FREE-ELECTRON NETWORK MODEL FOR CONJUGATED SYSTEMS. II. NUMERICAL CALCULATIONS[†]

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ABSTRACT

Numerical calculations are carried out on a large number of aromatic- and polyene-type conjugated molecules by the methods of the first paper of this series. These calculations include all energy levels, the wavelengths of the first four electronic transitions, the complete π-electron wavefunctions, the bond densities and bond orders, free valence and reactivities, and dipole moments. A method of estimation of bond lengths with a root mean square error of 0.016Å is presented. Wherever possible comparisons are made with experiment and with the results of the LCAO molecular orbital theory in the approximation developed by Coulson and Longuet-Higgins. The results in general are at least as good as those of the LCAO calculations.

THE FIRST PAPER of the present series[1] has presented a detailed consistent mathematical framework for the application of the free-electron model to conjugated π-electron systems. The present paper presents the results of a series of calculations designed to demonstrate the applicability and test the potentialities of the free-electron model.

Many of the previous theoretical calculations on conjugated hydrocarbons have been done by the LCAO (linear combination of atomic orbitals) molecular orbital theory in the approximation developed by Coulson and Longuet-Higgins.[2] It is emphasized that this method will be referred to throughout this paper as the LCAO method, and that this abbreviation will refer only to the Coulson-Longuet-Higgins approximation just mentioned. It has been pointed out in I that the LCAO three-dimensional, one-electron model actually closely approximates a one-dimensional model, such as the present theory, so it is not surprising that there exists a very close equivalence between LCAO results and the results of the present paper. For this reason a detailed

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[†] This work was assisted in part by the Office of Naval Research under Task Order IX of Contract N6ori-20 with The University of Chicago.

[1] K. Ruedenberg and C. W. Scherr, J. Chem. Phys. 21, 000 (1953), hereinafter referred to as I.

[2] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A191, 39 (1947).

comparison of the two theories is presented at the end of this report.

The complete π-electron wavefunctions for each of the molecules considered here are presented. These wavefunctions will be useful to calculate the π-electron density at any point, to make perturbation treatments, and to calculate oscillator strengths of the electronic transitions.

In referring to particular atoms, the standard organic numbering, as indicated on Fig. 1, part (a), is followed; bonds are referred to by their terminal atoms. For example the bond connecting the α and β positions in naphthalene is referred to as bond 1–2.

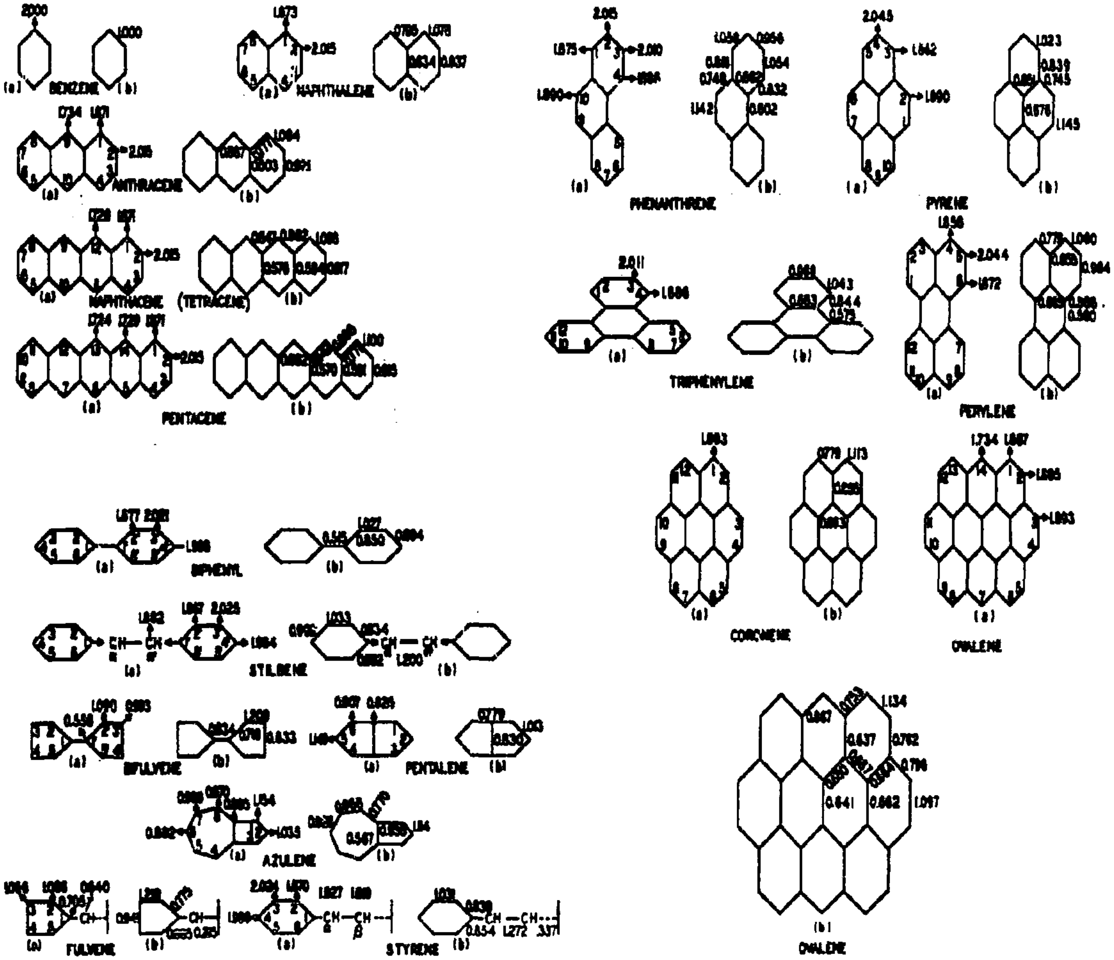

Fig. 1. Bond densities and bound valences. The members of each pair marked (a) present the bound valences of the atoms indicated. The members marked (b) present the total mobile bond densities. The bound valences for joint atoms of the alternant molecules are not presented; they are generally greater than 2.0, usually around 2.3.

1. THE SECULAR EQUATION AND THE ENERGY LEVELS

No particular difficulty was encountered in solving the secular equations for the eigenvalues. The largest determinant after factorization according to symmetry species was 9×9 (ovalene). The first $\underline{n}$ energy levels ($\underline{n}$ is the number of π-electrons) and their symmetries are presented in Table I. The remaining levels and their symmetries are trivially found from these tabulated values. By the pairing theorem for energy levels of alternant molecules (see paper I), for every solution κ_i, where

$$\left.\begin{aligned} \kappa_i &= 2\pi D/\lambda_i\ , \\ D &= \text{the internuclear distance,} \\ \text{and} \qquad \lambda_i &= \text{the wavelength of } \phi_i\text{, the } \underline{i}\text{th } \pi\text{-electron wavefunction,} \end{aligned}\right\} \qquad (1)$$

there exist solutions $\kappa_{mn\pm i} = m\pi\pm\kappa_i$ where $\underline{m}$ may take any integral value, positive or negative, or zero and with the restriction that $\kappa_{mn\pm i} > 0$. The $\underline{i}$th level between $m\pi$ and $(m+1)\pi$ (altogether the $(mn+i)$th level) has the same symmetry as the $\underline{i}$th level between zero and π; the energy relation being, as indicated above, $\kappa_{mn+i} = m\pi+\kappa_i$. The energy levels of nonalternant molecules are not mirrored at half-integral multiples of π; that is, for every κ_i there only exist solutions $\kappa_{mn+i} = m\pi+\kappa_i$, $m = 0, \pm1, \pm2\cdots$.

Instead of κ_i, the value actually entered in Table I is $\cos\kappa_i$. The symmetries tabulated refer to the axes of Fig. 2 and are convenient for purposes of calculation.

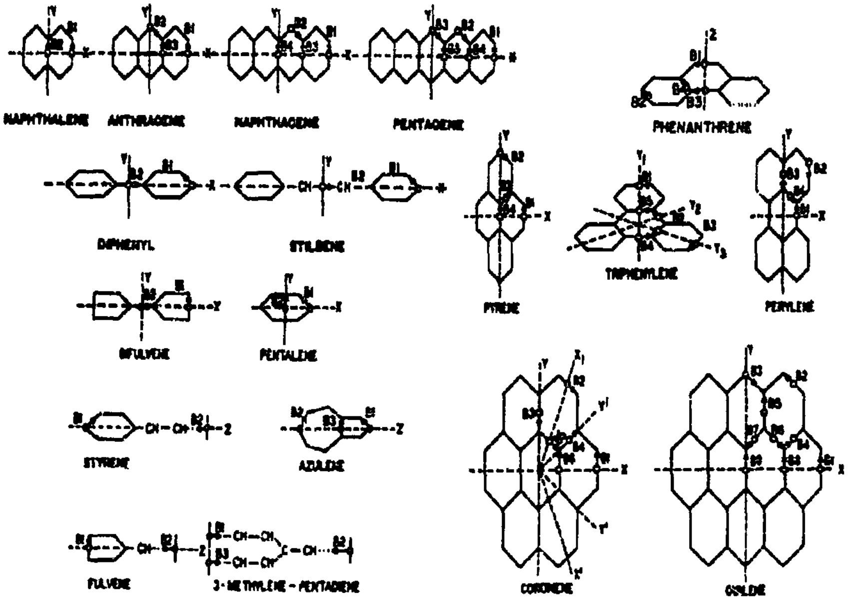

Fig. 2. The arbitrary coordinates.

The group theory notation is also referred to these same axes.[3]

2. THE WAVEFUNCTIONS

The wavefunction of the *i*th orbital, ϕ_i, may be represented by

$$\phi_i = \sum_B \phi_{Bi} , \qquad (2)$$

where ϕ_{Bi} is that part of ϕ_i located on branch *B* and is zero elsewhere. Each ϕ_{Bi}, then, is of the form

$$\phi_{Bi} = a_{Bi} \cos(\kappa_i x + \delta_{Bi}), \qquad (2a)$$

where δ_{Bi} is the phase of ϕ_{Bi} referred to an (arbitrary) coordinate axis located on branch *B*.

The complete π-electron wavefunctions of all molecules considered in this paper are presented in Tables I, II, and III. Table I lists $\cos\kappa_i$, Table II lists $a_{Bi}{}^2$, and Table III lists $\tan\delta_{Bi}$. Figure 2 depicts the numbering of the branches and the origins of the x_B's. The bases of the arrows are the origins, and the heads indicate the direction of positive x_B. In no calculations, except those of the spectral lines, was it necessary to know κ_i or δ_{Bi} explicitly.[4] Wherever the phase is obvious by a symmetry consideration, no entry has been made in Table III.

There are two methods, described in the Appendix, which may be employed to find the wavefunctions. The first method consists of solving for $a_{Bi}{}^2$ and $\tan\delta_{Bi}$ directly from the joint conditions [I, Eqs. (1.32), (1.33), and (1.34)] and from Eq. (2.7) of I. The second method consists of finding the eigenvectors of the secular equations by the usual methods, [see I, particularly Eqs. (2.56) and (2.57)] as in LCAO calculations. The first method is generally most convenient if the molecule possesses symmetry. The second is generally more convenient if the molecule is large and/or possesses little or no symmetry The only molecule for which the second method was used in the present calculations is ovalene.

The second method only gives the value of the wavefunction at the atoms. The π-electron density at the mid-point of a bond is found from:

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[3] The *Z* axis is always taken perpendicular to and out of the plane of the paper except for molecules with C_{2v} symmetry, where the *Z* axis is as indicated in Fig. 2 and the *X* axis is perpendicular to the plane of the paper. The orbitals are antisymmetric with respect to σ_h, designating reflection at the plane of the molecule.

[4] The phase angle is arbitrary by an additive factor $\pm m\pi$, m integral. One takes $\pi/2 \geq \delta_{Bi} > -\pi/2$.

value of ϕ_i at bond r–s, $$\phi_i(r\text{–}s) = \frac{\phi_i(r)+\phi_i(s)}{2\cos\frac{1}{2}\kappa_i}. \qquad (3a)$$

The quantities of Tables II and III are then found from

$$\tan\delta_{Bi} = \frac{\phi_{Bi}{}^2(-\kappa_{i/2}) - \phi_{Bi}{}^2(+\kappa_{i/2})}{2(\sin\kappa_i)\phi_{Bi}{}^2(0)} \qquad (3b)$$

and

$$a_{Bi}{}^2 = (1+\tan^2\delta_{Bi})\phi_{Bi}{}^2(0)\ , \qquad (3c)$$

where $\phi_i(r)$ is the value of the ith orbital at atom r, for example, and in (3b) and (3c) $\phi_i(x)$ is its value in branch B at coordinate x.

3. SPECTRA

The wavelengths of radiation for the four transitions between the two highest filled and the two lowest unfilled energy levels are presented in Table IV. The nomenclature and assignment is due to Platt and Klevens.[5] These wavelengths are compared with the center of gravity of the corresponding singlets and triplets.[6] Unfortunately, most of these triplet data are estimates. Where the estimates of the triplets were not available, only the singlets are listed. There will, of course, always be triplets, which generally lie in such a direction as to improve the agreement of the theoretical calculations. Some corresponding LCAO calculations[5] are also tabulated for comparison.

The free-electron model (and the LCAO model) gives agreement to within 10,000cm^{-1}, usually better. Indeed the prediction of the longest wavelength transition is generally quite good. These results are the more remarkable when one considers that there is only one (quasi-) adjustable parameter in the free-electron model, D, the internuclear distance. Actually, no attempt at adjustment was made; D has been taken to be 1.39Å (the benzene C–C distance) in the aromatic systems, and, 1.34Å (the ethylene C–C distance) in the n-polyenes. When comparing the LCAO model predictions with the free-electron model predictions, it should be borne in mind that in the former there are two adjustable parameters, S and β; S is usually fixed at about 0.25, and β is varied to give a best fit.

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[5] H. B. Klevens and J. R. Platt, J. Chem. Phys. 17, 470 (1949); J. R. Platt, J. Chem. Phys. 18, 1168 (1950).

[6] K. Ruedenberg and J. R. Platt, private communication.

4. BOND DENSITIES

The total mobile bond order, defined by Coulson and Longuet-Higgins[1] for their LCAO theory would be, in free-electron terms, as follows:

$$p_{rs} = 2 \sum_{j=1}^{n/2} \phi_j(r)\phi_j(s) \ , \tag{4}$$

where p_{rs} is the total mobile bond order of bond r–s, *j* refers to the orbital and $\phi_j(r)$ and $\phi_j(s)$ are the values of the *j*th orbital wavefunction at atoms *r* and *s*, respectively. This definition is an approximation to the electron density in the bond.

The total mobile bond density for the free-electron model is defined by

$$b(rs) = 2 \sum_{j=1}^{n/2} \phi_j^2(r{-}s) \ , \tag{5}$$

where $\phi_j(r{-}s)$ is the value of the *j*th orbital at the midpoint of bond r–s. This definition is also an approximation to the electron density in the bond which, however, is consistent with the definition of the electron density at the atoms. For comparison with Eq. (4), Eq. (5) may be written approximately as

$$b(rs) \approx f\left[\tfrac{1}{2} + \sum_{j=1}^{n/2} \phi_j(r)\phi_j(s)\right] \ , \tag{6}$$

where *f* is some constant, equivalent to a mean value of $1/\cos^2\tfrac{1}{2}\kappa_1$, and may be taken as ≈ 1.25. It would seem that the most exact, but probably unnecessary, definition for the electron density would be an integrated density extending half a bond length to either side of the point in question.

The bond densities calculated from Eq. (5) are presented in Figs. 1 and 3, part (b).

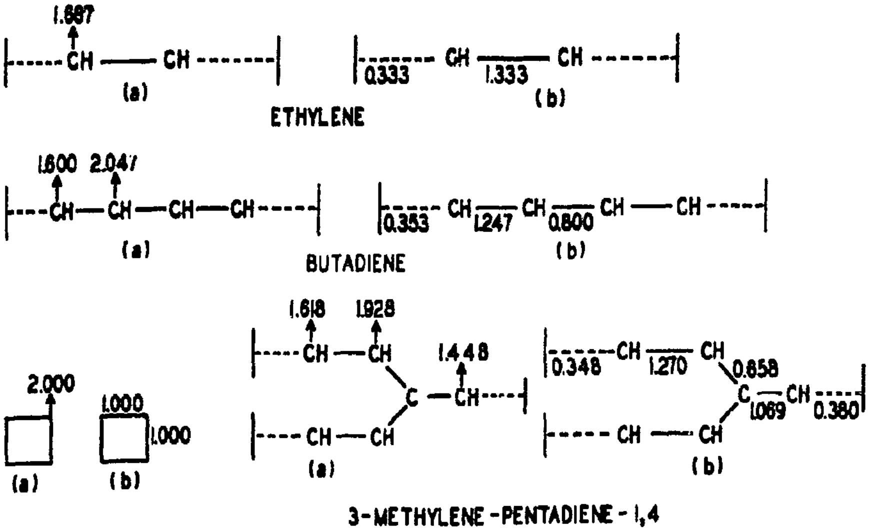

Fig. 3

5. BOUND VALENCE AND REACTIVITIES

Coulson and Longuet-Higgins[7] have defined a useful quantity, *the free valence*, which has been successfully correlated by many authors with chemical reactivity. It is a second-order effect which becomes of importance in alternant hydrocarbons because the "electron density" at the atoms (the first-order effect) is the same (but *v.i.*). The free valence is the potential bond-forming power a particular atom in a molecule has. The free valence is obtained by forming the sum of the bond orders of the bonds terminating on the atom under consideration and then subtracting this sum from a certain number, N_{max}. N_{max} is obtained in the following manner: If one were to have available calculations on all possible hydrocarbons, then he would be able to pick out the maximum possible value for the sum just mentioned above. This maximum value is taken to be N_{max}. Analytically the

$$\text{free valence of atom } r = N_{max} - \sum_{\substack{\text{all } s \text{ neighboring} \\ \text{to } r}} p_{rs}$$

This concept may be taken over, *in toto*, into the free-electron picture. The present author has chosen to tabulate merely the sums of the bond densities, and in order to indicate the complementary nature of these sums to the free valence, has called them, following a suggestion of Ruedenberg's, *the bound valence*. Hence, the smaller the bound valence, the more reactive the atom (to electrophilic reagents). These *bound valences* are presented in Figs. 1 and 3. The base of the arrows indicates the corresponding atom.

In the first paragraph of this section it has been mentioned that the first-order effect for reactivities is the "electron *density*"; however, it should be noted that the LCAO model has tacitly implied that the first-order effect is due to the electron *population* (see paper I, since to the author's knowledge this distinction between density and population has never been made before). This point is being investigated further. In this paper once D has been taken as the unit of length there is no numerical difference between density and population for bond or for non-joint atom densities. At the joints the population is $\frac{3}{2}$ of the density. No *bound valences* are reported for joint atoms (they are generally greater than 2.0, usually around 2.3). In nonalternant molecules, it is the total electron density at the atoms which is reported rather than the *bound valence*.

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[7] C. A. Coulson and H. C. Longuet-Higgins, *Rev. Scientifique* *85*, 929 (1947).

Table V compares the (theoretically) most reactive atoms in each molecule with the known chemistry of the hydrocarbons. The only serious discrepancy with experiment is found in the phenanthrene molecule, where the 1,8 positions are indicated to be slightly more reactive than the 9,10 positions. If one attempts to explain this by noticing that there is an over-all very high concentration of π-electron density about the 9,10 positions (*i.e.*, atoms 9 and 10 contiguous and connected by the very high density 9–10 bond) then a difficulty arises in explaining why the somewhat similar pyrene molecule is not reactive at the pyrene 1,2 positions. An exactly similar difficulty is encountered in the LCAO model.

6. DIPOLE MOMENTS

Of all the molecules considered here, only fulvene and azulene can (theoretically) have dipole moments, and indeed, this is an experimental fact, that alternant hydrocarbons have at most, small dipole moments. The calculated moments are: Fulvene 4.4 D (Debyes); azulene 6.3 D. These may be compared with the (unrefined) LCAO values of 4.8 D and 6.9 D, respectively.[8] Experimentally, fulvene would be expected to have a dipole moment of about 1.2 D on the basis of the dipole moments of its derivatives, while that of azulene is of the order of unity.[8] There are many well-known reasons for these discrepancies among which the σ-electron contribution to the dipole moment and the effect of the true bond length should be mentioned.

7. BOND LENGTHS

Coulson[9] has successfully demonstrated that on the basis of the total π-electron density (Coulson's total mobile bond order) at the bonds, predictions of the bond lengths in these molecules can be made which agree fairly well with experiment; usually within the experimental error. The present author has found the following, completely empirical equation to be satisfactory for use with the bond densities calculated on the basis of the free-electron model. It reproduces the known bond lengths with a root mean square deviation of 0.016Å:

$$\text{length of bond } r\text{–}s(\text{A}) = 1.665 - 0.1398[1+b(rs)] \quad . \tag{7}$$

Equation (7) has been obtained from the curve of Fig. 4. Figure 4 is analogous to the well-known figure due to Coulson[9] constructed on the basis of the LCAO model results,

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[8] LCAO data taken from B. Pullman and A. Pullman, *Les théories électroniques de la chimie organique* (Masson and Company: Paris, 1952), pp. 399 and 406.

[9] C. A. Coulson, *Proc. Roy. Soc.* (London) *A207*, 91 (1951), and also in *J. Phys. Chem.* *56*, 311 (1952).

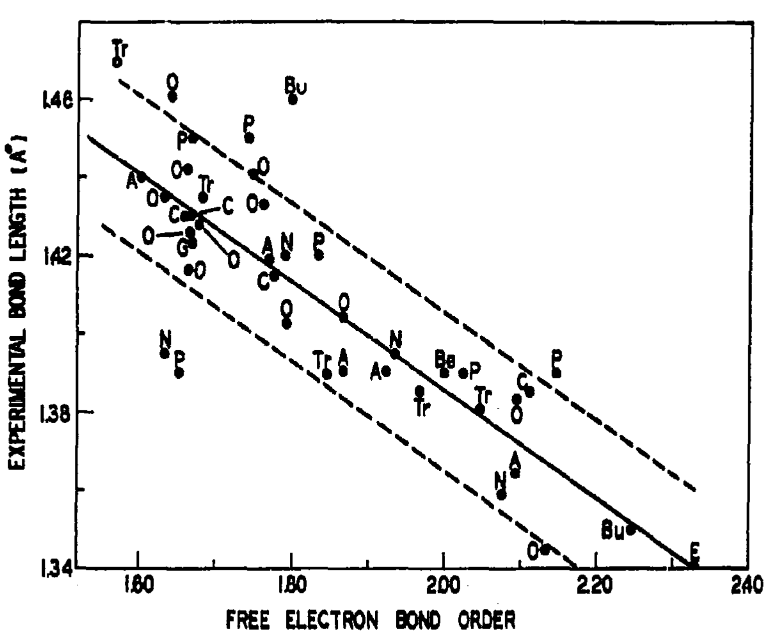

Fig. 4. This curve shows the relationship between the calculated total mobile bond density and the experimental data now available. A, anthracene; Be, benzene; Bu, butadiene; C, coronene; G, graphite; N, naphthalene, O, ovalene; P, pyrene; Tr, triphenylene; and E, ethylene.

and indeed, the present Fig. 4 is constructed to facilitate comparison. Experimental bond lengths are plotted against calculated bond densities. The solid line is a straight line which can be drawn through the points.[10] The dashed lines represent 0.020Å deviations from the solid line, and correspond to the experimental error for most of the molecules considered. The present author has calculated the root mean square deviations on both Fig. 4 and the analogous plot of Coulson.[11] These deviations are, for the free-electron model, 0.016Å; LCAO, 0.018Å. Table VI presents a breakdown of these figures.[12] The predictions of bond lengths by the free-electron model are

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[10] A better fit to the experimental data could perhaps be obtained if one disregards the somewhat doubtful polyene points and the certainly dubious pyrene points. Because of this uncertainty of how to weight the experimental data, the best line has been estimated by an inspection.

[11] The bulk of the necessary data is taken from J. M. Robertson, Proc. Roy. Soc. (London) A207, 101 (1951). It has been necessary to make a few corrections to these data; see, for example, note b to Table VI.

[12] The experimental lengths for butadiene, and in particular the 1-2 bond (1.46Å), are somewhat dubious. [See, e.g., Coulson, and Daudel, and Robertson, Proc. Roy. Soc. (London) A207, 311 (1951).] For a discussion of the polyene bond lengths from a free-electron point of view see H. Kuhn, J. Chem. Phys. 16, 840 (1948); 17, 1198 (1949). See also Noel S. Bayliss, Aust. J. Sci. Res. A4, 344 (1951), and earlier references given there; his treatment does not conform to that of the present paper. For these and other reasons the butadiene point was not included in this calculation. With this point in they become: free-electron 0.017Å; LCAO unchanged.

consistently better than the predictions by the LCAO model.

8. DISCUSSION OF SPECIAL POINTS

Detailed calculations on a series of n-polyenes has not been given. One may conveniently find the total mobile bond density from the following formula:

$$b(rs)_{s=r+1} = 1 - \frac{(-1)^r}{(n+1)\ \sin\{\pi(r+\frac{1}{2})/(n+1)\}} , \qquad (8)$$

where r in Eq. (8) is the systematic number of the rth atom, and n is the number of atoms in the polyene chain. This equation clearly shows the "alternating single and double bonds" of polyene chains. It also shows that the strongest bond in any n-polyene is the 1-2 bond and its sister, the (n-1)-n bond. The formula implies that very long chains would show only a slight conjugation effect.

In the cyclo-butadiene molecule there exists a filled level, $\kappa_2 = \frac{1}{2}\pi$, degenerate with the lowest unfilled level, and, hence, cyclo-butadiene has a triplet ground state.[13] Properly speaking, that is, there are two half-filled orbitals in the ground state, and Eq. (5) must be used in its general form,

$$b(rs) = \sum_{j=1}^{\infty} n_j \phi_j^{\,2}(r-s) , \qquad (5a)$$

where n_j is the number of π-electrons in the jth orbital. Longuet-Higgins[14] has considered the following three hypothetical hydrocarbons from the LCAO approach which also have, on that model, a triplet ground state; 1,3-$(CH_2)_2C_6H_4$, and 1,1-$(CH_2)_2C = CH_2$, Clar's hydrocarbon,[15] none of which have a Kekule structure, but all of which have unstrained σ-bonds and an even number of π-electrons. As might be expected, all three of these also have a triplet ground state on the basis of the free-electron model calculations.

The lowest bound valence in the cata-condensed ring systems considered here was found in pentacene, which agrees with the observation that the higher members of the polyacene series are not only highly unstable, but progressively more unstable.

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[13] See for example, C. A. Coulson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. 36, 193 (1940), p. 198.

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

[15] E. Clar, Aromatische Kohlenwasserstoffe (Verlag. Julius Springer: Berlin, 1941), p. 311. This hydrocarbon consists of six benzene rings, peri-condensed into an equilateral triangle.

9. A COMPARISON WITH THE LCAO MODEL

A general statement can be made concerning the comparison of the LCAO model of Coulson and Longuet-Higgins and the free-electron model on the basis of the calculations carried out here; namely, that the free-electron model predictions are equivalent to or slightly better than the LCAO results. The superiority is slight and may not be real.

Specifically, the accuracy of the predictions of spectra seems to be about equal, particularly when the center of gravity of the singlet and triplet lines are considered. This equality actually is in favor of the free-electron model, since (in the present calculations) no parameter has been varied in order to give optimal fit, whereas in the LCAO calculations at least one of the available parameters has been freely adjusted to give optimal fit.

The relative bond densities in any series of related bonds are both qualitatively and quantitatively reproduced with amazing fidelity in the two theories, despite their divergent approaches. Figure 5 shows the LCAO bond orders[8] plotted against the free-

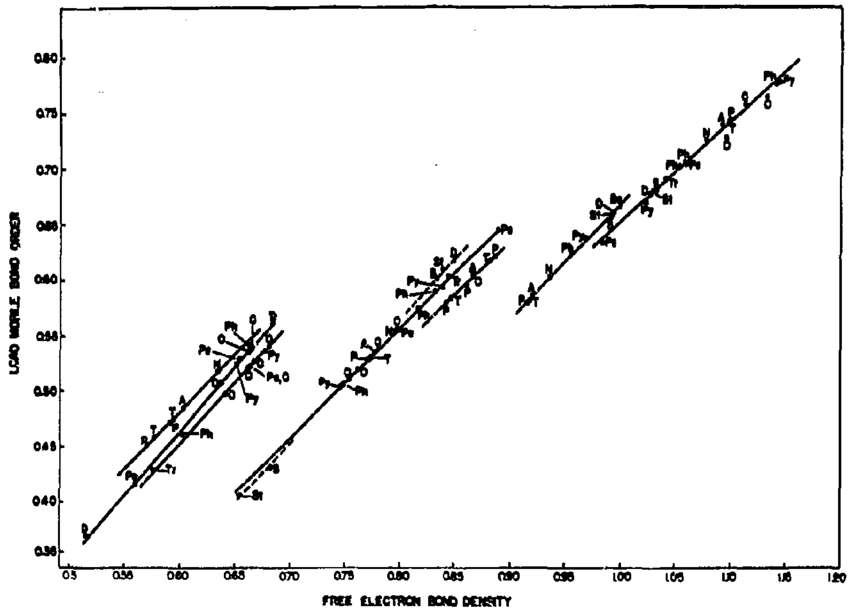

Fig. 5. These curves indicate the close correspondence of the free-electron model and the LCAO model calculated bond densities (orders) for alternant molecules; both coordinates to the same scale. A, anthracene; Be, benzene; C, coronene; D, diphenyl; N, naphthalene; O, ovalene; P, pentacene; Pe, perylene; Ph, phenanthrene; Py, pyrene; S, stilbene· St, styrene; T, tetracene; and Tr, triphenylene.

electron bond densities, both to the same scale. The points closely align themselves, according to broad generalizations of bond type (terminating in two joints; terminating in one joint, etc.), on lines whose slopes are very close to unity. The deviations of the points from these straight lines rarely exceeds 0.02 density units, much too small to be decisive in comparisons with experiment. However, there do exist certain differences which can be subjected to experimental test; whenever a point on a left-lying line is higher than a point on a right-lying line (of Fig. 5), then the relative bond lengths of the bonds involved are reversed in the two theories. Such pairs of points will be particularly decisive when they include bonds from the same molecule. The present experimental data however are not precise enough to differentiate and could only permit such comparisons to indicate a trend.

Nevertheless, in predictions of bond lengths based on these electron densities the free-electron model is superior. In the important case of the naphthalene molecule, important because of the high degree of precision claimed for the x-ray investigation, both models give unsatisfactory predictions. The root mean square deviations for this molecule are: Free-electron model 0.023Å; LCAO 0.025Å. It has been pointed out in Table VI that the LCAO root mean square deviation of 0.018Å claimed[9, 11, 16] for the LCAO predictions of the bond lengths in this molecule is obtained, not from Coulson's graph,[9] but from a special graph[16] which heavily weights the naphthalene, the anthracene, and the graphite predictions. These very poor root mean square deviations are directly attributable to their (almost identically) poor prediction of the length of the cross-linked bond.[17] As has been discussed elsewhere[11, 16] it is this particular bond which is subject to an experimental error about twice those of the other three bonds in naphthalene.

There is a possible fruitful field of comparison of bond length predictions. As can be clearly seen in Fig. 6, the predictions of bond lengths in the odd-membered ring systems by the two theories are widely divergent. Even comparatively rough bond length measurements on azulene would suffice for a discrimination.[18]

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[16] Coulson, Daudel, and Robertson, Proc. Roy. Soc. (London) A207, 306 (1951).

[17] The value predicted by both models is about 1.437Å, which value seems to be more reasonable, on the basis of a comparison with the similar bond in anthracene (1.440Å) than the experimental value (1.395Å) of reference 11.

[18] Dr. Heilbronner (ETH, Zurich) has kindly supplied the author with some advanced tentative results of electron diffraction measurements made on the azulene molecule, which indicate that the cross-linked bond in azulene is about 1.45Å. Free-electron

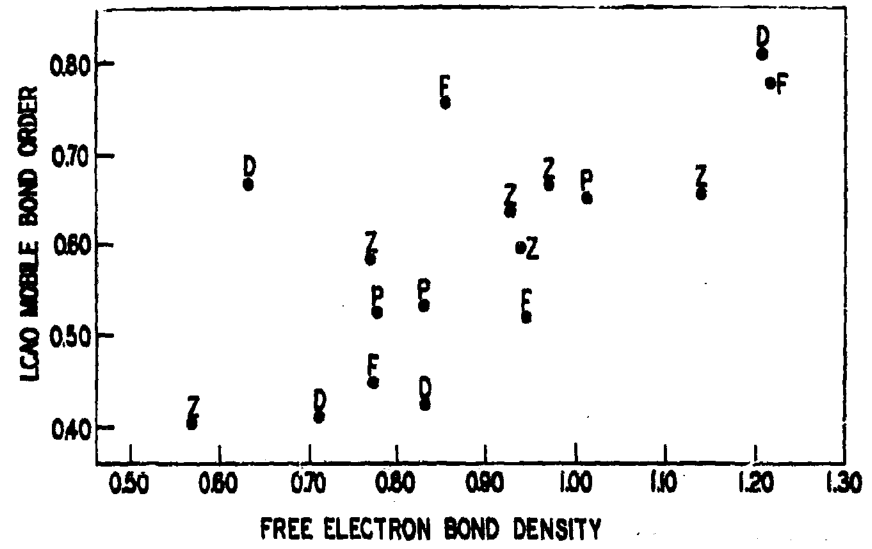

Fig. 6. This plot shows the lack of correspondence of the free-electron model and the LCAO model calculations of the bond densities (orders) for nonalternant molecules; both coordinates to the same scale. D, difulvene; F, fulvene; P, pentalene; Z, azulene.

A comparison of the physical labor involved in solving molecular problems by the two methods is difficult to make. The time involved for a complete calculation on one molecule ran from one minute for the polyenes through four and a half hours for pentacene to six days for ovalene.

10. CONCLUSION

The free-electron model has been shown to be a versatile and respectable tool for use in the investigation of molecular structure. It is capable of extension to other systems of interest than those considered here and seems to be capable of extension to include electron interaction; it deserves more attention than has hitherto been given to it. It seems quite reasonable to expect that the theory may be refined to the same degree as the LCAO model theory. On the other hand, the free-electron model seems to have the same limitations and inaccuracies that the LCAO method has, and further its present treatment of polyenes is unsatisfactory.

ACKNOWLEDGMENT

The author would like to thank Professor J. R. Platt for suggesting this problem, and for his continued helpful interest.

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model prediction 1.446Å; LCAO, from reference 9, greater than 1.49; LCAO from reference 16, about 1.45.

TABLE I

THE π-ELECTRON WAVEFUNCTIONS: $\cos\kappa_i$

The symmetries (SS, SA, *etc.*) and the group theory notation refer to the axes of Fig. 2. The symmetries indicate the behavior of the orbital upon reflection at the plane of the molecule, taken in the order X, Y. Hence, AS would mean antisymmetric upon reflection at the XZ plane, symmetric upon reflection at the YZ plane; S^3A^3, symmetric upon reflection at any of three equivalent XZ planes, antisymmetric at any of three equivalent YZ planes. A single letter (*e.g.*, in molecules with C_{2v} symmetry) indicates the behavior upon reflection at the Z axis (at the XZ plane).

Benzene		D_{6h}
1. S^3S^3	A_{2u}	1.0
2. AS	E_{1g}	0.5
3. SA		
4. AA	E_{2u}	-0.5
5. SS		
6. A^3S^3	B_{2g}	-1.0
7. S^3A^3	B_{1g}	-1.0

Naphthalene		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.80902
3. AS	B_{3g}	0.59023
4. SS	B_{1u}	0.42356
5. AA	A_u	0.30902
6. SA	B_{2g}	-0.30902
7. AS	B_{3g}	-0.42356
8. SS	B_{1u}	-0.59023
9. AA	A_u	-0.80902
10. AS	B_{3g}	-1.0

Anthracene		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.90627
3. SS	B_{1u}	0.65841
4. AS	B_{3g}	0.62139
5. AA	A_u	0.46685
6. SA	B_{2g}	0.39392
7. AS	B_{3g}	0.20369
8. SS	B_{1u}	-0.20369
9. AA	A_u	-0.39392
10. SA	B_{2g}	-0.46685
11. SS	A_{1u}	-0.62139
12. AS	B_{3g}	-0.65841
13. AA	A_u	-0.90627
14. AS	B_{3g}	-1.0

Naphthacene		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.94490
3. SS	B_{1u}	0.79002
4. AS	B_{3g}	0.63640
5. SA	B_{2g}	0.57008
6. AA	A_u	0.53783
7. SS	B_{1u}	0.37823
8. AS	B_{3g}	0.36518
9. AA	A_u	0.14382
10. SA	B_{2g}	-0.14382
11. SS	B_{1u}	-0.36518
12. AS	B_{3g}	-0.37823
13. SA	B_{2g}	-0.53783
14. AS	B_{3g}	-0.57008
15. SS	B_{1u}	-0.63640
16. AS	B_{3g}	-0.79002
17. AA	A_u	-0.94490

Pentacene		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.96385
3. SS	B_{1u}	0.85968
4. SA	B_{2g}	0.70083
5. AS	B_{3g}	0.64491
6. AA	A_u	0.57601
7. SS	B_{1u}	0.51454
8. AS	B_{3g}	0.45582
9. SA	B_{2g}	0.36855
10. AA	A_u	0.29056
11. AS	B_{3g}	0.10681
12. SS	B_{1u}	-0.10681
13. SA	B_{2g}	-0.29056
14. AA	A_u	-0.36855
15. SS	B_{1u}	-0.45582
16. AS	B_{3g}	-0.51454
17. SA	B_{2g}	-0.57601

Diphenyl		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.92249
3. SS	B_{1u}	0.57180
4. AA	A_u	0.5
5. AS	B_{3g}	0.5
6. SA	B_{2g}	0.31597
7. SS	B_{1u}	-0.31597
8. AA	A_u	-0.5
9. AS	B_{3g}	-0.5
10. SA	B_{2g}	-0.57180
11. SS	B_{1u}	-0.92249
12. SA	B_{2g}	-1.0

18. AS	B_{3g}	-1.0

18. SS	B_{1u}	-0.64491
19. AA	A_u	-0.70083
20. AS	B_{3g}	-0.85968
21. AA	A_u	-0.96385
22. AS	B_{3g}	-1.0

Stilbene		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.96096
3. SS	B_{1u}	0.72011
4. SA	B_{2g}	0.5
5. AS	B_{3g}	0.5
6. AA	A_u	0.5
7. SS	B_{1u}	0.24085
8. SA	B_{2g}	-0.24085
9. AS	B_{3g}	-0.5
10. AA	A_u	-0.5
11. SS	B_{1u}	-0.5
12. SA	B_{2g}	-0.72011
13. SS	B_{1u}	-0.96096
14. SA	B_{2g}	-1.0

Styrene		C_{2v}
1. S	B_2	0.97903
2. S	B_2	0.66594
3. A	A_2	0.5
4. S	B_2	0.31308
5. S	B_2	-0.31308
6. A	A_2	-0.5
7. S	B_2	-0.66594
8. S	B_2	-0.97903

Difulvene		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.89830
3. SS	B_{1u}	0.42356
4. AA	A_u	0.30902
5. AS	B_{3g}	0.30902
6. SA	B_{2g}	0.11020
7. SS	B_{1u}	-0.59023
8. AS	B_{3g}	-0.80902
9. AA	A_u	-0.80902
10. SA	B_{2g}	-0.84183

Fulvene		C_{2v}
1. S	B_2	0.96262
2. S	B_2	0.44376
3. A	A_2	0.30902
4. S	B_2	-0.12480
5. S	B_2	-0.78158
6. A	A_2	-0.80902

Methylene-3 pentadiene 1,4		C_{2v}
1. S	B_2	0.83041
2. A	A_2	0.5
3. S	B_2	0.24581
4. S	B_2	-0.24581
5. A	A_2	-0.5
6. S	B_2	-0.83041

Pentalene		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.70711
3. AS	B_{3g}	0.43426
4. SS	B_{1u}	0.19371
5. AA	A_u	0.0
6. SA	B_{2g}	-0.70711
7. AS	B_{3g}	-0.76759
8. SS	B_{1g}	-0.86038

Azulene		C_{2v}
1. S	B_2	1.0
2. S	B_2	0.81254
3. A	A_2	0.63253
4. S	B_2	0.39186
5. A	A_2	0.22398
6. S	B_2	-0.18536
7. A	A_2	-0.35032
8. S	B_2	-0.77636
9. A	A_2	-0.83952
10. S	B_2	-0.90934

Phenanthrene		C_{2v}
1. S	B_2	1.0
2. A	A_2	0.89689
3. S	B_2	0.72015
4. S	B_2	0.56250
5. A	A_2	0.5
6. A	A_2	0.33647
7. S	B_2	0.28404
8. A	A_2	-0.28404
9. S	B_2	-0.33647
10. S	B_2	-0.5
11. A	A_2	-0.56250
12. A	A_2	-0.72015

Pyrene		V_h
1. SS	B_{1u}	1.0
2. AS	B_{3g}	0.87017
3. SA	B_{2g}	0.78868
4. SS	B_{1u}	0.64306
5. AA	A_u	0.5
6. SS	B_{1u}	0.41731
7. AS	B_{3g}	0.35687
8. SA	B_{2g}	0.21132
9. AA	A_u	-0.21132
10. SS	B_{1u}	-0.35687
11. AS	B_{3g}	-0.41731
12. SA	B_{2g}	-0.5

13. S	B_2	-0.89689
14. A	A_2	-1.0

13. AS	B_{3g}	-0.64306
14. AA	A_u	-0.78868
15. SS	B_{1u}	-0.87017
16. AS	B_{3g}	-1.0

Perylene		V_h
1. SS	B_{1u}	1.0
2. AS	B_{3g}	0.92104
3. SA	B_{2g}	0.82261
4. AA	A_u	0.75120
5. SS	B_{1u}	0.64460
6. AS	B_{3g}	0.43524
7. SS	B_{1u}	0.42469
8. SA	B_{2g}	0.42178
9. AS	B_{3g}	0.37968
10. AA	A_u	0.15986
11. SA	B_{2g}	-0.15986
12. SS	B_{1u}	-0.37968
13. AA	A_u	-0.42178
14. AS	B_{3g}	-0.42469
15. SS	B_{1u}	-0.43524
16. AS	B_{3g}	-0.64460
17. SA	B_{2g}	-0.75120
18. AA	A_u	-0.82261
19. SS	B_{1u}	-0.92104
20. AS	B_{3g}	-1.0

Triphenylene		D_{3h}
1. S^3	A_2''	1.0
2. S	E''	0.89610
3. A		
4. S^3	A_2''	0.59023
5. S	E''	0.55400
6. A		
7. A^3	A_1''	0.42356
8. S	E''	0.29074
9. A		
10. A	E''	-0.29074
11. S		
12. S^3	A_2''	-0.42356
13. A	E''	-0.55400
14. S		
15. A^3	A_1''	-0.59023
16. A	E''	-0.89610
17. S		
18. A^3	A_1''	-1.0

Coronene		D_{6h}
1. S^3S^3	A_{2u}	1.0
2. AS	E_{1g}	0.89349
3. SA		
4. SS	E_{2u}	0.70998
5. AA		
6. S^3S^3	A_{2u}	0.61693
7. S^3A^3	B_{1g}	0.5
8. A^3S^3	B_{2g}	0.45026
9. AS	E_{1g}	0.38018
10. SA		
11. SS	E_{2u}	0.23036
12. AA		
13. SA	E_{1g}	-0.23036
14. AS		
15. AA	E_{2u}	-0.38018
16. SS		
17. S^3S^3	A_{2u}	-0.45026
18. A^3A^3	A_{1u}	-0.5
19. A^3S^3	B_{2g}	-0.61693
20. SA	E_{1g}	-0.70998
21. AS		
22. AA	E_{2u}	-0.89349
23. SS		
24. A^3S^3	B_{2g}	-1.0

Ovalene		V_h
1. SS	B_{1u}	1.0
2. SA	B_{2g}	0.93890
3. AS	B_{3g}	0.90269
4. AA	A_u	0.80139
5. SS	B_{1u}	0.79300
6. SS	B_{1u}	0.67428
7. SA	B_{2g}	0.63641
8. AS	B_{3g}	0.59895
9. SA	B_{2g}	0.52671
10. SS	B_{1u}	0.41907
11. AS	B_{3g}	0.41900

Ovalene		V_h
12. AA	A_u	0.41279
13. SS	B_{1u}	0.34698
14. AA	A_u	0.30085
15. SA	B_{2g}	0.24635
16. AS	B_{3g}	0.14602
17. SS	B_{1u}	-0.14602
18. AA	A_u	-0.24635
19. SA	B_{2g}	-0.30085
20. AS	B_{3g}	-0.34698
21. SA	B_{2g}	-0.41279
22. SS	B_{1u}	-0.41900

Ovalene		V_h
23. AS	B_{3g}	-0.41907
24. AA	A_u	-0.52671
25. SS	B_{1u}	-0.59895
26. AA	A_u	-0.63641
27. AS	B_{3g}	-0.67428
28. AS	B_{3g}	-0.79300
29. SA	B_{2g}	-0.80139
30. SS	B_{1u}	-0.90269
31. AA	A_u	-0.93890
32. AS	B_{3g}	-1.0

TABLE II

THE π-ELECTRON WAVEFUNCTIONS: a_{Bi}^2

Molecule	Orbital	Symmetry	B1	B2	B3	B4	B5	B6	B7	B8	B9
Benzene	1.	SS	0.16667								
	all others	—	0.33333								
Naphthalene	1.	SS	0.09091	0.09091							
	2.	SA	0.20000	0							
	3.	AS	0.16029	0.39709							
	4.	SS	0.17737	0.22629							
	5.	AA	0.20000	0							
Anthracene	1.	SS	0.06250	0.06250	0.06250						
	2.	SA	0.13145	0.15669	0.02938						
	3.	SS	0.15062	0.09786	0.05116						
	4.	AS	0.08829	0.13827	0.28202						
	5.	AA	0.16417	0.03631	0.10652						
	6.	SA	0.11615	0.13053	0.15822						
	7.	AS	0.11526	0.20137	0.02098						
Naphthacene	1.	SS	0.04762	0.04762	0.04762	0.04762					
	2.	SA	0.09818	0.11588	0.04560	0					
	3.	SS	0.10744	0.10172	0.00075	0.11041					
	4.	AS	0.05350	0.10216	0.19168	0.25441					
	5.	SA	0.12148	0.07672	0.08575	0					
	6.	AA	0.12154	0.05190	0.18469	0					
	7.	SS	0.08364	0.09986	0.11729	0.13022					
	8.	AS	0.12245	0.07548	0.00852	0.15466					
	9.	AA	0.07260	0.15206	0.02878	0					
Pentacene	1.	SS	0.03846	0.03846	0.03846	0.03846	0.03846				
	2.	SA	0.07850	0.08976	0.09635	0.04878	0.00696				
	3.	SS	0.08343	0.09394	0.07243	0.00468	0.05757				
	4.	SA	0.09212	0.06625	0.09885	0.01759	0.05914				
	5.	AS	0.03473	0.07385	0.09174	0.13253	0.21491				
	6.	AA	0.08952	0.07172	0.01353	0.19585	0.04265				
	7.	SS	0.10135	0.07257	0.04580	0.09537	0.01601				
	8.	AS	0.10750	0.02507	0.10962	0.05930	0.08371				
	9.	SA	0.06366	0.07884	0.08447	0.09071	0.10668				
	10.	AA	0.09041	0.10248	0.03000	0.00059	0.07744				
	11.	AS	0.04882	0.11040	0.14194	0.02679	0.00362				
Diphenyl	1.	SS	0.07692	0.07692							
	2.	SA	0.12834	0.45990							
	3.	SS	0.15162	0.18062							
	4.	AA	0.16667	0							
	5.	AS	0.16667	0							
	6.	SA	0.14312	0.28256							
Stilbene	1.	SS	0.06667	0.06667							
	2.	SA	0.10000	0.26667							
	3.	SS	0.10000	0.26667							
	4.	SA	0.13333	0.13333							
	5.	AS	0.16667	0							
	6.	AA	0.16667	0							
	7.	SS	0.10000	0.26667							

Molecule	Orbital	Symmetry	B1	B2	B3	B4	B5	B6	B7	B8	B9
Styrene	1.	S	0.16667	0.33333							
	2.	S	0.16667	0.33333							
	3.	A	0.33333	0							
	4.	S	0.16667	0.33333							
3-methylene-pentadiene 1,4	1.	S	0.24267	0.27200							
	2.	A	0.33333	0							
	3.	S	0.18590	0.44229							
n-polyenes	all	—	$a^2 = (n+1)/2$								
Fulvene	1.	S	0.21263	0.46841							
	2.	S	0.25771	0.35574							
	3.	A	0.40000	0							
	4.	S	0.17011	0.57472							
	5.	S	0.28262	0.29344							
	6.	A	0.40000	0							
Difulvene	1.	SS	0.09091	0.09091							
	2.	SA	0.14847	0.51526							
	3.	SS	0.17737	0.22628							
	4.	AA	0.20000	0							
	5.	AS	0.20000	0							
	6.	SA	0.17074	0.29254							
	7.	SS	0.16026	0.39738							
	8.	AS	0.20000	0							
	9.	AA	0.20000	0							
	10.	SA	0.18078	0.19218							
Azulene	1.	S	0.09091	0.09091	0.09091						
	2.	S	0.21251	0.17624	0.01997						
	3.	A	0.24759	0.05576	0.29139						
	4.	S	0.13757	0.25045	0.17278						
	5.	A	0.09852	0.31370	0.15409						
	6.	S	0.25032	0.08126	0.17303						
	7.	A	0.23673	0.12498	0.07972						
	8.	S	0.07224	0.35786	0.13512						
	9.	A	0.17010	0.19968	0.18068						
	10.	S	0.23644	0.04328	0.40821						
Pentalene	1.	SS	0.11111	0.11111							
	2.	SA	0.25000	0							
	3.	AS	0.19678	0.42575							
	4.	SS	0.21201	0.30392							
	5.	AA	0.25000	0							
	6.	SA	0.25000	0							
	7.	AS	0.21989	0.24088							
	8.	SS	0.17688	0.58498							

Molecule	Orbital	Symmetry	B1	B2	B3	B4	B5	B6	B7	B8	B9
Phenanthrene	1.	S	0.06250	0.06250	0.06250	0.06250					
	2.	A	0.08388	0.13763	0.28522	0.04344					
	3.	S	0.26855	0.09889	0.00024	0.10258					
	4.	S	0.00604	0.14006	0.17369	0.20381					
	5.	A	0.12526	0.14035	0	0.14035					
	6.	A	0.06350	0.13652	0.23718	0.10354					
	7.	S	0.23379	0.11248	0.06470	0.05457					
Pyrene	1.	SS	0.05263	0.05263	0.05263	0.05263					
	2.	AS	0.07753	0.14284	0.05336	0.17865					
	3.	SA	0.17108	0.05423	0.13492	0					
	4.	SS	0.07786	0.17511	0.02558	0.02954					
	5.	AA	0.09091	0.12121	0.12121	0					
	6.	SS	0.14839	0.00677	0.19991	0.25581					
	7.	AS	0.07214	0.12265	0.09708	0.19766					
	8.	SA	0.12263	0.14507	0.02591	0					
Perylene	1.	SS	0.04167	0.04167	0.04167	0.04167					
	2.	AS	0.20944	0.07468	0.10377	0.04468					
	3.	SA	0.04289	0.08942	0	0.12089					
	4.	AA	0.05927	0.11336	0	0.01692					
	5.	SS	0.07808	0.07634	0.18266	0.06427					
	6.	AS	0.02954	0.10032	0.10148	0.03320					
	7.	SS	0.00091	0.09080	0.10994	0.08135					
	8.	SA	0.11647	0.08526	0	0.10071					
	9.	AS	0.14035	0.04476	0.17476	0.16339					
	10.	AA	0.08905	0.10427	0	0.03839					
Triphenylene	1.	S^3	0.04762	0.04762	0.04762	0.04762	0.04762	0.04762			
	2.	S	0.18166	0.21504	0.04872	0.02054	0.03201	0.06096			
	3.	A_3	0.00440	0.08538	0.13734	0.27988	0.07061	0.04166			
	4.	S^3	0.10686	0.06618	0.10686	0.06618	0.06618	0.06618			
	5.	S	0.04318	0.02800	0.11865	0.10658	0.03346	0.20079			
	6.	A_3	0.14381	0.08038	0.06833	0.00180	0.25657	0.08924			
	7.	A^3	0.11825	0.03771	0.11825	0.03771	0.03771	0.03771			
	8.	S	0.10506	0.17010	0.08435	0.04660	0.16241	0.04098			
	9.	A_3	0.07745	0.08777	0.09816	0.21127	0.00050	0.12194			
Coronene	1.	S^3S^3	0.03333	0.03333	0.03333	0.03333	0.03333	0.03333			
	2.	AS	0.04460	0.08193	0.10637	0.02659	0.04619	0.12266			
	3.	SA	0.09438	0.05704	0	0.07978	0.09717	0.02070			
	4.	SS	0.11648	0.07566	0.09186	0.02296	0.02834	0.00209			
	5.	AA	0.06205	0.10288	0	0.06889	0.01084	0.03709			
	6.	S^3S^3	0.03575	0.03575	0.13826	0.13826	0.08781	0.08781			
	7.	S^3A^3	0.11111	0.11111	0	0	0	0			
	8.	A^3S^3	0.07675	0.07675	0.07840	0.07840	0.02469	0.02469			
	9.	AS	0.00083	0.04581	0.17363	0.04341	0.16545	0.13126			
	10.	SA	0.06081	0.01583	0	0.13023	0.14265	0.17684			
	11.	SS	0.10474	0.07754	0.08527	0.02132	0.04098	0.01065			
	12.	AA	0.06847	0.09568	0	0.06395	0.02075	0.05107			

Molecule	Orbital	Symmetry	B1	B2	B3	B4	B5	B6	E7	B8	B9
Ovalene	1.	SS	0.02439	0.02439	0.02439	0.02439	0.02439	0.02439	0.02439	0.02439	0.02439
	2.	SA	0.06112	0.04629	0.05903	0.05548	0.00789	0.06620	0.06656	0.02859	0
	3.	AS	0.02949	0.05420	0.06282	0.01651	0.07766	0.03514	0.03086	0.08646	0.10773
	4.	AA	0.04515	0.08005	0.06200	0.04064	0.02387	0.00902	0.02514	0.06293	0
	5.	SS	0.10014	0.03944	0.03729	0.05989	0.02353	0.06586	0.03479	0.00140	0.03772
	6.	SS	0.00072	0.04866	0.04314	0.03813	0.12447	0.02594	0.08395	0.02681	0.09563
	7.	SA	0.11886	0.05881	0.05649	0.01869	0.03367	0.01529	0.02067	0.00099	0
	8.	AS	0.05110	0.07309	0.06700	0.06240	0.02424	0.02796	0.01109	0.00891	0.02771
	9.	SA	0.01407	0.04831	0.00031	0.11440	0.04433	0.08158	0.04029	0.10609	0
	10.	SS	0.13469	0.04634	0.06245	0.02628	0.01248	0.03294	0.00496	0.03652	0.00634
	11.	AS	0.01197	0.03162	0.02500	0.02764	0.09961	0.06727	0.08059	0.08798	0.17225
	12.	AA	0.05460	0.05478	0.06481	0.05847	0.05914	0.03791	0.03182	0.00320	0
	13.	SS	0.00433	0.03539	0.04882	0.06331	0.00714	0.06746	0.11828	0.08638	0.15663
	14.	AA	0.01726	0.05798	0.00078	0.04236	0.06208	0.07559	0.06561	0.10744	0
	15.	SA	0.05235	0.05089	0.09020	0.02158	0.05873	0.04567	0.02374	0.01991	0
	16.	AS	0.05059	0.05775	0.12909	0.03677	0.01737	0.01762	0.03238	0.00688	0.05678

TABLE III.

The reference coordinates are shown in Fig. 2. Wherever the phase

Molecule	Orbital: Branch	2	3	4	5	6	7	8
Naphthacene	B2		1.0925	0.066212			15.631	0.63293
Pentacene	B2	-1.6333	3.0250	0.28906	0.10148	-0.25623	-1.4330	5.9578
Phenanthrene	B1	-0.092822	0.41338	-1.2236	1.7321	-0.99169	1.5007	
	B4	-0.87844	-2.8417	1.9800	-1.7321	0.10223	0.13161	
Pyrene	B3	-1.0895		0.78433		1.2107	-0.02519	
Perylene	B2	0.46039			1.5269	-1.4366	-0.69744	
	B3	1.15656			17.292	0.81522	0.063547	
	B4	1.3300			-0.50211	28.402	1.3007	
Triphenylene	B2	-6.3933	2.1311		-0.22518	0.075061		-3.6881
	B3	-0.26968	0.089892		3.1611	-1.0537		-1.4872
	B4	-2.5724	0.85747		-4.7962	1.5987		-0.096145
Coronene	B2	0.39688		1.2642				
	B3	1.0704		1.2523				
	B4	-1.0704	-1.0704	-1.2523	-1.2523	2.7752		-0.87759
	B5	1.4055		7.2845				
Ovalene	B2	0.75161	-0.45800	0.054668	9.7656	-0.38012	-0.69565	1.0065
	B4	0.69905	1.0701	1.1320	1.9561	2.0230	4.2473	1.3591
	B5	0.16904	-1.1287	-0.66845	-0.27687	138.63	-0.52226	-0.39123
	B6	-1.7143	1.5406	0.27330	5.2209	-0.039311	1.2565	4.7215
	B7	5.6332	1.3231	3.0116	-0.54088	-0.73290	2.1215	0.33171

is obvious from symmetry considerations, no entry has been made.

9	10	11	12	13	14	15	16
9.7850	0.25472	-0.2350					
-0.70262							
-1.2338							
0.46804							
1.2294							
0.49572							
0.032048							
-0.067714		-1.4004					
-1.1245		0.32469					
1.1245	1.1245	-0.32469	-0.32469				
0.49741		3.7931					
-0.021495	0.38941	-0.57068	92.121	0.16745	-0.21940	1.4730	-0.35993
-1.8669	0.82172	0.29987	1.1876	1.2520	-0.29737	0.049343	0.64402
2.1416	-1.3251	2.6748	-0.27299	-1.7090	1.0954	-0.25094	3.2016
-0.44961	-1.7400	0.35086	2.2731	-1.5176	0.15720	8.8338	3.3322
1.7960	-1.2067	0.09435	1.5511	-1.3786	1.3640	1.2860	-0.18934

TABLE IV. SPECTRAL PREDICTIONS

The LCAO model predictions (with S = 0.25; β(ring) = 23,000cm^{-1}; and β(polyene) = 32,000cm^{-1}) and the experimental data have all been taken from references 5 and 6. The experimental data in parentheses are estimations.

Molecule	Transition	Predicted transition energy (cm^{-1}) FEMO	Predicted transition energy (cm^{-1}) LCAO	Observed singlets	Observed triplets	Center of gravity of singlets and triplets	Correction FEMO	Correction LCAO
Benzene	L_a, L_b, B_b, B_a (fourfold degen. in this approx.)	52 300	49 100	48 000 (c.g.)	29 300	(43 400)	-9000	-5500
				38 200	(43 800)			
				54 000	(40 000)			
				54 000	(40 000)			
Naphthalene	L_a	31 400	29 000	35 000	21 300	28 200	-3000	-1000
	L_b	36 100	35 000	32 200	(36 200)	33 200	-3000	-2000
	B_b	39 100	43 000	45 000	(35 000)	39 200	0	-4000
	B_a	43 700	49 000	59 000	(49 300)	54 500	+11 000	+5500
Anthracene	L_a	20 500	19 000	26 700	14 700	20 700	0	+1500
	L_b	28 500	29 000	(29 000)	(33 000)	31 000	+2500	+2000
	B_b	32 400	39 300	38 500	(30 000)	34 500	+2000	-5000
	B_a	40 500	49 000	53 700	(44 700)	49 200	+9000	0
Naphthacene	L_a	14 420	13 500	21 000	(9500)	15 500	+1000	+2000
	L_b	24 000	26 000	(25 500)	(29 500)	27 500	+3500	+1500
	B_b	27 800	37 000	36 700	(28 200)	32 500	+4500	-4500
	B_a	37 400	49 000	47 400	(39 000)	43 200	+6000	-6000
Pentacene	L_a	10 690	10 000	17 300	(6200)	11 800	+1000	+2000
	L_b	18 880	24 000	24 000?	(28 000)	26 000	+9000	+2000
	B_b	21 300	35 500	33 000	(24 300)	28 300	+7000	-7000
	B_a	29 500	49 000	(43 000)	(35 000)	39 000	+9500	-10 000
Phenanthrene	L_a	28 800		33 000	(22 000)	27 500	-1500	
	L_b	31 000		28 300	(33 700)	31 900	0	
	B_b	32 100		39 400	(29 700)	34 500	+2500	
	B_a	34 300		53 400	(44 400)	48 900	+14 500	

Triphenylene	L_a, L_b, B_b, B_a (fourfold degen. in this approx.)	29 500	34 000 (c.g.)	(29 800) (c.g.)	32 800	+3500

Molecule	Transition	Predicted transition energy (cm^{-1}) FEMO	 LCAO	Observed singlets	Correction for singlets only FEMO	 LCAO
Diphenyl	^1L_a?	32 100	33 800	39 200	+7000	+5500
	^1L_b?	39 500	38 200	(41 000)	+1500	+3000
		44 900	44 400	48 000	+3000	+3500
		52 300	49 000	56 000	+2500	+7000
Fulvene	The three filled levels to the lowest unfilled	20 600	18 600	27 000	+6500	+7500
		26 300	24 300	35 500	+9000	+11 000
		44 800	38 000	54 000	+9000	+16 000
Styrene	^1L_a	31 800	31 300	34 000	+2000	+2500
	^1L_b	39 300	36 700	38 500	-1000	+1000
	^1B_b	44 800	43 800	46 500	+1500	+2500
	^1B_a	52 300	49 000	58 000	+5500	+9000
Azulene	^1L_b	20 300	20 000	14 400	-6000	-5500
	^1L_a	27 400	27 000	27 500	0	+ 500
	^1B_b	30 400	30 600	34 000	+3500	+3500
	^1B_a	37 500	37 500	48 000	+10 500	+10 500
Coronene	^1L_a, ^1L_b, ^1B_b, ^1B_a (fourfold degen. in this approx.)	23 200	25 200	29 000 (c.g.)	+6000	+4000
Ethylene	$N_1 \rightarrow V_1 {}^1B_b$	55 900	68 000	57 000	+1000	-11 000
Butadiene	$N_1 \rightarrow V_1 {}^1B_b$	33 800	40 500	43 000	+9000	+2500
Hexatriene	$N_1 \rightarrow V_1 {}^1B_b$	24 200	28 700	38 000	+14 000	+9500

TABLE V. BOUND VALENCES AND CHEMICAL REACTIVITIES

Under the heading "Theoretically most reactive atom(s)–bond," the atom position with lowest bound valence or, respectively, the bond with the highest π-electron density is listed for each molecule. Positionally equivalent atoms are indicated by enclosure in parentheses.

Molecule	Theoretically most reactive atom(s)	bond	Positions attacked upon oxidation	halogenation	nitration	sulfonation
Naphthalene	(1,4,5,8)		1,4	1 1,5 1,4	1 1,5 1,8	1
Anthracene	(9,10) then (1,4,5,8)		9,10	9 9,10	9 9,10	1,5 1,8
Naphthacene	(9,10,11 12)		9,10	9,10		
Pentacene	(6,13)		6,13			
Diphenyl	(2,2') then (4,4')		all reactions at the 4 atom; (steric effects?)			
Stilbene	(2,2')	α–α'	addition to the α–α' bond			
Styrene	β	α–β	addition to the α–β bond			
Phenanthrene	(1,8)	9–10	9,10	9 9,10	9	1 2 3 9
Pyrene	(3,5,8,10)		3,8 3,10	3,5,8 3,5,8,10		3,5,8,10
Perylene	(3,4,9,10)		3,9 3,10	3,9 3,10 3,4,9,10	3,10 3,4,9,10	3,9 3,10

TABLE VI. A COMPARISON OF THE PREDICTIONS OF BOND LENGTHS BY THE FREE-ELECTRON MODEL AND THE LCAO MODEL

Molecule	Root Mean Square Deviations (A) Free-electron Model	LCAO Model[a]
Benzene	0.004	0.004
Naphthalene	0.023	0.025[b]
Anthracene	0.008	0.013
Pyrene	0.025	0.025
Triphenylene[c]	0.015	0.020
Coronene	0.007	0.014
Ovalene	0.014	0.016
Graphite	0.009	0.010
Ethylene	0.000	0.000
Butadiene		
2–3 bond	0.004	0.000
1–2 bond	0.046	0.016
All molecules except polyenes	0.016	0.018
All molecules	0.017	0.018

[a] These numbers were calculated by the present author, mainly from the data of reference 11.

[b] It should be noted that the often quoted value of 0.018 for this molecule[9,11,16] refers, not to Coulson's plot,[9] but to a special, less general curve from reference 16, which has been heavily weighted in favor of this molecule and a few others.

[c] Klug, *Acta Cryst*. 3, 165 (1950).

APPENDIX

ILLUSTRATION OF THE METHOD: NAPHTHACENE

Matrix Formulation

The naphthacene molecule has V_h symmetry; expressed in terms of cartesian coordinates the symmetry species are SS, SA, AS, AA (where the letters refer to the behavior (symmetric or antisymmetric) upon reflection at XY and YZ planes, respectively). See Fig. 2.

In the case of SS symmetry

$$\left.\begin{array}{l}
\phi(1) = \phi(4) = \phi(5) = \phi(8) \ , \\
\phi(2) = \phi(3) = \phi(6) = \phi(7) \ , \\
\phi(9) = \phi(10) = \phi(11) = \phi(12) \ , \\
\phi(1,12) = \phi(4,11) = \phi(5,10) = \phi(8,9) \ , \\
\phi(9,12) = \phi(10,11) \ ,
\end{array}\right\} \qquad (A.1)$$

(where $\phi(r,s)$ designates the value of the wavefunction at the joint atom located between atoms *r* and *s*, and is to be distinguished from $\phi(r-t)$, the value of the wavefunction at bond $r-t$). Hence, there are only five independent variables. If we write the secular equations [I, Eq. (2.44), (2.45), (2.46)], keeping the relations of (A.1) in mind, we arrive at

$$\left.\begin{array}{l}
(-3\cos\kappa+1)\phi(9,12)+ \quad 2\phi(12) = 0 \\
\phi(9,12)-2\cos\kappa\,\phi(12)+ \quad \phi(1,12) = 0 \\
\phi(12)+(1-3\cos\kappa)\phi(1,12)+ \quad \phi(1) = 0 \\
\phi(1,12)-2\cos\kappa\,\phi(1)+ \quad = 0 \\
\phi(1)+(1-2\cos\kappa)\phi(2) = 0
\end{array}\right\}. \qquad (A.2)$$

By similar considerations, we can write for AS symmetry

$$\left.\begin{array}{l}
-(1+3\cos\kappa)\phi(9,12)+ \quad 2\phi(12) = 0 \\
\phi(9,12)-2\cos\kappa\,\phi(12)+ \quad \phi(1,12) = 0 \\
\phi(12)+(1-3\cos\kappa)\phi(1,12)+ \quad \phi(1) = 0 \\
\phi(1,12)-2\cos\kappa\,\phi(1)+ \quad \phi(2) = 0 \\
\phi(1)-(1+2\cos\kappa)\phi(2) = 0
\end{array}\right\}. \qquad (A.3)$$

For SA symmetry,

$$\left.\begin{array}{r}\phi(9,12)=\phi(10,11)=0\\ -2\cos\kappa\,\phi(12)+\phi(1,12)=0\\ \phi(12)+(1-3\cos\kappa)\phi(1,12)+\phi(1)=0\\ \phi(1,12)-2\cos\kappa\,\phi(1)+\phi(2)=0\\ \phi(1)+(1-2\cos\kappa)\phi(2)=0\end{array}\right\}. \qquad (A.4)$$

For AA symmetry,

$$\left.\begin{array}{r}\phi(9,12)=\phi(10,11)=0\\ -2\cos\kappa\,\phi(12)+\phi(1,12)=0\\ \phi(12)-(1+3\cos\kappa)\phi(1,12)+\phi(1)=0\\ \phi(1,12)-2\cos\kappa\,\phi(1)+\phi(2)=0\\ \phi(1)-(1+2\cos\kappa)\phi(2)=0\end{array}\right\}. \qquad (A.5)$$

The Eigenvalues

From this point on we will discuss only the symmetry SS. From (A.2) we obtain the following secular equation:

$$\left.\begin{vmatrix}(1-3\cos\kappa) & 2 & & & \\ 1 & -2\cos\kappa & 1 & & \\ & 1 & (1-3\cos\kappa) & 1 & \\ & & 1 & -2\cos\kappa & 1\\ & & & 1 & (1-2\cos\kappa)\end{vmatrix}=0\right\}, \qquad (A.6)$$

giving

$$-72(\cos\kappa)^5+84(\cos\kappa)^4+34(\cos\kappa)^3-48(\cos\kappa)^2-3\cos\kappa+5=0$$

or

$$(\cos\kappa-1)[72(\cos\kappa)^4-12(\cos\kappa)^3-46(\cos\kappa)^2+2\cos\kappa+5]=0.$$

(In the absence of free end points, the solution $\cos\kappa=1$ can be anticipated for SS symmetry.) The solutions of (A.6) are given in Table I for the SS orbitals. The negatives of these roots are the roots of the AS symmetry secular equation.

Wavefunction Obtained via the Eigenvectors

The secular equation (A.2) may now be solved, for each eigenvalue, to give the relative values of the eigenvectors. Application of the normalization condition [I, Eq. (2.34)] fixes their absolute values.

Thus

$$\left.\begin{aligned}
\phi(2) &= (-1+2\cos\kappa)^{-1}\phi(1)\ , \\
\phi(1,12) &= [2\cos\kappa-(-1+2\cos\kappa)^{-1}]\phi(1)\ , \\
\phi(12) &= \{(-1+3\cos\kappa)[2\cos\kappa-(-1+2\cos\kappa)^{-1}]-1\}\phi(1)\ , \\
\phi(9,12) &= 2\{(-1+3\cos\kappa)[2\cos\kappa-(-1+2\cos\kappa)^{-1}]-1\}(-1+3\cos\kappa)^{-1}\phi(1)\ ,
\end{aligned}\right\} \qquad (A.7)$$

and

$$4\phi^2(1) + 4\phi^2(2) + 4\phi^2(12) + 4(3/2)\phi^2(1,12) + 2(3/2)\phi^2(9,12) = 1\ . \qquad (A.8)$$

For example, for the eigenvalue $\cos\kappa = 1$

$$\phi(r) = \phi(1) \text{ for all } r,$$

$$\phi^2(1) = 1/21 = 0.04762.$$

For the eigenvalue, $\cos\kappa = 0.79002$,

$$\begin{aligned}
\phi(1) &= \phi(1)\ , \\
\phi(2) &= 1.7240\phi(1)\ , \\
\phi(1,12) &= -0.1440\phi(1)\ , \\
\phi(12) &= -1.1973\phi(1)\ , \\
\phi(9,12) &= -1.7478\phi(1)\ ,
\end{aligned}$$

and from (A.8)

$$\phi^2(1) = 0\text{[illegible]}235\ , \qquad \phi(1) = \pm 0.1799\ .$$

If we arbitrarily select $\phi(1)$ to be positive, all the other eigenvectors are uniquely determined. We may now find the value of the wavefunction at the mid-point of a bond from Eq. (3a). We can find a_B and δ_B from the considerations of I, Eq. (2.21)-(2.30) and the accompanying text; of $a_B{}^2$ and $\tan\delta_B$ (the quantities listed in Tables II and III) from Eq. (3b) and (3c), and a_B and δ_B from these. Since $\pi/2 \geqslant \delta_B > -\pi/2$, we obtain, for example, for $\cos\kappa = 0.79002$,

$$\left.\begin{aligned}
\delta_1 &= 0\ , \\
\delta_2 &= 0.8296\ , \\
\delta_3 &= 0\ , \\
\delta_4 &= 0\ ,
\end{aligned}\right\} \qquad (A.9a)$$

in radians. Hence, $0.1799 = \phi(1) = a_1 \cos(3\kappa/2) = 0.5488$, *etc.*, so that one finds

$$\left.\begin{aligned} a_1 &= 0.3278 \ , \\ a_2 &= -0.3189 \ , \\ a_3 &= -0.0274 \ , \\ a_4 &= -0.3323 \ . \end{aligned}\right\} \tag{A.9b}$$

Wavefunction Obtained via the Joint Conditions

This method works without excessive labor if the molecule is small and/or there is enough symmetry to supplement it. Consider the case in question (SS symmetry). Here $\delta_1 = \delta_3 = \delta_4 = 0$, since we have chosen our branch origins to lie on the symmetry axis. (If the axis had been an A axis, we would have $\delta_B = \pi/2$.) There remains δ_2 to be determined. We write, *e.g.*, at the joint atom (9,12) the boundary conditions

$$-2\tan(-\kappa+\delta_2)+\tan(\kappa/2) = 0 \ , \tag{A.10a}$$

$$a_2\cos(-\kappa+\delta_2) = a_4\cos(\kappa/2) \ . \tag{A.10b}$$

By use of

$$\tan(\kappa x_B+\delta_B) = (\tan\kappa x_B+\tan\delta_B)/(1-\tan\kappa x_B \tan\delta_B) \ , \tag{A.11}$$

Eq. (A.10a) is transformed from a *transcendental* equation in δ_2 into an *algebraic* equation in $\tan\delta_2$, which is readily solved to yield the value in (A.9a). By virtue of (A.11), the system of joint conditions is, in all cases, equivalent to a system of algebraic equation.

The values of the δ_B, when substituted into the equations of the type (A.10b), readily determine the *ratios* of the a_B's. The normalization condition I, Eq. (2.7), then gives the *absolute* values listed in (A.9b).

The value of the wavefunction at any point is now easily found, *e.g.*,

at atom 12: $\phi(12) = a_2\cos\delta_2$,

at atom 9,12: $\phi(9,12) = a_2\cos(-\kappa+\delta_2) = a_4\cos(\kappa/2)$,

at bond 9,12–12: $\phi(9,12\text{–}12) = a_2\cos(-\kappa/2+\delta_2)$.

Use of Tables I, II, III for the Construction of the Wavefunctions

The δ_B's may be obtained from the $\tan\delta_B$'s listed in Table III. The signs of the δ_B's are the same as the signs of the $\tan\delta_B$'s [See I, Eq. (2.11)]. The magnitudes of the a_B's are the square roots of the $a_B{}^2$'s listed in Table II. We arbitrarily choose one of the a_B (say a_1) to be positive. To find the sign of a_2, we write the continuity condition I, Eq. (1.32) or (2.4), at atom (1,12):

$$a_1 \cos 5\kappa/2 = a_2 \cos(\kappa+\delta_2) .$$

The <u>signs</u> of the cosines determine the sign of the a_2. We may then consider (A.10b) to find the sign of a_4, <u>etc</u>....

Convenient checks on the calculations are provided by I, Eqs. (2.43), (2.89), and (2.90).