

MOLECULAR ORBITAL THEORY (M.O.T.)

Diatomic molecules

H₂ & He₂⁺ molecules

In M.O.T., valence e⁻s are affected by all nuclei & delocalized over the entire system.

For simplicity, inner e⁻s are localized on a particular atom, and some valence e⁻s are also mainly localized.

M.O.s are: wave functions resulting from L.C.A.O.s.

the combination is limited by the symmetry of the molecule and the symmetries of the orbitals, besides energy levels.

H & H $1s_A + 1s_B \rightarrow$ two L.C.A.O combinations

M.O.s = # combining A.O.s. Conservation of orbitals

sum of A.O.s. \rightarrow bonding $1s_A + 1s_B = \text{M.O. (B)}$



in bonding, e⁻ density is concentrated between nuclei \rightarrow attraction
 in antibonding, e⁻ is depleted, i.e. nuclei are not well screened, i.e. repulsive force

σ -orbitals = M.O. with rotational C_∞ axis \rightarrow

Similar to A.O.s., the wave functions of M.O.s. are normalized by multiplying by a normalization constant N such that:

$$\int (\psi^* \psi) d\tau = 1$$

(probability of finding the e⁻ somewhere outside the nucleus

Probability of finding the electron somewhere outside the nucleus is unity = 1.

for bonding MO, the normalized wave eqn. is:

$$\int [\psi_{1sA} + \psi_{1sB}]^2 d\tau = N^2 \int (\psi_{1sA}^2 + 2\psi_{1sA}\psi_{1sB} + \psi_{1sB}^2) d\tau = 1$$

$$N^2 \left(\int \psi_{1sA}^2 d\tau + 2 \int \psi_{1sA} \psi_{1sB} d\tau + \int \psi_{1sB}^2 d\tau \right) = 1$$

but, since normalization is used,

$$\therefore \int \psi_{1sA}^2 d\tau = \int \psi_{1sB}^2 d\tau = 1$$

$$\therefore N^2 (1 + 1 + 2 \int \psi_{1sA} \psi_{1sB} d\tau) = 1$$

$$\therefore N = \frac{1}{\sqrt{2(1 + \int \psi_{1sA} \psi_{1sB} d\tau)}}$$

by choice:

the positive sign gives a positive wave function

$\left\{ \int \psi_{1sA} \psi_{1sB} d\tau \right\}$ is called the overlap integral

If we approximate by neglecting overlap integrals, then

$$N = \frac{1}{\sqrt{2}}$$

as we have seen from the top eqn.:

$$\psi_{\text{bonding}} = N(\psi_{1sA} + \psi_{1sB}) = \frac{1}{\sqrt{2}}(\psi_{1sA} + \psi_{1sB})$$

$$\psi_{\text{antibonding}} = N(\psi_{1sA} - \psi_{1sB}) = \frac{1}{\sqrt{2}}(\psi_{1sA} - \psi_{1sB})$$

$$\text{since } \psi_{\text{bonding}} = N_A \psi_{1sA} + N_B \psi_{1sB} = N(\psi_{1sA} + \psi_{1sB})$$

since H_A & H_B combine with the same amount, in the resulting σ -orbital

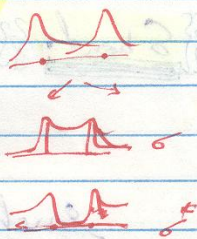
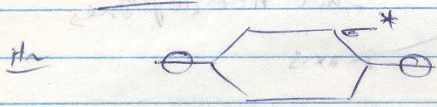
however, in general, the combined A.O.s. combine with different extents, thus:

$$\psi = a\psi_1 + b\psi_2 + c\psi_3 + \dots$$
 (bonding) or: $\psi_i = \sum_j a_{ji} \phi_j$

$\psi_i = i\text{th A.O.} / \phi_j = j\text{th A.O.}$
 $a_{ji} = \text{coefficient of atom } j \text{ in } i\text{th A.O.}$

∴ in the general case, the normalization constant

N is:
$$N = \frac{1}{\sqrt{a^2 + b^2 + c^2 + \dots}}$$



consider B.O. for H_2 , H_2^+ , H_2^-

consider He , He^+ , He^-

which of them is not stable? why?

Diatomic Molecules of the 2nd-Period Elements

σ-bonding

Assuming z-axis of interaction, σ bonds may be formed by $s+s$, p_z+p_z , $d_z^2+d_z^2$, $s+d_z^2$, $p_z+d_z^2$

furthermore, hybrid orbitals may give σ bonding sp , sp^2 , sp^3 from one to another atom, with C_{∞} rotational symmetry

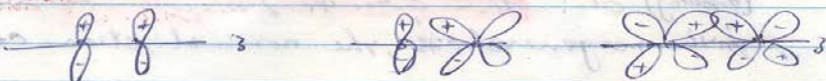


but, if zero overlap, → nonbonding

π -bonding

how do we call it π -bond? one nodal plane

consider z-axis of interaction



δ bond



two nodal planes

z-axis

such as compounds of quadruple bonds
such as $\text{Re}_2\text{Cl}_8^{2-}$ { 1 σ , 2 π , 1 δ bonds together }.

Question: what about $\text{C}\equiv\text{C}$

M. O. Levels

atomic orbitals of two atoms combine together if they have:

- (1) the same symmetry
- (2) comparable energy levels

In case of Xe (it is in the 2nd period), order of some of the energy levels depends on # of s & relative energies. it depends on mixing of s & p orbitals of the same atom (hybridization)

Li_2 no problem, $2s + 2s \rightarrow \begin{matrix} \text{M.O. (a)} \\ \text{M.O. (b)} \end{matrix}$
similar to the case of $1s + 1s$ in H_2
the $2s$ enter M.O. (b) $\rightarrow \sigma_b \rightarrow \text{B.O.} = 1$

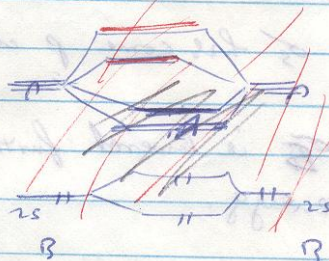
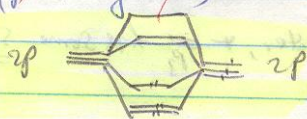
Inner Shells \rightarrow non-bonding

See table 4.1 p. 140

$\text{Be}_2 \sim 2$ has B.O. = zero, $\# \text{bonding} = \# \text{antibonding}$
 $\text{Be: } 1s^2 2s^2$

$\text{B}_2 \sim 2$ B. $1s^2 2s^2$ there is s/p mixing \rightarrow so:
 B_2 has two unpaired e's

the two π_{2p} orbitals must be lower than σ_{2p}
 (paramagnetic)



$\text{C}_2 \equiv$ diamagnetic $\sigma_{1s}^2 \sigma_{1s}^{*2} \pi_x^2 \pi_y^2$

$\text{N}_2 \rightarrow$ diamagnetic, B.O. = 3 regardless of the energy levels of π_{2p} & σ_{2p}

but since N_2^+ has a single e, σ_{2p} is higher than π_x & π_y

$\therefore \text{N}_2: \sigma_{1s}^2 \sigma_{1s}^{*2} \pi_x^2 \pi_y^2 \sigma_{2p}^2$

$\text{O}_2 \rightarrow$ paramagnetic (no s/p) mixing

V.B.T. $\rightarrow \ddot{\text{O}} = \ddot{\text{O}}; \therefore$ diamagnetic

M.O.T. \rightarrow two unpaired e's

$\therefore \text{O}_2: \sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_x^2 \pi_y^2 \pi_x^* \pi_y^*$



see Huheey 2nd ed. p. 129

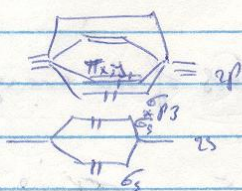
\therefore here, relative energies of σ_{2p} & $\pi_{x,y}$ are reversed here (for O_2 and also for F_2) compared to N_2 .

Note that O_2^+ is shorter than O_2 bond, why??
 O_2^- is longer than O_2 , why??

In case of $B, C \text{ \& } N^+$ it is evident that $\pi_{x,y}$ has lower energies than σ_{p_z} . This is probably due to low difference in energy between 2s & 2p orbitals in atomic $B, C \text{ \& } N$. Thus, mixing of 2s & 2p occurs (hybridization)

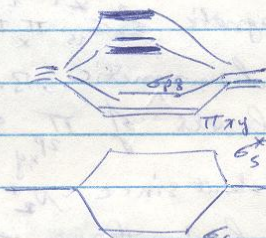
\therefore σ_s has some p character, & σ_{p_z} has some s character

\therefore σ_s is lowered further in energy, & σ_{p_z} is raised in energy.



without 2s/2p mixing

O_2



with 2s/2p mixing

N_2

Consider N_2

within each N -atom, mixing (hybridization) of 2s & 2p to give two sp hybrid orbitals but actually not equivalent 50:50% in each case.

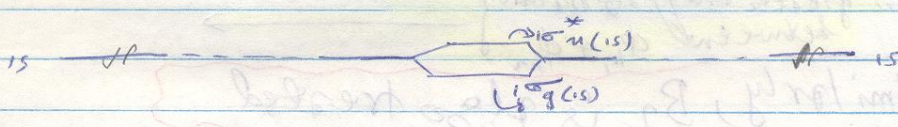
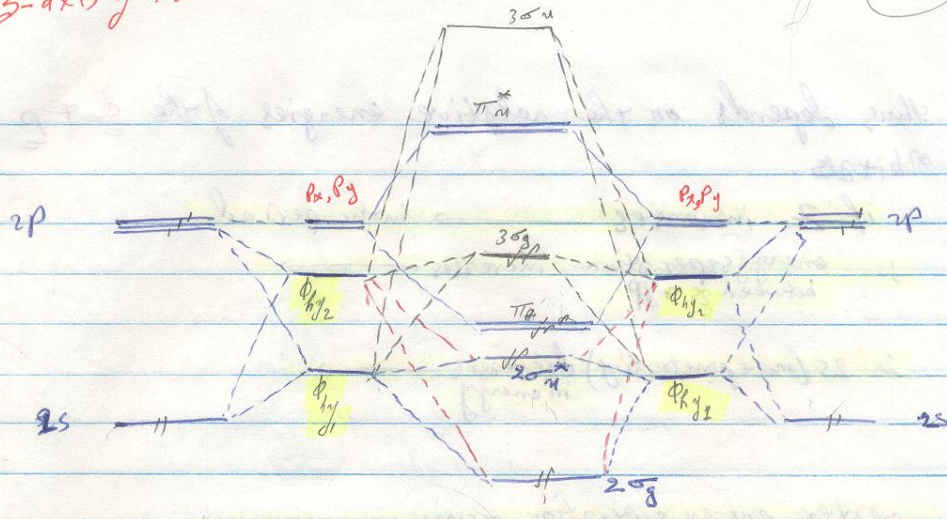
the resulting sp orbitals will inter combination with orbitals on the other N atom.

As a result, the energy of the bonding orbital will be stabilized further, and antibonding destabilized further.

Consequently, σ_{p_z} is raised, and $\pi_{x,y}$ orbitals are lowered.

3-axis of interaction

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~~Also~~ applies to B_2, C_2 molecules, with N (different distributions of e^-)

note that when s & p are hybridised, to give two sp hybrid orbitals, the two sp hybrid orbitals must have equal energy, such as $\overset{sp}{C} \equiv \overset{sp}{C}$ in H_2C_2 molecules.

but in X_2 (such as N_2), the two sp hybrid orbitals are different in energy

~~but in X_2 (such as N_2), the two sp hybrid orbitals are different in energy~~

but in X_2 (such as ^{Br} ~~Cl_2~~), the two sp hybrid orbitals are not equal in energy.

→ one hybrid orbital is used for bonding to the other X atom, this hybrid orbital must be sp with greater p character (ϕ_{hy} with $\lambda < 1$).

→ the other hybrid orbital must be sp with greater s character, this contains the lone pairs.
The difference in energy between the two sp orbitals

thus depends on the relative energies of the s & p orbitals.

if Z increases \rightarrow in the period,

energy separation increases between 2s & 2p

\therefore 2s (more penetrating) decreases in energy

\therefore greater energy separation occurs \rightarrow

\therefore less mixing occurs \rightarrow

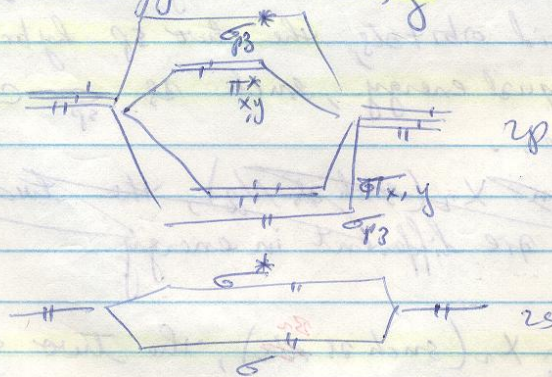
\therefore greater energy separation between ϕ_{h_1} & ϕ_{h_2} \rightarrow

Similarly, B_2 is also treated

\therefore in O_2 & F_2 , 2s & 2p are ^{relatively} highly separated

\therefore no 2s/2p mixing occurs

\therefore σ_p has lower energy than $\pi_{x,y}$



going to O , $F \rightarrow$ No s-p mixing

going to $N_2 \leftarrow C, N$ mixing (yes)

Heteronuclear Molecules

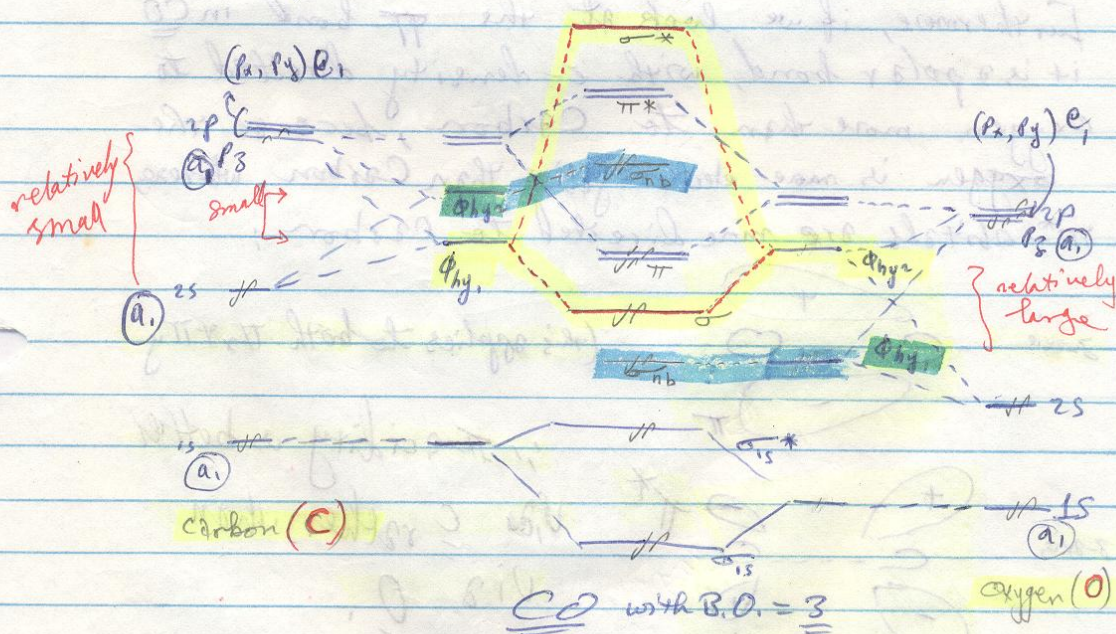
(B. Douglas)
(J. Barrell)

Atomic & Molecular Structure

Heteronuclear diatomics can similarly be described.
B.O. & π unpaired e^- can be calculated as before from the m.o. energy level diagrams.

Increase of mixing (hybridization) within the same atom and if significant energy level difference exists between orbitals of X & Y atoms, a Hybridization approach is preferable.

In m.o. level diagrams, (e.g. CO) orbital energies are lower for the more electronegative atom (O):



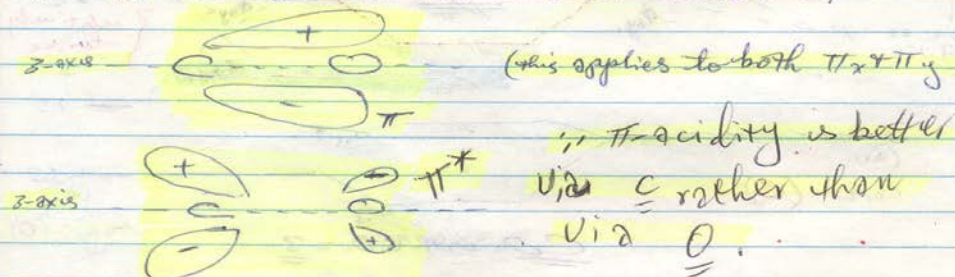
Note that $\phi_{hy}(C)$ is comparable in energy to $\phi_{hy}(O)$ thus they combine to give σ & σ^* m.o.s. whereas, $\phi_{hy}(C)$ & $\phi_{hy}(O)$ are only nonbonding thus, they remain localized on C & O separately occupying the lone pairs $\text{C} \equiv \text{O}$.

It is interesting to know why CO is a Lewis ^{base} ~~acid~~ donating $2e^-$ via C rather than O. This is because:

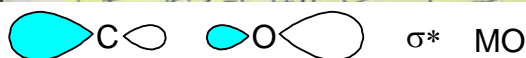
$\phi_{yz}(C)$ is at relatively high energy, and although it is sp but due to high energy, it is more like p than s , (mainly p -character), \therefore it is not very tightly bound to C nucleus, \therefore it can be donated easily to other Lewis acids.

$\phi_{yz}(O)$ is at lower energy, \therefore mainly s -character, \therefore tightly bound to O nucleus, \therefore it can't be easily donated to other Lewis acids.

Furthermore, if we look at the π bond in CO it is a polar bond, with e^- density directed to Oxygen more than to Carbon, because the oxygen is more electronegative than Carbon, whereas π^* orbitals are more directed to Carbon:



the same thing applies to σ -bond:

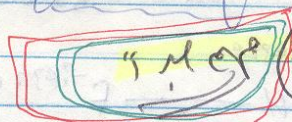
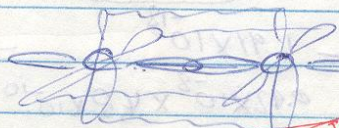


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the nonbonding orbitals are distributed in ^{almost} localized manner :



note that the π_x & π_y are in perpendicular planes, but may form some kind of a cylinder around the σ -bond axis (z-axis), however, there is a node in the cylinder _{overall}



Note the difference between two \perp π bonds and one σ bond $|||$

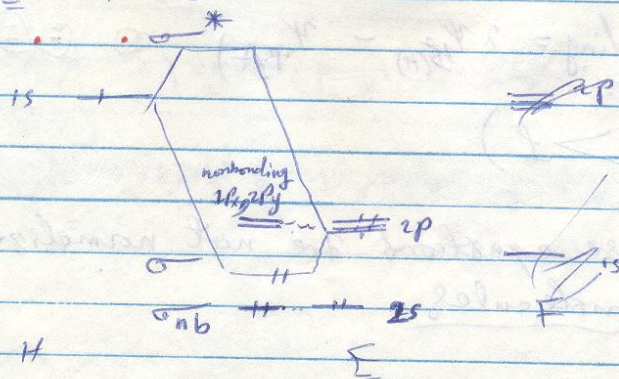
Another example is H-F molecule

J. Barret, p. 133

H-F is a heteronuclear diatomic molecule

H has $1s^1$, F has $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

$1s(H)$ & $2p_z$ of F may combine together although they have difference in energy levels (I.E. H = 13.6 eV, I.E. F = 17.42 eV), the resulting σ bonding M.O. is more closely related to F than to H



Thus, the $H-F$ bond is a polar covalent bond.

HF has a dipole moment $D = \delta e \times r \neq 0$

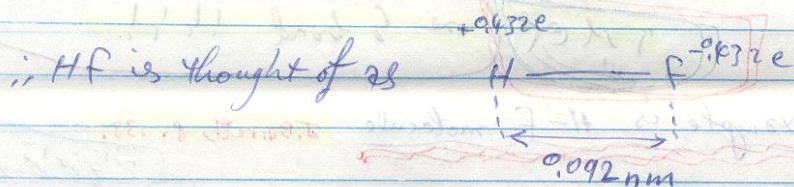
where: D = dipole moment

δe = point charge ($+\delta e$ or $-\delta e$ on H or F)

r = distance between $+\delta e$ & $-\delta e$

In HF , D is measured to be 1.91×10^{-18} e.s.u.

but $r = 0.092$ nm, $\therefore \delta = \frac{1.91 \times 10^{-18}}{0.92 \times 10^{-8} \times 4.8 \times 10^{-10}} = 0.422$



In wave-mechanical description, the resulting orbitals from L.C.A.O. are:

$\psi_{\text{bonding}} = \psi_{1s(H)} + \lambda \psi_{2p_z(F)}$

② or $\psi_{\text{antibonding}} = \lambda \psi_{1s(H)} - \psi_{2p_z(F)}$

where $(\lambda > 1)$

however, these equations are not normalized as in H_2 molecules.

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Alternatively,

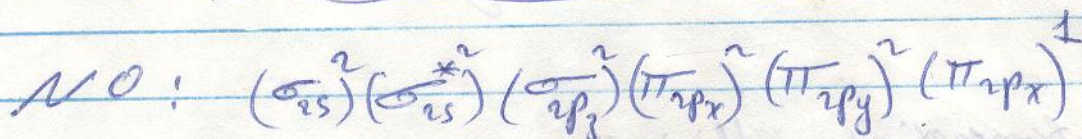
~~One may use~~ sp orbital of F to combine with
1s of H in **HF**, instead of using sp^3 .



however, even with elements of well calculated ϵ ,
the ϵ values are not accurately measured.

to independently

Example NO (nitric oxide)



with B.O. ≈ 2.5

NO^+ is similar to CO

