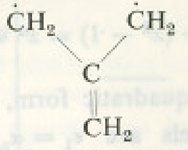
the structure, I, since two double bonds cannot be written for this structure without invoking "long bonds."

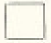


I

Exercises. Determine the π-energy levels for each of the following π-networks and determine the total π-energy and the *DE*

1.  *Ans.* $x = -2, 1, 1$
$E_\pi^+ = 2\alpha + 4\beta;\ DE = 2\beta$
$E_\pi^{\cdot} = 3\alpha + 3\beta;\ DE = \beta$
$E_\pi^- = 4\alpha + 2\beta;\ DE = 0$

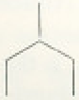
2.  *Ans.* $x = -2.170, -0.311, +1.000, +1.481$
$E_\pi = 4\alpha + 4.962\beta;\ DE = 0.962\beta$

3.  *Ans.* $x = 0, 0, \pm 2$
$E_\pi = 4\alpha + 4\beta;\ DE = 0$

4.  *Ans.* $x = -2.562, 0, 1, 1.562$
$E_\pi = 4\alpha + 5.123\beta;\ DE = 1.123\beta$

5.  *Ans.* $x = 0, \pm\sqrt{3}, \pm 1$
$E_\pi^+ = 4\alpha + 5.464\beta;\ DE = 1.464\beta$
$E_\pi^{\cdot} = 5\alpha + 5.464\beta;\ DE = 1.464\beta$
$E_\pi^- = 6\alpha + 5.464\beta;\ DE = 1.464\beta$

6.  *Ans.* $x = \pm 1.802, \pm 1.247, \pm 0.445$
$E_\pi = 6\alpha + 6.988\beta;\ DE = 0.988\beta$

7.  *Ans.* $x = \pm 1, \pm(2 \pm \sqrt{3})^{1/2}$
$E_\pi = 6\alpha + 6.899\beta;\ DE = 0.899\beta$

(Note that this cross-conjugated triene turns out to be less stable than the preceding hexatriene.)

2.6 Roots of Polynomial Equations

A vital particular of the HMO method is finding the roots of the secular polynomial. For a second-order equation, of course, the quadratic formula is easily applicable. Although the general solution for cubic equations is well known, the author has found that for most cases the application of the formula is more work than it is worth. For fourth and higher polynomials other methods must be employed.

The obvious first step is to test the several possible integral values for x, $0, \pm 1, \pm 2$. Note that since no carbon in a π-lattice can be bound to more than three other carbons no root can equal or exceed three in magnitude; that is, all $|m_j| < 3$. A rapid procedure for testing these values is the following: starting at the far left, the first coefficient of the secular polynomial, which is generally unity for our cases, is multiplied by the assumed value for the argument and the product is added algebraically to the next lower coefficient. The sum is multiplied by the assumed argument and the product is added to the next lower coefficient, etc. If the final sum vanishes, the assumed value for the argument is a root, and, moreover, the set of sums constitutes the coefficients for the next lower secular polynomial obtained by factoring the found root. An example follows in which $x = -2$ is found to be a root:

$$\begin{array}{cccc} x^3 + x^2 & -3x & -2 \\ -2 & 2 & 2 \\ \hline -1 & -1 & 0 \end{array}$$

The polynomial obtained by factoring this root is $x^2 - x - 1 = 0$.

With a calculating machine this method affords a rapid (with practice) means of testing assumed values of the argument. When an approximate value is found, a method such as Newton's may be used to obtain the root to any desired precision. Alternatively, a plot of the function may be constructed for the first approximation to the roots.[5]

An additional help: the reader will recall from his algebra days that the number of alternations of sign between successive coefficients equals the number of negative roots.

Some generalizations are also helpful. An important theorem which is not proved here (see Chap. 3) is

$$\sum_j m_j = 0 \tag{33}$$

that is, the algebraic sum of all the roots vanishes. The form of the roots takes an even more restricted pattern for special types of systems.

An especially important distinction is the classification into alternant hydrocarbons[6] (AH) and nonalternant hydrocarbons (non-AH). Alternant

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[5] Other methods for finding roots of polynomials are known. See H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, Van Nostrand, New York (1943), p. 477; and J. W. Mellor, *Higher Mathematics for Students of Chemistry and Physics*, Dover Publications, New York (1955), Chap. VI.

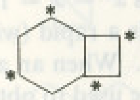
[6] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, A192, 16 (1947).

hydrocarbons are planar conjugated hydrocarbons, having no odd-membered rings, in which the carbons can be divided into two sets, s (starred), and u (unstarred), such that each s-carbon has only u neighbors and vice-versa. In an even-AH the numbers of starred and unstarred positions are usually equal ($n_s = n_u$); for such cases the roots take the form

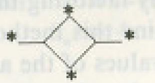
$$x_j = \pm\mu, \pm\mu', \pm\mu,'' \text{ etc.} \tag{34}$$

that is, the roots occur in pairs of opposite sign.[7] An example of such a system is II. In some cases the starred set is larger than the unstarred set ($n_s > n_u$); such cases have ($n_s - n_u$) MO's with no bonding energy[8] [$(n_s - n_u)x\text{'s} = 0$] and may normally be described as polyradicals. An example is III. Note that for such systems one cannot write normal Kekulé structures having more than n_u double bonds.

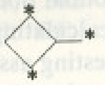
In most odd-AHs the starred set exceeds the unstarred set by one; the starred carbons are referred to as *active positions*.[8] For these systems, the roots also occur in pairs and the extra root has the value zero. An example is IV. For some systems n_s exceeds n_u by an odd number greater than one. For these cases $2n_u$ roots occur as ± pairs and the remainder are zero. For these systems, also, Kekulé structures can be written only with n_u double bonds. An example is V.



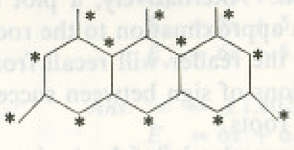
II



III



IV



V

For alternant systems the energy levels are symmetrically disposed about the zero level.

For some simple systems the energies may be written in closed form.[3,6,9] For straight chains of n atoms

$$x_j = -2\cos\frac{j\pi}{n+1}; \qquad j = 1, 2, 3, \cdots, n \tag{35}$$

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[7] C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

[8] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

[9] C. A. Coulson, *Proc. Roy. Soc.*, **A164**, 383 (1938); F. G. Fumi, *Nuovo cimento*, **8**, 1 (1951); A. A. Frost and B. Musulin, *J. Chem. Phys.*, **21**, 572 (1953). The last reference puts the formulas in a convenient mnemonic form.

For rings of n atoms

$$x_k = -2\cos\frac{2k\pi}{n}; \qquad k = 0, \pm1, \pm2, \cdots, \begin{matrix} \pm\dfrac{n-1}{2} \text{ for } n \text{ odd} \\ \pm\dfrac{n}{2} \text{ for } n \text{ even} \end{matrix} \tag{36}$$

Heilbronner[10] has shown how the secular polynomials for a complex system may be derived from those of component parts. If K_n, K_{n-1}, and K_{n-2} are the secular polynomials for chains of n, $n-1$, and $n-2$ atoms, respectively,

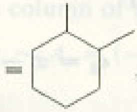
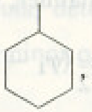
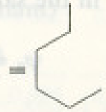
$$K_n = xK_{n-1} - K_{n-2} \tag{37}$$

If R_n is the polynomial for a ring of n atoms,

$$R_n = K_n - K_{n-2} - 2(-1)^n \tag{38}$$

Let P_n be any system of n atoms having the secular polynomial, $\mathbf{P}_n$; let $\mathbf{P}^r_{n-1}$ be the polynomial for the system P^r_{n-1} which is P_n with atom r removed from the π-lattice. Then, if Q_{n+1} (having polynomial $\mathbf{Q}_{n+1}$) is derived from P_n by attachment of a carbon atom at atom r,

$$\mathbf{Q}_{n+1} = x\mathbf{P}_n - \mathbf{P}^r_{n-1} \tag{39}$$

Example. Let $Q_{n+1} =$ , $P_n =$ , $P^r_{n-1} =$ , $\mathbf{P}_n = x^7 - 7x^5 + 13x^3 - 7x$; $\mathbf{P}^r_{n-1} = x^6 - 5x^4 + 6x^2 - 1$. Therefore, $\mathbf{Q}_{n+1} = x^8 - 8x^6 + 18x^4 - 13x^2 - 1$.

Consider the system Q_{n+m} formed by joining atom r of system R_n to atom s of system S_m. We find that

$$\mathbf{Q}_{n+m} = \mathbf{R}_n\mathbf{S}_m - \mathbf{R}^r_{n-1}\mathbf{S}^s_{m-1} \tag{40}$$

Example. Let $R_n =$ , $S_m =$ , $Q_{n+m} =$ . $\mathbf{R}_n = x^5 - 5x^3 + 5x + 2$; $\mathbf{R}^r_{n-1} = x^4 - 3x^2 + 1$; $\mathbf{S}_m = x^3 - 3x + 2$; $\mathbf{S}^s_{m-1} = x^2 - 1$.

Therefore,

$$\mathbf{Q}_{n+m} = x^8 - 9x^6 + 2x^5 + 24x^4 - 8x^3 - 19x^2 + 4x + 5.$$

These relations are of general use for simplifying computational problems.[11]

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[10] E. Heilbronner, *Helv. Chim. Acta*, **36**, 170 (1953).

[11] For additional properties of some use see I. Samuel, *Compt. rend.*, **238**, 2422 (1954); **229**, 1236 (1949); R. Gouarné, *Compt. rend.*, **230**, 844 (1950); H. O. Pritchard and F. H. Sumner, *Phil. Mag.*, **45**, 466 (1954); T. H. Goodwin and V. Vand, *J. Chem. Soc.*, **1955**, 1683; H. H. Günthard and H. Primas, *Helv. Chim. Acta*, **39**, 1645 (1956); A. L. Chistyavkov, *Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, **1959**, 1349.

2.7 Calculation of Coefficients

To find the coefficients for the molecular orbital that corresponds to each energy, we return to the original set of simultaneous equations, insert each energy in turn, and solve for the set of coefficients.

The case of ethylene is trivial. The secular determinant (25) corresponds to the equations

$$\begin{aligned} c_1x + c_2 &= 0 \\ c_1 + c_2x &= 0 \end{aligned}$$

For $x = -1$ (lowest level)

$$-c_1 + c_2 = 0 \qquad \therefore c_1 = c_2$$

Applying the normalization condition,

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

we find $\quad c_1 = c_2 = 1/\sqrt{2}$

Thus $\quad \psi_1 = \dfrac{1}{\sqrt{2}}(\varphi_1 + \varphi_2); \qquad \epsilon_1 = \alpha + \beta$

Using $x = 1$ in the same manner, we find

$$\psi_2 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2); \qquad \epsilon_2 = \alpha - \beta$$

The two MO's for ethylene are now completely characterized.

Butadiene is somewhat more laborious by this method. The secular determinant (28) corresponds to

$$\begin{aligned} c_1x + c_2 \qquad\qquad &= 0 \\ c_1 + c_2x + c_3 \qquad &= 0 \\ c_2 + c_3x + c_4 &= 0 \\ c_3 + c_4x &= 0 \end{aligned}$$

For the first (lowest-lying) MO, $x = -[(1 + \sqrt{5})/2]$. Working down, we find

$$c_2 = \left(\frac{1 + \sqrt{5}}{2}\right)c_1$$

$$c_3 = -c_1 + c_2\left(\frac{1 + \sqrt{5}}{2}\right) = \left(\frac{1 + \sqrt{5}}{2}\right)c_1$$

$$c_3 - \left(\frac{1 + \sqrt{5}}{2}\right)c_4 = 0$$

$$c_4 = \left(\frac{2}{1 + \sqrt{5}}\right)c_3 = \left(\frac{2}{1 + \sqrt{5}}\right)\left(\frac{1 + \sqrt{5}}{2}\right)c_1 = c_1$$

From the normalization condition,

$$c_1^2 + c_2^2 + c_3^2 + c_4^2 = 1$$

$$c_1^2 + \left(\frac{1 + \sqrt{5}}{2}\right)^2 c_1^2 + \left(\frac{1 + \sqrt{5}}{2}\right)^2 c_1^2 + c_1^2 = 1$$

$$\therefore c_1 = \left(\frac{1}{5 + \sqrt{5}}\right)^{1/2} = c_4$$

and $\quad c_2 = c_3 = \left(\dfrac{1 + \sqrt{5}}{2}\right)\left(\dfrac{1}{(5 + \sqrt{5})^{1/2}}\right)$

Hence $\quad \psi_1 = \dfrac{1}{\sqrt{5 + \sqrt{5}}}\left(\varphi_1 + \dfrac{1 + \sqrt{5}}{2}(\varphi_2 + \varphi_3) + \varphi_4\right)$

This procedure can be repeated for each energy to compute each MO. However, the equivalent method of cofactors is much more systematic and straightforward. In principle, the cofactors along any row can be used, although there is generally little advantage to using any row other than the first. For cofactors, A_r, along the first row, the coefficient of the rth atom (and the rth column of the secular determinant)

$$c_r \sim A_r = (-1)^{r+1}(\text{minor of } a_{1r}) \tag{41}$$

Example. Butadiene:

$$\begin{aligned} A_1 &= x^3 - 2x \\ A_2 &= -(x^2 - 1) \\ A_3 &= x \\ A_4 &= -1 \end{aligned}$$

For ψ_1, $x = -\left(\dfrac{1 + \sqrt{5}}{2}\right)$

r	A_r	A_r^2	$c_r = A_r/(\sum A^2)^{1/2}$
1	-1	1	$\dfrac{1}{\sqrt{5 + \sqrt{5}}} = 0.371$
2	$-\left(\dfrac{1 + \sqrt{5}}{2}\right)$	$\dfrac{3 + \sqrt{5}}{2}$	$\dfrac{1 + \sqrt{5}}{2\sqrt{5 + \sqrt{5}}} = 0.600$
3	$-\left(\dfrac{1 + \sqrt{5}}{2}\right)$	$\dfrac{3 + \sqrt{5}}{2}$	$\dfrac{1 + \sqrt{5}}{2\sqrt{5 + \sqrt{5}}} = 0.600$
4	-1	1	$\dfrac{1}{\sqrt{5 + \sqrt{5}}} = 0.371$
		$\sum A_r^2 = \sqrt{5} + 5$	

$$\therefore \quad \left(\sum A_r^2\right)^{1/2} = (5 + \sqrt{5})^{1/2}$$

By this procedure normalized coefficients are obtained directly. Furthermore, the work is kept neat and orderly and can be inspected for errors rather conveniently. Each value of x is substituted in turn to determine each MO. It should be noted that occasionally the cofactors along a particular row vanish; in such cases cofactors along a different row must be used.

For some special systems several theorems are useful for the determination of the coefficients. These are stated without proof. For an AH, in which the energies occur in pairs, $\pm\mu$, the coefficients for the MO of $m = \mu$ are readily found from the MO of $m = -\mu$ by changing the sign of the coefficients of the unstarred atoms.[8] In the nonbonding MO ($m = 0$) of an odd-AH coefficients of unstarred positions are zero and each sum of the coefficients of starred atoms attached to any one unstarred position vanishes[6,7] (see p. 54).

For straight chains of n carbons the coefficients take the form[3,6,9]

$$c_{jr} = \sqrt{\frac{2}{n+1}}\sin\frac{rj\pi}{n+1} \tag{42}$$

whereas for rings of n atoms

$$c_{jr} = \frac{1}{\sqrt{n}}\,e^{\frac{2\pi i r(j-1)}{n}} \tag{43}$$

in which $j = 1, 2, 3, \cdots, n$. In the latter case note that the coefficients are given in complex form. When using such coefficients in other equations, attention must be given to the use of complex conjugates where appropriate.[12]

Exercise. Determine the coefficients of all of the MO's for each of the following compounds (see Exercise 2.5):

Ans.

Allyl,

ψ_i	x_i	c_1	c_2	c_3
1	$-\sqrt{2}$	$1/2$	$1/\sqrt{2}$	$1/2$
2	0	$1/\sqrt{2}$	0	$-1/\sqrt{2}$
3	$\sqrt{2}$	$1/2$	$-1/\sqrt{2}$	$1/2$

Cyclopropenyl,

ψ_i	x_i	c_1	c_2	c_3
1	-2	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$
2	1	$1/\sqrt{6}$	$1/\sqrt{6}$	$-2/\sqrt{6}$
3	1	$1/\sqrt{2}$	$-1/\sqrt{2}$	0

---

[12] The use of complex exponents is discussed in Sec. 3.10.

Note: In this case of degenerate energy levels the MO's cannot be uniquely defined. We shall find that the requirement that MO's be orthogonal means that the two MO's in this case have nodes at right angles to each other. Any linear combinations of the degenerate MO's which satisfy the orthogonality and normalization conditions are equally valid MO's. The MO's are related by these equations:

$$\psi_2' = \lambda\psi_2 + (1-\lambda^2)^{1/2}\psi_3, \qquad 0 < \lambda < 1$$
$$\psi_3' = (1-\lambda^2)^{1/2}\psi_2 - \lambda\psi_3$$

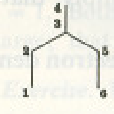
Butadiene,

ψ_i	x_i	c_1	c_2	c_3	c_4
1	-1.618	0.371	0.600	0.600	0.371
2	-0.618	0.600	0.371	-0.371	-0.600
3	0.618	0.600	-0.371	-0.371	0.600
4	1.618	0.371	-0.600	0.600	-0.371

Pentadienyl,

ψ_i	x_i	c_1	c_2	c_3	c_4	c_5
1	-1.732	0.288	0.500	0.576	0.500	0.288
2	-1	0.500	0.500	0	-0.500	-0.500
3	0	0.576	0	-0.576	0	0.576
4	1	0.500	-0.500	0	0.500	-0.500
5	1.732	0.288	-0.500	0.576	-0.500	0.288

3-Methylene-1,4-pentadiene



ψ_i	x_i	c_1	c_2	c_3	c_4	c_5	c_6
1	-1.932	0.230	0.444	0.628	0.325	0.444	0.230
2	-1.000	0.500	0.500	0	0	-0.500	-0.500
3	-0.518	0.444	0.230	-0.325	-0.628	0.230	0.444
4	$+0.518$	-0.444	0.230	0.325	-0.628	0.230	-0.444
5	1.000	0.500	-0.500	0	0	0.500	-0.500
6	1.932	0.230	-0.444	0.628	-0.325	-0.444	0.230

2.8 Electron Densities

We recall that the probability that an electron will be found in a small region of space, $\delta\tau$, is given by $\psi_r\psi_r^*\,\delta\tau$, in which ψ_r is the value of the normalized wave function in the small region τ. Since our wave functions are generally real, we can omit the complex conjugate notation. For our linear combination MO's

$$\psi = \sum_r c_r\varphi_r$$

$$\int \psi^2\,d\tau = \int\left(\sum c_r\varphi_r\right)^2 d\tau \tag{44}$$

$$= \int \sum_r c_r^2\varphi_r^2\,d\tau + \int \sum_r \sum_{s\neq r} c_r c_s \varphi_r\varphi_s\,d\tau$$

Our previous orthogonality assumption was

$$\int \varphi_r \varphi_s \, d\tau = 0 \quad \text{for } r \neq s \tag{45}$$

Hence

$$\int \psi^2 \, d\tau = \int \sum_r c_r^2 \varphi_r^2 \, d\tau = \sum_r c_r^2 \int \varphi_r^2 \, d\tau \tag{46}$$

which we recognize as the normalization condition; however, $\int \varphi_r^2 \, d\tau$ represents the probability of finding an electron in the region of space associated with the atomic orbital φ_r. Because the integration is made over all space, the value of each integral is unity, but each term is multiplied by a factor, c_r^2. In the simple LCAO (HMO) approximation c_r^2 consequently has the physical significance of the probability that an electron in an MO is associated with atomic orbital φ_r or, more simply, that c_r^2 is the electron density at atom r in the MO.[13]

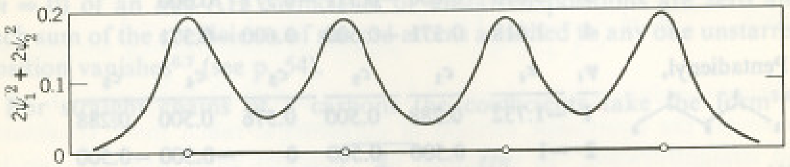


Fig. 2.6 Electron density function, $2\psi_1^2 + 2\psi_2^2$, for butadiene, using Slater orbitals.

The total electron density at an atom, q_r, is the sum of electron densities contributed by each electron in each MO:

$$q_r = \sum_j n_j c_{jr}^2 \tag{47}$$

c_{jr} is the coefficient of atom r in the jth MO, which is occupied by n_j electrons. The sum is taken over all of the MO's.

Examples. Butadiene: ψ_1 and ψ_2 are each occupied by two electrons. Hence $q_1 = 2c_{11}^2 + 2c_{21}^2 = 2(0.140) + 2(0.360) = 1.000$ and $q_2 = 2c_{12}^2 + 2c_{22}^2 = 2(0.360) + 2(0.140) = 1.000$. By symmetry, atoms 3 and 4 give the same answer; that is, the electron density is unity at each atom.

We should emphasize that the electron density as we *define* it is a convenient fiction which has only approximate physical significance. This point is demonstrated by an inspection of the function $2\psi_1^2 + 2\psi_2^2$ in Fig. 2.6, in which the electron density is the area beneath the curve. Although this function clearly peaks at the nuclei, it has substantial value between the atoms where one clearly cannot discern a boundary between the domains of individual atoms.

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[13] G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, 57, 2086 (1935).

Allyl: For allyl cation, ψ_1 is doubly occupied.

r	c_r	c_r^2	q_r	ζ_r
1	$\frac{1}{2}$	$\frac{1}{4}$	0.5	+0.5
2	$\sqrt{2}/2$	$\frac{1}{2}$	1	0
3	$\frac{1}{2}$	$\frac{1}{4}$	0.5	+0.5
			$\Sigma q_r = 2$	$\Sigma \zeta_r = +1$

Since the neutral carbon would contain one electron, both carbons 1 and 3 in allyl cation have half a positive charge. We say that the *charge density* $\zeta_r = 1 - q_r$ is +0.5. The central carbon is neutral, that is, $\zeta_2 = 0$.

This result corresponds to a resonance hybrid of the two structures:

$$\overset{\oplus}{\mathrm{C}} - \mathrm{C} = \mathrm{C} \leftrightarrow \mathrm{C} = \mathrm{C} - \overset{\oplus}{\mathrm{C}}$$

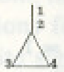
Note that the sum of the electron densities over all of the atoms must equal the total number of π-electrons. If it does not, an error has been made in the computations.

Allyl radical contains, in addition, one electron in ψ_2 which has $c_1 = \sqrt{2}/2 = -c_3$ and $c_2 = 0$. For the total π-electron densities the square of each coefficient is added to the electron densities of the cation. We find $q_1 = q_2 = q_3 = 1$ for allyl radical.

In allyl anion ψ_2 houses two electrons; hence each square above is doubled and added to the electron densities for allyl cation, yielding $q_1 = q_2 = 1.5$; $q_2 = 1$. Both end carbons in allyl anion have a half unit of additional negative charge; that is, $\zeta_1 = \zeta_3 = -0.5$, $\zeta_2 = 0$.

Exercise. Find the electron densities for each of the following systems:

Methylenecyclopropene,



Ans.

ψ_i	x	c_1	c_2	c_3	c_4
1	−2.170	0.278	0.612	0.524	0.524
2	−0.311	0.814	0.253	−0.368	−0.368
q_r		1.478	0.882	0.820	0.820
ζ_r		−0.478	+0.118	+0.180	+0.180

Cyclopropenyl,

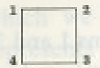
Cation: $q_1 = q_2 = q_3 = 0.677$

Radical: Degeneracy, see note.

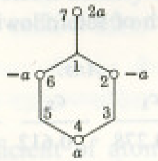
Anion: $q_1 = q_2 = q_3 = 1.333$

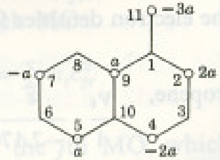
Note: In cyclopropenyl radical the third π-electron may be placed in either of two degenerate orbitals. A molecule cannot exist in one of several degenerate states (Jahn-Teller theorem) and will distort slightly to destroy the symmetry which gives rise to the degeneracy (Jahn-Teller distortion). In some cases a time-average electron density is useful. For such cases the Jahn-Teller effect may be ignored, and the electron density is calculated by assuming that $1/n$th of the available electrons is in each of the n degenerate MO's. The cyclopropenyl radical case would then be treated as if half an electron were in each of the degenerate MO's ψ_2 and ψ_3. This procedure yields $q_1 = q_2 = q_3 = 1$. The cyclopropenyl anion is straightforward—the third electron is put in ψ_2 and the fourth, having the same spin as the third, is put into ψ_3. The anion, consequently, is a diradical, but the Jahn-Teller effect does not apply.

Cyclobutadiene, *Ans.* $q_1 = q_2 = q_3 = q_4 = 1$



Coulson and Rushbrooke[7] have shown that for even alternant hydrocarbons (AH) and for odd-AH radicals the electron density at each position is unity. In general, the electron densities in nonalternant systems differ from unity. An odd-AH cation or anion is formed by removing one electron from or adding one electron to the singly occupied nonbonding MO of an odd-AH radical having uniform electron distribution. The charge densities in such cases, consequently, are determined entirely by the coefficients of the NBMO which may be found without solving secular equations. The procedure has been discussed by Longuet-Higgins.[14] We use the fact that in the NBMO the coefficients of active atoms sum to zero about each inactive position. In the examples of benzyl and α-naphthylmethyl which follow the active positions are circled. In benzyl c_4 is taken as a. About inactive position 3, $c_2 + c_4 = 0$; therefore, $c_2 = -a$. The other coefficients are determined in the same manner.





$$(2a)^2 + 3a^2 = 1 \qquad (3a)^2 + 2(2a)^2 + 3a^2 = 1$$

$$\therefore \quad a^2 = \tfrac{1}{7} \qquad \therefore \quad a^2 = \tfrac{1}{20}$$

$$a = 1/\sqrt{7} \qquad a = 1/2\sqrt{5}$$

$$\zeta_2 = \zeta_4 = \zeta_6 = \tfrac{1}{7} \qquad \zeta_2 = \zeta_4 = \tfrac{1}{5}$$

$$\zeta_7 = \tfrac{4}{7} \qquad \zeta_5 = \zeta_7 = \zeta_9 = \tfrac{1}{20}$$

$$\zeta_{11} = \tfrac{9}{20}$$

In these examples ζ_r is positive or negative, depending on whether we are considering the cation or anion, respectively.

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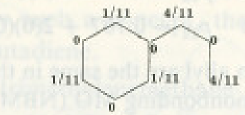
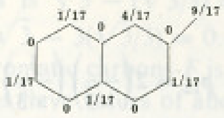
[14] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 275 (1950); cf. also M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345, 3357 (1952); *Ann. Repts. Prog. Chem., Chem. Soc. London*, **48**, 112 (1951).

Exercise. Find the charge densities for the heptatrienyl, cinnamyl, and β-naphthylmethyl cations.

Ans.





2.9 Bond Orders and Free Valence

In 1939 Coulson[15] introduced the *partial mobile bond order* p^j_{rs} for the r—s bond in the jth MO, defined as

$$p^j_{rs} = c_{jr}c_{js} \tag{48}$$

The corresponding *total mobile bond order* or, more simply, the *bond order* is

$$p_{rs} = \sum_{\substack{\text{all} \\ \text{electrons}}} p^j_{rs} = \sum_j n_j c_{jr} c_{js} \tag{49}$$

in which n_j is the number of electrons in the jth MO.

The bond order is merely a convenient defined quantity, although this particular definition has some important mathematical advantages (*vide infra*). Nevertheless, as so defined, this quantity has a rough physical significance that we might associate with the binding power of a bond, since the product of the coefficients of adjacent bonded atoms may be construed as a bond electron density. When both coefficients are large and of like sign, the product is large and corresponds to substantial electronic cement binding the atoms. When one of the coefficients is zero, indicative of a node at an atom, the partial mobile bond order vanishes in agreement with our expectations for a nonbinding situation. Finally, if the coefficients are of opposite sign, indicative of a node between the atoms, we have a negative bond order in agreement with what we would demand for an antibonding situation.

Examples.

Ethylene: $p_{12} = 2c_1c_2 = 1$

Butadiene: $p_{12} = 2(0.371)(0.600) + 2(0.600)(0.371) = 0.894$

$p_{23} = 2(0.600)(0.600) + 2(0.371)(-0.371) = 0.447$

Note: In this case the 1–2 bond, which is a double bond in the conventional structural symbolism, has a large p-value, whereas the "single" bond, 2–3, has a rather small p-value.

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[15] C. A. Coulson, *Proc. Roy. Soc.*, **A169**, 413 (1939).

Allyl: Cation: $p_{12} = 2(0.5)(0.707) = 0.707$

Radical: $p_{12} = 0.707 + (0)(0.707) = 0.707$

Anion: $p_{12} = 0.707 + 2(0)(0.707) = 0.707$

Bond orders in allyl are the same in the cation, radical, and anion because the upper level is a nonbonding MO (NBMO). This equality is true of all odd-AH systems.

Cyclopropenyl:

$$\text{Cation:}\quad p_{12} = 2\left(\frac{1}{\sqrt{3}}\right)\left(\frac{1}{\sqrt{3}}\right) = 0.667$$

$$\text{Radical (see note on p. 53):}\quad p_{12} = 0.667 + \frac{1}{2}\left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + \frac{1}{2}\left(\frac{1}{\sqrt{2}}\right)\left(-\frac{1}{\sqrt{2}}\right) = 0.500$$

$$\text{Anion:}\quad p_{12} = 0.667 + \left(\frac{1}{\sqrt{6}}\right)\left(\frac{1}{\sqrt{6}}\right) + \left(\frac{1}{\sqrt{2}}\right)\left(-\frac{1}{\sqrt{2}}\right) = 0.333$$

In this case a variation in electron population occurs in antibonding MO's and a corresponding variation in bond order results.

Exercise. Calculate the bond orders for methylenecyclopropene, pentadienyl, and trimethylenemethane.

Ans.

Coulson and Longuet-Higgins[16] have shown that the total π-electron energy may be expressed as a function of electron densities and bond orders:

$$E_\pi = \sum_r q_r\alpha + 2\sum_{r<s}\sum p_{rs}\beta \tag{50}$$

This theorem provides a valuable check on one's computations, for, after obtaining the coefficients, these may be used to calculate the bond orders, the sum of which over all the bonds should equal the total binding energy.

The free valence index, F_r, has been defined by Coulson[17] as

$$F_r = N_{\max} - N_r \tag{51}$$

in which N_r is the sum of the orders of all bonds joining atom r and $N_{\max}$ is the maximum value, which is usually taken as $\sqrt{3}$.[18]

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[16] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **191**, 39 (1947).

[17] C. A. Coulson, *Discussions Faraday Soc.*, **2**, 9 (1947); *J. Chim. Phys.*, **45**, 243 (1948).

[18] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952); H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 677 (1952).

For butadiene, $F_1 = 1.732 - 0.894 = 0.838$ and $F_2 = 1.732 - 0.894 - 0.447 = 0.391$. The free valence is a modern version of Thiele's concept of residual affinity. As required by such a concept, the free valence is higher at the terminal position of butadiene.

The bond order for a bond in trimethylenemethane is $\sqrt{3}/3$; hence F for a terminal position is $\sqrt{3} - (\sqrt{3}/3) = \frac{2}{3}\sqrt{3} = 1.16$, whereas F for the central position is $\sqrt{3} - 3(\sqrt{3}/3) = 0$. The value for $N_{\max}$ comes from this system.[18] For aromatic carbons F is typically about 0.4, and in free radicals some positions have values of about unity. F has been used as a measure of ease of attack by free radicals (see Chaps. 10 and 13).[19]

2.10 Nodal Properties of MO's

The MO wave functions for butadiene were diagrammed in Fig. 1.18. The four wave functions, ψ_1, ψ_2, ψ_3, and ψ_4, had 0, 1, 2, and 3 nodes, respectively, which, in this representation occur as points along a line. All straight chain π-systems can be represented along a straight line because of our neglect of non-neighbor interactions. For such systems each MO, ψ_j, can be represented in a similar manner with $j - 1$ nodal points. In straight-chain even systems the nodal points occur only between atoms and divide the segments between nuclei into *bonds* and *antibonds*: ψ_1 of butadiene can be described as having a net of three bonds; ψ_2, with two bonds and one antibond, has a net of only one bond; ψ_3 has one bond and two antibonds, hence is net antibonding; ψ_4 has three antibonds. The order of orbital energies clearly parallels the bonding and antibonding characteristics of the MO's.

A more schematic representation of the MO's of pentadienyl is given in Fig. 2.7. For this odd-membered system the nodal points in some of the MO's coincide with nuclear positions giving regions that we may call nonbonds; ψ_3 is totally nonbonding in agreement with its energy and with our prior classification as a NBMO.

As soon as we introduce branches or rings, the nuclei of the π-network must be described as points in a plane. The nodes now become lines, and further possibilities for nodes open up. We now have two MO's with one node, the nodal lines in these cases being at right angles. The orientation of the nodal lines is simply that which leaves the most net bonding and fulfills symmetry requirements. If both orthogonal nodal lines give MO's with identical energy, we have a degeneracy, and any orientation of the

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[19] For a recent review of the free-valence concept, see B. Pullman and A. Pullman, "Free Valence in Conjugated Organic Molecules," Chap. 2 in J. W. Cook, *Progress in Organic Chemistry*, Vol. 4, Butterworths Scientific Publications, London (1958).

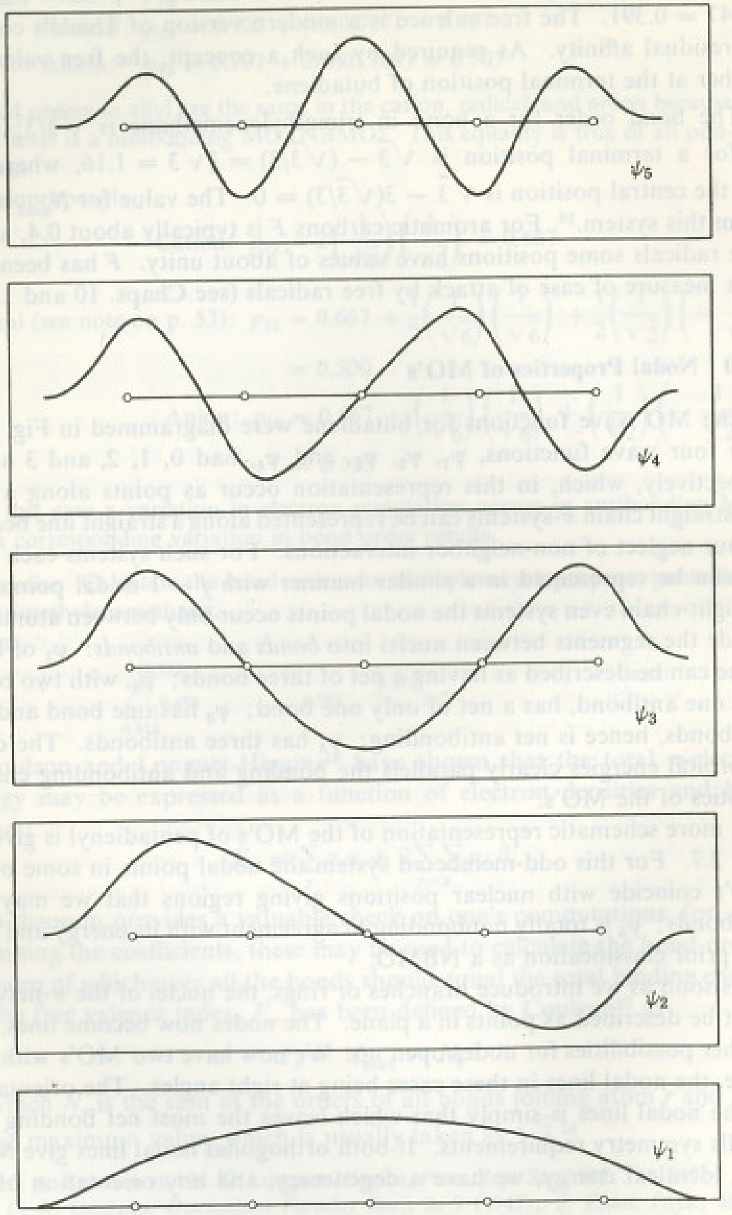

Fig. 2.7 Schematic HMO's for pentadienyl.

nodal lines corresponding to rotation about a point is equally valid. These features are illustrated below.

The six MO's of 3-methylene-1,4-pentadiene are represented schematically in Fig. 2.8: ψ_1 is totally bonding; ψ_2 has two bonds and three nonbonds; ψ_3, with a node at right angles to that in ψ_2, has three bonds and two antibonds and, consequently, has less net bonding than ψ_2; ψ_4, with two parallel nodes, has two bonds and three antibonds, hence has net antibonding; ψ_5 has two orthogonal nodes with two antibonds and three nonbonds; ψ_6 is totally antibonding. Note that in this case we do not get two parallel nodes along the long axis of the molecule. The reason has to do with symmetry considerations which become evident in Chap. 3.

An interesting case is that of cyclobutadiene, whose MO's are shown in Fig. 2.9; ψ_1 is completely bonding; ψ_2 has one node which forms two bonds and two antibonds or a net of zero bonding; ψ_3 has an orthogonal node and is clearly identical with ψ_2, except for orientation in space, and must have identical energy. Consequently, any pair of MO's obtained by a rotation of the nodes about the center of the molecule are likewise perfectly acceptable MO's and have the same energy. Examples are ψ_2' and ψ_3' formed by rotating the nodes counterclockwise by 45°.

Supplemental Reading

Although descriptions of the HMO method have been presented frequently, the following references treat the method in some detail.

Dictionary of Values of Molecular Constants, edited by C. A. Coulson and R. Daudel, Vol. I, Centre de Chemie Théorique de France, Paris.

G. W. Wheland, *Resonance in Organic Chemistry*, John Wiley and Sons, New York (1955), p. 660.

B. Pullman and A. Pullman, *Les theories electroniques de la chimie organique*, Masson et Cie, Paris (1952), p. 178.

H. Hartmann, *Theorie der chemischen Bindung*, Springer-Verlag, Berlin (1954), p. 250.

C. A. Coulson, *Valence*, Oxford University Press, London (1952), p. 238.

C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947).

R. Daudel, R. Lefebvre, and C. Moser, *Quantum Chemistry*, Interscience Publishers, New York (1959).

A. Streitwieser, Jr., and J. I. Brauman, *Tables of Molecular Orbital Calculations*, Pergamon Press, New York (in press).

This book gives an extensive list of HMO energies and coefficients.