
QUARTERLY REVIEWS

THE FREE-ELECTRON APPROXIMATION FOR CONJUGATED COMPOUNDS

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1. Introduction

CONJUGATED compounds occupy a special and important place in the application of theoretical methods to the study of organic chemistry. They include all the compounds (*e.g.*, dyes and pigments) that are intensely coloured in the visible and the near ultra-violet region of the spectrum; they are the compounds that have always presented difficulties from the viewpoint of classical valency theory in that their properties cannot be uniquely represented by structures with conventional chemical bonds; they have furthermore proved to be remarkably amenable to the methods of quantum mechanics. Indeed, current theoretical methods have achieved greater success with relatively complex conjugated molecules than they have with very much simpler saturated compounds,¹ and the reason for this apparently contradictory circumstance lies in the possibility of discussing the properties of conjugated compounds largely in terms of the "unsaturation" or π electrons, which from many points of view can be regarded as forming a separate shell "outside" the other electrons. Their relation to the conjugated molecule is much the same as that of the outer valency shell of electrons to an atom.

When a conjugated hydrocarbon system is represented by a conventional valency structure, each carbon atom forms one double and two single bonds. According to the theory of the double bond,² three out of the four valency electrons on each carbon share in three sp^2 hybrid (single) bonds which make angles of 120° in one plane. These electrons, or rather their wave functions or orbitals, have cylindrical (σ) symmetry about the three bond directions. The fourth valency electron on each carbon atom occupies an orbital with π symmetry, in which there is a node in the plane of the σ bonds. In the ordinary double bond, the overlap between the orbitals of the π electrons on adjacent carbons provides both the extra strength of the double bond and also its resistance to free rotation. In a conjugated system, the presence of a π electron on each carbon tends

¹ Lennard-Jones and Pople, *Discuss. Faraday Soc.*, 1951, **10**, 9.

² Pauling, "The Nature of the Chemical Bond", Cornell, 1940, p. 89.

to smear the π electron cloud over the whole molecule, with the resulting difficulty in giving definite locations to the double bonds; Lennard-Jones³ used the term "mobile" electrons to describe this property.

Of the six extranuclear electrons in all contributed by a carbon atom in a conjugated system, two are tightly bound to the nucleus in the inner K or $1s$ shell; three of the valency electrons have σ symmetry, and the fourth is a π electron. The respective ionisation energies are about 280 volts for the K electrons (soft X-rays), 14 volts⁴ for the σ , and of the order of 10 volts⁵ or less for the π electrons in simple conjugated systems. These figures provide real evidence that we can speak of the K , σ , and π shells as having progressively looser binding with the π shell as it were on the "outside". In current approximate theoretical treatments it is customary to obtain the necessary simplification by neglecting the inner K and σ shells, and by dealing with the problem solely in terms of the behaviour of the π shell in much the same way as atomic problems are handled by focusing attention on the outer valency shell. While the K and σ electrons are undoubtedly localised respectively near individual nuclei and in definite sp^2 bonds, the π shell must be considered in relation, not to individual atoms or bonds, but to the conjugated system as a whole.

Two general methods have been developed during the last twenty years. The "valence bond" (VB) method involving the principle of resonance has been reviewed^{2, 6} and will not be considered here. Attention will be confined in general to the molecular orbital (MO) method,^{7, 8} and in particular to the more recently developed free-electron (FE) approximation. The essence of this approach is to find the energy levels, with their associated wave functions or molecular orbitals, that are available to the π electrons considered in relation to the molecule as a whole. Each level can contain at most two electrons with opposite spins (Fermi-Dirac statistics), and subject to this condition the ground state of the molecule has its π electrons in the lowest possible energy levels. The higher vacant energy levels are available for occupation in the excited states of the molecule. From the sequence of energy levels it is possible to make predictions about spectral frequencies, and from the nature of the orbitals one can deduce transition probabilities and spectral intensities, and obtain a picture of the π electron distribution over the conjugated system. As an introduction to the theory it will be convenient to discuss briefly the problem of the electron in a box.

The Problem of the Electron in a Box.—In quantum mechanics, the behaviour of an electron is deduced by solving the Schrodinger equation

$$\nabla^2\psi + (8\pi^2m/h^2)(E - V)\psi = 0 \quad . \quad . \quad . \quad (1)$$

³ *Proc. Roy. Soc.*, 1937, *A*, **158**, 280; see also Mulliken, *J. Chem. Phys.*, 1939, **7**, 121.

⁴ *Idem, ibid.*, 1935, **3**, 517.

⁵ Walsh, *Quart. Reviews*, 1948, **2**, 73.

⁶ Maccoll, *ibid.*, 1947, **1**, 16.

⁷ Coulson, *ibid.*, p. 144.

⁸ Mulliken, *J. Chem. phys.*, 1949, **46**, 497; this paper contains key references to the development of MO theory.

where V is the potential energy of the electron, and m and h have their usual significance. The solution of (1) gives the allowed energy levels E and the associated wave functions ψ . If the electron is confined to a box with impenetrable walls but within the box is free to move with uniform potential energy, we may choose the zero of energy so that $V = 0$ within the box. At the sides of the box, V is pictured as rising abruptly to infinity in order to keep the electron inside. For simplicity we may consider the box to have only one dimension, namely the x direction, and (1) then reduces to

$$\frac{d^2\psi}{dx^2} + (8\pi^2mE/h^2)\psi = 0 \quad . \quad . \quad . \quad (2)$$

The solution of this problem as given in standard texts⁹ shows that the allowed energy levels for the electron are given by

$$E_n = n^2(h^2/8mL^2) \quad . \quad . \quad . \quad (3)$$

where L is the length of the box, and n is a quantum number that can have the integral values 1, 2, 3 . . . The corresponding wave functions ψ_n resemble the standing waves of a vibrating string fastened at both ends; they are the sine curves

$$\psi_n = (2/L)^{1/2} \sin(n\pi x/L) \quad . \quad . \quad . \quad (4)$$

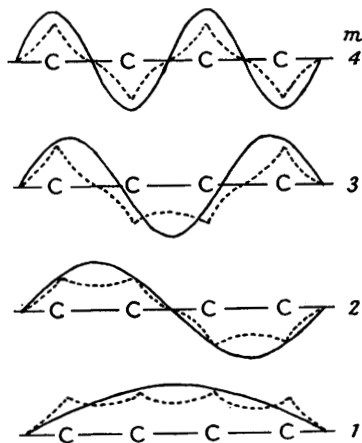


FIG. 1

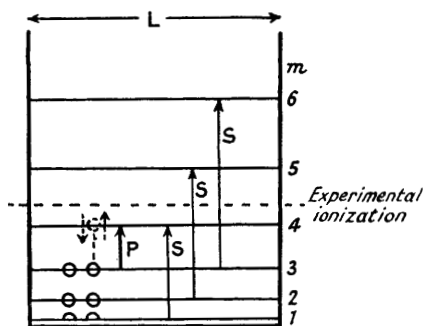


FIG. 2

which are constrained to be zero at the sides of the box, and have $n - 1$ internal nodes; the four lowest are shown in Fig. 1. The energy levels going upwards are separated by increasing intervals according to the increase in the squared integer n^2 ; they are closer together, *i.e.*, the energy-level pattern is more compressed, the greater the length L of the box. If there are $2N$ electrons in the box, and if we neglect the repulsion between them so that they can all be assumed to have the same uniform potential

⁹ Pauling and Wilson, "Introduction to Quantum Mechanics", McGraw-Hill, N.Y., 1935, p. 95.

energy $V = 0$, then the lowest state of this electron gas is found by assigning the electrons, two to each level, until the N lowest levels are filled, as shown for six electrons in Fig. 2. As is well known, the simple theory of an electron gas forms the basis of Sommerfeld's treatment¹⁰ of the conduction electrons in a metallic crystal; in this case the size L of a real crystal is so great that the energy levels are drawn close enough together to form a practically continuous band of allowed energies.

2. Linear Conjugated Systems

Simple FE Theory.—If we consider a linear conjugated molecule such as a polyene or a polymethine, the basic concept of the free electron MO theory is that the mobile π electrons are analogous to the conduction electrons of a tiny metallic crystal. In reality the π electrons are confined, not by the walls of an impenetrable box, but by the attraction of the positively charged atomic nuclei which are partly shielded by the K and σ electrons. The confining potential-energy field, along the molecular axis,

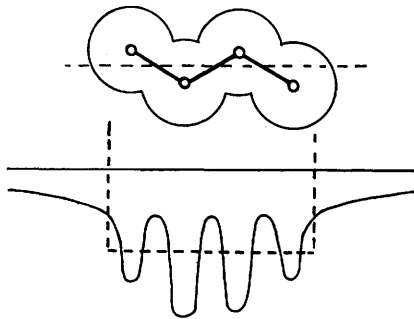


FIG. 3

most probably has the oscillating form shown in Fig. 3 for the case of the butadiene molecule. However, it is a feature of quantum theory that, regardless of how the electrons are confined to a given locality, the nodal properties of the successive orbitals are unchanged. Thus the orbital of lowest energy will have no internal nodes, the next lowest will have one node, and so on. This fact has been emphasised by Walsh⁵ under the name of the "fitting in" principle. Thus the orbitals available to the π electrons of a linear conjugated molecule may be expected to have the same general shapes as those of a one-dimensional electron gas, even if the detailed shapes and the values of the corresponding energies are somewhat modified.

It therefore appears that it is worth investigating more closely the consequences of assuming that the π electrons of a linear conjugated system resemble a free electron gas; or, in other words, that the oscillating potential-energy field can be replaced approximately by the idealised "potential energy box" shown by the broken line in Fig. 3. This concept

¹⁰ Mott and Jones, "Theory of Metals and Alloys", Oxford, 1936, p. 51.

was used by Schmidt,¹¹ who treated the π electrons of benzene and condensed aromatic hydrocarbons in terms of an electron gas in a cylindrical box. More recently, Bayliss,¹² Kuhn,¹³ and Simpson¹⁴ independently and almost simultaneously used the model of an electron gas in one dimension to account for the spectra of linear conjugated molecules.

To be specific, we take the case of a linear conjugated system whose length is L and which has $2N$ π electrons. If π electrons behave like a free electron gas in a one-dimensional box, the π electron energy levels are those given by equation (3). According to Pauli's exclusion principle, each level can accommodate two electrons at most, so that the lowest energy state (the ground state) has the N lowest levels fully occupied, as shown in Fig. 1 for the case of the six π electrons in hexatriene. The absorption spectrum of the molecule is the result of electronic transitions from occupied to higher vacant levels. As shown below, the most intense transition is from the uppermost filled level N to the lowest vacant level $(N + 1)$; its frequency in wave numbers is derived from equation (3) to be

$$\nu \text{ (cm.}^{-1}\text{)} = (E_{N+1} - E_N)/hc = (h/8mcL^2)(2N + 1) \quad (5)$$

Introducing the numerical values of the constants h , m , and c , and expressing L in Ångström units, one obtains for the wave-number ν and the corresponding wave-length λ (in Å)

$$\nu = 3.033 \times 10^5(2N + 1)/L^2 \quad (6)$$

$$\lambda = 329.7L^2/(2N + 1) \quad (7)$$

The intensity of an absorption band is conveniently described by its oscillator strength f , which is calculated from the integrated area under the band by⁶

$$f = 4.31 \times 10^{-9} \int \epsilon \cdot d\nu \quad (8)$$

where ϵ is the molar extinction coefficient. Theoretically, the intensity of a transition between levels n and k is expressed in terms of the transition moment integral Q ,¹⁵ which in the present case is

$$Q = \int_0^L \psi_k x \psi_n dx \quad (9)$$

by the relation

$$f = 1.085 \times 10^{11} \nu Q^2 \quad (10)$$

In the case of the linear electron gas, it has been shown¹² that Q and f are predicted to be zero if the difference Δn between the quantum numbers n and k is even; thus, allowed transitions obey the selection rule that Δn must be odd. The most intense transition turns out to be $(N, N + 1)$ with $\Delta n = 1$; its oscillator strength is calculated to be

$$f = 0.134(2N + 1) \quad (11)$$

¹¹ *Ber.*, 1940, **73**, 97.

¹² *J. Chem. Phys.*, 1948, **16**, 287.

¹³ *Helv. Chim. Acta*, 1948, **31**, 1441; *J. Chem. Phys.*, 1948, **16**, 840.

¹⁴ *Ibid.*, p. 1124.

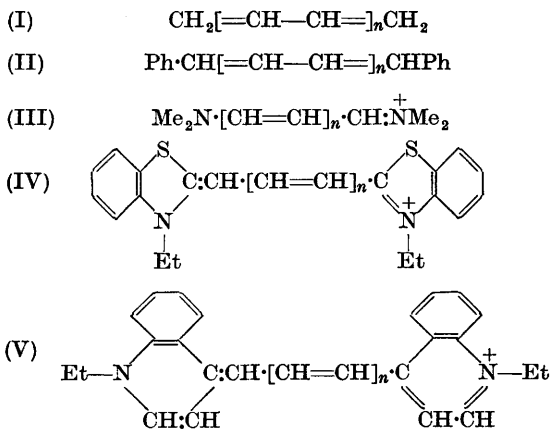
¹⁵ *Rep. Prog. Physics*, 1941, **8**, 231.

The model predicts¹² that the next most intense transitions are those with $\Delta n = 3$, namely, those designated as $(N, N + 3)$, $(N - 1, N + 2)$, and $(N - 2, N + 1)$. Equation (3) places them at approximately three times the frequency of the most intense band, and their intensities are

$$f = 0.005(2N + 1) \quad . \quad . \quad . \quad (12)$$

The results of the preceding paragraph may be summarised by saying that the FE model predicts that the spectrum of a linear conjugated molecule should have one intense absorption band, accompanied by weaker bands at higher frequency. Since the length L of the conjugated system is roughly proportional to the number of π electrons $2N$, equations (6) and (7) predict that in a homologous series of linear conjugates the principal band should move steadily to longer wave-lengths as N increases, and that λ should vary roughly as N . Equation (11) predicts that the intensity of the band should also increase roughly as N . Each spectrum should have weaker bands at higher frequency whose intensity is about 1/25 of the main band.

Comparison with Experiment.—Homologous series of linear conjugated compounds include the polyenes (I), diphenyl polyenes (II), polymethine ions (III), and cyanine dyes such as (IV) and (V). Data relating to their spectra have been summarised by Mulliken and Rieke,¹⁵ Brooker,¹⁶



Maccoll,⁶ Simpson,¹⁴ and Kuhn.¹³ Typical cases and more detailed references are given in Tables 1, 2, and 3. In each case the absorption spectrum consists of a principal band which in each series progresses with increasing intensity to longer wave-lengths as the length of the conjugated system increases. Higher members of the series have one or more weaker bands of about one-fifth to one-tenth of the intensity of the main band, and at rather less than double its frequency. The principal bands are represented

¹⁶ "Advances in Nuclear Chemistry and Theoretical Organic Chemistry", ed. by Burk and Grummitt, Intersci. Publ. Corp., New York, 1945, pp. 89 *et seq.*

TABLE 1. *Polyenes*

	2N	$\lambda_{\max.}$ (m μ)	f (exp.)	f (calc.)	L(CC) ^a (Å)	L (calc.) ^b (Å)
Ethylene ^c	2	162.5*	0.34	0.40	1.33	3.8
Butadiene ^d	4	210*	0.53	0.67	3.7	5.6
Hexatriene ^e	6	250*	(0.62) ^f	0.94	6.1	7.3
Octatetraene ^g	8	290	(1.55) ^h	1.21	8.6	8.9
Vitamin A ⁱ	10	325	1.05	1.47	11.1	10.4
Anhydrovitamin A ^j	12	369	—	1.74	13.6	12.1
<i>trans</i> -Lycopene ^k	22	470	2.71	3.08	26.0	18.1
<i>trans</i> - γ -Carotene ^l	22	460	2.49	3.08	26.0	17.9
Dehydro- β -carotene ^m	24	475	—	3.35	28.5	19.0
Dehydrolycopene ⁿ	30	504	—	4.15	35.9	22.5

* Gas values ; all others are in solution.

^a Direct distance between terminal C atoms, calculated from data of Schomaker and Pauling, *J. Amer. Chem. Soc.*, 1939, **61**, 1769.

^b Calculated from eq. (7) to fit experimental $\lambda_{\max.}$

^c Platt, Klevens, and Price, *J. Chem. Phys.*, 1949, **17**, 466.

^d Refs. (5), (15).

^e Price and Walsh, *Proc. Roy. Soc.*, 1946, **A**, **185**, 182.

^f Estimated by the Reviewer, ref. (12).

^g Woods and Schwartzman, *J. Amer. Chem. Soc.*, 1949, **71**, 1396.

^h Ref. (15).

ⁱ Zscheile and Henry, *Ind. Eng. Chem. Anal.*, 1942, **14**, 422.

^j Ref. (31). ^k Ref. (22).

^l Karrer and Jucker, "Carotinoide", Birkhauser, Basel, 1948.

TABLE 2. *Diphenyl polyenes*,^a C₆H₅[CH=CH]_nC₆H₅

n	2N ^b	$\lambda_{\max.}$ (m μ)	f (exp.)	f (calc.)	L(CC) ^c (Å)	L (calc.) (Å)
0	2	251.5	0.41	0.40	1.5	4.8
1	4	319	0.58	0.67	3.8	6.9
2	6	352	0.77	0.94	6.3	8.6
3	8	377	1.26	1.21	8.7	10.1
4	10	404	1.39	1.47	11.2	11.6
5	12	424	1.41	1.74	13.7	12.9
6	14	445	1.58	2.01	16.2	14.2
7	16	465	1.90	2.28	18.7	15.5

^a Experimental values are benzene solution values quoted by Maccoll, ref. (6). Slightly different values in some cases are given by Mulliken and Rieke, ref. (15).

^b Equivalent number of π electrons assumed by the Reviewer [ref. (12)] on basis of intensities.

^c Direct distance between phenyl carbons terminating the linear chain.

in Fig. 4 by vertical lines whose lengths are proportional to the oscillator strengths. Other linear conjugated series that show the same progression of wave-length and intensity include the quinolyl-phenyl polyenes¹⁷ and the polyene aldehydes and azines ;¹⁸ Schwarzenbach¹⁹ and Ferguson and Branch²⁰ have investigated similar linear systems. The predicted propor-

¹⁷ Compton and Bergmann, *J. Org. Chem.*, 1947, **12**, 363.

¹⁸ Blout and Fields, *J. Amer. Chem. Soc.*, 1948, **70**, 189.

¹⁹ Schwarzenbach, Lutz, and Felder, *Helv. Chim. Acta*, 1944, **27**, 576.

²⁰ *J. Amer. Chem. Soc.*, 1944, **66**, 1467.

TABLE 3. *Polymethines and cyanines*

<i>n</i>	<i>2N</i>	$\lambda_{\max}(\text{m}\mu)$	<i>f</i> (exp.)	<i>f</i> (calc.)	<i>L</i> (NN) ^a (in Å)	<i>L</i> (calc.) (in Å)
<i>Polymethines</i> (III) ^b						
1	6	309	0.87	0.94	5.6	8.1
2	8	409	1.12	1.20	8.3	10.6
3	10	511	1.32	1.47	11.1	13.1
<i>Cyanines</i> (IV) ^c						
0	6	425	1.2	0.94	5.6	9.5
1	8	555	1.2	1.21	8.3	12.3
2	10	650	1.6	1.47	11.1	14.7
3	12	760	1.9	1.74	13.9	17.3
4	14	870	—	2.01	16.7	19.9
5	16	995	—	2.28	19.5	22.6

^a Zig-zag distances between terminal N atoms; all bond distances being assumed = C-C (aromatic) = 1.39 Å.

^b Simpson, ref. (14); *f*(exp.) values recalculated by the Reviewer.

^c Brooker's experimental data quoted by Kuhn, ref. (13); *f*(exp.) values from ref. (24).

tionality between λ and *N* is found in polymethines (III) and cyanines (IV, V) with symmetrical end groups, where there is an approximately constant interval of 1000 Å between the principal bands of successive members of a series; these have been called "non-convergent" series by

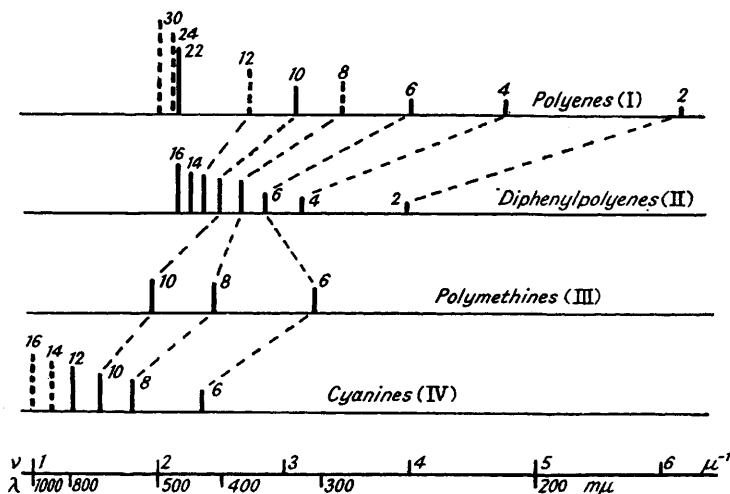


FIG. 4

Brooker.¹⁶ The series of polyenes (I) and (II), and cyanines with unsymmetrical end groups, conform less accurately to FE theory in that the wave-length shift decreases as *N* increases; in fact, λ is more nearly proportional to $N^{\frac{1}{2}}$ than to *N*—Brooker calls these series "convergent".

A quantitative comparison of the experimental results with FE theory

is given in Tables 1—3, which show the experimental and theoretical values of f , and also compare the actual lengths of conjugated systems with the values of L that would be required by equations (6) and (7) to fit the experimental ν or λ data exactly. It is seen that the agreement between the theoretical and experimental intensities is particularly good, and this is one of the most satisfying features of the FE theory. Later in this Review the FE theory will be compared briefly with the well known LCAO MO theory⁷ which has been widely applied to conjugated systems; it should be pointed out that Mulliken and Rieke¹⁵ found that intensities predicted by the LCAO method are in general 2—3 times the experimental values, a discrepancy that has since been found to be due to the neglect in LCAO theory of the effect called "configuration interaction".²¹ The FE theory also takes no account of configuration interaction, and in view of its definitely over-simplified theoretical basis the success of equation (11) is a phenomenon that deserves further investigation.

In the cases of the polyenes and the diphenyl polyenes, it was shown by the Reviewer¹² that the length L (calc.) of the one-dimensional electron gas calculated to fit the experimental data was, at least for conjugated chains of moderate length, in good agreement with the actual geometrical distance measured in a straight line between the terminal carbons of the conjugated system. This feature is shown in Tables 1 and 2; owing to the convergent nature of these spectral series, the agreement is less satisfactory for both the longest and the shortest molecules. For polymethines and cyanines (Table 3), the values of L (calc.) are, as shown by Kuhn,¹³ in very satisfactory agreement with the actual zig-zag distance along the conjugated chain between the terminal atoms, in these cases nitrogens. The discrepancy between the two interpretations of L (calc.) is a reflexion of the experimental fact that polyenes and polymethines with the same number of π electrons do not absorb at the same frequency (see Fig. 4); the theoretical reason is that it is undoubtedly over-simple to describe the π electrons in these systems as moving in a field of uniform potential energy.

Owing to the selection rule that Δn must be odd, transitions such as $(N, N + 2)$ are forbidden in *trans*-conjugated systems. The secondary bands in the longer polymethines¹⁴ and in long polyenes such as *trans*-lycopen²³ are therefore to be identified with transitions with $\Delta n = 3$ such as $(N, N + 3)$, $(N - 1, N + 2)$, $(N - 2, N + 1)$, although the model predicts wave-numbers that are much too high and intensities that are much too low.¹² The "*cis*-peak" that appears between the principal and secondary bands in *cis*-lycopen^e, etc., is probably the $\Delta n = 2$ transition, polarised perpendicular to the molecular axis, which becomes allowed in *cis*-chains.^{15, 22}

It should be remarked that the simple FE model takes no account of electron spin. Actually, the excited state $(N, N + 1)$ may be either singlet

²¹ Coulson, Craig, and Jacobs, *Proc. Roy. Soc.*, 1951, *A*, **206**, 297.

²² Zechmeister, Le Rosen, Schroeder, Polgar, and Pauling, *J. Amer. Chem. Soc.*, 1943, **65**, 1940.

or triplet, according as the spins of the electrons in the two orbitals are antiparallel or parallel (see Fig. 2). The ground state must be singlet, and the intense principal band is undoubtedly the singlet-singlet transition, since singlet-triplet transitions are very weak or forbidden. Since spin is neglected in the FE model, the predicted band positions should really be compared with the *mean* of the positions of the experimental singlet and triplet bands. The latter have been observed for only very few of the cases cited, although it is believed that they would lie at somewhat longer λ than the singlet (principal) band.

Free-electron Orbitals.—Chemists are interested in the form and symmetry of the orbitals as the basis for the distribution of electron charge over the molecule, and because of the ultimate possibility of predicting, or accounting for, chemical reactivity. The FE orbitals (see Fig. 1) are characterised by their internal nodes and by their symmetry (n odd) or antisymmetry (n even). The importance of orbital nodes has been emphasised by Herzfeld²³ and by Walsh;⁵ the nodes also play an important part in the extension of FE theory to aromatic compounds (see next section). The nodal positions and symmetries of the first four orbitals in Fig. 1, for example, bear a close qualitative resemblance to the four LCAO orbitals of butadiene, which are also sketched in Fig. 1, and which, expressed in terms of the atomic orbitals $\phi_1 \dots \phi_4$, coefficients being neglected, are

$$\left. \begin{aligned} \psi_1 &= \phi_1 + \phi_2 + \phi_3 + \phi_4 \\ \psi_2 &= \phi_1 + \phi_2 - \phi_3 - \phi_4 \\ \psi_3 &= \phi_1 - \phi_2 - \phi_3 + \phi_4 \\ \psi_4 &= \phi_1 - \phi_2 + \phi_3 - \phi_4 \end{aligned} \right\} \dots \dots \dots (13)$$

Since ψ^2 is an electron density, π electron charge densities can be computed along the conjugated chain. In Fig. 5, drawn for the case of six

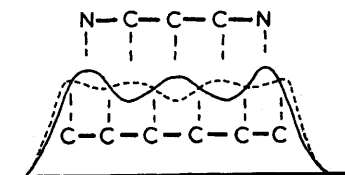


FIG. 5

π electrons, the charge densities of the ground and the first excited states have been drawn from the following sums of FE orbitals:

$$\left. \begin{aligned} \text{Ground state: } & 2\psi_1^2 + 2\psi_2^2 + 2\psi_3^2 \\ \text{Excited state: } & 2\psi_1^2 + 2\psi_2^2 + \psi_3^2 + \psi_4^2 \end{aligned} \right\} \dots \dots (14)$$

In a review of FE theory, Kuhn²⁴ has pointed out the deductions that are possible by fitting the alternating charge density to the conjugated chains of a polyene and of a polymethine ion with the same number of

²³ *Rev. Modern Phys.*, 1949, **21**, 527.

²⁴ *Chimia*, 1950, **4**, 203.

π electrons; in the case chosen here they would be hexatriene and the ion $\text{H}_2\text{N}^+\text{-CH:CH:CH:NH}_2$. The three maxima and two minima of the ground state fit most naturally to the *five bonds* of the polyene, and to the *five atomic nuclei* of the polymethine. The curves in Fig. 5 suggest the following qualitative conclusions: (a) The bonds in hexatriene alternate in charge density and hence in double-bond character. (b) The end "double" bonds in hexatriene have greater double-bond character than the central one. (c) The *atoms* of the polyene chain are at positions of roughly equal charge density. (d) The *bonds* of the polymethine chain are at positions of roughly equal charge density, *i.e.*, have equal bond order. (e) The atoms of the polymethine chain have the alternating charge density represented by the sequence $- + - + -$. Lennard-Jones,³ in his LCAO treatment of polyenes, reached conclusions similar to (a) and (b); (c) is also a consequence of simple LCAO theory. The VB concept of the equivalent resonance forms of polymethine ions finds its expression in (d). These results are readily generalised to longer or shorter chains.

The optical transition to the excited state is seen in Fig. 5 to consist of a migration of charge away from the centre of the chain towards its ends. This gives the principal band its great intensity and its polarisation along the molecular axis. In hexatriene, the central bond loses double-bond character as a result of the transition; the adjoining bonds gain it. In the polymethine shown, the central carbon atom loses charge, the adjoining carbon atoms gain it.

The diagram leads to interesting predictions of the effect of hetero-substitution in the polymethine chain on the spectrum.²⁴ (a) If a nitrogen atom is substituted for the *central* carbon in the case illustrated with $N = 3$, its greater positive nuclear charge will cause the energy of the ground state to be lowered more than that of the excited state, owing to the greater electron density at that point in the ground state. The frequency of the principal band is therefore *raised* as compared with the parent polymethine. (b) Substitution of nitrogen at either of the adjoining carbons would have the reverse effect of *lowering* the frequency of the principal band, since the energy of the excited state is now lowered more than that of the ground state. (c) Both these effects are reversed in the next polymethine with $N = 4$, since the alternations of charge are reversed. Thus the ground state is now $- + - + - + -$ as compared with $- + - + -$ in the first case. These rules are identical with those derived by Dewar²⁵ from LCAO theory, and supported by a number of examples. They may be summarised by saying that:

Hetero-substitution *raises* the absorption frequency if the affected carbon atom (a) is at a position of *maximum* charge density in the ground state, or (b) is at an *antinode* of the highest occupied orbital of the ground state, or (c) is "starred" in the sense used by Dewar. [Statements (a), (b), and (c) are equivalent.] In the reverse cases, hetero-substitution lowers the absorption frequency.

²⁵ *J.*, 1950, 2329.

3. Aromatic Conjugated Systems

Benzene is the conjugated compound *par excellence*. The six C-C bonds are of equal length and form a regular hexagon in one plane, and the six π electrons must therefore be distributed quite evenly with respect to the σ skeleton. Just as a one-dimensional model has given useful information about linear conjugated molecules, so it has been found that the π electrons of benzene and other aromatic hydrocarbons can be interpreted in terms of a one-dimensional free electron gas confined to the molecular perimeter, which in the case of benzene for example can be regarded as being distorted from a hexagon into a circle. As early as 1931, Hückel²⁶ represented aromatic π electrons by complex wave functions travelling around the molecular perimeter; more recently, Platt²⁷ has applied this concept to FE theory, using his model primarily to further the understanding of the molecular states and the spectra of benzene and condensed aromatic hydrocarbons in which Klevens and Platt²⁸ have pointed out important regularities.

If the molecular perimeter of benzene is regarded as a circle, the π orbitals must "fit in" to the circular path. In FE theory with its assumption of uniform potential energy, the orbitals are sine or cosine functions such as $\sin m\phi$ or $\cos m\phi$, where ϕ is the angular co-ordinate that ranges around the circle from 0 to 2π , and where the number m (Platt's "orbital ring quantum number") can take on the values $m = 0, \pm 1, \pm 2, \dots$. The solution of the Schrodinger equation gives the following values for the orbital energies:

$$E_m = m^2 h^2 / 2mL^2 \quad . \quad . \quad . \quad (15)$$

where L is now the length of the

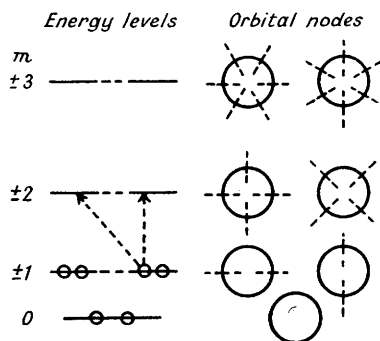


FIG. 6

molecular perimeter; the energy levels and the nodes of the orbitals are shown in Fig. 6. The lowest orbital with $m = 0$ has no nodes and represents a uniform electron distribution around the ring. Corresponding to $m = \pm 1$ there are two levels with equal energy, and each orbital has two nodes (see Fig. 6). These levels are said to be *degenerate*, a property which arises because the circular perimeter has no beginning and no end, and there is a resulting uncertainty about where the nodes should be drawn. This vagueness about the positions of the nodes in space can be expressed mathematically by using the

complex functions $e^{im\phi}$ or $e^{-im\phi}$ for the orbitals instead of $\sin m\phi$ or $\cos m\phi$. Each orbital with $m \neq 0$ is degenerate; if we considered a substituted benzene in which a definite direction is fixed by the position of the substituent, one level of each degenerate pair would be established as having

²⁶ *Z. Physik*, 1931, **70**, 204. ²⁷ *J. Chem. Phys.*, 1949, **17**, 484. ²⁸ *Ibid.*, p. 470.

the lower energy, and the degeneracy would be "split." This degeneracy does not arise in the case of linear conjugated systems since the positions of the nodes are definitely fixed by the requirement that the orbitals must be zero at the two ends of the system.

Two of the six π electrons of benzene occupy E_0 , and four occupy the degenerate pair of levels E_1 (see Fig. 6); the ten π electrons of naphthalene fill the levels E_0 , E_1 , and E_2 , and so on. According to Hückel,²⁶ aromatic properties recur when each degenerate energy level pair is filled. Thus *cyclooctatetraene* with eight π electrons is not aromatic; ²⁹ *cyclodecapentaene* should be.

The absorption spectrum of benzene contains three well-known electronic transitions, a weak transition near 2600 Å with oscillator strength $f = 0.001$, a moderately intense one near 2000 Å with $f = 0.07$, and an intense transition at 1850 Å with $f = 0.8$. If the excitation of an electron from one of the levels $m = \pm 1$ to one with $m = \pm 2$ in Fig. 6 is identified with the band at 1850 Å, the calculated $f = 0.6$,²⁷ and the value of L required to fit equation (15) is 8.1 Å, corresponding to a circle of diameter 2.6 Å, in good agreement with the actual diameter of 2.8 Å across the benzene ring.

This simple application of FE theory accounts for only one excited state; however, as Platt²⁷ has shown, there are actually *eight* possible excited states with the configuration of three electrons in the level $m = \pm 1$ and one electron with $m = \pm 2$. To make the discussion applicable to aromatic hydrocarbons in general as well as to benzene, we can use Platt's nomenclature of labelling the top filled orbital in the ground state by f , assigning it the quantum numbers $\pm m$. The lowest vacant level with quantum numbers $\pm (m + 1)$ is labelled g . The ground state of the aromatic hydrocarbon is designated by f^4 to denote that four electrons are in the degenerate pair of levels with the quantum numbers $\pm m$. Excited states with one electron promoted to the lowest vacant level are denoted by f^3g . In order to show that the f^4 state is unique but that there are eight different states with the configuration f^3g , it is necessary to consider the *complete molecular wave functions* which are formed by taking the products of the occupied orbital wave functions. We shall use the complex orbitals $e^{im\phi}$, $e^{-im\phi}$, $e^{i(m+1)\phi}$, $e^{-i(m+1)\phi}$, which are mathematically simpler, although they are more difficult to visualise, than the sine or cosine functions referred to previously. For the ground state, the complete wave function (insofar as it depends on ϕ) is

$$f^4: e^{im\phi} \cdot e^{im\phi} \cdot e^{-im\phi} \cdot e^{-im\phi} = 1 \quad . \quad . \quad . \quad (16)$$

This equation expresses the fact that each orbital $\pm m$ accommodates two electrons; the complete function f^4 is totally symmetrical with no nodes. The electron spins are all paired, the total spin is zero, and the state is therefore a singlet. Platt denotes such states as 1A . In the excited state f^3g , the electron in the g level may have either of the two quantum numbers

²⁹ Pink and Ubbelohde, *Trans. Faraday Soc.*, 1948, **44**, 708.

$\pm (m + 1)$; there are hence two complete wave functions, *viz.*,

$$f^3g : (e^{im\phi} \cdot e^{im\phi} \cdot e^{-im\phi})e^{i(m+1)\phi} = e^{i(2m+1)\phi} \quad . \quad . \quad (17)$$

$$f^3g : (e^{im\phi} \cdot e^{im\phi} \cdot e^{-im\phi})e^{-i(m+1)\phi} = e^{-i\phi} \quad . \quad . \quad (18)$$

In the former case, equation (17), the complete wave function has $2(2m + 1)$ nodes as ϕ ranges from 0 to 2π ; in the latter case it has two nodes. Platt labels these states as L and B, respectively. Furthermore, if the spin of the g electron is parallel to the spin of its "hole" in the f shell, the total electronic spin is zero and the state is a singlet; if the spin of the g electron is antiparallel to that of its hole, the total spin is unity and the state is a triplet. Thus there are the excited states 1L , 3L , 1B , 3B . Lastly, in a real molecule in which the atoms around the perimeter cause the potential energy to be periodic rather than uniform, the B and L states split into $^1,^3B_a$, $^1,^3B_b$, $^1,^3L_a$, $^1,^3L_b$, eight states in all, the distinction between a and b depending on where the nodes cut the molecular skeleton. In most cases the nodes of a states cut *bonds* and those of b states cut *atoms*; but see Platt²⁷ for the details. Similar sets of states can be based on other excited configurations.

This description and designation of states, based on a very simple form for the orbitals, has formed the basis for Platt's successful correlation of aromatic spectra and for his semi-quantitative prediction of the intensities and polarisations of absorption bands. Fig. 7 shows the more important states of benzene and naphthalene, the nodes of the complete wave functions, the conventional group-theory designations, and the corresponding absorption bands where they have been observed.

The FE theory can thus give an adequate description in simple terms of the aromatic excited states that are of interest to the spectroscopist. However, the chemist is primarily concerned with the ground states of molecules and their reactions, and in this connexion a vast literature has grown up around the effect of substituents on the reactivity of aromatic compounds. In theoretical terms these effects are concerned with (a) the π electron density in relation to the molecular framework, and (b) the polarisability of the π electron cloud. In the case of benzene, the FE orbitals of Fig. 6 predict a uniform π electron density around the ring in keeping with the known equality of the six C-C bond distances; this is to be compared with the predicted alternating electron density along a linear polyene (Fig. 5) and the known alternation of bond distances. If the benzene ring has a substituent at one point, its effect will be to fix in space the nodes of the levels $m = \pm 1$ in Fig. 6, and to make one of these levels of lower energy than the other, thus removing the degeneracy. However, the simple FE orbitals will still have the forms $\cos m\phi$ and $\cos m(\phi + \pi/2)$, and when these are squared and added to the square of the lowest orbital in the manner of equation (14), the result is still a uniform π electron density around the ring. It is thus apparent that the FE theory needs some future development to cope with the problem of aromatic reactivity.

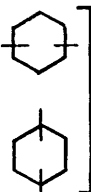
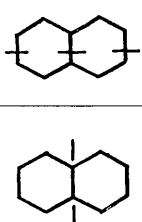

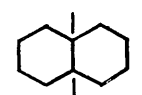

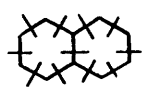

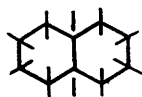



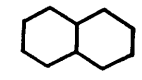
Benzene		Naphthalene	
	Degenerate pair ${}^1B_g, {}^1B_u$ (1E_u) Intense absorption at 1800 Å		1B_a (${}^1B_{2u}$) Intense absorption at 1700 Å
	1L_a (${}^1B_{1u}$) Moderately intense absorption at 2000 Å		1B_b (${}^1B_{1u}$) Most intense absorption at 2200 Å
	1L_a (${}^1B_{2u}$) Moderately intense absorption at 2000 Å		1L_a (${}^1B_{2u}$) Absorption at 2700 Å
	1L_b (${}^1B_{2u}$) Weak absorption at 2600 Å		1L_b (${}^1B_{1u}$) Weak absorption at 3100 Å
	3L_a (${}^3B_{1u}$) Very weak absorption at 3400 Å Phosphorescence level		3L_a (${}^3B_{2u}$) Phosphorescence level at 4900 Å
	1A (${}^1A_{1g}$) Ground state		1A (${}^1A_{1g}$) Ground state

FIG. 7

4. Extension of FE Theory

Referring back to Schroedinger's equation (1) (p. 320), we see that the answer to the problem of finding the energy levels and the orbitals of the π electrons depends in principle on a knowledge of V , the potential-energy field in which the electrons move. The FE approximation of confining the electrons by the vertical-walled potential-energy box of Fig. 3 is obviously a gross oversimplification, one reason being that the model makes no provision for ionisation, *i.e.*, for the electrons to escape from the box or from the vicinity of the molecule. On the other hand, real conjugated molecules have ionisation energies that are generally less than 10 e.v.⁵ Thus for the case of hexatriene depicted in Fig. 2, the ionisation energy needed to allow the π electron to escape is less than the energy of the second excited level of the FE model. Furthermore, the "box" approxima-

tion results in a wrong "pattern" for the energy levels in that the intervals between them increase as the energy increases. In real cases, whether of atoms or molecules, the levels tend to draw closer together the greater their energy, merging into a continuum of levels above the energy of ionisation.

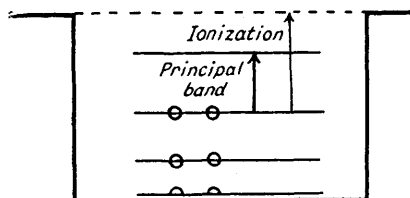


FIG. 8

to escape altogether, *i.e.*, it ionises. Models of this kind have been examined by Bayliss³⁰ in relation to linear polyenes. Their energy level pattern is more acceptable in that the levels draw closer together as the energy increases, and they account for both the absorption spectra and ionisation energies with a length L which agrees rather better with molecular dimensions than the simple FE model.

It is also possible to improve the original model by taking into account the fact that the actual electronic potential energy is really oscillating or periodic (see Fig. 3). Kuhn³¹ tackled this aspect of the problem, as far as linear polyenes and unsymmetrical cyanines are concerned, by assuming that the potential energy along the conjugated chain has the same periodicity as the vinyl $C=C-C$ units. The effect of this was to introduce an extra potential-energy parameter, and when suitable and reasonable values were introduced, Kuhn was able to account quantitatively for convergent spectral series such as those in Fig. 4. Bayliss and Riviere³² approached the problem in a rather different way by attempting to evaluate numerically the oscillating potential-energy function along the molecular axis as shown in Fig. 3. This was done by regarding the π electron as moving in the electrostatic field of all the carbon nuclei of the conjugated system, the effect of the K , σ , and other π electrons being taken into account by assigning to each nucleus an effective, screened nuclear charge Z' . It was not possible to obtain an analytical solution of the problem; however, numerical solutions by the method of finite differences, the value $Z' = 1$ being used for carbon and $Z' = 1.5$ for nitrogen, led to improved agreement with the spectral and ionisation data for butadiene and several polymethines. Their values of Z' were justified by a rather arbitrary extension³³ to molecules of Slater's screening rules for atoms.³⁴ It is only fair to state

³⁰ *Australian J. Sci. Res.*, 1950, **A**, **3**, 109.

³¹ *Z. Elektrochem.*, 1949, **53**, 165; *J. Chem. Phys.*, 1949, **17**, 1198.

³² *Australian J. Sci. Res.*, 1951, **A**, **4**, 344.

³³ Bayliss, *J. Chem. Phys.*, 1949, **17**, 1353.

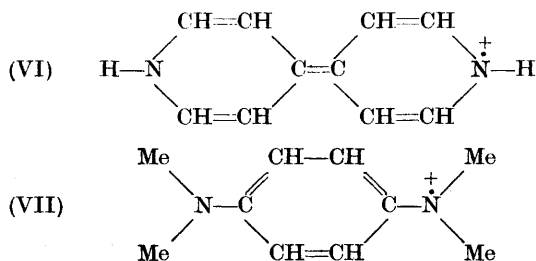
³⁴ *Phys. Review*, 1930, **36**, 58.

It is possible to allow for ionisation by regarding the π electrons as moving, not in a box, but rather in a "well" with potential-energy walls of finite height, as shown in Fig. 8 for the case of hexatriene. While the electron is inside the well, its potential energy is regarded as uniform; if its total energy is greater than the height of the walls, it is free

that these low values for Z' , as compared with the Slater atomic values of 3.2 and 3.9 for C and N, respectively, seem to depend on the fact that all the nuclei of the conjugated chain, not merely the nearest nuclei, were considered to contribute to the π electron energy. The Slater atomic values seem to be definitely required in LCAO treatments of the same problem.³⁵

The more advanced treatments just described still employ the linear or one-dimensional model of the simple FE theory, and they give orbitals that are essentially similar to those of the simple theory with nodes in roughly the same places. They show little improvement over the simple uniform potential model in the computed transition intensities. This conclusion would appear to be general. Electrons confined to a given space are represented by standing waves in that space. When the orbitals are normalised, their amplitudes and the positions of their nodes are not very sensitive to the way in which the electrons are imagined to be confined, *i.e.*, whether they are confined by the walls of a "box" imposed from "outside", or by a system of charged nuclei placed "inside", that space. It is these considerations, which provide the justification for the use, at least qualitatively, of the simple theory of the electron gas to derive information about π electron orbitals, their nodes, and the resultant π electron densities. The energy levels and the predicted spectral frequencies are much more sensitive to the assumptions concerning the details of the potential-energy field.

The FE model has been applied to the problem of phthalocyanines and porphines by Kuhn,²⁴ by Simpson,³⁶ and by Platt.³⁷ It has been extended to two-dimensional cases by Kuhn,³⁸ and the absorption spectrum of decaborane has been considered by Pimentel and Pitzer³⁹ in terms of an electron gas in a three-dimensional space. Kuhn's treatment²⁴ of dyes



such as dipyrindyl-violet (VI) and Würster's blue (VII), where there is both linear and ring conjugation, is a good illustration of the importance of the orbital nodes. In both the linear and the ring portions of the conjugated system the orbitals are standing waves, with the added condition in these cases that the waves must agree in phase at the junctions between

³⁵ Shull and Ellison, *J. Chem. Phys.*, 1951, **19**, 1215. ³⁶ *Ibid.*, 1949, **17**, 1218,

³⁷ Chap. 4 of "Radiation Biology, Vol. 3. Biological Effects of Visible Radiation", ed. by Hendricks, McGraw-Hill, N.Y., 1951.

³⁸ *Helv. Chim. Acta*, 1949, **32**, 2247.

³⁹ *J. Chem. Phys.*, 1949, **17**, 882.

the different parts of the conjugated system. The mathematical solution of the problem is difficult, and Kuhn⁴⁰ has therefore investigated the behaviour of mechanical analogues made up of vibrating branched strings and vibrating membranes where similar nodal patterns are to be expected.

5. Summary and Comparison with the LCAO Method

In order to appreciate the real nature of the assumptions made in the FE method, it is instructive to compare it with the procedure used in the well known LCAO molecular orbital method. Taking the simple case of butadiene, with one π electron associated with each of the four carbons, and imagining at first that the carbons are widely separated from one another, then the π electron orbitals on the individual carbons would be atomic orbitals of the type described as $2p\pi$ with a node in the plane of the nuclei. Denote these by $\phi_1 \dots \phi_4$. If the widely separated carbons are now brought together to form the butadiene molecule, it is assumed in the LCAO method that the molecular orbitals ψ of the π electrons can be constructed as linear combinations of the atomic orbitals $\phi_1 \dots \phi_4$. In other words the MO's ψ will have the form

$$\psi = a\phi_1 + b\phi_2 + c\phi_3 + d\phi_4 \quad . \quad . \quad . \quad (19)$$

Four independent ψ 's can be constructed from the four ϕ 's, and the mathematical problem is to determine the four appropriate sets of the coefficients a, b, c, d . If the Schrodinger equation (1) is rearranged in the form

$$\left(-\frac{\hbar^2}{8\pi^2m} \nabla^2 + V \right) \psi = E\psi \quad . \quad . \quad . \quad (20)$$

it may be rewritten as

$$\mathbf{H}\psi = E\psi \quad . \quad . \quad . \quad (21)$$

where the one electron Hamiltonian operator \mathbf{H} is

$$\mathbf{H} = -\frac{\hbar^2}{8\pi^2m} \nabla^2 + V$$

Now in general the energy E is given by

$$E = \int \psi \mathbf{H} \psi d\tau / \int \psi^2 d\tau \quad . \quad . \quad . \quad (22)$$

where for simplicity it is supposed that the ψ functions are real.

If now ψ is expressed in the approximate LCAO form of (19), then the corresponding E is

$$E = \left\{ \int (a\phi_1 + \dots + d\phi_4) \mathbf{H} (a\phi_1 + \dots + d\phi_4) d\tau \right\} / \left\{ \int (a\phi_1 + \dots + d\phi_4)^2 d\tau \right\} \quad (23)$$

Without going into the mathematical details of the LCAO theory, which have been fully described elsewhere,^{7, 41} the so-called variation procedure

⁴⁰ *Z. Elektrochem.*, 1951, **55**, 220.

⁴¹ Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39; and following papers.

is to find the sets of values of a, b, c, d that make the E of (23) a minimum. The solution of the problem, and the resulting values of E , involve integrals such as

$$\int \phi_i \mathbf{H} \phi_j d\tau = H_{ij} \quad . \quad . \quad . \quad . \quad (24)$$

and

$$\int \phi_i \phi_j d\tau = S_{ij} \quad . \quad . \quad . \quad . \quad (25)$$

which appear when the brackets of (23) are multiplied out. Since $\phi_1 \dots \phi_4$ are located on different carbon nuclei that are separated in space, it is usual in simple LCAO theory to assume that $H_{ij} = 0$ unless $i = j$ or unless i and j refer to nearest neighbours, also that $S_{ij} = 0$ unless $i = j$, in which case S_{ij} or rather S_{ii} is unity, since the atomic orbitals ϕ are supposed to be normalised. By these assumptions, the problem is thus broken down into one involving the integrals conventionally designated as Q and β , namely,

$$Q = H_{ii} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\beta = H_{ij} \quad (i, j \text{ nearest neighbours}) \quad . \quad . \quad . \quad (27)$$

The result of the simple LCAO treatment of our example of butadiene is that the four molecular orbitals are given by

$$\left. \begin{aligned} \psi_1 &= 0.37\phi_1 + 0.60\phi_2 + 0.60\phi_3 + 0.37\phi_4 \\ \psi_2 &= 0.60\phi_1 + 0.37\phi_2 - 0.37\phi_3 - 0.60\phi_4 \\ \psi_3 &= 0.60\phi_1 - 0.37\phi_2 - 0.37\phi_3 + 0.60\phi_4 \\ \psi_4 &= 0.37\phi_1 - 0.60\phi_2 + 0.60\phi_3 - 0.37\phi_4 \end{aligned} \right\} \quad . \quad . \quad (28)$$

and that the corresponding energy levels are—

$$\left. \begin{aligned} E_1 &= Q - 1.62\beta & E_2 &= Q - 0.62\beta \\ E_3 &= Q + 0.62\beta & E_4 &= Q + 1.62\beta \end{aligned} \right\} \quad . \quad . \quad (29)$$

It is to be noted that the potential energy V of the π electrons, which appears in the Schrodinger equations (1) and (20), is contained in the operator \mathbf{H} , and that its form does not enter the discussion until an attempt is made to evaluate mathematically the integrals Q and β . The ψ 's of equation (28) are independent of any assumption about V ; the fact that they have the same nodal features as the FE orbitals [see equation (13) and Fig. 1] emphasises the conclusion reached in the preceding section, namely, that the forms of the molecular orbitals are rather insensitive to the way in which the π electrons are supposed to be held together in the region of the molecular framework. Although the E 's of equation (29) do involve Q and β , their differences involve only the integral β ; in a set of related compounds such as a homologous series of polyenes it is possible to estimate β either from the spectrum or else from the thermal resonance energy data pertaining to one member of the series, and to use this value consistently for the whole series. The empirical values of β have been discussed by Mulliken and Rieke.⁴² In this way the simple LCAO treatment has been extended to many conjugated systems without the necessity

⁴² *Rev. Modern Phys.*, 1942, **14**, 259. See also ref. (8).

of mathematically evaluating either Q or β , and hence by implication without the need to make any assumption about the form of the potential energy V .*

After this analysis of LCAO theory, we may summarise the main features of the FE and the LCAO methods as follows :

(1) Both methods treat conjugated compounds in terms of the unsaturation, mobile, or π electrons, which are supposed to move independently of the rest of the molecular framework, and are assigned to molecular orbitals that belong to the conjugated system as a whole.

(2) The LCAO method is essentially one in which the molecular orbitals ψ are assumed to have a particular form, namely, that they can be constructed from linear combinations of the π orbitals of the individual carbon atoms.

(3) The FE method, on the other hand, is one in which a simple form is assumed for V , the potential-energy field in which the π electrons move. The form of the orbitals ψ is then derived by solving the one-electron form of the Schrodinger equation.

(4) Because of the formal nature of the LCAO assumption embodied in equation (19) and of the subsequent mathematical analysis, the LCAO method provides a calculus which is applicable to any conjugated system.

(5) The FE concept of a π electron gas in a uniform potential-energy field in a box is also in principle applicable to any conjugated system. Mathematical difficulties have so far in practice confined the FE treatment to linear molecules which can be treated approximately as one dimensional, and to very simple non-linear molecules.

(6) In the case of linear molecules, both methods predict orbitals with similar forms and nodal properties. Hence both methods predict values of π electron densities along a linear conjugated chain that are qualitatively similar, although quantitatively different.⁴³

(7) In linear molecules such as polyenes and polymethines, the FE method predicts transition intensities and spectral frequencies that are superior to those of the simple LCAO theory.^{14, 15}

(8) Neither the FE method, nor the LCAO treatment in its simple form, introduces the concept of electron spin except in applying the Pauli principle to the filling of the orbitals. FE orbitals have not yet been made the basis of a general treatment including spin corresponding to the LCAO method with antisymmetrised molecular orbitals (ASMO).⁴⁴

Owing to its relatively crude approximation to V , it is not easy to give theoretical reasons for the relative success of the FE method. Indeed, one wonders how any simple theoretical approach can achieve quantitative success when applied to a system as complex as an organic molecule. Two

⁴³ McLean, Thesis, University of Western Australia, 1952 (paper by Bayliss and McLean in preparation).

⁴⁴ Coulson and Jacobs, *Proc. Roy. Soc.*, 1951, A, **206**, 287.

* The more advanced forms of LCAO theory do require the evaluation of integrals such as Q and β ; these methods have necessarily been applied to relatively few cases as yet. See ref. (8), also Parr and Mulliken, *J. Chem. Phys.*, 1950, **18**, 1338.

reasons can perhaps be advanced tentatively: the first is that the real π electron potential energy within a conjugated system is in fact more uniform than would be suspected from the conventional chemical-bond picture; the second has already been referred to, namely, that the *nodes* of the electronic wave functions are their most important properties, and the positions of the nodes depend more on the *dimensions* of the space in which the electrons are confined than on the forces which act on them within that space.