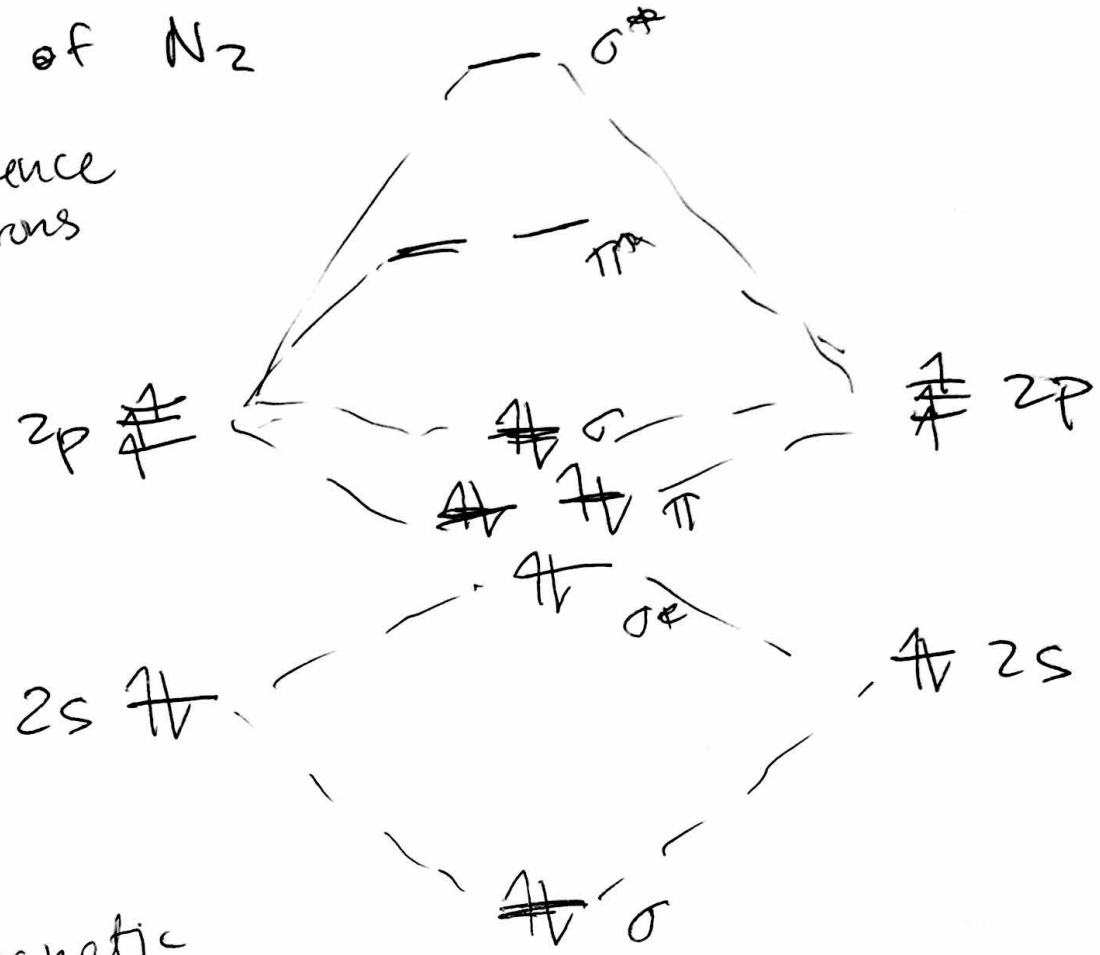
Lecture 12 CH431 10/6/16

Lewis of N_2 :N≡N:

MO of N_2

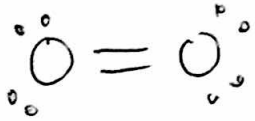


10 valence electrons

↳ no unpaired electrons predicted from MO diagram

↳ diamagnetic

O_2 12 total valence electrons

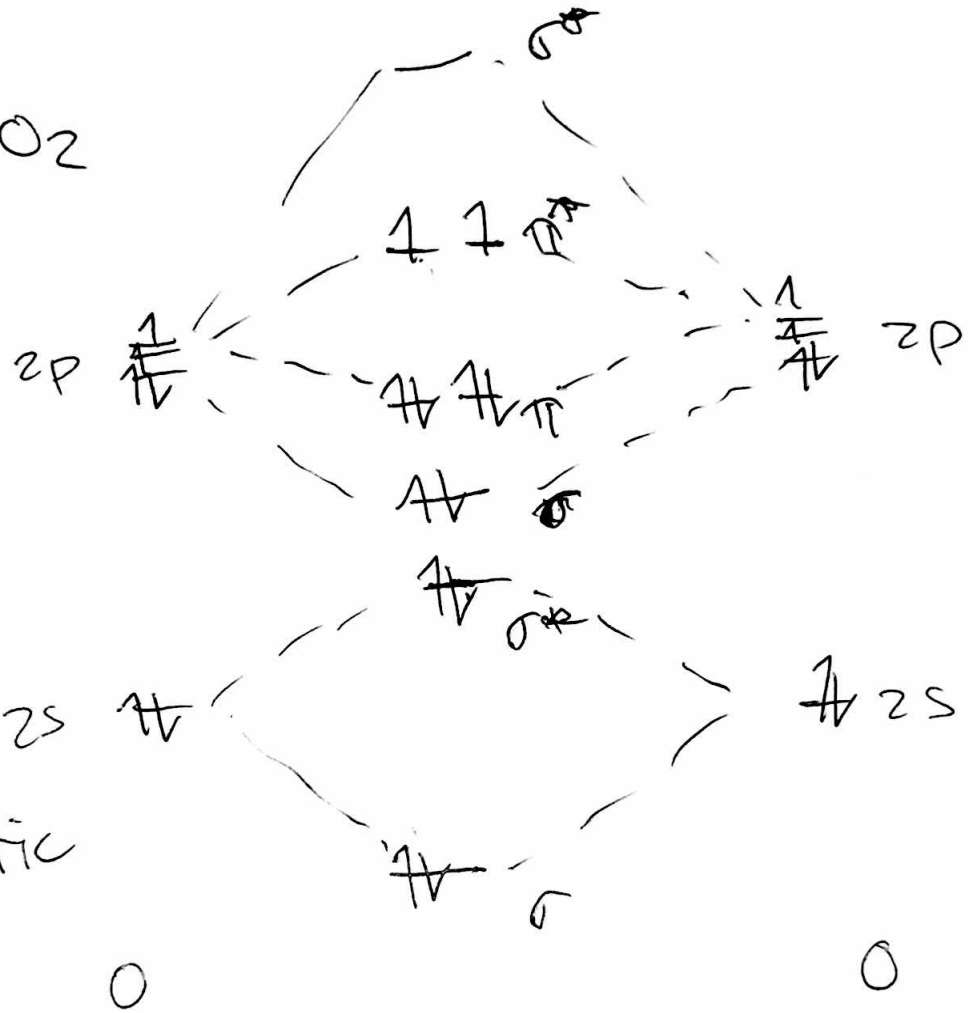


Lewis Dot

MOs of O_2

↳ tell us that O_2 should have 2 unpaired electrons

↳ paramagnetic



bond order $\frac{1}{2}(8 - 4) = 2$

↑ ēs in bonding orbitals

↑ ēs in antibonding orbitals)

O_2: B.O. is 2

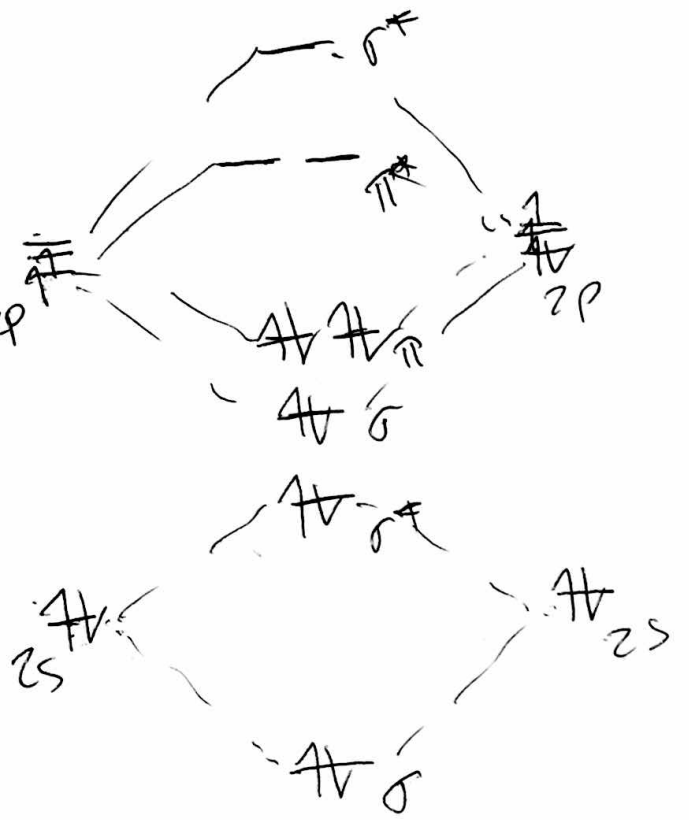
O_2^- (13 $\bar{e}$s) → B.O. of 1.5

$\frac{1}{2}(8-5)$ ↗

O_2^{2-} : B:O of 1

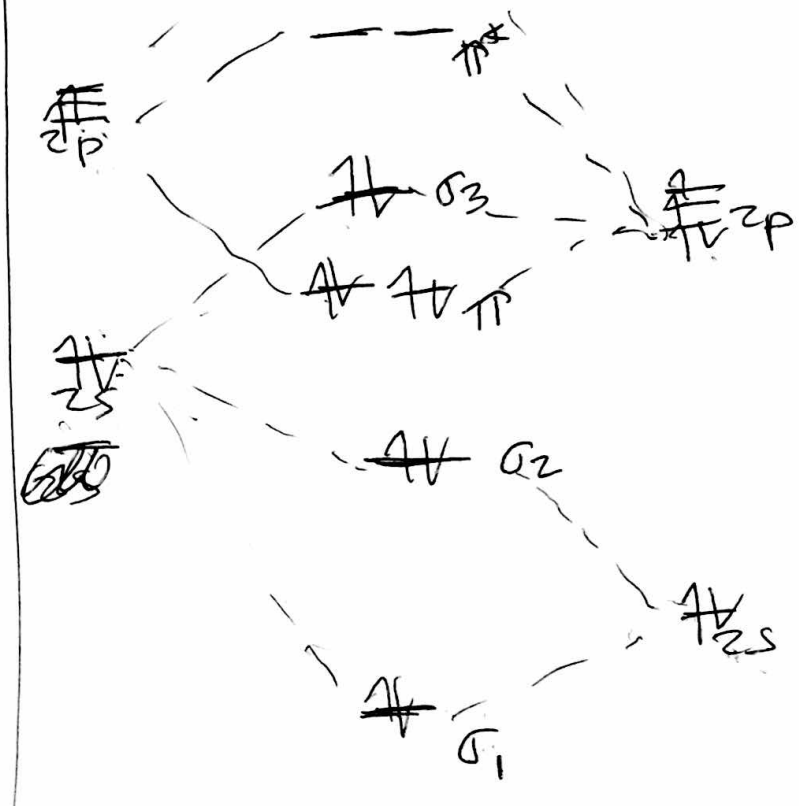
MO diagram of CO

What if orbital energies were the same in both C + O?



C O

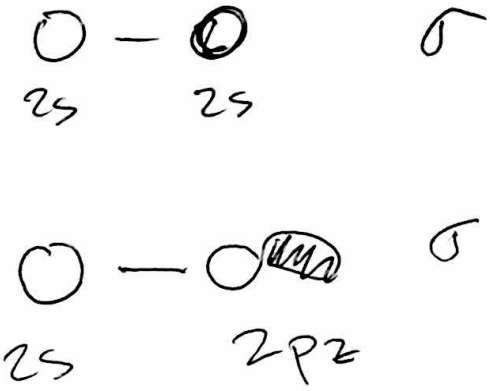
But the energies are different → C 2s orbital is much closer to O 2p orbitals

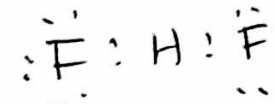


C O

$\sigma_1, \sigma_2, \sigma_3, \sigma_4 \rightarrow$ comes from the combined interactions of both 2s and 2pz orbitals on C & O

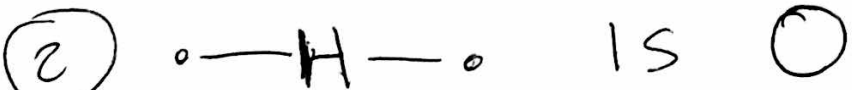
:C≡O:

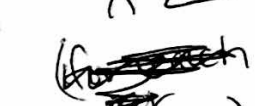


MO of $FHF^{\ominus}$  Lewis dot structure

(1) linear $D_{\infty h}$ point group

→ simplify and use D_{2h} character table

(2)  is

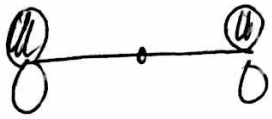
 2s,  2pz, 2px, 2py  X2 (for each F atom)

(3) Γ_{2s}, Γ_{2pz}, Γ_{2px}, Γ_{2py} for 

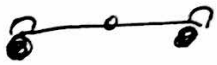
- if orbitals move? character = 0
- if orbitals stay in place but change phase = -1
- if orbitals stay in place and keep same phase = 1

D_{2h}	E	$C_{2(z)}$	$C_{2(y)}$	$C_{2(x)}$	i	$\sigma_{(xy)}$	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ_{2s}	2	2	0	0	0	0	2	2
Γ_{2pz}	2	2	0	0	0	0	2	2
Γ_{2px}	2	-2	0	0	0	0	2	-2
Γ_{2py}	2	-2	0	0	0	0	-2	2

2s 2s
F F



2px 2px
F F



2py 2py
F F

2pz 2pz
F F

(4) Reduction formula

$\Gamma_{2s} = A_g + B_{1u}$

A_g ↓ s orbital; B_{1u} ↓ pz orbital

$\Gamma_{2pz} = A_g + B_{1u}$

A_g ↓ s orbital; B_{1u} ↓ pz

$\Gamma_{2px} = B_{2g} + B_{3u}$

B_{2g} ↓ dxz; B_{3u} ↓ px

$\Gamma_{2py} = B_{3g} + B_{2u}$

B_{3g} ↓ dyz; B_{2u} ↓ py

(5) The purpose of this step is to see how we can combine the orbitals on the F atoms so that they can interact with the orbitals on the central atom that match the irreducible representations derived in (4)

$\Gamma_{2s} = A_g + B_{1u}$

$A_g \Rightarrow s$ $\quad B_{1u} \Rightarrow p_z$

=> we need to find combinations of the F 2s orbitals that will match the symmetry of the s and p_z orbital on H

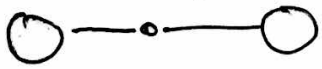
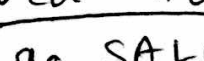
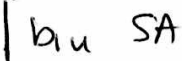
(ignore the fact at this point that H doesn't really have accesible p or d orbitals)

F—H—F

* s orbital on central atom

what combo of 2s orbitals from F atoms will have good overlap with this?

* p_z orbital on central atom

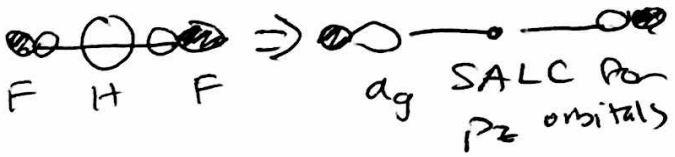
 and  are the SALCs derived from the 2F 2s orbitals, referred to as ag SALC  and b1u SALC 

We can now go through this process with all of the Γ orbitals

$\Gamma_{2p_z} = A_g + B_{1u}$

$A_g \Downarrow$ S $B_{1u} \Downarrow$ p_z

* S orbital



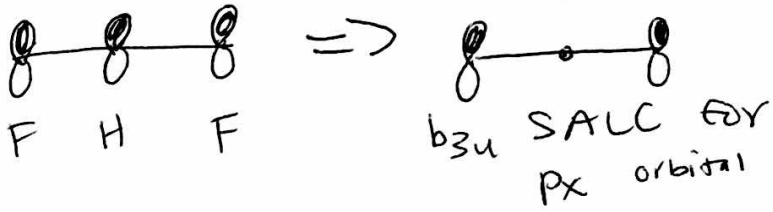
* p_z orbital

$\Gamma_{2p_x} = B_{2g} + B_{3u}$

$B_{2g} \Downarrow$ d_{xz} $B_{3u} \Downarrow$ p_x

* d_{xz}

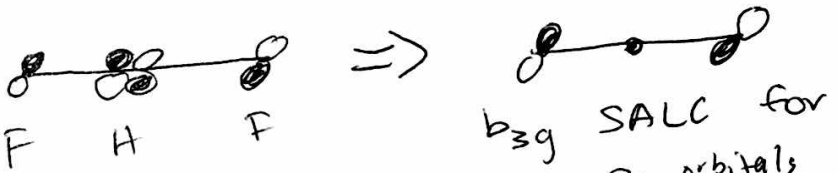
* p_x



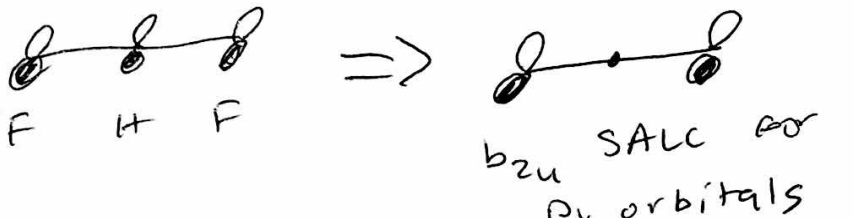
$\Gamma_{2p_y} = B_{3g} + B_{2u}$

$B_{3g} \Downarrow$ d_{yz} $B_{2u} \Downarrow$ p_y

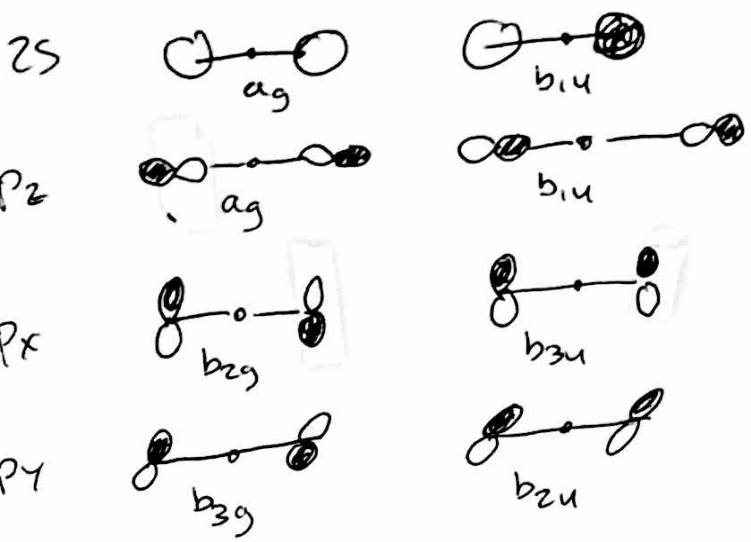
* d_{yz}



* p_y

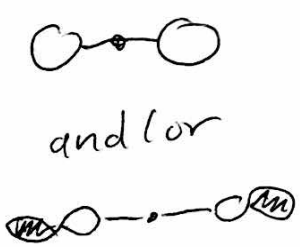


All SALCs determine using this process



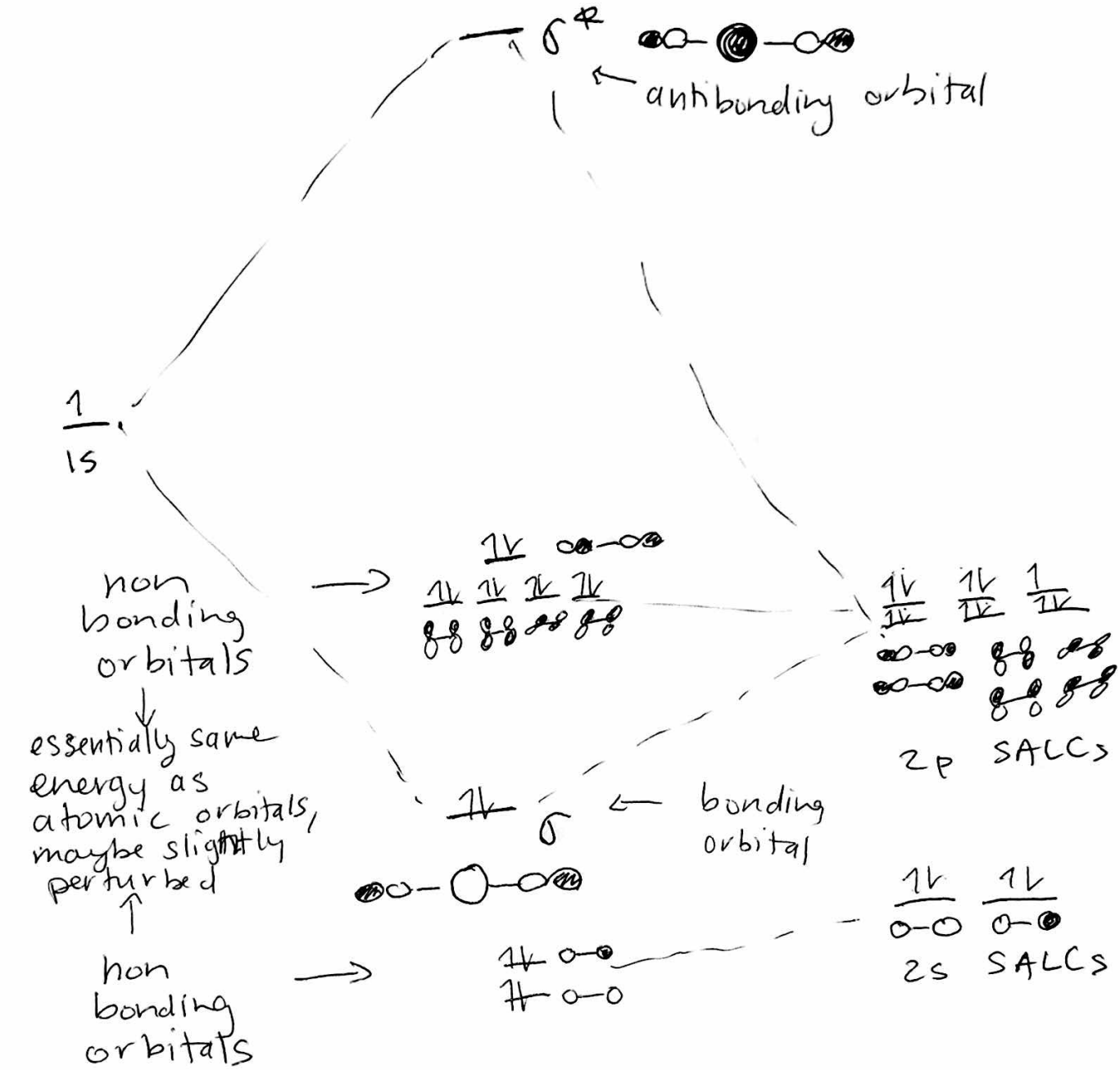
8 total SALCs derived from 8 total atomic orbitals

NOW how do we make an MO diagram out of this? Let's think back to the orbitals available for bonding on H: 1s only! So the only SALCs that can have bonding and antibonding interactions w/ H must be able to interact w/ S orbital ⟹ only the SALCs w/ a_g symmetry! All other SALCs will be essentially non-bonding



Which of these SALCs are closer in energy to the 1s of H?

The SALC derived from $2p_z$'s! Therefore, the only major bonding / antibonding combination should be between H 1s and p_z a_g SALC



BO of FHF^-? $\frac{1}{2}(2-0) = 1$!

Thus while Lewis structure suggest H has 4 electrons around it in bonds, in fact, a better description is that there is a 3-center 2-electron bond between the H and 2 F's.