Chapter 5

Huckel Aromaticity

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D.S. Urch, Orbitals & Symmetry,

SIMPLE HÜCKEL THEORY

(W.L. Jolly, "Modern Inorganic Chemistry, pp. 96 – 102 & pp. 129 – 133).
(1st edition)

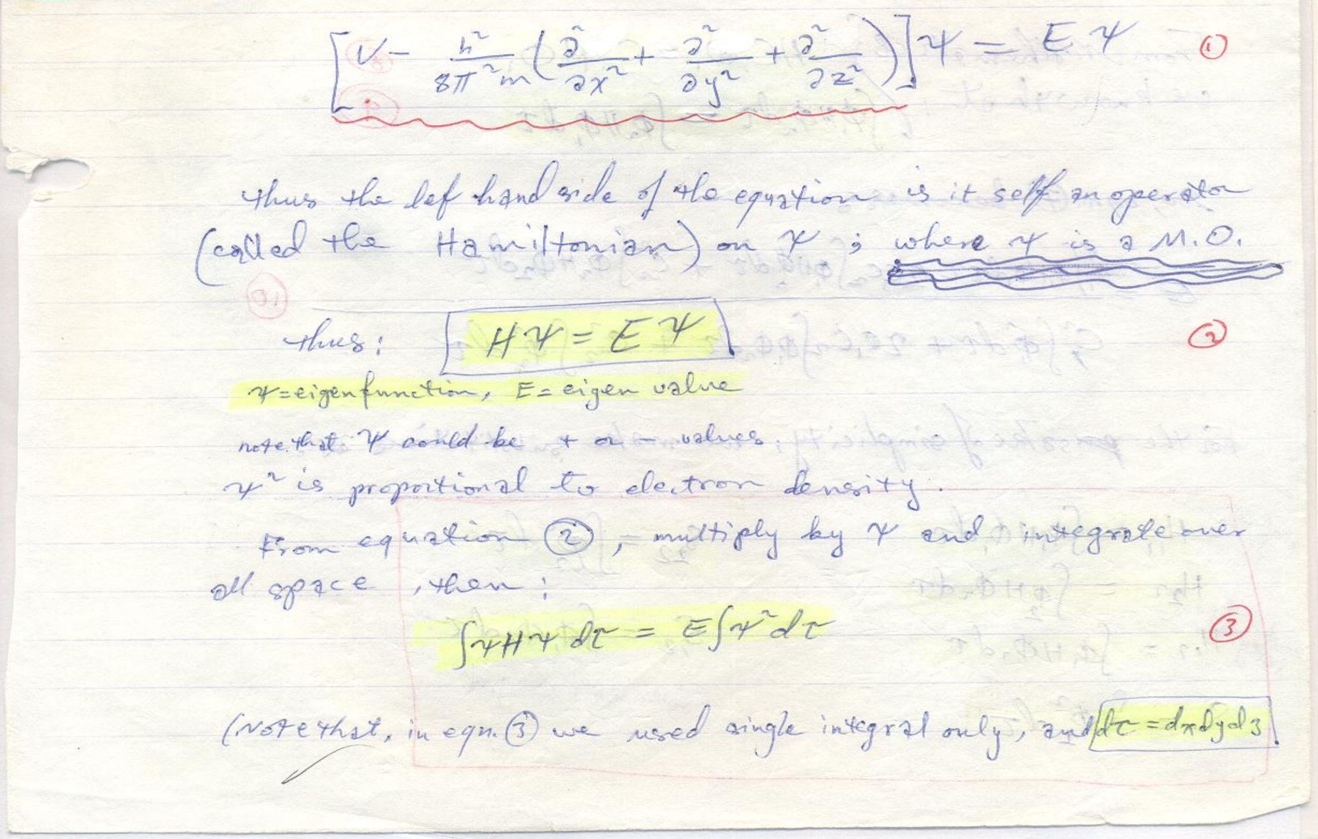
Simple L.C.A.O. (A closer look) and the hamiltonian operator

considering a M.O. as a L.C.A.O., thus the M.O. is affected by more than one ~~sto~~ nucleus.

However, the valence $\bar{e}$ circulates among the nuclei, but it will at any one time be much closer to one nucleus than any other, and the M.O. wave function will be fairly well represented by a valence atomic orbital for that nucleus.

Consider M.O's. & their energies for a single valence $\bar{e}$ associated with two atoms, such as H_2^+, Li_2^+ or LiH^+

Shrödinger equation is:



$$\left[V - \frac{h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\right]\psi = E\psi \qquad ①$$

thus the lef hand side of the equation is it self an operator (called the Hamiltonian) on ψ ; where ψ is a M.O.

thus: $$\boxed{H\psi = E\psi} \qquad ②$$

ψ = eigenfunction, E = eigen value

note that ψ could be + or − values.

ψ^2 is proportional to electron density.

From equation ②, multiply by ψ and integrate over all space, then:

$$\int \psi H \psi \, d\tau = E \int \psi^2 d\tau \qquad ③$$

(Note that, in eqn. ③ we used single integral only, and $\boxed{d\tau = dx\,dy\,dz}$

$$\therefore \quad E = \frac{\int \psi H \psi \, d\tau}{\int \psi^2 d\tau} \qquad ④$$

Remember that ψ is a molecular orbital wave function, resulting from linear combination of two atomic orbitals ϕ_1 & ϕ_2

$$\therefore \quad \psi = C_1\phi_1 + C_2\phi_2 \qquad ⑤$$

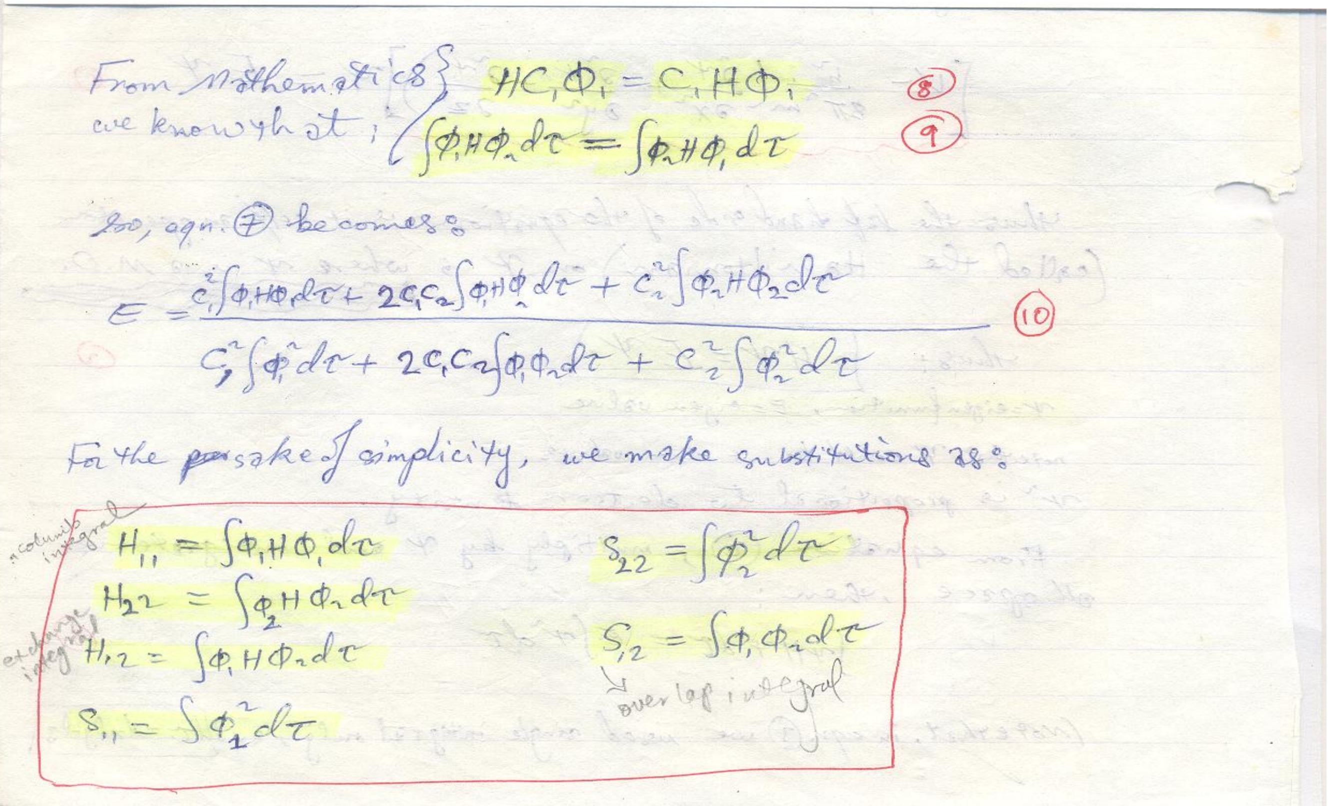
$\boxed{C_1 \,\&\, C_2 \text{ are coefficients to be determined}}$

From equations ④ & ⑤, then:

$$E = \frac{\int (c_1\phi_1 + c_2\phi_2) H (c_1\phi_1 + c_2\phi_2) d\tau}{\int (c_1\phi_1 + c_2\phi_2)^2 d\tau} \qquad ⑥$$

$$= \frac{\int (c_1\phi_1 H c_1\phi_1 + c_1\phi_1 H c_2\phi_2 + c_2\phi_2 H c_1\phi_1 + c_2\phi_2 H c_2\phi_2) d\tau}{\int (c_1^2\phi_1^2 + 2c_1c_2\phi_1\phi_2 + c_2^2\phi_2^2) d\tau} \qquad ⑦$$

From mathematics we know that;
$$\begin{cases} HC_1\phi_1 = C_1 H\phi_1 & ⑧ \\ \int \phi_1 H \phi_2 \, d\tau = \int \phi_2 H \phi_1 \, d\tau & ⑨ \end{cases}$$



From Mathematics we know that; $\left\{ \begin{array}{l} HC_1\Phi_1 = C_1 H\Phi_1 \\ \int \phi_1 H \phi_2 \, d\tau = \int \phi_2 H \phi_1 \, d\tau \end{array} \right.$ ⑧ ⑨

So, eqn. ⑦ becomes:

$$E = \frac{c_1^2\int \phi_1 H \phi_1 \, d\tau + 2c_1c_2\int \phi_1 H \phi_2 \, d\tau + c_2^2\int \phi_2 H \phi_2 \, d\tau}{c_1^2\int \phi_1^2 \, d\tau + 2c_1c_2\int \phi_1 \phi_2 \, d\tau + c_2^2\int \phi_2^2 \, d\tau} \quad ⑩$$

For the ~~pur~~ sake of simplicity, we make substitutions as:

coulumb integral

$H_{11} = \int \phi_1 H \phi_1 \, d\tau$ $\qquad$ $S_{22} = \int \phi_2^2 \, d\tau$

$H_{22} = \int \phi_2 H \phi_2 \, d\tau$

exchange integral

$H_{12} = \int \phi_1 H \phi_2 \, d\tau$ $\qquad$ $S_{12} = \int \phi_1 \phi_2 \, d\tau$

overlap integral

$S_{11} = \int \phi_1^2 \, d\tau$

So, eqn. (10) becomes:

$$E = \frac{C_1^2 H_{11} + 2C_1C_2H_{12} + C_2^2 H_{22}}{C_1^2 S_{11} + 2C_1C_2S_{12} + C_2^2 S_{22}} \qquad (11)$$

If we differentiate eqn. (11) when minimum value of E is used, as;

$$\left(\frac{\partial E}{\partial c_1}\right)_{c_2} = 0 \quad \text{and} \quad \left(\frac{\partial E}{\partial c_2}\right)_{c_1} = 0$$

differentiation of eqn. (11) yields:

$$C_1(H_{11} - ES_{11}) + C_2(H_{12} - ES_{12}) = 0 \qquad (12)$$

$$C_1(H_{12} - ES_{12}) + C_2(H_{22} - ES_{22}) = 0 \qquad (13)$$

Equations (11) & (12) are called secular equations

A solution to these eqns. (11 + 12) can be expressed in terms of the Secular Determinant:

$$\begin{vmatrix} (H_{11} - ES_{11}) & (H_{12} - ES_{12}) \\ (H_{12} - ES_{12}) & (H_{22} - ES_{22}) \end{vmatrix} = 0 \qquad (14)$$

where H_{11} + H_{22} are called "Coulomb Integrals".

From eqn. (4) a coulumb integral is approximately, ~~the~~ Coulomb integral is approximately equl to the energy of an electron in the valence ~~shell~~ atomic orbital ((α)). This is logical for a neutral molecule, where e–e ~~rep~~ and nucleus–nucleus repulsions ~~are~~ compensate.

thus, we may write:

$$H_{11} = \alpha_1 \quad \text{and} \quad H_{22} = \alpha_2$$

The term H_{12} is called "Exchange Integral", which is essentially the energy of interaction of two atomic orbitals, (β).

Both α + β have negative values, with reference to original ground level (zero level).

Assuming that the atomic wave functions $\phi_1 + \phi_2$ of equation ⑤ are normalized, then:

$$S_{11} = \int \phi_1^2 \, d\tau = S_{22} = \int \phi_2^2 \, d\tau = 1 \qquad ⑮$$

Equation ⑮ states that the probability of finding an electron in the orbital is exactly unity.

The term S_{12} is called "overlap integral" because it is a measure of the extent to which orbitals 1 & 2 overlap, for simplicity, S_{12} is written as S.

Thus, equation 14 becomes:

$$\begin{vmatrix} \alpha_1 - E & \beta - ES \\ \beta - ES & \alpha_2 - E \end{vmatrix} = 0 \qquad ⑯$$

In case of homonuclear diatomic molecules (H_2^+), we equal $\alpha_1 = \alpha_2 = \alpha$

thus, equation ⑯ becomes:

$$(\alpha - E)^2 = (\beta - ES)^2 \qquad ⑰$$

thus, two solutions are:

$$\alpha - E = -(\beta - ES) \rightsquigarrow E = (\alpha + \beta)/(1+S) \qquad ⑱$$

2nd $\alpha - E = +(\beta - ES) \rightsquigarrow E = (\alpha - \beta)/(1-S)$ ⑲

If we substitute equations ~~⑱ & ⑲~~ in equations (~~16~~) 20

we get: $C_1(\alpha - E) + C_2(\beta - ES) = 0$

From eqn. ⑫

or:

$$C_1 = -\frac{(\beta - ES)}{(\alpha - E)} C_2 \qquad ⑳$$

from eqn. no. 12

thus, from equation ⑳ if $E = (\alpha + \beta)/(1+S)$ (eqn. 18),

$$\therefore C_1 = \left(\frac{-\beta + \left(\frac{\alpha+\beta}{1+S}\right)S}{\alpha - \frac{\alpha+\beta}{1+S}}\right) C_2 = \frac{\frac{\cancel{-\beta} - \beta S + \alpha S \cancel{+\beta}}{1+S}}{\frac{\alpha + \alpha S - \alpha - \beta}{1+S}} C_2 = \left(\frac{\cancel{\alpha S - \beta}}{\cancel{\alpha S - \beta}}\right) C_2 = C_2$$

then $C_1 = C_2$ ㉑

and, from eqn. ⑳, if $E = (\alpha - \beta)/(1-S)$ (eqn. 19),

then $C_1 = -C_2$ ㉒

thus, the M.O. wave equation (eqn. 5) may be written as:

$$\Psi = C_1\Phi_1 \pm C_1\Phi_2 \qquad ㉓$$

The question is: How can we find C_1 ??

we normalize the wave function (23) as: ⇐ لاحظنا وأول هذه المربعات

$$\boxed{\psi = c_1\phi_1 \pm c_2\phi_2}$$

$$\int \psi^2 d\tau = c_1^2 \int \phi_1^2 d\tau \pm 2c_1^2 \int \phi_1\phi_2 d\tau + c_1^2 \int \phi_2^2 d\tau = 1$$

from defining eqns. ( ) $\therefore \int \psi^2 d\tau = c_1^2 S_{11} \pm 2c_1^2 S + c_1^2 S_{22} = 1$

Hence: $C_1^2(2 \pm 2S) = 1$

$$\therefore C_1 = \pm \frac{1}{\sqrt{2 \pm 2S}} \qquad (24)$$

thus, equation (23) becomes:

$$\psi_{bonding} = \frac{1}{\sqrt{2+2S}}(\phi_1 + \phi_2) \qquad (25)$$

and: $$\psi_{antibonding} = \frac{1}{\sqrt{2-2S}}(\phi_1 - \phi_2) \qquad (26)$$

If these functions are squared, then the valence-electron density is obtained as:

$$\psi^2_{bonding} = \frac{1}{2+2S}(\phi_1^2 + \phi_2^2 + 2\phi_1\phi_2) \qquad (27)$$

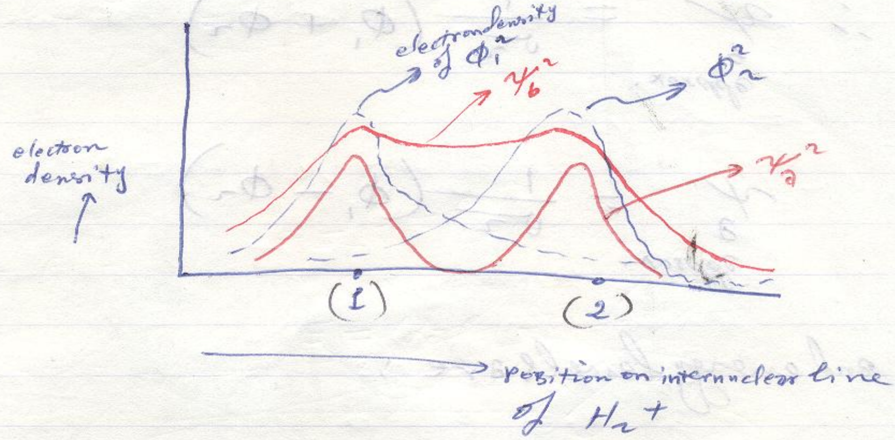
and $$\psi^2_{anti.} = \frac{1}{2+2S}(\phi_1^2 + \phi_2^2 - 2\phi_1\phi_2) \qquad (28)$$

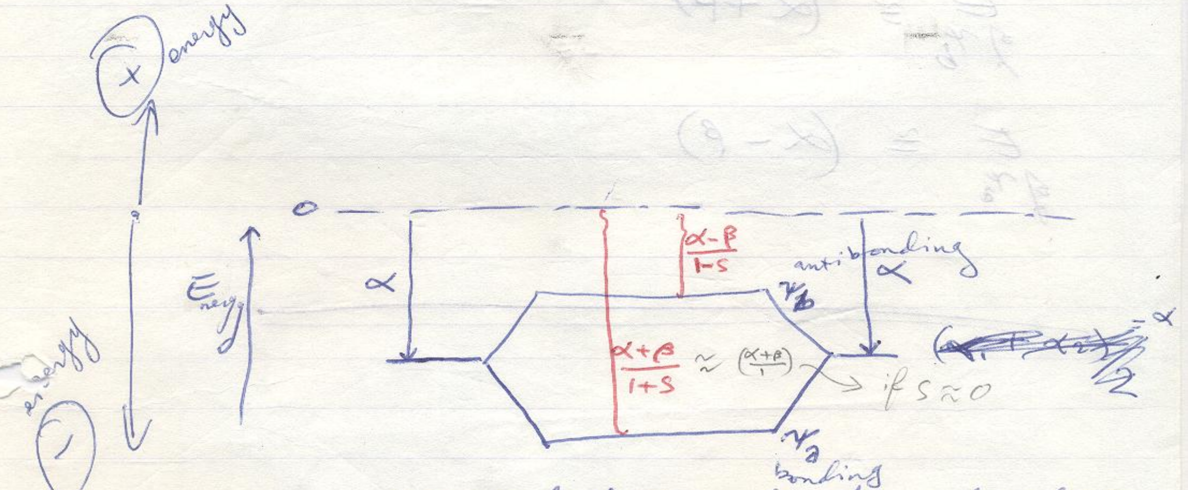
$\psi^2_{Bonding}$ → shows increase in e-density between the two nuclei thus stabilization occurs $\therefore \psi_b$ is bonding M.O.

energy level of ψ_B is

$$E = (\alpha + \beta)/(1+S) \qquad (29)$$

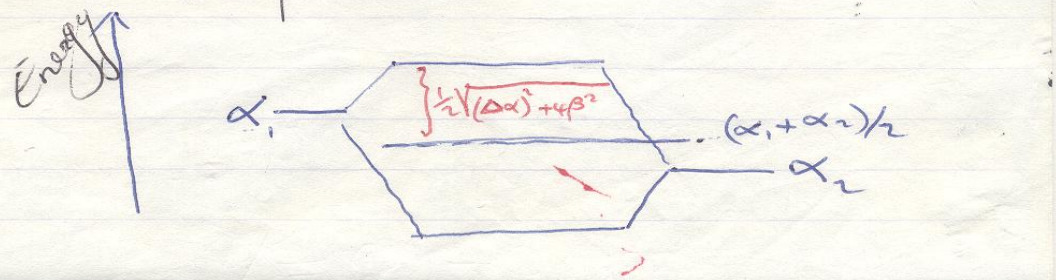
$\psi_{\text{anti/bonding}}$ shows a decrease in e^--density between nuclei,
∴ unstable ψ_a (antibonding)
with $E = (\alpha - \beta)/(1 - S)$





M.O. energy level diagram for homonuclear diatomic

but for heteronuclear diatomic molecule



S is always small (0.2 — 0.3 generally)
so, approximated to be zero,

$$\therefore \underset{\text{approx.}}{\psi_b} = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$

$$\underset{\text{approx.}}{\psi_a} = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

and energy levels are:

$$E_{\text{of } \psi_b} \cong (\alpha + \beta)$$

$$E_{\text{of } \psi_a} \cong (\alpha - \beta)$$

Homework: Construct the Secular Det. for π-bonding in C_3H_3 and C_6H_6 systems as we did for diatomic molecules

back to Simple Hückel Theory:

one of applications of $\overset{\text{simple}}{\text{M.O.T.}}$ is to study π-bonding in cyclic aromatic hydrocarbons, C_nH_n as was carried out by Hückel.

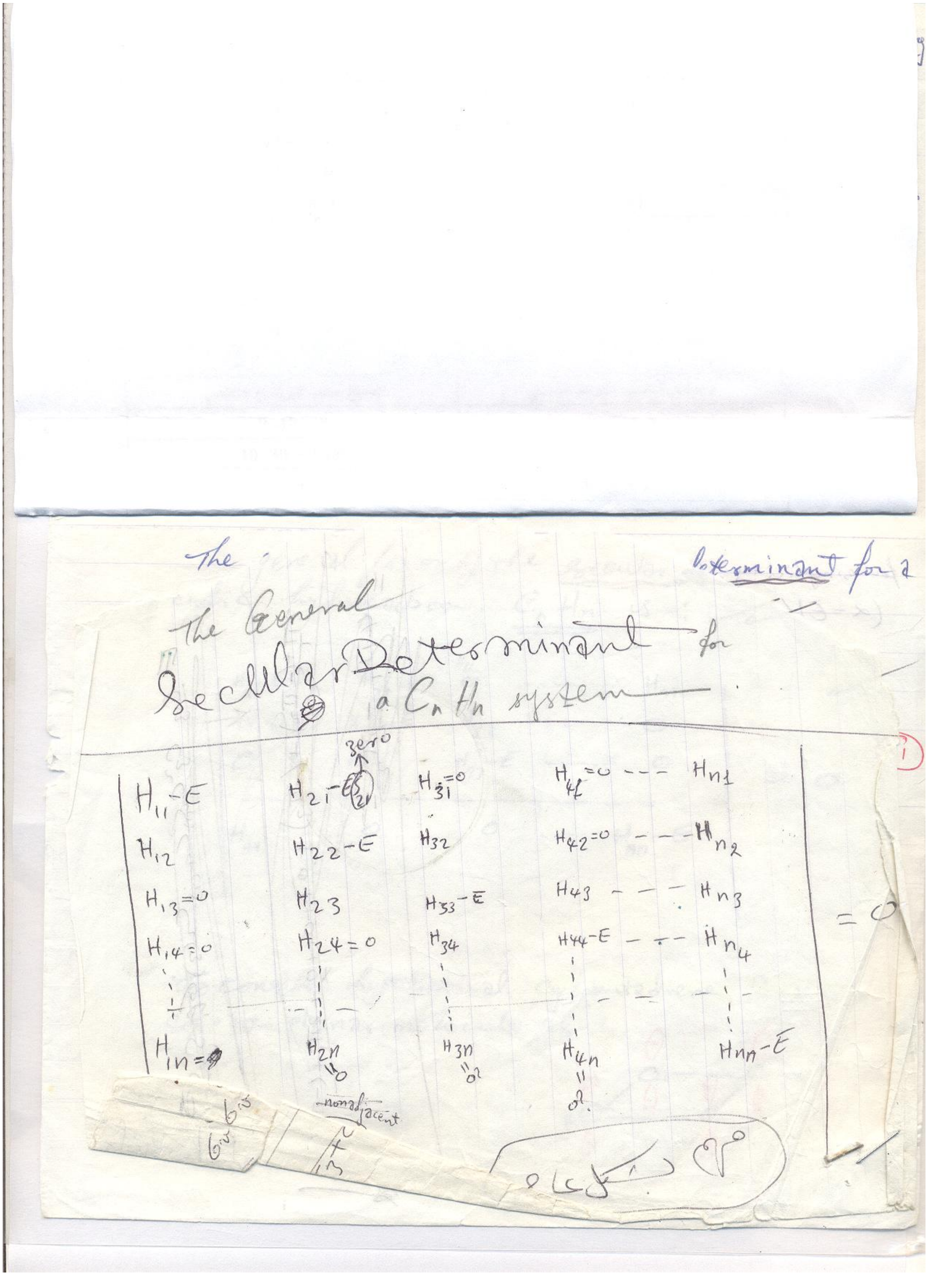
Aromatic hydrocarbons are planar, thus, σ M.O's. & π M.O's. are separated in discussions.

In simple Hückel theory, we consider only π M.O's., derived from $\underline{\underline{n}}$ orbitals of pπ symmetry

approximations are:

$\int \phi_i \phi_j d\tau = S_{ij} = 0$, and $\overset{\int \phi_i H \phi_j d\tau}{H_{ij}} = 0$ except when the $\underline{\underline{i}}$th & jth pπ orbitals are on adjacent atoms.

(H_{13}, H_{24}, —— are all zero).



The Determinant for a

The General Secular Determinant for a C_nH_n system

①

$$\left|\begin{array}{cccccc} H_{11}-E & H_{21}-E\overset{\substack{\text{zero}\\ \uparrow}}{S_{21}} & H_{31}=0 & H_{41}=0 & \cdots & H_{n1} \\ H_{12} & H_{22}-E & H_{32} & H_{42}=0 & \cdots & H_{n2} \\ H_{13}=0 & H_{23} & H_{33}-E & H_{43} & \cdots & H_{n3} \\ H_{14}=0 & H_{24}=0 & H_{34} & H_{44}-E & \cdots & H_{n4} \\ \vdots & \vdots & \vdots & \vdots & & \vdots \\ H_{1n}= & H_{2n}=0 & H_{3n}=0? & H_{4n}=0? & & H_{nn}-E \end{array}\right| = 0$$

nonadjacent

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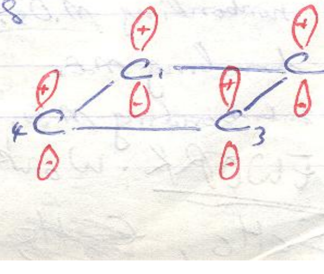
~~(H_{13}, H_{24}, ... are all zero)~~.

The general form of the secular determinant for a cyclic hydrocarbon C_nH_n is:

$$\begin{vmatrix} H_{11}-E & H_{21} & \overset{H_{31}}{0} & \cdots & H_{n1} \\ H_{12} & H_{22}-E & H_{32} & \cdots & 0 \\ 0 & H_{23} & H_{33}-E & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ H_{1n} & 0 & 0 & \cdots & H_{nn}-E \end{vmatrix} = 0 \quad ③①$$

To consider hypothetical cyclobutadiene C_4H_4, square planar molecule as



We write:

$$\Psi = C_1\Phi_1 + C_2\Phi_2 + C_3\Phi_3 + C_4\Phi_4$$

as ~~in the~~ previously, we make substitutions as

$H_{ii} = \alpha$, ✓ ✓

if ith & jth are adjacent, then $H_{ij} = \beta$

the secular determinant for π orbitals of C_4H_4 then becomes:

$$\begin{vmatrix} \overset{H_{11}}{\alpha - E} & \overset{\to H_{12}}{\beta} & \overset{\to H_{13}}{0} & \overset{\to H_{14}}{\beta} \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \underset{H_{44}}{\alpha - E} \end{vmatrix} = 0$$

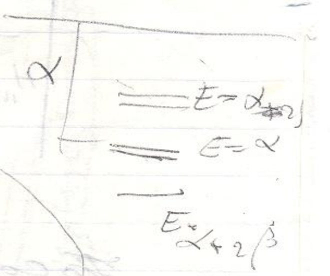
for simplicity, divide by β, and replace $(\alpha - E)/\beta$ by x where $\boxed{x = \frac{\alpha - E}{\beta}}$

✓

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

$\therefore\ x^2(x^2 - 4) = 0$??

with roots $x = -2, +0, -0, +2$



$\therefore$ E ~~for~~ two nonbonding M.O's, with energy $= \alpha$
one bonding M.O. with energy $= \alpha + 2\beta$
one antibonding M.O. with energy $= \alpha - 2\beta$

HOMEWORK: Work out Secular determinant for CH ~~C_6H_6~~ systems

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} =$$

$$+x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} + 0 \Big| \quad \Big| -1 \begin{vmatrix} 1 & x & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{vmatrix} =$$

✓

for $C_3H_3^+$

$$\begin{vmatrix} H_{11}-E & H_{12} & H_{13} \\ H_{12} & H_{22}-E & H_{32} \\ H_{13} & H_{23} & H_{33}-E \end{vmatrix} = 0 \equiv \begin{vmatrix} \alpha-E & \beta & \beta \\ \beta & \alpha-E & \beta \\ \beta & \beta & \alpha-E \end{vmatrix} = 0$$

$$\boxed{x = \frac{\alpha-E}{\beta}}$$

So: $$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$

$$x(x^2-1) - \overset{?,}{\boxed{1\overset{(1-x)}{(x-1)}}}^{?} + 1\overset{(1-x)?}{(\cancel{x}-\cancel{x})} = 0$$

$$x(x^2-1) - x + 1 + 1 - x = 0$$

$$(x-1)(x-1)(x+2) = 0 \quad ✓$$

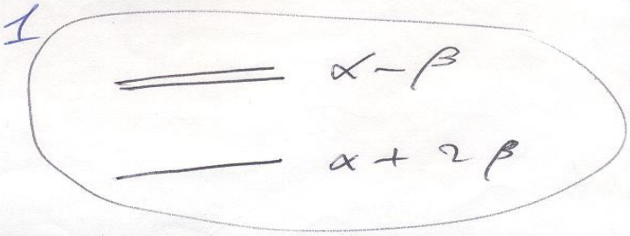
$$x = -2, +1, +1$$

$$\frac{(\alpha-E)}{\beta} = -2 \qquad E = \alpha + 2\beta$$

$$\frac{\alpha-E}{\beta} = 1 \qquad E = \alpha - \beta$$

$$\frac{\alpha-E}{\beta} = 1 \qquad = \alpha - \beta$$

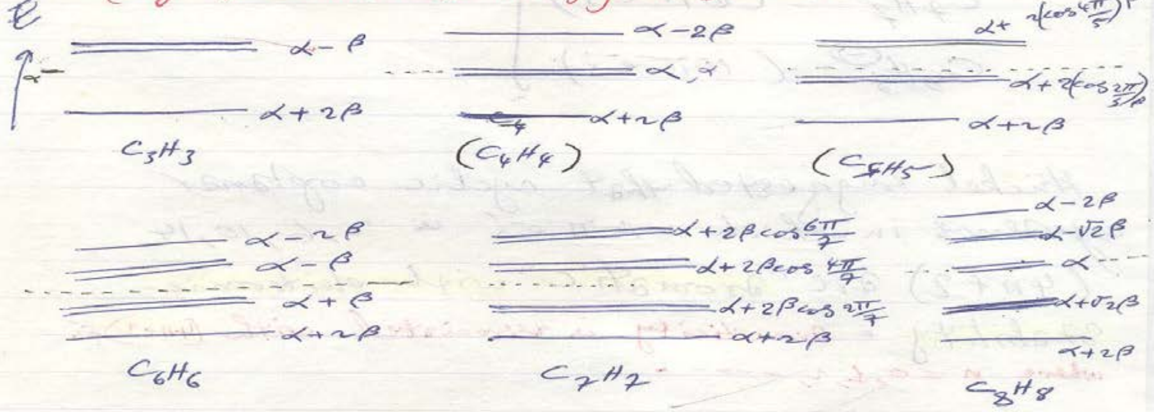
three different energy levels



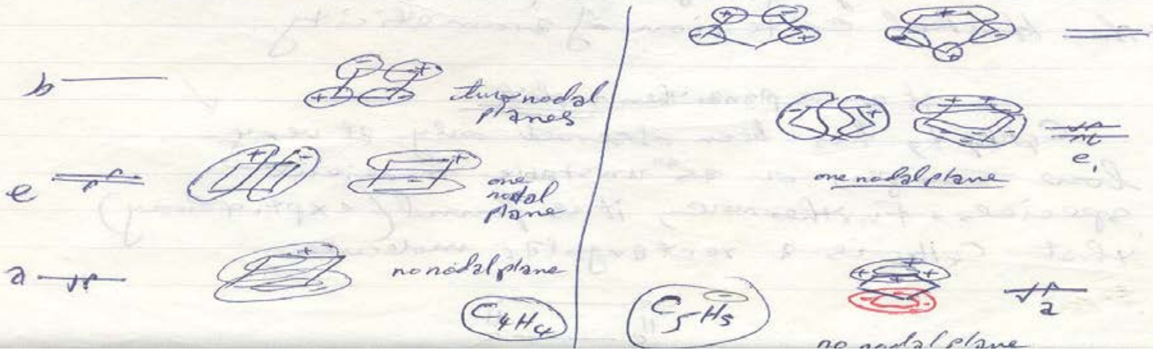
for C_nH_n molecules, the π-energy level diagram must always have strongly bonding nondegenerate level and one or more doubly degenerate levels lying at higher energyies, ~~wheen~~ and when $\underline{\underline{n}}$ is even number, a strongly antibonding nondegenerate level.

thus for $\underline{\underline{C_nH_n}}$ ($n = 3, 4, 5, 6, 7$ & 8) the M.O. energy level diagrams are shown as:

(only if aromatic planar conjugated systems)



consider ~~the~~ as examples, the π M.Os. of C_4H_4 and $C_5H_5^-$ molecules:



Note, that: If ~~the~~ all M.O's. at or below the "Centre of Gravity" of the levels are filled, then the system is stable.

Thus, $CH_3^{\oplus}$, ($2\pi\ \bar{e}$'s),

$C_5H_5^{\ominus}$, ($6\pi\ \bar{e}$'s)

C_6H_6, ($6\pi\ \bar{e}$'s)

$C_7H_7^{\oplus}$ ($6\pi\ \bar{e}$'s)

$C_8H_8^{\circleddash 2}$ ($10\pi\ \bar{e}$'s)

} are stable species.

Hückel suggested that cyclic coplanar systems in which # $\pi\ \bar{e}$'s is 2, 6, 10, 14 __ ($4n+2$) are "aromatic" with electronic stability. Aromaticity is associated with $(4n+2)\bar{e}$'s where $n = 0, 1, 2, ----$.

(don't confuse n with $\underline{\underline{n}}$ of C_nH_n)

so ~~the~~ called relation of cyclic coplanar ($4n+2$) rule or the Hückel criterion of aromaticity.

if square planar then triplet ✓

C_4H_4 has been observed only at very low Temps., or as an unstable transient species. Furthermore, it is found (expt. & theory) that C_4H_4 is a rectangular molecule

with two-or-less localized double bonds.

(thus, it is distorted from square planar structure) and the doubly degenerate level is split, ~~into~~ and the stabilization occurs by having the two unpaired e^-'s pair up in the lower of the split levels.

the square form of C_4H_4 can be stabilized when complexation to Transition metals occurs $C_4H_4Fe(CO)_3$.

C_8H_8 also should have a triplet if exists in the planar form, with all C—C bonds equivalent. In fact, it is conjugated but nonplanar molecule. If reduced, $C_8H_8^{-2}$, then it becomes planar aromatic, forming sandwich complexes

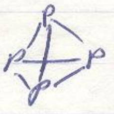
sas: $(C_8H_8^{-2})\,U^{+4}(C_8H_8^{-2})$]

Hückel theory also applies to inorganic molecules, such as P_4, ignoring the lone pairs at phosphorous atoms:

thus, the hypothetical square planar P_4 is unstable.

otherwise, it must be a rectangular configuration

Actually, P_4 is in Td structure



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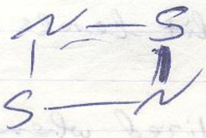
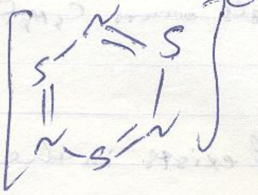
other examples are also known:

S_2N_2, $S_3N_3^-$, $S_4N_3^+$ and $S_5N_5^+$ are known to be planar.

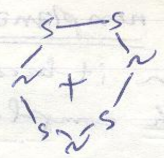


square planar ($6\pi e^-$'s)



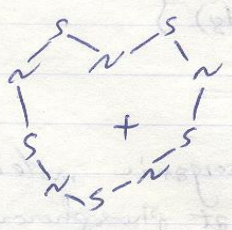
hexagonal planar ($10\pi e^-$'s)

$S_4N_3^+$

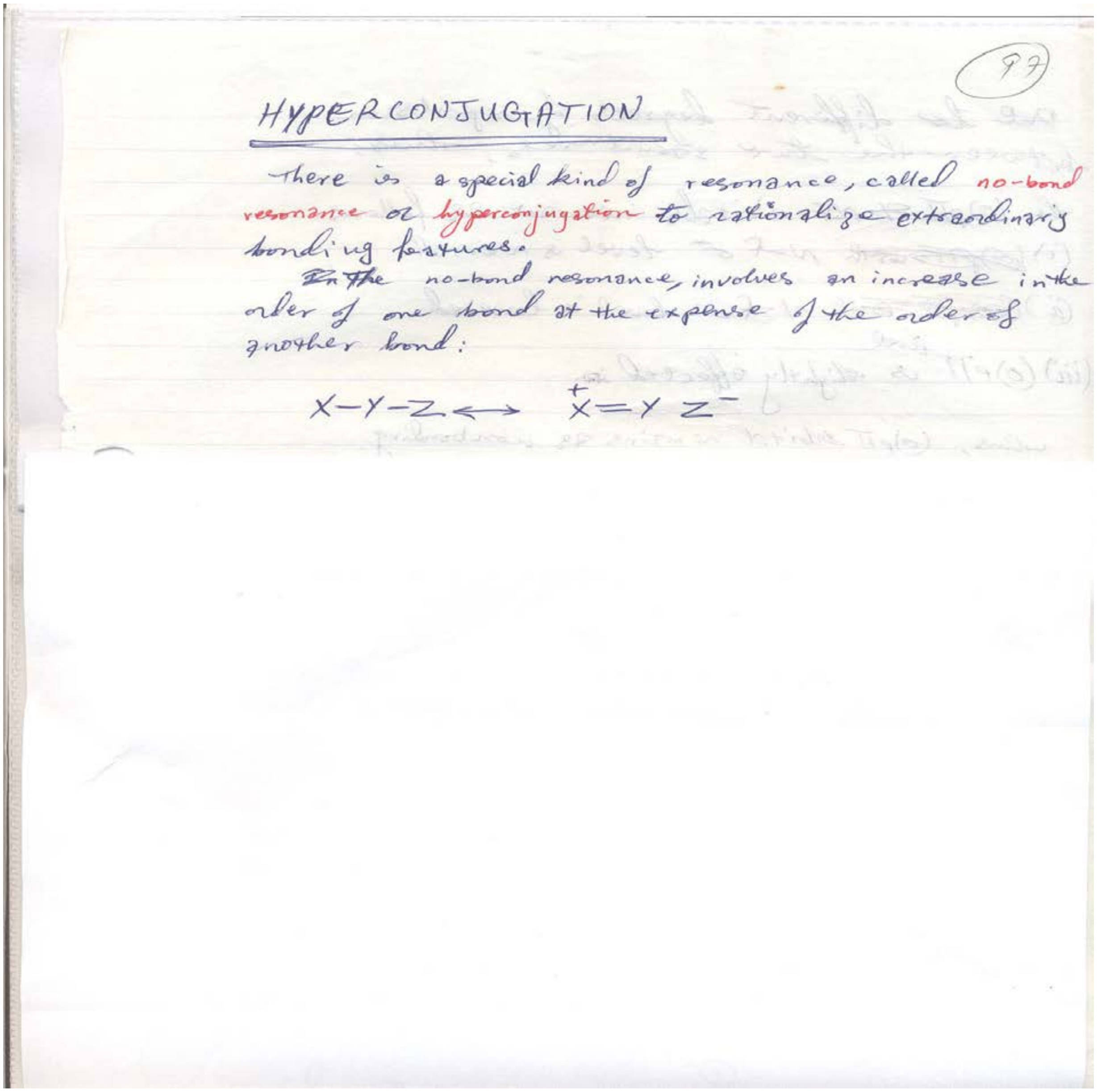


($10\pi e^-$'s)

$S_5N_5^+$



($14\pi e^-$'s)



HYPERCONJUGATION

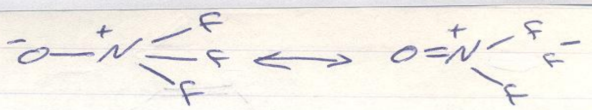
There is a special kind of resonance, called no-bond resonance or hyperconjugation to rationalize extraordinary bonding features.

~~In~~ the no-bond resonance, involves an increase in the order of one bond at the expense of the order of another bond:

$$X{-}Y{-}Z \longleftrightarrow \overset{+}{X}{=}Y\ Z^{-}$$

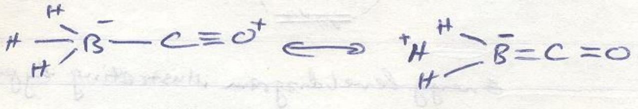
Example: ONF$_3$

http://www.najah.edu/za/adver/ramadanTimeTab.htm 9/16/2007



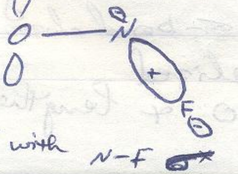
since N–F bonds appear to be abnormally long.

In BH_3/CO interaction is unexpectedly strong acid base interaction, explained by hyperconj.

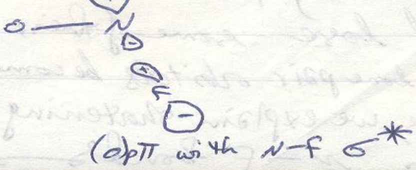


Hyperconjugation may be defined generally as the interaction within a molecule of a π-system with a σ-system.

Consider ONF_3 with nonbonding $p\pi$ orbitals on (O) atom; the nonbonding $p\pi$ of (O) may interact with bonding + antibonding M.O's. of N–F bonds.



$(O)p\pi$ with $N{-}F$ σ^*



$(O)p\pi$ with $N{-}F$ σ^*

Due to different degrees of repulsion between the two structures, thus;

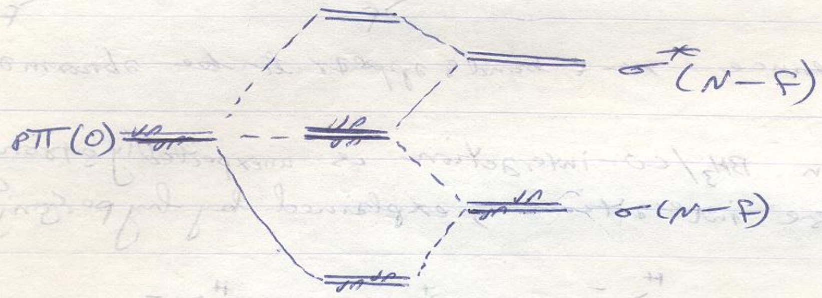
the (O)$p\pi$ ~~&~~ N-F orbitals interact as follows:

(i) ~~(O)$p\pi$ with~~ N-F σ^* level is raised

(ii) ~~(O)$p\pi$~~ with N-F σ level is lowered

(iii) (O)$p\pi$ level is slightly affected

thus, (O)$p\pi$ orbital remains as nonbonding.



Energy level diagram illustrating hyperconjugation in ONF₃, to give:

(i) Note that there ~~lowest~~ is a net stabilization of energy for the whole system, taking place.

(ii) lowest orbitals (derived from (O) pπ + N–F σ orbitals) aquire considerable N—O π-bonding and lose some of their N–F σ-bond character

(iii) (O) lone pair orbitals become delocalized

(iv) thus, we explain shortening of N—O + lengthening of N—F bonds.