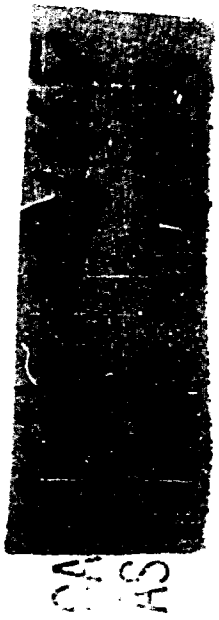

FREE-ELECTRON NETWORK MODEL FOR CONJUGATED SYSTEMS. I. THEORY[†]

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ABSTRACT

The free-electron model for conjugated systems is consistently developed as the limiting case of a three-dimensional quantum-mechanical treatment of the π-electrons in such systems. Joint conditions (for branching points) and boundary conditions (for free endpoints) are derived, and the hermiticity of the Hamiltonian is shown. A matrix formulation of the theory is established which makes the application to large systems feasible and at the same time leads to a close analogy with the LCAO model (= LCAO MO treatment considering only nearest neighbor interactions). Quantities analogous to the quantities q (= charge in an atomic orbital) and p (= bond order) are defined, and special attention is given to alternant conjugated systems, for which a population theorem, analogous to the one in LCAO theory, is valid.

INTRODUCTION

SYSTEMS of conjugated double bonds in organic molecules are, in a good approximation, described by assuming that the σ-electrons form bonds which maintain the molecular frame and that the π-electrons move in the potential of this frame. Interesting properties of the molecules depend, in a first approximation, on the π-electrons, e.g., the relative bond lengths, certain types of chemical reactivity, ultraviolet spectra, and (to a lesser degree) dipole moments; and it is therefore of interest to investigate the motion of the π-electrons by itself. A basic characteristic of this motion is the high mobility or delocalization, i.e., the fact that the different electrons are not bound to definite bonds, but move rather freely over the whole conjugated structure. The description by molecular orbitals (MO's) seems therefore particularly suited for this case.

The classical method of constructing MO's consists of forming them as LCAO MO's (linear combination of atomic orbitals). The rigorous application of this method leads to an extremely large number of difficult integrals, and only benzene has been

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successfully treated in this way.[1] In order to achieve a more general method applicable to larger classes of molecules, one generally makes the assumption that only nearest neighbors interact and considers the remaining integrals as parameters in the final result. This simplified method[2] has been rather successful, and in the following we always mean this simplified LCAO theory whenever we mention the LCAO model without further specification.

On the other hand, the existence of the core potential suggests the possibility of expressing this potential in terms of coordinates which are fitted to the particular frame of the molecule, e.g., cylindrical coordinates in the case of benzene. As a consequence, the molecular orbitals would be expressed in terms of the same coordinates. Again, this approach can be carried through for benzene,[3] but it becomes very complicated for larger molecules. Here too, however, there exists a simplified formulation applicable to any conjugated system: the one-dimensional free-electron model.

This model is not new,[4] but it has mostly been regarded as a pictorial, but rough, description. It is the purpose of the present paper to show that the free-electron model deserves the same recognition and standing as the simplified LCAO model. A close analogy between the mathematics of the two models will be derived,[4c] and in the second paper of the present series[5] a close agreement will be established between the

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[1] M. Goeppert-Mayer and A. L. Sklar, J. Chem. Phys. 6, 645 (1938); C. C. J. Roothaan, and R. G. Parr, J. Chem. Phys. 17, 1001 (1949); Parr, Craig, and Ross, J. Chem. Phys. 18, 1561 (1950); C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).

[2] See, e.g., Coulson and Longuet-Higgins, Proc. Roy. Soc. A191, 39 (1947); see also reference 8.

[3] See K. Ruedenberg and R. G. Parr, J. Chem. Phys. 19, 1268 (1951).

[4a] L. Pauling, J. Chem. Phys. 4, 673 (1936); O. Schmidt, Ber. Deutsch. Chem. Ges. 73A, 97 (1950); J. R. Platt, J. Chem. Phys. 17, 484 (1949); H. Kuhn, Helv. Chim. Acta 31, 1441, 1780 (1948), 32, 2247 (1949), 34, 1308, 2371 (1951), J. Chem. Phys. 16, 840 (1948), 17, 1198 (1949), Zeit. f. El. Chem. 53, 165 (1949), 55, 220 (1951); S. Nikitiue, J. Chim. Phys. 47, 614 (1950).

[4b] N. S. Bayliss, J. Chem. Phys. 16, 287 (1948), 17, 1853 (1949), Aust. J. Sci. Res. A3, 109 (1950); N. S. Bayliss and J. C. Riviere, Aust. J. Sci. Res. A4, 344 (1951); W. T. Simpson, J. Chem. Phys. 16, 1124 (1948).

[4c] An analogy between the LCAO model and the FE model in the simplest cases (no branch points) was already noticed by W. T. Simpson, J. Chem. Phys. 17, 1218 (1949), and H. H. Jaffe, J. Chem. Phys. 20, 1646 (1952).

[5] C. W. Scherr, J. Chem. Phys. 21, 000 (1953).

numerical results obtained by the two models. Thus, from an empirical point of view, the free-electron model seems to serve as well to describe conjugated systems as the simplified LCAO model.

But also from the theoretical point of view, the free-electron model offers several attractive properties: 1) once the free-electron model is chosen, the quantum-mechanical problem is rigorously solved; one makes no further approximations of virtually uncontrolled implications, as, e.g., the assumption of considering only nearest-neighbor interactions in the LCAO model; 2) in the case of hydrocarbons, the free-electron model has only one parameter, the neighbor distance D, as compared to the two parameters β, S of the LCAO model;[6] 3) the meaning of the parameter D in terms of measurable quantities is more precisely defined than the meaning of the parameters occurring in the LCAO model; therefore there is but little "leeway" to "adjust" D and the free-electron model comes closer to being an "absolute theory" (= no adjustable parameters); 4) the free-electron wavefunctions are easy to visualize--a fact which is demonstrated by the model of J. R. Platt explained in the third paper of this series.[7] Of course the LCAO model has the advantage that it is in a position to describe simultaneously all electrons, not only the π-electrons, in a molecule.

The second part of the present paper is restricted in scope to the case that all atoms in a conjugated structure are mathematically equivalent, i.e., practically to the case of hydrocarbons. A method to include the effect of heteroatoms is in preparation.

1. GENERAL CONCEPTS

a. The Model

The organic molecules to which the present theory applies are characterized by the fact that each of them contains a so-called conjugated system of bonds, i.e., a system of alternating single and double bonds. Each atom within a conjugated system contributes two σ-electrons and one π-electron for the chemical binding of the conjugated structure. In the approximation considered here, the σ-electrons form σ-bonds which maintain the geometrical arrangement; and the molecular framework, stripped of the π-electrons, forms a "skeleton" or "core" which, because of positive charge,

[6] For a fair comparison it should be noted that the correlation of the LCAO model with experimental data can be obtained by assigning a fixed value to S and treating β as the only empirical parameter. The LCAO model actually contains a third parameter, α, which however serves only to calibrate the zero point of the energy.

[7] J. R. Platt, J. Chem. Phys. 21, 000 (1953).

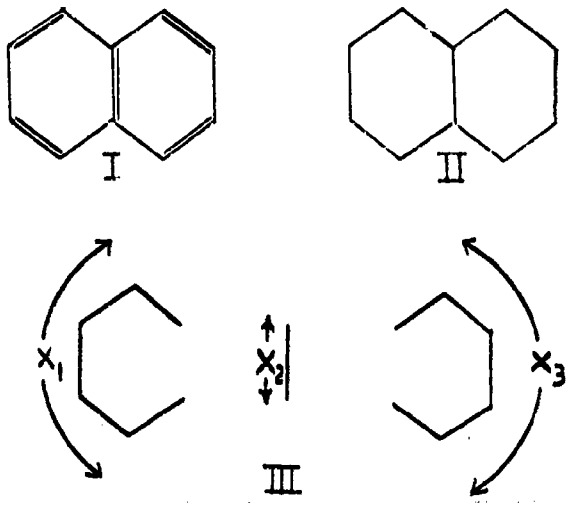

Fig. 1

creates a potential under whose influence all π-electrons move throughout the entire conjugated structure. Thus, if formula I of Figure 1 describes for example the naphthalene molecule, formula II in the same figure would be an appropriate description of the corresponding molecular skeleton. Indeed, this formula gives even a correct geometrical picture of the physical skeleton, since it is well known that all atoms belonging to a conjugated system lie in one plane.

The starting point of the theory to be developed here is the assumption that the core potential is infinitely high everywhere except on the bond lines of the skeleton structure II, where it is finite. Obviously such a potential has to be considered as the limiting case of a potential which is infinitely high everywhere except within a thin tube extending along the bond lines. Furthermore the interelectronic interaction is, in a first approximation, neglected between the π-electrons so that the latter move, independent of each other under the influence of the core potential.

b. Linear Bond Paths

In order to determine the implications of the assumptions just made, let us, as a first example, consider the motion of an electron in a long thin box of length ℓ and with a square cross-section of side-length $\epsilon \ll \ell$ (see Figure 2). This model corresponds to the π-electronic motion in a polyene, e.g., butadiene. The eigenfunctions

$$\Phi_{nmm'}(x,y,z) = (2/\ell)^{\frac{1}{2}}(2/\epsilon)\sin(\pi nx/\ell)\sin(\pi my/\epsilon)\sin(\pi m'z/\epsilon) \qquad (1.1)$$

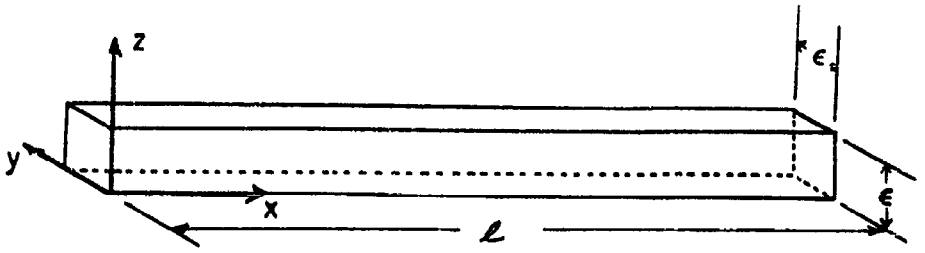

Fig. 2

must be antisymmetric with respect to the plane $z = \epsilon/2$, which we take to be the nodal plane of the π-electrons so that the quantum numbers assume the values

$$n = 1,2,3,\ldots;\ m = 1,2,3,\ldots;\ m' = 2,4,6,\ldots \tag{1.2}$$

From the expression for the eigenvalues

$$E_{nmm'} = (h^2/8m)\,[(n/\ell)^2+(m/\epsilon)^2+(m'/\epsilon)^2] \quad , \tag{1.3}$$

it follows that, because of $\epsilon \ll \ell$, the motions in the y- and z-directions remain in their ground state ($m = 1$, $m' = 2$) while the x-motion is excited to its lower levels, so that

$$E = E_{n12} = (h^2/8m)[(n/\ell)^2+(5/\epsilon^2)] = E_n + \text{const.} \quad , \tag{1.4}$$

$$E_n = (h^2/8m\ell^2)n^2 \quad , \tag{1.5}$$

and the wavefunctions have a single nodal plane perpendicular to the z-axis in agreement with the nodal properties of $2p\pi$ atomic orbitals. Hence the y- and z-motion may be neglected for low excitations, and it is sufficient to work with the energies (1.5) and the wavefunctions

$$\phi_n(x) = (2/\ell)^{\frac{1}{2}} \sin(\pi n x/\ell) \quad , \tag{1.6}$$

which may be defined by the equations

$$\phi_n^2(x) = \int dx \int dy \Phi_{n12}^2(x,y,z) = \int_Q dQ \Phi_{n12}^2 \quad , \tag{1.7}$$

$$\text{sign of } \phi_n(x) = \text{sign of } \Phi_{n12}(x, y=\tfrac{1}{2}\epsilon, z=\tfrac{1}{2}\epsilon) \quad , \tag{1.7'}$$

where Q denotes a cross-section of the tube and $dQ = dxdy$, a cross-section element. The functions (1.6) are the normalized eigenfunctions of the <u>one-dimensional</u> eigenvalue problem considered by the free-electron model, and the energies E_n (1.5) are the corresponding energy eigenvalues.

The limiting process $\epsilon \to 0$ leaves $\phi_n(x)$ and E_n unaffected and therefore meaningful, whereas Φ_{n12} and E_{n12} become infinite. The latter circumstance means that the y- and z-excitation energies become <u>infinitely</u> high so that $\phi_n(x)$ and E_n give (for $\epsilon = 0$) a correct description of the system for <u>all finite</u> excitations of the x-motion, <u>i.e.</u>, for all finite quantum numbers n.

Since high excitations effect, however, structural changes in organic molecules,

they do not have to be considered and the assumption $\epsilon \ll \ell$ is actually sufficient to justify the use of the one-dimensional description given by (1.5,6), i.e., the physical assumption is only that the π-electrons form a cloud whose length is large compared to its width. The passage to the limit $\epsilon \to 0$ is only a matter of mathematical convenience and does not imply that the π-electron cloud is actually infinitely thin.

c. Comparison with the LCAO Model

The present theory is thus, physically, a three-dimensional theory, and the electron cloud of a π-electron is its MO. These MO's are not entirely different in nature from the MO's formed as linear combinations of atomic orbitals (LCAO MO's), if all matrix elements between non-neighboring atoms are neglected--the assumption adopted in the LCAO MO model.[8] Indeed, such an assumption implies that the radii of the (finite) atomic orbitals are smaller than one bond length in straight chains and smaller than $\frac{1}{2}\sqrt{3} = 0.87$ bond lengths in benzene rings, so that the molecular orbitals formed by them obtain also a tubular shape as shown in Figure 3, where the circles indicate the atomic orbitals, and the shaded area is inaccessible to the π-electrons.

The MO's constructed as LCAO MO's correspond to a potential which is not constant within the accessible region. This generalization can be readily introduced in our model by assuming a potential $V = V(x)$ inside the box of Figure 2. Thereby the eigenvalues (1.5) and the eigenfunctions (1.6) will be changed, but they will remain finite so that all arguments presented above remain unaltered.

There is no need to introduce a potential which depends also on y and z, since, because of $\epsilon \ll \ell$, the motions in the y- and z-directions will in any case stay in the ground state so that the (y,z)-dependence remains irrelevant. The LCAO MO model (with neglect of non-neighbor interaction) also considers essentially only "longitudinal excitations", since one can see from Figure 3 that the "transversal profile", i.e., the (y,z)-dependence, of the LCAO MO is much less changed by varying the coefficients of the different atomic orbitals than the "longitudinal profile".

The purpose of the foregoing remarks is not to justify the free-electron model by vague analogies with the LCAO MO model, but to give a plausible reason for the agreement which exists, as we hope to show, between the two methods.

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[8] An introduction to the LCAO MO treatment and further literature may be found in B. and A. Pullmann: Les théories électroniques de la chimie organique (Masson and Co., Paris: 1952), ch. IV, 2.

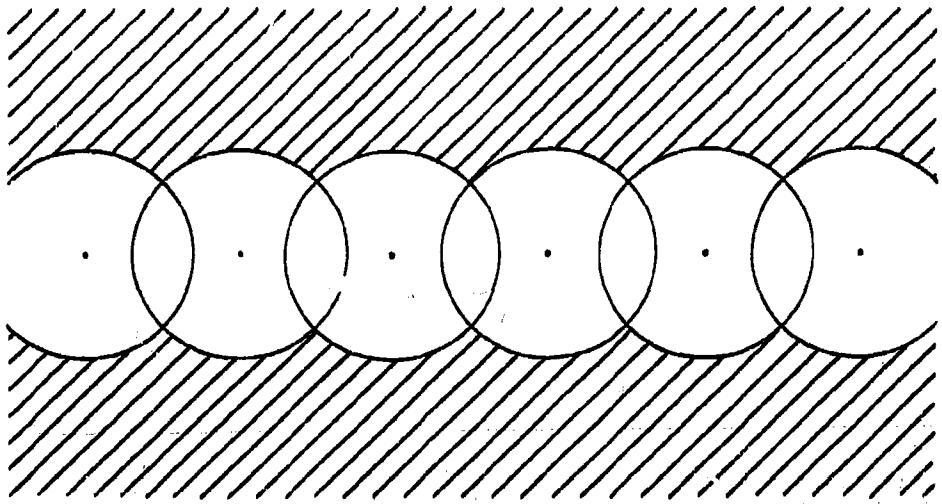

Fig. 3

d. Non-Linear Bond Paths

Let us take benzene as an example of the case that the bond path is no longer a straight line, and let us for the moment assume that the π-electrons move in a thin circular tube (torus of radius R) rather than in a hexagonal tube. Let us further replace the annular well potential representing the torus by the analytic potential

$$V(r,\phi,z) = U(2\alpha)^{-2}\{(Z/R)^2+[(r/R)-(R/r)]^2\} \quad , \tag{1.8}$$

$$U = \hbar^2/2mR^2 \quad , \tag{1.9}$$

where the cylindrical coordinates z, r, and ϕ (z perpendicular to the molecular plane) are used, and α is a dimension less constant $<< 1$. It is sensible to define

$$\epsilon = \alpha R \tag{1.10}$$

as the diameter of the corresponding tube, whereas $\ell = 2\pi R$ is its length, so that indeed $\epsilon/\ell = \alpha/2\pi << 1$.

It has been shown[4] that the potential (1.8) leads to energy levels

$$E_{n_\phi n_r n_z} = E_{n_\phi} + E_{n_r} + E_{n_z} \quad , \tag{1.11}$$

where E_{n_ϕ} corresponds to angular excitations, E_{n_r} corresponds to radial excitations, and E_{n_z} corresponds to out-of-plane excitations. The energy levels E_{n_ϕ} of the "longitudinal motion" are given by

$$E_{n_\phi} = Un_\phi^2 f(\alpha^2 n_\phi^2) \ , \quad n_\phi = 0, \pm 1, \pm 2, \ldots \ , \tag{1.12}$$

$$f(x) = [(1+4x)^{\frac{1}{2}}-1]/2x = 1 - x + \ldots \ , \tag{1.13}$$

and for the two transversal motions one finds the excitation energies

$$\Delta E_{n_r} = \Delta E_{n_z} = 2U/\alpha >> \Delta E_{n_\phi} \ . \tag{1.14}$$

It is therefore again true that the excitations of the transversal motions can be neglected, and that the energy levels of the longitudinal motion approximate the limiting levels

$$\lim_{\epsilon \to 0} E_{n_\phi} = Un_\phi^2 \ . \tag{1.15}$$

These are, however, identical with the levels obtained by considering the one-dimensional motion of a particle along the line which is the limit of the tube as $\epsilon \to 0$.

These conclusions can be expected to be independent of the particular example chosen, i.e., to hold not only for a circular tube, but for a tube along any arbitrary bond path, e.g., for the hexagonal tube of benzene. This expectation will be justified at the end of the next subsection. We have then the general result that the assumption of a potential, infinite everywhere except on the bond skeleton, is equivalent to describing the electronic motion by an one-dimensional MO, $\phi(x)$, depending on the "bond-path coordinate" x, and assuming for $\phi(x)$ the Schrödinger equation

$$\{(d/dx)^2+(2m/\hbar^2)[E-V(x)]\}\phi(x) = 0 \ , \tag{1.16}$$

where V(x) is an appropriate potential along the bond skeleton. The complete description of the electron is then furnished by a three-dimensional molecular orbital which can approximately be written as

$$\Phi(x,y,z) \approx \phi(x)(2/\epsilon)\sin(\pi y/\epsilon)\sin(2\pi z/\epsilon) \ , \tag{1.17}$$

$$0 \le y \le \epsilon \ , \quad -\tfrac{1}{2}\epsilon \le z \le \tfrac{1}{2}\epsilon \ , \quad \epsilon << \ell \ . \tag{1.17'}$$

Here the x-coordinate is tangential to the bond paths, y is perpendicular to x in the molecular plane, and z is perpendicular to the molecular plane, which is chosen to be the plane z = 0. The orbital $\Phi(x,y,z)$ is antisymmetric with respect to this plane. A more rigorous form for $\Phi(x,y,z)$ is obtained by solving the thin-tube problem corresponding to the bond skeleton; between such a $\Phi(x,y,z)$ and the one-dimensional orbital

$\phi(x)$ one has, in analogy with (1.7,7'), the relation

$$\phi^2(x) = \lim_{\epsilon \to 0} \int_{Q(x)} dQ \Phi^2(x,y,z) \quad , \tag{1.18}$$

$$\text{sign of } \phi(x) = \text{sign of } \Phi(x, y=\epsilon/2, z=\epsilon/4) \quad , \tag{1.19}$$

where ϵ is the diameter of the tube, and $Q(x)$, its cross-section at the point x.

e. Branching Points (Joints)

Those points in a conjugated structure where three branches meet (we call them branching points or joints) present the one-dimensional formulation with a particular problem. Let us split the skeleton of Figure 1 (II) up into three branches and define on each branch an independent arbitrary coordinate system as shown by Figure 1 (III). Let $\phi_B(x_B)$ be the part of the wavefunction $\phi(x)$ which lies on the branch B(=1,2,3); more precisely: let $\phi_B(x_B)$ be defined by:

$$\left.\begin{aligned} \phi_B(x_B) &= \phi(x), \quad \text{if } x = x_B, \quad \underline{i.e.}, \text{ on branch B,} \\ \phi_B(x_B) &= 0, \quad \text{if } x \neq x_B, \quad \underline{i.e.}, \text{ on all other branches,} \end{aligned}\right\} \tag{1.20}$$

so that

$$\phi(x) = \sum_B \phi_B(x_B) \ . \tag{1.21}$$

Then the Schrödinger equation (1.16) holds for each branch function $\phi_B(x_B)$, and the question arises: how to fit together those $\phi_B(x_B)$ which meet in one joint.

A first condition is quite clearly the "continuity condition": the three branch functions $\phi_1(x_1)$, $\phi_2(x_2)$, $\phi_3(x_3)$ must assume the same value at their meeting point, i.e:

$$\phi_1(x_{1J}) = \phi_2(x_{2J}) = \phi_3(x_{3J}) \quad , \tag{1.22}$$

where x_{BJ} is the coordinate of the joint on branch B.

However, since Eq. (1.16) is a second order differential equation, we have to derive also a condition involving the first derivatives of the functions $\phi_B(x_B)$. For this purpose we consider again the system of thin tubes corresponding to a bond skeleton. Let Figure 4a illustrate the part of this system in the neighborhood of a joint.

As before, let $\Phi(x,y,z)$ be the solution of the three-dimensional Schrödinger equation inside the tube, fulfilling the boundary condition $\Phi(x,y,z) = 0$ at the walls. From

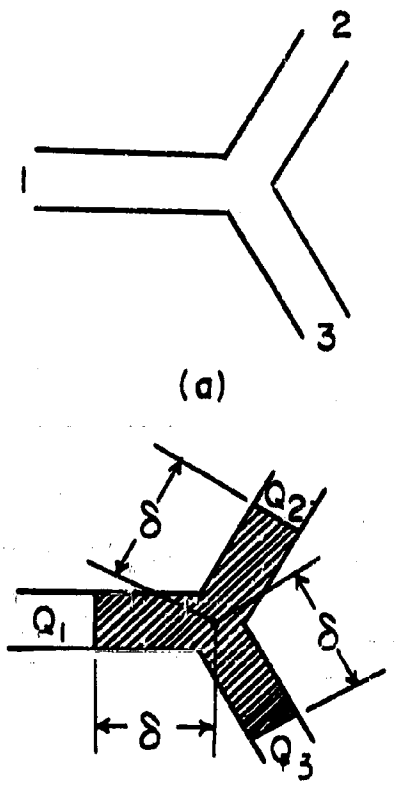

Fig. 4

$$\mathrm{div}(\Phi\ \mathrm{grad}\ \Phi) = \mathrm{grad}^2\phi + \Phi\Delta\Phi \quad , \tag{1.23}$$

we obtain by virtue of Gauss' theorem

$$\int_V dV\ (\mathrm{grad}^2\Phi + \Phi\Delta\Phi) = \int_S dS\Phi(\partial\Phi/\partial n) = \tfrac{1}{2}\int_S dS(\partial\Phi^2/\partial n) \tag{1.24}$$

where S is the surface of the volume, V, and $(\partial/\partial n)$ is the derivative in the direction of the outer normal on S. For the volume, V, we choose the volume indicated by the shaded area in Figure 4b. Since Φ vanishes on the walls, and Q_1, Q_2, Q_3, are planar cross-sections, Eq. (1.24) simplifies to

$$\sum_B \frac{\partial}{\partial x_B} \int_{Q_B} dQ\Phi^2 = 2J \quad , \tag{1.25}$$

$$J = \int_V dV(\mathrm{grad}^2\Phi + \Phi\Delta\Phi) \quad , \tag{1.25'}$$

where the coordinate x_B is tangential to the tube branch B, and pointing away from the joint. Now consider <u>first</u> the limit $\epsilon \to 0$ (ϵ = tube diameter). By virtue of Eq. (1.18,20) the left-hand side of Eq. (1.25) goes into

$$\sum_B [\frac{\partial}{\partial x_B}\phi^2(x)]_{Q_B} = \sum_B [\frac{\partial}{\partial x_B}\phi_B^2(x_B)]_{x_B = x_{BJ}+\delta} = \text{finite}; \tag{1.26}$$

hence it follows that also

$$\lim_{\epsilon\to 0} J = \text{finite},$$

and therefore the integrand of J becomes infinite of the order ϵ^{-2} as $\epsilon \to 0$. <u>Secondly</u>, consider the limit: {lim $\epsilon \to 0$ <u>and</u> lim $\delta \to 0$}, where δ is the distance of each of the three surfaces Q_B from the joint midpoint (see Figure 4b). Since the surfaces Q_B are purely fictitious, and Φ does not fulfill any boundary conditions on them, the limit $\delta \to 0$ (in distinction from the limit $\epsilon \to 0$) does in no way cause Φ to become infinite. Hence, in the limit {$\epsilon \to 0$, $\delta \to 0$}, the integrand of J, once again, goes to infinity as ϵ^{-2}, and hence

$$\lim_{\delta\to 0,\epsilon\to 0} J = 0 \quad .$$

Therefore, the expression (1.26) must vanish for $x_B \to x_{BJ}$, and we find the new boundary condition

$$\sum_B \frac{\partial}{\partial x_B}\phi^2(x_B) = \sum_B \phi_B(x_B)\frac{\partial}{\partial x_B}\phi_B(x_B) = 0 \quad \text{at the joint } x_B = x_{BJ} \ , \tag{1.27}$$

which by virtue of the continuity condition (1.22) is equivalent to

$$\left[\sum_B \left(\frac{\partial}{\partial x_B}\right)\phi_B(x_B)\right]_{\text{Joint}} = 0 \ . \tag{1.28}$$

Since Eq. (1.28) may be derived also in the case of complex wavefunctions, it is clear that Eq. (1.28) expresses the conservation of the quantum-mechanical current density:

$$(i\hbar/2m)[\phi(d\phi^*/dx) - \phi^*(d\phi/dx)] \ . \tag{1.29}$$

However, since all wavefunctions $\phi(x)$ which occur as solutions of our problems are (with a few exceptions) real, their current density vanishes everywhere so that the current conservation becomes trivial. We shall call Eq. (1.28) the "conservation condition."

The derivation of the conservation conditions is independent of the number of branches meeting at one joint. Although for our purposes only the case of three branches per joint is useful, it is still of interest to note that also in the general case the conditions (1.22) and (1.28) suffice precisely to determine the solution of the eigenvalue problem, if the wavefunction is required to have a unique value everywhere. In order to recognize this independence, consider a system containing

a_3 joints collecting 3 branches
a_4 joints collecting 4 branches
. . .
a_j joints collecting j branches,
and b "free endpoints."

If B_{max} is the total number of branches, then

$$2B_{max} = 3a_3 + 4a_4 + \ldots + ja_j + b \ . \tag{1.30}$$

Since Eq. (1.16) is a second-order differential equation, the left-hand side of Eq. (1.30) gives the number of constants in the total wavefunction $\phi(x)$; the right-hand side of Eq. (1.30), on the other hand, gives the total number of joint and endpoint conditions. Since there is one more parameter (the eigenvalue) and one more condition (the normalization of the wavefunction) in the problem, the number of unknowns to be determined equals the number of equations to be fulfilled.

It is furthermore easily seen that, in the case of one closed branch, as in benzene, the joint conditions are equivalent to the condition that the wavefunction have a period that is an integral fraction of the branch length.

On the basis of the joint conditions (1.22,28) it is possible to give a more rigorous justification for the statements leading up to Eq. (1.16), namely, that there is no difference in the treatment of linear and non-linear bond paths. Consider any non-branching point on a bond path as a joint with two branches; the conditions (1.22, 28) then are applicable and yield the result that both $\phi(x)$ and $(d\phi/dx)$ are continuous at any such point. These continuities, however, entail the validity of the Schrödinger equation (1.16) throughout the entire bond path containing only such points. Consider in particular a "corner" in the bond path, e.g., in naphthalene [see Figure 1 (II)]: on the two straight portions of the bond path meeting at the corner, Eq. (1.16) is valid; at the corner, ϕ and $(d\phi/dx)$ have to be continuous; and, if $V(x)$ is continuous, Eq. (1.16) yields that the left limit of $(d/dx)^2\phi$ equals the right limit of $(d/dx)^2\phi$. It follows that $(d/dx)^2\phi$ exists at the corner and equals the common limit so that Eq. (1.16) is valid at the corner. Hence, corners in a bond path have no implications, if the π-electronic potential is continuous.

The conditions (1.22,28) were first used by Hans Kuhn.[9] As yet no proof or discussion of the conservation condition (1.28) seems to have been given.

f. Formulation of the General Mathematical Problem

It may be useful to collect at this point the equations which determine the one-dimensional free-electron molecular orbital (FEMO). They are:

1) the Schrödinger equation on the branches:

$$H\,\phi(x) = \{(-\hbar^2/2m)(d/dx)^2 + V(x)\}\phi(x) = E\,\phi(x)\ , \tag{1.31}$$

2) the joint conditions:

$$[\phi_1(x_1) = \phi_2(x_2) = \phi_3(x_3)] \text{ at joint (continuity condition)}\ , \tag{1.32}$$

$$\sum_B (\partial\phi_B/\partial x_B)_{\text{Joint}} = 0 \text{ (conservation condition)}\ , \tag{1.33}$$

3) the boundary conditions for free endpoints:

$$\phi(x) = 0 \quad \text{at free endpoint.} \tag{1.34}$$

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[9] H. Kuhn, Helv. Chim. Acta 32, 2247 (1949).

Concerning the branches having free endpoints, there is still a question that remains to be settled--namely, where to locate the endpoint. For reasons which will become clear later [see appendix] we adopt the following postulate: The free-electron paths terminate one bond length beyond the last atom. Thus, for the styrene molecule of Figure 5a, whose bond skeleton is given by Figure 5b, the free-electron path is pictured in Figure 5c: it extends up to the point E, whereas the last atom is situated at the point C.

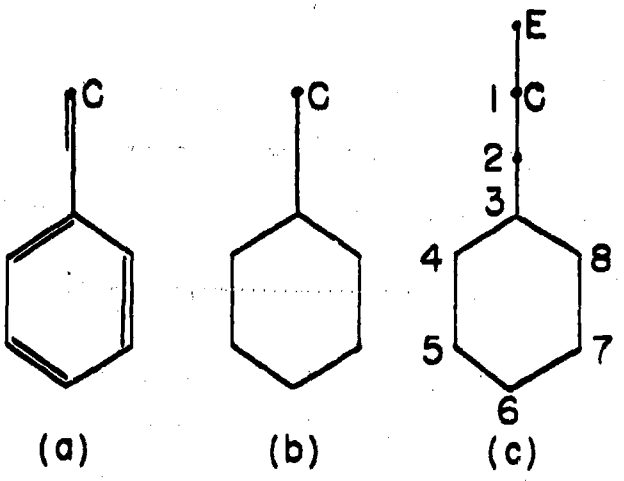

Fig. 5

The definition initially given for the free-electron model has therefore to be modified. It should now read: The potential for the π-electronic motion is assumed to be infinite everywhere except on the free-electron path, where it is finite; the free-electron path is identical with the bond skeleton except that it exceeds the latter at its free endpoints by one bond length. Some authors[5b] have used different conventions concerning the free endpoints in order to fit certain experimental data; our choice is based on theoretical grounds, as will be shown in the appendix.

5. Hermiticity, Orthogonality, Normalization

The problem just formulated is an eigenvalue problem in a one-dimensional, but multiconnected configuration space. Let [see Eqs. (1.20,21)]

$$f(x) = \sum_B f_B(x_B) \tag{1.35}$$

be a function in this space satisfying the joint and endpoint conditions (1.32,33,34), but otherwise arbitrary. The integral over the configuration space is then defined as

$$\int_\ell dx f(x) = \sum_B \int_{\ell_B} dx_B f_B(x_B) \ , \tag{1.36}$$

where ℓ indicates the total length of the free-electron paths and ℓ_B indicates the length of branch number B. In connection with such integrals the following generalization of Green's theorem is important.

Consider the integration over the one-dimensional space indicated in Figure 6,

where the coordinates x_B runs from 0 (at the joint) to a_B (at the endpoints). Let $f(x)$ and $g(x)$ be two functions of the type (1.35) which, however, do not vanish at the points a_B, since Figure 8 is assumed to be part of a larger bond skeleton. Then the following theorem holds:

$$\sum_{B=1}^{3} \int_0^{a_B} dx_B [f_B (d/dx_B)^2 g_B - g_B (d/dx_B)^2 f_B] = \sum_{B=1}^{3} [f_B (d/dx_B) g_B - g_B (d/dx_B) f_B]_{x_B = a_B} . \quad (1.37)$$

Indeed, Green's theorem yields

$$\int_0^{a_B} dx_B [f_B (d/dx_B)^2 g_B - g_B (d/dx_B)^2 f_B] = [f_B (d/dx_B) g_B - g_B (d/dx_B) f_B]_0^{a_B} \quad (1.38)$$

for each branch. If one now sums over the three branches, those terms on the right-hand side of (1.38) which are taken at the joint ($x_B = 0$) vanish by virtue of the joint conditions (1.32,33,34):

$$\sum_B [f_B (d/dx_B) g_B - g_B (d/dx_B) f_B]_{x_B = 0} = f(0) \sum_B (dg_B/dx_B)_0 - g(0) \sum_B (df_B/dx_B)_0 = 0$$

and hence Eq. (1.37) results.

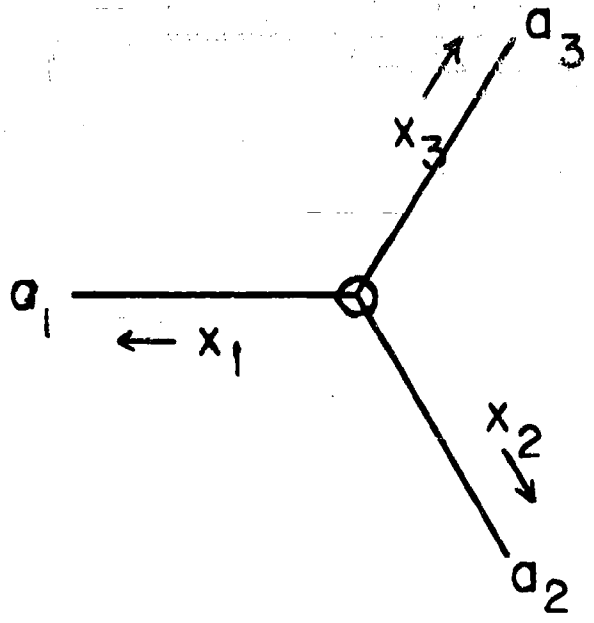

Fig. 6

If one now decomposes the total free-electron path of a bond skeleton into parts of the form of Figure 6 and applies (1.37) to each part, then all right-hand side contributions of Eq. (1.37) cancel each other or vanish at the free endpoints, where $f = g = 0$. Hence

$$\int_{\ell} dx f(x)(d/dx)^2 g(x) = \int_{\ell} dx g(x)(d/dx)^2 f(x) \ , \tag{1.39}$$

where the integration extends over the total bond skeleton; i.e., $(d/dx)^2$ is a hermitian operator with respect to our multiconnected configuration space, and so is the Hamiltonian H of the Schrödinger equation (1.31). As a consequence, the eigenvalues of that equation are real, and eigenfunctions belonging to different eigenvalues are mutually orthogonal. (Eigenfunctions belonging to the same eigenvalue can, of course, be chosen so as to be mutually orthogonal.) The validity of these properties depends essentially upon both joint conditions (1.32,33).

The eigenfunctions are required to be normalized:

$$\int_{\ell} dx \ \phi^2(x) = \sum_B \int_{\ell_B} dx_B \phi_B^2(x_B) = 1 \ . \tag{1.40}$$

2. CASE OF CONSTANT POTENTIAL

a. General Form of the Solution

If the potential V(x) is constant throughout the entire free-electron path, it can be assumed to vanish identically, and the Schrödinger equation (1.31) is readily solved. The eigenfunction of the energy level E_n has the form

$$\phi_n(x) = \sum_B \phi_{Bn}(x_B) \ , \tag{2.1}$$

$$\phi_{Bn}(x_B) = a_{Bn}\cos(k_n x_B + \delta_{Bn}) \ , \tag{2.2}$$

with

$$E_n = (\hbar^2/2m)k_n^2 \ . \tag{2.3}$$

In the following we shall omit the subscript n wherever it is not needed. The conditions which determine the parameters k, a_B, δ_B (B = 1, 2, 3,...) become very simple. The continuity conditions (1.32):

$$a_1\cos(kx_{1J} + \delta_1) = a_2\cos(kx_{2J} + \delta_2) = a_3\cos(kx_{3J} + \delta_3) \ ; \tag{2.4}$$

the conservation conditions (1.33):

$$a_1\sin(kx_{1J} + \delta_1) + a_2\sin(kx_{2J} + \delta_2) + a_3\sin(kx_{3J} + \delta_3) = 0 \ , \tag{2.5}$$

or, by virtue of (2.4):

$$\tan(kx_{1J}+\delta_1) + \tan(kx_{2J}+\delta_2) + \tan(kx_{3J}+\delta_3) = 0 \quad . \tag{2.6}$$

In these equations, x_{BJ} denotes the coordinate of the joint on the branch B. The normalization condition becomes

$$\tfrac{1}{2} \sum_B a_B^2 \ell_B = \int_\ell dx\ \phi^2(x) = 1 \quad , \tag{2.7}$$

where ℓ_B denotes, as usual, the length of the B-th branch. Eq. (2.7) is established in the following way. On branch B one obtains

$$\begin{aligned} \int_0^{\ell_B} dx_B\ a_B^2 \cos^2(kx_B+\delta_B) &= \tfrac{1}{2}a_B^2 \int_0^{\ell_B} dx_B[1+\cos 2(kx_B+\delta_B)] \quad , \\ &= \tfrac{1}{2}a_B^2\{\ell_B + k^{-1}[\sin(kx_B+\delta_B)\cos(kx_B+\delta_B)]_0^{\ell_B}\} \quad , \\ &= \tfrac{1}{2}a_B^2\ell_B - \tfrac{1}{2}k^{-2}[\phi_B(d\phi_B/dx_B)]_0^{\ell_B} \quad , \end{aligned}$$

<u>i.e.</u>,

$$\int_0^{\ell_B} dx_B \phi_B^2(x_B) = \tfrac{1}{2}a_B^2\ell_B + \tfrac{1}{2}k^{-2}\{[\phi_B(d\phi_B/dn)]_0 + [\phi_B(d\phi_B/dn)]_{\ell_B}\} \quad , \tag{2.8}$$

where (d/dn) denotes the derivative at a joint (or endpoint) in <u>that</u> direction on the branch which points <u>away</u> from the joint (or endpoint). By virtue of the normalization, the left hand side of (2.8) will become unity after summation over all branches; hence

$$k^2\{2 - \sum_B a_B^2\ell_B\} = \sum_B \{[\phi_B(d\phi_B/dn)]_0 + [\phi_B(d\phi_B/dn)]_{\ell_B}\} \quad . \tag{2.9}$$

Here each branch enters on the right-hand side only by its first and last point. These are either joints or free endpoints. The latter do not contribute anything since $\phi = 0$ at a free endpoint. The terms arising from joints, on the other hand, may be ordered according to joints, so that the right-hand side of (2.6) may be written

$$\sum_J \{\sum_{B=1} \phi_B(d\phi_B/dn)\}_{\text{on joint } J} \quad , \tag{2.10}$$

where B = 1, 2, 3 denote the three branches merging in joint J and $\sum_J$ denotes the sum over all joints of the bond skeleton. By virtue of Eqs. (1.32,33), each term in the summation over J vanishes separately, and thus Eq. (2.7) is proved. This equation may be considered a generalization of the familiar result obtained in the case of a single branch, namely that the mean value of $\cos^2 t$ between 0 and π is $\frac{1}{2}$.

It is useful to introduce, at this point, a few conventions. First of all we note that

$$a_B \cos(kx_B + \delta_B) = a'_B \cos(kx_B + \delta'_B) \quad ,$$

with

$$a'_B = -a_B \quad , \qquad \delta'_B = \delta_B \pm \pi \quad .$$

In order to eliminate any ambiguity we shall always choose the phase δ_B such that

$$\tfrac{1}{2}\pi \geqslant \delta_B > -\tfrac{1}{2}\pi \quad , \tag{2.11}$$

thereby simultaneously fixing the relative signs of the amplitudes a_B of the different branches. At the same time this establishes a one-to-one correspondence between δ_B and $\tan\delta_B$.

There is, of course, still a factor $e^{i\gamma}$ (γ = real) which is arbitrary in the normalized functions (2.1). However, we require the wavefunction to be real, and thus only a factor (-1) remains arbitrary in the total function $\phi(x)$ on Eq. (2.1).

In the second place, it is seen that the sign of k and δ may be simultaneously reversed without affecting the wavefunction (2.2) or the eigenvalue (2.3). We adopt the convention always to choose

$$k \geqslant 0 \tag{2.12}$$

which entails in each case a definite sign for δ. The de Broglie wavelength λ_ϕ of the motion described by the molecular orbital (2.1) is then given by

$$\lambda_\phi = 2\pi/k \quad . \tag{2.13}$$

Since a <u>constant</u> potential V(x) treats all atoms as equal, it is natural to consider the distance D between neighboring atoms as a constant throughout the conjugated structure. We adopt this assumption and define the dimensionless constant

$$\kappa = kD \quad , \tag{2.14}$$

which will prove to be convenient. Eq. (2.3) can then be written

$$(E_n/E_H) = (a/D)^2 \kappa_n^2 \quad , \tag{2.14'}$$

where $a = \hbar^2/e^2m$ is the Bohr radius, and $E_H = e^2/2a$ is the ionization potential of the hydrogen atom. It will soon become clear that for our purposes, κ lies always in the range

$$0 \leq \kappa \leq \pi \quad , \tag{2.15}$$

so that a one-to-one correspondence exists between κ, $\sin\kappa$, and $\cos\kappa$.

b. Eigenvectors of a Free-Electron Eigenfunction

Let

$$\phi(1), \phi(2), \ldots \phi(N) \quad , \tag{2.16}$$

denote the values which the eigenfunction $\phi(x)$, (2.1), assumes at the N atoms of the conjugated structure. We define the N-dimensional row vector

$$\phi = \begin{bmatrix} \phi(1) \\ \phi(2) \\ \cdots \\ \phi(N) \end{bmatrix} , \tag{2.17}$$

and call it the free-electron eigenvector corresponding to the eigenfunction $\phi(x)$, (2.1). This vector is uniquely determined by the function $\phi(x)$; however, inversely $\phi(x)$ is also uniquely determined by the eigenvector ϕ in conjunction with its eigenvalue (2.3). Indeed, each branch B contains at least two atoms, say P and Q, so that the constants a_B and δ_B can, by virtue of (2.2), be expressed in terms of $\phi(P)$, $\phi(Q)$, and $k = (2mE/\hbar^2)^{\frac{1}{2}}$. In order to obtain explicit expressions for a_B and δ_B it is convenient to employ the relation

$$\phi_B(x_B+\xi) = \cos(k\xi)\phi_B(x_B) + k^{-1}\sin(k\xi)(d\phi_B/dx_B)_{x_B} \quad , \tag{2.18}$$

where ξ is arbitrary. Eq. (2.18), which will also prove to be useful later, follows from (2.2) by virtue of the addition theorem for the cosine or else by means of the Taylor expansion

$$\phi_B(x_B+\xi) = \sum_{n=0}^{\infty} (\xi^n/n!)\partial^n\phi_B(x_B) = e^{\xi\partial}\phi_B(x_B) \quad ,$$

$$\phi_B(x_B+\xi) = (\cos i\xi\partial - i \sin i\xi\partial)\phi_B(x_B) \quad , \tag{2.19}$$

where $\partial = (d/dx)$. The equivalence of (2.18) and (2.19) follows from the Schrödinger equation

$$(d/dx)^2\phi(x) + k^2\phi(x) = 0 \quad . \tag{2.20}$$

In practice one chooses the origin of the coordinate on a branch, always such as

to have it coincide with an atom or with the midpoint of a bond. Consider therefore first the case that $x_B = 0$ coincides with an atom P so that

$$\phi_B(P) = a_B \cos\delta_B \quad , \tag{2.21}$$

and let Q denote the atom next to P at $x_B = D$, so that by virtue of (2.18) and (2.14)

$$\phi_B(Q) = \phi_B(P)[\cos\kappa - \sin\kappa \tan\delta_B] \quad . \tag{2.22}$$

From (2.21) and (2.22) one obtains the relations

$$\tan\delta_B = [\cos\kappa - \phi_B(Q)/\phi_B(P)]/\sin\kappa \quad , \tag{2.23}$$

$$a_B^2 = \phi_B^2(P)/\cos^2\delta_B = (1 + \tan^2\delta_B)\phi_B^2(P) \quad , \tag{2.24}$$

for the calculation of $\tan\delta_B$ and a_B^2. The sign of a_B must be the same as the sign of $\phi_B(P)$, since in Eq. (2.21) one has $\cos\delta_B > 0$ because of the convention (2.11). On the other hand, if $x_B = 0$ coincides with the midpoint of the bond between the atoms P and Q, then application of (2.18) for $x_B = 0$, $\xi_P = -\frac{1}{2}D$, and $\xi_Q = \frac{1}{2}D$ yields

$$\phi_B(P) = a_B[\cos\tfrac{1}{2}\kappa \cos\delta_B + \sin\tfrac{1}{2}\kappa \sin\delta_B] \quad , \tag{2.25}$$

$$\phi_B(Q) = a_B[\cos\tfrac{1}{2}\kappa \cos\delta_B - \sin\tfrac{1}{2}\kappa \sin\delta_B] \quad , \tag{2.26}$$

or

$$\phi_B(P) + \phi_B(Q) = 2a_B \cos\tfrac{1}{2}\kappa \cos\delta_B \quad , \tag{2.27}$$

$$\phi_B(P) - \phi_B(Q) = 2a_B \sin\tfrac{1}{2}\kappa \sin\delta_B \quad . \tag{2.28}$$

Hence one obtains for $\tan\delta_B$ and a_B^2:

$$\tan\delta_B = \frac{1 + \cos\kappa}{\sin\kappa} \frac{\phi_B(P) - \phi_B(Q)}{\phi_B(P) + \phi_B(Q)} \quad , \tag{2.29}$$

$$a_B^2 = [\phi_B^2(P) + \phi_B^2(Q) \cdot 2\cos\kappa\, \phi_B(P)\phi_B(Q)]/\sin^2\kappa \tag{2.30}$$

since $\cos\delta_B > 0$, the sign of a_B is the same as the sign of $[\phi_B(P) + \phi_B(Q)]$, see Eq. (2.27).

It is useful to define another N-dimensional row vector, namely

$$\phi = \begin{bmatrix} \varphi_1 \\ \varphi_2 \\ \cdots \\ \varphi_N \end{bmatrix} \quad , \tag{2.31}$$

whose elements $\varphi_1, \varphi_2, \ldots \varphi_N$ have subscripts corresponding again to the N atoms of the system and are defined in the following manner (see 2.16):

$$\left.\begin{aligned} \varphi_P &= D^{\frac{1}{2}}\phi(P) \ , \quad \text{if P is not a joint ("ordinary atoms") ,} \\ \varphi_Q &= (D3/2)^{\frac{1}{2}}\phi(Q) \ , \quad \text{if Q is a joint .} \end{aligned}\right\} \tag{2.32}$$

The vector $\boldsymbol{\phi}$ has, as we shall show, the property

$$\boldsymbol{\phi}^*\boldsymbol{\phi} = \sum_{P=1}^{N} \varphi_P^2 = \sum_B \tfrac{1}{2}a_B^2 \ell_B = \int_\ell dx\phi^2(x) = \sum_B \int_{\ell_B} dx_B \phi_B^2(x_B) \ , \tag{2.33}$$

where $\boldsymbol{\phi}^*$ denotes the hermitian conjugate matrix of $\boldsymbol{\phi}$, which here is identical with the transposed matrix. Since $\phi(x)$ is assumed to be a normalized eigenfunction (see 1.31), we obtain

$$\boldsymbol{\phi}^*\boldsymbol{\phi} = \sum_{P=1}^{N} \varphi_P^2 = 1 \ , \tag{2.34}$$

and therefore call $\boldsymbol{\phi}$ the normalized free electron eigenvector.

In order to establish (2.33) consider first the n atoms $Q_1, Q_2, Q_3, \ldots Q_n$ on one branch B. If x_F is the coordinate of the first atom $Q_1 = F_B$ and $x_E = x_F + (n-1)D$ is the coordinate of the last atom $Q_n = E_B$, then let us denote the argument of the cosines in (2.2) by (see 2.14)

$$\left.\begin{aligned} f &= kx_F + \delta_B \qquad\qquad (\text{first atom } F_B) \\ e &= kx_E + \delta_B = f + (n-1)\kappa \quad (\text{last atom } E_B) \ . \end{aligned}\right\} \tag{2.35}$$

For the sum

$$S_B = \sum_{\nu=1}^{N} \phi_B^2(Q_\nu) \ , \tag{2.36}$$

one obtains

$$S_B = a_B^2 \sum_{\nu=0}^{n-1} \cos^2(\kappa\nu+f) = \tfrac{1}{4}a_B^2 \sum_{\nu=0}^{n-1} \{2 + e^{i2(\kappa\nu+f)} + e^{-i2(\kappa\nu+f)}\}$$

$$= \tfrac{1}{4}a_B^2\{2n + e^{i2f}(e^{i2n\kappa}-1)/(e^{i2\kappa}-1) + e^{-i2f}(e^{-i2n\kappa}-1)/(e^{-i2\kappa}-1)\}$$

and by virtue of (2.35)

$$S_B = \tfrac{1}{4}a_B^2\{2n + [e^{i(f+e)} + e^{-i(f+e)}][e^{i(e-f+\kappa)} - e^{-i(e-f+\kappa)}]/[e^{i\kappa}-e^{-i\kappa}]\}$$

$$S_B = \tfrac{1}{2}a_B^2\{n + \tfrac{1}{2}[\sin(2e+\kappa) - \sin(2f-\kappa)]/\sin\kappa\}$$

$$S_B = \tfrac{1}{2}a_B^2\{(n-1) + \cot\kappa(\sin e \cos e - \sin f \cos f) + \cos^2 e + \cos^2 f\} \ . \qquad (2.37)$$

Giving ℓ_B the same meaning as in Eq. (2.7) and giving (d/dn) the same meaning as in Eq. (2.8) one can, in the case of a branch between two joints, write (2.37) as

$$DS_B = \tfrac{1}{2}a_B^2\ell_B + \tfrac{1}{2}D[\phi_B^2(F_B) + \phi_B^2(E_B)] + (D/2k)\cot\kappa\{[\phi_B(d\phi_B/dn)]_{F_B} + [\phi_B(d\phi_B/dn)]_{E_B}\} \ . \qquad (2.38)$$

If a branch B contains a free endpoint and Q_n is the last atom, then the free endpoint with the boundary condition $\phi = 0$ is located one bondlength beyond Q_n, i. e., at the site of a fictitious atom Q_{n+1}. Since $\phi(Q_{n+1}) = 0$, one has in this case

$$S_F(n) = \sum_{\nu=1}^{n} \phi_B^2(Q_\nu) = \sum_{\nu=1}^{n+1} \phi_B^2(Q_\nu) = S_B(n+1) \ ;$$

and we obtain Eq. (2.38) again; but all terms coming from the free end vanish.

Let us now sum Eq. (2.38) over all branches of a conjugated structure and write the result in the form

$$D \sum_B \{S_B - \tfrac{1}{2}\phi_B^2(F_B) - \tfrac{1}{2}\phi_B^2(E_B)\}$$
$$= \sum_B \tfrac{1}{2}a_B^2\ell_B + (D/2k)\cot\kappa \sum_B \{[\phi_B(d\phi_B/dn)]_{F_B} + [\phi_B(d\phi_B/dn)]_{E_B}\} \ . \qquad (2.39)$$

Taking into consideration that all contributions from free endpoints vanish, one recognizes that by virtue of (2.36) and (2.32) the left-hand side of (2.39) is identical with

$$\sum_{P=1}^{N} \varphi_P^2 = \boldsymbol{\phi}^* \boldsymbol{\phi}$$

where the sum over P includes all atoms of the conjugated system. Furthermore, the second term on the right-hand side of (2.39) is of the same nature as the right-hand side of (2.9), and vanished for the reasons given there. Thus Eq. (2.39) becomes identical with Eq. (2.33), and the proof is completed.

The normalization theorem is not limited to the eigenvector $\boldsymbol{\phi}$ (2.31). Choose, on the free electron path, any set of L-equidistant points R_1, R_2, ... R_L, whose neighbor distance, d, is adjusted in such a manner that all joints and endpoints are contained in the set, and define the L-dimensional row vector

$$\tilde{\boldsymbol{\phi}} = \begin{bmatrix} \tilde{\varphi}_1 \\ \tilde{\varphi}_2 \\ \cdots \\ \tilde{\varphi}_L \end{bmatrix} \ , \qquad (2.40)$$

with

$$\left.\begin{aligned} \tilde{\varphi}_R &= d^{\frac{1}{2}}\phi(R) , \qquad \text{if R is not a joint,} \\ \tilde{\varphi}_R &= (d3/2)^{\frac{1}{2}}\phi(R) , \quad \text{if R is a joint.} \end{aligned}\right\} \tag{2.41}$$

From the preceding derivation it is apparent that the normalization theorem (2.42,43) holds equally for $\tilde{\phi}$.

For example, one may choose $d = \frac{1}{2}D$, and then the points R_1, R_2, ... R_L are all atoms plus all bond midpoints. One obtains

$$\tilde{\varphi}_R^2 = \tfrac{1}{2}\varphi_R^2 \qquad \text{at atoms: } R = P ,$$

$$\tilde{\varphi}_R^2 = \tfrac{1}{2}D\phi^2(R) \quad \text{at bond midpoints: } R = M ,$$

hence

$$\sum_R \tilde{\varphi}_R^2 = \tfrac{1}{2}\sum_P \varphi_P^2 + \tfrac{1}{2}D\sum_M \phi^2(M) . \tag{2.42}$$

By virtue of the normalization theorem, the left-hand side of (2.42) is unity, and the first term on the right-hand side is $\frac{1}{2}$; hence one finds

$$D\sum_M \phi^2(M) = 1 , \tag{2.43}$$

where the sum extends over all bond midpoints. Eq. (2.43), which may be called the normalization theorem for the bond midpoint, serves as a convenient numerical check in any computation involving the $\phi^2(M)$.

A different example is provided by the stilbene molecule (see Figure 7). There it is possible to choose a four-dimensional normalized row vector $\tilde{\phi}$, corresponding to the four atoms A, B, C, D, with the neighbor distance $d = 3D$.

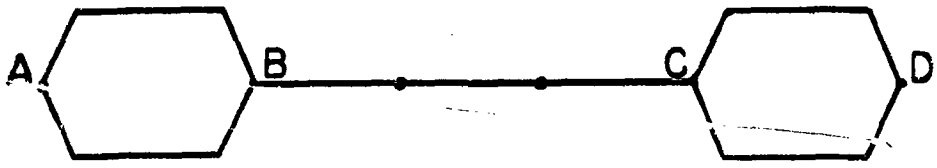

Fig. 7

c. Matrix Form of the Eigenvalue Problem

Consider three consecutive points P_{-1}, P_0, P_{+1}, on a branch with coordinates $(x_B\text{-}D)$, x_B, (x_B+D) respectively. Applying the relation (2.18) for $\phi_B(P_{-1})$ and $\phi_B(P_{+1})$, one obtains

$$\phi_B(P_{-1}) - 2\cos\kappa\ \phi_B(P_0) + \phi_B(P_{+1}) = 0\ . \tag{2.44}$$

If P_0 is the last atom at a free end, then $\phi(P_{-1}) = 0$, and hence

$$-2\cos\kappa\ \phi(P_0) + \phi_B(P_{+1}) = 0 \tag{2.45}$$

in that case. Consider furthermore a joint J and its three neighboring atoms P_1, P_2, P_3. Applying Eq. (2.18) for (P_1), (P_2), (P_3), and adding all three relations one obtains

$$\sum_{B=1}^{3} \phi_B(P_B) = 3\cos\kappa\ \phi(J) + k^{-1}\sin\kappa \sum_{B=1}^{3} (d\phi_B/dx_B)_J\ .$$

Because of the conservation condition (1.33), the second term on the right-hand side vanishes, and the result is

$$\phi(P_1) + \phi(P_2) + \phi(P_3) - 3\cos\kappa\ \phi(J) = 0\ . \tag{2.46}$$

Since for each atom one has one relation of the type (2.44,45,46), one finds exactly as many equations as there are atoms. Hence one has a system of N homogeneous linear equations for N quantities $\phi(P_1)$, $\phi(P_2)$, ... $\phi(P_N)$. This may be written

$$\mathbf{F}\,\boldsymbol{\phi} = 0\ , \tag{2.47}$$

where $\boldsymbol{\phi}$ is the eigenvector defined in Eq. (2.17), and $\mathbf{F}$ is a matrix whose structure is most easily explained by writing it down in a special case, say styrene. If the atoms are numbered in the way indicated in the free-electron path of Figure 5c, then the matrix assumes the form:

	1	2	3	4	5	6	7	8
1	-F	1						
2	1	-F	1					
3		1	-(3/2)F	1				1
4			1	-F	1			
5				1	-F	1		
6					1	-F	1	
7						1	-F	1
8			1				1	-F

(2.48)

where all elements which are omitted vanish, and

$$F = 2\cos\kappa \ . \tag{2.49}$$

Let T be the diagonal matrix defined by

$$\left.\begin{aligned} T_{PQ} &= T_P\,\delta_{PQ} \ , \\ T_P &= \begin{cases} 1, & \text{if P is not a joint} \ , \\ (\tfrac{2}{3})^{\frac{1}{2}}, & \text{if P is a joint} \ , \end{cases} \end{aligned}\right\} \tag{2.50}$$

so that the normalized eigenvector (2.31,32) is given by

$$\phi = D^{\frac{1}{2}}T^{-1}\phi \ . \tag{2.51}$$

Then Eq. (2.47) can be rewritten as the eigenvalue equation

$$\mathbf{F}\phi = F\phi \ , \tag{2.52}$$

where $\mathbf{F}$ is the matrix

$$\mathbf{F} = \mathbf{TFT} + \mathbf{FI} \ , \tag{2.53}$$

($\mathbf{I}$ = unit matrix). In the case of styrene:

$$\mathbf{F} = \begin{array}{c|cccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ \hline 1 & 0 & 1 & & & & & & \\ 2 & 1 & 0 & (2/3)^{\frac{1}{2}} & & & & & \\ 3 & & (2/3)^{\frac{1}{2}} & 0 & (2/3)^{\frac{1}{2}} & & & & (2/3)^{\frac{1}{2}} \\ 4 & & & (2/3)^{\frac{1}{2}} & 0 & 1 & & & \\ 5 & & & & 1 & 0 & 1 & & \\ 6 & & & & & 1 & 0 & 1 & \\ 7 & & & & & & 1 & 0 & 1 \\ 8 & & & (2/3)^{\frac{1}{2}} & & & & 1 & 0 \end{array} \tag{2.53'}$$

Since $\mathbf{F}$ is a symmetric matrix, it follows that the eigenvalues F are real [by virtue of (2.49) they are ≤ 2], and that the eigenvectors belonging to different eigenvalues are mutually orthogonal. From (2.34) we know that the eigenvectors are normalized. Different eigenvectors of one degenerate level can of course be orthogonalized. Hence the eigenvectors $\phi_1, \phi_2, \ldots \phi_n$ of (2.52), corresponding to the eigenfunctions $\phi_1(x)$,

$\phi_2(x) \ldots \phi_n(x)$ satisfy the relations

$$\phi_n^* \phi_m = \sum_{p=1}^{N} \varphi_{np} \varphi_{mp} = \delta_{mn} , \tag{2.54}$$

in analogy with

$$\int_\ell dx \phi_n(x) \phi_m(x) = \delta_{mn} . \tag{2.55}$$

The eigenvalues F_n are found as solutions of the secular equation corresponding to (2.52) or (2.47):

$$|F - FI| = 0 , \tag{2.56}$$

or

$$|F| = 0 . \tag{2.57}$$

From the eigenvalues F_n one finds the energy levels E_n by means of (2.49) and (2.14').

When the eigenvalues are found, the eigenvectors ϕ_n can be determined as solutions of the system of equations (2.52), or the eigenvector ϕ can be determined as solutions of (2.47). Finally, the free-electron wavefunctions $\phi_n(x)$ can be calculated from the eigenvectors by the method outlined in Eqs. (2.21-30).

In this way, energy levels and eigenfunctions of the free-electron problem with constant potential can be determined without explicit use of the boundary condition (1.34) and the joint conditions (2.4,5,6); and application of the model to larger molecules is made possible. Whereas the determination of the eigenvalues must always be done by means of the secular equation (2.56,57) (except in the very simplest cases), it is sometimes more convenient to determine the free-electron wavefunctions directly than to calculate the eigenvectors. This is the case when the phases of the wavefunction are immediately given by the symmetry of the system (for example in naphthalene); once the eigenvalues and all phases δ_B of a wavefunction are known, it is easy to determine its amplitudes, a_B, by use of the equations (2.4) and (2.7).

It should be noted that the matrix form of the eigenvalue problem can equally well be developed for eigenvectors of the type discussed in Eq. (2.40). A nice application of this fact to the stilbene molecule of Figure 7 will be discussed later. Another consequence is that the orthonormality relations (2.54) hold also for the eigenvectors $\tilde{\phi}_n$ (2.40). Incidentally it may be mentioned that the orthogonality of eigenvectors belonging to different eigenvalues can also be derived directly by the

method employed in the proof of the normalization theorem (2.34).

d. Discussion, Applications

The N values which are obtained for $F = 2\cos\kappa$ give rise to infinitely many values of κ. There are N values $\kappa_n (n = 1, 2 \ldots N)$ in the range $0 \leq \kappa_n \leq \pi$ and each of these N values κ_n gives rise to an infinite set of κ values, namely

$$\kappa_{n\nu}^{\pm} = \pm\kappa_n + 2\pi\nu \ , \quad \nu = 1, 2, 3 \ldots \ . \tag{2.58}$$

A possible situation in the case N = 2 is shown in Figure 8. We note that by definition $\kappa \geq 0$ (see 2.12). To each value $\kappa_{n\nu}^{s} (s = \pm)$ belongs, by means of (2.14'), one eigenvalue $E_{n\nu}^{\pm}$ and, by means of Eqs. (2.21-30), one wavefunction $\phi_{n\nu}^{\pm}(x)$.

Thus each eigenvector $\boldsymbol{\phi}_n$ gives rise to an infinite set of eigenfunctions $\phi_{n\nu}^{s}(x)$. For the N lowest-energy levels, i. e., those in the range $(0 \leq \kappa \leq \pi)$, the de Broglie wavelength λ_ϕ (2.13) is

$$\lambda_\phi \geq 2D \ . \tag{2.59}$$

Hence there can be no more than one node from each wavefunction between two neighboring atoms. For the wavefunctions corresponding to $\kappa > \pi$, on the other hand, there always exists pairs of neighboring atoms between which are at least two nodes.

The eigenvalue $\kappa_n = 0$ (corresponding to $F_n = 2$) implies $\lambda_\phi = \infty$, i. e., a constant wavefunction. Hence it does not occur if the electron path has a free endpoint, since a constant wavefunction would have to vanish identically. This eigenvalue always occurs, however, if the electron path has no free endpoints.

Fig. 8

Since the molecule contains N π-electrons, the one-half N lowest levels are doubly occupied in the ground state. If N is odd, then the highest level is only singly occupied in the ground state. Later, it will be shown that for alternant hydrocarbons all ground-state levels have

$$\kappa \leq \pi/2 \ ; \tag{2.60}$$

but also for those non-alternant hydrocarbons which were investigated by one of us,[6]

the condition (2.60) was always found to be valid for the ground-state levels.

The excitations of the highest electrons to the next higher levels correspond to the π-electron spectra of the conjugated molecule. The transition energy $\Delta E = E_m - E_n$ between two levels E_m, E_n is given by

$$\Delta E = E_D \Delta(\kappa^2) \ , \tag{2.61}$$

with

$$E_D = E_H (a/D)^2 \ ; \tag{2.62}$$

the corresponding wavenumber $(1/\lambda) = \Delta E/hc$ by

$$(1/\lambda) = (1/\lambda_D)\Delta(\kappa^2) \ , \tag{2.63}$$

or

$$(1/\lambda) = \tfrac{1}{2}\lambda_c \Delta(1/\lambda_\phi^2) \ , \tag{2.64}$$

with

$$(1/\lambda_D) = \lambda_c/8\pi^2 D^2 \ . \tag{2.65}$$

Here the symbol Δx always has the meaning $x_m - x_n$; λ_ϕ is the de Broglie wavelength (2.13) of a free-electron orbital; $a = 0.529151\text{Å}$ is the Bohr radius; $E_H = 13.6035\text{eV}$ is the atomic ionization potential of hydrogen; and $\lambda_c = 0.0242607\text{Å}$ is the Compton wavelength. For $D = D_C = 1.40000\text{Å}$ (the subscript C stands for "conjugated", the value 1.40000 being a mean value for the bond distance in conjugated systems) one obtains the numerical values

$$E_C = 1.9432\text{eV} = 44.827\text{kcal/mole} \tag{2.66}$$

$$(1/\lambda_C) = 15{,}677\text{cm}^{-1} \ . \tag{2.66'}$$

For other values of D one finds E_D and λ_D by means of the relation

$$(E_D/E_C) = (\lambda_C/\lambda_D) = (D_C/D)^2 \ . \tag{2.67}$$

Because of Eq. (2.60) it follows then that the lowest π-electronic excitation energies are of the order of magnitude given in Eq. (2.66,66'), or rather a little larger. This result is in agreement with experiment. In contrast, the excitation of an electron

from a ground-state level to a level with $\kappa \geq \pi$ needs an energy $\Delta E \geq (\pi^2 - \frac{1}{4}\pi^2)E_D = 14.3\text{eV}$. Since the ionization energy for benzene is 9.24eV, such a level cannot have a physical meaning, i. e., the approximations of the free-electron model which do not allow for ionization become insufficient for excitations of this magnitude.

The lowest N levels of the free-electron model correspond to the N levels found in LCAO theory. The similarity between the form of the matrix $\mathbf{F}$ (2.53) and the matrix which determines the eigenstates in LCAO theory is striking; indeed, the only difference is that each joint introduces a factor $(2/3)^{\frac{1}{2}}$ into the matrix $\mathbf{F}$, whereas it does not do so in the LCAO matrix. The set of linear equations (2.44,45,46) is of the same nature as the corresponding system in LCAO theory, and the simplifications on the basis of the molecular symmetry can therefore be achieved by exactly the same methods which are used in LCAO theory.[10] It should be noted that each free-electron eigenfunction belongs to a definite representation of the three-dimensional symmetry group of its molecule. In order to find this representation one has to take into account that the total three-dimensional free-electron wavefunction (see Eq. (1.17) ff.) is antisymmetric with respect to the molecular plane. It follows that a one-to-one correspondence exists between the free-electron states and the LCAO states according to their group-theory classification. However, the order of the energies is not always the same same; an example is given by the fourth and fifth levels in perylene (cf. refs. 6 and 8): The LCAO model furnishes $E_{A_u} > E_{B_{1u}}$, the free-electron theory, $E_{B_{1u}} > E_{A_u}$. Also the free-electron method may yield accidental degeneracies not shown by the LCAO model and vice versa. (E. g., the sixth to ninth levels inclusive in perylene are degenerate in the LCAO model, but not in the free-electron model.)

Let M_- and M_+ be the two bond midpoints on both sides of a non-joint atom P, and let P and Q be the two atoms on both sides of a bond midpoint M. Then it is sensible to define an atom population, a', on P and a bond population, b', on the bond PQ by the equations

$$a'(P) = \sum_n f_n \int_{M_-}^{M_+} dx \phi_n^2(x) , \tag{2.68}$$

$$b'(M) = b'(PQ) = \sum_n f_n \int_P^Q dx \phi_n^2(x) , \tag{2.68'}$$

where $f_n = 0, 1, 2$ denotes the number of electrons occupying the orbital $\phi_n(x)$. The sum extends only over the filled orbitals, since $f_n = 0$ for the other cases. For an

[10] See, e. g., ref. 8, page 196.

atom P_J at a joint the atom population has to be defined by

$$a'(P) = \sum_n f_n \sum_{B=1}^{3} \int_{P_J}^{M_B} dx_B \phi_{Bn}^2(x_B) \tag{2.68"}$$

where M_1, M_2, M_3 are the three bond midpoints between P_J and its three neighbor atoms.

Instead of using the quantities a' and b', it is simpler to work with the quantities a and b, defined by (See Eq. (2.32))

$$a(P) = \sum_n f_n \varphi_{nP}^2 = T_P^{-2} D\, \omega(P) , \tag{2.69}$$

$$b(PQ) = b(M) = D\, \omega(M) , \tag{2.69'}$$

where

$$\omega(x) = \sum_n f_n \phi_n^2(x) \tag{2.70}$$

denotes the total π-electronic linear density at the point x, and T_P is defined in Eq. (2.50). One would have $a = a'$ and $b = b'$, if $\phi(P)$, $\phi(M)$, $\phi(P_J)$ would represent the mean value of the function $\phi(x)$ in the integrals (2.68), (2.68'), (2.68"), respectively. Although this is, in general, not true for a single atom or bond, it can be considered to hold <u>on the average</u>, in the sense of the following argument. According to Eqs. (2.33) and (2.43) the total π-electronic population of the molecule can be expressed as

$$N = \sum_n f_n \int_{\ell} dx \phi_n^2(x) = \sum_P a(P) = \sum_M b(M) , \tag{2.71}$$

whence

$$\sum_P a'(P) = \sum_P a(P) = N , \tag{2.71'}$$

$$\sum_M b'(M) = \sum_M b(M) = N , \tag{2.71"}$$

where the summation over P contains all atoms and the summation over M contains all bond midpoints (N is the number of electrons). Hence, <u>on the average</u>, a(P) may be considered as the contribution of atom P to the total population, and b(PQ) may be considered as the contribution of the bond PQ to the total population. In the following, we shall apply the terms atom population and bond population to a and b respectively.

The quantities a, b have a similar physical meaning as the analogous quantities q (= the number of electrons on an atom) and p (= bond order between two atoms) of the

LCAO model.[2] It follows then that the reactivities of the different atoms and the total π-electronic dipole moment of the molecule are connected with the a's in the same way as they are connected with the q's, and the application can be taken over directly from LCAO theory. It should be noted however that at the joints there is a difference between the electron density and the electron population (t' is difference is unknown in LCAO theory), and one may raise the question whether the former or the latter decides the chemical reactivity. The quantities b, on the other hand, are related to the bond lengths and the so-called free valences of the same atoms in the same way as the LCAO quantities, p.

On this basis it is possible to correlate the free-electron wavefunctions with experimental facts. The numerical comparison shows that the free-electron results are in no way inferior to the results obtained from the LCAO model.

e. Alternant Conjugated Systems

We conclude the present paper by showing that the free-electron theory describes the particular character of the alternant conjugated system with an even number of atoms in the very same way as the LCAO model does.[11] This important group of molecules, which includes all conjugated structures composed of even-membered rings, is defined by the following properties: The conjugated structure contains an even number of atoms, and it must be possible to divide all atoms into two classes, e. g., "starred ones" and "unstarred ones", in such a fashion that no two neighbors belong to the same class.

The theoretical characteristics of these molecules have their origin in the "pairing theorem", which we shall now establish. Let J be the matrix

$$J = \begin{pmatrix} 1 & 0 & 0 & 0 & \dots & 0 \\ 0 & -1 & 0 & 0 & \dots & 0 \\ 0 & 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 0 & -1 & \dots & 0 \\ & & \cdot & \cdot & \cdot & \\ 0 & 0 & 0 & 0 & \dots & \pm 1 \end{pmatrix} , \qquad (2.72)$$

i. e., J is a diagonal matrix in which all elements corresponding to the starred atoms are 1 and all elements corresponding to the unstarred atoms are -1. Then

$$J^2 = I , \qquad (2.73)$$

[11] Alternant systems with an odd number of atoms present no difficulties and will be dealt with in a subsequent paper.

where I denotes the unit matrix, and

$$\mathbf{J}\mathbf{F}\mathbf{J} = -\mathbf{F} \ , \tag{2.74}$$

where $\mathbf{F}$ is the matrix (2.53). Hence it follows from (2.52) that

$$\mathbf{F}\boldsymbol{\phi}' = \mathbf{F}'\boldsymbol{\phi}' \ , \tag{2.75}$$

with

$$\boldsymbol{\phi}' = \mathbf{J}\boldsymbol{\phi} \ , \tag{2.76}$$

$$\mathbf{F}' = -\mathbf{F} \ . \tag{2.77}$$

That is: If $\boldsymbol{\phi}$ is an eigenvector with the eigenvalue F, then $\boldsymbol{\phi}'$ is an eigenvector with the eigenvalue $F' = -F$. Hence, if κ_n is an eigenvalue of κ (see Eq. (2.49)), then

$$\kappa_n' = \pi - \kappa_n \tag{2.78}$$

is also an eigenvalue. Combined with Eq. (2.58), this leads to the result that with $\kappa_n (\leq \pi/2)$ one has simultaneously the eigenvalues

$$\left.\begin{aligned} \kappa_{n\nu} &= \kappa_n + \nu\pi \\ \kappa'_{n\nu} &= (\pi - \kappa_n) + \nu\pi \end{aligned}\right\} \quad \nu = 0, 1, 2, 3 \ldots \ . \tag{2.79}$$

Figure 9 shows all the eigenvalues generated by one κ_n, which must appear together in an alternant system.

Fig. 9

Let κ_n be the smaller one and let κ_n' be the larger one of the two paired eigenvalues $\leq \pi$, i. e.,

$$0 \leq \kappa_n \leq \tfrac{1}{2}\pi \ , \tag{2.80}$$

$$\tfrac{1}{2}\pi \leq \kappa_n' \leq \pi \ . \tag{2.81}$$

Then it follows for the two paired eigenfunctions $\phi_n(x)$ and $\phi_n'(x)$ that

$$\lambda_{\phi_n} \geq 4D \ , \tag{2.82}$$

$$4D \geq \lambda_{\phi'_n} \geq 2D \ , \tag{2.83}$$

i. e., for $\phi_n(x)$ two nodes are at least two bond lengths apart, and for $\phi'_n(x)$ the distance of two nodes lies between one and two bond lengths. Moreover, one sees from Eq. (2.76) that

$$\left.\begin{aligned} \phi_n(P) &= \phi'_n(P) \quad \text{at each starred atom,} \\ \phi_n(P) &= -\phi'_n(P) \quad \text{at each unstarred atom,} \end{aligned}\right\} \tag{2.84}$$

or vice versa, depending on the choice of the arbitrary signs in the wavefunctions.

The explicit form of the wavefunction $\phi'_n(x)$ becomes simple on a branch where the point $x_B = 0$ coincides with an atom: If $\phi_n(x)$ is given by Eq. (2.2), then $\phi'_n(x)$ is given by

$$\phi'_{Bn}(x) = a_{Bn} \cos[(D^{-1}\pi - k_n)x_B - \delta_{Bn}] \ , \tag{2.85}$$

as may be verified by taking account of Eqs. (2.78,84) in Eqs. (2.23, 24) which determine k_n, δ_{Bn}, k'_n, δ'_{Bn}. From (2.85) follows indeed that

$$\phi'_{Bn}(\nu D) = (-1)^{\nu}\phi_{Bn}(\nu D), \quad \nu = 1, 2, 3 \ldots \ , \tag{2.86}$$

which is identical with (2.84), if one chooses the point $x_B = 0$ to be a starred atom. On the other hand, on a branch where $x_B = 0$ coincides with a bond midpoint one finds, by virtue of (2.29,30) and (2.78,84), that

$$\phi'_{Bn}(x) = a_{Bn} \cos[(D^{-1}\pi - k_n)x_B + (\tfrac{1}{2}\pi - \delta_{Bn})] \ , \tag{2.87}$$

whence

$$\phi'_{Bn}[(\nu - \tfrac{1}{2})D] = (-1)^{\nu}\phi_{Bn}[(\nu - \tfrac{1}{2})D], \quad \nu = 1, 2, 3 \ldots \ , \tag{2.88}$$

which agrees with (2.84) if $x_B = -\frac{1}{2}D$ is chosen as a starred atom.

An immediate consequence of the pairing theorem is the population theorem, which states that the total π-electronic population at each atom is unity in the ground state of an alternant conjugated system. This theorem, which excludes, for example, the existence of a π-electronic dipole moment for alternant systems, is established in the following way: By virtue of the pairing theorem, in particular Eq. (2.84), the

π-electronic atom population (2.70) in the ground state can be written

$$a(P) = \sum_{n=1}^{N/2} 2\varphi_{nP}^2 = \sum_{n=1}^{N} \varphi_{nP}^2 \,. \tag{2.89}$$

Now Eq. (2.64) states that the quantities φ_{nP}, taken for n = 1, 2, ... N, form an orthogonal matrix and hence

$$a(P) = 1 \,. \tag{2.90}$$

This population theorem is the counterpart of the identical theorem in the LCAO model.

Since the secular equation simultaneously has the eigenvalues F and -F, it must be possible to write it as a system of $\frac{1}{2}N$ equations containing only F^2. Such a system can be obtained in the following manner: The matrix $\mathbf{F}^2$ commutes with J (2.72):

$$\mathbf{F}^2\mathbf{J} = \mathbf{J}^2\mathbf{F}\mathbf{J}^2\mathbf{F}\mathbf{J} = \mathbf{J}(-\mathbf{F})(-\mathbf{F}) = \mathbf{J}\mathbf{F}^2 \,, \tag{2.91}$$

and hence has no elements (different from zero) connecting starred and unstarred atoms. Hence the vector transformation described by $\mathbf{F}$ leaves both the "starred subspace" and the "unstarred subspace" invariant, and hence the eigenvectors of $\mathbf{F}$ can be assumed to have only starred components or only unstarred components. The eigenvalue of $\mathbf{F}^2$ is of course F^2. Indeed from (2.52) and (2.75, 76, 77) it follows that

$$\mathbf{F}^2\boldsymbol{\phi} = F^2\boldsymbol{\phi} \,, \tag{2.92}$$

$$\mathbf{F}\mathbf{J}\boldsymbol{\phi} = F^2\mathbf{J}\boldsymbol{\phi} \,, \tag{2.92'}$$

whence

$$\mathbf{F}^2\boldsymbol{\phi}_+ = F^2\boldsymbol{\phi}_+ \tag{2.93}$$

$$\mathbf{F}^2\boldsymbol{\phi}_- = F^2\boldsymbol{\phi}_- \tag{2.93'}$$

with

$$\boldsymbol{\phi}_\pm = \tfrac{1}{2}(\mathbf{I} \pm \mathbf{J})\boldsymbol{\phi} \,. \tag{2.94}$$

Since

$$(\mathbf{I} + \mathbf{J}) = \begin{bmatrix} 1 & & & & \\ & 0 & & & \\ & & 1 & & \\ & & & 0 & \\ & & & & \ddots \end{bmatrix}, \qquad (\mathbf{I} - \mathbf{J}) = \begin{bmatrix} 0 & & & & \\ & 1 & & & \\ & & 0 & & \\ & & & 1 & \\ & & & & \ddots \end{bmatrix}, \tag{2.95}$$

one may write Eq. (2.93) and (2.93') as

$$(\mathbb{F}^2)_* \, \phi_* = F^2 \phi_* \, , \tag{2.96}$$

$$(\mathbb{F}^2)_o \, \phi_o = F^2 \phi_o \, , \tag{2.96'}$$

where ϕ_* is the $\frac{1}{2}$N-dimensional vector obtained from ϕ_+ by omitting all unstarred components, and ϕ_o is the $\frac{1}{2}$N-dimensional vector obtained from ϕ_- by omitting all starred components. Similarly, $(\mathbb{F}^2)_*$ and $(\mathbb{F}^2)_o$ are obtained from $\mathbb{F}^2$ by omitting all unstarred or all starred elements respectively. The eigenvalues F^2 are therefore solutions of the two equations

$$|(\mathbb{F}^2)_* - F^2 \mathbb{I}| = 0 \, , \tag{2.97}$$

$$|(\mathbb{F}^2)_o - F^2 \mathbb{I}| = 0 \, . \tag{2.97'}$$

The eigenvectors ϕ_*, ϕ_o of (2.96) and (2.96'), corresponding to the same eigenvalue F^2, furnish the two eigenvectors ϕ_+ and ϕ_- of $\mathbb{F}^2$. From these, one obtains the two eigenvectors

$$\phi = \phi_+ + \phi_- \, , \tag{2.98}$$

$$\phi' = \mathbb{J}\phi = \phi_+ - \phi_- \, , \tag{2.98'}$$

of $\mathbb{F}$, corresponding to the two eigenvalues +F and -F. Which eigenvalue belongs to which eigenvector is decided by checking the relation (2.44), i. e., one of the equations of the set (2.52), between three neighboring points.

As an illustration let us finally consider the problem of finding the eigenvalues of the stilbene molecule, whose free-electron path has already been shown in Figure 7. In the first place, we note that one may set up a secular equation for the four points A, B, C, D, which have the neighbor distance 3D. Since they form an alternant system, the four eigenvalues, $\tilde{F}_n$, of this problem form two pairs, and since there are no free endpoints, one pair must be $\tilde{F}_1 = 2$, $\tilde{F}_4 = -2$, corresponding to $\tilde{\kappa}_1 = 0$, $\tilde{\kappa}_4 = \pi$, where $\tilde{\kappa} = 3Dk$. Hence there actually remains one eigenvalue to be determined. The matrix (2.53) becomes for these four points,

$$\tilde{F} = \begin{array}{c|cccc} & A & B & C & D \\ \hline A & 0 & 2(\frac{2}{3})^{\frac{1}{2}} & 0 & 0 \\ B & 2(\frac{2}{3})^{\frac{1}{2}} & 0 & \frac{2}{3} & 0 \\ C & 0 & \frac{2}{3} & 0 & 2(\frac{2}{3})^{\frac{1}{2}} \\ D & 0 & 0 & 2(\frac{2}{3})^{\frac{1}{2}} & 0 \end{array} \qquad (2.99)$$

whence

$$\tilde{F}^2 = \begin{bmatrix} \frac{8}{3} & 0 & \frac{4}{3}(\frac{2}{3})^{\frac{1}{2}} & 0 \\ 0 & \frac{28}{9} & 0 & \frac{4}{3}(\frac{2}{3})^{\frac{1}{2}} \\ \frac{4}{3}(\frac{2}{3})^{\frac{1}{2}} & 0 & \frac{28}{9} & 0 \\ 0 & \frac{4}{3}(\frac{2}{3})^{\frac{1}{2}} & 0 & \frac{8}{3} \end{bmatrix}, \qquad (2.100)$$

and

$$(\tilde{F}^2)_* = \begin{bmatrix} \frac{28}{9} & \frac{4}{3}(\frac{2}{3})^{\frac{1}{2}} \\ \frac{4}{3}(\frac{2}{3})^{\frac{1}{2}} & \frac{8}{3} \end{bmatrix} = (\tilde{F}^2)_o . \qquad (2.101)$$

The secular equation (2.97) becomes

$$(3\tilde{F})^4 - 52(3\tilde{F})^2 + 576 = 0 , \qquad (2.102)$$

and, since $(3\tilde{F})^2 = 36$ (corresponding to $\tilde{F} = \pm 2$) must be one root, it follows that $(3\tilde{F})^2 = 52 - 36 = 16$ is the second root. Thus, we find for $\frac{1}{2}\tilde{F} = \cos\tilde{\kappa}$, and for $\tilde{\kappa}$, the four eigenvalues

$\cos\tilde{\kappa}$	1	2/3	-2/3	-1
$\tilde{\kappa}_n$	0	0.268π	0.732π	π

in the range ($0 \leq \tilde{\kappa} \leq \pi$). These eigenvalues plus those generated in the range between π and 3π are drawn in Figure 10 on horizontal lines. The first vertical scale shows the values of $\tilde{\kappa}$ and the second (middle) vertical scale shows the corresponding values of $k = \tilde{\kappa}/3D$.

Since the eigenvalues of k depend only on the free-electron path and not on the manner in which one assumes equidistant points on the path, no other eigenvalues, k, can be found by solving the 14-dimensional secular equation corresponding to the 14

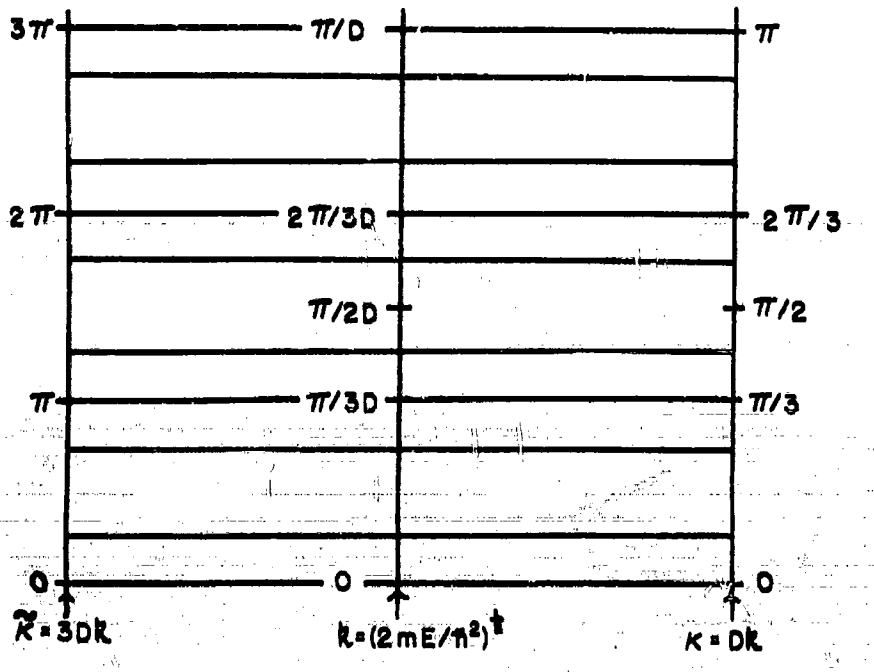

Fig. 10

atoms of the molecule. However, in this problem one works with the quantities $\kappa = Dk = \tilde{\kappa}/3$. The 14 states with $0 \leq \kappa \leq \pi$ correspond to the 14 LCAO states of the molecules. Now the third (right) scale in Figure 10 shows the values of κ for the eigenvalues which were found; one recognizes that there exists only 10 levels in this range; hence some of these must be degenerate. Indeed, the levels $\kappa_n = \pi/3$ and $\kappa_n = 2\pi/3$ are both triply degenerate, thus providing the extra four levels. This degeneracy is easily recognized: The eigenfunctions for $\kappa_n = \pi/3$ have $\lambda_\phi = 6D$, and one sees immediately that one can construct three mutually orthogonal wavefunctions with this wavelength; they are shown in Figure 11 where a

full line is drawn, wherever the wave function is positive,

hollow line is drawn, wherever the wave function is negative,

dotted line is drawn, wherever the wave function is identically zero.

Since there are three independent wavefunctions for $\kappa = \pi/3$, the same must be true for $\kappa = 2\pi/3$ by virtue of the pairing theorem. In order to find all wavefunctions one solves the system of two linear equations obtained from (2.96) by substituting $(\tilde{F}^2)_*$ of (2.101) for $(F^2)_*$; by the method described after (2.97), one then obtains the eigenvectors of $\tilde{F}$ (2.99) and hence by the usual methods [see Eqs. (2.21-30)] the wavefunctions for the 14 lowest states. Finally one can determine the symmetries of the

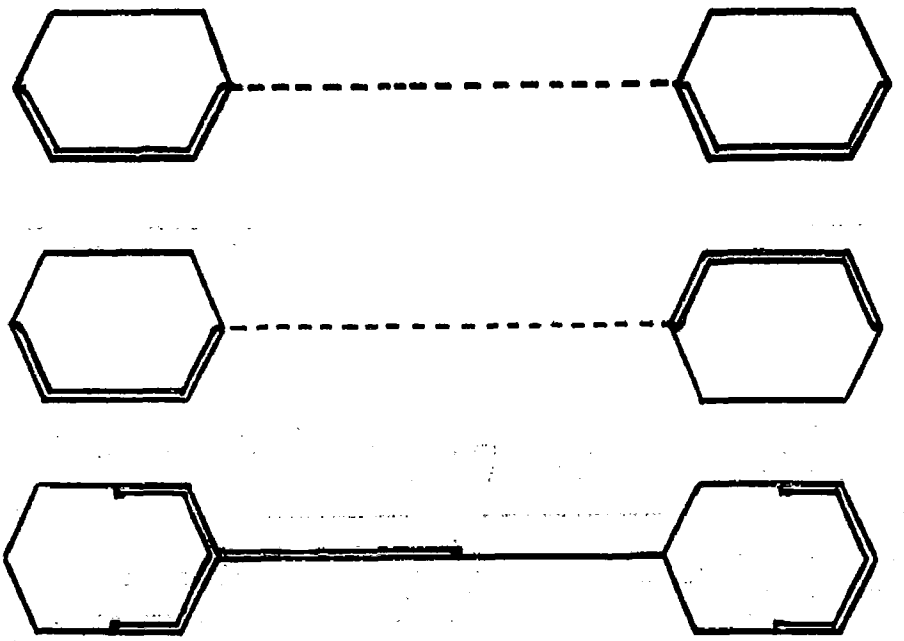

Fig. 11

different wavefunctions.

Of course it would have been possible from the beginning to separate out the eigenvalue equations corresponding to the different symmetry types; this procedure would be advantageous in dealing with a molecule of sufficiently high symmetry. Since this method operates in precisely the same way as in the LCAO model,[10] we do not have to go into details at this point, and refer the reader to the following paper[5] for an illustrative example.

APPENDIX

JUSTIFICATION OF THE BOUNDARY CONDITION FOR FREE ENDPOINTS

The assumption that the wavefunction $\phi(x)$ goes to zero one bond length D beyond the last atom at a free end [see comments after Eq. (1.34)] has been essential in deriving the normalization of the eigenvectors [see after Eq.(2.38)] and in deriving the matrix formulation of the eigenvalue problem [see Eq.(2.45)]. Hence, also the orthogonality of the eigenvectors depends on the present choice of the boundary conditions [see comments after (2.53')].

It will now be shown that this boundary condition is the only one which guarantees the normalization of the eigenvectors as well as the existence of the pairing theorem for alternant systems.

Consider the proof starting after Eq. (2.34). Let us assume that the branch B considered there has a free endpoint; let the "first atom F_B" [definition: between Eqs. Eqs. (2.34) and (2.35)] be the one nearest to the free endpoint; and let the endpoint of the electron path be located at a distance ξD beyond the atom F_B. Then the branch length becomes

$$\ell_B = D(n - 1 + \xi) \ . \tag{A.1}$$

We choose the path endpoint to be the origin $x_B = 0$ of the coordinate x_B, which increases in the direction away from the endpoint. Hence, the wavefunction vanishes for $x_B = 0$, and has therefore the form

$$\phi_B(x_B) = a_B \cos(kx_B - \tfrac{1}{2}\pi) \ , \tag{A.2}$$

so that the argument of the cosine becomes, for the first atom F_B,

$$f = \xi\kappa - \tfrac{1}{2}\pi \ , \tag{A.3}$$

[see Eq. (2.35)].

The course of the proof subsequent to Eq. (2.37) shows that under the present circumstances [note Eq. (A.1)] the Eqs. (2.33) result from Eq. (2.37) only if the relation

$$-\cot\kappa \sin f \cos f + \cos^2 f = \xi \tag{A.4}$$

is fulfilled.[12] Hence,

$$-\frac{\sin(2f-\kappa)}{\sin\kappa} = (2\xi - 1) \ , \tag{A.5}$$

and by virtue of (A.3):

$$\sin\eta\kappa = \eta \sin\kappa \ , \tag{A.6}$$

with

$$\eta = 2\xi - 1 \ . \tag{A.7}$$

[12] If there are several branches with free endpoints, the Eq. (A.4) must still hold for each branch separately in order that our results remain generally valid.

Eq. (A.6) is satisfied by the values

$$\eta = 0 \ , \ +1 \ , \ -1 \ . \tag{A.8}$$

Now there are always eigenfunctions with κ in the range $0 < \kappa \leq \frac{1}{2}\pi$ ($\kappa = 0$ is excluded, if there is a free endpoint). For such values of κ there exist no other solutions of (A.6), as may be seen in the following way: Figure 12 shows the two curves

$$f(\eta) = \sin\eta\kappa \ , \tag{A.9}$$

$$g(\eta) = \eta \sin\kappa \ . \tag{A.10}$$

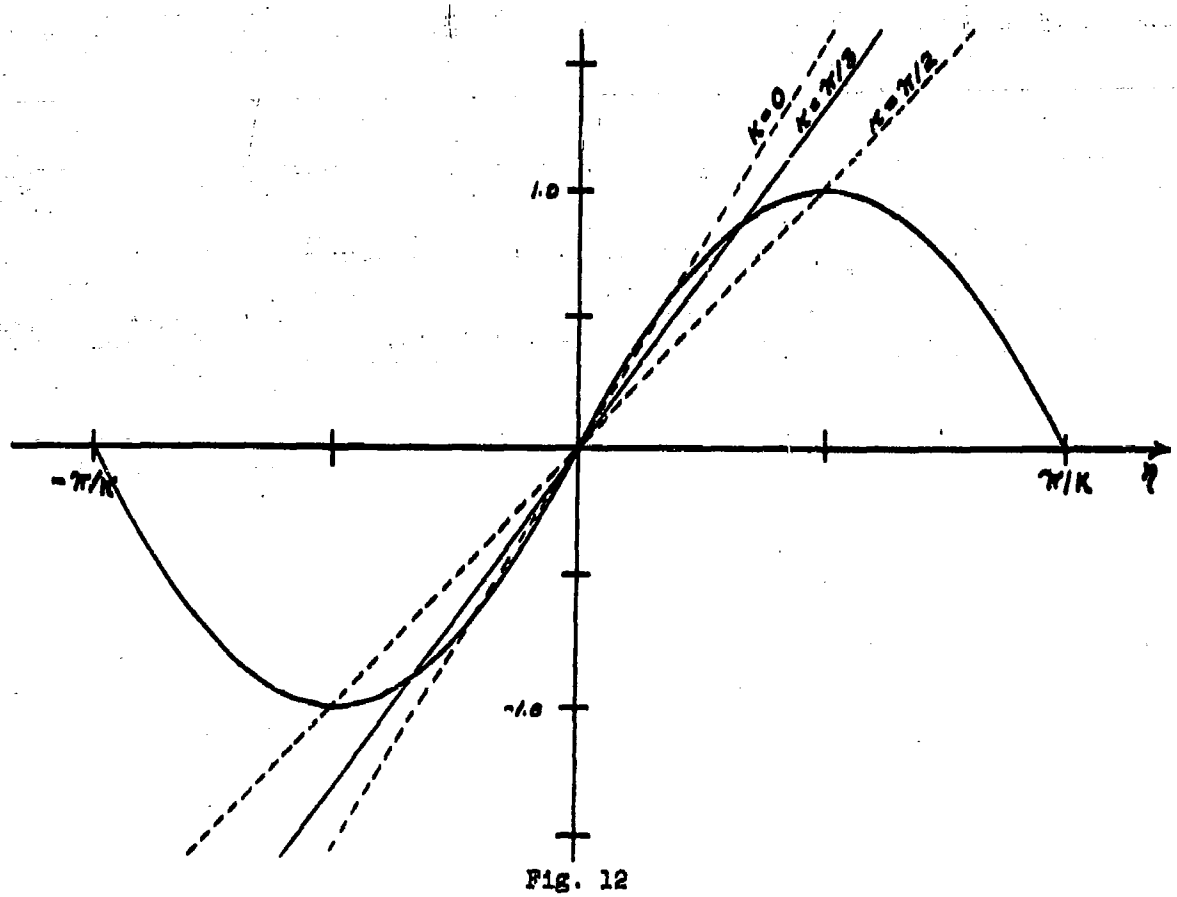

Fig. 12

For $\eta = (\pi/2\kappa)$ the straight line (A.10) assumes the value

$$g(\pi/2\kappa) = (\pi \sin\kappa)/2\kappa \ , \tag{A.11}$$

which decreases from

$$g(\pi/2\kappa) = \tfrac{1}{2}\pi \ , \text{ for } \kappa = 0 \ ,$$

to

$$g(\pi/2\kappa) = 1 \ , \ \text{for} \ \kappa = \tfrac{1}{2}\pi \ .$$

Hence the line (A.10) must lie in the sector between the two dotted lines of Figure 12; as an example the curve for $\kappa = \pi/3$ has been indicated. (It should be noted that, as $\kappa \to 0$, the argument point $\pi/2\kappa$ moves out towards infinity.) It follows then that the two curves (A.9) and (A.10) have no other intersections than the ones given by (A.8).

Thus, Eq. (A.5) is only fulfilled by [See(A.6)]

$$\xi = 0 \ , \ \tfrac{1}{2} \ , \ 1 \ . \qquad \text{(A.12)}$$

Since the wavefunction shall certainly not vanish at the last atom, the first value $\xi = 0$ has to be discarded. The second value $\xi = \frac{1}{2}$ is inconsistent with the validity of the pairing theorem. Indeed, it is easily recognised that such a boundary condition would lead to the relation

$$\phi_B(P_{+1}) - (1 + 2\cos\kappa)\phi_B(P_0) = 0 \qquad \text{(A.13)}$$

instead of to Eq. (2.45). Consequently, the matrix $\mathbf{F}$ entering in the eigenvalue equation (2.51) would contain the <u>diagonal</u> element (-1) for each end atom; and hence Eq. (2.74), the basis for the pairing theorem, would not hold.

Therefore the normalization of the eigenvectors <u>and</u> the pairing theorem for alternant systems result only from the choice $\xi = 1$; and this is the definition of the path end point adopted in this paper.

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