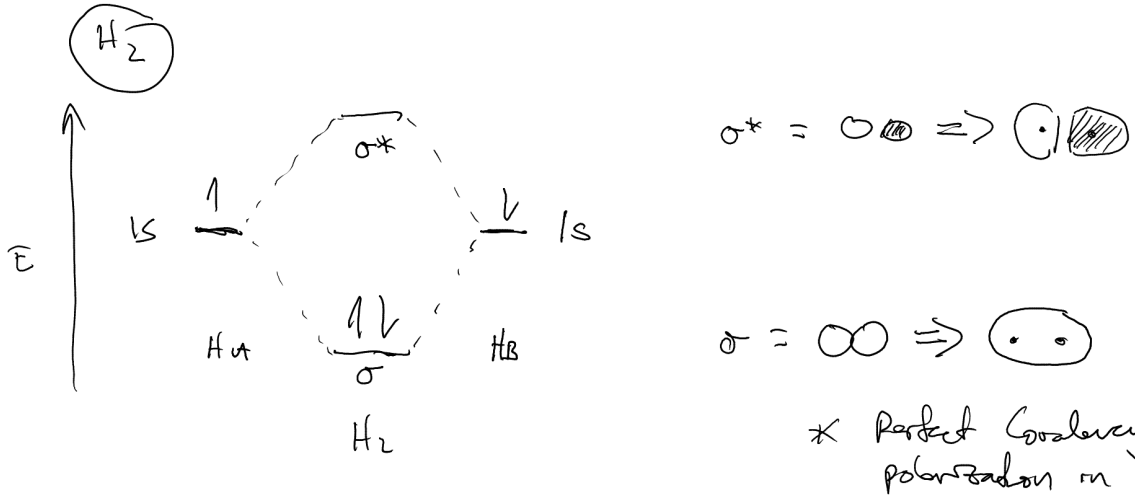
MOT- Heterodiatomics

MOs can be built from 2 identical atoms



* Perfect Covalency + no polarization in MOs

Heterodiatomics ⇒ Complexities arise

In general when 2 different AOs combine to generate a new MO 2 major factors dictate the energies of the atomic basis sets:

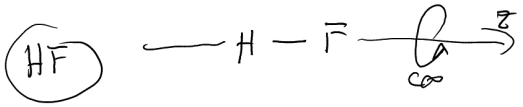
① Z^* Effective Nuclear Charge ⇒ AOs that experience greater Z^* are lower in energy

② More electronegative atoms typically have lower atomic energy levels.

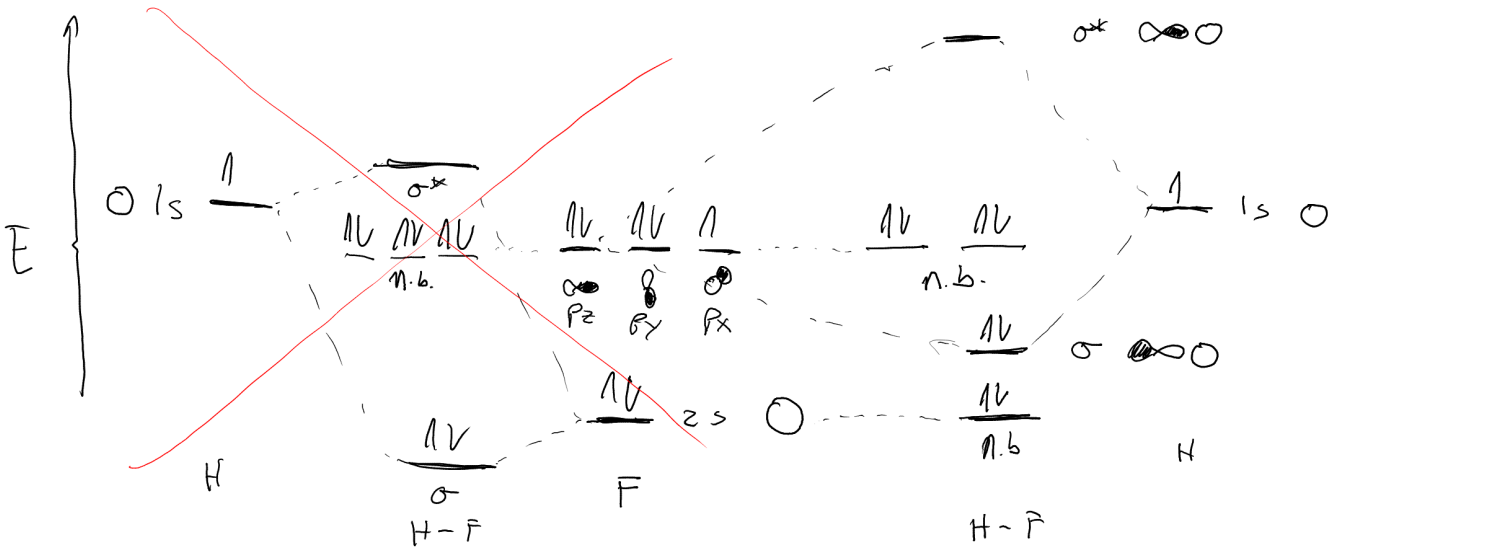
$H-F$ very different from H_2

σ $H-\ddot{F}:$ bond $\quad \psi_\sigma = C_H \psi_{1s} + C_F \psi_{2pz}$

$C_H < C_F$ different than H_2 $\quad C_{H_1} = C_{H_2}$



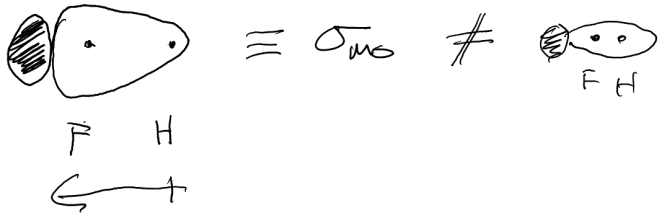
B.O. = 1



Energetic proximity of a MO to one of AOs that was used to build it means that MO has greater parentage from that AO

σ  closer in energy to 2pz on F

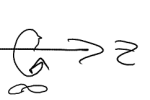
2pz 1s

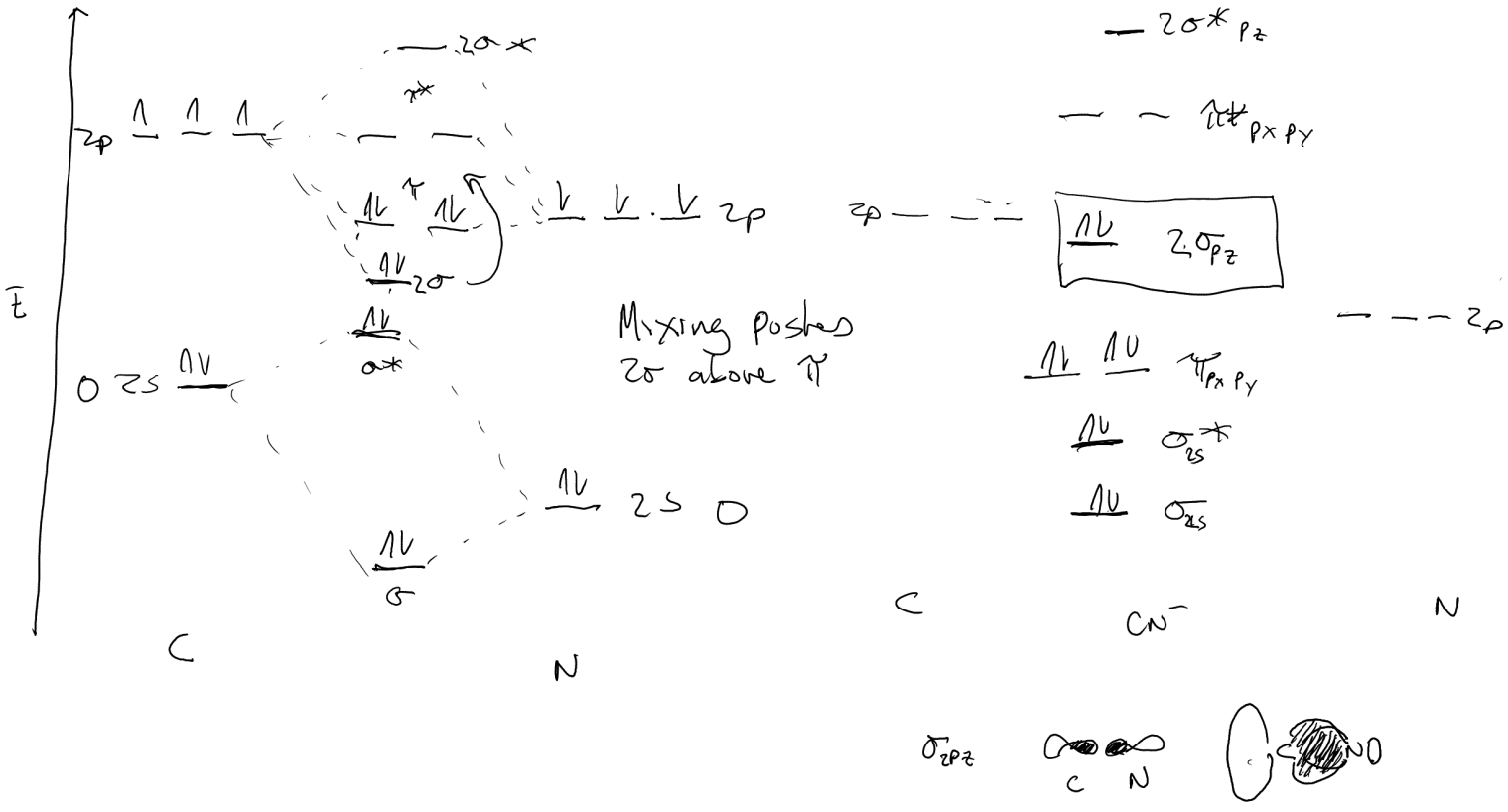


$H-\ddot{F}: + H^+ \longrightarrow H_2\ddot{F}^+$

gas gas

σ_{HF} + 1s O

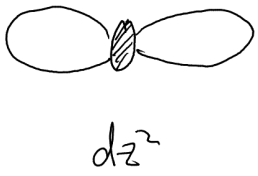
Consider CN^- $-:\overset{\ominus}{C}\equiv N:$  z $(C_{\infty v})$ C: $2s^2 2p^2$ N: $2s^2 2p^3$



CN^- is an excellent ligand

$[Fe^{II}(CN)_6]^{4-}$ ferrocyanide

d-orbitals have distinct shapes



d_{z^2}

d_{xy}, d_{xz}, $d_{x^2-y^2}$, d_{yz}

Metal-Metal Bonding

σ 

$d_{z^2} + d_{z^2}$

σ^* 

$d_{z^2} - d_{z^2}$

π 

d_{xz}

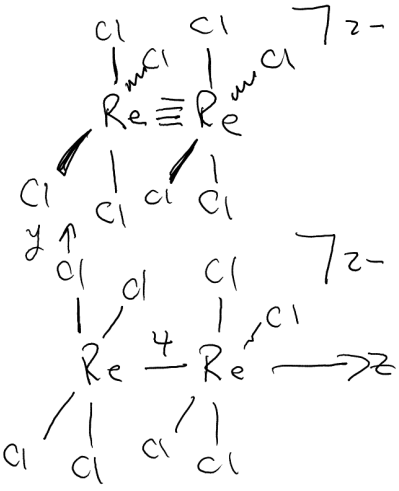
π^* 

δ 

δ^* out of plane

"Multiple Bonds between Metal Atoms"
1963 (2nd Edition)

Al Cotton



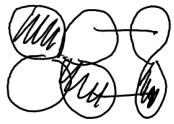
Quadruple Bond
$\sigma + 2\pi + \delta - xy$
xz, yz
d_{z^2}

Science 1964, 145, 1305

d-orbitals w/ other AOs

$d_{z^2} + s$
(σ)

$d_{z^2} + p_z$ (σ)



d_{xz} p_x (π)

Consider the Frontier Orbitals of CN

→ HOMO-LUMO Gap

HOMO for CN^- = 2σ derived from p_z

* this is closer in energy to C 2pz

σ-donor

LUMO for CN^- = π*

* Closer in energy to C 2px + 2py

2py - 2py

2px - 2px

d_{z^2} 2σ

6 de^- ← $[Fe^{II}(CN)_6]^{4-}$

$\downarrow -e^-$

$[Fe^{III}(CN)_6]^{3-}$

5 de^-

d_{yz} π*

d_{xz} π*