A THEORY OF THE ANNULENES

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ABSTRACT

It has been proposed that large annulenes have alternation of bond length. The height of the annulene singlet transition energies has been cited as evidence for bond alternation.

This thesis shows that the mechanism of bond alternation is inadequate to reproduce the experimental spectrum of the annulenes. I am able to explain the height of the annulene singlet transitions by the use of the alternant molecular orbital method.

It appears that simple MO methods and even limited C.I. treatments seriously underestimate the energy depression of the ground state through electron correlation.

It is shown that the tendency towards bond length alternation exhibited by the simple MO method is an artifact of this method, and should not be taken seriously. Some of the limitations of the AMO method are examined and it is shown how the AMO method may be extended to sigma as well as pi electrons.

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INTRODUCTION

In small linear molecules double bonds are shorter than single bonds. In ring molecules such as benzene, the conjugated bonds are of equal length. The question arises as to whether, in long conjugated polyenes, the bond lengths away from the ends are equal as in benzene, or unequal as in butadiene.

This question was first investigated by Lennard Jones (1) in 1937, and Coulson (2) in 1938. They concluded that the bond lengths away from end effects would be equal.

In 1949 Kuhn (3) discovered that the electronic energy levels of large polyenes were too high, unless it was assumed that the bond lengths were unequal. In 1956 Platt (4) suggested a mechanism he called "configuration interaction" to explain the apparent inequality in bond length. This suggested mechanism consists of the interaction of various excited states with the ground state through bond length alternation.

It has been shown by many (5,6,7,28,34) that free electron models predict bond length alternation must occur even without end effects for sufficiently large conjugated molecules. Most predict a critical size of about thirty (30) conjugated bonds.

The ring molecules cyclooöctadecanonaene ($C_{18}H_{18}$), and cyclotriacontapentadecaene ($C_{30}H_{30}$) have been synthesized (Sondheimer (30,31,32,33)). These annulenes exhibit "abnormally high" excited singlet energies.

The amount of bond alternation necessary to explain these spectra is unreasonable* (Gouterman and Wagniere (10)). Such bond alternation would require either a very high value for the first derivative of the resonance integral β , or a correspondingly high value of the first derivative of the coulomb integral between p orbitals on neighboring carbon atoms.

It therefore becomes reasonable to look for other explanations of the spectra. Longuet-Higgins (8) dismisses the possibility that the spectra might be explained by configuration interaction. He does a sample calculation showing that interacting certain configurations of $C_{18}H_{18}$ makes only a slight change in the molecular energy levels. This method is inadequate because there is a very large number of configurations that can interact with the ground state configuration, and the cumulative effect might be quite large, although each individual interaction is small.

A calculation by the complete configuration interaction method is impractical with a large number of pi

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*See chapter II, part 5.

electrons, because of the extreme length of such a calculation.

A different approach is the alternant molecular orbital (AMO) method (11,12,13,22,23,24,25,26). This method accounts for most of the electron correlation energy without having to choose excited configurations to mix with the ground state configuration. Using this method I have calculated the ground state energy and lowest excited state transition energies of cyclooctadecanoaene (CON), and cyclotriacontapentadecaene (CTP).

The results of alternant molecular orbital method calculations are qualitatively different from those of independent electron models. I will show that the greatest difference is the existence, in alternate hydrocarbons obeying Hückel's rule, of a finite energy gap between the ground state and the lowest excited singlet states.* This energy gap prevents bond alternation by Platt's mechanism, and explains the "abnormally high" excited singlet energies.

I will show in chapter VII how sigma-pi interactions may be added to the alternant molecular orbital method by a device akin to sigma bond spin polarization (19).

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*See chapter III, part 6.

CHAPTER I

ON PREDICTION OF BOND ALTERNATION WITH INDEPENDENT ELECTRON MODELS

PART 1. GENERAL CONSIDERATIONS

Suppose we imagine a conjugated ring of 4N+2 carbon atoms, such as benzene. We introduce a slight distortion, x, causing the bonds to alternate in length. The distortion will cause a mixing of bonding molecular orbitals X_n with antibonding molecular orbitals $\overline{X}_n$. The mixing is proportional to the distortion, x. By elementary perturbation theory, this gives an energy lowering to the n'th m.o. of:

$$\delta E_n \approx -x^2/\Delta E \qquad (1.1)$$

$1/\Delta E$ for the highest bonding orbital is proportional to the number of conjugated atoms in the ring. In the Hückel theory it is:

$$1/\Delta E \backsim (\mathrm{cosc}(\pi/4N+2))/4 \simeq (N+1/2)/\pi \qquad (1.2)$$

We may find by this method the total energy lowering per bond by adding up the δE_n.

$$\delta \frac{1}{4N+2} \sum E_n \sim -x^2(1+1/3 +1/5 +.....+1/(2N+1)) \qquad (1.3)$$

The summation in equation 1.3 diverges as $\frac{1}{2}\ln(2N+1)$. For sufficiently large N this term will dominate all others in the distortion energy, and bond length alternation would be expected. More detailed calculations leading to the same general conclusion are given in references (5,6,7,28). Various approximations are used but all agree that bond length alternation should develop with about thirty conjugated bonds. Coulson and Dixon (34) have made a similar calculation with valence bond theory, leading to bond alternation with a slightly smaller ring, but their calculation depends strongly on the use of a Morse function instead of a parabolic one. This dependence upon a particular type of curve would seem to make his conclusions unreliable, even within the framework of valence bond theory.

PART 2. A QUANTITATIVE CALCULATION OF THE PLAUSIBILITY OF BOND ALTERNATION IN CON ($C_{18}H_{18}$)

For our molecular orbital theory we shall make three approximations.

1. That the sigma bonds are independent of each other and of the pi bonds. This assumption ignores changes of hybridization during distortion of the sigma bonds.
2. We shall consider only interactions between neighboring atoms.
3. We shall neglect coulomb and exchange interac-

tions, but include overlap.

The problem of bond alternation is closely related to the molecular force constants. In particular, the B_{2u} distortion leading to bond alternation only occurs if the B_{2u} stretching force constant is negative. Because the force constants play such a major part in the problem of bond alternation, it is appropriate that force constants play the major part in our theory. We shall use as our only empirical constants the B_{2u} and A_{1g} stretching force constants of benzene. I feel that this approach is more reliable than those used in the literature that involve spectroscopic constants, although the conclusions are very similar.

If the first derivatives of the overlap integral and the resonance integral, dS/dr and $d\beta/dr$, were zero, then the A_{1g} and the B_{2u} force constants would be identical. Thus we see that the terms involving second derivatives of S or β must contribute equally to K_{A1g} and K_{B2u}.

The contribution of these terms is proportional to the bond order. Since the bond order of a conjugated bond not near any end effects will tend to be constant, the contribution of these terms to the total force constants will vary little from molecule to molecule. The actual values of the second derivatives of S and β are therefore unimportant for our purposes.

Following Mulliken (14), we shall assume that β/S is a constant.

The Calculation of K_{A1g} Benzene

$$E = 4\frac{\beta}{S}\left(\frac{S}{1+S}+\frac{S}{1+2S}\right)$$

$$E' = 4\frac{\beta}{S}(1/(1+S)^2+1/(1+2S)^2)S' \qquad (1.4)$$

$$E'' = 4\beta\frac{S''}{S}((1+S) \quad +(1+2S)^{-2})$$

$$-8\beta'S'((1+S)^{-3}+2(1+2S)^{-3})$$

If we make the usual assumption for benzene that $S = 0.25$, then:

$$E'' = 4.338\beta''-8.837\beta'S' \qquad (1.5)$$

We introduce here the force constant K_{σ}, which is the force constant of a single sigma bond.

$$K_{A1g \text{ benzene}} = K_{\sigma}+\frac{1}{6}E'' = K+0.723\beta''-1.473\beta'S' \qquad (1.6)$$

The Calculation of K_{B2u} Benzene

What follows applies equally well to an annulene with any other N. Let us consider an annulene with a B_{2u} distortion. The short C-C bonds will have an overlap S_1 and a resonance integral β_1. The long bonds will have overlap S_2 and resonance integral β_2. We set $S_1/S_2 =$

$\beta_1/\beta_2 = \phi^2$, $S_1 = \phi T$, $S_2 = \phi^{-1}T$, $\beta_1 = \phi B$, $\beta_2 = \phi^{-1}B$.

We set up the secular equation for the pi molecular orbitals, using p atomic orbitals as the basis functions. A portion of the matrix follows:

$$\begin{array}{cccccc}
\cdots\cdots & \cdots\cdots & \cdots\cdots & & & \\
0 & \phi B-\phi TE & -E & \phi^{-1}B-\phi^{-1}TE & 0 & 0 \\
0 & 0 & \phi^{-1}B-\phi^{-1}TE & -E & \phi B-\phi TE & 0 \\
0 & 0 & 0 & \phi B-\phi TE & -E & \cdots\cdots \\
0 & 0 & 0 & 0 & \cdots\cdots & \cdots\cdots
\end{array}$$

We divide each row of the matrix by B-TE, and let $Q = E/(B-TE)$. The same portion of the matrix now is:

$$\begin{array}{cccccc}
\cdots & \cdots & \cdots & & & \\
0 & \phi & -Q & \phi^{-1} & 0 & 0 \\
0 & 0 & \phi^{-1} & -Q & \phi & 0 \\
0 & 0 & 0 & \phi & -Q & \phi^{-1} \\
 & 0 & 0 & 0 & \phi & -Q
\end{array}$$

The eigenvalues of this matrix are:

$$Q_n^2 = (\phi-\phi^{-1})^2+4\cos^2\pi n/(2N+1) \tag{1.7}$$

$$-N\leq n\leq N$$

$$E_n = Q_nB/(1+Q_nT) \tag{1.8}$$

$$E_n' = \frac{B}{T}(1+Q_nT)^{-2}(Q_nT)' \tag{1.9}$$

$$E'' = \frac{B}{T}((1+Q_nT)^{-2}(Q_nT)''-2(1+Q_nT)^{-3}((Q_nT)')^2)$$

Now at $\phi = 1$,

$$(Q_nT)' = 0,\ (Q_nT)'' = T''Q_n+Q_n''T$$

Now $B/T = \beta/S$ is a constant, so: at $\phi = 1$:

$$E'' = (1+Q_nT)^{-2}(B''Q_n+BQ_n'')$$

From equation 1.7 and the definitions of ϕ and B, the following may be derived at $\phi = 1$:

$$B'' = \beta''-\beta^{-1}(\beta')^2;\ Q_n''B = 4(\beta Q_n)^{-1}(\beta')^2 \qquad (1.11)$$

$$E'' = (1+Q_nS)^{-2}(\beta''Q_n+\beta^{-1}(\beta')^2(4Q_n^{-1}-Q_n)) \qquad (1.12)$$

$$Q_n = 2\cos\frac{\pi n}{2N+1} \qquad (1.13)$$

$$K_{B2u} = K_\sigma+(2N+1)^{-1}\sum_n E_n'' \qquad (1.14)$$

For benzene, N = 1.

$$K_{B2u} = K_\sigma+0.723\ ''+1.28\beta^{-1}(\beta')^2 \qquad (1.15)$$

We may use the relationship $\beta^{-1}\beta' = S^{-1}S' = 4S'$; combining equations 1.6 and 1.15 gives:

$$K_{A1g}-K_{B2u} = -6.593\beta'S' \qquad (1.16)$$

These force constants of benzene are known experimental quantities (Whiffen (15)).

$$K_{A1g} = 7.62\text{x}10^5\text{dynes/cm} \qquad K_{B2u} = 3.94\text{x}10^5\text{dynes/cm}$$

Combining equation 1.16 and the above gives:

$$K_{A1g}-K_{B2u} = -6.593\beta'S' = 3.68\text{x}10^5\text{dynes/cm} \qquad (1.17)$$

$$\beta'S' = -0.558\text{x}10^5\text{dynes/cm} = \tfrac{1}{4}\beta^{-1}(\beta')^2 \qquad (1.18)$$

$$\beta^{-1}(\beta')^2 = -2.23\text{x}10^5\text{dynes/cm} \qquad (1.19)$$

The Calculation of $K_{B2u}\ C_{18}H_{18}$

The molecule cycloöctadecanonaene, known as CON, or (18)-annulene (Sondheimer (31)) or $C_{18}H_{18}$, is believed to be planar (Sondheimer (30), Weiss and Gouterman (37)). We apply equations 1.12, 1.13 and 1.14 with N = 4 to derive:

$$K_{B2u}\ C_{18}H_{18} = K_\sigma+2.68\beta^{-1}(\beta')^2+0.681\beta'' \qquad (1.20)$$

With equation 1.15, and the experimental benzene force constant, we find:

$$K_{B2u}\ C_{18}H_{18} = 1.40\beta^{-1}(\beta')^2-0.042\beta'' +3.94\text{x}10^5\text{dynes/cm} \qquad (1.21)$$

From equations 1.19 and 1.21, we find:

$$K_{B2u}\ C_{18}H_{18} = 0.82\text{x}10^5\text{dynes/cm}-0.042\beta'' \qquad (1.22)$$

The $-0.042\beta''$ term can be expected to be small. If $B'' = 0$, corresponding to β decreasing exponentially with distance, then $\beta'' = \beta^{-1}(\beta')^2 = -2.23\text{x}10^5$dynes/cm, then:

$$K_{B2u}\ C_{18}H_{18} = 0.91\text{x}10^5\text{dynes/cm} \qquad (1.23)$$

PART 3. POSSIBLE ERRORS

There could be an error in the calculation of $\beta^{-1}(\beta')^2$ (equations 1.4 through 1.19) due to assuming one can use the same K_σ for both the A_{1g} and B_{2u} benzene distortions. The K_σ for the B_{2u} vibration would have to be about $1\text{x}10^5$dynes/cm greater than for the A_{1g} vibration to increase the value of $\beta^{-1}(\beta')^2$ sufficiently to cause bond alternation. This seems somewhat unlikely, because one would expect the B_{2u} distortion to change the sigma bond hybridization, causing the $B_{2u}K_\sigma$ to be less than the $A_{1g}K_\sigma$.

No major error in the calculations is to be expected because of the assumed value of 0.25 for the overlap integral, because those molecular orbitals that contribute most to lowering the B_{2u} force constant (stretching) are the higher energy ones that are least sensitive to the value of the overlap integral. The assumption that β/S is a constant should be safe for the same reason.

Longuet-Higgins (8) does a similar calculation including coulomb and exchange interactions in a simple way, with very similar results. It therefore seems unlikely that a similar use of coulomb and exchange interactions in the preceding calculation would make much difference.

The term β'' would have to be $+20\times10^5$dynes/cm to bring about bond alternation (see equation 1.22). This seems to be much too large to be believed.

CHAPTER II

PROPERTIES OF THE ANNULENES

PART 1. THE ULTRAVIOLET ADSORPTION SPECTRA OF THE ANNULENES

In the Hückel theory each annulene will have four degenerate lowest excited singlet states. Electron repulsion breaks the degeneracy, leaving the states $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$. The transition from the ground state to the degenerate $^1E_{1u}$ state is dipole allowed, and gives the strongest absorption. The other two transitions are dipole forbidden, and of lower energy. The $^1B_{1u}$ transition may borrow intensity effectively from the $^1E_{1u}$ transition by vibrational interactions (see Moffitt (35)). For this reason, the $^1B_{1u}$ absorption is fairly intense, while the absorption of the $^1B_{2u}$ transition remains quite weak. This analysis allows us to make spectroscopic assignments primarily on the basis of intensities.

The assignment for benzene is as follows (see Pariser (18)):

$^1B_{2u}$ 4.71 e.v.

$^1B_{1u}$ 5.96 e.v.

$^1E_{1u}$ 6.76 e.v.

The (18)- and (30)-annulenes show only two easily identifiable peaks, Sondheimer, Wolovsky and Amiel (30). We make the assignment supported by Longuet-Higgins (8):

(18)-annulene		(30)-annulene	
$^1E_{1u}$	27,000 cm^{-1}	$^1E_{1u}$	23,300 cm^{-1}
$^1B_{1u}$	22,300 cm^{-1}	$^1B_{1u}$	19,100 cm^{-1}

The $^1B_{2u}$ transitions are not identifiable at room temperature, but Gouterman and Wagniere (10) report an ultraviolet spectrum at 77°K for the (18)-annulene. From their spectrum, they make assignments:

(18)-annulene	
$^1E_{1u}$	27,060 cm^{-1}
$^1B_{1u}$	21,345 cm^{-1}
$^1B_{2u}$	20,350 cm^{-1}

Gouterman and Wagniere's (10) 77°K spectrum has much better resolution than the room temperature spectra of Sondheimer etc. (10), but the bands assigned to the $^1B_{2u}$ transition are still rather weak, and there may be some reason to suspect this assignment.*

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*See chapter V, part 4.

PART 2. OTHER PROPERTIES OF THE ANNULENES

There are several reports of X-ray analysis of the structure of the (18)-annulene. Sondheimer, etc. (30) reports the (18)-annulene to be planar and to have a center of symmetry. The center of symmetry precludes bond alternation. They also report an NMR experiment showing a splitting between the inner and outer protons of the (18)-annulene. Such splittings are caused by ring currents. Ring currents are characteristic of aromatic compounds and constitute strong evidence against bond alternation.

Weiss and Gouterman (37) report an X-ray analysis of the (18)-annulene showing the molecule to be planar and without bond alternation. In addition, they report carbon-carbon bond lengths.*

There appears to be little data available on the (30)-annulene, because of its chemical instability and low solubility in organic solvents, Sondheimer, etc. (30,32).

See Sondheimer (33) for further references on "Recent Advances in the Chemistry of Large Ring Conjugated Systems."

PART 3. PREDICTION OF HÜCKEL THEORY

As the Hückel theory predicts only one energy for the three transitions, we may consider the Hückel theory

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*See figure 1.

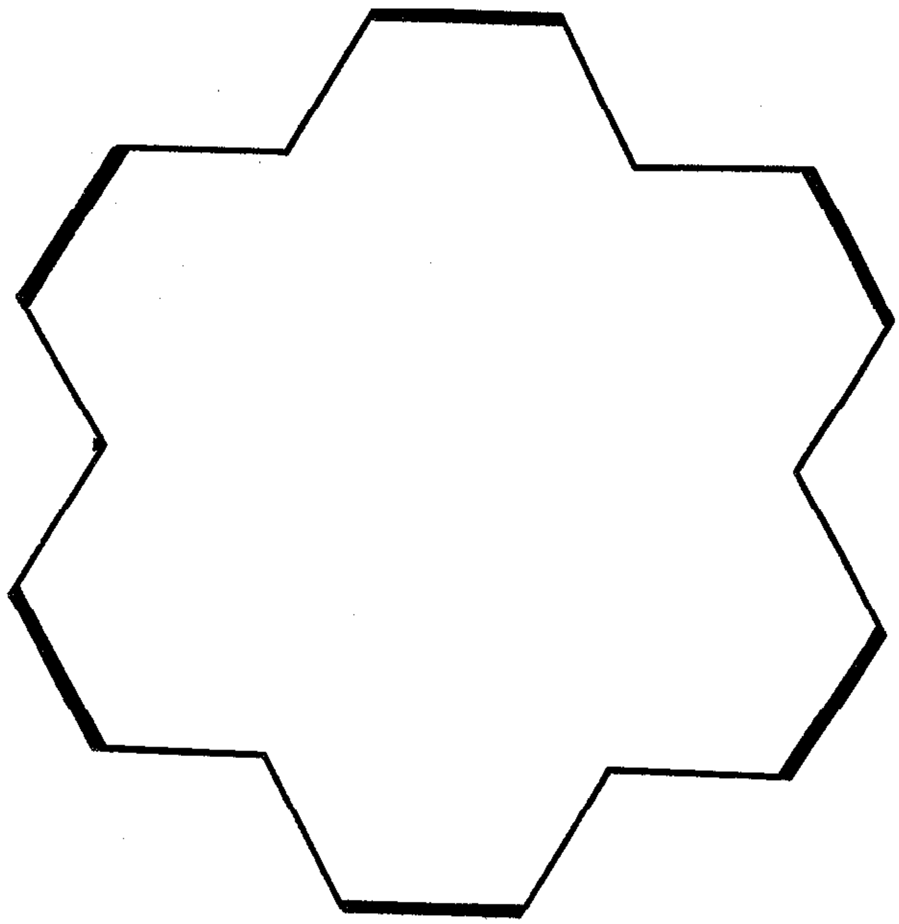

FIGURE 1

THE (18)-ANNULENE

The "transoid" bonds (light lines) are 1.382 ± .003 Å

The "cisoid" bonds (heavy lines) are 1.419 ± .004 Å

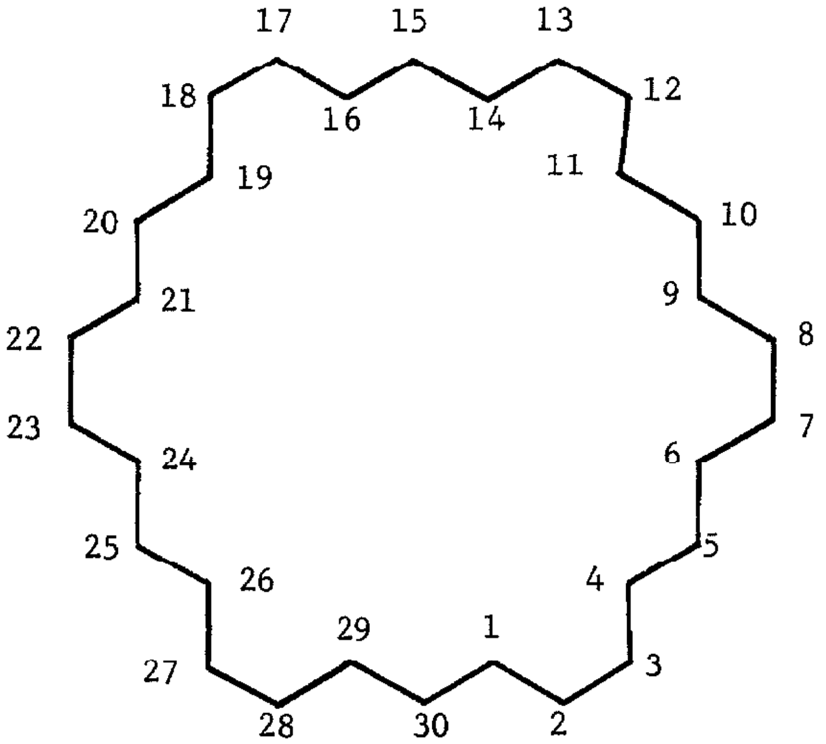

FIGURE 2

THE (30)-ANNULENE, CYCLOTRIACONTAPENTADECAENE

This annulene is of D_{6h} symmetry. We will assume that all the bond lengths and bond angles are equal.

to predict an average energy. In benzene the $^1B_{1u}$ transition at 48,070 cm^{-1} is very near the average energy of the $^1B_{2u}$, $^1B_{1u}$, and $^1E_{1u}$ transitions.

In the (18)- and (30)-annulenes, we do not know where the $^1B_{2u}$ transitions are; but we know (part 1) that the $^1B_{1u}$ energies are below the $^1E_{1u}$ energies.

It seems fairly safe to assume in these cases that the average transition energies cannot be much below the $^1B_{1u}$ energies, and may be above these energies. It therefore seems logical to apply the Hückel theory to the $^1B_{1u}$ transitions only.

We should expect the $^1B_{1u}$ transition energies of benzene, the (18)-annulene, and the (30)-annulene to be in about the ratio of one to one-third to one-fifth. We would predict the $^1B_{1u}$ transition energies of the (18)-annulene and the (30)-annulene to be respectively at 16,000 cm^{-1} and 9,600 cm^{-1}. This is far from the experimental values given in part 1.

It has been proposed by Kuhn (3) and Longuet-Higgins (8) that this disagreement is the result of bond alternation. I shall make calculations to see if this mechanism could account for the disagreement between the experimental and Hückel $^1B_{1u}$ energies of the (18)- and (30)-annulenes, and also to determine the amount of molecular distortions necessary to account for these anomalies.

PART 4. THE EFFECT OF MOLECULAR DISTORTION

For the ${}^1B_{1u}$ benzene transition:

$$\Delta E = 48{,}070\ \mathrm{cm}^{-1} = -2\beta/(1-S^2) \qquad (2.1)$$

$$S = 0.25 = T$$

then:

$$\beta = -22{,}530\ \mathrm{cm}^{-1} = B \qquad (2.2)$$

From equation 1.8 we find:

$$\Delta E = -(1-Q_N^2T^2)^{-1}2Q_NB \qquad (2.3)$$

For the ${}^1B_{1u}$ (18)-annulene transition:

$$\Delta E = 22{,}300\ \mathrm{cm}^{-1},\ Q_4 = 0.4876 \qquad (2.4)$$

From equations 2.4 and 1.7 we find:

$$\phi = 1.1856 \qquad (2.5)$$

We will assume an exponential form for the resonance and exchange integrals. This is a reasonable approximation because we have shown that the second derivatives of S and β do not play an important part. We write, for the distortion δr:

$$\delta r = a \ln\phi \qquad (2.6)$$

then:

$$\delta r = 0.1703a \qquad (2.7)$$

At the equilibrium position, the net force on each atom is zero.

$$0 = F_{B2u} = K_{\sigma}\delta r + (2N+1)^{-1}\sum_{n} E'_{n} \qquad (2.8)$$

$$E'_{n} = 2B(1+Q_{n}T)^{-1}a^{-1}Q_{n}^{-1}\sinh(2\delta r/a) \qquad (2.9)$$

$$0 = F_{B2u} = \delta r(K_{\sigma}+2.63B/a^{2}) \qquad (2.10)$$

We may make the same calculation for the (30)-annulene. We find that:

$$\left.\begin{aligned} &Q_{7} = 0.4204, \ \delta r = 0.2065a \\ &0 = F_{B2u} = \delta r(K_{\sigma}+2.60B/a^{2}) \end{aligned}\right\} \qquad (2.11)$$

Equations 2.10 and 2.11 agree very well as to the size of B/a^2. From equations 1.15 and 2.10 we get:

$$B/a^{2} = -6.3\text{x}10^{5}\text{dynes/cm} \qquad (2.12)$$

$$a = 0.27\text{Å}$$

PART 5. DISCUSSION

Equation 2.12 differs from equation 1.19 almost by a factor of three. If we had started from equation 2.11, the difference would have been even greater. We conclude that bond alternation is not responsible for the disagreement between the experimental and Hückel $^1B_{1u}$ energies of the (18)- and (30)-annulenes.

There are two other facts supporting this conclusion. Gouterman and Wagniere (10) show that if there was tunneling between potential minima, there would be vibronic effects on the optical bands. As these effects have not been observed, the potential barrier must either be very large or nonexistent.

The $^1B_{1u}$ transition of an annulene belongs to Clar's p-bands (Moffitt (35)). Streitwieser (17) gives an empirical formula for the p-band energies of polyenes that agrees well with the experimental $^1B_{1u}$ energies of the (18)- and (30)-annulenes. This agreement would be very unlikely if some unusual mechanism such as bond alternation were affecting the spectra of these annulenes, without affecting the spectra of the cata-condensed hydrocarbons, on which the empirical formula is based.

In a later section I shall discuss this empirical formula in more detail, and give a theoretical justification for it.*

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*See chapter III, part 6.

CHAPTER III

INTRODUCTION TO THE ALTERNANT MOLECULAR ORBITAL THEORY

PART 1. EXPLANATION

In the first chapter we showed that the simple Hückel molecular orbital theory is inadequate for dealing with long conjugated polyenes. The main failing of the simple Hückel molecular orbital scheme is the lack of account for electron correlation.

The alternant molecular orbital (AMO) method treats the problem of electron correlation by using different orbitals for different spins. The orbitals for electrons of different spin are concentrated in different regions of space, thereby minimizing the electron repulsion energy.

PART 2. NOTATION

We shall follow the notation of Lowdin (12,13) as far as possible. ϕ will be used for atomic orbitals (AO's); ψ for molecular orbitals (MO's); and a for alternant molecular orbitals (AMO's). Greek letters μ, ν, σ specify the AO; small Roman letters i, j, k identify the MO; and capitals I, J, K label the AMO.

In alternant systems the molecular orbitals appear in pairs:

$$\Psi_K = \sum^{o} \phi_\mu c_{\mu k} + \sum^{*} \phi_\mu c_{\mu k} \qquad (3.1)$$

$$\Psi_{\bar{k}} = \sum^{o} \phi_\mu c_{\mu k} - \sum^{*} \phi_\mu c_{\mu k}$$

The $\sum^{o}$ and $\sum^{*}$ denote summation over the "unstarred" and "starred" atoms respectively. The molecular orbital functions that take account of overlap are not quite this simple, but we may still group them in pairs.

From each pair of MO, a pair of AMO are constructed.

$$a_K = \cos\theta_K \Psi_k + \sin\theta_K \Psi_{\bar{k}} \qquad (3.2)$$

$$\bar{a}_K = \cos\theta_K \Psi_k - \sin\theta_K \Psi_{\bar{k}}$$

$$0 \angle \theta_K \angle \pi/4$$

The a_K have the following orthogonality relationships:

$$\langle a_K | a_J \rangle = \langle \bar{a}_K | a_J \rangle = \langle \bar{a}_K | \bar{a}_J \rangle = 0 \qquad (3.3)$$

$$K \neq J$$

$$\langle a_K | a_K \rangle = \langle \bar{a}_K | \bar{a}_K \rangle = 1$$

$$\langle a_K | \bar{a}_K \rangle = \cos 2\theta_K = \lambda_K$$

PART 3. ELECTRON SPIN

The "a" orbitals have their largest amplitudes on "unstarred" atoms, and the "$\bar{a}$" orbitals have their largest amplitudes on the "starred" atoms. The "a" electrons are given parallel spins so that no two "a" electrons can occupy the same atomic orbital simultaneously. The spins of electrons in "$\bar{a}$" orbitals are also parallel so no two "$\bar{a}$" electrons may be in the same atomic orbital simultaneously.

Let us suppose we have an alternant hydrocarbon with 2n conjugated electrons. We put the first n conjugated electrons in "a" orbitals, and the second n electrons in "$\bar{a}$" orbitals. The total spin of the first n electrons will be n/2, as will be the total spin of the second n electrons.

$$S_a = S_{\bar{a}} = \frac{1}{2}n \qquad (3.4)$$

The simplest spin function with this property is:

$$\delta_1 = \alpha(1)\alpha(2)\cdot\cdots\cdot\alpha(n-1)\alpha(n)\beta(n+1)\cdots\beta(2n) \qquad (3.5)$$

This spin function is not an eigenfunction of S^2. To make δ_1 an eigenfunction of S^2 we must take the proper projection. If we want to find a singlet state, we take the singlet projection Sp_o of δ_1:

$$S^2_{(a+\bar{a})}\ Sp_o = 0 \qquad (3.6)$$

PART 4. LIMITING BEHAVIOR OF AMO GROUND STATE WAVE FUNCTIONS

As the λ_K approach zero, the "a" orbitals become completely concentrated on the "unstarred" atoms, while the "$\bar{a}$" orbitals become concentrated on the "starred" atoms. In the presence of overlap this perfect alternation occurs when the λ_K are slightly greater than zero.

If we were to separate the atoms of a molecule, the λ_K would decrease to zero. At complete separation, each atom would get exactly one of the conjugated electrons. This correct result is also predicted by valence bond theory, but not by simple Hückel MO theory.

We may compare the AMO theory with the valence bond theory. At perfect alternation, the AMO theory puts exactly one electron on each atom. The antisymmetrized wave function is antisymmetric with respect to the exchange of the spatial coordinates of any two "starred", or any two "unstarred" atoms. This antisymmetrized wave function will therefore consist of equal contributions from every nonionic valence bond configuration in which each electron on an "unstarred" atom is paired with an electron on a "starred" atom.

Compared to the full configuration interaction treatment, the AMO method is least accurate when the simple Hückel MO and valence bond theories give equally poor wave functions.

PART 5. AMO'S FOR EXCITED STATES

For excited states, it is useful to introduce "antibonding" AMO's.

$$a_{\bar{K}} = \cos\theta_K \Psi_{\bar{K}} + \sin\theta_K \Psi_k \qquad (3.7)$$

$$\bar{a}_{\bar{K}} = \cos\theta_K \Psi_{\bar{K}} - \sin\theta_K \Psi_k$$

The orthogonality relationships among the antibonding AMO are the same as among the bonding AMO. In addition there are the relationships:

$$\langle \bar{a}_J \mid a_{\bar{K}} \rangle = \langle a_J \mid a_{\bar{K}} \rangle = \langle a_J \mid \bar{a}_{\bar{K}} \rangle = \langle \bar{a}_J \mid \bar{a}_{\bar{K}} \rangle = 0$$

$$K \neq J$$

$$\langle a_K \mid \bar{a}_{\bar{K}} \rangle = \langle \bar{a}_K \mid a_{\bar{K}} \rangle = 0 \qquad (3.8)$$

$$\langle a_K \mid a_{\bar{K}} \rangle = - \langle \bar{a}_K \mid \bar{a}_{\bar{K}} \rangle = \sin 2\theta$$

Let us imagine we excite an electron from a bonding to an antibonding orbital. The excited electron must go into an orbital that is orthogonal to all other AMO orbitals of the same spin. Thus if the excited electron is to have the same spin as the electrons in the "a" orbitals, it must be in an $\bar{a}_{\bar{K}}$ orbital. The $\bar{a}_{\bar{K}}$ orbital will have its smallest amplitudes on the "unstarred" atoms, and so the excited electron will achieve only a small energy lowering through exchange interactions with electrons of its own spin. We see that in the AMO theory, exciting a single electron raises not only the one-electron energy, but increases the electron repulsion energy as well. This rise in the electron repulsion energy will not diminish as the size of the molecule increases, because of the increase in the number of electrons. We would therefore expect the AMO theory to always produce a finite energy gap between the ground state and the lowest excited states, no matter how large the molecule. This question will be discussed in detail later.

PART 6. AMO EXCITED STATES

There are several methods available for constructing excited states. Pauncz (23,24) constructs states of different multiplicity by starting with the simple spin function δ_1, and taking the projection with the desired total spin. He uses this method to construct the $^3B_{1u}$ state of benzene. He finds it is necessary to use a many-parameter wave function in the construction of multiplet states (24). This is probably because a multiplet state must have, in molecular orbital language, at least one electron in an antibonding orbital. The AMO wave function will have to emphasize MO configurations in which the antibonding electron(s) came from one of the higher energy molecular orbitals, in order to keep the energy of the state low. This means that the higher AMO of the multiplet wave function must have considerably more alternation than the lower AMO.

There is an obvious method for constructing the $^1B_{2u}$ and $^1B_{1u}$ states. One converts one of the AMO pairs into a bonding MO Ψ_k and an antibonding MO $\Psi_{\bar{k}}$ singlet. These MO's are no longer alternant. The remaining electrons maintain their ground state spin orientations, and one retains only the singlet spin projection. In cyclic polyenes the molecular orbitals come in degenerate pairs. One may therefore construct a degenerate pair of singlet excited state wave functions as above. Mixing two such degenerate configurations will give the $^1B_{2u}$ and $^1B_{1u}$ states of a cyclic polyene.

The electrons in the nonalternant orbitals have lost their spin correlation with the rest of the electrons in the system. This loss will raise the electron repulsion energies of the two involved electrons. The increase in electron repulsion energy will approach a constant value as the size of the polyene increases indefinitely, so with this model there will always be a finite energy gap between the ground state and the lowest $^1B_{1u}$ and $^1B_{2u}$ states.

The construction of the $^1E_{1u}$ states is by my own method, and a description of this method will be left to chapter IV. We will only say here that there will always be a finite energy gap between the ground state and the lowest degenerate $^1E_{1u}$ states.

The above discussion suggests a semiempirical method of correcting for electron correlation in the Hückel theory. For transitions of a given type, such as the p-band transitions of Clar, we add a constant energy term to the energy calculated for the upper state by the Hückel method. In this way we introduce the finite energy gap found with AMO theory. We choose our constant energy term and our resonance and other integrals so as to satisfy as nearly as possible the experimental energies of as large a class of polyenes as possible.

Just such an empirical method as we have proposed has been carried out by Streitwieser (17) for Clar's p-bands. His method has up to now lacked our theoretical justification. The constant energy term he uses for the p-bands is 10,000 cm^{-1}. To apply the method to cyclic polyenes, we note that the $^1B_{1u}$ transition of cyclic polyenes, is the p-band. The method predicts the $^1B_{1u}$ transition for the (18)-annulene at 23,000 cm^{-1} and for the (30)-annulene at 18,000 cm^{-1}. Comparison with the table on page 14 shows how well the method has worked.

In the next chapter I shall present a detailed mathematical apparatus to be used in calculating the ground state of the annulenes, with the purpose of calculating excited state transition energies.

CHAPTER IV

CALCULATION OF TRANSITION ENERGIES

PART 1. THE GROUND STATE WAVE FUNCTION

The ground state wave function Ψ_o will be an antisymmetrized product of a space function ϕ_o, and the spin function Sp_o. ϕ_o is a product of alternant molecular orbitals.

$$\phi_o = a_I(1) \cdots\cdots a_N(n) \bar{a}_I(n+1) \cdots\cdots \bar{a}_N(2n) \qquad (4.1)$$

By making full use of the spin function Sp_o, one may obtain equations which involve integrals over spatial coordinates of the electrons only (Pauncz, De Heer and Lowdin (12)).

$$\left\langle \Psi^* \middle| H_{op} \Psi \right\rangle = \frac{1}{n+1} \sum_{P} (-)^{p+p_{1P}} \binom{n}{p_{1P}}^{-1} \left\langle \phi_o^* \middle| H_{op} \middle| P^r \phi_o \right\rangle \qquad (4.2)$$

The operator H_{op} may be any Hermitian operator that is symmetric in the coordinates of the electrons. P^r is any permutation of the spatial coordinates of the electrons. The symbol p_{1P} stands for Lowdin's "characteristic number"; it is the number of "$\bar{a}$" functions among the first n AMO of $P^r \phi_o$.

We wish to be able to calculate properties of low energy transitions. In such a calculation the higher energy electrons play a special part, because they go from a bonding to an antibonding orbital. We therefore want to take special care to use good orbitals for the higher energy orbitals.

If one uses a single Θ for all the AMO, as Pauncz, De Heer, and Lowdin (12,13) do, one is likely to make a considerable error in calculating excited state energies, because the ground state energy of the excited electron will not be good. (We are assuming most of the transition energy involves a single electron.)

If one uses the many-parameter method, with a separate Θ_K for each AMO, the calculation for any molecule larger than benzene becomes very cumbersome (22,23).

A good compromise should be to use two parameters, one for the lower energy AMO, and a second for the higher energy AMO. The Θ used for all the lower energy AMO will be called Θ_1, and the Θ used for the higher energy AMO will be called Θ_2. The lower energy AMO will be called "1" orbitals, and the higher energy orbitals will be called "2" orbitals. The electrons in these orbitals will be designated in the same way.

PART 2. THE NORMALIZATION INTEGRAL

We may use equation 4.2 to find the normalization integral, S. Because of the orthogonality relationships (equation 3.3), only certain permutations contribute to S. These allowed permutations are of the form:

$$P^r = \prod_{k=1}^{n} P_k \tag{4.3}$$

where P_k may be either a transposition of k and n+k, or the identity operator.

Let us have p pairs of "1" orbitals, and q pairs of "2" orbitals. Then:

$$p+q = n \tag{4.4}$$

$$S_{p,q} = \frac{1}{n+1} \sum_{u_1=0}^{p} \sum_{u_2=0}^{q} \binom{n}{u_1+u_2}^{-1} \binom{p}{u_1} \binom{q}{u_2} \lambda_1^{2u} \lambda_2^{2u}$$

If q or $1-\lambda_2^2$ is small, it is convenient to introduce the variable R in place of λ_2:

$$R = (1-\lambda_2^2) \tag{4.5}$$

$$\lambda_2^{2u_2} = \sum_f \binom{u_2}{f} (-R)^f \tag{4.6}$$

We may substitute equation 4.6 into equation 4.4:

$$S_{p,q} = \frac{1}{n+1} \sum_{u_1=0}^{p} \sum_{u_2=0}^{q} \sum_{f=0}^{u_2} \binom{n}{u_1+u_2}^{-1} \binom{p}{u_1} \binom{q}{u_2} \cdot \binom{u_2}{f} \lambda_1^{2u_1} (-R)^f \tag{4.7}$$

We may rearrange the terms in equation 4.7:

$$\binom{n}{u_1+u_2}^{-1}\binom{p}{u_1}\binom{q}{u_2}\binom{u_2}{f} = \binom{n}{p}^{-1}\binom{u_1+f}{f}\binom{u_1+u_2}{u_2-f}\binom{n-u_1-u_2}{q-u_2} \tag{4.8}$$

It is easy to show that for any $|x| < 1$:

$$(1-x)^{-(u_1+f+1)} = \sum_{u_2=f}^{\infty}\binom{u_1+u_2}{u_2-f} x^{(u_2-f)} \tag{4.9}$$

$$(1-x)^{-(p+1-u_1)} = \sum_{u_2=-\infty}^{q}\binom{n-u_1-u_2}{q-u_2} x^{(q-u_2)} \tag{4.10}$$

$$\begin{aligned}(1-x)^{-(p+f+2)} &= \sum_{g=0}\binom{p+f+g+1}{g} x^{g} \\ &= (1-x)^{-(u_1+f+1+p+1-u_1)}\end{aligned} \tag{4.11}$$

When we consider the coefficient of x^{q-f}, we find that:

$$\binom{n+1}{q-f} = \sum_{u_2=f}^{q}\binom{u_1+u_2}{u_2-f}\binom{n-u_1-u_2}{q-u_2} \tag{4.12}$$

We may substitute equation 4.12 back into equation 4.7, again rearranging terms, and find:

$$S_{p,q} = \frac{1}{p+1}\sum_{u_1=0}^{p}\sum_{f=0}^{q}\binom{f+p+1}{f}^{-1}\binom{q}{f}\binom{u_1+f}{f}\cdot \lambda_1^{2u_1}(-R)^{f} \tag{4.13}$$

From equation 4.13 it is obvious that if R=0, $S_{p,q}$ is independent of q. For this reason, we may ignore non-alternant orbitals.

We may define the function

$$T_{f,p}(x) = \sum_{u_1=0}^{p} \binom{u_1+f}{f} x^{u_1} \qquad (4.14)$$

$$T_{f,0}(x) = 1$$

$$T_{f,p+1}(x) = T_{f-1,p+1}(x) + xT_{f,p}(x) \qquad (4.15)$$

From equation 4.15, the $T_{f,p}(x)$ may easily be generated. This is particularly useful when using a computer. Then:

$$S_{p,q} = \frac{1}{p+1} \sum_{f=0}^{q} \binom{f+p+1}{f}^{-1} \binom{q}{f} (-R)^f \, T_{f,p}(\chi_1^2) \qquad (4.16)$$

PART 3. THE ONE-ELECTRON ENERGY

Our calculation of the one-electron energy E_I follows very closely that of Lowdin, etc. (12). The only important difference is that we use two parameters instead of one.

We first introduce the one-electron operator h_1.

$$h_{kk} = (k|h_1|k) = \int \psi_k^* \, h_1 \psi_k \, dv \qquad (4.17)$$

$$h_{KK} = (K|h_1|K) = \int a_K^* \, h_1 \, a_K \, dv$$

$$h_{K\bar{K}} = (\bar{K}|h_1|K) = \int \bar{a}_K^* \, h_1 \, a_K \, dv$$

We divide the one-electron energy into two parts. $E_I = E_1 + E_2$. E_1 is the one-electron energy of the "1" orbitals, and E_2 is the one-electron energy of "2" orbitals. We introduce the energies:

$$W_1 = \sum_{\text{"1" orbitals}} (h_{kk} + h_{\bar{k}\bar{k}}) \qquad (4.18)$$

$$\Delta W_1 = \sum_{\text{"1" orbitals}} (h_{\bar{k}\bar{k}} - h_{kk})$$

$$W_2 = \sum_{\text{"2" orbitals}} (h_{\bar{k}\bar{k}} + h_{kk})$$

$$\Delta W_2 = \sum_{\text{"2" orbitals}} (h_{\bar{k}\bar{k}} - h_{kk})$$

We carry out the routine algebra as in Lowdin, etc. (12), and find:

$$E_1 = W_1 - \lambda_1 \Delta W_1 S_{p-1,q} (S_{p,q})^{-1} \qquad (4.19)$$

$$E_2 = W_2 - \lambda_2 \Delta W_2 S_{p,q-1} (S_{p,q})^{-1}$$

The $S_{p,q}$ notation brings out in detail the exact nature of the factor multiplying the W. It is easy to see how equation 4.19 is to be generalized in the many-parameter model. For the many-parameter model, one uses a separate ΔW for each AMO pair, and one replaces $S_{p-1,q}$ by the normalization integral calculated with the appropriate pair of AMO vacated. We might write this as:

$$E_I = W - (\sum_K \lambda_K \Delta W_K \; S_K) S^{-1} \tag{4.20}$$

PART 4. THE ELECTRON INTERACTION ENERGY

We shall use for the AMO coulomb integrals:

$$\gamma_{KL} = (KK|LL) \tag{4.21}$$

and for the AMO exchange integrals:

$$\delta_{KL} = (KL|LK) \tag{4.22}$$

We distinguish three types of electron interaction. First, there are interactions between electrons in "1" orbitals. We call these 1-1 interactions. The interactions between "1" electrons and "2" electrons we call 1-2 interactions. The interactions among "2" electrons we call 2-2 interactions.

In what follows, the superscripts K-L, 1-1, 1-2, or 2-2 will refer to these three types of interaction. Following Pauncz's method with this addition, we write for the interaction between two pairs of occupied AMO designated by K and L. The Λ_J^{K-L} will be defined later.

$$
\begin{aligned}
E^{K-L} = 2\Lambda_o^{-1}\Big\{ & \Lambda_1^{K-L}\left(\gamma_{KL} + \gamma_{K\bar{L}} - \delta_{KL}\right) \qquad (4.23) \\
& \Lambda_2^{K-L}\Big[\delta_{K\bar{L}} + \lambda_K\left((K\bar{K}|\bar{L}\bar{L}) + (\bar{K}K|LL) - (KL|L\bar{K}) - (\bar{K}\bar{L}|\bar{L}K) \right) \\
& \quad + \lambda_L\left((KK|L\bar{L}) + (\bar{K}\bar{K}|\bar{L}L) - (KL|\bar{L}K) - (\bar{K}\bar{L}|L\bar{K}) \right) + \lambda_K\lambda_L(KL|\bar{L}\bar{K})\Big] \\
& \Lambda_3^{K-L}\left(2(K\bar{K}|L\bar{L}) - (K\bar{L}|L\bar{K}) \right)\Big\}
\end{aligned}
$$

The interaction between the two electrons in the K AMO is:

$$
E^{K-K} = \Lambda_o^{-1}\left(\Lambda_4^{K-K}\gamma_{K\bar{K}} + \Lambda_5^{K-K}\,\delta_{K\bar{K}}\right) \qquad (4.24)
$$

The definition of the other Λ are arbitrary until we have defined Λ_o. The simplest definition of Λ_o is to set Λ_o equal to $S_{p,q}$. With this definition:

$$(1-\lambda_1^2)\Lambda_4^{1-1} = S_{p,q} - \lambda_1^2 S_{p-1,q} \qquad (4.25)$$

$$(1-\lambda_2^2)\Lambda_4^{2-2} = S_{p,q} - \lambda_2^2 S_{p,q-1} \qquad (4.26)$$

$$(1-\lambda_1^2)\Lambda_5^{1-1} = S_{p-1,q} - S_{p,q} \qquad (4.27)$$

$$(1-\lambda_2^2)\Lambda_5^{2-2} = S_{p,q-1} - S_{p,q} \qquad (4.28)$$

The previous four equations may be written in the many-parameter notation used in equation 4.20.

$$(1-\lambda_K^2)\Lambda_4^{K-K} = S - \lambda_K^2 S_K \qquad (4.29)$$

$$(1-\lambda_K^2)\Lambda_5^{K-K} = S_K - S \qquad (4.30)$$

Our many-parameter notation has the advantage of great compactness and simplicity. We shall write out the equations for the other Λ in the many-parameter notation, followed by the two-parameter notation.

(4.31)

$$(1-\lambda_K^2)(1-\lambda_L^2)\Lambda_1^{K-L} = S - \lambda_K^2 S_K - \lambda_L^2 S_L + \lambda_K^2 \lambda_L^2 S_{KL}$$

$$(1-\lambda_K^2)(1-\lambda_L^2)\Lambda_2^{K-L} = S_L - S + \lambda_K^2 (S_K - S_{KL})$$

$$(1-\lambda_K^2)(1-\lambda_L^2)\Lambda_3^{K-L} = (S - S_K - S_L + S_{KL})\lambda_K \lambda_L$$

In the above, S_{KL} is the normalization integral after the K and L AMO have been vacated. We may write a relationship for S_{KL} in terms of the other S.

$$(1-\lambda_L^2)S_L - (1-\lambda_K^2)S_K - (\lambda_K^2-\lambda_L^2)S_{KL} \qquad (4.32)$$

Equation 4.32 may be rewritten:

$$(1-\lambda_L^2)(S_{KL}-S_L) = B_{KL} = (1-\lambda_K^2)(S_{KL}-S_K) \qquad (4.33)$$

If we also define:

$$S - S_K - S_L + S_{KL} = D_{KL} \qquad (4.34)$$

We may rewrite equations 4.29-4.31:

$$(1-\lambda_K^2)(1-\lambda_L^2)\Lambda_4^{K-K} = (1-\lambda_K^2)(1-\lambda_L^2)(S-D_{KL}) + (1-\lambda_L^2)D_{KL}-\lambda_K^2 B_{KL} \qquad (4.35)$$

$$(1-\lambda_K^2)(1-\lambda_L^2)\Lambda_5^{K-K} = B_{KL} - (1-\lambda_L^2)D_{KL} \qquad (4.36)$$

$$(1-\lambda_K^2)(1-\lambda_L^2)\Lambda_1^{K-L} = (1-\lambda_K^2)(1-\lambda_L^2)(S-D_{KL}) + D_{KL}- (\lambda_K^2+\lambda_L^2)B_{KL} \qquad (4.37)$$

$$(1-\lambda_K^2)(1-\lambda_L^2)\Lambda_2^{K-L} = B_{KL} - D_{KL} \qquad (4.38)$$

$$(1-\lambda_K^2)(1-\lambda_L^2)\Lambda_3^{K-L} = D_{KL}\lambda_K\lambda_L \qquad (4.39)$$

For the two-parameter notation we write:

$$S_1 = S_{p-1,q} \qquad S_2 = S_{p,q-1} \tag{4.40}$$

$$S_{11} = S_{p-2,q} \qquad S_{12} = S_{p-1,q-1} \qquad S_{22} = S_{p,q-2}$$

$$(S_{12}-S_1)/(1-\lambda_2^2) = b = (S_{12}-S_2)/(1-\lambda_1^2) \tag{4.41}$$

$$S - S_1 - S_2 + S_{12} = d \tag{4.42}$$

$$S - 2S_1 - S_{11} = D_{11} = (1-\lambda_1^2)^2 d_{11} \tag{4.43}$$

$$S - 2S_2 + S_{22} = D_{22} = (1-\lambda_2^2)^2 d_{22} \tag{4.44}$$

$$S = s \tag{4.45}$$

The lower case variables s, b, d, d_{11}, d_{22} will be used exclusively in what follows.

The Λ's used in equations 4.23-4.24 are arbitrary until we choose Λ_o. For computations we shall find it convenient to define:

$$\Lambda_o = s \tag{4.46}$$

We may then find the other Λ in terms of the quantities defined in equations 4.43-4.45.

$$\Lambda_1^{1-2} = s - (\lambda_1^2 + \lambda_2^2)b + d/((1-\lambda_1^2)(1-\lambda_2^2)) \tag{4.47}$$

$$\Lambda_{2}^{1-2} = b - d/((1-\lambda_1^2)(1-\lambda_2^2))$$

$$\Lambda_{3}^{1-2} = \lambda_1\lambda_2 d/((1-\lambda_1^2)(1-\lambda_2^2))$$

$$\Lambda_{1}^{1-1} = s + \lambda_1^2(\lambda_1^2 d_{11} - 2b + 2d/\ (1-\lambda_1^2)) \tag{4.48}$$

$$\Lambda_{2}^{1-1} = b - \lambda_1^2 d_{11}$$

$$\Lambda_{3}^{1-1} = d_{11}\lambda_1^2$$

$$\Lambda_{4}^{1-1} = s + \lambda_1^2(-b+d/(1-\lambda_1^2)) \tag{4.49}$$

$$\Lambda_{5}^{1-1} = b - d/(1-\lambda_1^2)$$

$$\Lambda_{1}^{2-2} = s + \lambda_2^2(d_{22}\lambda_2^2 - 2b + 2d/(1-\lambda_2^2)) \tag{4.50}$$

$$\Lambda_{2}^{2-2} = b - d_{22}\lambda_2^2 - d/(1-\lambda_2^2)$$

$$\Lambda_{3}^{2-2} = d_{22}\lambda_2^2$$

$$\Lambda_{4}^{2-2} = s + \lambda_2^2(-b+d/(1-\lambda_2^2)) \tag{4.51}$$

$$\Lambda_{5}^{2-2} = b - d/(1-\lambda_2^2)$$

In order to evaluate b and d, we start from equations 4.22, 4.44, and 4.45.

$$b = \frac{1}{p} \sum_{f=0}^{q-1} \binom{q-1}{f} \binom{p+f+1}{p}^{-1} (-R)^{f} T_{f+1,p-1}(\lambda_1^2) \qquad (4.52)$$

$$d = \frac{1}{p} \sum_{f=0}^{q-1} \binom{q-1}{f} (-R)^{f+1} \left(\lambda_1^{2p} - \binom{p+f+2}{p}^{-1} T_{f+1,p}(\lambda_1^2) \right)$$

The Λ's we used in equations 4.47-4.51 are closely related to those of Pauncz. To get Pauncz's Λ, we set $\lambda_1 = \lambda_2 = \lambda$, and multiply by $(n^2-1)n(1-\lambda^2)^3$.

PART 5. THE MOLECULAR ORBITAL ELECTRON REPULSION INTEGRALS

We shall use the method of Pariser (18) in calculating coulomb and exchange integrals. This method involves the formal consistent neglect of differential overlap between atomic orbitals and the adjustment of some theoretical quantities by empirical or semiempirical procedures.

The neglect of differential overlap reduces considerably the number of integrals that need be considered. For any pair of molecular orbitals k and $\bar{k}$ we may write:

$$(kk|kk) = (\bar{k}\bar{k}|kk) = (\bar{k}\bar{k}|\bar{k}\bar{k}) \qquad (4.53)$$

We may expect equation 4.53 to be especially good if the orbital k is of high energy, because then the charge density on the bonds will be small.

For any two pairs of orbitals we write:

$$(kk|jj) = (kk|\bar{j}\bar{j}) = (\bar{k}\bar{k}|jj) = (\bar{k}\bar{k}|\bar{j}\bar{j}) \qquad (4.54)$$

$$(j\bar{k}|\bar{k}j) = (\bar{j}k|k\bar{j}) = (\bar{j}k|\bar{k}j) = (j\bar{k}|k\bar{j}) \qquad (4.55)$$

$$(jk|kj) = (jk|\bar{k}\bar{j}) = (\bar{j}\bar{k}|kj) = (\bar{j}\bar{k}|\bar{k}\bar{j}) \qquad (4.56)$$

The symmetry of the (18)- and (30)-annulenes is assumed to be D_{6h}. However, in constructing the molecular orbitals, we shall assume that the symmetry of the 2n-annulene is D_{2nh}. With this perimeter model, the $C_{\mu k}$ appearing in equation 3.1 will be:

$$c_{\mu k} = (2n)^{-1/2}\omega^{\mu k} \qquad (4.57)$$

with $\omega = \exp(i\pi/n)$

From the actual atomic coulomb integrals $(\mu\mu|\nu\nu)$ we define average integrals:

$$C_{\mu} = \frac{1}{2n}\sum_{\nu=1}^{2n}(\nu\nu|\nu+\mu,\nu+\mu) \qquad (4.58)$$

The C_{μ} depend somewhat upon the molecule involved. For example, C_3 for benzene is the coulomb repulsion integral between electrons in p orbitals on opposite sides of the ring. The carbon atoms involved are in a cis configuration. In the (18)-annulene, two-thirds of the atom pairs contributing to C_3 are in a trans configuration, leading to a lower value for C_3.

We introduce the additional quantities:

$$\overline{C}_e = \frac{1}{n}\sum_{\mu=1}^{n} C_{2\mu} \tag{4.59}$$

$$\overline{C}_o = \frac{1}{n}\sum_{\mu=1}^{n} C_{2\mu-1}$$

For the quantities mentioned in equations 4.53-4.59 we may write:

$$(kk|kk) = \frac{1}{2}(\overline{C}_e+\overline{C}_o) \tag{4.60}$$

and

$$(k\bar{k}|\bar{k}k) = \frac{1}{2}(\overline{C}_e-\overline{C}_o) \tag{4.61}$$

$$(kk|jj) = \frac{1}{2}(C_e+C_o) \tag{4.62}$$

$$(k\bar{k}|\bar{j}j) = \frac{1}{2}(C_e-C_o) \tag{4.63}$$

$$(jk|kj) = \frac{1}{2n}\sum_{\mu=1}^{2n} C_\mu W^{\mu(k-j)} \tag{4.64}$$

$$(j\bar{k}|\bar{k}j) = \frac{1}{2n}\sum_{\mu=1}^{2n} C_\mu(-)^\mu W^{\mu(k-j)} \tag{4.65}$$

Of the molecular orbital coulomb and exchange integrals that are not equal to one of the integrals in equations 4.60-4.65, most are zero because of the D_{6h} molecular symmetry. The rest are small because they depend upon terms such as $(\mu\mu|\nu\nu) - C_{\mu-\nu}$.

Because of the above considerations, we do not expect the best SCF molecular orbitals to differ much from those defined by equation 4.57. The exception will be when the D_{6h} molecular symmetry allows mixing of molecular orbitals of the same, or very nearly the same energy. This will occur, for instance, with the k=3m and k=3m molecular orbitals in the (18)-annulene.

PART 6. THE AMO INTEGRALS

From equations 4.53-4.57 and the definitions of the AMO orbitals (equation 3.2), we may prove:

$$\gamma_{KL} + \gamma_{K\bar{L}} = 2(kk|ll) = \bar{C}_e + \bar{C}_o \tag{4.66}$$

$$(K\bar{K}|\bar{J}\bar{J}) + (\bar{K}K|JJ) = 2\lambda_K(kk|jj)$$

$$2(K\bar{K}|J\bar{J}) = 2\lambda_K\lambda_J(kk|jj)$$

$$\gamma_{K\bar{K}} = \lambda_K^2(k\bar{k}|\bar{k}k) + (kk|kk) - (k\bar{k}|\bar{k}k)$$

$$\delta_{K\bar{K}} = \lambda_K^2(kk|kk)$$

$$\delta_{KJ} = (kj|jk)\cos^2(\theta_k-\theta_j) + (kj|jk)\sin^2(\theta_k+\theta_j)$$

$$\delta_{K\bar{J}} = (kj|jk)\cos^2(\theta_k+\theta_{\bar{j}}) + (k\bar{j}|\bar{j}k)\sin^2(\theta_k-\theta_j)$$

$$\begin{aligned}(KJ|J\bar{K}) + (\overline{KJ}|\bar{J}K) = {} & ((kj|jk)+(k\bar{j}|\bar{j}k)) \\ & + \lambda_L((kj|jk)-(k\bar{j}|\bar{j}k))\end{aligned}$$

$$(KJ|\overline{JK}) = (kj|jk)\cos^2(\theta_K-\theta_J) - (k\bar{j}|\bar{j}k)\sin^2(\theta_K+\theta_J)$$

$$(K\bar{J}|J\bar{K}) = (kj|jk)\cos^2(\theta_K+\theta_J) - (k\bar{j}|\bar{j}k)\sin^2(\theta_K-\theta_J)$$

PART 7. THE INTERACTION ENERGY

If the K orbital is a "1" orbital, we may write for equation 4.24:

$$E^{K-K} = (kk|kk) - (k\bar{k}|\bar{k}k)(1-\lambda_1^2) + (k\bar{k}|\bar{k}k)S^{-1}\left[\lambda_1^2(1-\lambda_1^2)b-d\right] \qquad (4.67)$$

If the J orbital is also a "1" orbital, we write for equation 4.23:

$$E^{J-K} = 4(kk|jj) - 2(kj|jk) - 2(1-\lambda_1^2)(\bar{k}j|j\bar{k}) - 2s^{-1}d\lambda_1^2(\bar{k}j|j\bar{k}) + 2s^{-1}b(1-\lambda_1^2)\lambda_1^2(\bar{k}j|j\bar{k}) \qquad (4.68)$$

If the K orbital is a "2" orbital, we write:

$$E^{K-K} = (kk|kk) - (k\bar{k}|\bar{k}k)(1-\lambda_2^2) + (k\bar{k}|\bar{k}k)S^{-1}\lambda_2^2(b(1-\lambda_2^2)-d) \qquad (4.69)$$

If the J orbital is also a "2" orbital, we write:

$$E^{J-K} = 4(kk|jj) - 2(jk|kj) - 2(j\bar{k}|\bar{k}j)(1-\lambda_2^2) + 2s^{-1}\lambda_2^2(j\bar{k}|\bar{k}j)(-d+b(1-\lambda_2^2)) \qquad (4.70)$$

If the J orbital is a "1" orbital, and the K orbital is a "2" orbital, then:

$$\begin{aligned} E^{J-K} = {} & 4(kk|jj) - 2(jk|kj)\cos^2(\theta_1-\theta_2) \\ & - 2(j\bar{k}|\bar{k}j)\sin^2(\theta_1+\theta_2) \\ & - 2(jk|kj)s^{-1}\sin^2(\theta_1-\theta_2) \cdot \\ & (b(\lambda_1^2+\lambda_2^2+\lambda_1\lambda_2-1)+d) \\ & + 2s^{-1}(j\bar{k}|\bar{k}j)\cos^2(\theta_1+\theta_2) \cdot \\ & (-d+b(1-\lambda_2^2-\lambda_1^2+\lambda_1\lambda_2)) \end{aligned} \tag{4.71}$$

The next step is to sum equations 4.67-4.71 over the appropriate molecular orbitals. We must first decide which orbitals are to be "1" orbitals, and which "2" orbitals. We shall let the top two pairs of AMO be "2" orbitals and let all the other orbitals be "1" orbitals. Then $q = 2$, $p = n-2$.

We define the quantities:

$$A = \frac{1}{n}\sum_{\mu=1}^{2n} C_\mu \cos\frac{\pi\mu}{n} \qquad B = \frac{1}{n}\sum_{\mu=1}^{2n}(-)^\mu C_\mu \cos\frac{\pi\mu}{n} \tag{4.72}$$

$$G_\mu = \sum_{K=-\frac{n-3}{2}}^{\frac{n-3}{2}} \omega^{\mu K} = \frac{\sin\frac{\pi\mu}{2n}(n-2)}{\sin\frac{\pi\mu}{2n}}$$

$$F = \frac{1}{2n}\sum_{\mu=1}^{2n} C_{\mu}G_{\mu}^{2} \qquad F = \frac{1}{2n}\sum_{\mu=1}^{2n} (-1)^{\mu} C_{\mu}G_{\mu}^{2}$$

From equation 4.64, we may find that:

$$\sum\sum_{j,k=-\frac{n-3}{2}}^{\frac{n-3}{2}} (kj|jk) = F \tag{4.73}$$

$$\sum\sum_{j,k=-\frac{n-3}{2}}^{\frac{n-3}{2}} (k\bar{j}|\bar{j}k) = \bar{F}$$

$$\sum_{k=\text{"1" orbitals}} \sum_{j=\text{"2" orbitals}} (jk|kj) = C_0-\bar{C}_e-B$$

$$\sum_{k=\text{"1" orbitals}} \sum_{j=\text{"2" orbitals}} (j\bar{k}|\bar{k}j) = C_0-\bar{C}_e-A$$

$$\sum\sum_{k,j=\text{"2" orbitals}} (jk|kj) = \bar{C}_o+\bar{C}_e+B$$

$$\sum\sum_{k,j=\text{"2" orbitals}} (j\bar{k}|\bar{k}j) = -C_o+C_e+A$$

We are now ready to express the total electronic pi interaction energy.

In the absence of MO alternation, the interaction energy is:

$$E^{o} = (n^{2}-1)(\bar{C}_{e}+\bar{C}_{o}) - F + B - 2C_{0} + 2\bar{C}_{e} \qquad (4.74)$$

$$\begin{aligned}
E_{int} = E^{o} &+ 2(C_{0}-\bar{C}_{e}-B)(\sin^{2}(\theta_{1}-\theta_{2}) \\
&((1-s^{-1}d-s^{-1}b(\lambda_{1}^{2}+\lambda_{2}^{2}+\lambda_{1}\lambda_{2}-1)) \\
&- \bar{F} + \lambda_{1}^{2}\bar{F}(1+s^{-1}b(1-\lambda_{1}^{2})-s^{-1}d) \\
&- \bar{C}_{e} + \bar{C}_{o} - A + \lambda_{2}^{2}(\bar{C}_{e}-\bar{C}_{o}+A)(1+(1-\lambda_{2}^{2})s^{-1}b \\
&\qquad -s^{-1}d) \\
&- 2C_{0} + 2\bar{C}_{e} + 2A + 2(\cos^{2}(\theta_{1}+\theta_{2})) \\
&(C_{0}-\bar{C}_{e}-A)(1+s^{-1}b(1-\lambda_{1}^{2}-\lambda_{2}^{2}+\lambda_{1}\lambda_{2})-s^{-1}d)
\end{aligned}$$

An examination of equation 4.75 shows a part independent of b and d. This part of the interaction energy is what we would get if we did not take the singlet projection of the spin function δ_{1}. The terms proportional to b have a positive sign, because the singlet projection of the wave function can be expected to have a higher electron repulsion energy, and a lower one-electron energy than any of the multiplet projections. The term proportional to d becomes small for large n.

PART 8. THE $^3B_{1u}$ STATE

Following Pauncz (2), we construct $^3B_{1u}$ states by using Sp_1, the triplet projection of σ_1. The wave function *of the* $^3B_{1u}$ *state is then the antisymmetrized product of* $\phi_o\ Sp_1$. (See equation 4.1.)

By making use of the properties of the spin function Sp_1, one may obtain an equation (Pauncz (2)) similar to equation 4.2.

$$\left\langle \Psi \middle| H_{op} \middle| \Psi \right\rangle = C \sum_P (-)^{p+p_{1P}} (n-2p_{1P}) \binom{n}{p_{1P}}^{-1} \cdot \left\langle \phi_o^* \middle| H_{op} \middle| P^r \phi_o \right\rangle \tag{4.76}$$

The constant C may be taken as arbitrary, the other symbols having the same meaning as in equation 4.2. For convenience we will let $C = 1/((n+2)(n+1))$.

By following a procedure very similar to that of equations 4.4-4.18, we find:

$$S_{p,q} = \frac{1}{p+1} \sum_{f=0}^{q} (-R)^{f} \binom{q}{f} \binom{f+p+1}{f}^{-1} T_{f,p}(\lambda_1^2) \quad (4.77)$$

$$- 2 \binom{f+p+2}{f+1}^{-1} T_{f+1,p}(\lambda_1^2)$$

$$b = \sum_{f=0}^{q-1} \frac{1}{p} \binom{q-1}{f} \left(\binom{p+f+1}{p}^{-1} T_{f+1,p-1}(\lambda_1^2) \right. \quad (4.78)$$

$$\left. -2 \binom{p+f+2}{p}^{-1} T_{f+2,p-1}(\lambda_1^2) \right) (-R)^{f}$$

$$d = \sum_{f=0}^{q-1} \frac{1}{p} \binom{q-1}{f} \left(- \lambda_1^{2p} + 2 \binom{p+f+3}{p}^{-1} T_{f+2,p}(\lambda_1^2) \right. \quad (4.79)$$

$$\left. - \binom{p+f+2}{p}^{-1} T_{f+1,p}(\lambda_1^2) \right) (-R)^{f+1}$$

If we use equations 4.77, 4.78, and 4.79 to define $S_{p,q}$, b, and d, equations 4.19-4.51 are true for the $^3B_{1u}$ state. These equations follow as a result of our choice for the constant C. If we again let the top two pairs of AMO be "2" orbitals, and all the rest be "1" orbitals, then p=n-2, q=2, and equations 4.19 and 4.75 define the energy of the $^3B_{1u}$ state.

This $^3B_{1u}$ AMO wave function is peculiar, in that it does not correspond to any Hückel MO wave function.

If we set all but one of the λ's of the AMO's equal to unity, the AMO wave function becomes a Hückel function with the two unpaired electrons occupying the remaining pair of AMO.

PART 9. THE LOWEST $^1B_{1u}$ AND $^1B_{2u}$ STATES

We construct wave functions for the $^1B_{1u}$ and $^1B_{2u}$ **states from functions resem**bling the Θ_3 and Θ_4 of Moffitt (31). For the (2n=4N+2)-annulene, Θ_3 equals the antisymmetrized product of:

$$\Theta_3 = \Big[a_{-N}a_{-N+1}\cdots a_{N-1}\psi_N\bar{a}_{-N}\bar{a}_{-N+1}\cdots\bar{a}_{N-1}\psi_{\bar{N}} \qquad (4.80)$$

$$+a_{-N}a_{-N+1}\cdots a_{N-1}\psi_{\bar{N}}\bar{a}_{-N}\bar{a}_{-N+1}\cdots\bar{a}_{N-1}\psi_N\Big]$$

$$Sp_o/\sqrt{2}$$

Θ_4 equals the antisymmetrized product of:

$$\Theta_4 = \begin{bmatrix} \psi_{-N}a_{-N+1}\cdots a_N\psi_{-\bar{N}}\bar{a}_{-N+1}\cdots\bar{a}_N \\ +\psi_{-\bar{N}}a_{-N+1}\cdots a_N\psi_{-N}\bar{a}_{-N+1}\cdots\bar{a}_N \end{bmatrix} Sp_o/\sqrt{2} \qquad (4.81)$$

For the $^1B_{1u}$ or p state:

$$U = (\Theta_3+\Theta_4)/\sqrt{2} \qquad (4.82)$$

For the ${}^1B_{2u}$ or alpha state:

$$V = (\Theta_3 - \Theta_4)/\sqrt{2} \tag{4.83}$$

The functions Θ_3 and Θ_4 are degenerate and orthogonal. The normalization integral **S** for Θ_3 will be:

$$S = S_{p,q-1} = \frac{1}{p+1} \sum_{f=0}^{q-1} \binom{f+p+1}{f}^{-1} \binom{q-1}{f} (-R)^f T_{f,p}(\lambda_1^2) \tag{4.84}$$

We shall have all but the N and -N orbitals be "1" orbitals. For Θ_3 the N orbitals are molecular orbitals leaving the -N orbitals to be "2" orbitals. We have $p = n-2$, $q = 2$.

We define the following quantities:

$$S' = S_{p,0} = \frac{1}{p+1} T_{0,p}(\lambda_1^2) \tag{4.85}$$

$$P = \frac{1}{p}(T_{0,p-1}(\lambda_1^2) - \frac{1}{p+1} T_{1,p-1}(\lambda_1^2))$$

$$Q = \frac{1}{p(p+1)} T_{1,p-1}(\lambda_1^2)$$

$$R' = \frac{R}{p(p+1)(p+2)} 2T_{2,p-1}(\lambda_1^2)$$

$$U = \frac{(1-\lambda_1^2)}{p(p+1)(p+2)} (2RT_{2,p-1}(\lambda_1^2) - (p+2)(1+R)T_{1,p-1}(\lambda_1^2)$$

$$+(p+1)(p+2)T_{0,p-1}(\lambda_1^2))$$

The energy of the θ_3 function is:

$$E_{\theta_3} = E^{o} - (C_0-\overline{C}_e-A) - \Delta W_2 \lambda_2 S'/2S \tag{4.86}$$

$$-\Delta W_1 \lambda_1 (P+\lambda_2^2 Q)/S$$

$$+ S^{-1}(P+\lambda_1 \lambda_2 Q)(C_0-\overline{C}_e-A)(\cos^2(\theta_1+\theta_2))$$

$$+ S^{-1}(P-\lambda_1 \lambda_2 Q+R')(C_0-\overline{C}_e-B)(\sin^2\theta_1-\theta_2)$$

$$+ S^{-1}(\tfrac{1}{2}(\overline{C}_e-\overline{C}_o)\lambda_2^2 S'-U\overline{F})$$

The interaction energy between θ_3 and θ_4 is:

$$H_{34} = \langle\theta_3|H|\theta_4\rangle = \tfrac{1}{2}(A-B) + (\overline{C}_e-\overline{C}_o-\tfrac{1}{2}A)\lambda_2^2 S'/S \tag{4.87}$$

$$E_U = E_{\theta_3} + H_{34} = E(^1B_{1u}) \tag{4.88}$$

$$E_V = E_{\theta_3} - H_{34} = E(^1B_{2u}) \tag{4.89}$$

PART 10. THE LOWEST $^1E_{1u}$ STATE

For the $(2n=4N+2)$-annulene we consider in analogy to the usual Hückel function, the AMO function $\emptyset_1$ equals the antisymmetrized product of:

$$a_{-N}\cdots a_{N-1}\overline{a}_{N+1}\overline{a}_{-N}\overline{a}\cdots\overline{a}_{N-1}\overline{a}_N \quad Sp_o \tag{4.90}$$

ϕ_1 has a ${}^1E_{2g}$ component as well as a ${}^1E_{1u}$ component. To get rid of the extraneous ${}^1E_{2g}$ component we introduce the function ϕ_2. ϕ_2 equals the antisymmetrized product of:

$$a_{-N} \cdots a_{N-1} a_N \bar{a}_{-N} \cdots \bar{a}_{N-1} a_{N+1} \quad Sp \qquad (4.91)$$

ϕ_1-ϕ_2 has ${}^1E_{2g}$ symmetry, but is probably a poor approximation to an electronic state. In MO language, it contains no single excitations from the Hückel ground state, whereas we would expect such MO configurations to play an important part in the lowest ${}^1E_{2g}$ state.

$$\Psi({}^1E_{1u}) = (\phi_1+\phi_2)/\sqrt{2} \qquad (4.92)$$

For the actual algebraic manipulations it is found most convenient to express ϕ_1 as the antisymmetrized product of:

$$\bar{a}_{-N} \cdots a_{N-1} a_{N+1} \bar{a}_{-N} \cdots \bar{a}_{N-1} \bar{a}_N \quad Sp \qquad (4.93)$$

This expression for ϕ_1 is identical except in form to 4.90.

The normalization integral S for the ${}^1E_{1u}$ state is identical to that of the ${}^1B_{1u}$ and ${}^1B_{2u}$ states (see equation 4.84). We define the following integrals:

$$p = n-2, \quad q = 2$$

$$R_0 = \frac{1}{p+1}(T_{0,p}(\lambda_1^2) - \frac{1}{p+2} T_{1,p}(\lambda_1^2)) \qquad (4.94)$$

$$R_4 = \frac{1}{p(p+1)}(-2T_{1,p}(\lambda_1^2) + (p+1)T_{0,p}(\lambda_1^2)$$

$$+2T_{2,p}(\lambda_1^2)/(p+2))$$

$$R_5 = \frac{1}{p(p+1)}(T_{1,p}(\lambda_1^2) - \frac{2}{p+2}T_{2,p}(\lambda_1^2))$$

$$S_o = \frac{1}{(p+1)(p+2)} T_{1,p}(\lambda_1^2)$$

$$S_5 = \frac{2}{p(p+1)(p+2)} T_{2,p-1}(\lambda_1^2)$$

Then:

(4.95)

$$E(^1E_{1u}) = E^o + A - \Delta W_1 \lambda_1 (R_4 + (1+\lambda_2^2)R_5 + \lambda_2^2 S_5)/S$$

$$-\Delta W_2 \lambda_2 (R_0 + S_0)/2S - \frac{1}{2}(\overline{C}_e - \overline{C}_o)\lambda_2^2$$

$$- (R_4 + \lambda_2^2 R_5)(1-\lambda_1^2)\overline{F}/S - (1-\lambda_2^2)R_0 A/S$$

$$+ (\sin^2\theta_1 - \theta_2)(C_0 - \overline{C}_e - B)(R_4 + R_5)/S$$

$$- (\sin^2\theta_1 - \theta_2)\lambda_1 \lambda_2 (R_5 + S_5)(A-B)/S +$$

$$(1-\lambda_1^2)(1-\lambda_2^2)(C_0 - \overline{C}_e - A)R_5/S$$

$$-(\sin^2\theta_1+\theta_2)(R_4+R_5)(C_0-\overline{C}_e-A)/S - \tfrac{1}{2}R_5(\sin 2\theta_1 \sin 2\theta_2)$$

$$((C_0-C_e-A)\lambda_2^2+\tfrac{1}{2}(A-B)(\lambda_2^2+\lambda_1\lambda_2))/S$$

In chapter IV I have shown how to find AMO wave functions and energy levels for the lower excited states of the annulenes. In the next chapter, the results of numerical computations on the 7094 computer will be given. The weaknesses in the present AMO approach will be examined, and possible improvements mentioned.

CHAPTER V

RESULTS OF 7094 COMPUTATIONS

PART 1. BENZENE

The first calculation is of the energy levels of benzene using the empirical integrals of Pariser (18).

The energy depression of the ground state relative to the Hückel ground state is 0.668 e.v. The transition energies to the excited states are:

(5.1)

$^3B_{1u}$	$^1B_{2u}$	$^1B_{1u}$	$^1E_{1u}$
3.325 e.v.	5.28 e.v.	6.503 e.v.	6.843 e.v.

The calculation for the $^3B_{1u}$ state has been done before (De Heer and Pauncz (24)); my result is in complete agreement.

The experimental values for these quantities are:

3.59 e.v.	4.71 e.v.	5.96 e.v.	6.76 e.v.

(Pariser (18))

Direct comparison shows us that the empirical integrals of Pariser (18) do not reproduce the actual spectrum with any precision. Since the integrals of Pariser were originally chosen to match this particular spectrum, it would appear to be more reasonable to choose integrals that, with AMO wave functions, would match the experimental transitions.

It is now known that the $^3B_{1u}$ state of benzene is distorted (DeGroot and van der Waals (36)). It has been estimated (De Heer and Pauncz (24)) that the symmetrical form of benzene in the $^3B_{1u}$ state is 0.2 e.v. higher in energy than the distorted form. We will therefore try to match the theoretical spectrum to 3.79 e.v. for the $^3B_{1u}$ transition.

I follow the method of Pariser (18) by choosing C_2 and C_3 theoretically. I use their values of:

$$C_2 = 5.682 \text{ e.v.} \qquad C_3 = 4.978 \text{ e.v.}$$

By matching the experimental transitions to the calculated AMO transitions we determine the values of C_0, C_1, and β. A Fortran program was written to calculate the transition energies and their first derivatives with respect to C_0, C_1, and β. In successive iterations, new C_0, C_1, and β are calculated by linear interpolation.

First, an attempt was made to use the 3 singlet transitions to fit the experimental transitions. The successive iterations diverged instead of converging, with the $^1B_{2u}$ level remaining too high.

Then, the $^3B_{1u}$ state was substituted for the $^1B_{2u}$ state, and the iterations converged nicely.

The resulting integrals were:

AMO Empirical Integrals

$$C_0 = 10.2346 \text{ e.v.} \qquad C_1 = 7.16524 \text{ e.v.} \tag{5.2}$$

$$\beta = 2.4207 \text{ e.v.}$$

These integrals may be compared to those of Pariser (18).

Pariser Empirical Integrals

$$C_0 = 10.959 \text{ e.v.} \qquad C_1 = 6.895 \text{ e.v.}$$

$$\beta = 2.371 \text{ e.v.}$$

The depression of the ground state energy relative to the Hückel ground state with the AMO empirical integrals is:

$$\delta E_g = -0.398 \text{ e.v.} \tag{5.3}$$

We find for the AMO wave functions and transition energies of the various benzene states:

(5.4)

	λ_1	λ_2	E	$E_{exp.}$
$^1A_{1g}$	.9448	.8159	0	....
$^3B_{1u}$	.9628	.7357	3.790	3.79*
$^1B_{2u}$	.9483	.8685	5.156	4.71
$^1B_{1u}$	.9463	.9563	5.960	5.96
$^1E_{1u}$	.9468	.7137	6.760	6.76

An interesting point is that in the $^1B_{1u}$ singlet, λ_2 is greater than λ_1. An examination of equation 4.87 shows that the matrix element H_{34} is smallest when λ_2^2 is large. Since H_{34} enters the energy of the $^1B_{1u}$ state with a plus sign (equation 4.88), λ_2 must be large, explaining the anomaly.

The question also arises why the $^1B_{2u}$ AMO energy should be so much above the experimental energy. One way to approach this question is to examine the behavior of the AMO wave functions in various limits. We know

---

*This experimental transition energy is adjusted to what one would expect for symmetrical benzene.

that in the absence of electron repulsion, the AMO wave functions become Hückel wave functions. We now consider the opposite limit, in which we let the resonance integral β approach zero. In this limit, λ_1, and λ_2 approach zero, and the $^1A_{1g}$ and $^3B_{1u}$ states become what is described in valence bond language as nonionic. Simple group theoretical arguments show that the $^1B_{2u}$ AMO state becomes a mixture of singly-ionized structures of the figure 3(a) type, while the $^1B_{1u}$ and $^1E_{1u}$ AMO states include also structures of the 3(b) type.

Valence bond theory allows five singlet nonionic structures. From the two Kekule structures one may construct a $^1A_{1g}$ state and a $^1B_{2u}$ state. From the three Dewar structures one may construct a $^1A_{1g}$ state and a degenerate pair of $^1E_{2g}$ states (see figure 4).

In figure 5 we display the energies of the AMO states with those of the corresponding valence bond states. We see that the energy of the $^1B_{2u}$ AMO state is very much worse than that of the $^1B_{1u}$ or $^1E_{1u}$ states.

From this point of view, it is not surprising that the AMO energy for the $^1B_{2u}$ state came out .45 e.v. above the experimental value.

A possible method of improving the apparently poor $^1B_{2u}$ AMO wave function would be to introduce configuration interaction. One might use as a basis set just those AMO

FIGURE 3(a)

FIGURE 3(b)

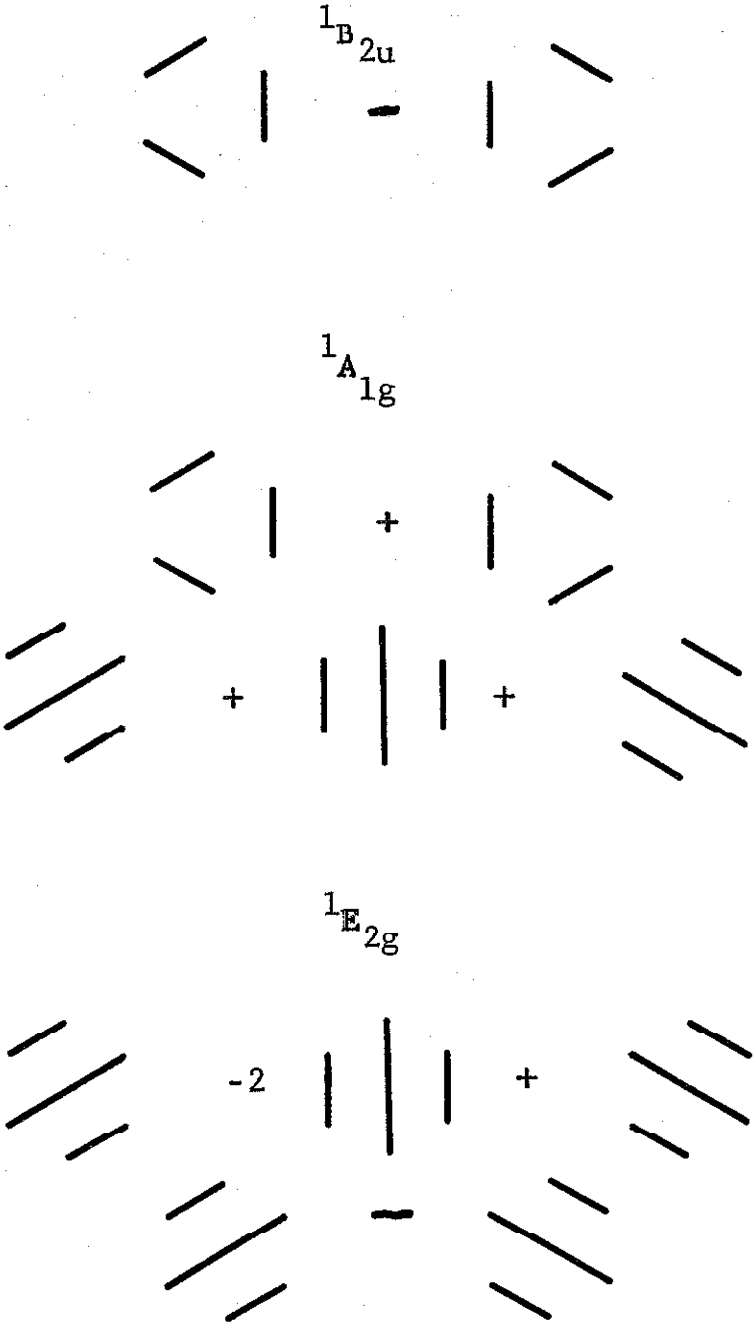

FIGURE 4

SYMMETRIES OF NONIONIC VALENCE BOND STRUCTURES

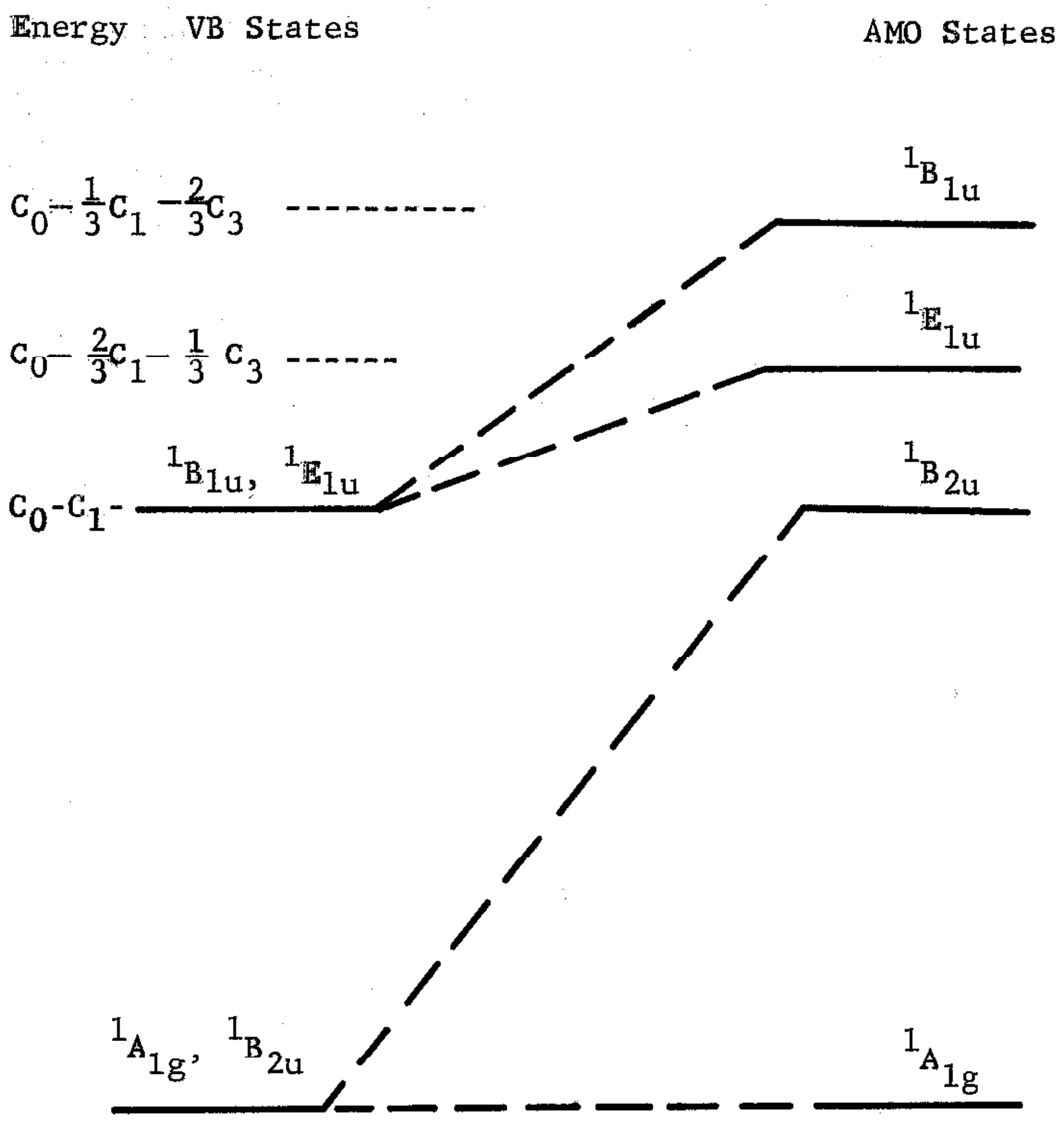

FIGURE 5

A COMPARISON OF THE ENERGIES OF VB WAVE FUNCTIONS AND AMO WAVE FUNCTIONS IN THE LIMIT AS THE RESONANCE INTEGRAL β APPROACHES ZERO configurations necessary to produce the appropriate VB wave function as well as the appropriate Hückel MO function in the proper limits. The difficulty with this method is that it may very well be as complicated as the usual configuration interaction method.

PART 2. THE (18)-ANNULENE (CON)

From chapter II part 2 we know that the (18)-annulene has D_{6h} symmetry. To classify the symmetries of the molecular orbitals we must treat the real and imaginary components of the complex orbitals separately. Let:

$$\Psi_{k^+} = \text{the real part of } \sqrt{2}\,\Psi_k \qquad (5.5)$$

$$\Psi_{k^-} = \text{the imaginary part of } \sqrt{2}\,\Psi_k$$

Then we may classify the MO symmetries as follows:

A_{1u}	A_{2u}	E_{1g}	E_{2u}	B_{1g}	B_{2g}
0		$1^{\pm}$	$2^{\pm}$	3^{+}	3^{-}
6^{+}	6^{-}	$5^{\pm}$	$4^{\pm}$	9	
		$7^{\pm}$	$8^{\pm}$		

(5.6)

The energy splittings between the 0 and $\underline{6}^{+}$, and between the 3^{+} and 9 MO are so great that we may assume that these MO are very close to the best self-consistent field MO.

The 3^- and 6^- orbitals are exact self-consistent field (SCF) orbitals because they are the only orbitals of their respective symmetries. We may construct the pair of alternant molecular orbitals a_{3^-} and $\bar{a}_{3^-}$ from the 3^- and 6^- orbitals. We may also construct from the 3^+ and 6^+ orbitals the alternant orbitals a_{3^+} and $\bar{a}_{3^+}$. If we use the same θ in constructing the a_{3^-} and a_{3^+} orbitals, this pair of orbitals will span the same function space as the a_3 and a_{-3} orbitals. In the ground state, the a_{3^-} and a_{3^+} orbitals are occupied by electrons of parallel spin, so we are justified in replacing these two orbitals by the a_3 and a_{-3} orbitals. We may replace the $\bar{a}_{3^-}$ and $\bar{a}_{3^+}$ orbitals by the $\bar{a}_3$ and $\bar{a}_{-3}$ orbitals for the same reason.

The energy splitting between the +2 and -4 molecular orbitals is about 1.53β. The interaction leading to their mixing in the best SCF molecular orbitals is of long range, involving the difference between atomic coulomb integrals for atoms separated by 3 or more bonds.

If we used a ground state wave function with the same θ for the a_2 and a_{-4} orbitals, the error in not using the best SCF orbitals here would vanish, as it vanished in the case of the +3 and -3 orbitals. In any case, we expect the error introduced by not using the SCF orbitals in the ground state to be small. In the case of excited states in which an electron is taken out of a -4 orbital, the error should be more important, leading to a too high theoretical energy.

The 8^+ MO is much higher in energy than the 2^+ and 4^- MO, and is not expected to contribute much in the formation of the lower SCF orbitals. The discussion of the remaining E_{2u} and E_{1g} orbitals follows the same line and leads to the same conclusions.

The following values of C_μ were taken from the benzene program (part 1), or were calculated from the atomic coulomb integrals tabulated by Pariser (18):

$$
\begin{array}{llll}
C_0 & = 10.2346 \text{ e.v.} & C_1 & = 7.16524 \text{ e.v.} \\
C_2 & = 5.682 & C_3 & = 4.209 \\
C_4 & = 3.243 & C_5 & = 2.745 \\
C_6 & = 2.478 & C_7 & = 2.256 \\
C_8 & = 2.155 & C_9 & = 2.152 \\
C_{-\mu} & = C_{2n-\mu} = C_\mu & & \\
\overline{C}_e & = 4.1500 & \overline{C}_o & = 3.8781 \\
C_0-\overline{C}_e & = 6.0845 & \overline{C}_e-\overline{C}_o & = 0.2719 \\
A & = 2.7516 & B & = 0.2820 \\
\overline{F} & = 7.1571 & &
\end{array}
\qquad (5.7)
$$

A program was written to calculate the wave functions and energy levels of various annulene AMO states. The integrals of 5.7 are used as input. The depression of the (18)-annulene ground state relative to the Huckel ground state was found to be 1.404 e.v.

We find for the AMO wave functions and transition energies of the various (18)-annulene states: (See table on page 71.)

The E_{exp} are taken from Gouterman and Wagniere (10); their spectrum was taken at 77°K. The $E_{C.I.}$ are taken from some configuration interaction calculations performed by Weiss and Gouterman (37). I have converted both from wave numbers to e.v.

PART 3. THE (30)-ANNULENE (CTP)

The (30)-annulene has D_{6h} symmetry. We classify the MO symmetries in the same way we did with the (18)-annulene.

(5.9)

A_{1u}	A_{2u}	E_{1g}	E_{2u}	B_{1g}	B_{2g}
0		$1^{\pm}$	$2^{\pm}$	3^{+}	3^{-}
6^{+}	6^{-}	$5^{\pm}$	$4^{\pm}$	9^{+}	9^{-}
12^{+}	12^{-}	$7^{\pm}$	$8^{\pm}$	15	
		$11^{\pm}$	$10^{\pm}$		
		$13^{\pm}$	$14^{\pm}$		

(5.8)

	λ_1	λ_2	E_{AMO}	E_{exp}	$E_{C.I.}$	$E_{P.P.}$
$^1A_{1g}$	.9544	.5897	0	-	0	0
$^3B_{1u}$	.9689	.4900	1.4055 e.v.	-		1.23
$^1B_{2u}$	.9604	.7161	2.5626	2.52 e.v.	1.42	1.65
$^1B_{1u}$	.9642	.9632	3.1799	2.64	2.18	2.06
$^1E_{1u}$	.9656	.4148	4.1916	3.35	3.28	4.22

The question of the effect of mixing MO of the same symmetry species is very similar in the (18)- and (30)-annulenes. The same arguments lead qualitatively to the same conclusions, with the possibility that mixing is a little more important in the (30)-annulene because the MO energies are closer together. We still expect that using the best SCF orbitals would lower the transition energies to the excited states somewhat.

The following values for electron repulsion integrals were taken from the benzene program (part 1), or were calculated from the atomic coulomb integrals tabulated by Pariser (18):

$$
\begin{aligned}
C_0 &= 10.2346 \text{ e.v.} & C_1 &= 7.1652 \text{ e.v.} \\
C_2 &= 5.682 & C_3 &= 4.0548 \\
C_4 &= 3.1254 & C_5 &= 2.5890 \\
C_6 &= 2.1898 & C_7 &= 1.9302 \\
C_8 &= 1.7444 & C_9 &= 1.6023 \\
C_{10} &= 1.5062 & C_{11} &= 1.4211 \\
C_{12} &= 1.3662 & C_{13} &= 1.3292 \\
C_{14} &= 1.3068 & C_{15} &= 1.3056 \\
C_{-\mu} &= C_{2n-\mu} = C_{\mu} \\
\overline{C}_e &= 2.9384 & \overline{C}_o &= 2.7659
\end{aligned}
\tag{5.10}
$$

$$C_0-\overline{C}_e = 7.2872 \qquad \overline{C}_e-\overline{C}_o = 0.1725$$

$$A = 2.4306 \qquad B = 0.1713$$

$$\overline{F} = 16.4843$$

We find the wave functions and AMO energies of the (30)-annulene by the annulene program. The energy depression of the AMO ground state relative to the Hückel ground state is 1.8588 e.v.

(5.11)

	λ_1	λ_2	E_{AMO}	E_{exp}
$^1A_{1g}$	.9612	.4962	0	-
$^3B_{1u}$	.9722	.4052	1.0749	-
$^1B_{2u}$	.9679	.6951	2.1680	-
$^1B_{1u}$	.9716	.9467	2.7406	2.37 e.v.
$^1E_{1u}$	.9719	.3548	3.4505	2.89 e.v.

PART 4. DISCUSSION OF THE AMO METHOD

We have found that in both the (18)- and (30)-annulenes, the AMO method overestimates the transition energies of the $^1B_{1u}$ and $^1E_{1u}$ states. In contrast, the C.I. calculation of Weiss and Gouterman does well on the transition energy of the (18)-annulene, $^1E_{1u}$ state, but underestimates the transition energy of the $^1B_{1u}$ state. The assignment of the $^1B_{2u}$ state to the series of weak bands leading to 2.52 e.v.* seems doubtful since both our AMO calculation and Weiss and Gouterman's C.I. calculation indicate there should be a splitting of about .6-.7 e.v. between the $^1B_{1u}$ and $^1B_{2u}$ states.

The AMO transition energies of the (18)-annulene seem to be uniformly about 1 e.v. above the C.I. energies of Weiss and Gouterman.* This is probably because the limited C.I. method is inferior to the AMO method for depressing the energy of the ground state. (See Swalen and de Heer (25)).

We found in the case of benzene, that the AMO excited singlet wave functions are not sufficiently flexible to reach the minimum electron repulsion energy VB configurations. This lack of flexibility applies equally to the excited singlet states of the (18)- and (30)-annulenes. As these annulenes have more closely spaced interacting configurations than benzene, we may expect the lack of flexibility of the excited singlet state AMO wave functions to be more serious.

It is difficult to predict what error was introduced by using a two-parameter AMO theory rather than

---

*See page 71.

the many-parameter AMO theory. We know that we have underestimated the energy depression of the ground states relative to the Hückel ground states. We suspect we have overestimated the $^3B_{1u}$ transition energy, since the energy of the $^3B_{1u}$ AMO state should be greatly improved* by the many-parameter AMO theory.

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*See chapter III, part 6.

CHAPTER VI

POSSIBILITY OF BOND LENGTH ALTERNATION WITH ALTERNATE MOLECULAR ORBITAL (AMO) MODEL

PART 1. THE BEHAVIOR OF THE λ_K

We have seen (page 4) that the highest bonding orbitals play an especially important part in the problem of bond length alternation. For this reason we shall use separate θ_k for each alternate molecular orbital, and pay particular attention to the behavior of θ_k for large n and $\pi k/n \approx \pi/2$.

For very large n, we may replace the spin function Sp_o (equations 3.4-3.6) by δ_1. (See Pauncz, etc. (12).)

$$\delta_1 = \alpha_{(1)} \cdot \cdots \cdot \alpha_{(n)} \beta_{(n+1)} \cdot \cdots \cdot \beta_{(2n)} \tag{6.1}$$

This simplified spin function leads to a simplified expression for the energy.

$$E_1 = W - 2\sum_k \lambda_k (h_{\bar{k}\bar{k}} - h_{kk}) \tag{6.2}$$

$$E_{12} = \sum_{K>L}\sum 2\,\gamma_{KL} + 2\,\gamma_{K\bar{L}} - \delta_{KL}$$

$$+ \sum_K \gamma_{K\bar{K}}$$

From equation 4.66:

$$\gamma_{KL} + \gamma_{K\bar{L}} = \bar{C}_e + \bar{C}_o \tag{6.3}$$

$$\gamma_{K\bar{K}} = (kk|kk) - (1-\lambda_k^2)(k\bar{k}|\bar{k}k)$$

Let $S_k = \sin 2\theta_k$

$$\begin{aligned} 4\delta_{JK} = {} & (1+\lambda_K)(1+\lambda_J)(jk|kj) \\ & + (1-\lambda_K)(1+\lambda_J)(j\bar{k}|\bar{k}j) \\ & +(1+\lambda_K)(1-\lambda_J)(\bar{j}k|k\bar{j}) \\ & +(1-\lambda_K)(1-\lambda_J)(\bar{j}\bar{k}|\bar{k}\bar{j}) \\ & + 2S_J S_K((jk|\bar{k}\bar{j}) + (\bar{j}k|k\bar{j})) \end{aligned} \tag{6.4}$$

$$\begin{aligned} \frac{dE}{d\lambda_K} = {} & -2(h_{\bar{k}\bar{k}} - h_{kk}) + 2\lambda_K(k\bar{k}|\bar{k}k) \\ & - \frac{1}{2}\sum_{j\neq k} (1+\lambda_J)((kj|jk) - (\bar{k}j|j\bar{k})) \\ & \qquad (1-\lambda_J)((k\bar{j}|\bar{j}k) - (\bar{k}\bar{j}|\bar{j}\bar{k})) \\ & \qquad -2\lambda_K S_J((kj|\bar{j}\bar{k}) + (k\bar{j}|j\bar{k}))/S_K \end{aligned} \tag{6.5}$$

$= 0$ at energy minima

At $j=-k$, $(k\bar{j}|\bar{j}k) = (\bar{k}j|j\bar{k})$, $\lambda_J = \lambda_K$.

If $\cos\frac{\pi K}{n} \ll 1$, then $(kj|jk) \approx (\bar{k}\bar{j}|\bar{j}\bar{k})$; and for any j, $((kj|jk) - (\bar{k}j|j\bar{k}) + (k(-j)|(-j)k) - (\bar{k}(-j)|(-j)\bar{k}))$ and $((k\bar{j}|\bar{j}k) - (\bar{k}\bar{j}|\bar{j}\bar{k}) + (k(\overline{-j})|(\overline{-j})k) - (\bar{k}(\overline{-j})|(\overline{-j})\bar{k}))$ are proportional to $\cos\frac{\pi k}{n}$, as is $h_{\bar{k}\bar{k}} - h_{kk}$.

We therefore find that equation 6.5 may be written as:

$$\frac{dE}{d\lambda_K} = \text{terms } 0(\lambda_K) + \text{terms } 0(\cos\frac{\pi k}{n}) = 0 \qquad (6.6)$$

This can be true only if λ_K is proportional to $\cos\frac{\pi k}{n}$ for $\cos\frac{\pi k}{n} \ll 1$.

We may notice that using the spin function S is equivalent to setting the Λ_1 and Λ_4 equal to Λ_o, and setting the other Λ's equal to zero. Actually, the other Λ's are proportional to $1/n$, and all the Λ's are functions of the λ_k^2. A more complete treatment could introduce, at most, a term proportional to $1/n$ in the expression for λ_k with $\cos\frac{\pi k}{n} \ll 1$. We may therefore write:

$$\lambda_k = A\cos\frac{\pi k}{n} + B/n \qquad (6.7)$$

when n is large and $\cos\frac{\pi k}{n} \ll 1$.

PART 2. BOND LENGTH ALTERNATION

Let us introduce into our annulene a slight distortion x (as in chapter I), causing the C-C bond lengths to alternate. For the short bonds we will have a resonance integral $\beta_1 = \beta - x\beta'$, and for the long bonds $\beta_2 = \beta + x\beta'$. Each of the atomic coulomb integrals between starred and unstarred atoms will change similarly. We introduce distorted molecular orbitals.

$$X_k = \cos x_k \, \Psi_k + i \sin x_k \, \Psi_{\bar{k}} \tag{6.8}$$

$$X_{\bar{k}} = \cos x_k \, \Psi_{\bar{k}} + i \sin x_k \, \Psi_k$$

From the distorted molecular orbitals X_k we construct distorted alternate molecular orbitals b_k.

$$b_k = \cos\theta_k \, X_k + \sin\theta_k \, X_{\bar{k}} \tag{6.9}$$

$$= \cos x_k \, a_K + i \sin x_k \, a_{\bar{K}}$$

$$\bar{b}_k = \cos\theta_k \, X_k - \sin\theta_k \, X_{\bar{k}}$$

$$= \cos x_k \, \bar{a}_K + i \sin x_k \, \bar{a}_{\bar{K}}$$

The ground state wave function of the distorted molecule is construed from the b_k in the same way we previously constructed the ground state of the undistorted molecule from the a_k . For small distortions the θ_k will be unchanged from their values for the undistorted molecule. We know by symmetry that $\theta_k=\theta_{-k}$, and that $x_k = -x_{-k}$, the x_k being proportional to the bond length distortion x. The expressions in terms of the various b_k integrals will be formally the same as the expressions for the undistorted molecule in terms of the a_k integrals (chapter IV). It is easy to prove from the orthogonality and normalization of X_k and $X_{\bar{k}}$ that the Λ are independent of the x_j. This allows us to treat the Λ as constants when minimizing the energy with respect to the x_k.

PART 3. THE PI ENERGY

$$E_1 = W - \sum_k \lambda_k (\Lambda^K_4 + \Lambda^K_5) \Big[((\bar{k}|h|\bar{k}) - (k|h|k)) \cdot \cos 2x_k / \Lambda_0 + ((\bar{k}|h|k) - (k|h|\bar{k}))\, i \sin 2x_k / \Lambda_0 \Big] \tag{6.10}$$

For the higher bonding orbitals we may neglect overlap, and:

$$(\bar{k}|h|\bar{k}) - (k|h|k) = 4\beta \cos\frac{\pi k}{n} \tag{6.11}$$

$$(\bar{k}|h|k) - (k|h|\bar{k}) = 4i\beta' x \sin\frac{\pi k}{n}$$

It is this second term that is mainly responsible for the distortion of the molecular orbitals.

The coulomb and exchange integrals involving k molecular orbitals may be divided into two types: those involving a product of k orbitals $(b_k)^*(b_k)$ or $(\bar{b}_k)^*(\bar{b}_k)$, and those not containing one of these combinations but containing $(\bar{b}_k)^*(b_k)$ or $(b_k)^*(\bar{b}_k)$. The latter type integral is always multiplied by λ_k.

$$\begin{aligned} 2(b_k)^*(b_k) &= (k)^*(k)+(\bar{k})^*(\bar{k}) + S_k((\bar{k})^*(k)+(k)^*(\bar{k})) \\ &\quad - \lambda_k(\cos 2x_k)((\bar{k})^*(\bar{k})-(k)^*(k)) \\ &\quad - i\lambda_k(\sin 2x_k)((\bar{k})^*(k)-(k)^*(\bar{k})) \end{aligned} \tag{6.12}$$

We see that all the terms in the energy dependent upon x_k are of order λ_k or less. These terms will contribute only to exchange interactions between starred and unstarred atoms, $(\cos \pi k/n \ll 1)$.

$$\begin{aligned} 2(b_k)^*(\bar{b}_k) &= \lambda_k((\bar{k})^*(\bar{k})+(k)^*(k)) \\ &\quad +(\cos 2x_k - iS_k \sin 2x_k)((k)^*(k)-(\bar{k})^*(\bar{k})) \\ &\quad +(S_k \cos 2x_k - i \sin 2x_k)((\bar{k})^*(k)-(k)^*(\bar{k})) \end{aligned} \tag{6.13}$$

For small λ_k, we may represent S_k as $S = 1 - \frac{1}{2}\lambda_k^2$; the energy may be expanded in terms of λ_k.

$$E = A_k - B_k\lambda_k + C_k\lambda_k^2 \qquad (6.14)$$

At $E_{min.}$, $\lambda_k = B_k/2C_k$. (6.15)

An examination of equations 6.12 and 6.13 shows that only B_k is a function of x_k, A_k and C_k are independent of x_k.

$$B_k = B_{k1}\cos 2x_k + B_{k2}\sin 2x_k \qquad (6.16)$$

B_{k2} is of order x, therefore:

$$\frac{d^2E}{dx_k^2} = +4B_k\lambda_k = 2B_k^2/C_k \qquad (6.17)$$

The term C_k derives primarily from the S_k term $((\bar{k})*(k)+(k)*(\bar{k}))$ in the exchange integrals $(b_k b_j | b_k b_j)$.

This term is primarily responsible for lowering the probability of finding two pi electrons on the same carbon atom. The term $((\bar{k})*(k)+(k)*(\bar{k}))$ is insensitive to changes of k in the region $\cos\frac{\pi k}{n} \ll 1$. C_k will also be insensitive to changes of k in the same region. C_k will be approximately proportional to the average value of S_j, as this average times S_k determines the probability of finding a "k" electron sharing a carbon atom with another pi electron. Lowdin (13) has shown that as $n \to \infty$, his single λ approaches a constant value. It is therefore reasonable to assume that our average S_j also approaches a constant value, ($\overline{S}_j$ cannot exceed one in any event). We may therefore assume that C_k is nearly independent of k and n, when n is large and $\cos\frac{\pi k}{n} \ll 1$.

The term B_k is principally concerned with interactions between starred and unstarred atoms, and especially with the interaction between neighboring atoms. B_{k1} is proportional to $\cos\frac{\pi k}{n}$ ($\cos\frac{\pi k}{n} \ll 1$). (See discussion of δ_{KL} and λ_k, equation 6.5.) B_{kl} is proportional to $\sin\frac{\pi k}{n}$. Each term in B_{k2} contains either a factor of $\sin 2x_j$, or $x\beta'$, or xC'_u; for small molecular distortions these terms are small. The terms involving C'_u are significant only for small u, because C'_u drops off like u^{-2}. B_k, like C_k, is nearly independent of n with n large and $\cos\frac{\pi k}{n} \ll 1$ held constant.

We may now express the energy per bond in terms of x and the small x_k.

$$E = E_o + Kx^2 + \frac{1}{n}x\sum_j L_j(\lambda_j x_j) + \frac{1}{n}\sum_j (\lambda_j x_j)^2 B_{j1}/\lambda_j \tag{6.17}$$

$$+ \frac{1}{n^2}\sum\sum_{k \neq j} M_{jk}(\lambda_j x_j)(\lambda_k x_k)$$

The term $B_{j1}/\lambda_j = 2C_j$ when λ_j and x_j are small (equation 6.15). If λ_j is not small, then B_{j1}/λ_j will approach a function $F(k/n)$ as $n \rightarrow \infty$. K is a force constant depending upon the bond order. L_j and M_{jk} come out of B_{j2}. L_j approaches a function $L(j/n)$ as $n \rightarrow \infty$, because the C'_u drop off sufficiently rapidly. M_{jk} behaves like $\log|j-k|/n$, for small $|j-k|/n$. These off diagonal terms will be ignored. By differentiating with respect to x_j we find:

$$\lambda_j x_j = -xL_j/4C_j \tag{6.18}$$

$$E_{min} = E_o + (K - \frac{1}{8n}\sum_j L_j^2/C_j)x^2 \tag{6.19}$$

$\frac{1}{n}\sum_j L_j^2/C_j$ approaches a constant as $n \rightarrow \infty$, so there is no divergence to cause any great change in the B_{2u} force as n increases. For this reason it is very unlikely that for any $n > 3$, K_{B2u} would vary greatly from its benzene value.

PART 4. SUMMARY

We find that the proper variables to describe the AMO distortions are the $\lambda_k x_k$. The second derivatives of the energy with respect to these variables do not approach zero as k/n approaches 1/2, while the terms in the energy involving derivatives with respect to x remain bounded.

The lack of the singularity in the contribution of the k'th orbital to K_{B2u} as k/n approaches 1/2 removes the factor diverging as -log(n) in the calculation of K_{B2u}, (chapter I). As this factor is not very large in free electron models, (leading to bond alternation only for n about 15 or above), the slight residue that may be left of it in the AMO theory (terms proportional, perhaps, to 1/n) should not be big enough to make any great change in K_{B2u}. I predict no bond alternation for the annulenes.

The use of the $\lambda_k x_k$ to describe the AMO distor- may be intuitively justified by noting that at λ_k=0, variation of x_k only changes the phase of b_k. With the use of $\lambda_k x_k$ to describe molecular distortions, no such curiosity occurs.

CHAPTER VII

SIGMA-PI INTERACTION BY THE AMO METHOD

PART 1. SIGMA WAVE FUNCTIONS

We shall use the AMO method to calculate the sigma-pi exchange interactions. We shall start with valence bond function for the sigma electrons.

$$\sigma_s = \frac{1}{N_s}(\sigma_1(1)\sigma_2(2)+\sigma_2(1)\sigma_1(2)) \qquad (7.1)$$

$$\sigma_t = \frac{1}{N_t}(\sigma_1(1)\sigma_2(2)-\sigma_2(1)\sigma_1(2)) \qquad (7.2)$$

$$N_s^2 = 2 + 2\langle\sigma_1|\sigma_2\rangle^2, \quad N_t^2 = 2 - 2\langle\sigma_1|\sigma_2\rangle^2 \qquad (7.3)$$

σ_s is the spatial part of a low energy singlet sigma bond wave function between adjacent atoms 1 and 2. σ_t is the space part of a triplet wave function. We will assume that atom 2 is starred, and atom 1 is unstarred. We construct an alternant valence bond (AVB).

$$\sigma_a = \sigma_s \cos\theta_\sigma + \sigma_t \sin\theta_\sigma \qquad (7.4)$$

The AVB concentrates the first electron on the "1" atom, and the second electron on the "2" atom. Ths spin of the first electron is aligned parallel to that of the pi electrons in the "a" orbitals, and the spin of the second electron is aligned parallel to that of the pi electrons in "$\bar{a}$" orbitals.

If we had only one AVB, we would write:

$$(S_a+S_1)^2 = (\frac{n}{2}+1)^2 - 1/4 = (S_{\bar{a}}+S_2)^2 \tag{7.5}$$

$$s^2 = 0$$

The operators S_a and $S_{\bar{a}}$ were defined in chapter III (part 3) as the spin operators for the a and $\bar{a}$ electrons respectively.

We define S_1 and S_2 as the spin operators respectively for the first and second electrons in equations 7.1 and 7.2.

We may note that $\langle\sigma_s|\sigma_s\rangle = \langle\sigma_t|\sigma_t\rangle = 1$ (7.6)

$$\langle\sigma_s|\sigma_t\rangle = 0$$

The permutation of electrons 1 and 2 gives:

$$P_{12}\sigma_s = \sigma_s, \; P_{12}\sigma_t = -\sigma_t \tag{7.7}$$

From the above equations, we find:

$$\langle\sigma_a|\sigma_a\rangle = 1, \quad \sigma_a P_{12}\sigma_a = \cos 2\theta_\sigma = \lambda_\sigma \tag{7.8}$$

θ_σ determines the triplet character of the sigma bond. Since the energy gap between the singlet and triplet state of a sigma bond is high, (about 5-15 e.v. (19)), θ_σ

will be small. We shall use a single Θ for all our orbitals. It will be convenient to introduce the quantity:

$$R = (1-\lambda_\sigma) \tag{7.9}$$

This R will play the same part with the sigma bonds that the R introduced in the theory of the ground state energy played with the highest bonding orbitals.

There are 2n C-C bonds in one of our conjugated rings. If each of these bonds are AVB bonds, we may combine the spin of all the "1" electrons to make a total spin S_1, and all the spin function for which:

$$(S_a + S_1)^2 = \tfrac{3}{2}n(\tfrac{3}{2}n+1) = (S_a+S_2)^2 \tag{7.10}$$

$$S^2 = 0$$

PART 2. THE METHOD

We may use the results of chapter IV, with p=n, and q=2n, to find the values of $S_{p,q}$, b, d, and the Λ that we want. We may use the R defined in equation 7.9 for this purpose.

The pi electron energy may be calculated as in chapter IV. There remains the σ-π interaction energy and the sigma energy. We divide the sigma energy into two parts. The first part, E_1^σ, is the energy of the isolated sigma bonds. The second part, E_2^σ , is the interaction energy between neighboring sigma bonds. The major part of E_2^σ that will concern us results from the exchange energy of two sigma electrons from neighboring bonds on the same atom. The sigma-pi interaction energy, $E^{\pi-\sigma}$, is dependent upon the exchange energy of two electrons on the same carbon atom.

PART 3. THE SIGMA ENERGY

Let:

$$E_s = \langle \sigma_s | H | \sigma_s \rangle \ , \ E_t = \langle \sigma_t | H | \sigma_t \rangle \tag{7.11}$$

$$E_1^\sigma = n(E_t+E_s) - n\lambda_\sigma(E_t-E_s) - n(1-\lambda_\sigma^2)(E_t-E_s)\cdot \Lambda_5^\sigma/\Lambda_0$$

Sigma-Sigma Bond Interaction Energy

A change of sign of Q_σ does not change E^σ. From this it follows that E_2^σ may be expanded in integral powers of R. We may divide E_2^σ into a coulomb part and an exchange part.

$$E_2^\sigma = E_{2\ \mathrm{coul}}^\sigma + E_{2\ \mathrm{exch}}^\sigma \tag{7.12}$$

Nomenclature

We will number the atomic sigma orbitals in the C-C bonds in serial order as we go about the ring, starting on an unstarred atom.

$$C \; 1 \; 2 \; C^* \; 3 \; 4 \; C \; 5 \; 6 \; C^*$$

Orbitals σ_{2m-1}, σ_{2m} form the m'th sigma bond, between carbon atoms m and m+1.

$$E^{\sigma}_{2\ \mathrm{coul}} = A_c + B_c R + C_c R^2 + \ldots\ldots \qquad (7.13)$$

The coefficient A_c is independent of λ_π, because when R=0, the sigma electron spins are decoupled from the pi electron spins. As R increases, charge moves from the bonds in toward the atomic centers. For this reason, B_c and C_c involve only integrals such as:

$$\left(S^2(\sigma_1\sigma_1+\sigma_2\sigma_2) - 2S(\sigma_1\sigma_2) \,\middle|\, \sigma_m\sigma_m \right) \qquad (7.14)$$

Here $S = \langle\sigma_1|\sigma_1\rangle$. (We are assuming that orbitals not sharing a common bond have zero overlap.)

The charge density on the left of the above integral behaves as a quadrapole, and the integral rapidly vanishes as σ_m moves away from bond "1." If σ_m is adjacent to bond "1," the integral is still small. We shall assume that B_c and C_c are small compared to dE^{σ}_1/dR.

$E_{2\ \mathrm{exch}}^{\sigma}$

For consistency it will be assumed that exchange integrals between sigma orbitals not sharing a common bond or atom are zero. With this assumption, the only exchange integral that appears in E_2^{σ} is the $(\sigma_2\sigma_3|\sigma_3\sigma_2) = J_{23}$ integral.

$$E_{2\ \mathrm{exch}}^{\sigma} = -nJ_{23}\Lambda_{\sigma}^{-1}\Big[(1+\lambda_{\sigma})^2(\Lambda_1^{\sigma-\sigma}+2\Lambda_2^{\sigma-\sigma}+\Lambda_3^{\sigma-\sigma})/N_s^2 + 4(1-\lambda_{\sigma}^2)(\Lambda_1^{\sigma-\sigma}+\Lambda_2^{\sigma-\sigma}+\Lambda_3^{\sigma-\sigma})/N_sN_t + (1-\lambda_{\sigma})^2(\Lambda_1^{\sigma-\sigma}-6\Lambda_2^{\sigma-\sigma}+\Lambda_3^{\sigma-\sigma})/N_t^2\Big] \quad (7.15)$$

J_{23} equals about 1.24 e.v. (Altmann (21))

PART 4. THE SIGMA-PI ENERGY

In the expression of the sigma-pi energy there occur coulomb and exchange integrals involving a pair of sigma orbitals, such as $\sigma_1\sigma_2$, or $\sigma_1\sigma_1$. We introduce operators to transform these orbitals.

$$T_1\ \sigma_1\sigma_1 = \tfrac{1}{2}(\sigma_1\sigma_1+\sigma_2\sigma_2) = T_1\ \sigma_2\sigma_2 \quad (7.16)$$

$$T_1\ \sigma_1\sigma_2 = \tfrac{1}{2}(\sigma_1\sigma_2+\sigma_2\sigma_1) = T_1\ \sigma_2\sigma_1$$

$$T_2\ \sigma_1\sigma_1 = \frac{1}{2}(\sigma_1\sigma_2+\sigma_2\sigma_1)S = T_2\ \sigma_2\sigma_2$$

$$T_2\ \sigma_1\sigma_2 = \frac{1}{2S}(\sigma_1\sigma_1+\sigma_2\sigma_2) = T_2\ \sigma_2\sigma_1$$

The sigma-pi energy may now be written as:

$$\begin{aligned}
E^{\sigma-\pi} = {} & 4n\Lambda_o^{-1}(T_1+(\sin 2\theta_\sigma)(1-T_1)/\sqrt{1-S^4} \\
& +(\lambda_\sigma - S^2)(T_2-S^2T_1)/(1-S^4)) \\
& \sum_K \Big\{\Lambda_1^{\pi-\sigma}((a_Ka_K/\sigma_1\sigma_1)+(\bar{a}_K\bar{a}_K/\sigma_1\sigma_1)-(a_K\sigma_1/\sigma_1a_K)) \\
& +\Lambda_2^{\pi-\sigma}((\bar{a}_K\sigma_1/\sigma_1\bar{a}_K)+\lambda_K((a_K\bar{a}_K/\sigma_2\sigma_2)+(\bar{a}_Ka_K/\sigma_1\sigma_1) \\
& -(a_K\sigma_1/\sigma_1\bar{a}_K)-(\bar{a}_K\sigma_2/\sigma_2a_K))+S((a_Ka_K/\sigma_1\sigma_2) \\
& +(\bar{a}_K\bar{a}_K/\sigma_2\sigma_1)-(a_K\sigma_1/\sigma_2a_K)-(\bar{a}_K\sigma_2/\sigma_1\bar{a}_K)) \\
& +S\lambda_K(a_K\sigma_1/\sigma_2\bar{a}_K))+\Lambda_3^{\pi-\sigma}\ S(2(a_K\bar{a}_K/\sigma_1\sigma_2) \\
& -(a_K\sigma_2/\sigma_1\bar{a}_K))\Big\}
\end{aligned} \tag{7.17}$$

PART 5. DISCUSSION

In chapter VII I have developed a method of working the sigma electrons into the AMO method. The method has involved using one variable parameter for the pi electrons, and a second for the sigma electrons. The sigma electron integrals required for a numerical calculation do not seem to be available at the moment, so no attempt at numerical calculation was made.

Certain hopeful features of the calculation stand out. If one were to treat a molecule in a doublet or triplet state, the alternant valence bonds would introduce spin density on to the protons and other nuclei in a natural way. The AVB approach may also be useful in understanding the proton-proton splittings of NMR.

SUMMARY AND CONCLUSIONS

It has been shown fairly conclusively that the annulenes do not undergo bond length alternation. The difficulty in calculating transition singlet energies seems to be connected with the electron correlation energy. The AMO method seems to make errors in the opposite direction by not giving sufficient electron correlation in the excited singlets. A set of empirical integrals were derived that should be superior to those of Pariser.

A method is developed to extend the AMO method to cover sigma as well as pi electrons.

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ABSTRACTS OF PROPOSITIONS

I. The time correlation function for blackbody radiation is calculated.

II. An improvement of the AMO theory is suggested.

III. A useful theorem for the calculation of spin densities is derived, with applications.

IV. A wave function for an electron in a noncoulombic potential is derived. The problem is related to the Mossbauer effect.

V. Spin densities for the lowest triplet state of naphthalene are calculated by a C. I. method. It is suggested that this state of napthalene is a prime candidate for spin density calculations by the AMO and other similar methods.

PROPOSITION I

COHERENCE PROPERTIES OF BLACKBODY RADIATION

The correlation of the electromagnetic field for blackbody radiation may be regarded as a model correlation problem in that it depends only on the statistical properties of photons, and admits of an exact solution.

Time correlations are usually assumed to be of exponential form, and are of greatest general interest. It then seems worthwhile to find the time correlation of the components of the electromagnetic field for blackbody radiation. I define:

$$w = \pi kT/\hbar$$

$$E_{ij}(t) = \left\langle E_i(t_o)\ E_j(t_o+t)\right\rangle$$

$L(x) = \mathrm{cotgh}(x) - 1/x$, the Langevin function of statistical mechanics.

Then:

$$E_{ij}(t) = -\delta_{ij}\, 8\hbar w^4\, L'''(wt)/9c^3$$

The derivation of this calculation is given by Bourret* with acknowledgment of my contribution. $E_{ij}(t)$ does not decay even approximately exponentially, and has a minimum at $wt=2.36$.

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*R.C. Bourret, Nouvo Cimento 18, 347-356 (1960)

PROPOSITION II

A REFINEMENT OF THE AMO THEORY IS PROPOSED

The standard AMO wave function consists of the antisymmetrized product of a set of spatial orbitals, a_K, multiplied by a projection of the spin function, δ_1.

In some systems a particular pair of electrons may have much stronger mutual correlation than either electron has with the rest of ths system. One example of this would be the two 1s electrons of the Lithium atom.

In such a system we would expect such an electron pair to act almost as a subsystem, with the spin of the electron pair being almost a good quantum number.

In the standard AMO method the projections of the spin operator δ_1 are in general not eigenfunctions of the spin of a particular pair of electrons. We may refine the standard AMO method by altering the expectation value of the spin of a pair of strongly interacting electrons. We accomplish this with a spatial permutation operator.

Suppose the standard AMO method puts the strongly interacting electrons into spatial orbitals a_i and $\bar{a}_i$. When the product $a_i\bar{a}_i$ appears in the AMO wave function, we replace it by $a_i\bar{a}_i+C_i\bar{a}_i a_i$. The value of the constant C_i is chosen so as to minimize the electronic energy of the system. If $C_i = 1$, the electron pair have pure singlet character. If $C_i = -1$, the electron pair have pure triplet character. Intermediate values of C_i give intermediate values for the expectation of ths spin of the electron pair.

I will first consider as an example of the method an electronic wave function for the Lithium atom with radial correlation.

In place of the 1s orbital I will use two orbitals, 1s' and $1\bar{s}'$, differing slightly from the best SCF 1s orbital. The 1s' orbital will have a greater density at the nucleus, and the $1\bar{s}'$ orbital will have a lesser density at the nucleus than the 1s orbital. The normal wave function one would construct is:

$$\Psi_1 = 1\bar{s}'1s'2s\ (\alpha\beta-\beta\alpha)\alpha$$

This wave function is better than the standard AMO wave function:

$$\Psi_2 = 1\bar{s}'1s'2s\ (2\beta\alpha\alpha-\alpha(\alpha\beta+\beta\alpha))$$

The first function is superior because the density at the nucleus of 1s electrons is much greater than that of 2s electrons.

The refined AMO wave function is:

$$\Psi_3 = (1\bar{s}'1s'+C_{1s}1s'1\bar{s}')2s\ (2\beta\alpha\alpha-\alpha(\alpha\beta+\beta\alpha))$$

If $C_{1s}=0$, Ψ_3 of course degenerates into Ψ_2. If $C_{1s}=1$, Ψ_3 becomes identical after antisymmetrization and normalization to Ψ_1, one would expect the optimum value of C_{1s} to lie nearer one than zero, so Ψ_3 would be a much better wave function than Ψ_2. It should also be superior to Ψ_2, since Ψ_3 allows some spin correlation between the 1s and 2s electrons.

As a second example, we consider the ground state of the allyl radical. Dearman and Lefebvre* made an AMO calculation for the allyl radical, and compared it to a C.I. calculation. They obtained:

$$\lambda_o = 0.66$$

One may work backward from the C.I. calculation to find both the standard AMO and refined AMO wave functions having the maximum overlap with the C.I. wave function. For the standard AMO wave function one gets essentially the AMO wave function of Dearman and Lefebvre; for the refined AMO wave function I obtain:

$$\lambda_o = 0.638; \; C_o = .061$$

There is an appreciable difference between the

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*H. H. Dearman and R. Lefebvre, J. Chem. Phys. <u>34</u>, 72 (1961).

refined and standard wave functions for the allyl radical that would show up in calculations of such quantities as spin density.

The acetylene molecule would be an ideal test case for our refined AMO method. The π_x and π_y orbitals each contain an electron pair. The electrons in each electron pair have a strong mutual correlation, but only a weak correlation with the other electron pair.

I will call the bonding π_x orbital π_x, and the antibonding π_x orbital $\bar{\pi}_x$. Then:

$$a_x = \cos\theta\,\pi_x + \sin\theta\,\bar{\pi}_x$$

$$\bar{a}_x = \cos\theta\,\pi_x - \sin\theta\,\bar{\pi}_x$$

The π_y and a_y are defined in the same way.

$$\Psi_{RAMO} = (a_x\bar{a}_x + C\bar{a}_x a_x)a_y\bar{a}_y(2\alpha\beta\alpha\beta - \alpha\alpha\beta\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + 2\beta\alpha\beta\alpha)$$

If C=1, Ψ_{RAMO} reduces to a function for two independent electron pair singlets.

The wave function is cylindrically symmetrical despite its asymetric appearance.

PROPOSITION III

A USEFUL THEOREM FOR THE CALCULATION OF SPIN DENSITIES IN DOUBLET STATES

Consider the matrix element:

$$J = \left\langle A \middle| S_{nz} \middle| B \right\rangle$$

S_{nz} is the spin operator that operates only on the spin of the n'th electron. A and B are doublet spin functions with spin "up."

$$S_z\, A = \tfrac{1}{2}A; \; S_z B = \tfrac{1}{2}B$$

We introduce a fictitious electron β, and a fictitious spin operator S_f that operates only on β. The spin of β is opposite to that of A.

$$S_{fz}\beta = -\tfrac{1}{2}\beta$$

Then:

$$J = -2 \left\langle B \middle| S_{nz} S_{fz} \middle| A \right\rangle$$

We now introduce the time inversion operator K.

$$J = -\left\langle (1+K)B \middle| (1+K) S_{nz} S_{fz} A \right\rangle$$

Since K commutes with $S_{nz}S_{fz}$, we may write:

$$J = -\left\langle (1+K)B\beta \middle| S_{nz}S_{fz} \middle| (1+K)A\beta \right\rangle$$

The spin functions $(1+K)B\beta$ and $(1+K)A\beta$ are singlets. I define:

$$(1+K)B\beta/\sqrt{2} = {}^1B; \quad (1+K)A\beta/\sqrt{2} = {}^1A$$

Then:

$$J = -\,2\left\langle {}^1B \middle| S_{nz}S_{fz} \middle| {}^1A \right\rangle$$

We may replace $S_{nz}S_{fz}$ by $\frac{1}{3}S_n \cdot S_f = \frac{1}{6}P_{nf} - \frac{1}{12}$

The operator P_{nf} permutes the spins of the n'th and f'th electrons.

Then:

$$J = \frac{1}{6}\left\langle {}^1B \middle| {}^1A \right\rangle - \frac{1}{3}\left\langle {}^1B \middle| P_{nf} \middle| {}^1A \right\rangle$$

The properties of the permutation operator are usually better known than those of the spin operator.

As an example, we may apply this theorem to the spin densities of a many-parameter AMO doublet wave function. The doublet consists of 2n-1 electrons plus one fictitious electron. For the convenience of notation, we consider the odd electron in the o m.o. to be paired with the fictitious electron ($\lambda_o=0$).

I shall use the notation of Swalen and de Heer in finding the matrix elements of the molecular orbital spin density.

$$P_{kk} = P_{\bar{k}\bar{k}} = -\frac{1}{3} + \frac{1}{3Nn}\sum_{u}\binom{n-1}{u}^{-1} {}^{k}S'_{u}$$

$$P_{oo} = -\frac{1}{3} + \frac{2}{3Nn}\sum_{u}\binom{n-1}{u}^{-1} S'_{u}$$

$$P_{k\bar{k}} = -\frac{1}{3Nn}(1-\lambda_k^2)^{1/2}\sum_{u}\binom{n-1}{u}^{-1} {}^{k}S'_{u}$$

$$N = \frac{1}{n+1}\sum_{u}\binom{n}{u}^{-1} S_{u}$$

The proof that the trace of this density matrix is unity is straightforward.

McConnell* etc., made an approximate spin density calculation for the perinaphthyl and triphenylmethyl radicals with a one-parameter AMO function. The approximation used has been questioned by Lowdin,** etc. I have found by the use of the above spin density matrix that McConnell's results for the perinaphthyl radical are entirely correct.

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*R. Lefebvre, H. H. Dearman, and H. M. McConnell, J. Chem. Phys. 32, 176 (1960).

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PROPOSITION IV

WAVE FUNCTIONS FOR A NONCOULOMBIC POTENTIAL

In the Mossbauer effect, a splitting occurs because the nucleus changes size during emmission and absorption. This change in nuclear size changes the binding energy of the electrons, and leads to the observed splitting if the chemical environment of the emmitting and absorbing nuclei are different.

The nuclear size effect is usually treated by a simple minded first order perturbation technic, but it might be worthwhile to calculate an exact schodinger wave function for an atom with a finite nucleus. I will regard the energy eigenvalues to be fixed by a boundary condition near the nucleus. The problem will then be to calculate the wave function in the coulombic field outside the boundary. One could equally well use the same method to calculate the wave function of an outer electron with the nucleus partially shielded by inner electrons.

For orbitals other than the s orbitals, the density near the nucleus is small, so a change in the potential near the origin will have little effect. We will therefore only treat s orbitals. We define:

$\hbar w = (-2mE)^{1/2}$; $u = -Zw/2E$

$x = 2wr$; N is the integer such that $u-1 < N \leq u$

$\delta = u-N$

$\psi_u = P_u \, e^{-x/2}$

In order to obtain a convergent expression for P_u, P_u must be broken into two parts:

$$P_u = P_{u1} + P_{u2}$$

$$P_{u1} = R\,\Gamma(2-\delta) \sum_{n=0}^{N} (-)^n \left(\Gamma(u-n)\, \Gamma(u-n+1)\; n! \right)^{-1} \cdot x^{u-n-1}$$

$$P_{u2} = R(-)^N \left(\Gamma(\delta-1) \right)^{-1} \int_0^\infty dp \; e^{-xp} \left[-\left(\frac{p+1}{p}\right)^u \Big/ \Gamma(u+1) + \sum_{n=0}^{N} p^{n-u} / (n!\, \Gamma(u-n+1)) \right]$$

P_{u2} will be proportional to δ when δ is small, because of the factor $(\Gamma(\delta-1))^{-1}$. R is the normalization factor.

The integrand of P_{u2} is well behaved for all values of p, so there is no question of convergence. Both P_u exhibit singularities at the nucleus, but not essential singularities. When u is an integer ψ_u becomes the

Ns orbital.

The simple perturbation theory makes δ proportional to the square of the nuclear radius. As the singularities in both P_u are proportional to δ, and no stronger than $1/r$, the wave function at the surface of the nucleus will not be greatly perturbed.

PROPOSITION V

TRIPLET SPIN DENSITIES IN NAPHTHALENE

It is proposed that more work should be done in the theoretical calculation of spin densities. To learn the capabilities and limitations of each method, it is necessary to calculate spin densities of doublet and triplet states, by a variety of methods. The $^3B_{2u}^+$ state of napthalene has certain advantages for this purpose. First, it is accessible to experiment, being the lowest triplet. Naphthalene is of sufficiently low symmetry to have several different spin densities on experimentally accessible atoms, yet is of sufficiently high symmetry to ease the labor of calculations.

The $^3B_{2u}^+$ state is also the state most accessible to AMO calculations. The calculation one should do first is a simple, standard configuration interaction calculation. The calculation will be based on that of Pariser (1), but I will include some of the more important doubly excited states. The configurations I will use are labeled as follows:

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(1) R. Pariser, J. Chem. Phys. 24, 250 (1956).

Label	Configuration	
55	55'	$\alpha\alpha$
44	44'	$\alpha\alpha$
33	33'	$\alpha\alpha$
41	(41'+14')	$\alpha\alpha/\sqrt{2}$
22	22'	$\alpha\alpha$
11	11'	$\alpha\alpha$
25	$(255'5')\alpha\alpha\alpha\beta-5'2'\alpha\alpha$	
34	$55'(34'+43')\frac{1}{8}(\alpha\alpha(\alpha\beta+\beta\alpha)$ $-(\alpha\beta+\beta\alpha)\alpha\alpha)$	
13	55'(13'+31')" " " " " "	

The notation follows that of Pariser; paired bonding orbitals are not explicitly represented.

The contributions of the first 6 configurations have been worked out by Pariser. In the second part of the seventh configuration, both electrons came from the 5 MO.

The 55 configuration is by far the most important, and will be defined to have the zero point energy.

$$\langle 55|H|25\rangle = I_{25'} + \langle 25'|1\rangle - \sum_{f}\langle 2f|f5'\rangle + \langle 25|55'\rangle$$

$$E_{25} = I_{5'5'} - I_{22} + \langle 5'5'/1\rangle - \langle 22/1\rangle - \langle 22|5'5'\rangle$$

$$+ \sum_{f} \langle 2f|f2\rangle - \langle 5'f|f5'\rangle$$
$$+ \langle 5'5|55'\rangle + \langle 5'2|25'\rangle - \langle 25|52\rangle$$

$$\langle 55|H|34\rangle = \langle 54'|35\rangle + \langle 54|35'\rangle$$

$$E_{34} = I_{4'4'} - I_{33} + \langle 4'4'|1\rangle - \langle 33|1\rangle - \langle 33|4'4'\rangle$$
$$+ \langle 4'5|54'\rangle + \langle 5'3|35'\rangle$$
$$+ \sum_{f} \langle 3f|f3\rangle - \langle 4'f|f4'\rangle$$

The equations for the 13 configurations are similiar to the 34 equations, and will be ommitted.

The molecular integrals were calculated from the integrals tabulated by Pariser (1). For the wave function of the ${}^{3}B^{+}_{2u}$ state I obtain:

$$\Psi = .90\,|55\rangle + .201\,|44\rangle + .269\,|33\rangle$$
$$+ .0314\,|41\rangle + .170\,|22\rangle + .084\,|11\rangle$$
$$+ .079\,|13\rangle - .139\,|34\rangle - .115\,|25\rangle$$

The spin densities on the α, β, and γ carbon atoms are:

$$p_{\alpha} = .160 \;;\; p_{\beta} = .101 \;;\; p_{\gamma} = -.022$$

This calculation includes all the symmetry allowed singly excited configurations, and those doubly excited configurations that have a connection to the dominant 55 configuration through the spin density matrix. By including the doubly excited configurations I allow for the possibility of negative spin densities. The neglected doubly excited configurations should have little influence on the spin densities because they are of low amplitude and do not couple through the spin density matrix with any high amplitude configurations.