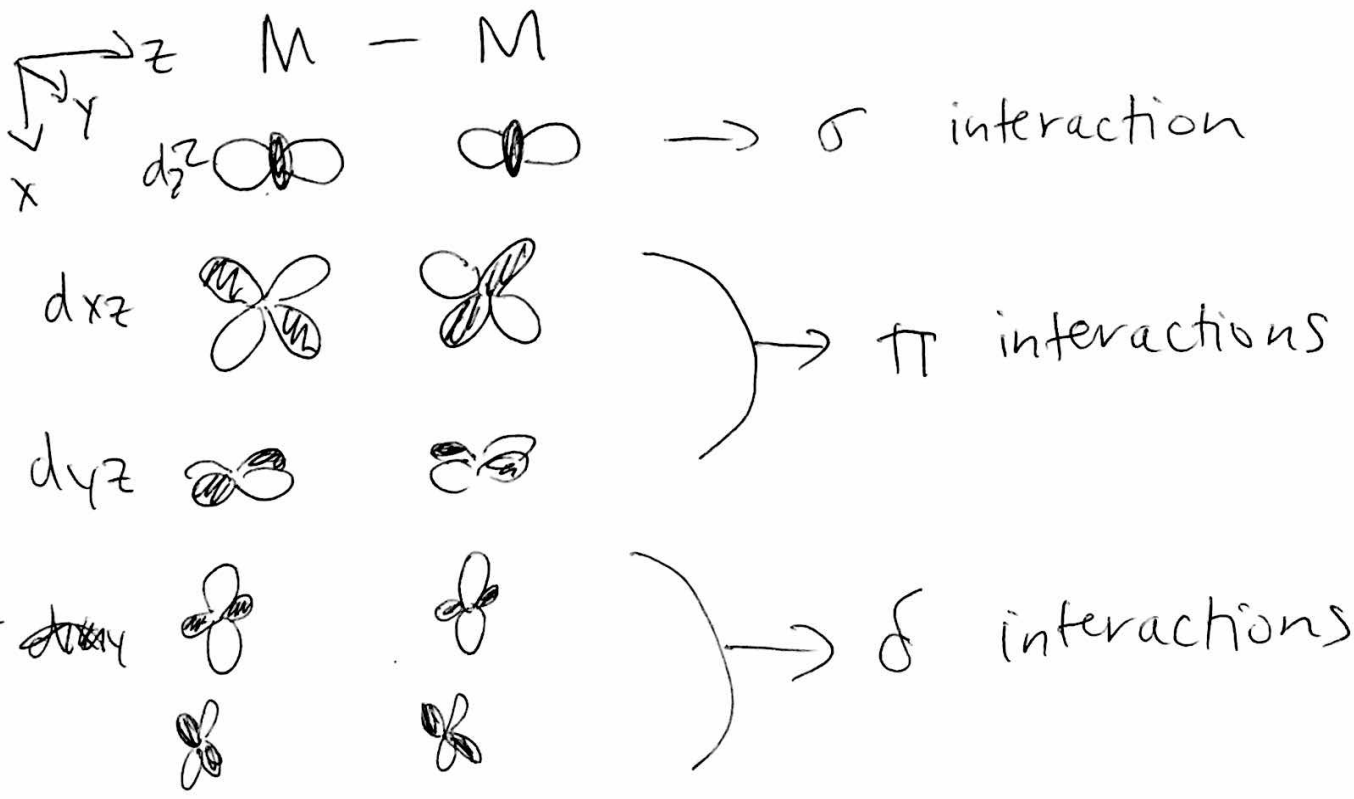
(exact representation may change depending on the coordinate axes you choose, but end result will be the same, namely you'll still get one Raman and one IR stretch)

Molecular orbitals

→ exact values of atomic orbital coefficients are not a focus of this class

$$\Psi_{MO} = c_a \Psi_a + c_b \Psi_b$$

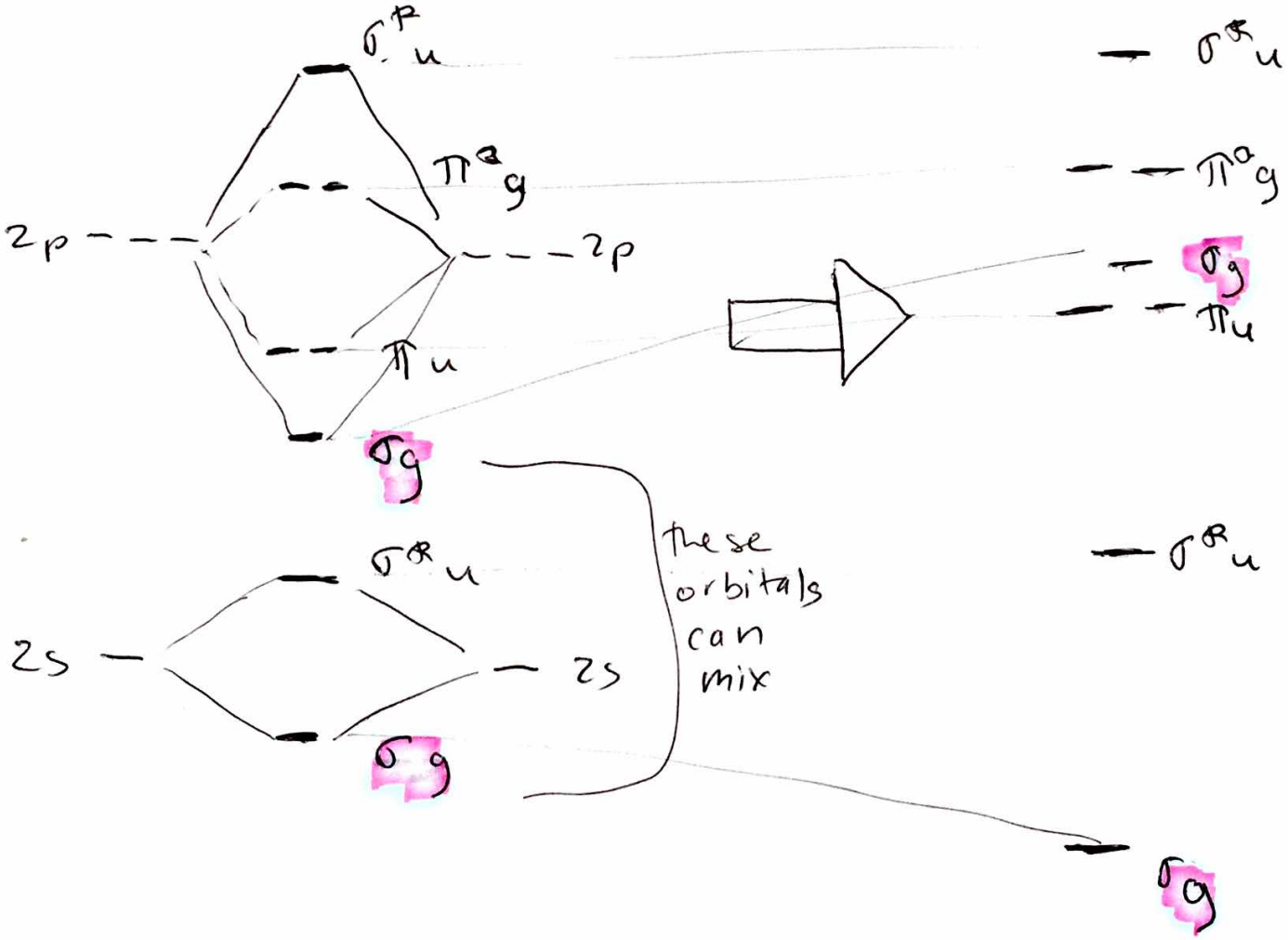
- c_a: coefficient
- Ψ_a: atomic orbital from atom A
- c_b: coefficient
- Ψ_b: atomic orbital from atom B



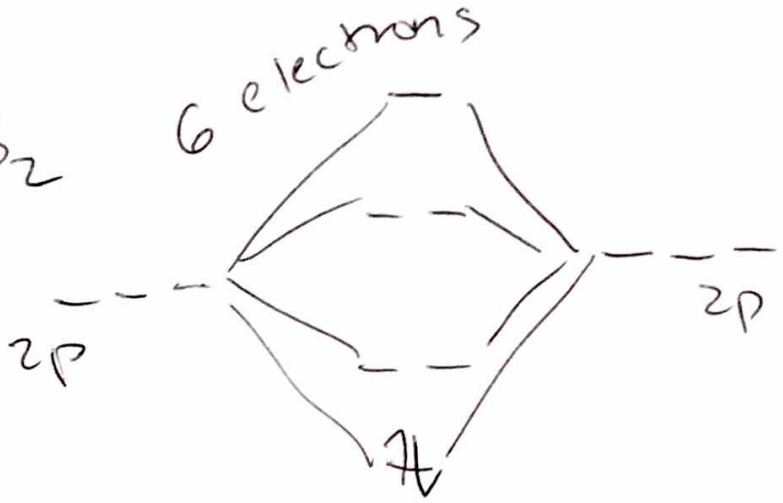
orbital mixing

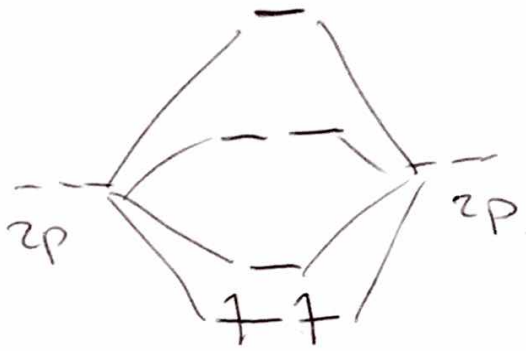
→ molecular orbitals w/ similar symmetries that are close enough in energy can mix, resulting in stabilization of lower energy orbital and destabilization of higher energy orbital

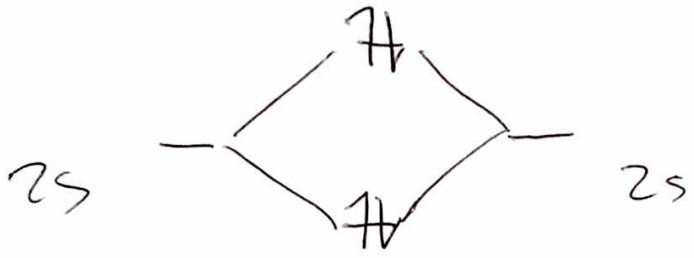
→ orbital energies are similar enough in Li_2, Be_2, B_2, C_2, and N_2 for this mixing to occur

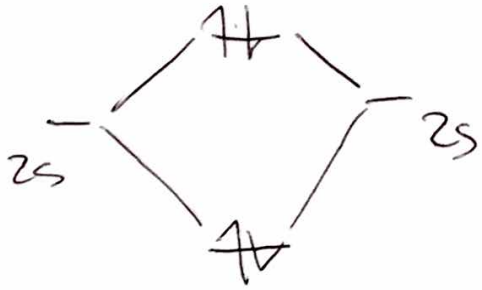


B_2 6 electrons









if there is no mixing

→ diamagnetic (no unpaired electrons)

with mixing

→ paramagnetic (2 unpaired electrons)

For C_2 8 electrons

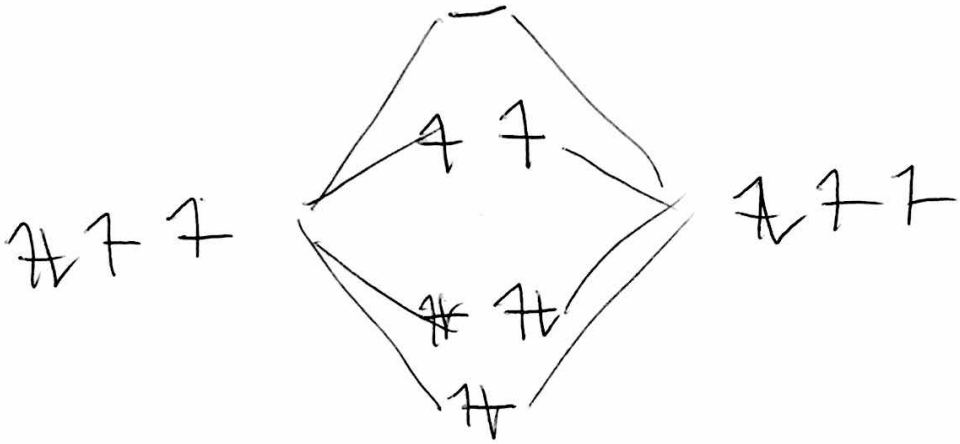
with no mixing, C_2 is paramagnetic

w/ mixing C_2 is diamagnetic

O_2 is paramagnetic!

↳ 12 electrons

Lewis dot structure
no indication that O_2 is paramagnetic



MO diagram explains why O_2 is paramagnetic