Chapter ???

MOT for Triatomic Molecules

TRIATOMIC MOLECULES

{1. B. Douglas, P. 145
2. J. Barrett, P. 150 – 161}

A stable bonding M.O. results from atomic orbitals of similar energies & good overlap.

In diatomics, symmetry restrictions are obvious.

Generally: good overlap is determined by symmetry of the molecule & symmetry of the atomic orbitals. ✓

∴ Symmetry & Groups theory are important in expecting permitted combinations in larger molecules, where possible combinations may not be obvious.

Linear Molecules:

CO_2 is a linear molecule O=C=O ($D_{\infty h}$) with a character table on page 127 (B. Douglas)

C_∞ (in the z-axis) O — C — O --- z-axis

C, $O_{(1)}$ & $O_{(2)}$ each have the available 2S & $2p_z$ orbitals available for σ-bonding.

✓ O is more electronegative than C

∴ 2S (O) is much lower in energy than Carbon orbitals; they are essentially nonbonding (although they do form two L.G.O's. (a_{1g} + a_{1u}) partly involved in bonding. → $\sigma_{1,2}$)

$2p_z$ (O) combine with C orbitals similar (γ)

If D∞h operations are applied then they give symmetries belonging to a_{1g} & a_{1u}: O + O (2S 2S) → σ_u + σ_g

consider the z-axis on each O directed to C to be (+),

O —(+z)→ C ←(+z)— O

apply the symmetry operations of D∞h on 2S & $2p_z$ of C (central atom) which becomes: O — C — O → z

D∞h	E	$2C_\infty$	...	∞σv	i	2S∞	∞C_2
A_{1g}	1	1		1	1	1	1

on $2p_z$

$D_{\infty h}$	E	C_∞	σ_v	i	S_∞	C_2
	1	1	1	-1	-1	-1

$\Sigma_{g,u}$

from $D_{\infty h}$ character table, 2S belongs to the totally symmetric representation (A_1g)

i.e. oxygen orbitals which can combine with 2S(C) must also belong to (A_1g) representation

We know that $2p_z$ of $2p_z$ (of both oxygens must undergo L.C.A.O. to give two new L.G.O's. which are:

$\phi_1 \{2p_{z(1)} + 2p_{z(2)}\}$ $\qquad$ $\phi_2 = \{2p_{z(1)} - 2p_{z(2)}\}$

if we apply symm. operations of $D_{\infty h}$ on each of these two L.G.O's. then we find their symmetries as

$\boxed{\phi_1 \rightsquigarrow a_1 g}$ of $\boxed{\phi_2 \rightsquigarrow \Sigma_u}$

i.e. ϕ_1 (L.G.O.) combines with $2s(O) \rightsquigarrow a_1 g$ to give bonding & antibonding M.O's.

$$\sigma_{a_1 g} = \underset{a_1 g}{2s(c)} + \underbrace{(2p_z + 2p_z)}_{\phi_1 \text{ L.G.O.}}$$

$a_1 g$

$$\sigma^*_{a_1 g} = \underset{a_1 g}{2s(c)} - \underbrace{(2p_z + 2p_z)}_{\phi_1 \text{ L.G.O.}}$$

the same thing applies to $2p_z(C)$ which has σ_u symmetry

it $2p_z(C)$ combines with ϕ_2 to give two M.O's. σ_u & σ_u^* as:

$\sigma_u = \underbrace{2p_z(C)}_{a_{1u}} + \underbrace{(+2p_{z_{O_1}} - 2p_{z_{O_2}})}_{\phi_2\ a_{1u}}$ $\phi_2\ a_{1u}$

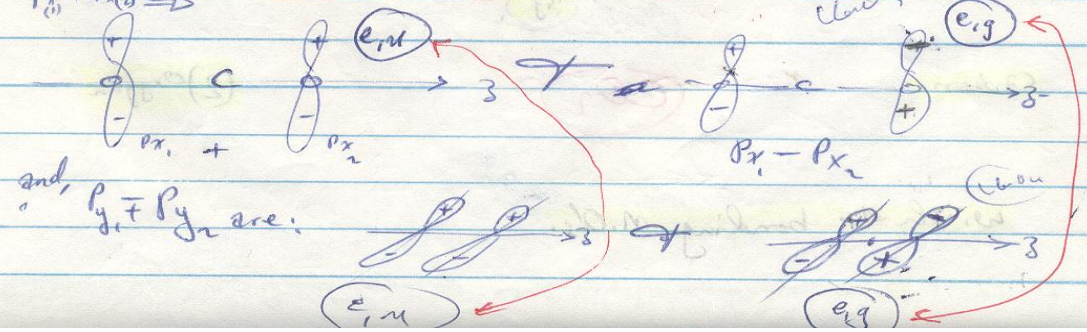
$\sigma_u^* = \underbrace{2p_z(C)}_{a_{1u}} - \underbrace{(+2p_{z_{O_1}} - 2p_{z_{O_2}})}_{\phi_2\ a_{1u}}$

What about π-bonding in CO_2 ??

In Carbon, two degenerate $2p_x$ & $2p_y$ orbitals exist, these two orbitals belong to E_{1u} (from $D_{\infty h}$ character table).
it each is labeled as e_{1u}.

what orbitals from the two oxygens are expected to combine with these orbitals?
it the remaining ones (p_x & p_y) from each oxygen are expected. { as $2s$ nonbonding; $2p_z$ are used in σ-bonds }
it the four orbitals of oxygen atoms ($2p_{x_1}, 2p_{y_1}, 2p_{x_2}, 2p_{y_2}$) combine together to form four L.G.O's.

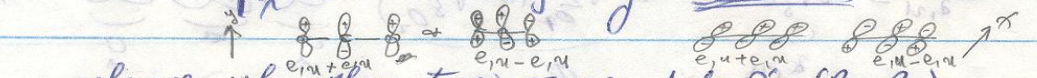
$p_{x_1} + p_{x_2} \Rightarrow$



and, $p_{y_1} \mp p_{y_2}$ are:

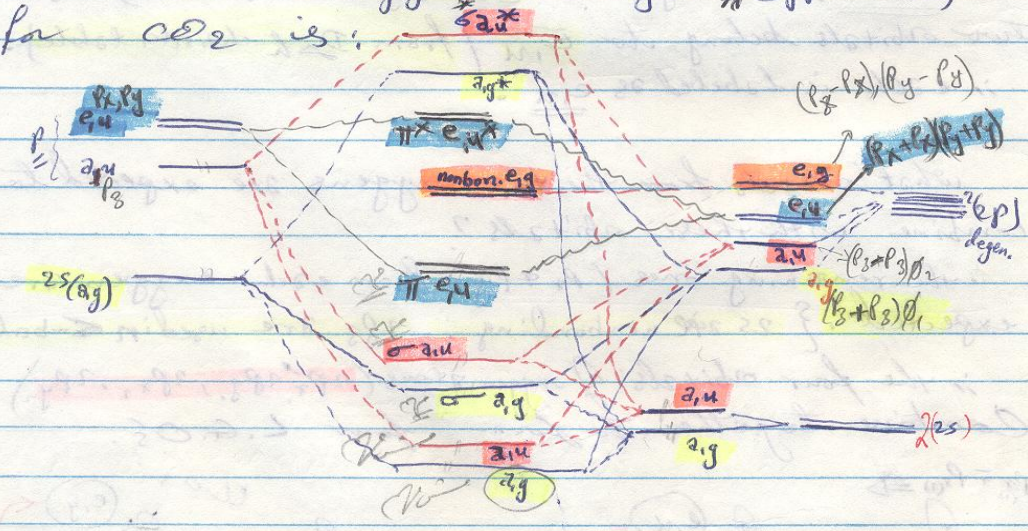
note that $(p_{x_1} + p_{x_2})$ L.G.O. & $(p_{y_1} + p_{y_2})$ L.G.O. together belong to e_{1u} representation ((Use Group theory to prove this))

∴ $(p_{x_1} + p_{x_2})$ L.G.O. & $(p_{y_1} + p_{y_2})$ L.G.O. combine with p_x & with p_y of Carbon.



whereas, the other two oxygen L.G.O's. $(p_{x_1} - p_{x_2})$ and $(p_{y_1} - p_{y_2})$ belong to e_{1g} representation which is different from e_{1u} for carbon p_x & p_y so they don't combine with $2s$ orbitals so they remain as nonbonding, and their electrons are localized at oxygen atoms.

thus, the M.O. energy level diagram (approximate) for CO_2 is:



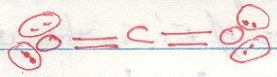
with 4 bonding M.O's.

Notes

(1) generally, splitting of $\pi - \pi^*$ is smaller than that of $\sigma - \sigma^*$ levels, This is due to smaller overlap in π bonding orbitals than in σ bonding orbitals, even with s/p mixing, σ_b will be lowered in energy.

(2) Furthermore, the M.O's $2_g, 2_u$ are very low in energy so they occupy the nonbonding e⁻'s, also the two e_g also occupy the nonbonding e⁻s.

the result is: four bonding orbitals, two giving σ $\{2_g + 2_u\}$, and two giving π $\{e_u\}$.



(3) Note that, Total number of M.O's. is exactly equal to total no. of At. orbitals = 12

(4) Similarly, other molecules are made $\{CS_2, N_2O, N_3^-, \text{[illegible]}, NO_2^+, \text{---etc.}\}$ which are isoelectronic with CO_2.

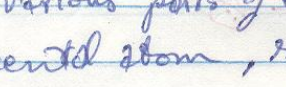
(5) this explains facts about stability of the molecule (B.O. (total) = 4)
Diamagnetic molecule

(6) Note the delocalization concept.

Generally

In dealing with triatomic molecules, two approaches have been suggested:

(i) The Sidgwick-Powell theory:

Shape & bonding of a molecule are determined by the minimization of the electrostatic repulsions between various pairs of $\bar{e}$'s in the valence shell of the central atom, such as  tetrahedral

(ii) The Walsh approach:

correlates the M.O's. of extreme possible shapes of the molecule (such as 180°—90°, as we see later)

In our course, we are interested only in the Walsh approach, which has partly been used in CO_2 molecule before.

Let's deal with a simpler case than CO_2, such as a linear triatomic hydride molecule (H-A-H) linear, which is a special case of AB_2 linear systems.

Assuming that A uses only $\bar{s}$ & $\bar{p}$ orbitals, these $\bar{s}$ & $\bar{p}$ orbitals must be combined to the two 1s orbitals of $H_{(1)}$ & $H_{(2)}$

thus, first thing is to find the symmetries of the orbitals $(2s, 2p_z, 2p_x, 2p_y)$ of (A).

So, we look at $D_{\infty h}$ character table, assuming that z-axis is axis of interaction,

$\therefore$ $2s \rightsquigarrow \Sigma_g$

$2p_z \rightsquigarrow \Sigma_u$

$\{2p_x, 2p_y\} \rightsquigarrow \Pi_u$

or by finding to which irreducible representation each orbital belongs, by applying all sym. oper. on each of these orbitals

now, we find out the L.G.O's of the two H atoms,

ϕ_1 L.G.O. $= \frac{1}{\sqrt{2}}\left(\psi_{1s_{(1)}} + \psi_{1s_{(2)}}\right)$ eq.1

bonding on H–H

$\phi_2 = \frac{1}{\sqrt{2}}\left(\psi_{1s_{(1)}} - \psi_{1s_{(2)}}\right)$ eq.2

L.G.O. antibonding on H–H

if we apply all sym. operations on each of these:

on ϕ_1:

$D_{\infty h}$	E	C_∞	σ_v	i	S_∞	C_2
	1	1	1	1	1	1

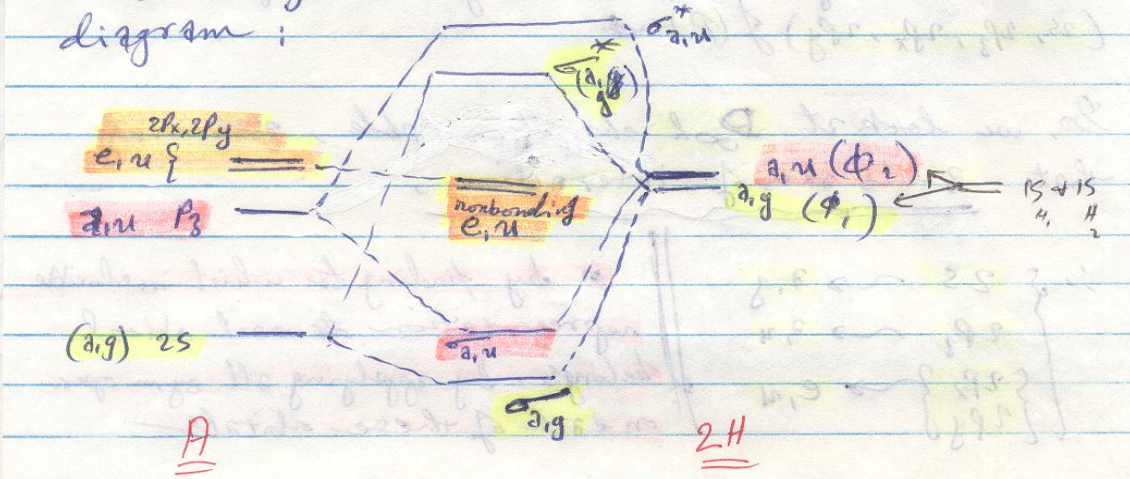
$\therefore \phi_1$ belongs to A_{1g}, $\therefore \phi_1 \rightsquigarrow \Sigma_g$

on ϕ_2:

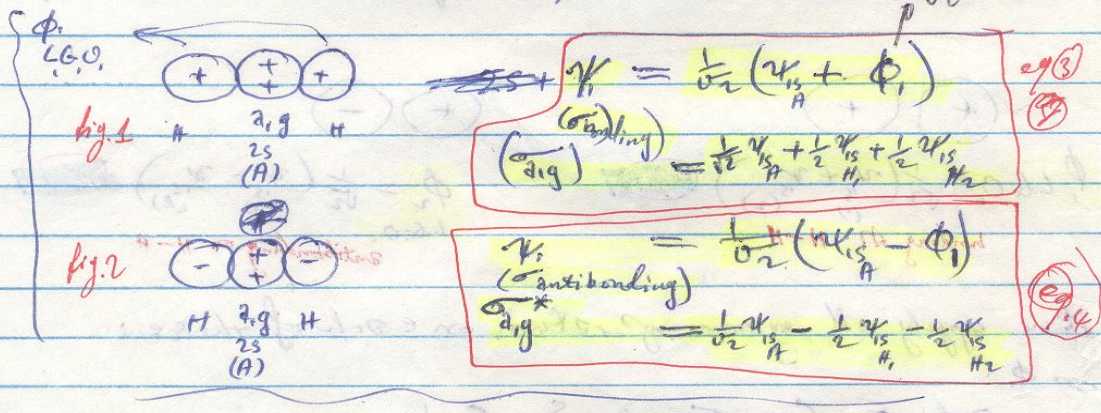
$D_{\infty h}$	E	C_∞	σ_v	i	S_∞	C_2
	1	1	1	−1	−1	−1

$\therefore \phi_2$ belongs to A_{1u}, $\therefore \phi_2 \rightsquigarrow \Sigma_u$

now, we try to construct the M.O. E. Level diagram:



to understand, we draw the functions:



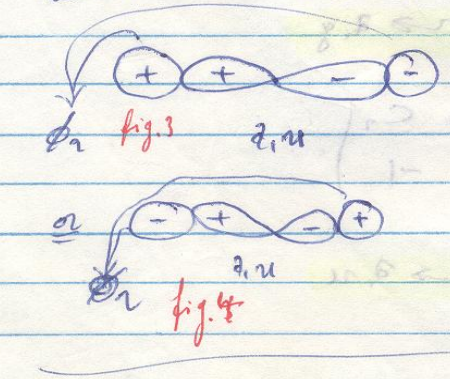
$$\psi_1 = \frac{1}{\sqrt{2}}\left(\psi_{1S_A} + \phi_1\right) \quad \text{eq (3)}$$

$$(\sigma_{bonding})\ (a_1g) = \frac{1}{\sqrt{2}}\psi_{1S_A} + \frac{1}{2}\psi_{1S_{H_1}} + \frac{1}{2}\psi_{1S_{H_2}}$$

$$\psi_1^* = \frac{1}{\sqrt{2}}\left(\psi_{1S_A} - \phi_1\right) \quad \text{eq 4}$$

$$(\sigma_{antibonding})^*\ a_1g = \frac{1}{\sqrt{2}}\psi_{1S_A} - \frac{1}{2}\psi_{1S_{H_1}} - \frac{1}{2}\psi_{1S_{H_2}}$$

the other M.O's (bonding & antibonding) are:

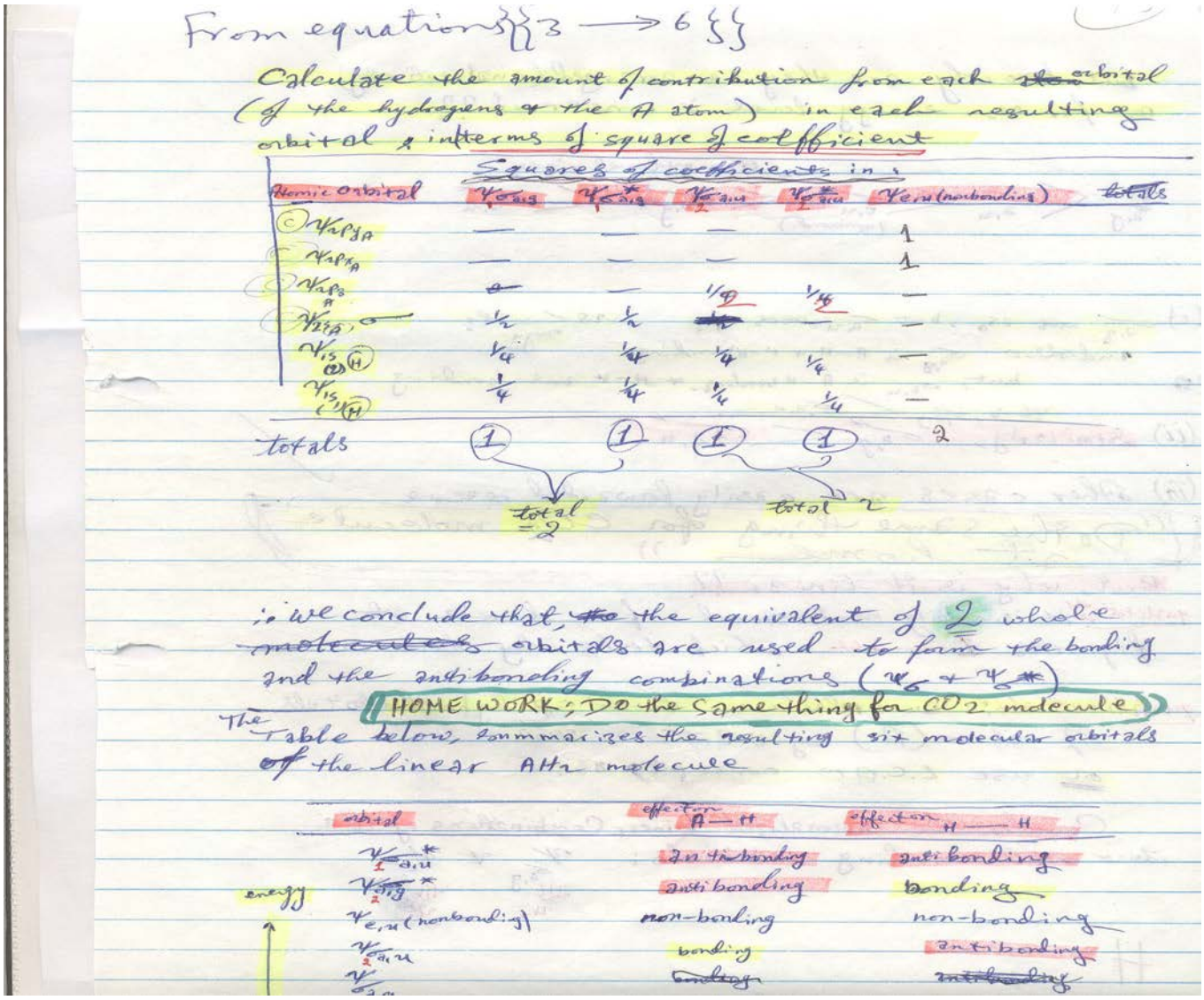


$$\psi_2 (\text{bonding}) = \frac{1}{\sqrt{2}}\left(\psi_{2p_z} + \phi_2\right) \quad \text{eq (5)}$$

$$(a_1u) = \frac{1}{\sqrt{2}}\psi_{2p_z} + \frac{1}{2}\psi_{1S_{H_1}} - \frac{1}{2}\psi_{1S_{H_2}}$$

$$\psi_2 (\text{antibonding}) = \frac{1}{\sqrt{2}}\left(\psi_{2p_z} - \phi_2\right) \quad \text{eq (6)}$$

$$(a_1u)^* = \frac{1}{\sqrt{2}}\psi_{2p_z} - \frac{1}{2}\psi_{1S_{H_1}} + \frac{1}{2}\psi_{1S_{H_2}}$$



$\Psi\sigma_{a1g}$ bonding bonding

; we conclude that, ~~the~~ the equivalent of 2 whole ~~molecules~~ orbitals are used to form the bonding and the antibonding combinations ($\psi_\sigma + \psi_\sigma^*$)

HOME WORK; DO the same thing for CO_2 molecule

The Table below, summarizes the resulting six molecular orbitals of the linear AH_2 molecule

orbital	effect on A—H	effect on H—H
$\psi_{1\sigma_u}^*$	antibonding	antibonding
$\psi_{2\sigma_g}^*$	antibonding	bonding
ψ_{e_u} (nonbonding)	non-bonding	non-bonding
$\psi_{2\sigma_u}$	bonding	antibonding
~~bonding~~	~~bonding~~	~~antibonding~~
$\psi_{1\sigma_g}$	bonding	bonding

energy ↑

But, why are they so arranged (qualitatively) as far as energy level is concerned??

energy level rises

$\psi_{\sigma_{1,g}} < \sigma_{1,u} < \sigma_{2,u}$ (nonbond.) $< \sigma^*_{1,g} < \sigma^*_{1,u}$

(i) $\sigma_{1,g}$ uses $2s_A$, but $\sigma_{1,u}$ uses $2p_z$, $2s <$ (energy) $2p_z$

and also $\sigma_{1,g}$ is A–H & H–H bonding

but, $\sigma_{1,u}$ is A–H bonding, & H–H antibonding

thus, $\sigma_{1,g} < \sigma_{2,u}$

(ii) Similarly, $\sigma^*_{1,g} < \sigma^*_{1,u}$

(iii) other cases are easily forwarded reasons.

("Do the same thing for CO_2 molecule at home")

But, why is it linear??

qualitatively, it is easily understood if we look at figures 1 → 4 which tells why linear.

quantitatively: we either use two sp hybrid orbitals (50:50) of atom (A) by V.B.T.

or use L.C.A.O. concept, as:

Consider the normalized linear combinations of the two M.O. bonding orbitals: $\psi_{\sigma_{1,g}}$ & $\psi_{\sigma_{1,u}}$

$\psi_{\sigma_{1,g}} \Rightarrow \psi_1$ $\quad$ $\psi_{\sigma_{1,u}} \Rightarrow \psi_2$

#

$\frac{1}{\sqrt{2}}(\psi_{s_A}) + \frac{1}{2}\psi_{1s_1} + \frac{1}{2}\psi_{1s_2}$

then: $K_1 = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$ ~~and $K_2 = \frac{1}{2}(\psi_1 - \psi_2)$~~

using equations (3) & (5)

$\therefore K_1 = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\psi_{s_A} + \frac{1}{2}\psi_{1s_{(1)}} + \frac{1}{2}\psi_{1s_{(2)}} + \frac{1}{\sqrt{2}}\psi_{p_{3_A}} + \frac{1}{2}\psi_{1s_{(1)}} - \frac{1}{2}\psi_{1s_{(2)}}\right]$

$\equiv \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\psi_{s_A} + \frac{1}{\sqrt{2}}\psi_{p_{3A}}\right] + \frac{1}{\sqrt{2}}\psi_{1s_{(1)}}$ ---- (eq. 7)

$\equiv \frac{1}{2}\left[\frac{1}{\sqrt{2}}(\psi_{s_A} + \psi_{p_{3A}})\right] + \frac{1}{\sqrt{2}}\psi_{1s_{(1)}}$ 0

And $K_2 = \frac{1}{\sqrt{2}}(\psi_2 - \psi_1)$

$\therefore K_2 = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\psi_{s_A} + \frac{1}{2}\psi_{1s_{(2)}} + \frac{1}{2}\psi_{1s_{(2)}} - \frac{1}{\sqrt{2}}\psi_{p_{3_A}} - \frac{1}{2}\psi_{1s_{(1)}} + \frac{1}{2}\psi_{1s_{(2)}}\right]$

$K_2 \equiv \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}\psi_{s_A} - \frac{1}{\sqrt{2}}\psi_{p_{3A}}\right] + \frac{1}{\sqrt{2}}\psi_{1s_{(2)}}$ ---- (eq. 8)

$\equiv \frac{1}{2}\left[\frac{1}{\sqrt{2}}(\psi_{s_A} - \psi_{p_{3A}})\right] + \frac{1}{\sqrt{2}}\psi_{1s_{(2)}}$ 0

Note that equations (7) & (8), have terms in parentheses which are actually the same as normalized linear combinations of the s & p_3 of the central atom (A) itself.

ii Compare them to the hybrid (sp) orbitals which we have happened to see before ~~when discussing the N_2 molecule in the past~~.

ملاحظات: ① يرجى مقارنة صعوبة M.O.T. بسهولة V.B.T. ولكن النتائج أهم.
هامتان ② حبذا قراءة الطلاب لكتاب J.Barrett ، يرجى فهم ملاحظة
أن الكتاب يجعل interaction y-axis وأما نحن فنستعمل z-axis

Walsh Diagrams of AH_2

Consider AH_2 molecule which could be linear (as CO_2) or bent as (NO_2, OH_2) but without π bonding.

Furthermore, H is orbitals are very high in energy, compared to oxygen orbitals energy.

M.O. theoretical treatment of AH_2 (A is a 2nd period element) is to consider (OH_2) 2s + 2p orbitals of the oxygen separately, and to construct two L.G.O's, which combine with O 2s + 2p, to give delocalized σ-orbitals,

or to start with sp^3 hybrid orbitals of O, two of which are to be used for production of two localized σ-orbitals

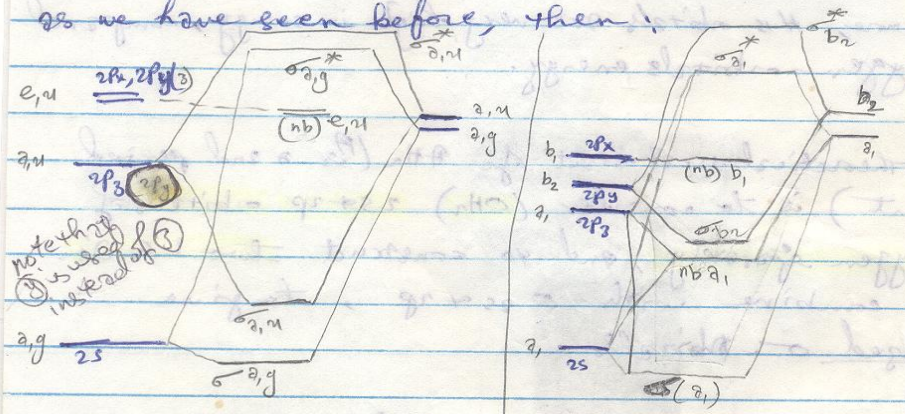
Consider AH_2 molecule, A is a 2nd period element with a maximum of 8 e's in four bonding & nonbonding orbitals relative energies of these orbitals will determine & their occupancy will determine the molecular shape.

For angular molecule, with a bond angle 90°, we use the axes of NO_2 as before:

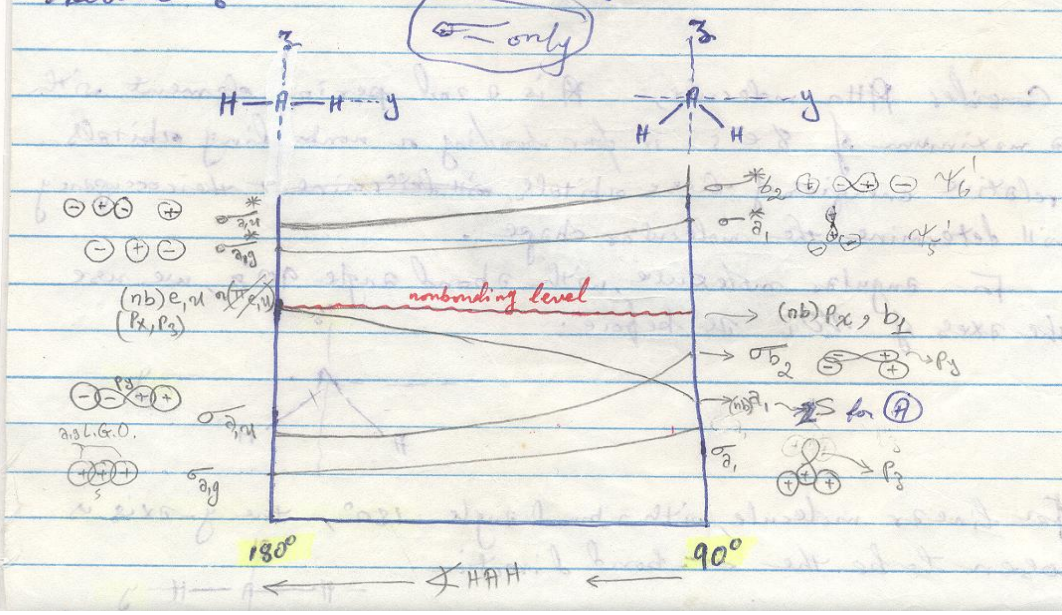
for linear molecule, with a bond angle 180°, the y-axis is chosen to be the σ-bond direction

So, when angle ~~AH~~ decreases, the choice of the axes will agree with the angular molecule.

If we recall the M.O. energy level diagrams for linear AH_2 & bent 90° AH_2 molecules as we have seen before, then:



these two M.O. energy levels, may be combined into the same energy level diagram as appears below:



Note that the common reference energy level is the nonbonding level, designated as e_{1u} or π_u in linear and as b_1 in bent.

Note that e_{1u} in linear involves $p_x + p_z(y)$, so the p_x (nonbonding) is unaffected by changing the angle so its energy is unaffected, thus the horizontal line remains.

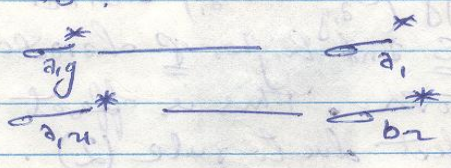
Other correlations take place, as

σ_{2g} (180°) ——— σ_{a_1} (90°)

$\sigma_{a_{1u}}$ (180) ——— σ_{b_2} (90°)

~~And the two nonbonding levels may be joined up as:~~

the corresponding antibonding levels, may also be correlated as:



there remain other correlations:

(nb) e_{1u} (π_u) ——→ (nb) a_1 (s)

Walsh's Rules: there are two important considerations upon the drawing of the correlations in the Walsh Diagram known as Walsh's Rules: (Important in deciding what happens to orbital energy if the molecule changes from linear → bent)

i) The energy of an orbital increases with (increasing p character and decreasing s character). Thus, σ_{b_2} & σ_{a_1} orbitals are higher in energy respectively than σ_u & σ_g orbitals which have higher s character. This rule is responsible for the main differences in orbital energies as the bond angle changes.

ii) If the M.O. is antibonding between the hydrogen atoms then a linear state is favoured, but if the M.O. is bonding with respect to the hydrogen atoms then a bent state is favoured, because in this case the hydrogens are brought closer together.

(These are in addition to previous discussions bonding A–H more stable than antibonding A–H.)

From these rules, we can expect structure of AH_2 molecules.

$(\sigma_{a_1 g} - \sigma_{a_1})$ is bonding with Hydrogens (rule 2) so it is most stable in bent state, where hydrogens are brought close together than in linear molecule.

But Rule (1) indicates that as the molecule bends, the energy $(\sigma_{a_1 g} - \sigma_{a_1})$ orbital increases due to lesser S and higher P character from the central atom. This is offset somewhat by the effect due to rule (2). $\therefore (\sigma_{a_1 g} - \sigma_{a_1})$ slightly favours a linear arrangement.

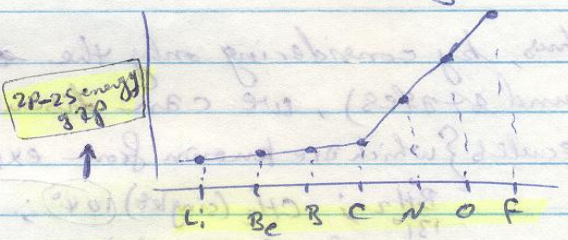
$(\sigma_{a_1 u} - \sigma_{b_2})$ bonding orbitals of (A–H) is H—H antibonding and the application of the two rules indicates that the orbital energy will increase as the bending of the molecule due to rule (2). Rule (1) is not relevant here, since $\sigma_{a_1 u}$ + σ_{b_2} orbitals are built from a p-orbital of the central atom. $\therefore (\sigma_{a_1 u} - \sigma_{b_2})$ favours linear arrangement

Similar reasoning applies to the corresponding antibonding orbitals.

$(\pi_{e,u} - b_1)$ is steady.

the other $(\overset{(nb)}{e_{,u}}(p) - \overset{(nb)}{a_1}(s))$: p–s energy gap is considerable, thus the correlation is drawn rather steeply but Rule (2) considerations here are not relevant, since both are non-bonding. ∴ $(e_{,u} - a_1)$ strongly prefers bent arrangement

Note that the position of $\overset{(nb)}{2_1}(s)$ is not certain. The p–s gap varies with nuclear charge of the atom as:



In the beginning, p–s gap is not too great, ∴ $2_1(s)$ is expected to be in the region of σ_{a_1} & σ_{b_2} bonding M.O's. As we go to the right of periodic table p–s gap increases, so $2_1(s)$ orbital will occur at a very much lower energies than the σ_{a_1} & σ_{b_2} (increasingly). Don't forget this point when applying Walsh diagrams, to molecules in which the charge on nucleus of central atom varies.

Application of Walsh Diagram to AH_2 molecules

The implications of Walsh Diagram in shapes of AH_2 molecules is concerned depends upon which whether the various orbitals are more stable in the linear or bent state. (Table 8.9)

Table 8.9 : Shape factors Favouring the Stability of Molecular Orbitals in AH_2 molecules

orbital	Shape factor giving more stable orbital (lowest energy)
$\sigma^*_{1u} - \sigma^*_{b_2}$	Linear molecule
$\sigma^*_{2g} - \sigma^*_{a_1}$	Linear molecule
$\pi_{1u} - b_1$ (nb)	energy independent of shape
$\pi_{1u} - a_1$ (s) (nb)	Bent molecule (strongly dependent upon bond angle)
$\sigma_{1u} - \sigma_{b_2}$	Linear molecule
$\sigma_{2g} - \sigma_{a_1}$	Linear molecule

Thus, by considering only the lowest energy levels (ground states), we can discuss shapes of molecules which are known from experiment as :

$\overset{131^\circ}{BH_2}$; CH_2 (singlet) 104° ; NH_2 103.3 ; OH_2 104.5°, and CH_2 (triplet) 180°

All we do is to fill electrons so as to achieve the ground state, and to use Walsh Diagram :

i) Molecules upto with upto 4 e's, $\rightarrow$ fill the lowest two molecular orbitals as $(\sigma_{2g} - \sigma_{a_1})^2$ $(\sigma_{2u} - \sigma_{b_2})^2$ in this case will be linear to be most stable as ;

i) = BeH_2 & $Hg(CH_3)_2$ are thus linear

ii) = BH_2 has 5 e's (besides the lone $1s^2$ pair). Four e's will enter the low lying $(\sigma_{2g} - \sigma_{a_1})^2$ & $(\sigma_{2u} - \sigma_{b_2})^2$ orbitals, and the fifth will occupy $(\pi_{(e_1u)} - a_1(s))$. The $(e_1u - a_1(s))$ is stabilized by bending of the molecule

thus the BH_2 is expected to be bent. But, it should be only slightly bent because the other four e⁻'s prefer to have linear arrangement $(\sigma_{a_1 g}^2)(\sigma_{a_u}^2)(\sigma_{b_2}^2)$ but, why one e⁻ is enough to bend the molecule (and overcome the effect of 4 e⁻'s)? This is because the $\left(\underset{(e,u)}{\pi_u} - a_1(s)\right)$ slope is very high that the bending effect of one e⁻ can overcome the effect of 4 e⁻'s. However, we can say that it must be slightly bent. (131°)

iii) $\ddot{C}H_2$ (singlet) has one pair of e⁻'s ⊕ CH_2

thus the configuration is $(\sigma_{a_1 g}^2)(\sigma_{a_1}^2)(\sigma_{a_u}^2)(\sigma_{b_2}^2)(\underset{\pi_u}{e,u} - a_1(s))^2$

thus, 2e⁻ in the $e,u - a_1(s)$, thus it is expected to be bent more than $\ddot{B}H_2$, which fits with experiment. (104°)

- but $\ddot{C}H_2$ (triplet) has two unpaired e⁻'s ⊕ $\ddot{C}H_2$

thus, the configuration is

$$(\sigma_{a_1 g}^2)(\sigma_{a_1}^2)(\sigma_{a_1 u}^2)(\sigma_{b_2}^2)(\underset{(\pi_u)}{e,u} - a_1(s))^1(e,u - b_1)^1$$

note that $(e,u - b_1)$ is shape independent, and occupies 1 e⁻, the other $(e,u - a_1(s))$ is strongly shape dependent, having 1e⁻ thus, we expect here to have a bond angle bigger than that in singlet $\ddot{C}H_2$, (a less bent). In fact this is true, and the triplet $\ddot{C}H_2$ is linear (180°). In this case, $(e,u - a_1(s))$ electron can't overcome the linear tendency of the lower 4e⁻s.

Note also as it not unstable here, not steep bending, so an e⁻ is not very significant

ii) $\ddot{N}H_2$ has 7e⁻s in the valence shells, to have:

$$(\sigma_{a_1 g}^2)(\sigma_{a_1}^2)(\sigma_{a_1 u}^2)(\sigma_{b_2}^2)(\underset{\pi_u}{e,u} - a_1^2)(\underset{\pi_u}{e,u} - b_1)^1$$

thus, 2e⁻s in the $(e,u - a_1(s))$ which is critically bending

bent as singlet CH_2. This is experimentally true ($103.7°$)
However, the $(e_{1u} - b_1)$ one e^- is ineffective.
(note that $s-p$ gap is here bigger than in C)

ii) H_2O : has 8 e's

configuration is:

$$(\sigma_{a_1 g} - \sigma_{2_1})^2 (\sigma_{a_1 u} - \sigma_{b_2})^2 (e_{1u} - a_1(s))^2_{(\pi u)} (e_{1u} - b_1)^2_{(\pi u)}$$

thus, NH_2 is expected to be similar to NH_2, with no much difference. This is also true.
((but, unfortunately, it should have smaller bond due to higher $s-p$ energy difference))

Note that the Sidgewick-Powell theory does not explain all these cases as satisfactorily as Walsh treatment.
such as the cases of:

① BH_2 → sp^2 ✓ ✓

② CH_2 (singlet) → sp^2 expected 120° but actually 104.0° due to difference in repulsion ✓ ✗

③ CH_2 (triplet) 180 is sp hybridized ✗
but if $\frac{3}{sp}$ $\frac{\pi}{sp}$ 90 ?
then it should be ok to get the min. repulsion
thus it should be at 109° ??
but they solve it as sp

but this is artificial, it should be sp^3 for min. repulsion, if Sedgewick-Powell theory is true. But, experimentally 180° is contradicting with Walsh's.

④ H_2O → Sedgewick-Powell ✓ ✗ < 109°

⑤ NH_2 → Sedgewick-Powell ✗
should be as H_2O, ∴ angle must be more than that of H_2O if theory is true. But, experimentally ✗ $\theta_{NH_2} < \theta_{H_2O}$

∴ Walsh Theory is More successful in many cases than Sedgewick-Powell Theory.

Furthermore, The Walsh theory (involving antibonding orbitals of molecules) can make successful qualitative predictions of absorption spectra of AH_2 species.

Consider table 8.10 with lowest energy transitions of the molecules, which may be linked with electronic configuration and bond angle changes:

Molecule	Absorption Region	
BH_2	600 – 900 nm	↓ energy of excitation increases
NH_2	450 – 740 nm	
OH_2	150 – 200 nm	

could we also link electronic configuration, lowest energy transition & bond angle changes ??

BH_2 → $(\sigma_{a_1g} - \sigma_{a_1}^{*})(\sigma_{a_1u} - \sigma_{b_2}^{*})(e_{1u} - a_1(s))^1$ ground st the bent structure

when excited, it becomes: $(\ \ )(\ \ )(e_{1u} - b_1)^1$ (excited)

∴ linear structure with the same bond strength as in ground st.

these predictions are in accord with facts.

Note also that $(e_{1u} - b) \rightarrow (e_{1u} - a_1(s))$ absorption transition in Walsh diagram, so, little energy is required for excitation is a measure for energy gap in BH_2.

NH_2: ground state: $(\sigma_{a_1 g})^2 (\sigma_{a_1 u})^2 (\sigma_{b_2})^2 (e_{1u})^4 (b_1)^1$

g.s. NH_2 bond angle < bond angle BH_2 g.s.

∴ corresponding transition needs higher energy (shorter wavelength) which is true from table.

to give bond angle 144° in excited NH_2

$(\omega)^1 (\quad)^2 (\quad)^2 (\quad)^1 (\quad)^2$

g.st. < excited state

(103.2°) (144°)

H_2O: $(\quad)^2 (\quad)^2 (e_{1u} - a_1(s))^2 (e_{1u} - b_1)^2$ are both filled

so corresponding transition does not occur.

∴ lowest energy transition is thus:

$(nb) \longrightarrow$ (antibonding)

$(e_{1u} - b_1)^2 \longrightarrow (e_{1u} - b_1)^1 (\sigma^*_{a_1 g} - \sigma^*_{a_1})^1$

thus ∠ increases, and is more than in g.st.,

actually it is stabilized in linear way if excited,

furthermore, the bond order is decreased, due to antibonding e⁻.

~~from photoelectron spectroscopy~~

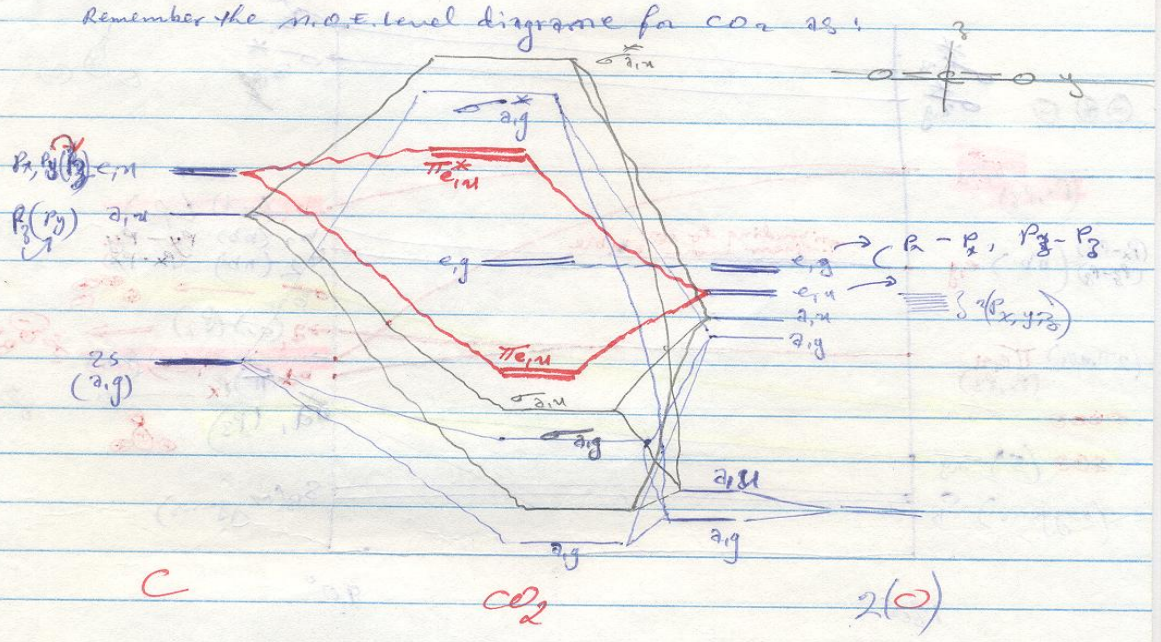
we get that H_2O is 104.5° is intermediate between 90°(p-p) & 180°(sp) extremes of the walsh diagram

Walsh Diagrams for AB_2 molecules including π-bonding M.O's.

From B. Douglas, we have seen M.O. Energy Level Diagrams for CO_2 & NO_2 molecules.

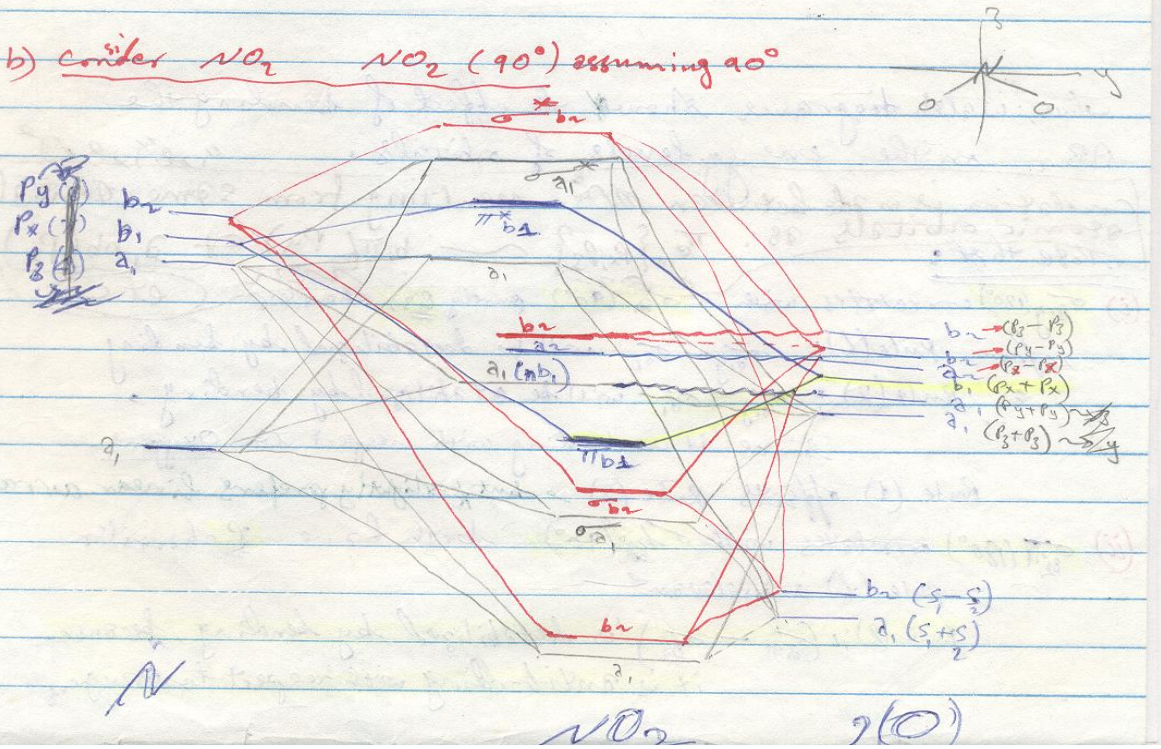
a) Consider CO_2 $O=C=O$: (180°)

Remember the M.O.E. Level diagrams for CO_2 as :



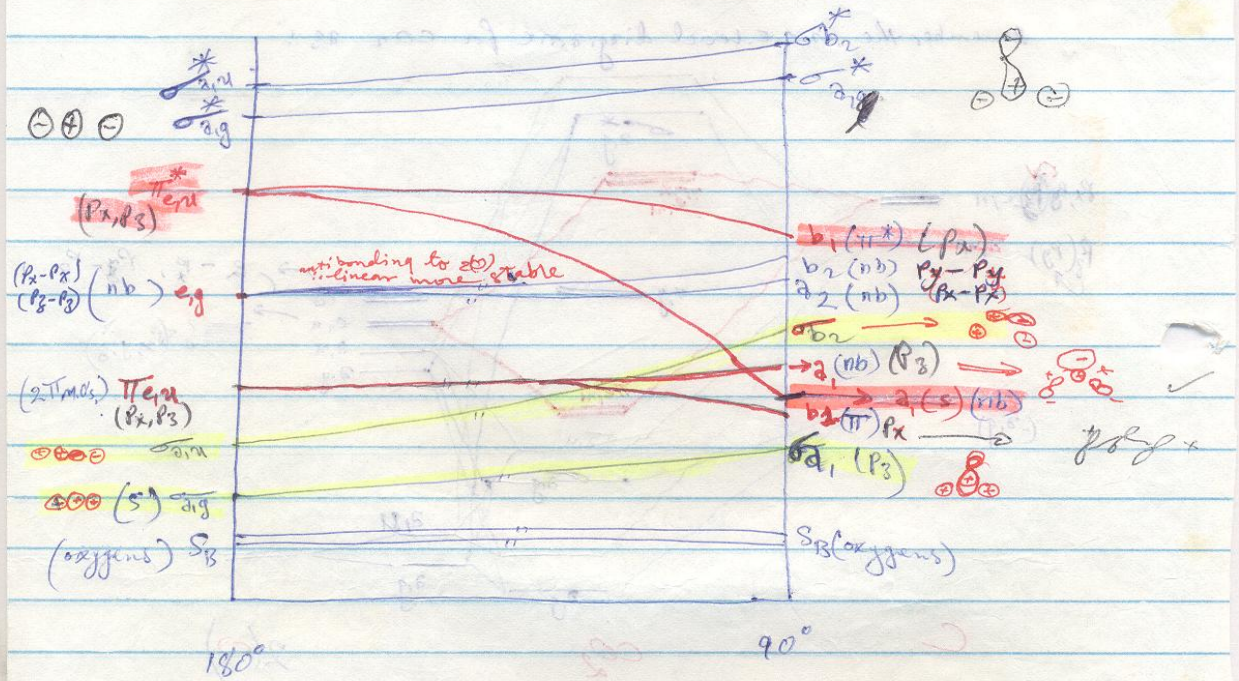
C CO_2 2(O)

b) Consider NO_2 NO_2 (90°) assuming 90°



NO_2 2(O)

Thus, the two M.O. Energy level diagrams may be now correlated in the Walsh Correlation Diagram as:



Thus, Walsh diagrams show the effect of bending the AB_2 on the energy levels of orbitals.

Correlation is made between M.O's resulting from same central atomic orbitals as: $\pi_{e,u}\{p_x, p_z\}$ ~ $b_1\pi(p_y)$ or $a_1 nb(p_x)$ etc.

Note that:

(i) $\sigma_{a_1g}(180°)$ correlates with $\sigma_{a_1}(90°)$ purely $p(z)$ character

∴ from Rule (1): $\sigma_{a_1g} - \sigma_{a_1}$ will be destabilized by bending

∴ Rule (2): $\sigma_{a_1g} - \sigma_{a_1}$ will be stabilized by bending, since it is bonding with respect to oxygens.

Rule (1) offsets Rule (2), but slightly prefers linear arrangement

(ii) $\sigma_{a_2u}(180°)$ correlates with $\sigma_{b_2}(90°)$ both have π characters

∴ Rule (1) is irrelevant

Rule (2): $(\sigma_{a_2u} - \sigma_{b_2})$ is destabilized by bending, because it is antibonding with respect to oxygens

iii) one of $\pi_{e,u}$ (180°) correlates with b_2 (90°) :
both are p characters, ∴ Rule(1) is irrelevant.
on bending, ($\pi_{e,u}$ — b_2) is stabilized by bending, since it is bonding with respect to oxygens.

iii) the other $\pi_{e,u}$ (180°) correlates with a_1 (90°) (n.b)
($\pi_{e,u}$ — a_1(n.b)) is bonding with respect to oxygens, ∴ must stabilize in bending (Rule 2) ✓
but from Rule (2) the π–B bonding character decreases on bending, ∴ stability decreases on bending ✓
∴ ($\pi_{e,u}$ — a_1(n.b)) destabilizes slightly on bending
Rule (1) is irrelevant, due to p characters (both $\pi_{e,u}$ and a_1(n.b) are coming from p_z orbitals of the central atoms in 180° & 90°. ✓

ii) the non-bonding e_g (180°) correlates with a_2 & b_2 (90°) ✓
both nonbonding.
e_g is nonbonding.
{ a_2 & b_2 are both antibonding to oxygens } Rule (2) ✓
{ a_2 & b_2 have p character } Rule (1) ✓
∴ (e_g — a_2) & (e_g — b_2) are destabilized by bending. ✓

iii) $\pi^*_{e,u}$ correlate with nonbonding a_1(s) and antibonding b_1^*
$\pi^*_{e,u}$ are p-character only, ✓
∴ ($\pi^*_{e,u}$ — a_1(s)) is from Rule (1) stabilized strongly by bending
($\pi^*_{e,u}$ — b_1^*) is not affected by Rule (1) (with p character), but from Rule (2), it is bonding with respect to oxygens, ∴ stabilized slightly by bending.

iii) $\sigma^*_{a,g}$ correlates with $\sigma^*_{a_1}$. $\sigma^*_{a_1}$ purely p (no s still) ✓
∴ from Rule (1) energy increases by bending.
from Rule (2) ($\sigma^*_{a,g}$ — $\sigma^*_{a_1}$) is antibonding to oxygens.
but Rule (1) predominates

viii) $(\sigma^*_{a_1u} - \sigma^*_{b_2})$ destabilized by bending, Due to Rule(2) antibonding with Oxygens

Now, we can use the Walsh diagram for studying e⁻ configurations & structures.

Considering Valency orbitals

a) Molecules containing 16 (or less) electrons must be linear, including S_R orbitals.

b) Molecules with 18 or 20 electrons would be bent since 2e⁻ will occupy $(\pi^*_{a_2u} - a_1, b_1)$.

c) 22 e⁻s give linear molecules since, the last 2 e⁻s go to $\sigma^*_{a_1g} - \sigma^*_{a_1}$

molecules	# Valency electrons	Walsh Prediction	observed bond angle
CO_2	16	linear	180°
N_2O, NO_2^+, N_3^-	16	linear	180°
NO_2	17	Bent	143°
O_3	18	Bent	117°
SO_2	18	Bent	119°
NO_2^-	18	Bent	115°
OF_2	20	Bent	101°
I_3^-, IO_2^-	22	linear	180°

ملاحظة: سؤال من طالب:

Why don't we use g & u subscripts in H_2O, NO_2, but we used them in BeH_2 & CO_2 ??

In C_{2v} group, there is no centre of inversion, so g & u are not needed, thus $2s$ & p_z belong to the same group represent.

In $D_{\infty h}$ group, there is centre of inversion, ∴ g & u are needed, thus, $2s$ & p_z don't belong to the same represent.

سؤال من عندي: لماذا الزاوية

OF_2 أكبر OCl_2

Note: O $\chi = 3.5$; $F = 4.1$; $Cl = 2.9$

good points

Question: which is more correct (for CO_2) to say; 2 localized π-M.O's., or 2 delocalized π-M.O's.?

Consider the π-electrons as e's in a one-dimensional potential well with $E_n = n^2h^2/8mL^2$

(i) localized: ∴ $n = 1$

∴ $E_1 = h^2/8mb^2$ where $b \equiv$ C—O bond length (lowest energy level)

four e's occupy the same energy levels, ignoring repulsion,

∴ $E_L \rightleftharpoons$ Total energy $= (4)E_1 = 4h^2/8mb^2$ (localized)

(ii) delocalized: first delocalized π-M.O's. is $2b$ long, and $n = 1$

∴ $E_1 = h^2/8m4b^2$

2nd delocalized π-M.O's is $2b$ long, $n = 2$

∴ $E_2 = 4h^2/8m4b^2$

$E_D \rightleftharpoons$ total π-energy $= 2E_1 + 2E_2 = \frac{2h^2}{8m4b^2} + \frac{8h^2}{8m4b^2} = \frac{10h^2}{32mb^2}$ (delocalized)

∴ $E_L / E_D = 1.6$ even with exclusion of pairing energy

∴ delocalized is more stable than localized