STEFANO CURTAROLO

- MULTIATOMS
- LCAO
- 2 ATOMS
- 4 ATOMS
- DEBYE-HUCKEL

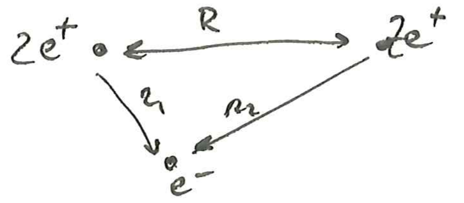
M1 - M16

H1 - H2

MULTIATOMS (MOLECULES)

LCAO

1e ⇒ 2 nuclei



H_2^+

$$V(r_1, r_2, R) = \mp e^2\left[-\frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}\right] \Rightarrow$$

FROZEN IONS
BORN–OPPENHEIMER
R constant ⇒ with C.M.
electrons follow ⇒

$\hookrightarrow E_{mol} = E_{el}(R) + \underbrace{\frac{e^2}{R}}_{\text{nuclei}}$

$$V(r_1, r_2) = e^2\left[-\frac{1}{r_1} - \frac{1}{r_2}\right] \Rightarrow$$

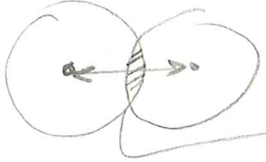
↓ function of R because $\vec{r}_2 = f(\vec{r}_1, \vec{R})$

$a_0 \rightarrow \frac{a_0}{Z}$

LCAO : Linear Combination Atomic Orbitals

ϕ_1 = wavefunction of atom 1 ⇒ GS $= \frac{1}{\sqrt{\pi a_0^3}} e^{-r_1/a_0}$ $1s_1$

ϕ_2 = wavefunction of atom 2 ⇒ GS = ↗



→ superposition (R)

R↓, super ↑ , R↑, superpos ↓ exponentially

take real for simplicity

$\Psi = c_1\phi_1 + c_2\phi_2$ ⇒ to normalize

$\hat{H}\Psi = E\Psi$ $\quad H|\psi\rangle = E|\psi\rangle$

$$\bar{E} = \frac{\int \Psi^* \hat{H} \Psi \, dV}{\int \Psi^* \Psi \, dV} = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} =$$

$$= \frac{\int (c_1\phi_1^* + c_2\phi_2^*) \hat{H} (c_1\phi_1 + c_2\phi_2) \, dV}{\int (c_1\phi_1^* + c_2\phi_2^*)(c_1\phi_1 + c_2\phi_2) \, dV} \Rightarrow$$

COULOMB INTEGRALS $H_{ii} \equiv \int \phi_i^* \hat{H} \phi_i \, dV$

BOND INTEGRAL $H_{ij} \equiv \int \phi_i^* H \phi_j \, dV$ } for numerator

(SUPERPOSITION) OVERLAP INTEGRAL $S_{ij} = \int \phi_i^* \phi_j \, dV$ } for DEN

$S_{ii} = 1$ (normalisation)

$$\Rightarrow E = \frac{c_1^2 H_{11} + c_2^2 H_{22} + c_1 c_2 \overbrace{(H_{12} + H_{21})}^{\text{same for simetry}}}{c_1^2 + c_2^2 + c_1 c_2 (S_{12} + S_{21})}$$

$H_{12}(R \to \infty) \to 0$

$S_{12}(R \to \infty) \to 0$

$$E_{LCAO} = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 + c_2^2 + 2c_1 c_2 S_{12}}$$

Variational principle
solution of the
problem

$\left(\frac{\delta E}{\delta \psi} = 0 \right) \Rightarrow$ minimize E over all possible choices of ψ (guesses)

$$\Rightarrow \frac{\partial E}{\partial c_1} = \frac{\partial E}{\partial c_2} = 0 \quad , \text{minimize}$$

$$\frac{\partial E}{\partial c_1} = 0 \Rightarrow \frac{1}{D}\frac{\partial N}{\partial c_1} - \frac{N}{D^2}\frac{\partial D}{\partial c_1} = 0 \quad * D \Rightarrow \frac{\partial N}{\partial c_1} - E\frac{\partial D}{\partial c_1} = 0$$

$$\Rightarrow \cancel{2}c_1 H_{11} + \cancel{2}c_2 H_{12} - E(\cancel{2}c_1 + \cancel{2}c_2 S_{12}) = 0$$

$$\begin{cases} c_1(H_{11} - E) + c_2(H_{12} - ES_{12}) = 0 \\ c_1(H_{12} - ES_{12}) + c_2(H_{22} - E) = 0 \end{cases}$$

and $\frac{\partial E}{\partial c_2} = 0$ 1≤ ?

$H = H_{11} + H_{22}$ COULOMB is identical for H_2^+

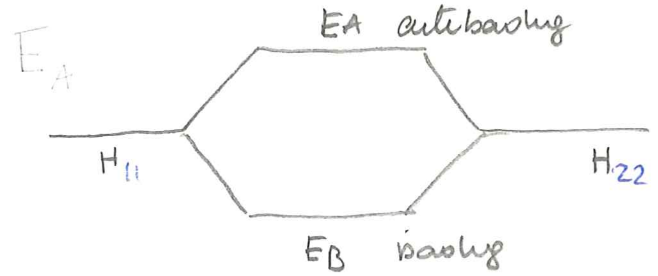
$$\Rightarrow \underbrace{\begin{bmatrix} (H_{11} - E) & (H_{12} - ES_{12}) \\ (H_{12} - ES_{12}) & (H_{22} - E) \end{bmatrix}}_{} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = 0$$

det( ) = 0
second order
equation
2 solution

$$E_A = H + \left(\frac{H_{12} - HS_{12}}{1 + S_{12}} \right) \quad \uparrow \; c_1 = -c_2$$

$$E_B = H - \left(\frac{H_{12} - HS_{12}}{1 - S_{12}} \right) \quad \downarrow \; c_1 = c_2$$

⇒

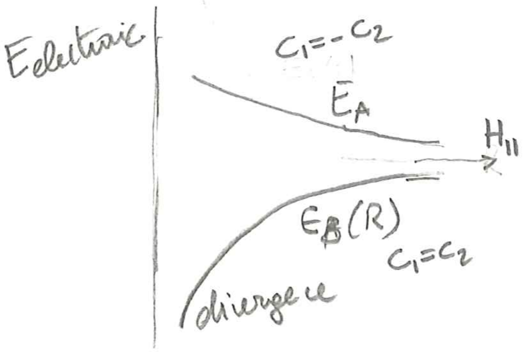


$H_{12}(R \to \infty) \to 0$

$S_{12}(R \to \infty) \to 0$

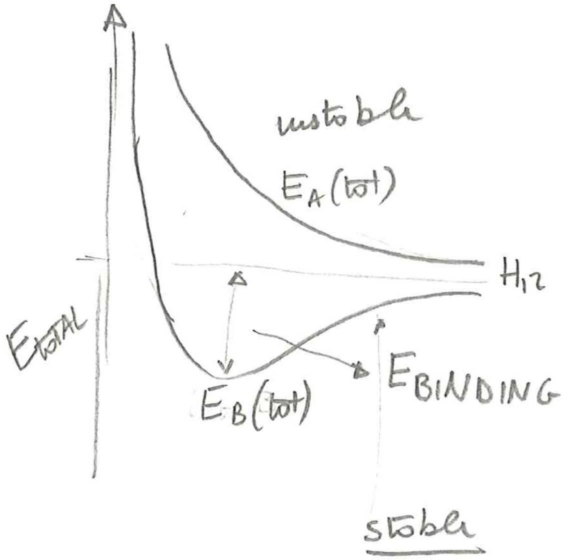
$S_{12}(R \to 0) \to 1$

$S(R \to 0) \to 1 \quad \Rightarrow$



$+\frac{e^2}{R}$

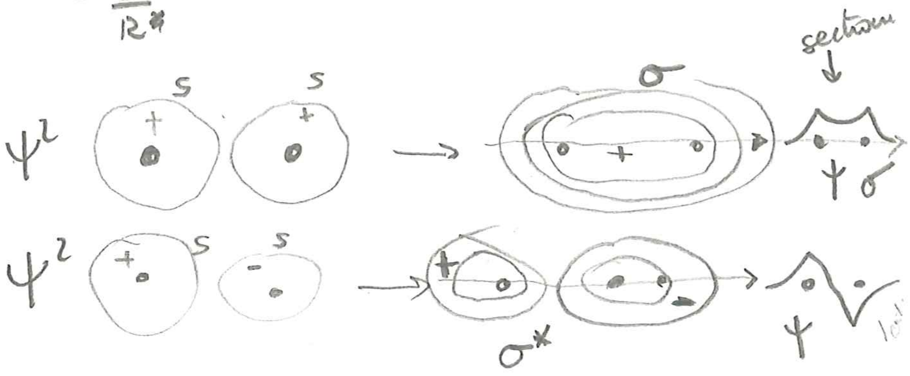
$\Rightarrow$



$$\text{total } E = E_{electronic} + E_{ions}(R) = \frac{e^2}{R^*}$$

$\psi_B = c_1(\phi_1 + \phi_2)$

$\psi_A = c_1(\phi_1 - \phi_2)$

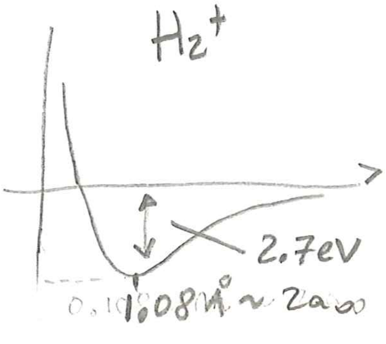


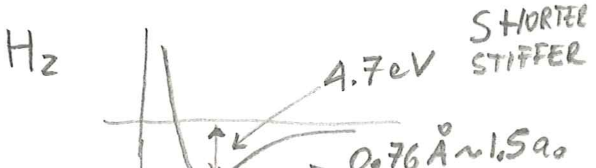
$s + s \to \sigma + \sigma^*$

$p + p \to (\pi + \pi^*) \,\&\, (\sigma + \sigma^*)$

$d + d \to$ troubles in solids (need $e_g + t_{2g}$)

$f + f \to$ more troubles.

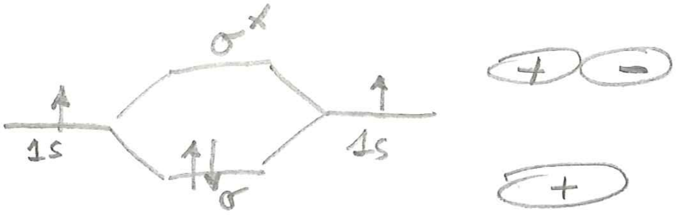




M3

LITHIUM

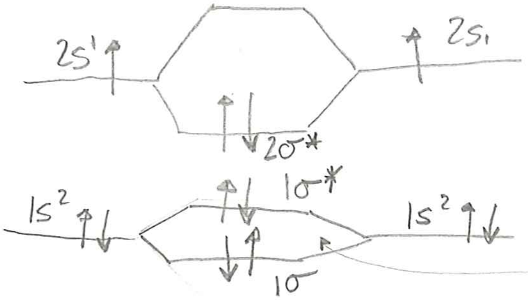
H_2



$$E_A = H + \frac{(H_{12} - H S_{12})}{1 + S_{12}}$$

$$E_B = H - \frac{(H_{12} - H S_{12})}{1 - S_{12}}$$

Li_2 $1s^2 2s^1$



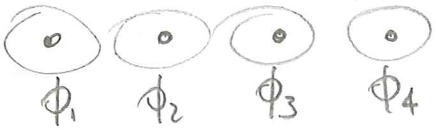
deeper electrons ⇒

$S(1s) < S(2s)$ ⇒

opening is <u>smaller</u>

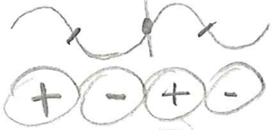
Li_4

now there are 4 atoms

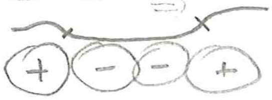


⇒ solution $\psi = \sum c_i \phi_i$

all $c > 0$ for convention

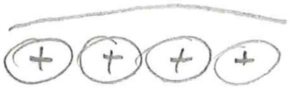


$\psi_4 = c_{41}\phi_1 - c_{42}\phi_2 + c_{43}\phi_3 - c_{44}\phi_4$ 3 nodes A



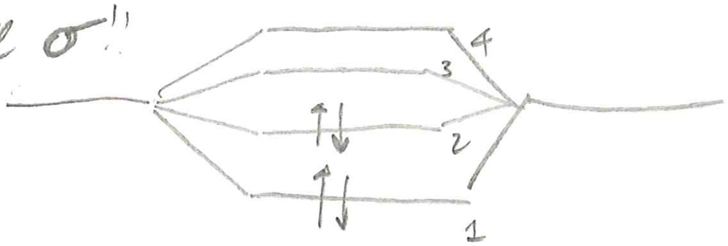
$\psi_3 = c_{31}\phi_1 - c_{32}\phi_2 - c_{33}\phi_3 + c_{34}\phi_4$ 2 nodes S

$\psi_2 = c_{21}\phi_1 + c_{22}\phi_2 - c_{23}\phi_3 - c_{24}\phi_4$ 1 node A



$\psi_1 = c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3 + c_{14}\phi_4$ 0 nodes S

spherical, all σ!!



M4

MORE COMPLICATE STRUCTURES!

$$LCAO\ (H_{ii}, H_{ij}, S_{ij}) \Longrightarrow \text{DEBYE HUCKEL MODEL } (\alpha, \beta)$$

$$\underbrace{H_{ii} = \int \phi_i^* \hat{H} \phi_i \, dV}_{\text{COULOMB}} \Longleftrightarrow \alpha \quad \text{all identical } \underline{\text{atoms}}$$

$$\underbrace{H_{ij} = \int \phi_i^* \hat{H} \phi_j \, dV}_{\text{BOND}} \Longrightarrow = \begin{cases} \alpha & |i-j|=0 \quad \text{same} \\ \beta & |i-j|=1 \quad \text{first neighbours} \\ 0 & \text{elsewhere} \end{cases}$$

$$\underbrace{S_{ij} = \int \phi_i^* \phi_j \, dV}_{\text{OVERLAP}} \Longrightarrow \cong \begin{cases} 1 & |i-j|=0 \quad \text{normalization} \\ 0 & \text{elsewhere} \end{cases}$$

<u>NO OVERLAP</u> drastic? yes but <u>works</u>

for $H_2 \Rightarrow$

$$\begin{vmatrix} H_{11}-E & H_{12}-ES_{12} \\ H_{12}-ES_{12} & H_{22}-E \end{vmatrix} \begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = 0 \Longrightarrow \begin{vmatrix} \alpha-E & \beta \\ \beta & \alpha-E \end{vmatrix} \Rightarrow 0$$

$$(\alpha-E)^2-\beta=0$$

$\Rightarrow E$

$\alpha-\beta$

$\alpha+\beta$

$\boxed{\beta \text{ is } \underline{\text{negative}}}$

for $Li_4 \Rightarrow$

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} \Rightarrow \det = 0$$

$E =$

$\alpha-1.6\beta$

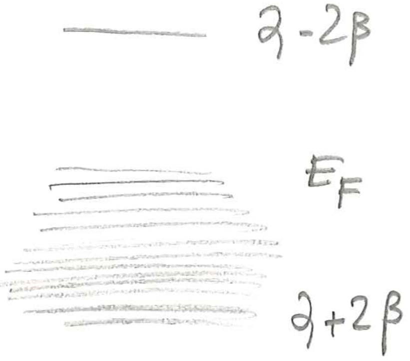
$\alpha-0.6\beta$

$\alpha+0.6\beta$

$\alpha+1.6\beta$

$N \to \infty$

$E =$ continuum



Solution

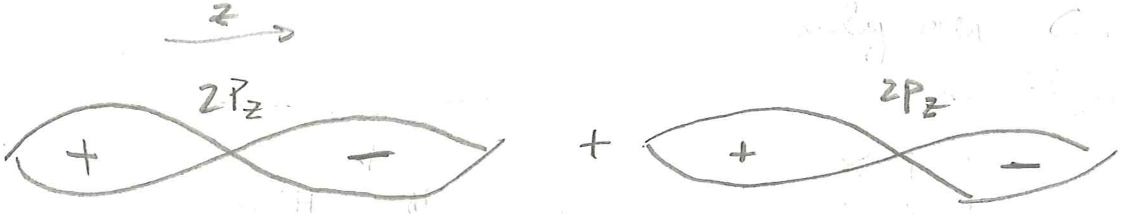
$$\psi_i = \sum_j c_{ij}\phi_j \qquad c_{ij} = \sqrt{\frac{2}{N+1}}\,\sin\left(\frac{\pi i j}{N+1}\right)$$

$$E_i = \alpha + 2\beta\cos\left(\frac{\pi i}{N+1}\right)$$

DEBYE
HUCKEL
MODEL.

↳ MORE NODES, WIGGLES
⇒ higher energy

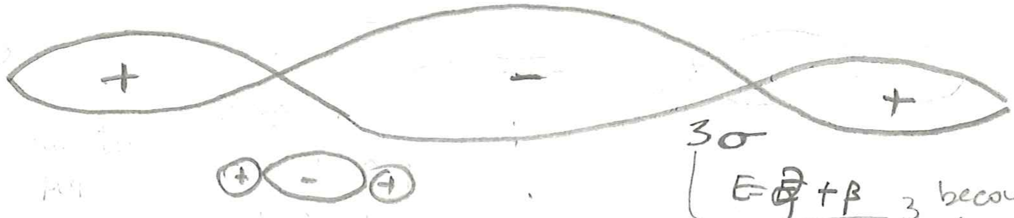
what about if I mix P orbitals?



SIMMETRYC PROBLEM

⇒ 2 SOLUTION SYMM & ANTI

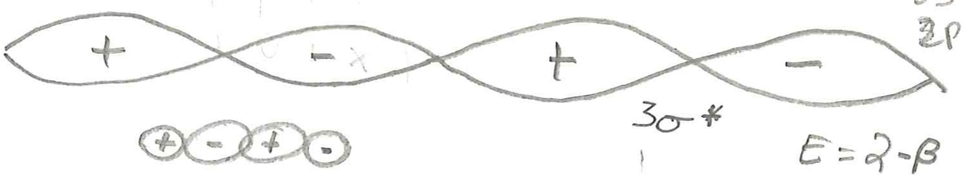
SIMM E_σ
lower energy



3σ

$E = \alpha + \beta$ 3 because
$1s \to 1\sigma$
$2s \to 2\sigma$
$2p \to 3\sigma, \pi$

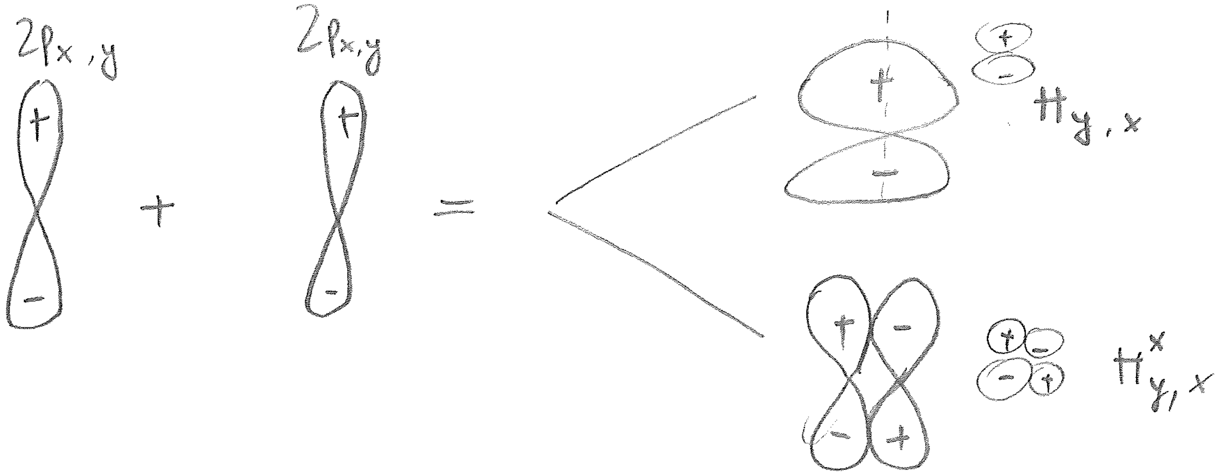
ANTI E_σ
Higher energy



$3\sigma^*$

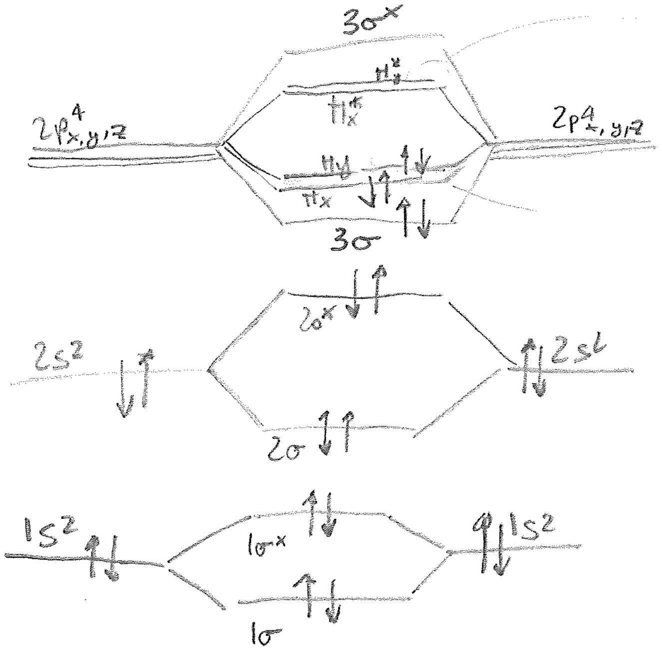
$E = \alpha - \beta$

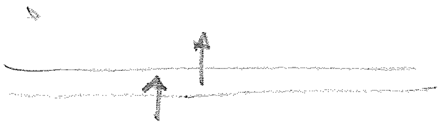
M6



OXIGEN O_2 $1s^2 2s^2 2p^4$

eigth electron





HUND'S RULE

"OF THE STATES ASSOCIATED WITH GROUND STATE CONFIGURATION OF AN ATOM OR ION, THOSE WITH GREATEST SPIN MULTIPLICITY LIE DEEPEST IN ENERGY

— LIFE ⇒ O_2 gets close to EMOGLOBINE !

⇒ O_2 is PARAMAGNETIC , S_2 again

N_2 $1s^2 2s^2 2p^3$ is DIAMAGNETIC ! !

F_2 $1s^2 2p^2 2p^5$ is DIA

— FOR O_2, F_2 3σ ↓ of π

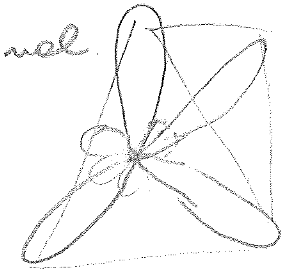
— FOR Li_2 to N_2 π ↓ then 3σ

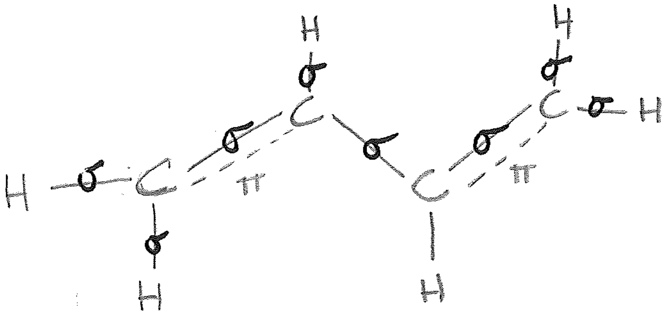
M7

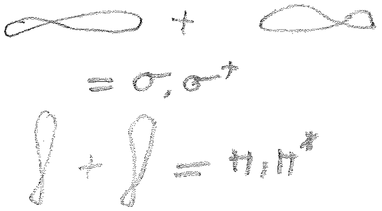
UPDATE with SP2

BUTADIENE

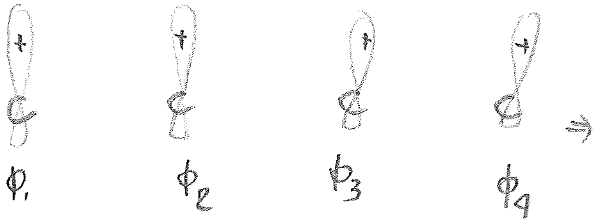
$C = 1s^2 \underbrace{2s^2\ 2p^2}_{sp^3\ \text{tetragonal}}$

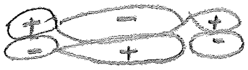
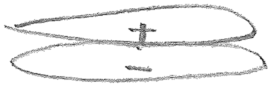






where are such π? localized?



E	NODES			
↑	3		$\psi_4 = c_1\phi_1 - c_2\phi_2 + c_3\phi_3 - c_4\phi_4$	$\alpha + 1.6\beta$
	2		$\psi_3 = c_1\phi_1 - c_2\phi_2 - c_3\phi_3 + c_4\phi_4$	$\alpha - 0.6\beta$
	1		$\psi_2 = c_1\phi_1 + c_2\phi_2 - c_3\phi_3 - c_4\phi_4$	↑↓ $\alpha + 0.6\beta$
	0		$\psi_1 = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + c_4\phi_4$	↑↓ $\alpha + 1.6\beta$

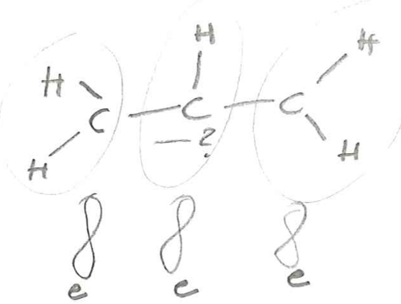
delocalized

$$\begin{vmatrix} \alpha-E & \beta & 0 & 0 \\ \beta & \alpha-E & \beta & 0 \\ 0 & \beta & \alpha-E & \beta \\ 0 & 0 & \beta & \alpha-E \end{vmatrix} \Rightarrow \quad x = \frac{\alpha-E}{\beta} \quad \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix}$$

M8

ALLYL

PLANAR



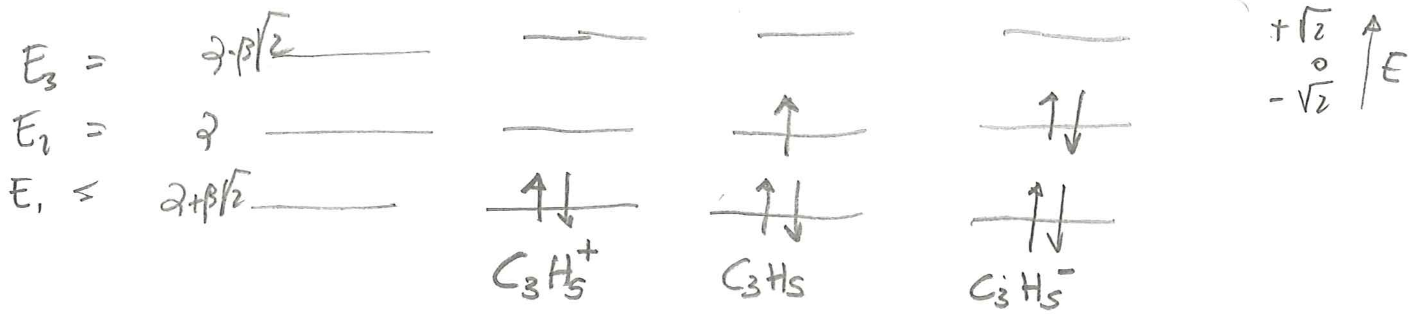
$x = (\alpha - E)/\beta$

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

$$x^3 - 2x = 0 \quad — \quad \begin{matrix} x = 0 \\ x = \sqrt{2}, -\sqrt{2} \end{matrix}$$

$$x = \frac{\alpha - E}{\beta} \qquad E = \alpha - \beta x = \begin{cases} E = \alpha \\ E = \alpha \pm \sqrt{2}\beta \end{cases}$$

$\beta < 0$



* * *

$c\,?$ $\qquad \Psi_1$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \qquad E_1 \left(x = -\sqrt{2} \right) \Rightarrow \begin{cases} c_1\sqrt{2} + c_2 = 0 \\ c_1 + c_2\sqrt{2} + c_3 = 0 \\ c_2 + c_3\sqrt{2} = 0 \end{cases}$$

remember $c_1^2 + c_2^2 + c_3^2 = 1$

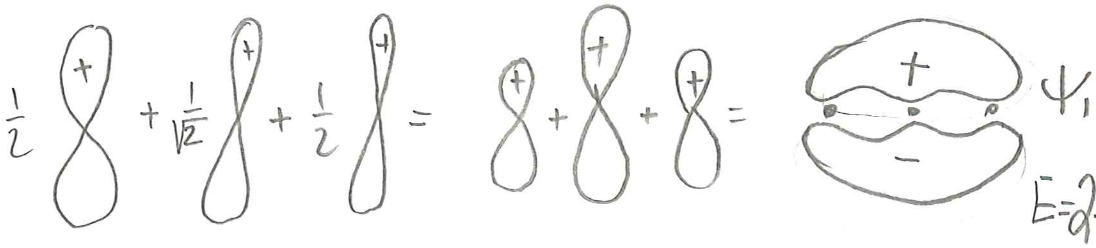
$c_1 = c_3$ from (1)-(3)

$c_2 = c_1\sqrt{2}$ from (2)

$(1, \sqrt{2}, 1) \Rightarrow \left(\frac{1}{2}, \frac{1}{\sqrt{2}}, \frac{1}{2}\right)$

$\sqrt{1\ \ 2\ \ 1} \Rightarrow 4 = 2$

$$\Psi_1 = \frac{1}{2}\phi_1 + \frac{1}{\sqrt{2}}\phi_2 + \frac{1}{2}\phi_3$$



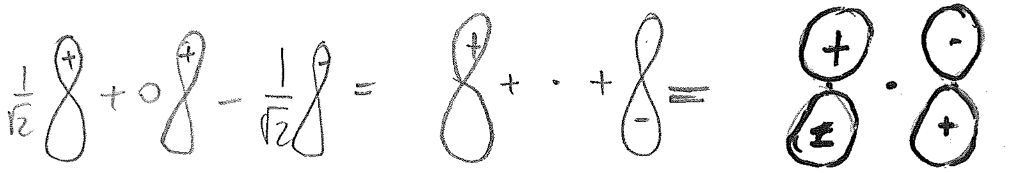
$E = \alpha + \beta\sqrt{2}$

M9

ψ_2 ?

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \xRightarrow{x=0} \begin{cases} c_2 = 0 \\ c_1 + c_3 = 0 \\ c_2 = 0 \end{cases} \Rightarrow (1, 0 -1) \Rightarrow \left(\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}}\right)$$

$$\Rightarrow \psi_2 = \frac{1}{\sqrt{2}}\phi_1 + 0\phi_2 - \frac{1}{\sqrt{2}}\phi_3 \Rightarrow$$

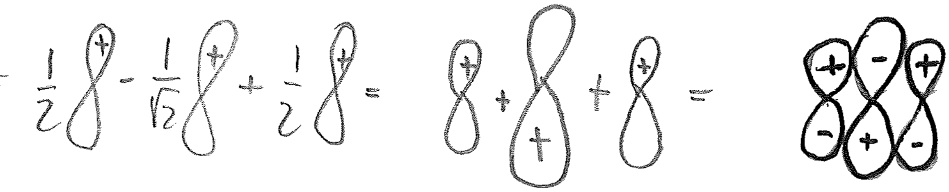


$E = \alpha$

ψ_3

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \quad x = \sqrt{2} \quad \begin{cases} c_1\sqrt{2} + c_2 = 0 \\ c_1 + \sqrt{2}c_2 + c_3 = 0 \Rightarrow \left(\frac{1}{2}, -\frac{1}{\sqrt{2}}, \frac{1}{2}\right) \\ c_2 + \sqrt{2}\,c_3 = 0 \end{cases}$$

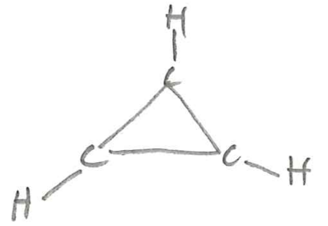
$\psi_3 =$



$E = \alpha - \beta\sqrt{2}$

M 10

CYCLO PROPENIL



$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} \xRightarrow{\text{det}} 0 \qquad x^3 - 3x + 2 = 0 \qquad x = -2, +1, +1$$

DOUBLE DEGENERATE

+1 is double

$E = \alpha - \beta x$

$$E_1 = \alpha + 2\beta$$

$x = -2$

$$\begin{vmatrix} -2 & 1 & 1 \\ 1 & -2 & 1 \\ 1 & 1 & -2 \end{vmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0 \qquad \left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right)$$

$\psi_1 =$

$$E_2 = E_3 = \alpha + \beta$$

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = 0$$

double

$c_1 + c_2 + c_3 = 0 \Leftarrow$ plane in $(c_1 c_2 c_3)$

$c_1^2 + c_2^2 + c_3^2 = 1$ (norm)

~~get b~~

get 2 vectors in the plane $v_1 = (1, -1, 0)$, $v_2 = (1, 0, -1)$ and orthogonalize

$\Rightarrow$

M 11.

$|V_1| = 1$ $\qquad$ $|V_2| = 1$

$$V_1 = \left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right) \qquad V_2 = \left(\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}}\right)$$

$V_1 \circ V_2 = \frac{1}{2}$ ⇒ not orthogonal ⇒

$$V_2^* \equiv V_2 - \underbrace{(V_1 \cdot V_2)}_{\frac{1}{2}} V_1$$

GRAM-SCHMIDT

$$V_2^* \cdot V_1 = V_2 \cdot V_1 - (V_1 \cdot V_2)\underbrace{(V_1 \cdot V_1)}_{1} = 0$$

$$V_2^* = \left(\frac{1}{\sqrt{2}}, 0, -\frac{1}{\sqrt{2}}\right) + \left(-\frac{1}{2\sqrt{2}}, +\frac{1}{2\sqrt{2}}, 0\right)$$

$$= \frac{1}{2\sqrt{2}}(1, 1, -2) \qquad |V_2^*| = \sqrt{\frac{\cancel{6}\,3}{4 \cdot \cancel{2}}} = \sqrt{\frac{3}{4}} = \frac{\sqrt{3}}{2}$$

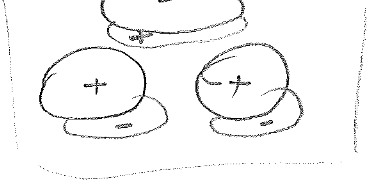
⇒

$$V_2 = \frac{1}{\sqrt{6}}(1, 1, -2)$$

$$V_1 = \left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right)$$

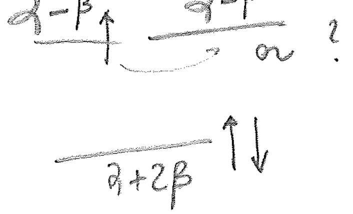
ψ_2 =

ψ_3 =



and all linear combinations!

⇒ E



CYCLIC DEBYE HUCKEL

Linear chain N (open)

$$\begin{vmatrix} x & 1 & & 0 \\ 1 & x & 1 & \\ & 1 & x & 1 \\ 0 & & \ddots & x \end{vmatrix} \Rightarrow$$

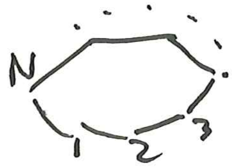
$$x_i = -2\cos\left[\frac{i\pi}{n+1}\right] \Rightarrow c_{ij} = \sqrt{\frac{2}{N+1}}\,\sin\left(\frac{\pi i j}{N+1}\right)$$

ORBITAL INDE
$i = [1,..,N]$

$j = [1,N]$
ATOM INDEX

$$E_i = \alpha - x_i\beta$$

Cyclic polyene



$$\begin{vmatrix} x & 1 & & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & & \ddots & x \end{vmatrix} \Rightarrow$$

$$x_i = -2\cos\left(\frac{2\pi i}{N}\right)$$ ~~$c_{ij} = \sqrt{\frac{1}{N}}$~~

- Real = uniques $\Longleftarrow$ $c_{ij} = \sqrt{\frac{1}{N}}\, e^{i\left(\frac{2\pi i (j-1)}{N}\right)}$

$\sqrt{-1}$

i = ORBITAL $[1 \ldots N]$

$j = [1 \ldots N]$ ATOM

- complex
  ⇒ degenerate, one has to take linear combination to have real coefficients

M13

GRAPHICAL

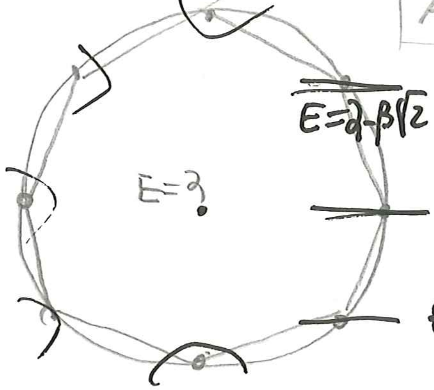
For linear : NO OUT OF DIAGONAL & "FIRST OUT DIAGONAL" elements ⇒ (NO degenerate levels

N system

draw circle, centered at $E = \alpha$, radius $2|\beta|$

inscribe polyhedron with $(2n+2)$ carbons from the bottom

Allyl $n=3 \Rightarrow 2n+2=8$



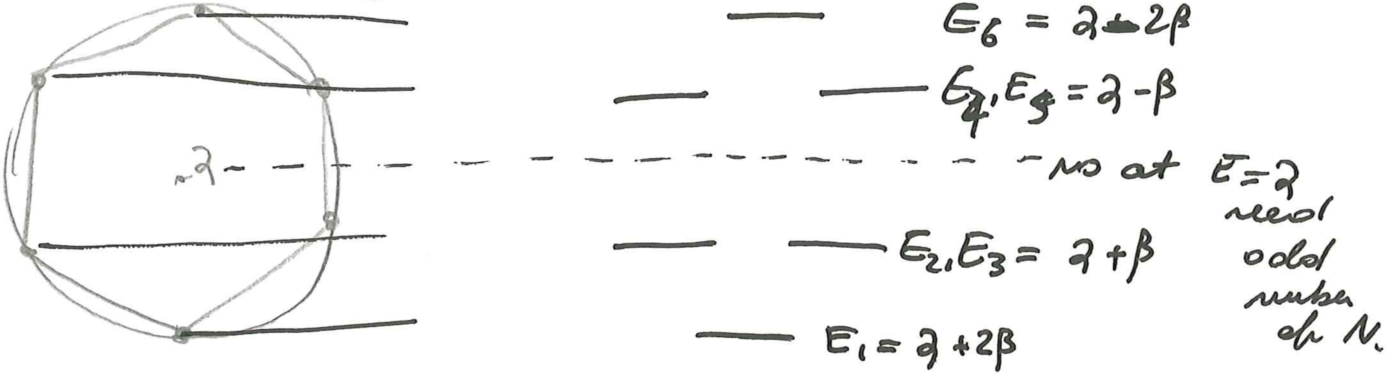
$E = \alpha - \beta\sqrt{2}$ forget, bottom and up, and degeneracies

$E = \alpha$

$E = \alpha + \beta\sqrt{2}$ ⇒ energies

For cyclic : inscribe polyedron with N carbons

get degeneracies



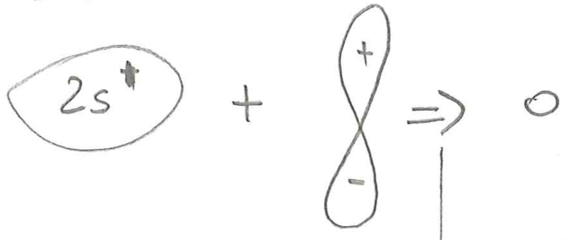
and fill up

BONDING OF ATOMS WITH DIFFERENT OVERLAP

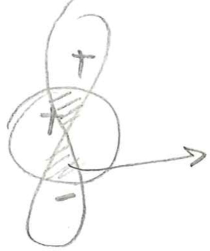
LiF Lithium Fluorine

Li $1s^2 2s^1$ F = $1s^2 2s^2 2p^5$ ⇒ only 1 e available

suppose $\int$ P_x or P_y



└> $\int = 0$ because



cancel each other

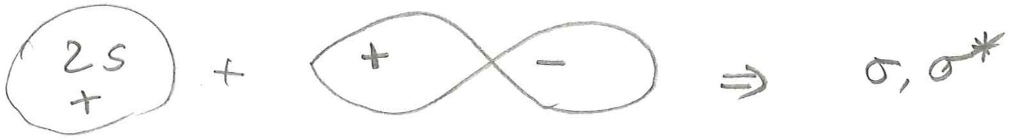
⇒ NO BONDING

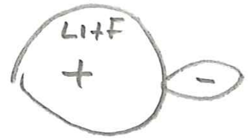
$2s^1 + P_x, P_y$

P_x has 2

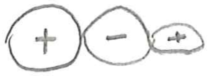
P_y has 2

P_z has 1



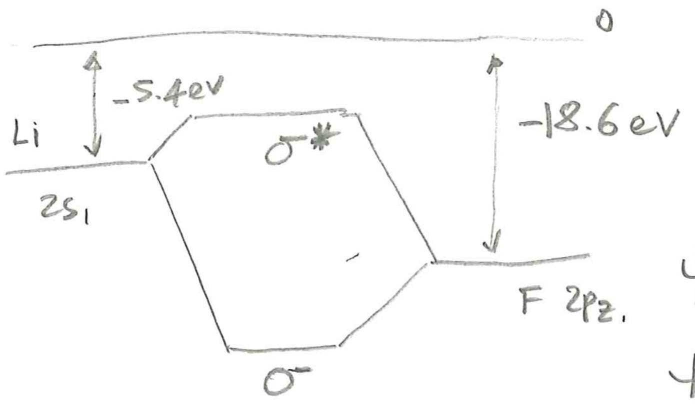


σ 1 node



σ* 2 nodes

⇒

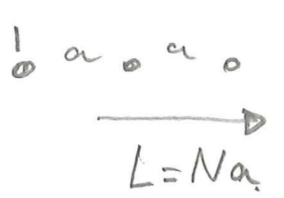


$\psi = C_{Li}\phi_{Li} + C_F\phi_F$

$\psi_{\sigma^*} \Rightarrow C_{Li} >> C_F$

$\psi_\sigma \Rightarrow C_{Li} << C_F$

GENERALIZATION OF D-H for large N.



$N >> 1 \Rightarrow \sim$ periodic
expect results
like periodic!

$$GS \Rightarrow \psi = \sum_j c_j \phi_j \qquad c_j = \sqrt{\frac{2}{N+1}}\,\sin\left(\frac{\pi j}{N+1}\right) \quad i=1$$

$$E = \alpha + 2\beta\cos\left(\frac{\pi}{N+1}\right) \quad i=1$$

$$N+1 \sim N \qquad \frac{N}{j} \rightarrow \frac{Na}{ja} = \frac{L}{ja} \Rightarrow \qquad k = \frac{\pi j}{L} \Rightarrow$$

$$c_j \sim \sqrt{\frac{2}{N}}\,\sin\left(\frac{\pi j a}{L}\right) \simeq \sqrt{\frac{2}{N}}\,\sin(ka)$$

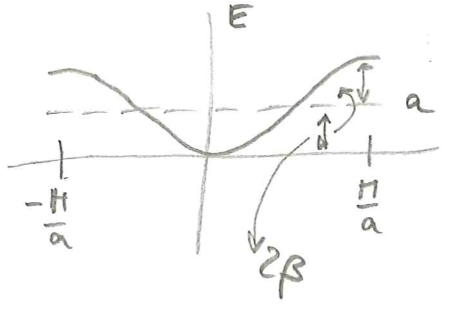
$j = 1, N \Rightarrow ka = 0, \pi$

$\Rightarrow$

$\sin(0,\pi) = \frown$

$\cos(0,\pi) \Rightarrow 1, -1$

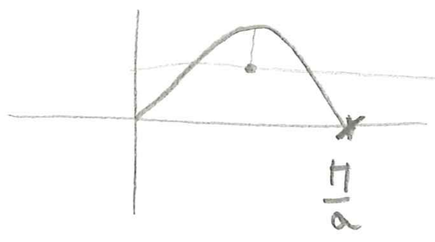
Remember $G^* =$ first reciprocal $= \frac{2\pi}{a} \Rightarrow BZ = \left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$?



$$E = \alpha + 2\beta\cos(ka)$$

$$k = \left[0, \frac{\pi}{a}\right]$$

$$V_{group} = \frac{1}{\hbar}\frac{\partial E}{\partial k} = -\frac{2a\beta}{\hbar}\sin(ka)$$



SOLUTION OF SCP

$E_n = -\frac{13.6\, Z^2}{n^2}$ valid only for Hyrogenoid

with more electrons compute numerically

and get. $E(n, e)$

: 1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 5d 4f....

+ Fill up with HUND (level are splitted in m sice $L \cdot S$ coupling ⇒ Zeeman)

but some orbitals have very close energy

2s & 2p ⇒ HYBRIDIZATION

HYBRIDIZATION of 2s & 2p

need at least 2s, 2p but not too much : 1, 2, 3, 4, 6 symetries possible No 5

Sum of $2s^{\#} + 2p^{\#} < 5$

$\mathrm{Max}\left[\#(2s) + \#(2p)\right] = 6 \Rightarrow$ filled no HYB

or $\left[\#(2s) + \#(2p)\right] = 5 \Rightarrow$ no possible

$\left[\#(2s) + \#(2p)\right] = 4 \Rightarrow 4e \underset{\text{Carbon}}{\Rightarrow} s^2p^2 \Rightarrow sp^3 \Rightarrow SP^3_{\text{HYB}}$

$\left[\#(2s) + \#(2p)\right] = 3 \Rightarrow 3e \underset{\text{Boron}}{\Rightarrow} s^2, p^1 \Rightarrow sp^2 \Rightarrow SP^2_{\text{HYP}}$

$\left[\#(2s) + \#(2p)\right] = 2 \Rightarrow \underset{\text{Berillium}}{2e} \Rightarrow s^2p^0 \Rightarrow sp^1 = \underset{\text{HYB}}{SP}$

H1 $\left[\#(2s) + \#(2p)\right] = 1 \Rightarrow$ NO HYB electrons stays in 2s

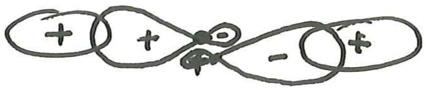
HYBRIDIZATION

Sp^1

Be (or C in SP)

Sp

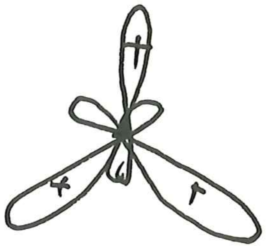
$H - Be - H$

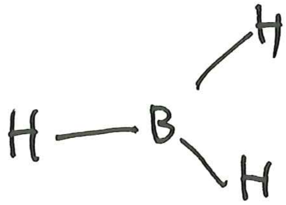


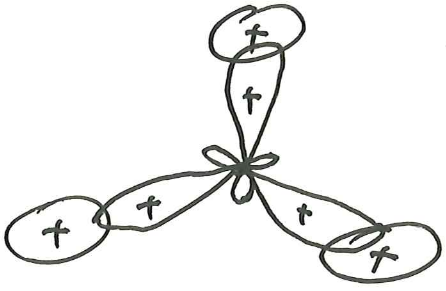
Sp^2

B (or C in Sp^2)
graphite

Sp^2

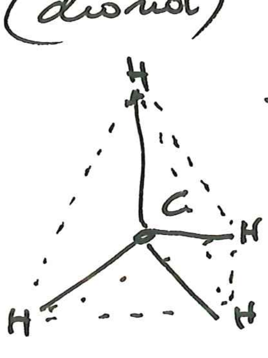




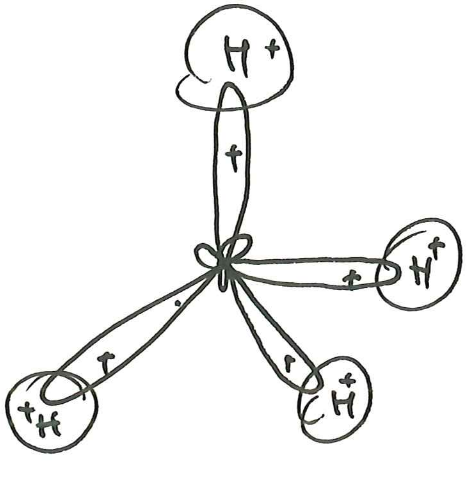


Sp^3

C (diamond)



tetrahedron



H2

J. LOWE QUANT. CHEM.

CHAPTER 8

THE SIMPLE HÜCKEL METHOD AND APPLICATIONS

8-1 The Importance of Symmetry

Our discussions of the particle in a box, the harmonic oscillator, the hydrogen atom, and homonuclear diatomic molecules have all included emphasis on the role which symmetry plays in determining the qualitative nature of the eigenfunctions. When we encounter larger systems, detailed and accurate solutions become much more difficult to perform and interpret, but symmetry continues to exert strong control over the solutions.

In this chapter, we will describe a rather simple quantum chemical method which was formulated in the early 1930s by E. Hückel. One of the strengths of this method is that, by virtue of its crudeness and simplicity, the effects of symmetry and topology on molecular characteristics are easily seen. Also, the simplicity of the model makes it an excellent pedagogical tool for illustrating many quantum chemical concepts, such as bond order, electron densities, and orbital energies. Finally, the method and some of its variants continue to be useful for certain research applications. Indeed, it is difficult to argue against the proposition that every graduate student of organic and inorganic chemistry should be acquainted with the Hückel molecular orbital (HMO) method.

8-2 The Assumption of σ–π Separability

The simple Hückel method was devised to treat electrons in unsaturated molecules like ethylene and benzene. By 1930 it was recognized that unsaturated hydrocarbons are chemically more reactive than are alkanes, and that their spectroscopic and thermodynamic properties are different too. The available evidence suggested the existence of loosely held electrons in unsaturated molecules.

We have already seen that, when atoms combine to form a *linear* molecule, we can distinguish between MOs of type $\sigma, \pi, \delta, \ldots$ depending on whether the MOs are associated with an m quantum number of $0, 1, 2, \ldots$. Thus, in acetylene (C_2H_2), the minimal basis set of AOs on carbon and hydrogen lead to σ and π MOs. Let us imagine that our acetylene molecule is aligned along the z cartesian axis. Then the p_x π-type AOs on the carbons are antisymmetric for reflection through a plane containing the molecular axis and the y axis. The p_y π-type AOs are antisymmetric for reflection through a plane containing the molecular axis and the x axis. The p_z AOs, which are σ-type functions, are symmetric for reflection through any plane containing the molecular axis. It has become standard practice to carry over the σ–π terminology to planar (but nonlinear) molecules, where m is no longer a "good" quantum number. In this expanded usage, *a π orbital is one that is antisymmetric for reflection through the plane of the molecule*, a σ orbital being symmetric for that reflection.

Hückel found that, by treating only the π electrons explicitly, it is possible to reproduce theoretically many of the observed properties of unsaturated molecules such as the uniform C–C bond lengths of benzene, the high-energy barrier to internal rotation about double bonds, and the unusual chemical stability of benzene. Subsequent work by a large number of investigators has revealed many other useful correlations between experiment and this simple HMO method for π electrons.

Treating only the π electrons explicitly and ignoring the σ electrons is clearly an approximation, yet it appears to work surprisingly well. Physically, Hückel's approximation may be viewed as one which has the π electrons moving in a potential field due to the nuclei and a "σ core," which is assumed to be frozen as the π electrons move about. Mathematically, the *σ–π separability* approximation is

$$E_{\text{tot}} = E_\sigma + E_\pi \tag{8-1}$$

where E_{tot} is taken to be the electronic energy E_{el} plus the internuclear repulsion energy V_{nn}.

Let us consider the implications of Eq. (8-1). We have already seen (Chapter 5), that a *sum* of energies is consistent with a sum of hamiltonians and a product-type wavefunction. This means that, if Eq. (8-1) is true, the wavefunction of our planar molecule should be of the form (see Problem 8-1)

$$\psi(1, \ldots, n) = \psi_\pi(1, \ldots, k)\psi_\sigma(k+1, \ldots, n) \tag{8-2}$$

and our hamiltonian should be separable into π and σ parts:

$$\hat{\mathscr{H}}(1, 2, \ldots, n) = \hat{\mathscr{H}}_\pi(1, 2, \ldots, k) + \hat{\mathscr{H}}_\sigma(k+1, \ldots, n) \tag{8-3}$$

Equations (8-2) and (8-3) lead immediately to Eq. (8-1):

$$\begin{aligned}\bar{E} &= \frac{\int \psi_\pi{}^*\psi_\sigma{}^*(\hat{\mathscr{H}}_\pi + \hat{\mathscr{H}}_\sigma)\psi_\pi\psi_\sigma\, d\tau(1, \ldots, n)}{\int \psi_\pi{}^*\psi_\sigma{}^*\psi_\pi\psi_\sigma\, d\tau(1, \ldots, n)} \\ &= \frac{\int \psi_\pi{}^*\hat{\mathscr{H}}_\pi\psi_\pi\, d\tau(1, \ldots, k)}{\int \psi_\pi{}^*\psi_\pi\, d\tau(1, \ldots, k)} + \frac{\int \psi_\sigma{}^*\hat{\mathscr{H}}_\sigma\psi_\sigma\, d\tau(k+1, \ldots, n)}{\int \psi_\sigma{}^*\psi_\sigma\, d\tau(k+1, \ldots, n)} \\ &= E_\pi + E_\sigma \end{aligned} \tag{8-4}$$

If these equations were valid, one could ignore ψ_σ and legitimately minimize E_π by varying ψ_π, but the equations are *not* valid because it is impossible to rigorously satisfy Eq. (8-3). We cannot define $\hat{\mathscr{H}}_\pi$ and $\hat{\mathscr{H}}_\sigma$ so that they individually depend completely on separate groups of electrons and still sum to the correct total hamiltonian. Writing these operators explicitly gives

$$\hat{\mathscr{H}}_\pi(1,\ldots,k) = -\tfrac{1}{2}\sum_{i=1}^{k} \nabla_i^2 + \sum_{i=1}^{k} V_{\mathrm{ne}}(i) + \tfrac{1}{2}\sum_{i=1}^{k}\sum_{\substack{j=1,\\ j\neq i}}^{k} 1/r_{ij} \tag{8-5}$$

$$\begin{aligned}\hat{\mathscr{H}}_\sigma&(k+1,\ldots,n)\\ &= -\tfrac{1}{2}\sum_{i=k+1}^{n} \nabla_i^2 + \sum_{i=k+1}^{n} V_{\mathrm{ne}}(i) + \tfrac{1}{2}\sum_{i=k+1}^{n}\sum_{\substack{j=k+1,\\ j\neq i}}^{n} (1/r_{ij}) + V_{\mathrm{nn}}\end{aligned} \tag{8-6}$$

where $V_{\mathrm{ne}}(i)$ represents the attraction between electron i and all the nuclei. These hamiltonians do indeed depend on the separate groups of electrons, but they leave out the operators for repulsion between σ and π electrons:

$$\hat{\mathscr{H}} - \hat{\mathscr{H}}_\pi - \hat{\mathscr{H}}_\sigma = \sum_{i=1}^{k}\sum_{j=k+1}^{n} 1/r_{ij} \tag{8-7}$$

In short, the σ and π electrons really do interact with each other, and the fact that the HMO method does not *explicitly* include such interactions must be kept in mind when we consider the applicability of the method to certain problems. Some account of σ–π interactions is included *implicitly* in the method, as we shall see shortly.

8-3 The Independent π-Electron Assumption

The HMO method assumes further that the wavefunction ψ_π is a product of one-electron functions and that the hamiltonian $\hat{\mathscr{H}}_\pi$ is a sum of one-electron operators. Thus, for n π electrons,

$$\psi_\pi(1, 2,\ldots, n) = \phi_i(1)\phi_j(2)\cdots\phi_l(n) \tag{8-8}$$

$$\hat{\mathscr{H}}_\pi(1, 2,\ldots, n) = \hat{H}_\pi(1) + \hat{H}_\pi(2) + \cdots + \hat{H}_\pi(n) \tag{8-9}$$

and

$$\int \phi_i^*(1)\hat{H}_\pi(1)\phi_i(1)\,d\tau(1)\bigg/\int \phi_i^*(1)\phi_i(1)\,d\tau(1) \equiv E_i \tag{8-10}$$

It follows that the total π energy E_π is a sum of one-electron energies:

$$E_\pi = E_i + E_j + \cdots + E_l \tag{8-11}$$

This means that the π electrons are being treated as though they are independent of each other, since E_i depends only on ϕ_i and is not influenced by the presence or absence of an electron in ϕ_j. However, this cannot be correct because π electrons in fact interact strongly with each other. Once again, such interactions will be roughly accounted for in an *implicit* way by the HMO method.

The implicit inclusion of interelectronic interactions is possible because we never actually write down a detailed expression for the π one-electron hamiltonian operator $\hat{H}_\pi(i)$. (We *cannot* write it down because it results from a π–σ separability assumption and an independent π-electron assumption, and both assumptions are incorrect.) $\hat{H}_\pi(i)$ is considered to be an "effective" one-electron operator—an operator that somehow includes the important physical interactions of the problem so that it can lead to a reasonably correct energy value E_i. A key point is that the HMO method ultimately evaluates E_i *via* parameters that are evaluated by appeal to experiment. Hence, it is a *semiempirical* method. Since the experimental numbers must include effects resulting from all the interelectronic interactions, it follows that these effects are implicitly included to some extent in the HMO method through its parameters.

It was pointed out in Chapter 5 that, when the independent electron approximation [Eqs. (8-8)–(8-11)] is taken, all states belonging to the same configuration become degenerate. In other words, considerations of space–spin symmetry do not affect the energy in that approximation. Therefore, the HMO method can make no explicit use of spin orbitals or Slater determinants, and so ψ_π is normally taken to be a single product function as in Eq. (8-8). The Pauli principle is provided for by assigning no more than two electrons to a single MO.

8-4 Setting up the Hückel Determinant

A. *Identifying the Basis Atomic Orbitals and Constructing a Determinant*

The allyl radical, C_3H_5, is a planar molecule[1] with three unsaturated carbon centers (see Fig. 8-1). The minimal basis set of AOs for this molecule consists of a 1s AO on each hydrogen and 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ AOs on each carbon. Of all these AOs only the $2p_z$ AOs at the three carbons are antisymmetric for reflection through the molecular plane.

Following Hückel, we ignore all the σ-type AOs and take the three $2p_z$ AOs as our set of basis functions. Notice that this restricts us to the carbon atoms. The hydrogens are not treated explicitly in the simple HMO method. We label our three basis functions $\chi_1\ \chi_2\ \chi_3$ as indicated in Fig. 8-2. We will assume these AOs to be normalized.

Suppose that we now perform a linear variation calculation using this basis set. We know this will lead to a 3×3 determinant whose roots will be MO

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[1] The minimum energy conformation of the allyl system is planar. We will ignore the deviations from planarity resulting from vibrational bending of the system.

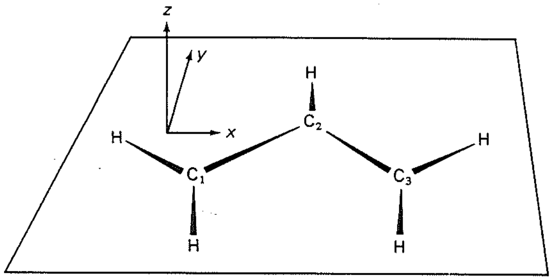

FIG. 8-1 Sketch of the nuclear framework for the allyl radical. All the nuclei are coplanar. The z axis is taken to be perpendicular to the plane containing the nuclei.

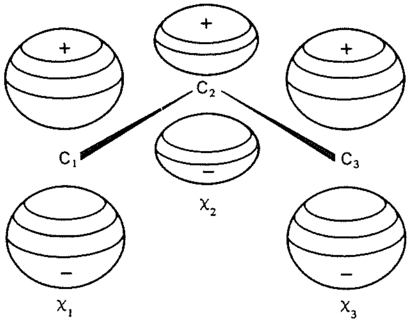

FIG. 8-2 The three π-type AOs in the minimal basis set of the allyl radical.

energies that can be used to obtain MO coefficients. The determinantal equation is

$$\begin{vmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & H_{13}-ES_{13} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & H_{23}-ES_{23} \\ H_{31}-ES_{31} & H_{32}-ES_{32} & H_{33}-ES_{33} \end{vmatrix} = 0 \tag{8-12}$$

where

$$H_{ij} = \int \chi_i \hat{H}_\pi \chi_j \, dv \tag{8-13}$$

$$S_{ij} = \int \chi_i \chi_j \, dv \tag{8-14}$$

Since H_{ij} and S_{ij} are integrals over the space coordinates of a single electron, the electron index is suppressed in Eqs. (8-13) and (8-14).

B. *The Quantity α*

We have already indicated that there is no way to write an explicit expression for $\hat{H}_\pi$ that is both consistent with our separability assumptions and physically correct. But, without an expression for $\hat{H}_\pi$, how can we evaluate the integrals H_{ij}? The HMO method sidesteps this problem by carrying certain of the H_{ij} integrals along as symbols until they can be evaluated empirically by matching theory with experiment.

Let us first consider the integrals H_{11}, H_{22}, and H_{33}. The interpretation consistent with these integrals is that H_{11}, for instance, is the average energy of an electron in AO χ_1 experiencing a potential field due to the entire molecule. Symmetry requires that $H_{11}=H_{33}$. H_{22} should be different since an electron in AO χ_2 experiences a different environment than it does when in χ_1 or χ_3. It seems likely, however, that H_{22} is not *very* different from H_{11}. In each case, we expect the dominant part of the potential to arise from interactions with the local carbon atom, with more distant atoms playing a secondary role. Hence, one of the approximations made in the HMO method is that all H_{ii} are identical if χ_i is on a carbon atom. The symbol α is used for such integrals. Thus, for the example at hand, $H_{11}=H_{22}=H_{33}=\alpha$. The quantity α is often called the *coulomb integral*.[2]

C. *The Quantity β*

Next, we consider the *resonance integrals* or *bond integrals* H_{12}, H_{23}, and H_{13}. (The requirement that $\hat{H}_\pi$ be hermitian plus the fact that the χ's and H_π are real suffices to make these equal to H_{21}, H_{32}, and H_{31}, respectively.) The interpretation consistent with these integrals is that H_{12}, for instance, is the energy of the overlap charge between χ_1 and χ_2. Symmetry requires that $H_{12}=H_{23}$ in the allyl system. However, even when symmetry does not require it, the assumption is made that all H_{ij} are equal to the same quantity (called β) when i and j refer to "neighbors" (i.e., atoms connected by a σ bond). It is further assumed that $H_{ij}=0$ when i and j are not neighbors. Therefore, in the allyl case, $H_{12}=H_{23}\equiv\beta$, $H_{13}=0$.

D. *Overlap Integrals*

Since the χ's are normalized, $S_{ii}=1$. The overlaps between neighbors are typically around 0.3. Nevertheless, in the HMO method, all S_{ij} $(i \neq j)$ are taken to be zero. Although this seems a fairly drastic approximation, it has been shown to have little effect on the qualitative nature of the solutions.

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[2] The term "coulomb integral" for α is unfortunate since the same name is used for repulsion integrals of the form $\int \chi_1(1)\chi_2(2)(1/r_{12})\chi_1(1)\chi_2(2)\,dv$. The quantity α also contains kinetic energy and nuclear–electronic attraction energy.

E. *Further Manipulation of the Determinant*

Our determinantal equation for the allyl system is now much simplified. It is

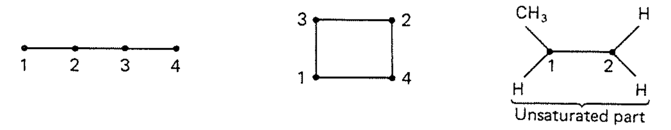
$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0 \tag{8-15}$$

Dividing each row of the determinant by β corresponds to dividing the whole determinant by β^3. This will not affect the equality. Letting $(\alpha - E)/\beta \equiv x$, we obtain the result

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{8-16}$$

which is the form we will refer to as the *HMO determinantal equation.* Notice that x occurs on the principal diagonal, 1 appears in positions where the indices correspond to a bond, 0 appears in positions (e.g., 1, 3) corresponding to no bond. This gives us a simple prescription for writing the HMO determinant for any unsaturated hydrocarbon system directly from a sketch of the molecular structure. The rules are (1) sketch the framework defined by the n *unsaturated* carbons; (2) number the atoms $1, \ldots, n$ (the ordering of numbers is arbitrary); (3) fill in the $n \times n$ determinant with x's on the diagonal, 1's in positions where row–column indices correspond to bonds, 0's elsewhere. See Fig. (8-3) for examples. As a check, it is useful to be sure the determinant is symmetric for reflection through the diagonal of x's. This is necessary since, if atoms i and j are neighbors, 1's must appear in positions i, j *and* j, i of the determinant.

Since the Hückel determinant contains only information about the number of unsaturated carbons and how they are connected together, it is sometimes referred to as a *topological determinant.* (Topology refers to properties that are due to the *connectedness* of a figure, but are unaffected by twisting, bending, etc.)



Butadiene (C_4H_6)

$$\begin{array}{c|cccc|} & 1 & 2 & 3 & 4 \\ 1 & x & 1 & 0 & 0 \\ 2 & 1 & x & 1 & 0 \\ 3 & 0 & 1 & x & 1 \\ 4 & 0 & 0 & 1 & x \end{array}$$

Cyclobutadiene (C_4H_4)

$$\begin{array}{c|cccc|} & 1 & 2 & 3 & 4 \\ 1 & x & 0 & 1 & 1 \\ 2 & 0 & x & 1 & 1 \\ 3 & 1 & 1 & x & 0 \\ 4 & 1 & 1 & 0 & x \end{array}$$

Propylene (C_3H_6)

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

(same as ethylene
in simplest form
of Hückel method)

FIG. 8-3 HMO determinants for some small systems.

8-5 Solving the HMO Determinantal Equation for Orbital Energies

The HMO determinantal equation for the allyl system (8-16) can be expanded to give

$$x^3 - 2x = 0 \tag{8-17}$$

or

$$x(x^2 - 2) = 0 \tag{8-18}$$

Thus, the roots are $x = 0$, $x = \sqrt{2}$, and $x = -\sqrt{2}$. Recalling the definition of x, these roots correspond respectively to the energies $E = \alpha$, $E = \alpha - \sqrt{2}\beta$, $E = \alpha + \sqrt{2}\beta$.

How should we interpret these results? Since α is supposed to be the energy of a pi electron in a carbon 2p AO in the molecule, we expect this quantity to be negative (corresponding to a bound electron). Since β refers to an electron in a bond region, it too should be negative. Therefore, the lowest-energy root should be $E_1 = \alpha + \sqrt{2}\beta$, followed by $E_2 = \alpha$, with $E_3 = \alpha - \sqrt{2}\beta$ being the highest-energy root. (It is convenient to number the orbital energies sequentially, starting with the lowest, as we have done here.)

We have just seen that bringing three $2p_\pi$ AOs together in a linear arrangement causes a splitting into three MO energy levels. This is similar to the splitting into two energy levels produced when two 1s AOs interact, discussed in connection with H_2^+. In general, n linearly independent separated AOs will lead to n linearly independent MOs.

The ground-state π-electron configuration of the allyl system is built up by putting electrons in pairs into the MOs, starting with those of lowest energy. Thus far, we have been describing our system as the allyl radical. However, since we have as yet made no use of the number of π electrons in the system, our results so far apply equally well for the allyl cation, radical, or anion.

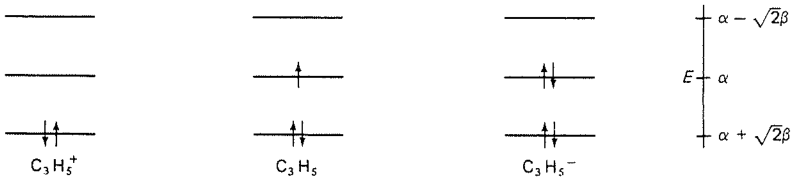


FIG. 8-4 π-Electron configurations and total energies for the ground states of the allyl cation, radical, and anion.

Configurations and total π energies for these systems in their ground states are depicted in Fig. 8-4. The total π-electron energies are obtained by summing the one-electron energies, as indicated earlier.

8-6 Solving for the Molecular Orbitals

We still have to find the coefficients which describe the MOs as linear combinations of AOs. Recall from Chapter 7 that this is done by substituting energy roots of the secular determinant back into the simultaneous equations. For the allyl system, the simultaneous equations corresponding to the secular determinant (8-16) are

$$c_1x + c_2 \qquad\quad = 0 \tag{8-19}$$

$$c_1 \; + c_2x + c_3 \;\; = 0 \tag{8-20}$$

$$c_2 \;\; + c_3x = 0 \tag{8-21}$$

(Compare these equations with the secular determinant in Eq. (8-16) and note the obvious relation.) As we noted in Chapter 7, homogeneous equations like these can give us only ratios between c_1, c_2, and c_3, not their absolute values. So we anticipate using only two of these equations and obtaining absolute values by satisfying the normality condition. Because we are neglecting overlap between AOs, this corresponds to requiring

$$c_1^2 + c_2^2 + c_3^2 = 1 \tag{8-22}$$

The roots x are, in order of increasing energy, $-\sqrt{2}$, 0, $+\sqrt{2}$. Let us take $x = -\sqrt{2}$ first. Then

$$-\sqrt{2}c_1 + \quad c_2 \qquad\quad = 0 \tag{8-23a}$$

$$c_1 - \sqrt{2}c_2 + \quad c_3 = 0 \tag{8-23b}$$

$$c_2 - \sqrt{2}c_3 = 0 \tag{8-23c}$$

Comparing Eqs. (8-23a) and (8-23c) gives $c_1 = c_3$. Equation (8-23a) gives $c_2 = \sqrt{2}c_1$. Inserting these relations into the normality equation (8-22) gives

$$c_1^2 + (\sqrt{2}c_1)^2 + c_1^2 = 1 \tag{8-24}$$

$$4c_1^2 = 1, \qquad c_1 = \pm\tfrac{1}{2} \tag{8-25}$$

It makes no difference which sign we choose for c_1 since any wavefunction is equivalent to its negative. (Both give the same ψ^2.) Choosing $c_1 = +\frac{1}{2}$ gives

$$c_1 = \tfrac{1}{2}, \qquad c_2 = 1/\sqrt{2}, \qquad c_3 = \tfrac{1}{2} \tag{8-26}$$

These coefficients define our lowest-energy MO, ϕ_1:

$$\phi_1 = \tfrac{1}{2}\chi_1 + (1/\sqrt{2})\chi_2 + \tfrac{1}{2}\chi_3 \tag{8-27}$$

A similar approach may be taken for $x = 0$ and $x = +\sqrt{2}$. The results are

$$(x = 0): \quad \phi_2 = (1/\sqrt{2})\chi_1 - (1/\sqrt{2})\chi_3 \tag{8-28}$$

$$(x = +\sqrt{2}): \quad \phi_3 = \tfrac{1}{2}\chi_1 - (1/\sqrt{2})\chi_2 + \tfrac{1}{2}\chi_3 \tag{8-29}$$

The allyl system MOs are sketched in Fig. 8-5.

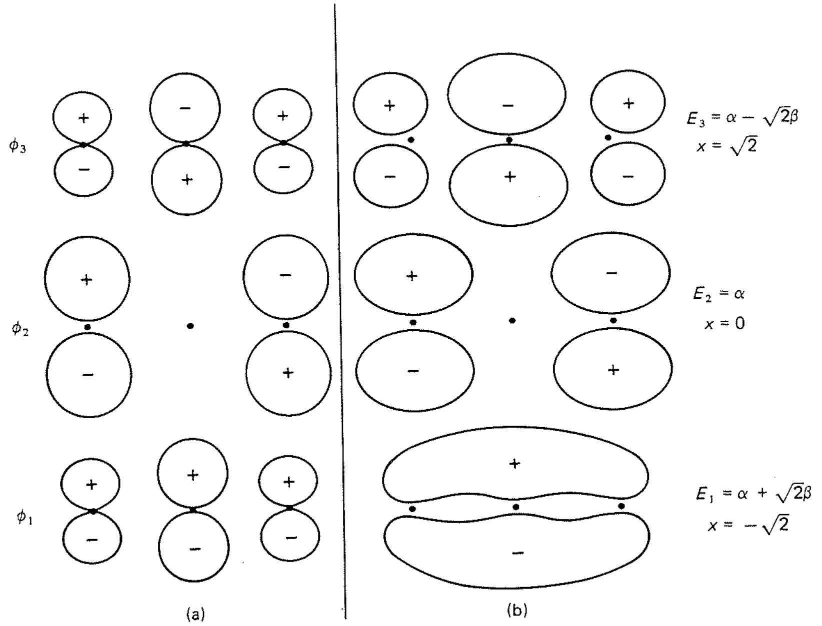


FIG. 8-5 *Sketches* of the allyl system MOs. (a) emphasizes AO signs and magnitudes. (b) resembles more closely the actual contours of the MOs.

The lowest-energy MO, ϕ_1, has no nodes (other than the molecular-plane node common to all π MOs) and is said to be bonding in the C_1–C_2 and C_2–C_3 regions. It is reasonable that such a bonding MO should have an energy wherein the bond-related term β acts to lower the energy, as is true here. The second-lowest energy MO, ϕ_2, has a nodal plane at the central carbon. Because there are no π AOs on *neighboring* carbons in this MO, there are no interactions at all, and β is absent from the energy expression. This MO is said to be *nonbonding*. The high-energy MO, ϕ_3, has nodal planes intersecting both bonds. Because the π AOs show sign disagreement across both bonds, this MO is everywhere antibonding and β terms act to raise the orbital energy above α.

8-7 The Cyclopropenyl System: Handling Degeneracies

The allyl system results when three π AOs interact in a linear arrangement wherein $H_{12} = H_{23} = \beta$, but $H_{13} = 0$. We can also treat the situation where the three π AOs approach each other on vertices of an ever-shrinking equilateral triangle. In this case, each AO interacts equally with the other two. This triangular system is the cyclopropenyl system C_3H_3 given in Fig. 8-6.

The HMO determinantal equation for this system is

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0, \qquad x^3 + 2 - 3x = 0 \tag{8-30}$$

This equation can be factored as

$$(x + 2)(x - 1)(x - 1) = 0 \tag{8-31}$$

Therefore, the roots are $x = -2, +1, +1$.

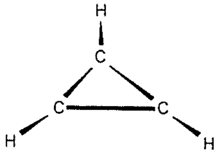


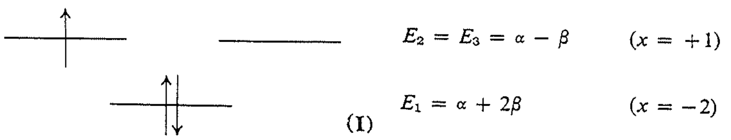
FIG. 8-6 The cyclopropenyl system (all nuclei are coplanar).

Since the root $x = 1$ occurs twice, we can expect there to be *two* independent HMOs having the same energy—a doubly degenerate level. The energy scheme and ground state electron configuration for the cyclopropenyl radical (three π electrons) (I) gives a total E_π of $3\alpha + 3\beta$. We can surmise from these orbital energies that ϕ_1 is a bonding MO, whereas ϕ_2 and ϕ_3 are predominantly antibonding. To see if this is reflected in the nodal properties of the MOs, let us solve for the coefficients. The equations consistent with the HMO determinant and with orbital normality are

$$\begin{aligned} c_1x + c_2 \quad + c_3 \quad &= 0 \\ c_1 \quad + c_2x + c_3 \quad &= 0 \\ c_1 \quad + c_2 \quad + c_3x &= 0 \\ c_1^2 + c_2^2 + c_3^2 &= 1 \end{aligned} \tag{8-32}$$

Setting $x = -2$ and solving gives

$$\phi_1 = (1/\sqrt{3})\chi_1 + (1/\sqrt{3})\chi_2 + (1/\sqrt{3})\chi_3 \tag{8-33}$$



(I)

For this MO, the coefficients are all of the same sign, so that the AOs show sign agreement across all bonds and all interactions are bonding.

To find ϕ_2 and ϕ_3 is trickier. We begin by inserting $x = +1$ into our simultaneous equations. This gives

$$c_1 \quad + c_2 \quad + c_3 \quad = 0 \quad \text{(three times)} \tag{8-34}$$

$$c_1^2 + c_2^2 + c_3^2 = 1 \tag{8-35}$$

With three unknowns and two equations, an infinite number of solutions is possible. Let us pick a convenient one: $c_1 = -c_2$, $c_3 = 0$. The normalization requirement then gives $c_1 = 1/\sqrt{2}, c_2 = -1/\sqrt{2}, c_3 = 0$. Let us call this solution ϕ_2:

$$\phi_2 = (1/\sqrt{2})\chi_1 - (1/\sqrt{2})\chi_2 \tag{8-36}$$

We still need to find ϕ_3. There remain an infinite number of possibilities, so let us pick one: $c_1 = 1/\sqrt{2}, c_2 = 0, c_3 = -1/\sqrt{2}$. We have used our experience with ϕ_2 to choose c's that guarantee a normalized ϕ_3. Also, it is clear that ϕ_3 is linearly independent of ϕ_2 since they contain different AOs. But it is desirable to have ϕ_3 *orthogonal* to ϕ_2. Let us test ϕ_2 and ϕ_3 to see if they are orthogonal:

$$\begin{aligned} S &= \int \phi_2\phi_3 \, dv = \tfrac{1}{2} \int (\chi_1 - \chi_2)(\chi_1 - \chi_3) \, dv \\ &= \tfrac{1}{2}\left\{\int \cancelto{1}{\chi_1^2 \, dv} - \int \cancelto{0}{\chi_1\chi_3 \, dv} - \int \cancelto{0}{\chi_1\chi_2 \, dv} + \int \cancelto{0}{\chi_2\chi_3 \, dv}\right\} = \tfrac{1}{2} \end{aligned} \tag{8-37}$$

Since $S \neq 0$, ϕ_2 and ϕ_3 are nonorthogonal. We can project out that part of ϕ_3 which is orthogonal to ϕ_2 by using the Schmidt orthogonalization procedure described in Section 6-10. We seek a new function ϕ_3', given by

$$\phi_3' = \phi_3 - S\phi_2 \tag{8-38}$$

where

$$S = \int \phi_2\phi_3 \, dv = \tfrac{1}{2} \tag{8-39}$$

Therefore,

$$\phi_3' = \phi_3 - \tfrac{1}{2}\phi_2 = 1/(2\sqrt{2})(\chi_1 + \chi_2 - 2\chi_3) \tag{8-40}$$

This function is orthogonal to ϕ_2 but is not normalized. Renormalizing gives

$$\phi_3'' = (1/\sqrt{6})(\chi_1 + \chi_2 - 2\chi_3) \tag{8-41}$$

In summary, to produce HMO coefficients for degenerate MOs, pick any two independent solutions from the infinite choice available, and orthogonalize them using the Schmidt (or any other) orthogonalization procedure.

The MOs for the cyclopropenyl system *as seen from above the molecular plane* are sketched in Fig. 8-7. The MO ϕ_2 can be seen to have both antibonding

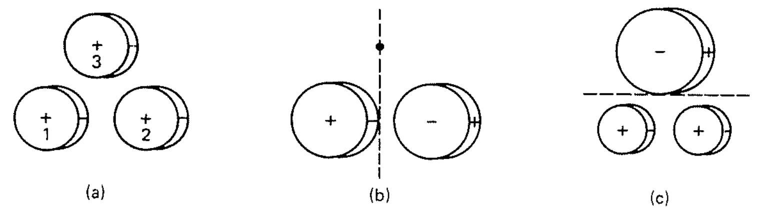


FIG. 8-7 The HMOs for the cyclopropenyl system: (a) $\phi_1 = (1/\sqrt{3})(\chi_1 + \chi_2 + \chi_3)$; (b) $\phi_2 = (1/\sqrt{2})(\chi_1 - \chi_2)$; (c) $\phi_3'' = (1/\sqrt{6})(\chi_1 + \chi_2 - 2\chi_3)$. The nodal planes intersect the molecular plane at the dashed lines.

(C_1–C_2) and nonbonding (C_1–C_3, C_2–C_3) interactions. ϕ_3'' has antibonding (C_1–C_3, C_2–C_3) and bonding (C_1–C_2) interactions. The interactions are of such size and number as to give an equal net energy value ($\alpha - \beta$) in each case. Since nodal planes produce antibonding or nonbonding situations, it is not surprising that higher and higher-energy HMOs in a system display more and more nodal planes. Notice that the MOs ϕ_2 and ϕ_3'' have the same *number* of nodal planes (one, not counting the one in the molecular plane) but that these planes are perpendicular to each other. This is a common feature of some degenerate orthogonal MOs in cyclic molecules.

It is important to notice the symmetry characteristics of these MOs. ϕ_1 is either symmetric or antisymmetric for every symmetry operation of the molecule. (It is antisymmetric for reflection through the molecular plane, symmetric for rotation about the threefold axis, etc.) This must be so for any nondegenerate MO. But the degenerate MOs ϕ_2 and ϕ_3'' are neither symmetric nor antisymmetric for certain operations. (ϕ_2 is antisymmetric for reflection through the plane indicated by the dashed line in Fig. 8-7, but is neither symmetric nor antisymmetric for rotation about the threefold axis by 120°.) In fact, one can easily show that, given a cycle with an odd number of centers, each with one AO of a common type, there is but *one* way to combine the AOs (to form a *real* MO) so that the result is symmetric or antisymmetric for all rotations and reflections of the cycle. Hence, an HMO calculation for a three-, five, seven-, ... membered ring can give only *one* nondegenerate MO. However, for a cycle containing an *even* number of centers, the analogous argument shows that *two* nondegenerate MOs exist.

8-8 Charge Distributions from HMOs

Now that we have a method that provides us with orbitals and orbital energies, it should be possible to get information about the way the π-electron charge is distributed in the system by squaring the total wavefunction ψ_π. In the

case of the neutral allyl radical, we have (taking ψ_π to be a simple product of MOs)

$$\psi_\pi = \phi_1(1)\phi_1(2)\phi_2(3) \tag{8-42}$$

Hence, the probability for simultaneously finding electron 1 in $dv(1)$, electron 2 in $dv(2)$ and electron 3 in $dv(3)$ is

$$\psi_\pi^2(1, 2, 3)\, dv(1)\, dv(2)\, dv(3) = \phi_1^2(1)\phi_1^2(2)\phi_2(3)^2\, dv(1)\, dv(2)\, dv(3) \tag{8-43}$$

For most physical properties of interest, we need to know the probability for finding *an* electron in a three-dimensional volume element dv. Since the probability for finding an electron in dv is the *sum* of the probabilities for finding each electron there, the *one-electron density function* ρ for the allyl radical is

$$\rho = 2\phi_1^2 + \phi_2^2 \tag{8-44}$$

where we have suppressed the index for *the* electron. If we integrate ρ over all space, we obtain a value of three. This means we are certain of finding a total π charge corresponding to three π electrons in the system.

To find out how the π charge is distributed in the molecule, let us express ρ in terms of AOs. First, we write ϕ_1^2 and ϕ_2^2 separately:

$$\left.\begin{aligned} \phi_1^2 &= \tfrac{1}{4}\chi_1^2 + \tfrac{1}{2}\chi_2^2 + \tfrac{1}{4}\chi_3^2 + (1/\sqrt{2})\chi_1\chi_2 + (1/\sqrt{2})\chi_2\chi_3 + \tfrac{1}{2}\chi_1\chi_3 \\ \phi_2^2 &= \tfrac{1}{2}\chi_1^2 + \tfrac{1}{2}\chi_3^2 - \chi_1\chi_3 \end{aligned}\right. \tag{8-45}$$

If we were to integrate ϕ_1^2, we would obtain

$$\begin{aligned} \int \phi_1^2\, dv &= \tfrac{1}{4}\int \cancelto{1}{\chi_1^2\, dv} + \tfrac{1}{2}\int \cancelto{1}{\chi_2^2\, dv} + \tfrac{1}{4}\int \cancelto{1}{\chi_3^2\, dv} + (1/\sqrt{2})\int \cancelto{0}{\chi_1\chi_2}\, dv \\ &\quad + (1/\sqrt{2})\int \cancelto{0}{\chi_2\chi_3}\, dv + \tfrac{1}{2}\int \cancelto{0}{\chi_1\chi_3}\, dv \\ &= \tfrac{1}{4} + \tfrac{1}{2} + \tfrac{1}{4} = 1 \end{aligned} \tag{8-46}$$

Thus, one electron in ϕ_1 shows up, upon integration, as being "distributed" $\frac{1}{4}$ at carbon 1, $\frac{1}{2}$ at carbon 2, and $\frac{1}{4}$ at carbon 3. We say that the *atomic π-electron densities* due to an electron in ϕ_1 are $\frac{1}{4}, \frac{1}{2}, \frac{1}{4}$ at C_1, C_2, and C_3, respectively. If we accumulate these figures for all the electrons, we arrive at a total π-electron density for each carbon. For the allyl radical, Table 8-1 shows that each atom has a π-electron density of unity.

Generalizing this approach gives for the total π-electron density q_i on atom i

$$q_i = \sum_k^{\text{all MOs}} n_k c_{ik}^2 \tag{8-47}$$

Here k is the MO index, c_{ik} is the coefficient for an AO on atom i in MO k, and

TABLE 8-1
HMO π Electron Densities in the Allyl Radical

Electron	Carbon atom 1	2	3
1 in ϕ_1	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$
2 in ϕ_1	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$
3 in ϕ_2	$\frac{1}{2}$	0	$\frac{1}{2}$
Sum	1	1	1

n_k, the "occupation number," is the number of electrons (0, 1, or 2) in MO k. (In those rare cases in which c_{ik} is complex, c_{ik}^2 in Eq. (8-47) must be replaced by $c_{ik}^* c_{ik}$.)

If we apply Eq. (8-47) to the cyclopropenyl radical, we encounter an ambiguity. If the unpaired electron is assumed to be in MO ϕ_2 of Fig. 8-7, we obtain $q_1 = q_2 = \frac{7}{6}$, $q_3 = \frac{4}{6}$. On the other hand, if the unpaired electron is taken to be in ϕ_3'', $q_1 = q_2 = \frac{5}{6}$, $q_3 = \frac{8}{6}$. The HMO method resolves this ambiguity by assuming that each of the degenerate MOs is occupied by half an electron. This has the effect of forcing the charge distribution to show the overall symmetry of the molecule. In this example, it follows that $q_1 = q_2 = q_3 = 1$. The general rule is that, for purposes of calculating electron distributions, the electron occupation is averaged in any set of partially occupied, degenerate MOs.

In actuality, the equilateral triangular structure for the cyclopropenyl radical is unstable, and therefore the above-described averaging process is only a theoretical idealization. It is fairly easy to see that a distortion from equilateral to isosceles form will affect the MO energies E_1, E_2, and E_3'' differently. In particular, a distortion of the sort depicted in Fig. 8-8 would have little effect on E_1 but would raise E_2 (increased antibonding) and lower E_3'' (decreased antibonding and increased bonding). Thus, there is good reason for the cyclopropenyl radical to be more stable in an isosceles rather than equilateral triangular form. This is an example of the Jahn–Teller theorem, which states, in effect, that a system having an odd number of electrons in degenerate MOs will change its nuclear configuration in a way to remove the degeneracy.[3] The preference of the cyclopropenyl radical for a shape less symmetrical than what we might have anticipated is frequently called "Jahn–Teller distortion."[4]

Many times we are interested in comparing the π-electron distribution *in the bonds* instead of on the atoms. In the integrated expression (8-46) are cross terms

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[3] Linear systems are exceptions to this rule. Problems are also encountered if there is an odd number of electrons and spin–orbit coupling is substantial.

[4] See Salem [1, Chapter 8].

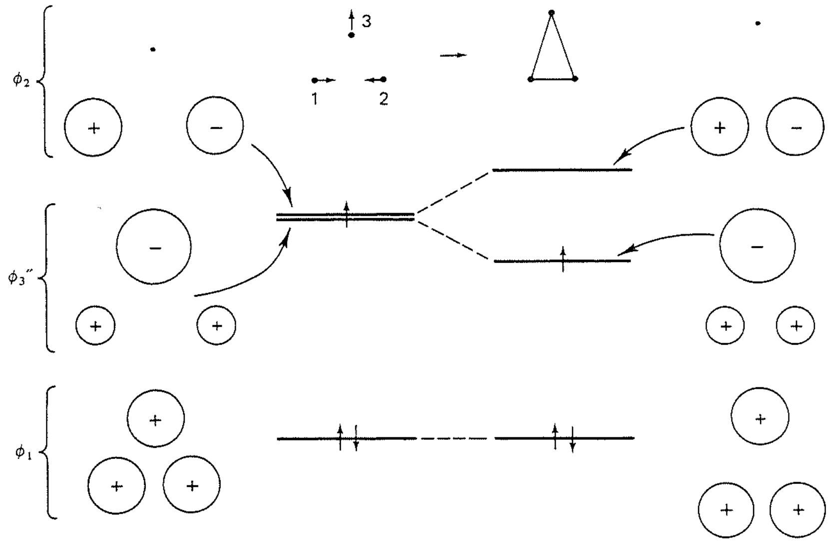

FIG. 8-8 When the equilateral structure is distorted by decreasing R_{12} and increasing R_{13}, R_{23}, the energies associated with ϕ_1, ϕ_2, ϕ_3'' shift as shown.

that vanish under the HMO assumption of zero overlap. But the overlaps are not actually zero, especially between AOs on nearest neighbors. Hence, we might view the factors $1/\sqrt{2}$ as indicating how much overlap charge is being placed in the C_1–C_2 and C_2–C_3 bonds by an electron in ϕ_1. The C_1–C_3 bond is usually ignored because these atoms are not nearest neighbors and therefore have much smaller AO overlap. Since $S_{12} = S_{23} = S_{ij}$ for neighbors i and j in any π system (assuming equal bond distances), we need not include S_{ij} explicitly in our bond index. If we proceed in this manner, two electrons in ϕ_1 would then give us a "bond order" of $2/\sqrt{2} = 1.414$. It is more convenient in practice to divide this number in half, because then the calculated π-bond order for ethylene turns out to be unity rather than two. Since ethylene has one π-bond, this can be seen to be a more sensible index.

As a result of these considerations, the π-bond order (sometimes called "mobile bond order") of the allyl radical is $\sqrt{2}/2$ $(= 0.707)$ in each bond. (Electrons in ϕ_2 make no contribution to bond order since c_2 vanishes. This is consistent with the "*nonbonding*" label for ϕ_2.)

Generalizing the argument gives, for p_{ij}, the *π-bond order* between *nearest-neighbor* atoms i and j:

$$p_{ij} = \sum_{k}^{\text{all MOs}} n_k c_{ik} c_{jk} \qquad (8\text{-}48)$$

where the symbols have the same meanings as in Eq. (8-46). In cases in which partially filled degenerate MOs are encountered, the averaging procedure described in connection with electron densities must be employed for bond orders as well.

8-9 Some Simplifying Generalizations

Thus far we have presented the bare bones of the HMO method using fairly small systems as examples. If we try to apply this method directly to larger molecules, it is very cumbersome. A ten-carbon-atom system leads to a 10×10 HMO determinant. Expanding and solving this for roots and coefficients is tedious. However, there are some short cuts available for certain cases. In the event that the system is too complicated to yield to these, one can use computer programs which are readily available.

For straight chain and monocyclic planar, conjugated hydrocarbon systems, simple formulas exist for HMO energy roots and coefficients. These are derivable from the very simple forms of the HMO determinants for such systems.[5] We state the results without proof.

For a straight chain of n unsaturated carbons numbered sequentially,

$$x = -2\cos[k\pi/(n+1)], \qquad k = 1, 2, \ldots, n \tag{8-49}$$

$$c_{lk} = [2/(n+1)]^{1/2} \sin[kl\pi/(n+1)] \tag{8-50}$$

where l is the atom index and k the MO index.

For a cyclic polyene of n carbons,

$$x = -2\cos(2\pi k/n), \qquad k = 0, 1, \ldots, n-1 \tag{8-51}$$

$$c_{lk} = n^{-1/2}\exp[2\pi ik(l-1)/n], \quad i = \sqrt{-1} \tag{8-52}$$

The coefficients derived from Eq. (8-52) for monocyclic polyenes will be complex when the MO is one of a degenerate pair. In such cases one may take linear combinations of these degenerate MOs to produce MOs with real coefficients, if one desires.

There is also a diagrammatic way to find the energy levels for linear and monocyclic systems. Let us consider monocycles first. One begins by drawing a circle of radius $2|\beta|$. Into this circle inscribe the cycle, point down, as shown in Fig. 8-9 for benzene. Project sideways the points where the polygon intersects the circle. The positions of these projections correspond to the HMO energy levels if the circle center is assumed to be at $E = \alpha$ (see Fig. 8-9). The number of intersections at a given energy is identical to the degeneracy. The numerical values for E are often obtainable from such a sketch by inspection or simple trigonometry.

For straight chains, a modified version of the above method may be used.

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[5] See Coulson [2].

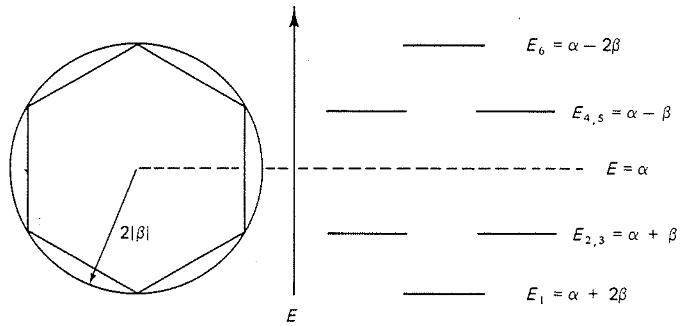

FIG. 8-9 HMO energy levels for benzene produced by projecting intersections of hexagon with a circle of radius $2|\beta|$.

For an n-carbon chain, inscribe a cycle with $2n+2$ carbons into the circle as before. Projecting out all intersections *except the highest and lowest*, and *ignoring degeneracies* gives the proper roots. This is exemplified for the allyl system in Fig. 8-10.

Examination of the energy levels in Figs. 8-9 and 8-10 reveals that the orbital energies are symmetrically disposed about $E = \alpha$. Why is this so? Consider the allyl system. The lowest-energy MO has two bonding interactions. The highest-energy MO differs *only* in that these interactions are now antibonding. [See Fig. 8-5 and note that the coefficients in ϕ_1 and ϕ_3 are identical except for sign in Eqs. (8-27) and (8-29).] The role of the β terms is thus reversed and so they act to raise the orbital energy for ϕ_3 just as much as they lower it for ϕ_1. A similar situation holds for benzene. As we will see shortly, the lowest energy corresponds to an MO without nodes between atoms, so this is a totally bonding MO. The highest-energy MO has nodal planes between all neighbor carbons, and so every interaction is antibonding. An analogous argument holds for the degenerate pairs of benzene MOs. These observations suggest that the energy of an MO should be expressible as a function of the net bond order

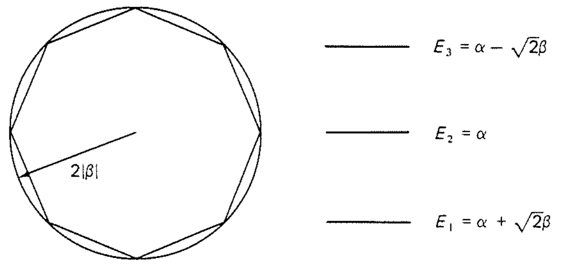

FIG. 8-10 HMO energy levels for allyl system ($n = 3$) produced by projecting the intersections of octagon ($n = 2 \times 3 + 2$) with a circle of radius $2|\beta|$.

associated with it, and this is indeed the case. The energy of the ith MO is given by the expression

$$E_i = \int \phi_i \hat{H}_\pi \phi_i \, dv = \int \sum_k c_{ki}\chi_k \hat{H}_\pi \sum_l c_{li}\chi_l \, dv \tag{8-53}$$

$$= \sum_k \sum_l c_{ki}c_{li} \int \chi_k \hat{H}_\pi \chi_l \, dv \tag{8-54}$$

When the atom indices k and l are identical, the integral is equal to α; when k and l are neighbors, it equals β. Otherwise it vanishes. Hence, we may write

$$E_i = \sum_k c_{ki}^2 \alpha + \sum_{k,l}^{\text{neighbors}} c_{ki}c_{li}\beta \tag{8-55}$$

However, c_{ki}^2 is $q_{k,i}$, the electron density at atom k due to one electron in MO ϕ_i, and $c_{ki}c_{li}$ is $p_{kl,i}$, the bond order between atoms k and l due to an electron in ϕ_i. Therefore,

$$E_i = \sum_k q_{k,i}\alpha + 2 \sum_{k<l}^{\text{neighbors}} p_{kl,i}\beta \tag{8-56}$$

We have seen that the sum of electron densities must equal the total number of electrons present. For one electron in ϕ_i, this gives additional simplification.

$$E_i = \alpha + 2\beta \sum_{k<l}^{\text{bonds}} p_{kl,i} \tag{8-57}$$

The *total* π-electron energy is the sum of one-electron energies. For n π electrons

$$E_\pi = n\alpha + 2\beta \sum_{k<l}^{\text{bonds}} p_{kl} \tag{8-58}$$

where p_{kl} is the *total* π-bond order between neighbors k and l. Hence, the individual orbital energies directly reflect the amount of bonding or antibonding described by the MOs, and the total energy reflects the net bonding or antibonding due to all the π electrons together.

Does this "pairing" of energy levels observed for allyl and benzene always occur? It is easy to show that it cannot in rings with an odd number of carbon centers. Consider the cyclopropenyl system. The lowest-energy MO is nodeless, totally bonding and has an energy of $\alpha + 2\beta$. [Note from Eq. (8-51) and also from the diagram method that every monocyclic system has a totally bonding MO at this energy.] To transform these three bonding interactions into antibonding interactions of equal magnitude requires that we cause a sign reversal across every bond. This is impossible, for, if c_1 disagrees in sign with c_2 and c_3, then c_2 and c_3 must agree in sign and cannot yield an antibonding interaction.

Not surprisingly, this has all been considered in a rigorous mathematical fashion. Systems containing a ring with an odd number of atoms are "nonalternant" systems. All other homonuclear unsaturated systems are "alternant" systems. An alternant system can always have asterisks placed on some of the centers so that no two neighbors are both asterisked or unasterisked. For nonalternants, this is not possible (see Fig. 8-11). It is convenient to subdivide alternant systems into even alternants or odd alternants according to whether the number of centers is even or odd. With this terminology defined, we can now state the *pairing theorem* and some of its immediate consequences.

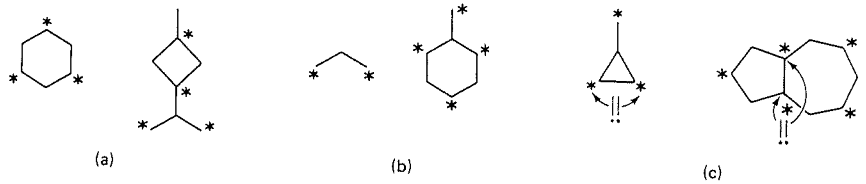

FIG. 8-11 (a) Even and (b) odd alternants have no two neighbors identical in terms of an asterisk label. (c) Nonalternants have neighbors that are identical.

The theorem states that, for alternant systems, (1) energy levels are paired such that, for each level at $\epsilon = \alpha + k\beta$ there is a level at $\epsilon = \alpha - k\beta$; (2) MOs that are paired in energy differ only in the signs of the coefficients for one of the sets (asterisked or unasterisked) of AOs.

It is easy to see that an immediate result of this theorem is that an odd-alternant system, which must have an odd number of MOs, must have a nonbonding ($E = \alpha$) MO that is not paired with another MO. It is also possible to show that the electron density is unity at every carbon for the neutral ground state of an alternant system. The proofs of the pairing theorem and some of its consequences are given in Appendix 5.

Another useful short cut exists that enables one to sketch qualitatively the MOs for any linear polyene. The HMOs for the allyl and butadiene systems are given in Fig. 8-12. Notice that the envelopes of positive (or negative) sign in these MOs are similar in appearance to the particle in a one-dimensional "box" solutions described in Chapter 2. This similarity makes it fairly easy to guess the first few MOs for pentadienyl, hexatriene, etc. Also, if one knows the lowest-energy half of the MOs for such molecules, one can generate the remaining MOs by appeal to the second part of the pairing theorem. (The edges of the one-dimensional box should extend one C–C bond length beyond the terminal atoms.)

For larger, more complicated systems, like naphthalene, it is possible to use symmetry properties of the molecule to help choose a basis of symmetry orbitals. As was mentioned in our discussion of homonuclear diatomic molecules, this has the effect of partitioning the secular determinant into a set of smaller determinants, thereby making the problem computationally less tedious. This

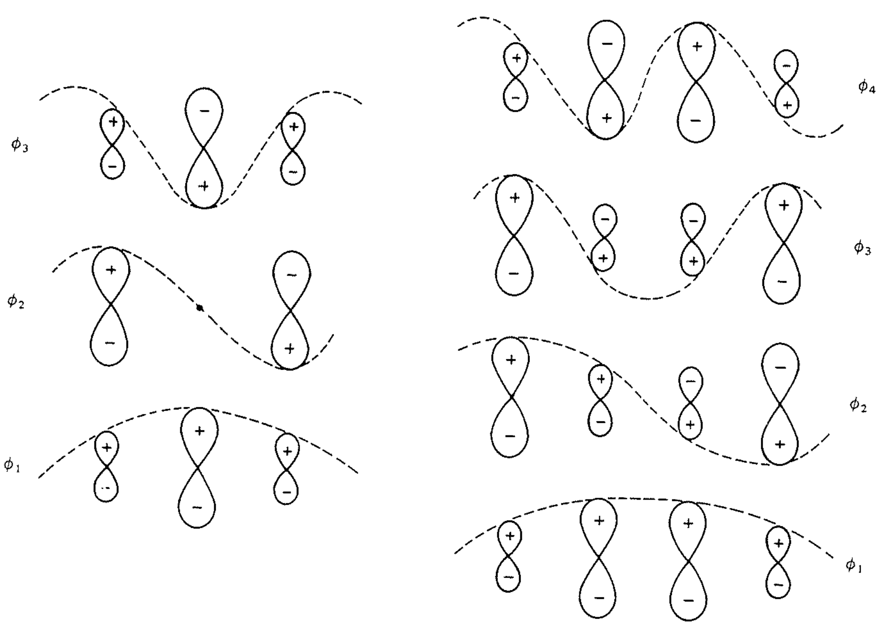

FIG. 8-12 MOs for the allyl and butadiene systems. The dashed lines emphasize the similarity between an envelope, or contour, of positive ψ_π for these systems and the particle in a one-dimensional box solutions.

procedure is described by Streitwieser [3] and Levine [4] and will not be described here since, in recent times, it has become common practice to do only the simplest HMO calculations by hand. Complicated systems are subjected to solution by computer[6] or else by appeal to HMO tabulations in print.[7]

8-10 HMO Calculations on Some Simple Molecules

Thus far, we have used the allyl and cyclopropenyl systems as examples. We will now describe the results of HMO calculations on some other simple but important systems.

A. *Ethylene (Even Alternant)*

The Hückel determinantal equation is

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

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[6] Many types of quantum-chemical computer programs are available from: Quantum Chemistry Program Exchange, Chemistry Department, Indiana University, Bloomington, Indiana 47401.

[7] See Coulson and Streitwieser [5], Streitwieser and Brauman [6], and Heilbronner and Straub [7]. See also Appendix 6 of this text.

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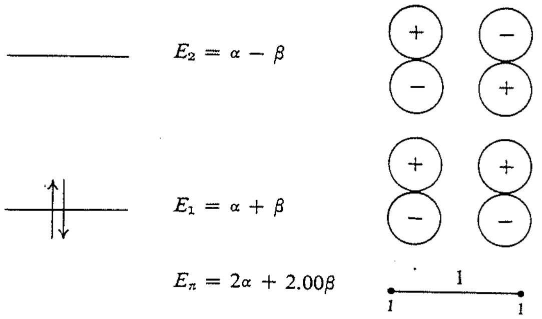
and so $x^2 - 1 = 0$; $x = +1, -1$. The resulting orbital energies and coefficients are

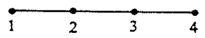
$$\begin{aligned} E_1 &= \alpha + \beta, \qquad \phi_1 = (1/\sqrt{2})\chi_1 + (1/\sqrt{2})\chi_2 \\ E_2 &= \alpha - \beta, \qquad \phi_2 = (1/\sqrt{2})\chi_1 - (1/\sqrt{2})\chi_2 \end{aligned} \tag{8-59}$$

These, with the ground state electronic configuration indicated, are shown in (II). π-Electron densities and π-bond order are indicated in the diagram beneath the MO sketches. Ethylene is an even alternant, so it has paired energies, unit electron densities, and coefficients related by a sign change.



(II)

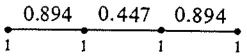
B. *Butadiene (Even Alternant)*



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

This problem can be solved by expansion to a polynomial in x and factoring, but it is simpler to use Eq. (8-49) or the decagon in a circle of radius $2|\beta|$. The coefficients are obtainable from Eq. (8-50). The results are

$$\begin{gathered} E_4 = \alpha - 1.618\beta, \qquad E_3 = \alpha - 0.618\beta, \qquad E_2 = \alpha + 0.618\beta, \\ E_1 = \alpha + 1.618\beta, \qquad E_\pi = 4\alpha + 4.472\beta \\ \phi_{\underset{(4)}{1}} = 0.372\chi_1 \underset{(-)}{+} 0.602\chi_2 + 0.602\chi_3 \underset{(-)}{+} 0.372\chi_4 \\ \phi_{\underset{(3)}{2}} = 0.602\chi_1 \underset{(-)}{+} 0.372\chi_2 - 0.372\chi_3 \underset{(+)}{-} 0.602\chi_4 \end{gathered} \tag{8-60}$$



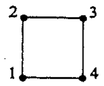
The MOs are given in Fig. 8-12. ϕ_1 is bonding in all bonds, ϕ_2 is bonding in the outer bonds, antibonding in the central bond. As a result, butadiene has a lower π-bond order in the central bond than in the outer bonds. This is in pleasing accord with the experimental observation that the central bond in butadiene is significantly longer than the outer bonds.

The formal structural formula for butadiene (**III**), indicating two pure double bonds and one pure single bond, is clearly not an adequate description since we have just found the central bond to have some π-bonding order (0.447) and the outer bonds to be less π bonding than ethylene (0.894). The MO parlance is that the π electrons in butadiene are *delocalized* over the entire carbon system rather than being restricted to the formal double bonds only.

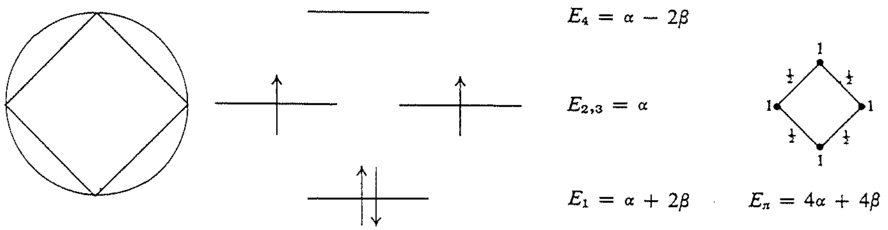
(III)

Because the HMO method allows for no interaction between terminal carbons (i.e., $H_{1,4} = 0$), there is no distinction between *cis*- and *trans*-butadiene in this calculation. However, if a weak interaction were postulated, it is not difficult to see that ϕ_1 would give a bonding end-to-end contribution, ϕ_2 a substantially larger antibonding interaction, leading to a prediction (in agreement with experiment) that *trans*-butadiene is the more stable form.

C. *Cyclobutadiene* (*Even Alternant*)



Inscribing this molecule in a circle gives us the orbital energies immediately (**IV**).



(IV)

Since ϕ_1 and ϕ_4 are nondegenerate, they must be symmetric or antisymmetric for the various rotations and reflections of the molecule. Also, ϕ_1 and ϕ_4 must have the same coefficients, except for sign changes.

$E = 4\alpha$

$2E_1 + E_3 + E_3$

$E_\pi = 4\alpha + 4\beta$

It follows at once that

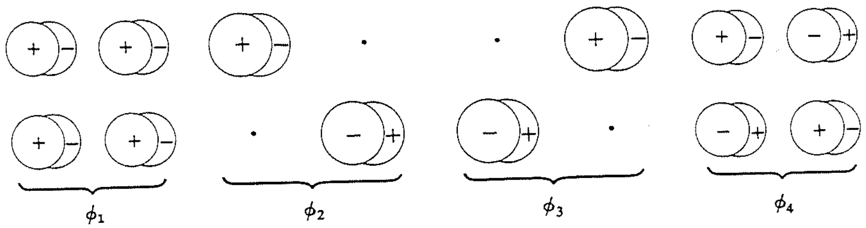
$$\phi_1 = \tfrac{1}{2}\chi_1 + \tfrac{1}{2}\chi_2 + \tfrac{1}{2}\chi_3 + \tfrac{1}{2}\chi_4, \qquad \phi_4 = \tfrac{1}{2}\chi_1 - \tfrac{1}{2}\chi_2 + \tfrac{1}{2}\chi_3 - \tfrac{1}{2}\chi_4$$

ϕ_2 and ϕ_3 are degenerate, so there is some arbitrariness here. However, we expect each of these MOs to have a nodal plane, and these planes should be perpendicular to each other if ϕ_2 and ϕ_3 are to be orthogonal. Therefore, we choose the pair having nodal planes indicated by dashed lines (**V**). The four MOs for cyclobutadiene *as seen from above* are shown in (**VI**). It is clear that ϕ_2 and ϕ_3 are nonbonding because the nodal planes prevent interactions between neighbors, but it looks like ϕ_2 and ϕ_3 violate the pairing theorem since they cannot be interchanged by changing signs of coefficients. This is only an apparent violation, because it is easy to find an equivalent pair of MOs that follow the rule. We need only choose nodal planes that are rotated 45° (**VII**) from those we selected previously. These MOs are linear combinations of ϕ_2 and ϕ_3 and are equivalent to them for purposes of calculating electron densities and bond orders. They are still nonbonding MOs (E still equals α), but now it is not because of a nodal plane preventing nearest-neighbor interactions, but because bonding and antibonding interactions occur in equal number and magnitude.

Notice that this is an example of an even alternant system with nonbonding MOs. Thus, whereas an odd alternant system *must* have *an* unpaired nonbonding MO, even alternants *may* have nonbonding MOs in pairs.

$\phi_2 = (1/\sqrt{2})\chi_1 - (1/\sqrt{2})\chi_3 \qquad \phi_3 = (1/\sqrt{2})\chi_2 - (1/\sqrt{2})\chi_4$

(V)



(VI)

$\phi_2' = \tfrac{1}{2}\chi_1 - \tfrac{1}{2}\chi_2 - \tfrac{1}{2}\chi_3 + \tfrac{1}{2}\chi_4 \qquad \phi_3' = \tfrac{1}{2}\chi_1 + \tfrac{1}{2}\chi_2 - \tfrac{1}{2}\chi_3 - \tfrac{1}{2}\chi_4$

(VII)

Since this system is alternant, it must have π-electron densities of unity in its ground neutral state. This would be necessary however, even if the molecule were not alternant, due to the fact that all carbons are equivalent by symmetry. Hence, they must all have the same electron density. Since it must sum to four electrons, the density of each atom must be unity. The same argument applies to the cyclopropenyl radical, a nonalternant that, nevertheless, has all electron densities equal to unity (if the unpaired electron is divided between degenerate MOs).

Symmetry also requires all four bonds to be identical. Since the total energy, $4\alpha + 4\beta$, is related to bond order through Eq. (8-58), it follows at once that the total bond order is 2, and so each bond has order $\frac{1}{2}$.

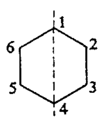
D. *Benzene* (*Even Alternant*)

Benzene is another molecule whose high symmetry enables one to use shortcuts. The orbital energies have already been found from the hexagon-in-a-circle diagram (see Fig. 8-9). The lowest- and highest-energy MOs must show all the symmetry of the molecule, as they are nondegenerate. Therefore,

$$\underset{(6)}{\phi_1} = (1/\sqrt{6})(\chi_1 \underset{(-)}{+} \chi_2 + \chi_3 \underset{(-)}{+} \chi_4 + \chi_5 \underset{(-)}{+} \chi_6)$$

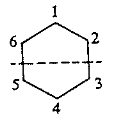
where the carbon atoms are numbered sequentially around the ring.

The degenerate MOs ϕ_2 and ϕ_3 should have one nodal plane each, and these should be perpendicular to each other.[8] If we take one plane as shown in **(VIII)**, we can immediately write down ϕ_2. The node for ϕ_3 is given in **(IX)**. It is obvious that χ_6, χ_1, χ_2 have coefficients of the same sign, and that $c_2 = c_6 = -c_5 = -c_3$, and also $c_1 = -c_4$. However, c_1 need not equal c_2 as these atoms are differently placed with respect to the nodal plane. To determine these coefficients, we will use the fact that the neutral ground-state π densities are all unity in this system. We consider first atom number 1. Its electron density due to two electrons in ϕ_1 and two electrons in ϕ_2 is $\frac{1}{6} + \frac{1}{6} + 0 + 0 = \frac{1}{3}$.



$$\underset{(4)}{\phi_2} = \tfrac{1}{2}(\chi_2 \underset{(-)}{+} \chi_3 \underset{(+)}{-} \chi_5 - \chi_6)$$

(VIII)



(IX)

Therefore, two electrons in ϕ_3 must produce a contribution of $\frac{2}{3}$. Hence the coefficient for this atom in ϕ_3 must be $1/\sqrt{3}$. A similar argument for atom 2 gives a coefficient of $1/\sqrt{12}$ (or, one can use the normality condition for ϕ_3). As a result,

$$\underset{(5)}{\phi_3} = (1/\sqrt{3})(\chi_1 \underset{(-)}{+} \tfrac{1}{2}\chi_2 - \tfrac{1}{2}\chi_3 \underset{(+)}{-} \chi_4 - \tfrac{1}{2}\chi_5 \underset{(-)}{+} \tfrac{1}{2}\chi_6)$$

Appeal to the pairing theorem generates ϕ_4 and ϕ_5 as indicated.

By symmetry, all bond orders must be identical, and their sum must be 4, since $E = 6\alpha + 8\beta$. Therefore, $p_{12} = p_{23} = \cdots = p_{61} = \frac{4}{6} = 0.667$.

The hexagon in a circle applies to ethylene ($n = 2$, $2n + 2 = 6$) as well as to benzene. As a result, the orbital energies for ϕ_2, ϕ_3 of benzene are identical to E_1 for ethylene. Examination of these MOs (Fig. 8-13) makes the reason for their energy agreement clear. Molecular orbital ϕ_2 of benzene is more revealing than is ϕ_3 in this context. The nodal plane produces an MO corresponding to two *noninteracting* ethylene MOs. Hence, an electron in this MO is always in a situation that is indistinguishable (under HMO approximations) from that in ϕ_1 of ethylene.

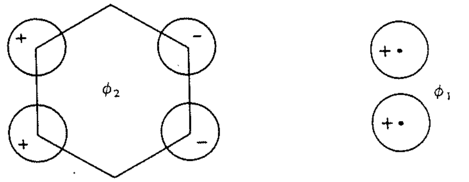


FIG. 8-13 ϕ_2 for benzene and ϕ_1 for ethylene have the same HMO energy. The MOs are sketched as seen from above.

In this section, we have tried to illustrate some of the properties of HMO solutions for simple systems and to indicate how symmetry and other relations are useful in producing and understanding HMO results. It is often convenient to have HMO results for various simple systems readily available in a condensed form. Therefore, a summary of results for a number of molecules is provided in Appendix 6.

8-11 Summary: The Simple HMO Method for Hydrocarbons

(1) The assumption is made that the π-electron energy can be minimized independently of σ electrons. This is an approximation.

(2) The assumption is made that each π electron sees the same field (the repulsion due to the other π electrons is presumably included "in effect," in a time averaged way) so that the π electrons are treated as independent particles. This approximation leads to a total wavefunction that is a simple product of one-electron MOs and a total π energy that is a sum of one-electron energies. Except for use of the Pauli principle to build up configurations, no explicit treatment is made of electron spin.

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[8] This statement applies to the real forms of ϕ_2 and ϕ_3. The complex forms [derivable from Eq. (8-52)] do not have a planar node. The situation is analogous to the $2p_{+1}$, $2p_{-1}$ versus $2p_x$, $2p_y$ orbitals for the H atom.

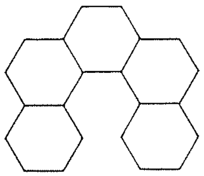
(3) The basis set is chosen to be a $2p_\pi$ AO from each carbon atom in the unsaturated system. Choosing a basis set of AOs means our MOs will be linear combinations of AOs, and so this is an LCAO–MO method.

(4) The Hückel determinant summarizes the connectedness of the unsaturated system, and is independent of *cis–trans* isomerism or bond length variation.

(5) The energy of each MO is expressed in terms of atomic terms, α, and bond terms, β. The amount of α in each MO energy is always unity because the sum of π-electron densities for one electron in the MO is always unity. The amount of β present is related to the net bonding or antibonding character of the MO.

(6) Alternant systems display paired energy levels and corresponding MOs having coefficients related by simple sign reversals. For ground-state neutral alternants, the electron densities are all unity.

(7) A caveat: One can perform HMO calculations on very large systems such as pentahelicene (**X**) thereby making the implicit assumption that this is a planar molecule. But repulsion between protons on the terminal rings is sufficient to cause this molecule to deviate from planarity. Hence, one must recognize that, in certain cases, an HMO calculation refers to a planar "ideal" not actually achieved by the molecule.



(X)

8-12 Relation between Bond Order and Bond Length

In this and following sections we will describe some of the relations between HMO theoretical quantities and experimental observations.[9]

It is natural to look for a correlation between calculated π-bond orders and experimentally determined bond lengths. A high bond order should correspond to a large π charge in the bond region, which should yield a shorter, stronger bond. The bond-order–bond-length results for certain simple systems, given as a graph in Fig. 8-14, do indeed show the anticipated behavior. However, as more and more data are added (Fig. 8-15) it becomes clear that an exact linear relation between these quantities does not exist at this level of refinement. Efforts to improve the situation by refining the theory have been made, but the relatively large uncertainty in experimentally determined bond lengths has been a severe handicap. Nevertheless, the correlation between bond order and bond length is good enough to make it useful for rough predictions of bond length *variations*. An example of this is given in Fig. 8-16, where calculated and observed bond

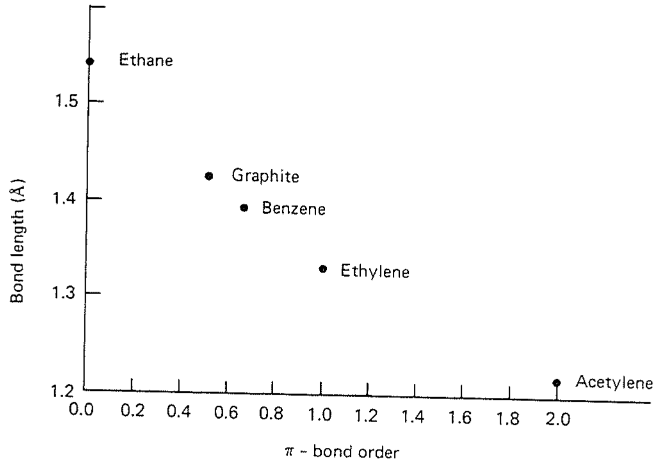


FIG. 8-14 π-Bond order versus bond length for some simple unsaturated hydrocarbons.

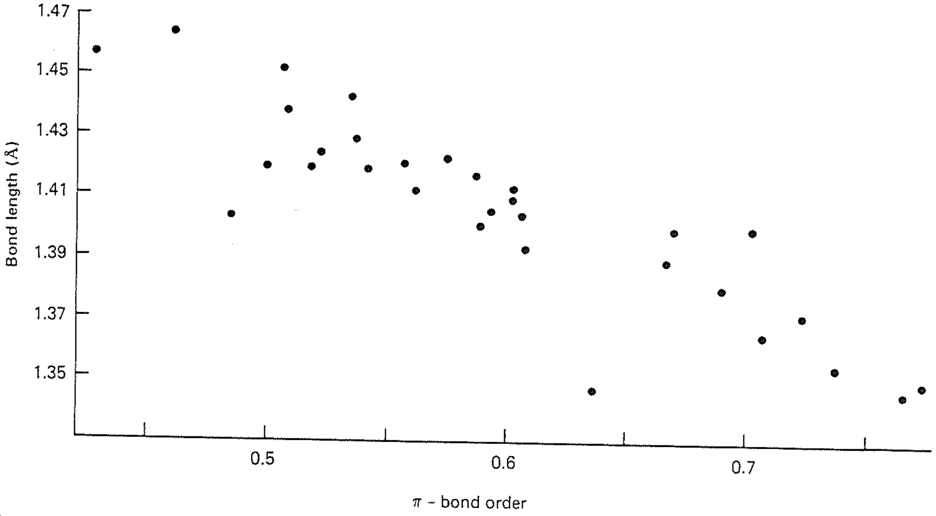


FIG. 8-15 Bond lengths versus π-bond orders for benzene, graphite, naphthalene, anthracene, phenanthrene, triphenylene, and pyrene.

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[9] For a more complete discussion of these phenomena as well as many others, see Streitwieser [3].

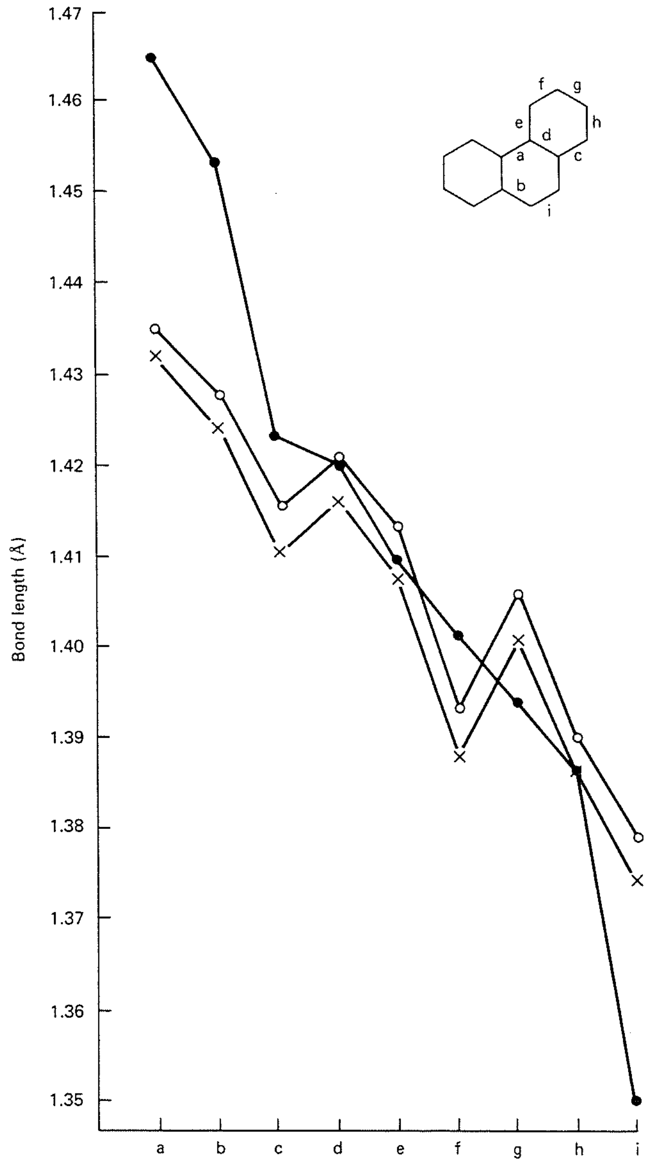

FIG. 8-16 Theoretical versus experimental bond lengths for phenanthrene in order of decreasing observed length: (●) experimental; (×) theoretical with $s = 1.54$ Å, $k = 0.765$; (o) theoretical with $s = 1.515$ Å, $k = 1.05$.

lengths for phenanthrene are plotted. Even though the predicted *absolute* values of bond lengths are imperfect, the theoretical values show a rough parallelism with observed values as we go from bond to bond. The relation used here to calculate the theoretical bond lengths from HMO bond orders is due to Coulson [8] and has the form

$$R = s - \frac{s - d}{1 + k(1 - p)/p} \tag{8-61}$$

Here, s is the single bond length, d the double bond length, p the π-bond order, k an adjustable parameter, and R the predicted length. The double bond length d is taken to be 1.337 Å, the bond length of ethylene. The single bond length may be taken to be the length of the C–C bond in ethane, 1.54 Å, or it may be set by fitting to data points (such as those in Fig. 8-15) on the assumption that the single bond between two CH_2 groups (i.e., ethylene with its π bond "turned off") is not necessarily the same length as the single bond between two CH_3 groups. Both of these alternatives have been used in Fig. 8-16. Other mathematical forms have also been suggested. Because of the scatter in the data, there is little basis for preferring one formula over another. It seems generally true that all the proposed relationships work best for bonds in condensed ring systems, and most poorly for bonds in acyclic polyenes (e.g., butadiene) or between rings (e.g., biphenyl).

8-13 π-Electron Densities and Electron Spin Resonance Hyperfine Splitting Constants[10]

The hyperfine structure of electron spin resonance (ESR) spectra results from the interaction between the magnetic moment due to an unpaired electron spin and the magnetic moments of certain nuclei (usually protons) in the molecule. The interaction between an *unpaired π electron* and a proton falls off rapidly with increasing separation. Therefore, the hyperfine structure is generally ascribed to interactions involving protons directly bonded to carbons in the π system (α protons) or else separated from the π system by two σ bonds (β protons). The equilibrium position of an α proton is in the nodal plane of the π system, and it is clear that any net spin density at the proton must be only *indirectly* due to the presence of an unpaired π electron. This indirect effect arises because the unpaired π electron interacts slightly differently with α- and β-spin σ electrons, and so the spatial distributions of these become slightly different, producing net spin density at the proton; the σ electrons are said to be *spin polarized* by the π electron (see Fig. 8-17).

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[10] A number of reviews on this subject have been published. See, for example, Gerson and Hammons [9].

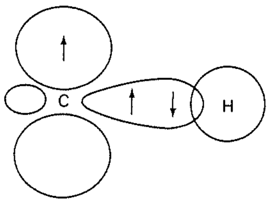


FIG. 8-17 The unpaired π-spin density at carbon repels both σ electrons in the C–H bond region, but does not repel them equally. As a result, slight spin imbalance due to σ electrons occurs at the proton.

The extent of spin polarization at a given hydrogen should depend on the percentage of time the unpaired π electron spends on the carbon to which that hydrogen is bonded. It is therefore reasonable to look for relationships between the distribution of *π-spin* density in a radical and the hyperfine coupling constants characterizing its ESR spectrum. The simplest assumption one can make in this regard, called the McConnell relation, is that the hyperfine splitting constant, $a_{H\mu}$, for a proton directly bonded to the μth carbon, is proportional to the net π-spin density ρ_μ on that carbon:

$$a_{H\mu} = Q\rho_\mu \tag{8-62}$$

Thus, if the unpaired π electron density is twice as great on carbon 1 as on carbon 2, the ESR splitting constant for a proton attached to carbon 1 should be twice as great as that for a proton attached to carbon 2.

The HMO method predicts that the spin density at the μth carbon due to an unpaired electron in the mth MO is simply $|c_{\mu m}|^2$. This is only a first approximation to ρ_μ, but a graph of observed splitting constants plotted against ρ_μ calculated in this way shows a respectable correlation (Fig. 8-18). The proportionality factor Q, given by the slope of the line of best fit, varies somewhat depending on the type of system and the charge of the radical. Thus, in Fig. 8-18, where all the data are from aromatic fused ring hydrocarbon radical anions, the correlation is quite good. As data for nonalternants and radical cations are added (Fig. 8-19) the scatter increases.

Some ESR spectra are interpreted to be consistent with the presence of some *negative* spin density. That is, if the extra π electron is taken to have α spin, some of the carbons appear to have an excess of β-spin π density. Now the amount of splitting seen in ESR spectra depends only on the *magnitudes* of spin densities at the protons, not on whether these spin densities are α or β, and the presence of negative spin density does not produce a *qualitative* change in an ESR spectrum (such as a "negative splitting," whatever that might be). Rather it leads to an increase in the total *amount* of spin density in the system, and this, in turn, leads to an increase in the sum of splitting constants (over what would be predicted in the absence of negative spin density). For example, the HMO prediction for allyl radical would give a net spin density of $\frac{1}{2}$ at each terminal carbon and zero at the central carbon. [The unpaired electron is in the nonbonding MO $(1/\sqrt{2})\chi_1 - (1/\sqrt{2})\chi_3$.] However, we might imagine the situation wherein there is a net spin of $\frac{2}{3}\alpha$ at each terminal carbon and $\frac{1}{3}\beta$ at the central atom. This retains a net spin value of 1α yet results in a larger splitting constant $a_{H\mu}$ for every proton in the molecule. It is possible to think of a physical explanation for this kind of spin distribution. The π electrons in lower-energy, filled MOs are being spin polarized similarly to the σ electrons mentioned earlier. If an α-spin electron in effect repels electrons of β spin more strongly than those of α spin, a buildup of β spin on the central carbon of allyl radical could be expected. Because this secondary effect is expected to be fairly small, a *net* negative spin density is likely only on carbons where the primary effect ($c_{\mu m}^2$) is zero or quite small. Methods for calculating this spin polarization (which will not be described here) indicate that certain of the splitting constants plotted in Figs. 8-18 and 8-19 do in fact result from negative spin densities. These data points are

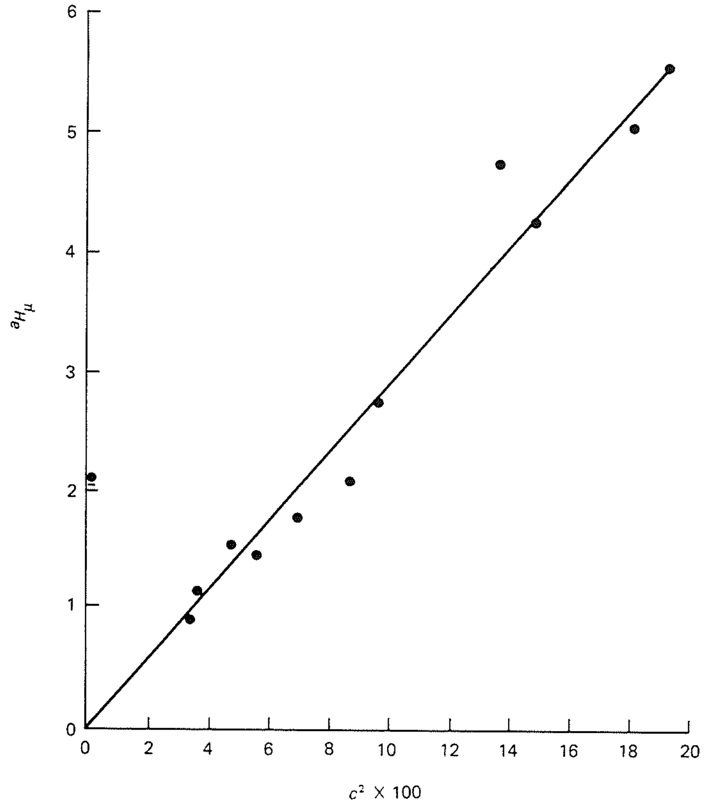


FIG. 8-18 ESR splitting constants a_{H_μ} versus HMO unpaired spin densities. The systems are fused ring alternant hydrocarbon radical anions (naphthalene, anthracene, tetracene, pyrene). The underlined point is thought to result from negative spin density. (Data from Streitwieser [3].)

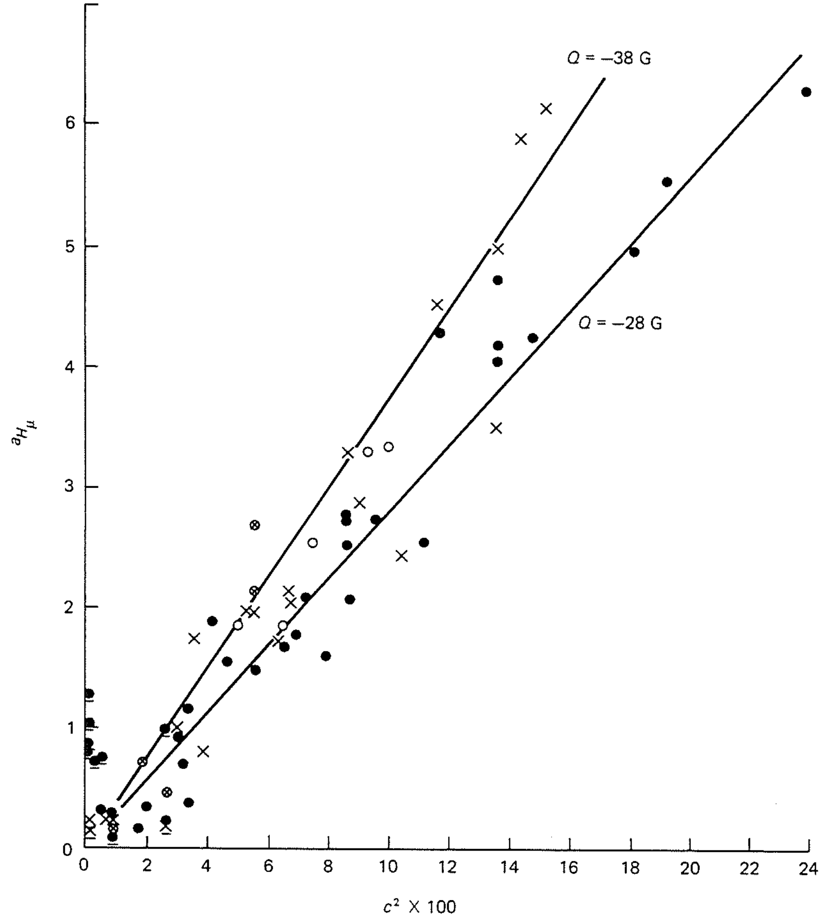


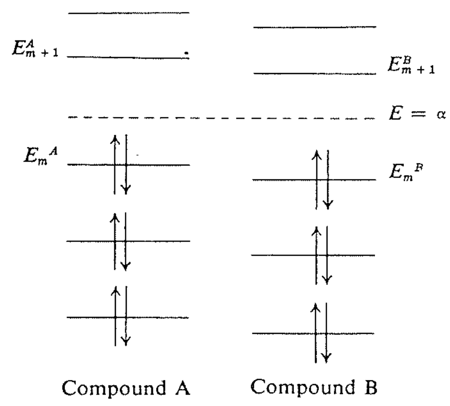
FIG. 8-19 ESR hyperfine splitting constants versus c^2 for the highest occupied MO of the radical. All data are from hydrocarbon radical anions or cations of alternant or nonalternant type. (●) Anion radical; (×) cation radical. Uncertain assignments: (○) anion; (⊗) cation. The two correlation lines are merely sight fitted to the anion and cation points separately and suggest that Q for cations should be larger than for anions. Points thought to result from negative spin density are underlined. [See Tables I, III, VIII, XII, XIII, XIV, XV, XVI, XVII, XVIII of Gerson and Hammons [9], and Table 6.2 of Streitwieser [3] for data plotted here.]

indicated in the figures, and it can be seen that they do indeed occur where $c_{\mu m}^2$ and $a_{H\mu}$ are small. This secondary effect is masked at higher values of $c_{\mu m}^2$ and $a_{H\mu}$, but presumably accounts for some of the scatter in the data. (Some scatter also results from solvent dependence of $a_{H\mu}$. Several solvents were used in experiments yielding the data in Fig. 8-19.)

Because of the pairing-theorem relation between coefficients of MOs, the ESR spectra of the radical cation and anion of an alternant system should appear very similar. Hückel molecular orbital theory would predict them to be identical except for a slight change of scale due to a change in the factor Q. In practice, this similarity has been observed to hold fairly well.

8-14 Orbital Energies and Oxidation–Reduction Potentials

Many conjugated hydrocarbons can be oxidized or reduced in solution using standard electrochemical techniques. Since oxidation involves removing an electron from the highest occupied (π) MO (HOMO), it is reasonable to expect molecules with lower-lying HOMOs to have larger oxidation potentials. Similarly, we might expect reduction to be easier for compounds wherein the lowest unoccupied MO (LUMO) is lower in energy [see (**XI**)]. Thus, compound A should have a lower oxidation potential than compound B since $E_m{}^A > E_m{}^B$, but compound B should have the lower reduction potential. A plot of oxidation potential versus E_m in units of β for a series of aromatic hydrocarbons (Fig. 8-20) yields a correlation which is remarkably free of scatter. Figure 8-21 indicates a similar correlation for reduction potential versus E_{m+1}.



(XI)

Since oxidation–reduction potentials correlate with HOMO–LUMO energies, and since these energies are paired in even alternant systems, we should expect a plot of oxidation vs reduction potential for such compounds to be linear also.

The data in Figs. 8-20 and 8-21 provide a connection between theoretical energy differences in units of β, and experimental energies. From the slope in Fig. 8-20 we obtain that $\beta \cong -2.03$ eV, or -46.8 kcal/mole. Similarly, the reduction potential data of Fig. 8-21 gives $\beta = -2.44$ eV $= -56.3$ kcal/mole.

One must be cautious in interpreting the above values of β. The problem is

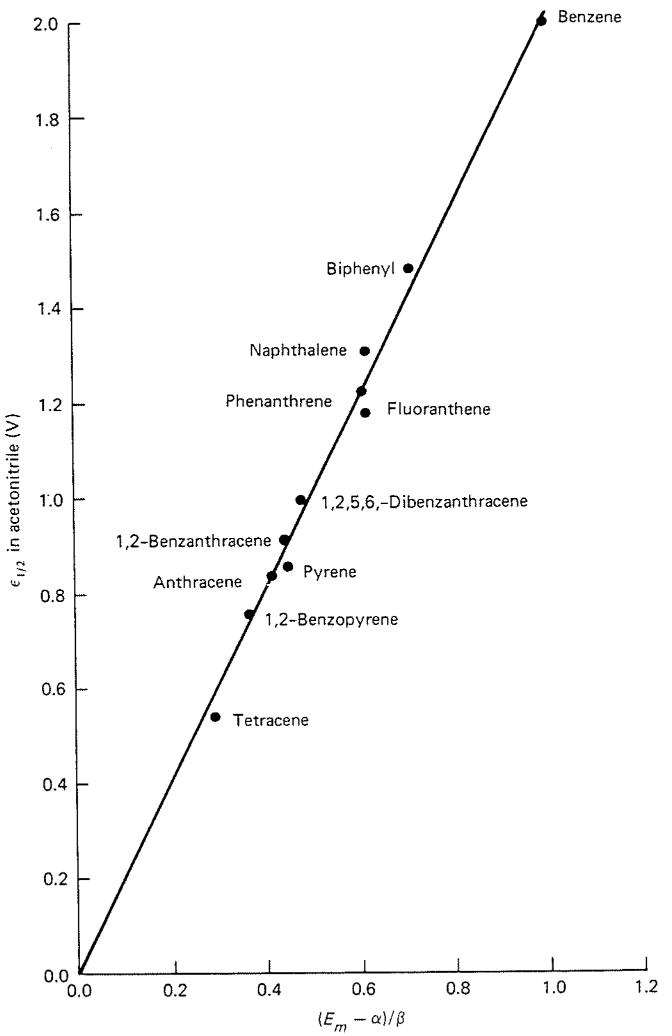


FIG. 8-20 Oxidation potentials in acetonitrile solution versus energy of HOMO (in units of β). ($\epsilon_{1/2}$ from Lund [10].)

that the experimental numbers include effects of physical processes not included in the theory. For example, when a neutral molecule in solvent becomes oxidized or reduced, solvation energy changes occur. One might argue that the fit of the data to straight lines in Figs. 8-20 and 8-21 implies this sort of contribution to be small, but the sensitivity of redox potentials to solvent nature indicates that this

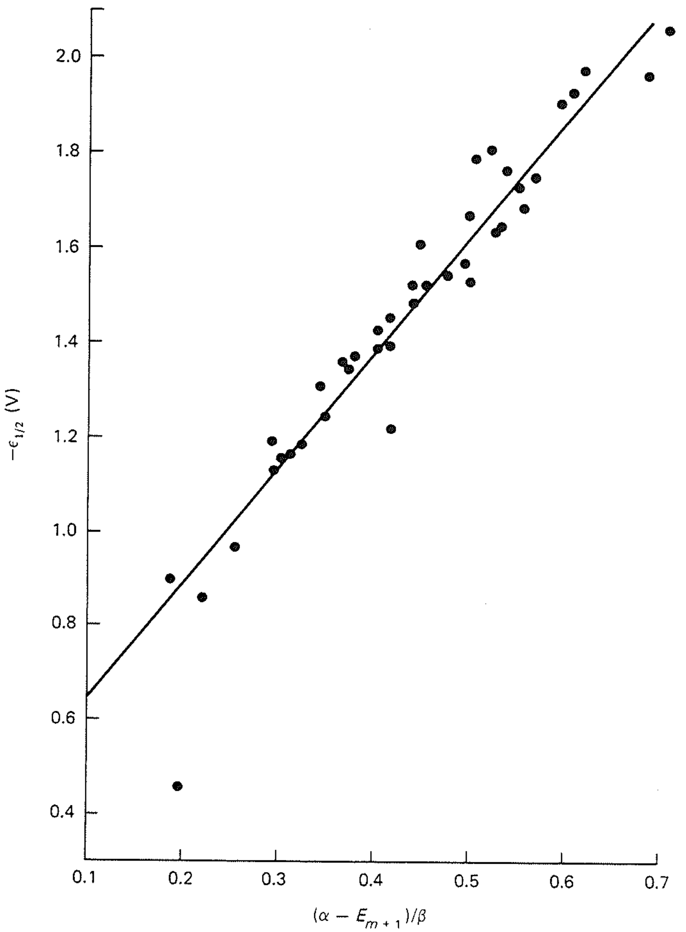


FIG. 8-21 First reduction potential in 2-methoxyethanol versus energy of LUMO (in units of β). ($\epsilon_{1/2}$ from Bergman [11].)

is not the case. However, in larger molecules, solvation energy change upon ionization tends to be smaller, and larger molecules also tend to have E_m and E_{m+1} closer to the $E = \alpha$ level. In other words, we expect both solvation energy change *and* redox potential to be proportional to E_m or E_{m+1}. Therefore, they can be combined in a single linear relation. There is, in general, no guarantee that "extra" contributing effects will be of a nature to be correctly assimilated into the theoretical formula, but, for this effect, it happens that this is at least partially the case.

Another extra effect to consider is the π-electron repulsion energy. Because the energies of the HOMO and LUMO are both associated with the neutral molecule, their energies fail to reflect the decrease or increase of π-electron repulsion energy resulting from loss or gain of a π electron. Here again, however, we expect the magnitude of the effect to be larger for smaller molecules, where the change in π densities is greatest, and also where E_m and E_{m+1} deviate most from α. Thus, as before, this extra effect will not necessarily upset the linear relation expected from simpler considerations.

In view of the crudity of the HMO method together with the fact that the empirical value of β includes the effects of several extra processes, the β values cited above for oxidation and reduction are considered to be in fairly good agreement, especially considering that the electron repulsion change operates to make oxidation easier and reduction harder.

8-15 Orbital Energies and Ionization Potentials

Suppose that monochromatic light is beamed into a gaseous sample of a compound. If the light is of sufficient energy, electrons will be "knocked out" of the molecules. The kinetic energy of such a photoelectron will be equal to the kinetic energy of the incident photon ($h\nu$) minus the energy needed to remove the electron from the molecule, that is, the ionization potential. Measurement of the kinetic energies of photoelectrons emitted in this manner is known as "photoelectron spectroscopy" [12].

In measuring the kinetic energies of photoelectrons from, say, benzene, it is found that a large number are near a particular energy value, another large number of electrons are near a different value, and so on for several kinetic energy values. Because the electrons tend to clump near several kinetic energy values, it follows that we are, in effect, measuring several ionization potentials. It is reasonable to associate these with removal of electrons from different MOs of the molecule.[11] A correlation plot (Fig. 8-22) between HMO orbital energies and experimentally measured ionization potentials for a number of alternant and nonalternant hydrocarbons has been produced by Brogli and Heilbronner [13]. Their best fit was achieved using $\alpha = -6.553 \pm 0.340$ eV, $\beta = -2.734 \pm 0.333$ eV, where the limits define a range for the predicted ionization potential (IP) that will include the experimental value nine times out of ten (a 90% confidence level). There is a fair degree of scatter in the correlation plot. By making some additional refinements in the theory, Brogli and Heilbronner succeeded in substantially improving the correlation. We will describe this refinement in Section 8-18.

In this section, we have dealt only with ionization potentials assigned to removal of a π electron. Removal of electrons from σ orbitals is also observed. If the impinging photons are of X-radiation frequencies, the inner shell electron ionization potentials are seen. Quantum-chemical treatments of these ionization potentials are possible using theoretical methods described later.

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[11] Note that each ionization potential is associated with removal of an electron from a different MO of the *neutral* molecule. This differs from the first, second, etc. ionization potentials produced by *successive* ionization.

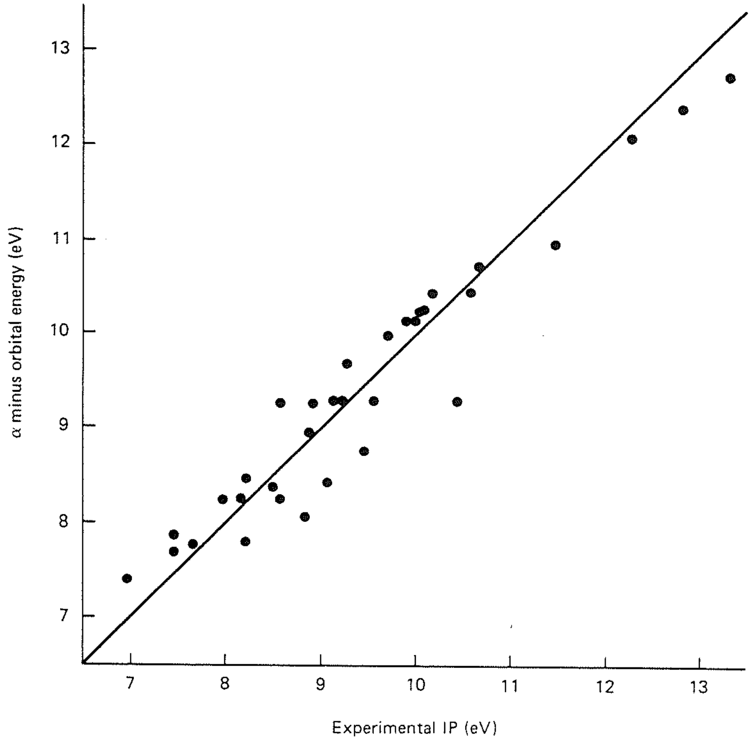


FIG. 8-22 Experimental ionization potentials for alternant and nonalternant hydrocarbons versus HMO orbital energies using $\alpha = -6.553$ eV, $\beta = -2.734$ eV.

8-16 π-Electron Energy and Aromaticity

When propene is hydrogenated to form propane, the increase in heat content ΔH°_{298} (called the *heat of hydrogenation*) is -30.1 kcal/mole. The heat of hydrogenation for 1-butene is -30.3 kcal/mole. In general, the heat of hydrogenation of an isolated double bond is about -30 kcal/mole. A similar constancy holds for the contribution of a double bond to the heat of formation of a molecule. Therefore, isolated double bonds fit easily into the usual chemical device of estimating the energy of a molecule by adding together contributions from the substituent parts. This additivity appears to be violated when double bonds are conjugated. Thus, the heat of hydrogenation for *trans*-1,3-butadiene is -57.1 kcal/mole compared with the value of -60.6 kcal/mole for a pair of butene double bonds. Since the hydrogenation product in each case is butane, the energy different of 3.5 kcal/mole must be due to the greater stability of conjugated double bonds.

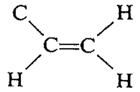
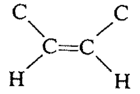
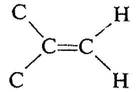
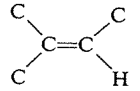
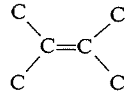
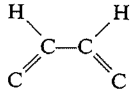
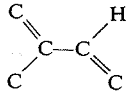
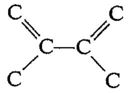
There is a theoretical parallel to this. The HMO energy for butadiene is $4\alpha + 4.472\beta$. For a pair of *isolated* double bonds, we double the energy of ethylene to obtain $4\alpha + 4\beta$. Therefore, the HMO method indicates that the conjugated double bonds are stabilized by 0.472β.

Because the π electrons in butadiene are delocalized over all three C–C bonds, this 0.472β has often been referred to as *delocalization energy*. It was common practice for many years to equate this theoretical delocalization energy for a molecule to its experimentally measured "extra" stability (e.g., for butadiene, $0.472|\beta| = 3.5$ kcal/mole).

In 1969, Dewar and co-workers [14, Chapter 5; 15; 16] demonstrated that conjugated double bonds may be successfully included in an additivity scheme. Hess and Schaad [17, 18] have considered this idea in the context of the HMO method. They distinguish between several kinds of C–C single and double bond energy as indicated in Table 8-2. Using these values of bond energy, the π energy of butadiene is calculated to be $2 \times 2.000\beta + 0.4660\beta + 4\alpha = 4\alpha + 4.4660\beta$ compared with the HMO result of $4\alpha + 4.472\beta$. The difference is 0.006β, less than 0.002β per π electron. Hess and Schaad show that this level of agreement holds for acyclic polyenes in general, even when there is much branching. Thus, it seems that conjugated double bonds in acyclic molecules fit into an additivity scheme after all.

There is an important difference between the energy additivity scheme for conjugated systems described above and the familiar additivity scheme used for C—H, C—C, and isolated C═C bonds. In the latter cases the energy "contributed" by the bond is generally thought of as being the same as the energy of that bond in the molecule (at least in an averaged way—some care must be exercised with definitions), and, furthermore, the bond is thought to be fairly independent of the identity of the molecule. For instance, a C—H bond in butane is very similar to one in heptane. But this is not the case for conjugated molecules. Inspection of Fig. 8-23 shows that a single bond between (formal) double bonds varies significantly in bond order from molecule to molecule. Since the total π-electron energy depends on bond order [Eq. (8-58)], we can tell at once that the *actual* theoretical energy contribution due to such a "single" bond varies from $2 \times 0.4472 = 0.8944\beta$ in butadiene to 1.088β in decapentaene. However, examination of Fig. 8-23 reveals that, in going from molecule to molecule, as the "single" bonds increase in π-bond order, the "double" bonds decrease in order. Thus, adding an additional C═C—C group to a chain adds a constant amount of bond energy (about 2.54β) to the total π energy, but this energy increment contains contributions from bond order changes over the whole molecule. We have, then, an *additive* scheme for a *delocalized* effect. For this reason, the bond energy contributions of Table 8-2 are called *effective* bond energies.

TABLE 8-2
π-Bond Types and Effective Binding Energies for Carbon–Carbon Double and Single Bonds[a]

Bond type		Effective binding energy in units of β
		2.0000
	(*cis* or *trans*)	2.0699
		2.0000
		2.1083
		2.1716
	(*cis* or *trans*)	0.4660
	(*cis* or *trans*)	0.4362
	(*cis* or *trans*)	0.4358

[a] The numbers associated with these bonds are not unique. They satisfy six simultaneous equations. Hence, any two of them may be given arbitrary values and the remaining six found by solving the simultaneous equations. Different arbitrary assignments lead to different sets of numbers, all equally valid and all giving identical pi-electron energies. These numbers can only be applied when a bond has an unambiguous formal identity, which means we must deal with acyclic polyenes (even number of centers and electrons).

We are now in a position to consider the concept of aromaticity. The term "aromatic" originally referred to organic molecules having pleasant odors. Later it referred to a class of molecules having a high degree of unsaturation. Benzene was recognized as the parent compound for many such molecules, and the term

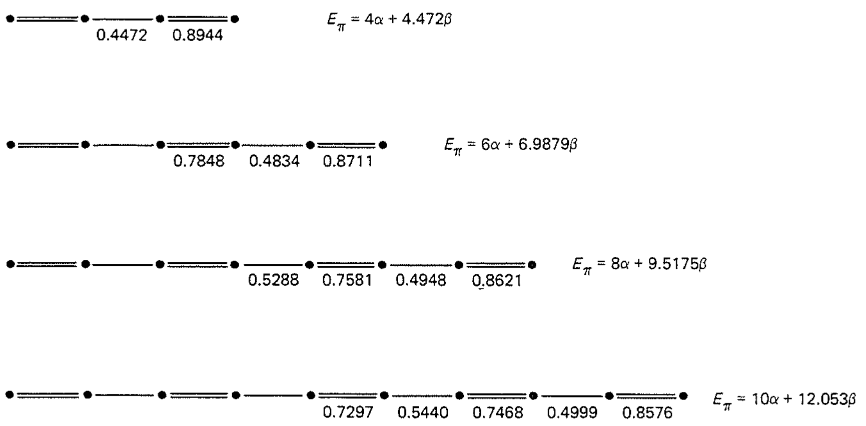


FIG. 8-23 HMO bound orders for butadiene, hexatriene, octatetraene, and decapentaene.

"aromatic" has come to mean "having chemical properties peculiar to benzene and some of its relatives." The chemical stability of these molecules, their relatively low heats of combustion or of hydrogenation, and their tendency to prefer substitution rather than addition (thereby preserving their π systems intact) distinguish these molecules from ordinary polyenes and have come to be called "aromatic properties," or manifestations of "aromaticity."[12] These properties suggest that the π electrons in aromatic systems are unusually low in energy, contributing to both the thermodynamic and the kinetic stability of the systems. We can test whether this is the case by calculating an "expected" π energy for benzene using the bond energies of Table 8-2 and an alternating single-double bond, or Kekulé, structure. The result, $6\alpha + 7.61\beta$, is significantly less stable (by 0.39β) than the HMO energy of $6\alpha + 8\beta$. We shall refer to this difference as the "resonance energy" (RE) of the system.

$$\mathrm{RE} = E_\pi(\mathrm{HMO}) - E_\pi(\text{from Table 8-2}) \qquad (8\text{-}63)$$

By this definition, a positive RE (in units of β) corresponds to extra molecular stabilization. If we divide the RE by the number of π electrons, we obtain the RE per electron (REPE). Hence, the REPE for benzene is 0.065β. Following Dewar we shall refer to a system having significantly positive REPE as "aromatic", significantly negative REPE as "antiaromatic," and negligible REPE as nonaromatic, or polyolefinic. (Recall that β is a negative quantity. When REPE is tabulated in eV, it is conventional to use the absolute value of β in eV so as to retain positive REPE for "aromatic" molecules.)

Cyclic polyenes differ from acyclic polyenes in that many of them show significant values for REPE. Some results of Schaad and Hess [18] are reproduced in Fig. 8-24. It is evident that a strong correlation exists between REPE and the presence or absence of aromatic properties.

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[12] The definition of the term "aromatic" is not generally agreed upon. This is partly due to the fact that some molecules are "like benzene" in some properties, "unlike benzene" in others. For discussion of this problem see Bergmann and Pullman [19].

The change from very aromatic to very antiaromatic nature as we go from a six-membered to a four-membered system is striking. If we examine the HMO energy levels, it is not difficult to see why these monocycles are so different. The six π electrons in benzene all occupy bonding MOs, whereas cyclobutadiene has two nonbonding electrons (**XII**). The situation is optimal for benzene not only because all its π electrons are bonding, but also because all the bonding levels

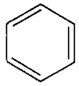
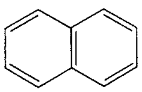
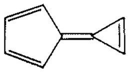
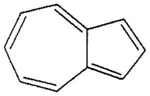
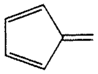
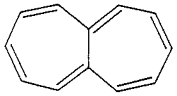
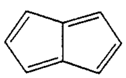
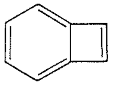
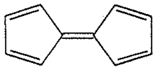
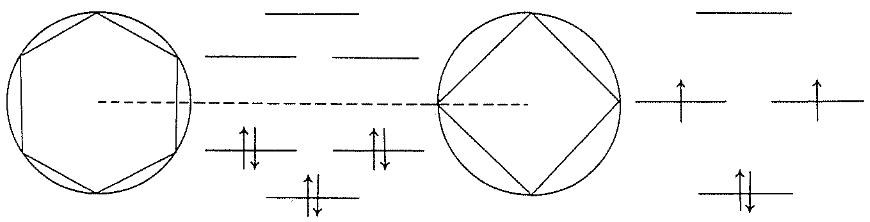
Molecule	REPE (eV) ($\lvert\beta\rvert = 1.4199$ eV)	*Chemical properties*
	0.092	Very stable; Undergoes substitution only under forcing conditions
	0.078	
	0.061	Simple derivatives isolated; undergo electrophilic substitution
	0.032	Known, stable compound
	−0.003	Isolated, but reactive
	−0.006	Isolated, but reactive
	−0.026	Me derivative observed spectroscopically at −196°C
	−0.038	Never prepared
	−0.047	Prepared in very dilute solution; extremely reactive
	−0.381	Prepared at 8°K, vanished at 35°K

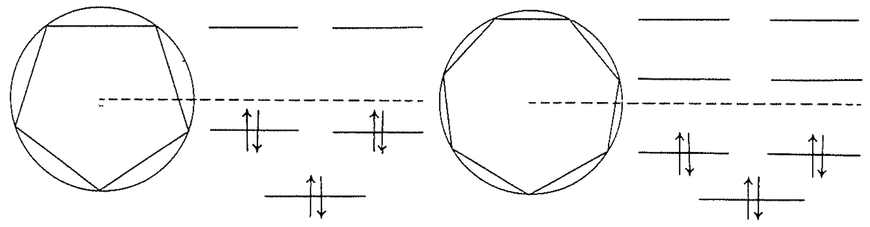
FIG. 8-24 Resonance energy per electron for a number of molecules. (From Schaad and Hess [18].)



(XII)

are fully occupied. Because all monocycles have a nondegenerate lowest level followed by higher-energy pairs of degenerate levels, it is not hard to describe the conditions that should produce maximum stability. There should be $4n + 2$ electrons (2 for the lowest level and 4 for each of the n higher bonding levels), and there should be more than $4n$ centers (either $4n + 1$, $4n + 2$, or $4n + 3$) to force the n doubly degenerate levels to all be bonding. The stability of cyclopentadienyl anion (6 electrons, 5 centers) and cycloheptatrienyl cation (6 electrons, 7 centers) was correctly predicted from these simple considerations (**XIII**). Extensive research has gone on in efforts to find examples where $n \neq 1$, but results are often complicated by angle strain and deviation from planarity in the molecule.[13]

In a molecule containing both cyclic and acyclic parts, does the RE arise only from the cyclic part? For certain cases, the answer is yes. Dewar has recognized that side or connecting chains contribute nothing to the RE of a system when the chain in question is the same in all formal structures for the molecule. For example, stilbene can be written in four equivalent formal ways, as shown below. The linking chain is identical in all cases, and it should not contribute to the RE. Calculations confirm that the RE for stilbene is just double that for benzene.



cyclopentadienyl anion
cycloheptatrienyl cation

(XIII)

The intimate relation between aromaticity and the possibility for more than one equivalent formal structure for a molecule has long been recognized. These "mobile" bonds tend to favor equal bond lengths in contrast to the strong alternation characteristic of acyclic polyenes. In benzene, the extra stabilization may be viewed as resulting from the fact that all six bonds are identical and have a higher bond order (0.667) than the average of 0.634 for double and single acyclic bonds. In antiaromatic cyclobutadiene, the four identical bonds have a bond order of 0.5, which is significantly below the average for acyclics. The very different bond orders in these two molecules is fully consistent with the energy argument based on the $4n + 2$ rule described earlier.[14]

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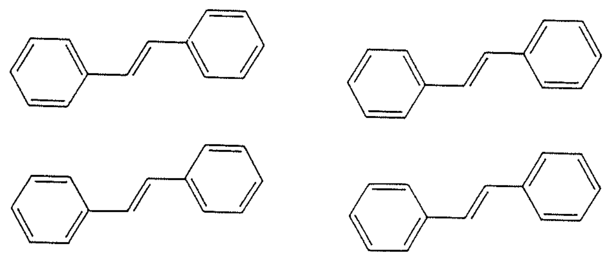
[13] See Breslow [20, p. 90].



(XIV)

To summarize, the π bonds in acyclic polyenes exhibit *delocalization* in the sense that bond orders are not transferable from one molecule to another, *additivity* in *effective* bond energies, *immobility* in formal bonds. Cyclic molecules do *not* exhibit additivity of effective energies or immobility of formal bonds. Their energy deviations from energy calculated assuming additivity and immobility are good indicators of kinetic and thermodynamic stability. Aromatic molecules possess extra stability because their π electrons[15] are more bonding than those in acyclic polyenes. Antiaromatics are unstable because their π electrons are less bonding.

From a consideration of experimental heats of atomization, Schaad and Hess have evaluated β to be -1.4199 eV. The physical processes involved in dissociating a gas-phase molecule into constituent atoms are quite different from those involved in adding or removing a π electron from a molecule in a solvent.

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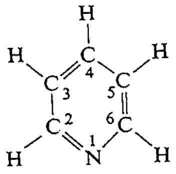
[14] It has been noted that bond length equalization associated with bond mobility results in π energy lowering when the C–C–C angles are near 120°. When the angle is very different from this, π energies are higher than expected. This has led to suggestions that "strain energy" may be an important factor in aromaticity. Because of the present lack of a quantum mechanical quantity equivalent to strain energy, and because the HMO method may include effects of σ electrons in an implicit but poorly understood way, it is very hard to know whether such suggestions are at variance with other statements or are simply equivalent to them but stated from a different viewpoint.

[15] It is not necessarily true that all the "extra" stability of aromatic molecules is attributable to π-electron effects; σ-Electron energies also depend on bond lengths and bond angles. Hence, we may be seeing, once again, a situation where the π-electron treatment includes other effects implicitly. Hess and Schaad [18] indicate that σ energies and π energies are indeed simply related over the bond-length range of interest.

Therefore, it is not surprising that the β value obtained from heats of atomization differs substantially from values obtained from redox experiments. Indeed, it is this variability of β as we compare HMO theory with different types of experiment that compensates for many of the oversights and simplifications of the approach. It is remarkable that, with but one such parameter, HMO theory does as well as it does.

8-17 Extension to Heteroatomic Molecules

The range of application of the HMO method could be greatly extended if atoms other than carbon could be treated. Consider pyridine as an example (**XV**). A π electron at a carbon atom contributes an energy α to E_π. The contribution due to a π electron at nitrogen is presumably something different.



(XV)

Let us take it to be $\alpha' = \alpha + h\beta$, where h is a parameter that will be fixed by fitting theoretical results to experiment. If the π electron is attracted more strongly to nitrogen than to carbon, h will be a positive number. In a similar spirit, we will take the energy of a π electron in a C–N bond to be $\beta' = k\beta$ and evaluate k empirically. Not surprisingly, the values of h and k appropriate for various heteroatoms depend somewhat on which molecules and properties are used in the evaluation procedure. A set of values compiled and critically discussed by Streitwieser [3] is given in Table 8-3. Other sets have been published.[16]

The dots over each symbol indicate the number of π electrons contributed by the atom. In pyridine, the formal bond diagram indicates a six π-electron system, implying that the nitrogen atom contributes one π electron. We also can argue that, of the five valence electrons of nitrogen, two are involved in σ covalent bonds with neighboring carbons, two more are in a σ lone pair, leaving one for the π system. Therefore, the atom parameter to use for this molecule is $h = 0.5$. The pyridine ring, like benzene, admits two equivalent structural formulas, and so the C—N bonds should be intermediate between double and single, symbolized C$\overset{\cdot}{\text{=\!\!=N}}$ in Table 8-3. Since $k = 1.0$ in this case, $\beta' = \beta$, and pyridine will have an HMO determinant differing from the benzene determinant only in the diagonal position corresponding to the nitrogen atom—the 1,1 position according to our (arbitrary) numbering scheme. For this position,

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[16] See McGlynn *et al.* [21, p. 87].

TABLE 8-3
Parameters for Heteroatoms in the Hückel Method[a]

Heteroatom	h	Heteroatomic bond	k
$\dot{N}$	0.5	$C\overset{\cdot}{=\!=}N$	1.0
$\ddot{N}$	1.5	$C—\ddot{N}$	0.8
$\overset{+}{N}$	2.0		
$\dot{O}$	1.0	$C=\dot{O}$	1.0
$\ddot{O}$	2.0	$C—\ddot{O}$	0.8
$\overset{+}{\dot{O}}$	2.5	$N—\ddot{O}$	0.7
$\ddot{F}$	3.0	$C—\ddot{F}$	0.7
$\ddot{Cl}$	2.0	$C—\ddot{Cl}$	0.4
$\ddot{Br}$	1.5	$C—\ddot{Br}$	0.3
S'^{b}	0.0	$C—S'$	0.8
S''	0.0	$C—S''$	0.8
		$S'—S''$	1.0
Methyl (inductive $\dot{C}_\alpha$—Me) −0.5	$h_{C_\alpha} = -0.5$	none	—
Methyl (heteroatom $\dot{C}_\alpha$—$\ddot{Me}$) 0.2	$h_{Me} = 0.2$	C_α—Me	0.7
Methyl (conjugative $\dot{C}_\alpha$—$C\overset{\cdot\cdot}{=}H_3$)	$h_{C_\alpha} = -0.1$	C_α—C	0.8
	$h_c = -0.1$	C—H_3	3.0
	$h_{H_3} = -0.5$		

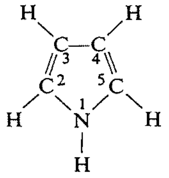
[a] Consistent with the philosophy of this approach is a distinction between single, double, and intermediate C—C bonds. Streitwieser recommends $k_{C-C} = 0.9$, $k_{C\overset{\cdot}{=}C} = 1.0$, $k_{C=C} = 1.1$.

[b] Sulfur is treated as a pair of AOs with a total of two π electrons, i.e., a sulfur in an aromatic ring is *formally* treated as *two* adjacent atoms S′ and S″ with the indicated parameters.

instead of x, we will have

$$x' = (\alpha' - E)/\beta = (\alpha + 0.5\beta - E)/\beta = (\alpha - E)/\beta + 0.5\beta/\beta = x + 0.5 \tag{8-64}$$

The pyrrole molecule has a nitrogen atom of the type $\ddot{N}$ (**XVI**). Since three valence electrons of nitrogen are in covalent σ bonds, two remain for inclusion in the π system. Therefore, pyrrole has a total of six π electrons. The unique



(XVI)

structural formula indicates that the C—$\ddot{\text{N}}$ bond is formally single, and $k = 0.8$, $h = 1.5$ are the appropriate parameters here. Also, the carbon–carbon bonds are now formally single or double. If we choose to distinguish among these bonds using the parameters in note *a* of Table 8-3, the resulting HMO determinant is

$$\begin{vmatrix} x+1.5 & 0.8 & 0 & 0 & 0.8 \\ 0.8 & x & 1.1 & 0 & 0 \\ 0 & 1.1 & x & 0.9 & 0 \\ 0 & 0 & 0.9 & x & 1.1 \\ 0.8 & 0 & 0 & 1.1 & x \end{vmatrix}$$

The methyl group can also be incorporated into the HMO method. Several approaches have been suggested. One is simply to modify the coulomb integral α for the carbon to which the methyl group is attached. A methyl group is thought to release sigma electrons to the rest of the molecule as compared to a substituent hydrogen. This suggests that an atom having a methyl group attached to it will be a bit electron rich and hence will be less attractive to π electrons. Use of a negative h parameter for this carbon is appropriate. This method is called the *inductive* model. Use of the inductive model does not add any new centers or any more π electrons to the conjugated system to which the methyl group is attached. The carbon to which the methyl is bonded is merely treated as a less attractive atom. A second approach is to treat the methyl group itself as a heteroatom. As we shall see shortly, the methyl group has two electrons that can participate (to a slight extent) in the π system, and so use of this *heteroatom* model adds one more center and two more π electrons for each methyl group included in this way. A third approach is the *conjugative* model. Because the methyl group has *local* threefold symmetry, one of the σ MOs for the methyl group resembles the π MOs of cyclopropenyl in symmetry characteristics. The three types of symmetry solutions are given in Fig. 8-25 for a methyl group on a benzene ring (compare with Fig. 8-7). Notice that the MO at the right of the figure is of the same symmetry as a π AO on the benzene ring. This means that the two electrons in this "methyl group MO" can participate in the π system of the molecule. To emulate this picture in our HMO determinant, we must add two π electrons and two more centers to our system (one for C and one for H_3) and find h and k values for the two new centers and bonds. The inductive effect of the methyl group on the neighboring ring carbon is often included in this model. In most cases, it is probably safe to say that the conjugative model is superior to the heteroatom model, which is, in turn, better than the inductive model, but no extensive critical comparison of these three models has been made. Parameters for all three approaches are included in Table 8-3. (C_α is the ring carbon.)

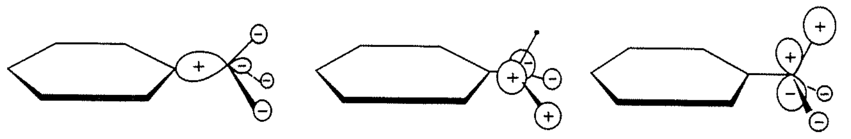


FIG. 8-25 Three MO symmetry solutions for a methyl group attached to a benzene ring.

8-18 Self-Consistent Variations of α and β

Efforts have been made to improve the HMO method by taking account of molecular π charge distribution. Suppose that we carry out an HMO calculation on a nonalternant molecule and find an electron density of 1.2 at one carbon and 0.8 at another. It is reasonable to argue that a π electron at the latter carbon is more strongly bound because it experiences less repulsion from other π electrons there. We can try to account for this by making α at that atom more negative. Thus, we could take

$$\alpha_i' = \alpha_i + \omega(1 - q_i)\beta \tag{8-65}$$

where q_i is the π-electron density at atom i and ω is a parameter (assumed positive) to be fixed empirically. If $q < 1$, then α' is more negative than α. If $q > 1$, α' is less negative. Having now modified α (using a trial value for ω), we must set up our new HMO determinant and solve it again. This yields new MOs, new values of q_i, and therefore new values of α'. We repeat this process over and over until electron densities remain essentially unchanged for two successive iterations. At this point, the electron densities *leading to* the HMO determinant are the same as those *produced by* the determinant, and the solution is said to be self-consistent with respect to electron densities. This procedure, often referred to as the "ω technique," discourages extreme deviations of electronic densities from the "norm" of unity at each carbon and thereby helps to compensate for the lack of explicit inclusion of pi electron repulsion in the HMO method. Streitwieser's calculations have led him to favor a value of ω of 1.4.

A similar idea has been applied to variations of the bond integral β. Suppose that we carry out an HMO calculation and find a π-bond order of 0.5 in one bond and 0.9 in another. We expect that the latter bond is in fact shorter than the former. We could roughly predict how much shorter it is by using the bond-order–bond-length relation described earlier. It is reasonable to modify β in these bonds on the basis of predicted length differences, set up a new HMO determinant, solve again, find new bond orders, and iterate until self-consistency is achieved with respect to bond orders.

These modifications to the simple HMO method improve predictions of some properties but not others. For example, Brogli and Heilbronner [13] have found that orbital energy correlation with ionization potential, determined by photoelectron spectroscopy, is significantly improved through inclusion of the effects of bond length variations in the *neutral molecule and the cation.* This improved correlation, shown in Fig. 8-26, showed no additional improvement upon subsequent variation of α as a function of electron density. This is reasonable, since β variation affects primarily bond order, hence MO energy, and that is the property measured by photoelectron spectroscopy. Variation of α shifts charge from atom to atom, but has smaller energy effects. On the other hand, π-electron contributions to dipole moments, calculated from electronic excess or deficiency at each center, are very sensitive to variation of α, and quite insensitive to variation of β. Again, this is reasonable because dipole moments are sensitive to electronic distribution rather than MO energy.

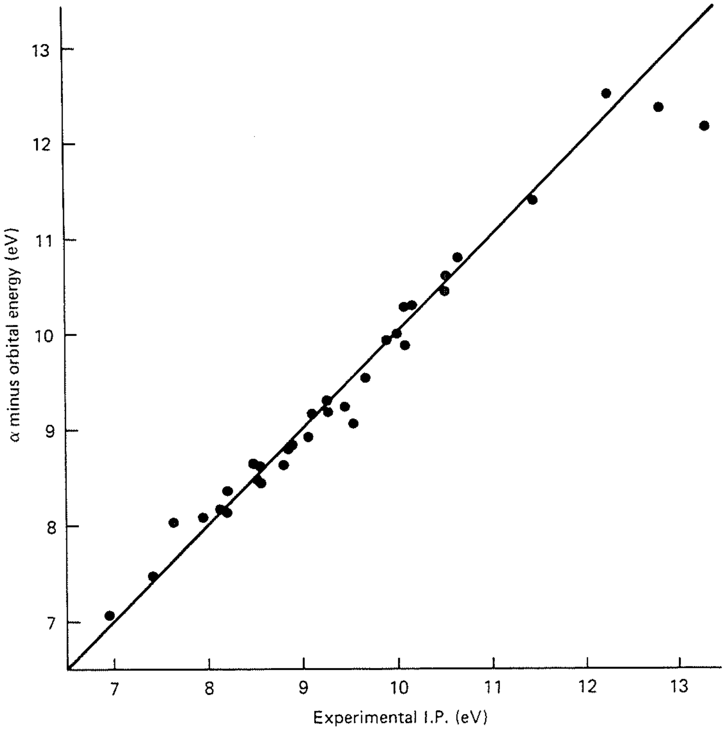
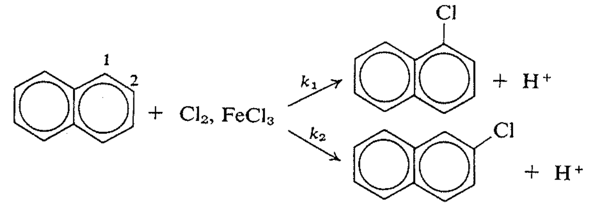


FIG. 8-26 Experimental ionization potential for alternant and nonalternant hydrocarbons versus orbital energy using a modified HMO technique which includes provisions for bond length variation in molecule and cation. (Compare with Fig. 8-22.)

8-19 HMO Reaction Indices

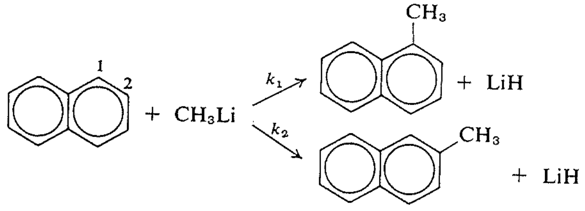
In this section, we discuss some applications of the HMO method to *reactivities* of conjugated molecules. The reactions of conjugated molecules that have received most of this theoretical treatment are:

(1) electrophilic aromatic substitution (**XVII**),



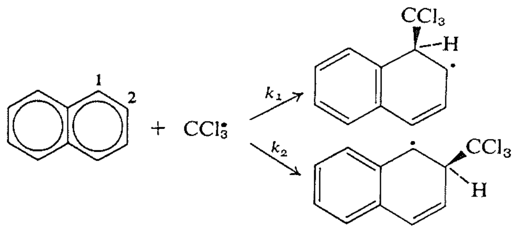
(XVII)

(2) nucleophilic aromatic substitution (**XVIII**);



(XVIII)

(3) radical addition (**XIX**).



(XIX)

For any of these reactions, we imagine there to be a path of least energy connecting reactants with products. For the two distinct reaction positions, 1 and 2 on naphthalene, the activation energies ϵ may differ, as indicated in Fig. 8-27.

The problem is somehow to relate the differences in ϵ (inferred from relative rate data) to a number based on quantum chemical calculations. To do this in a sensible way requires that we have some idea of the detailed way in which the reaction proceeds—we have to know what the reaction coordinate is. In some cases, this is fairly well known. For electrophilic aromatic substitution reactions, evidence suggests that a positive electrophile (e.g., Cl^+) approaches the substrate (say, naphthalene). As it draws closer, it causes a significant polarization of the π-electron charge distribution, drawing it toward the site of attack. Ultimately, it

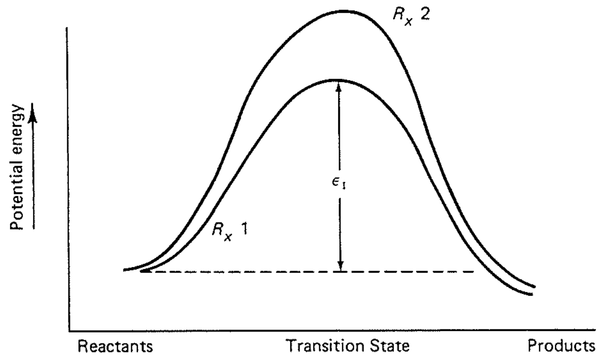
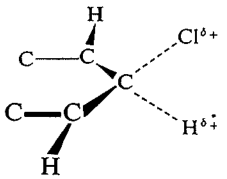


FIG. 8-27 Generalized energy versus reaction coordinate for reaction at two positions in naphthalene.

forms a partial bond with the carbon. At this stage, the carbon has already begun to loosen its bond to hydrogen, but it is at least partially bonded to four atoms (**XX**). This means that the ability of the carbon to participate in the aromatic system is temporarily hampered. At this point, the system is at or near the transition state. Thereafter, as H^+ leaves, the potential energy decreases and Cl moves into the molecular plane. A similar detailed mechanism is thought to apply for nucleophilic reactions except that the attacking group is negative.

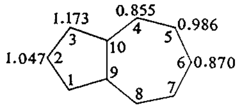


(XX)

For attack by a neutral radical, electrostatic attraction and charge polarization should not be significant factors. The radical bonds to the site of attack to produce a more-or-less tetrahedrally bonded carbon. This again leads to an interruption of the π system, but now it is not temporary as it was in the substitution reactions.

Based on these simple pictures, a number of MO quantities, often referred to as *reaction indices*, have been proposed as indicators of preferred sites for reaction. It is useful to divide these into two categories—those purporting to relate to early stages of the reaction, and those specifically related to the intermediate stage.

Perhaps the most obvious reaction index to use for the earliest stages of electrophilic or nucleophilic reactions is the *π-electron density*. If Cl^+ is attracted to π charge, it should be attracted most to those sites where π density is greatest. (Such an ion should be attracted to sites having excessive σ charge density also, but our basic HMO assumptions ignore any variations in σ density.) For an alternant hydrocarbon like naphthalene, all π densities are unity, so this index is of no use. For nonalternant molecules, however, it can be quite helpful. Azulene has varying HMO π densities (**XXI**). (More sophisticated calculations described in future chapters are in qualitative agreement with these π-electron density variations.) Experimentally, it is found that electrophilic substitution by Cl occurs almost entirely at position 1 (or 3). Nucleophilic substitution by CH_3 (from CH_3Li) occurs at the position of least π-electron density, namely 4 (or 8).



(XXI)

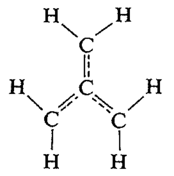
The charge density index refers to the nature of the molecule before allowance is made for perturbing effects due to the approaching reactant. Such a method is often called a "first-order" method, a terminology that is discussed more fully in Chapter 12. For alternant molecules, it is necessary to proceed to a high-order method, one that reflects the ease with which molecular charge is drawn toward some atom, or pushed away from it, as approach by a charged chemical reactant makes that atom more or less attractive for electrons. An index which measures this is called *atom self-polarizability*, symbolized $\pi_{r,r}$. The formulas for this and related polarizabilities are derived in Chapter 12. For now, we simply note that the formula is

$$\pi_{r,r} \equiv \partial q_r/\partial \alpha_r = 4 \sum_j^{\text{occ}} \sum_k^{\text{unocc}} c_{rj}^2 c_{rk}^2/(E_j - E_k) \tag{8-66}$$

A larger absolute value of $\pi_{r,r}$ means that a larger change in π density q_r occurs as a result of making atom r more or less attractive for electrons. ($\pi_{r,r}$ is negative since $E_j - E_k$ is negative. This makes physical sense because it means that if $\delta\alpha_r$ is negative, making atom r more attractive, δq_r is positive, indicating that charge accumulates there.) Since the most polarizable site should most easily accommodate either a positive- or a negative-approaching reactant, this index should apply for both electrophilic and nucleophilic reactions. For naphthalene, the values are $\pi_{11} = -0.433/|\beta|$, $\pi_{22} = -0.405/|\beta|$. This agrees with the experimentally observed fact that the 1 position of naphthalene is more reactive for both types of reaction.

Examination of Eq. (8-66) indicates that the MOs near the energy gap between filled and empty MOs will tend to contribute most heavily to $\pi_{r,r}$ because, for these, $E_j - E_k$ is smallest. For this reason, the highest occupied and lowest unfilled MO (HOMO and LUMO) are often the determining factor in relative values of π_{rr}. Fukui[17] named these the *frontier orbitals* and suggested that electrophilic substitution would occur preferentially at the site where the HOMO had the largest squared coefficient. In nucleophilic substitution, the approaching reagent seeks to *donate* electronic charge to the substrate, so here the largest squared coefficient for the LUMO should determine the preferred site. For even alternants like naphthalene, the pairing theorem forces these two MOs to have their absolute maxima at the same atom. The HOMO–LUMO coefficients for naphthalene are 0.425 and 0.263 for atoms 1 and 2, respectively, in accord with our expectations. For the nonalternant molecule azulene, discussed above, the largest HOMO coefficient occurs at atoms 1 and 3, which have already been mentioned to be the preferred sites for electrophilic attack. The largest LUMO coefficient occurs at atom 6, with atoms 4 and 8 having the second-largest value (see Appendix 6). Atoms 4 and 8 are the preferred sites for nucleophilic attack. Here, then, is a case where the charge density and frontier MO indices are not in agreement. The results suggest that, when significant π-density variations occur, this factor should be favored over higher-order indices. However, the whole approach is so crude that no ironclad rule can be formulated.

For radical attack, some other index should be used, for we do not expect electrostatic or polarization effects to be important in such reactions. An index called the *free valence*[18] has been proposed for free radical reactions. One assumes that the free radical begins bonding to a carbon atom in early stages of the reaction and that the ease with which this occurs depends on how much residual bonding capacity the carbon has after accounting for its regular π bonds. Thus, free valence is taken to be the difference between the maximum π bonding a carbon atom is capable of and the amount of π bonding it actually exhibits in the unreacted substrate molecule. The extent of π bonding is taken as the sum of all the orders of π bonds involving the atom in question. A common choice of reference for a maximally bonded carbon is the central atom in trimethylenemethane in its planar conformation (which is not the most stable). (**XXII**). Each bond in this neutral system has a π-bond order of $1/\sqrt{3}$, and so the total π-bond order associated with the central carbon is $\sqrt{3}$.[19] Using this as



(XXII)

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[17] See Fujimoto and Fukui [22].

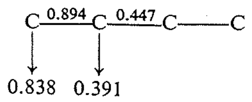
[18] See Coulson [23].

[19] Sometimes the three sigma bonds are included in this calculation, giving $3 + \sqrt{3}$. This has no effect on the question of *relative* values of F_r.

reference, the free valence for some atom r in *any* unsaturated hydrocarbon is defined as

$$F_r = \sqrt{3} - \sum_{s}^{\text{neighbors of } r} p_{rs} \tag{8-67}$$

A common way of representing the situation schematically is indicated in (**XXIII**) for butadiene. Bond orders are indicated on the bonds and free valences by arrows. It is clear that butadiene has a good deal more "residual bonding capacity" on its terminal atoms, and this is consistent with the fact that free radical attack on butadiene occurs predominantly on the end atoms. Other examples of correlation between free valence and rate of free radical addition have been reported.[20] A plot of rate data for methyl radical addition to conjugated molecules versus the largest free valence of the molecule is shown in Fig. 8-28. (We assume that the kinetics is dominated by the atom(s) having the maximum free valence.)



(XXIII)

The indices described above are most appropriate for indicating the relative ease of reaction *in the early stages*. By the time the reactants have reached the transition state, the substrate is quite far from its starting condition, so charge densities, polarizabilities, free valences calculated from the wavefunction of the unperturbed molecule may no longer be very appropriate. If the energy curves being compared through our indices behave in the simple manner described in Fig. 8.27, so that the higher-energy curve in early stages is also the higher-energy curve in the region of the transition state, such indices can be useful. Also, such simple behavior is very likely to occur when we compare a single type of reaction down a series of molecules of similar type, as in Fig. 8-28 (see also Problem 8-25). Experience, however, has indicated that indices more closely linked to the nature of the transition state are more generally reliable. We now describe one such reactivity index.

We mentioned earlier that addition and substitution reactions are expected to interrupt the π system at the site of attack. For substitution reactions, this interruption is only temporary and is presumably most severe in the transition state. For addition reactions, it is permanent. The *localization energy* is defined as the π energy lost in this process of interrupting the π system.

As an example, let us return to the naphthalene molecule. The situations resulting from interruption of the π system by *neutral radical* attack at positions 1 and 2 are illustrated in (**XXIV**). The remaining unsaturated fragment is, in each

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[20] See Streitwieser [3] and Salem [1].

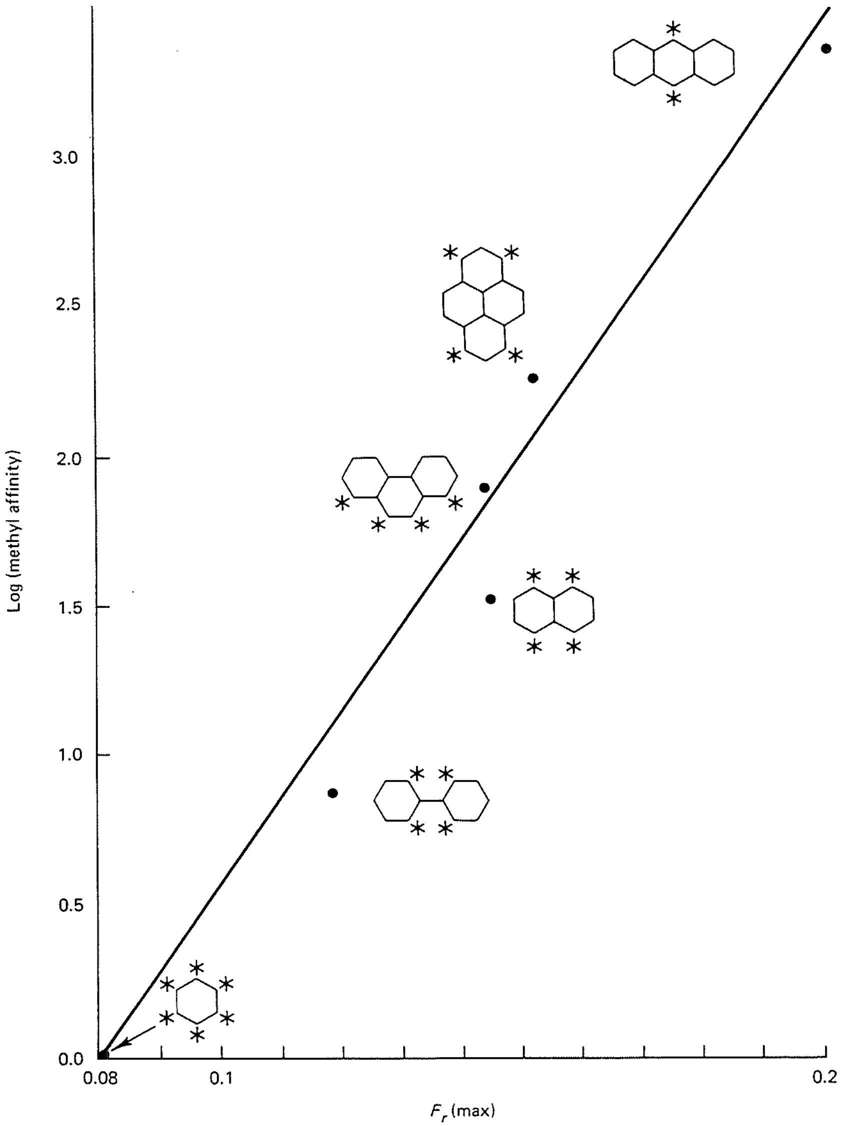
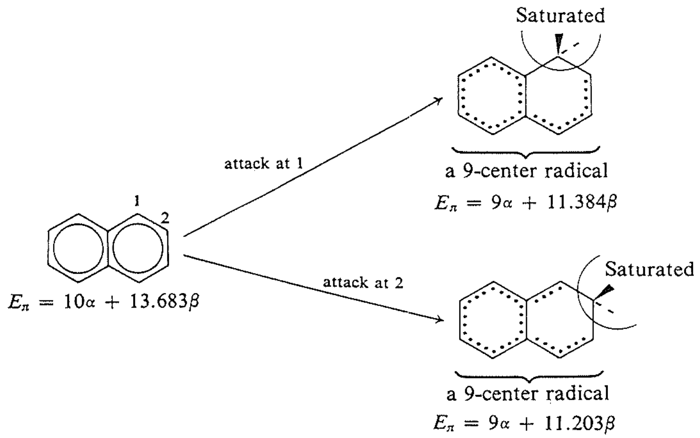


FIG. 8-28 Rate data for methyl radical addition are plotted against the maximum free valence found in each molecule. The original "methyl affinity" (Levy and Szwarc [24]) has been multiplied by $6/m$, where m is the number of sites having maximum free valence. (The asterisks in the figure identify these sites.)

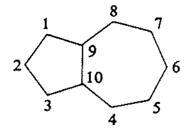


(XXIV)

case, a neutral radical. [If attack were by a negative ion (nucleophilic), the fragment would be topologically the same but would be negatively charged. Likewise, attack by a positive electrophilic reagent leads to a positively charged fragment.] No matter where attack occurs, our π energy must go from $10\alpha + \cdots\beta$ to $9\alpha + \cdots\beta$. This decrease by α is thus not expected to differ from case to case and hence is ignored in our localization energy calculation. The decrease in π energy is thus $2.299|\beta|$ for attack at position 1 and $2.480|\beta|$ for position two. These localization energies indicate that attack at position 1 should be favored since the energy cost is smaller there, and this is in accord with observation. (Localization energies are symbolized L, L^+, L^- depending, respectively, on whether attack is by a free radical, an electrophilic cation, or a nucleophilic anion.)

It is interesting to compare the various indices we have discussed for a single molecule to see how well they agree. Data for azulene are collected in Table 8-4. Experimentally, azulene is known to preferentially undergo electrophilic substitution at positions 1 and 3, nucleophilic substitution at positions 4 and 8, and radical addition in positions 1 and 3. Consider first electrophilic reaction. Examining the table indicates that position 1 is heavily favored by q_r, HOMO distribution, and L_r^+. The only other index relevant for this process, π_{rr}, favors position 4. For nucleophilic reaction, q_r, π_{rr}, L_r^- all favor position 4. The LUMO index favors position 6, but not decisively over position 4. For radical addition, LUMO favors position 6, whereas F_r and $L_r^{\cdot}$ favor position 4. The latter two indices, however, favor 4 over 1 by only a slight margin. Thus, for a nonalternant molecule like azulene, these numbers are not completely trustworthy and must be interpreted with caution. One difference between a molecule like anthracene and one like azulene is that all the C–C–C angles in the former

TABLE 8-4
Reactivity Indices for Azulene



r (atom no)	q_r	$-\|\beta\|\pi_{r,r}$	HOMO c_r^2	LUMO c_r^2	F_r	$L_r^+(\|\beta\|)$	$L_r^{\bullet}(\|\beta\|)$	$L_r^-(\|\beta\|)$
1	*1.173*	0.425	*0.2946*	0.0040	0.480	*1.924*	2.262	2.600
2	1.047	0.419	0.0000	0.0997	0.420	2.362	2.362	2.362
4	*0.855*	*0.438*	0.0256	0.2208	*0.482*	2.551	*2.240*	*1.929*
5	0.986	0.429	0.1126	0.0104	0.429	2.341	2.341	2.341
6	0.870	0.424	0.0000	*0.2610*	0.454	2.730	2.359	1.988

molecule are similar (~120°) whereas in azulene they differ. One might anticipate that the smaller angles in the five-membered subunit, being already closer to the tetrahedral angle characteristic of saturated carbons, would allow easier substitution or addition than would be the case in the seven-membered subunit. This factor is ignored in our calculations of L_r and might easily tip the balance to favor position 1 over position 4 for radical attack since $L_1^{\bullet}$ and $L_4^{\bullet}$ are so close in value. In short, these HMO reactivity index approaches are once again techniques that ignore many aspects of the physical processes being followed. It seems likely that many of these will cancel out of comparisons among similar molecules, but disimilarities between or within molecules (most often encountered in nonalternant systems) will cause such cancellations to be less complete. For more discussion of these and other HMO reaction indices, the reader is referred to more specialized discussions.[21] Application of some of these indices to carcinogenicities of polycyclic aromatic hydrocarbons has been reviewed in an article especially suitable for the nonspecialist.[22]

8-20 Conclusions

In this chapter, we have seen how certain basic features of molecular structure manifest themselves in molecular properties. The *connectedness*, or σ bond network, defines the bond positions where π electrons can congregate to lower the energy of the system. The extent of congregation is a useful measure of bond length and also is directly contributory to the total energy of the system.

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[21] See Streitwieser [3], Salem [1], Dewar [14], and Klopman [25].

[22] See Lowe and Silverman [28].

The symmetry restrictions for MOs have been emphasized. The fairly successful correlation of HMO results with certain experimental measurements suggests that the method effectively accounts for the controlling factors in some molecular properties.

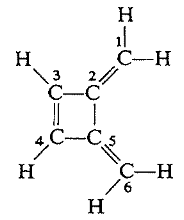
But we have omitted discussion of other properties that correlate only poorly with HMO theory. Notable in this regard are spectral energies. The natural idea of relating a spectral transition energy to a difference between orbital energies has not been very successful in HMO theory, except when one restricts attention to a particular band in a series of related molecules. This is at least partly due to improper handling of electron exchange symmetry in the HMO method leading to an inability to distinguish between different states of a given configuration.

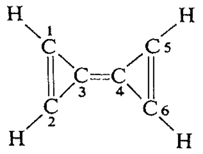
The HMO method can be an extremely instructive way to approach a problem since it can describe the manner in which certain important factors are operating. Also, for some situations, its predictive power is rather good. Certainly the successes of this method encourage further theoretical effort. However, the limitation to conjugated systems, the reliance on an increasing number of parameters as extensions are made, the inability to conform to some kinds of experimental measurement, and the conceptual slipperyness of the quantities used in the method have all contributed to a decline of interest in further tinkering with HMO theory. More powerful computers have made it possible for more complicated but better defined methods to be used.

PROBLEMS

8-1 Show that, if $\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_3$, and $\hat{H}_i\phi_j(i) = E_j\phi_j(i)$, then $\psi_{\text{prod}} = \phi_1(1)\phi_2(2)\phi_3(3)$ and $\psi_{\text{det}} = |\phi_1(1)\phi_2(2)\phi_3(3)|$ are both eigenfunctions of $\hat{H}$ and have the same eigenvalue. Show also that $\psi = (1/\sqrt{2})[\phi_1(1)\phi_2(2)\phi_3(3) + \phi_1(1)\phi_2(2)\phi_4(3)]$ is an eigenfunction of $\hat{H}$ if and only if $E_3 = E_4$.

8-2 Set up the HMO determinant for each of the following molecules:

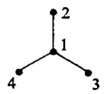
(a)


(b)


(c) $H_3C—CH_2—CH_2—CH=CH_2$ (d) $H_2C=CH—CH_2—CH_2—CH=CH_2$

(e) $H—C\equiv C—H$

8-3 Set up and solve the Hückel determinantal equation for 2-allylmethyl (also called trimethylenemethane) **(XXV)**. Display the orbital energy levels and indicate the electron configuration for the neutral ground state. Calculate E_π. Find the coefficients for all MO's. [Be sure that degenerate MOs are orthogonal.] *Calculate* the charge densities and bond orders.



(XXV)

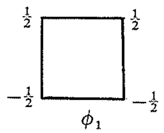
8-4 Suppose that two MOs of a molecule are given by the formulas

$$\phi_1 = (1/\sqrt{3})\chi_1 + (1/\sqrt{3})\chi_2 + (1/\sqrt{3})\chi_3,$$

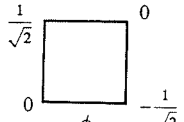
$$\phi_2 = (1/\sqrt{3})\chi_3 + (1/\sqrt{3})\chi_4 + (1/\sqrt{3})\chi_5,$$

where the χ's are AOs which are assumed to be orthonormal. By inspection, what is the overlap between these MOs?

8-5 Given the following two degenerate MOs for cyclobutadiene:



ϕ_1



ϕ_2

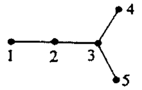
Use the Schmidt procedure to obtain an MO that has the same energy as ϕ_2 but is orthogonal to ϕ_1.

8-6 For cyclo-octatetraene, see if you can answer the following without reference to tabulations:

(a) What is the HMO energy of the *highest* energy pi MO?

(b) Sketch this MO (from above the molecule) showing signs and magnitudes (actual numbers) of the MO coefficients.

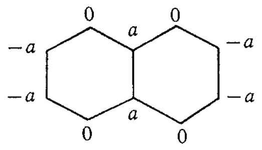
8-7 (a) What is the Hückel *orbital* energy for the following MO? (Assume that all centers are carbons.) [*Hint:* Use Eq. (8-56).]



c_1	c_2	c_3	c_4	c_5
$\frac{1}{3}$	$\sqrt{\frac{2}{3}}$	0	$-\frac{1}{3}$	$-\frac{1}{3}$

(b) Calculate the contributions to bond orders due to *one* electron in this MO.

(c) Calculate the Hückel energy of the following MO. (Figure out the value of a if you need to use it.)



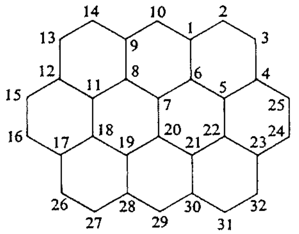
8-8 Without performing an HMO calculation, sketch the MOs for the pentadienyl radical. Use the particle-in-a-box solutions and the pairing theorem as a guide.

8-9 Which, if any, of the following systems would you expect to exhibit Jahn–Teller distortion? Indicate your thinking. (You should be able to answer without reference to HMO data tables.) (a) Benzyl radical, C_7H_7, . (b) Cyclopentadienyl radical, C_5H_5. (c) Cyclobutadienyl radical cation, $C_4H_4{}^+$. (d) Cyclobutadiene in triplet state, C_4H_4.

8-10 The bond lengths given in Table P8-10 have been reported for ovalene **(XXVI)**. Using a library source or a computer program, obtain HMO bond orders for ovalene and calculate theoretical bond lengths using a relation from Section 8-12. Make a comparison plot for ovalene of the type shown in Fig. 8-16. (See caption of Fig. 8-16 for values of k and s.)

TABLE P8-10

Bond	Length (Å)	Bond	Length (Å)
1–2	1.445	1–10	1.401
2–3	1.354	6–7	1.419
3–4	1.432	4–25	1.411
4–5	1.429	24–25	1.366
5–6	1.429	5–22	1.424
6–1	1.425	7–20	1.435

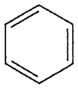


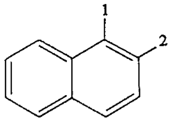
(XXVI)

8-11 Horrocks *et al.* [26] report experimental bond lengths for quinoline complexed to nickel. They display a comparison plot that uses theoretical data from an MO method more refined than the simple HMO method. Using the appropriate heteronuclear parameters, perform on the computer an HMO calculation for quinoline. Calculate theoretical C–C bond distances and compare them with the experimental and theoretical data of Horrocks *et al.*

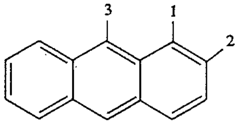
8-12 When the molecule $CH_2{=}CH{-}CH{=}O$ absorbs light of a certain frequency, a lone-pair electron on oxygen (called "n" for "nonbonding") is promoted to the lowest empty π MO of the molecule (called π^*; hence, an $n \to \pi^*$ transition). Assuming that the π MOs of this molecule are identical to those in butadiene, which C–C bond would you expect to become longer and which shorter as a result of this transition? Calculate the expected bond length changes using butadiene data, using either set of k, s values in the caption of Fig. 8-16. (*Observed:* $\Delta CH_2{-}CH \cong 0.06$ Å, $\Delta CH{-}CH \cong -0.04$ Å).

TABLE P8-13

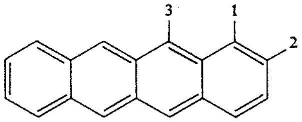

3.75



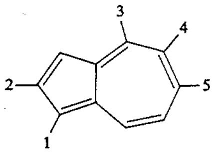
5.01
1.79



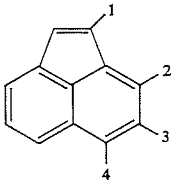
2.74
1.57
5.56



1.49
1.17
4.25



0.27
3.95
6.22
1.34
8.83



3.07
4.50
0.46
5.60

8-13 ESR coupling constants are shown in Table P8-13 for six hydrocarbon anion radicals. Use HMO tabulations in the literature (or a computer) to obtain π-electron MO coefficients for these systems. Construct a plot of coupling constant a_{H_μ} versus $c_{\mu i}^2$, where i is the MO containing the unpaired electron (a_{H_μ} values are in gauss). The numbered positions in Table P8-13 refer to hydrogen atoms.

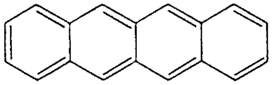
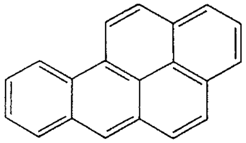
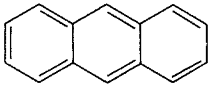
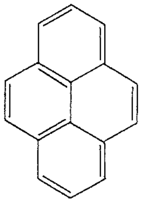
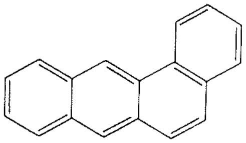
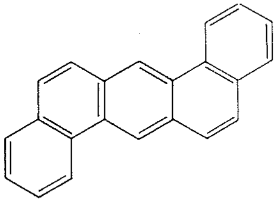
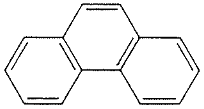
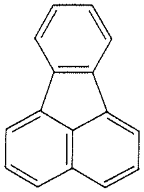
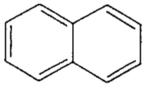
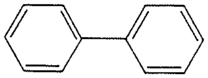
8-14 Polarographic half-wave potentials for oxidation and reduction of aromatic hydrocarbons are given in Table P8-14.

(a) Make separate plots of these data against energy (in units of β) of the highest occupied and lowest empty MO respectively. (Use tabulations or a computer program.)

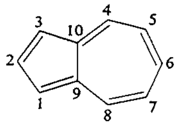
(b) Now plot reduction versus oxidation half-wave potential for this series. Explain adherence to or deviation from linearity.

TABLE P8-14

TABLE P8-14 (Continued)

Compound	Structure	Reduction half-wave potential in 2-methoxyethanol (V)	Oxidation half-wave potential in acetonitrile (V)
Tetracene		1.135	0.54
1,2-Benzpyrene		1.36	0.76
Anthracene		1.46	0.84
Pyrene		1.61	0.86
1,2-Benzanthracene		1.53	0.92
1,2,5,6-Dibenzanthracene		1.545	1.00
Phenanthrene		1.935	1.23
Fluoranthene		1.345	1.18
Naphthalene		1.98	1.31
Biphenyl		2.075	1.48

8-15 Use tabulated or computer generated HMO data for *neutral* azulene (**XXVII**) to answer the following questions (Tabulated data may be found in Appendix 6.):

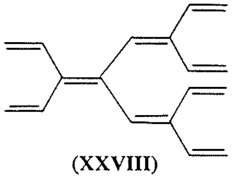


(XXVII)

(a) What values would you expect for oxidation and reduction half-wave potentials for this molecule under conditions described in Problem 8-14?

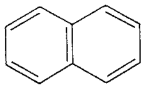
(b) If an electron were removed from the highest occupied MO to produce an ion, which bonds would you expect to lengthen, which to shorten?

8-16 Use the effective bond energies of Table 8-2 to calculate the expected π energy for (**XXVIII**). Compare this with the HMO energy of $18\alpha + 21.906\beta$.

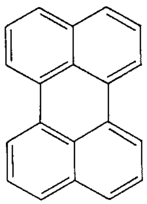


(XXVIII)

8-17 Obtain the HMO data for naphthalene (**XXIX**) and perylene (**XXX**):



(XXIX)



(XXX)

(a) For each molecule, compare E to the energy predicted by use of Table 8-2. Categorize each molecule as aromatic, nonaromatic or antiaromatic.

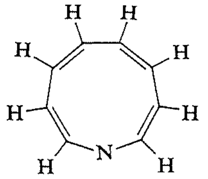
(b) Compare the RE for these two molecules. Does the central ring in perylene appear to be contributing?

(c) Draw formal bond structures for perylene. What can you conclude about the two bonds connecting naphthalene units in perylene?

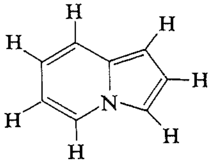
(d) Use HMO bond orders to calculate a predicted length for these two bonds. How do they compare with the observed 1.471 Å value? Is this observed length consistent with your conclusion of Part (c)?

8-18 The third, fourth, and fifth molecules in Fig. 8-24 have dipole moments. Assuming that the individual rings attract or repel charge in accordance with our expectations from the $4n + 2$ rule, predict the direction of the π-electronic contribution to the dipoles. (Dipoles are defined by chemists as being directed from positive toward negative ends of electric dipoles. Physicists use the opposite convention.) How would you expect the π-electron densities to vary in these molecules? Compare your expectations with tabulated densities.

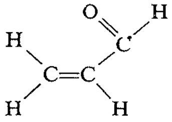
8-19 How many π electrons are there in each of the following neutral molecules?



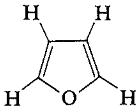
(a)



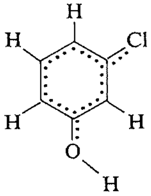
(b)



(c)

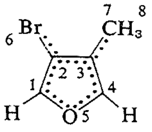


(d)



(e)

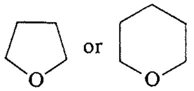
8-20 Use the parameters in Table 8-3 to construct the HMO determinant for molecule (**XXXI**). Use the conjugative model for the methyl group.



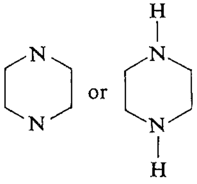
(XXXI)

8-21 Substitution of a nitrogen for a carbon in benzene changes the HMO energy levels, but not drastically. Hence the stability of the six π-electron molecule pyridine can still be rationalized by the $4n + 2$ rule. Which member of each of the following pairs of molecules would you expect to be stable on the basis of such arguments

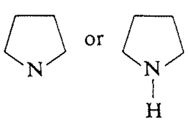
(a)



(b)



(c)



8-22 It is observed that many even alternant hydrocarbons tend to undergo nucleophilic substitution, electrophilic substitution, and radical addition at the same site(s). Rationalize this behavior in terms of the following indices (where appropriate): q_r, HOMO, LUMO, L_r.

8-23 Can π_{rr} be a successful index for nucleophilic *and* electrophilic substitution if these are observed to occur at different sites?

8-24 For the methylene cyclopropene system C_4H_4 (see Appendix 6 for HMO data and atomic numbering scheme):

(a) calculate the free valences for the neutral molecule;

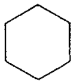
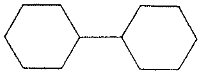
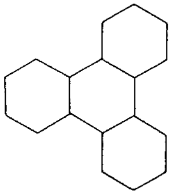
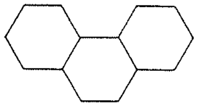
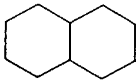
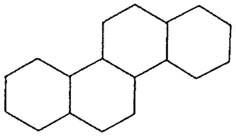
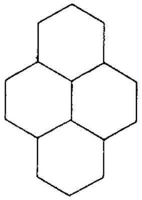
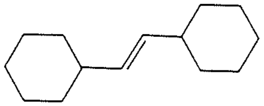
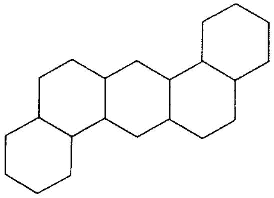
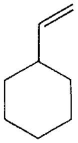
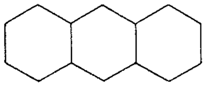
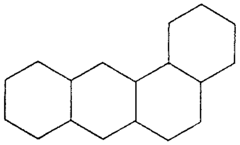
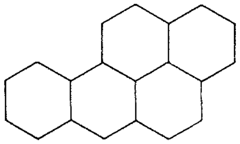
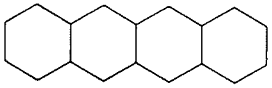
(b) decide, using three appropriate reactivity indices, which site is most susceptible to electrophilic attack.

(c) Decide which protons would lead to hyperfine splitting of the ESR spectrum of the radical anion, according to the simple Hückel approach.

(d) Decide whether the second-lowest MO is net bonding or net antibonding. Why?

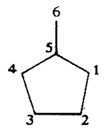
8-25 Published data for free radical ($CCl_3\cdot$) addition to hydrocarbons are shown in Table P8-25; see Kooyman and Farenhorst [27]. Using standard tabulations or computer programs, obtain F_r values for each molecule. Choose the largest value for each molecule and plot this against the log of the *modified* rate constant. In each case, modify the rate constant by dividing k by the *number* of sites on the molecule having the maximum F_r value. [If a molecule has F_r values differing by 0.002 or less, treat them as equal.] If any data points deviate greatly from the general trend, try to give an explanation.

TABLE P8-25

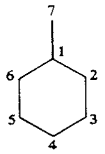
Molecule	Structure	Rate constant
Benzene		$<10^{-3}$ (use this limit)
Biphenyl		2.7×10^{-3}
Triphenylene		$<4 \times 10^{-2}$ (use this limit)
Phenanthrene		1.6×10^{-2}
Naphthalene		4×10^{-2}
Chrysene		6.7×10^{-2}
Pyrene		1.3
Stilbene		1.0
1,2,5,6-Dibenzanthracene		3.7
Styrene		12.5
Anthracene		22
Benzanthracene		30
3,4-Benzopyrene		70
Naphthacene		102

8-26 Which ring of the fourth molecule in Fig. 8-24 would you predict an electrophilic reagent would be more likely to attack, and why?

8-27* Which of the following neutral unsaturated planar hydrocarbons should experience greater changes in bond order when a pi electron is added to form the anion, and why?



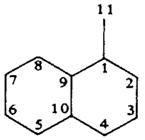
(a)



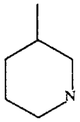
(b)

8-28* Consider an ESR experiment on the odd-alternant radical shown. Identify the site(s) that have attached hydrogen atoms that should give

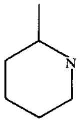
(a) the largest coupling constant,
(b) the second-largest coupling constant,
(c) no coupling constant.



8-29* Which of the following two seven-pi-electron systems should be easier to ionize, and why?



(a)



(b)

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* This problem assumes prior study of Appendix 5.

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