U.D.C. 541.2; 541.571.35

The Electronic Structure of Conjugated Systems in Terms of the Pariser-Parr-Pole Approximation

I.A.Misurkin and A.A.Ovchinnikov

The potentialities of the π-electron approximation for the description of the electronic structures of conjugated molecules are analysed and two modern schemes for the parametrisation of the model Pariser-Parr-Pople π-electron Hamiltonian are considered. The application of this theory in the calculation of the properties of the ground state (bond lengths and angles, heats of formation, and dipole moments) and excited states (the energies of singlet and triplet excitations, oscillator strengths, and ionisation potentials) is also discussed.
The bibliography includes 80 references.

CONTENTS

I.	Introduction	1072
II.	The π-electron approximation for conjugated systems	1073
III.	The properties of the ground state of conjugated molecules	1078
IV.	Calculations on excited states of conjugated molecules and two main schemes for the determination of the effective parameters of the model π-electron Hamiltonian	1081
V.	The difficulties of the theory in the calculation of the individual properties of excited states	1084

I. INTRODUCTION

Molecules with Saturated and Unsaturated Bonds

The theory of the electronic structures of conjugated molecules constitutes the most extensively studied field in quantum chemistry. The reasons for this are in many respects related to the fact that the absorption spectra of such compounds occur in the optical and ultraviolet regions, which are very readily susceptible to experimental study, and also to the fact that the properties of such molecules are determined by a comparatively small proportion of their electrons. These electrons, called π-electrons, form a closed autonomous group, which impart to conjugated molecules all their specific properties.

The purely chemical definition of conjugated compounds is self-evident; they include molecules with multiple bonds and contain atoms with "unsaturated valences". They are characterised by enhanced reactivity, the transmission of influences through several atoms, and a marked influence of substituents on the geometrical structure (bond lengths and angles).

We shall attempt to specify more precisely from the standpoint of electronic structure the factors on which the differences between the properties of compounds with saturated and unsaturated bonds depend. For a qualitative interpretation of the cuases of these differences, one may confine the treatment to a one-electron computational scheme. Organic molecules are usually many-electron systems and therefore in the calculation it is necessary to take into account a large number of atomic orbitals (AO). As a result, in terms of the one-electron approximation there arise numerous energy levels, which are combined into groups (bands). The state of each band is characterised by some one property, for example symmetry and type of atomic orbitals, from which one-electron functions called molecular orbitals (MO) are made up.

In molecules with saturated bonds the bands are either completely filled with electrons (two electrons with opposite spins in each molecular orbital) or are vacant, while in molecules with unsaturated bonds there are bands partly filled with electrons. As a rule, each molecular orbital is a linear combination of the atomic orbitals of all the atoms in the molecule (the LCAO-MO approximation), i.e. there is delocalisation over the entire molecule. It is then found that the wave functions (MO) corresponding to the completely filled band can be subjected to a specific unitary transformation such that the new one-electron functions assume a distinct localised character. In particular, the new orbitals can be made largely localised at individual bonds in the molecule (with two electrons having opposite spins in each new orbital)[1].

In molecules with unsaturated bonds it is also possible to localise electrons at individual ("double") bonds when the so called π-electrons are considered. However, the interaction of two electrons of one such bond (proportional to the resonance bond integral) will be almost the same as the interaction between adjacent double bonds, because the resonance integrals for "single" and "double" bonds are almost the same. In molecules with saturated bonds the resonance integral is several times greater (in absolute magnitude) than the resonance integrals for electrons in adjacent bonds, so that in these compounds the steric localisation of electrons is accompanied by "energy" localisation: the interaction between bonds only slightly alters their energy. This implies that in molecules with saturated bonds the approximation of non-interacting bonds constitutes a satisfactory zeroth approximation, while in molecules with unsaturated bonds the introduction of functions localised at the bonds is as a rule ineffective and it is better to employ delocalised functions immediately.

In the language of the solid state theory systems with unfilled bands are metals. If the number of atoms in the saturated molecule is increased regularly, we obtain a system where the structure of the energy bands is analogous to the structure of the energy bands in a dielectric (for example, paraffins and diamond). On the other hand, an increase in the size of the π-electron system, for example on passing from condensed aromatic molecules

to graphite, leads to a system with an unfilled energy band, which is characteristic of metals. Admittedly one-dimensional π-electron systems (macro-molecules with conjugated bonds) are always semiconductors, but this is related to a specific phenomenon—the Mott "metal—dielectric" transition (described in detail in the review of Ovchinnikov et al.[2]).

Numerous studies on the theory of molecules with π-electrons have been published. This reflects the major role which compounds with conjugated bonds play in chemistry, biology, and chemical physics. Furthermore, the effectiveness of various methods for calculations on molecules of other classes is tested on conjugated systems. Molecules with conjugated bonds form a relatively small fraction of the total number of molecular systems and for this reason the theory of the structure of conjugated systems is of great heuristic value.

Significant advances have been made in the modern theory of conjugated systems in the qualitative and quantitative explanation of molecular properties.

Various characteristics of conjugated molecules are calculated with a relative error of about 10%, which reflects the comparatively high predictive power of the theory. Nevertheless, the errors, which in individual cases can exceed 10%, make it necessary to seek new ways for improving the theory. Owing to the enormous difficulties of the many-electron problem, the theory of conjugated systems is essentially semiempirical. Therefore various schemes and methods, differing in the procedures for the introduction of empirical parameters and in the degree of approximation of the methods of calculation are quite admissible in this theory and are indeed used. In all such studies a satisfactory agreement with experiment is as a rule achieved. Their analysis makes it possible to identify the most significant and general features of different computational schemes. It is found that the general and most important aspects of these schemes are very similar, which is an advantage of the theory as a whole.

Apart from studies where individual molecular properties are calculated, which is probably the main task of the theory, studies which justify the empirical and semi-empirical relations used to calculate specific molecular properties are very important for the development of the theory.

The aim of the present review is to outline the present state of the semiempirical theory of conjugated systems from the standpoint of general principles without going into the details of various computational methods. We are interested primarily in problems such as the internal logical self-consistency of the theory, the accuracy of the prediction of various experimental data and properties, and the possibility of improving the methods for the calculation of these data and properties.

II. THE π-ELECTRON APPROXIMATION FOR CONJUGATED SYSTEMS

Molecules with conjugated bonds are as a rule planar. The atoms supplying $2p_z$ electrons to the general π-electron systems have nuclei located in a single plane (the xy plane). The σ-bonds between the atoms of the molecule are also located in this plane and form the so-called σ-skeleton of the conjugated molecule. The electrons of the σ-skeleton occupy completely filled bands and therefore the corresponding one-electron functions may be localised at the interatomic bonds.

All the $2p_z$ orbitals are orthogonal with respect to all the one-electron functions of the σ-bonds. This orthogonality is the main reason why the electrons of the molecule can be divided into those of the σ-skeleton and π-electrons. Furthermore it is found that π-electrons are more weakly bound to the molecule than σ-electrons, so that almost all the observed properties of molecules with conjugated bonds are determined by π-electrons. These postulates form part of the basis of the theory of conjugated systems considered here, which explains molecular properties in terms of an explicit consideration of π-electrons alone. This is the so-called π-electron approximation.

We shall quote only one group of experimental data, which confirm directly the validity of the π-electron approximation. In the theory of conjugated hydrocarbons in the π-electron approximation there is a theorem that the optical spectra of the cation and anion derived from the same molecule are identical. This theorem is valid when full account is taken of the interaction between the electrons[3]. The experimental data presented in Fig. 1 demonstrate a striking similarity of the absorption spectra, which constitutes a direct confirmation of the theoretical conclusions.

Fig. 1 shows that certain absorption band maxima are displaced relative to one another by about 10% of the transition energies. We believe that these values demonstrate directly the limit of the accuracy with which it is possible to carry out calculations in terms of the modern theory employing the π-electron approximation. Examination of π-electrons alone when considering molecular properties greatly facilitates the theoretical analysis, since the number of π-electrons is several times smaller than the total number of electrons in the molecule. The presence of other electrons in the molecule (the electrons of the σ-skeleton) is taken into account implicitly. It alters the π-electron interaction, which is described by an effective model Hamiltonian. The parameters of this Hamiltonian depend on the properties of the σ-skeleton, i.e. on the σ-electrons.

For a quantum-mechanical description of a π-electron system, it is natural to employ the set of the atomic $2p_z$ functions as the basis functions. These $2p_z$ functions are non-orthogonal, which leads to considerable technical difficulties in calculations. Therefore it is natural to construct from the $2p_z$ functions an orthogonal basis set $\varphi_p(\mathbf{r})$ using the linear transformation

$$\varphi_p(\mathbf{r}) = \sum_{i=1}^{M} U_{pi}\, 2p_{z_i}(\mathbf{r}) \quad (p = 1, 2, \ldots M),$$

where M is the number of $2p_z$ functions or the dimension of the new basis set of the functions $\varphi_p(\bar{\mathbf{r}})$. Löwdin[5] discovered the transformation U_{pi}, in which each of the functions $\varphi_p(\mathbf{r})$ consists largely of $2p_z$ functions of the atom p and contains only a slight admixture of the $2p_z$ functions of other atoms. Thus the functions $\varphi_p(\mathbf{r})$ are not only orthogonal (and normalised) but are also localised at the atoms. The slight delocalisation of these functions leads to effects associated with the mutual influence of the atoms.

We shall consider in greater detail the transition to an orthogonalised basis† set. This is done most naturally

† The idea of the treatment described below was communicated to the authors by M. V. Bazilevskii.

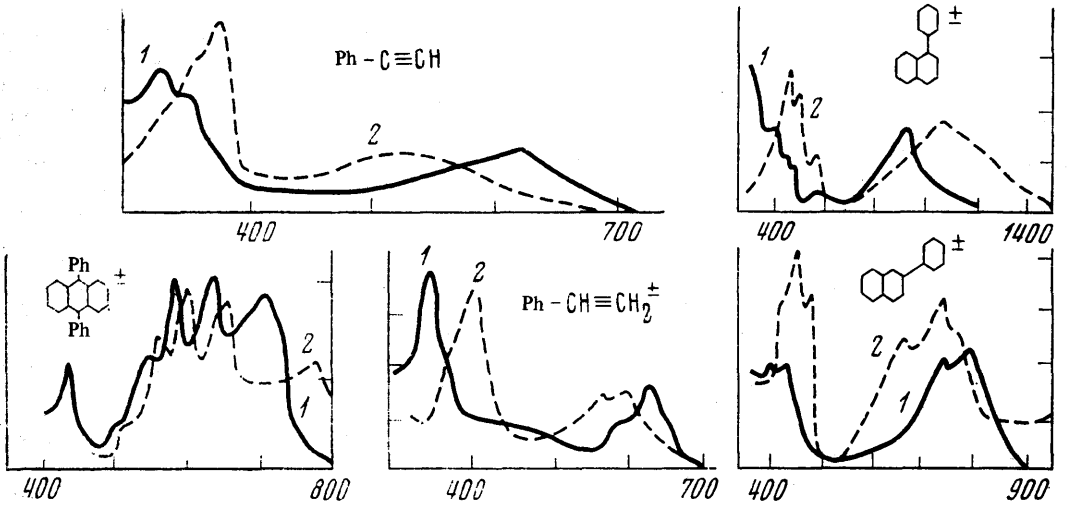


Figure 1. Experimental absorption spectra of the anions (curves *1*) and cations (curves *2*) of certain conjugated hydrocarbons[4].

by solving the standard quantum-chemical eigenvalue problem:

$$\hat{H}\psi = \varepsilon\psi,$$

where $\hat{H}$ is a Hamiltonian or Fockian and ψ is the row-matrix of the molecular orbitals $\{\psi_1, \psi_2, \ldots\}$, which can be expressed in terms of the non-orthogonal atomic orbitals χ_i specified by the row-matrix $\{\chi_1, \chi_2, \ldots\}$ and the required coefficient matrix C (the LCAO-MO approximation):

$$\psi = \chi C, \quad \psi_l = \sum_{k=1}^{M} \chi_k c_{kl},$$

where c_{ki} are the elements of the matrix C.

We now introduce the overlap integral matrix

$$\chi^{+}\chi = \begin{bmatrix} \chi_1^* \\ \chi_2^* \\ \vdots \end{bmatrix} (\chi_1, \chi_2 \ldots) = S.$$

The row- and column-matrices are multiplied in accordance with the usual rules of matrix multiplication and integration with respect to coordinates is carried out; the asterisk (*) denotes a complex conjugate. The elements of the matrix S, for example, are of the form

$$S_{ij} = \int \chi_i^*(\mathbf{r})\chi_j(\mathbf{r})\,d\mathbf{r}.$$

We now reformulate our equation for eigenvalues as follows:

$$\hat{H}\chi C = \chi C\varepsilon,$$

the left-hand side of the equation is multiplied by χ^{+}, and the matrix equation

$$HC = SC\varepsilon$$

is obtained. Here $\chi^{+}\hat{H}\chi$ is the matrix $\hat{H}$ in the non-orthogonal basis set. The solution of the last matrix equation constitutes the familiar problem of double diagonalisation (of the matrices H and S). It would appear that, by multiplying the left-hand side of the equation by S^{-1} and obtaining thereby the equation

$$(S^{-1}H)C = C\varepsilon,$$

we reduce the problem to the diagonalisation of a single matrix $S^{-1}H$. However, this matrix is generally speaking asymmetric‡: its transposition (designated by the symbol ~)

$$\widetilde{(S^{-1}H)} = \tilde{H}\tilde{S}^{-1} = H\,S^{-1}$$

yields another matrix, namely

$$H\,S^{-1} \neq S^{-1}H.$$

At the same time it is known that the diagonalisation of an asymmetric matrix is difficult and requires special computer programs, which are difficult to devise.

Therefore the double diagonalisation problem will be solved in a different way. We reformulate our matrix equation as follows:

$$HS^{-1/2}S^{1/2}C = S^{1/2}S^{1/2}C\varepsilon,$$

multiply its left-hand side by $S^{-1/2}$, and obtain the equation

$$\bar{H}\cdot\bar{C} = \bar{C}\varepsilon,$$

where $\bar{C} = S^{1/2}C$ and $\bar{H} = S^{-1/2}HS^{-1/2}$. The matrix $\bar{H}$ is symmetrical and therefore its diagonalisation is carried out with the aid of standard programs.

In order to obtain $\bar{H}$, it is necessary to calculate first the matrix $S^{-1/2}$. In qualitative studies one employs the method of expansion with respect to the non-diagonal part of S:

$$S = I + S',$$

where I is a unit matrix and S' the non-diagonal part of S.

---

‡ In all subsequent treatment it is assumed that all the atomic orbitals are real and therefore the matrices S and H are symmetrical and real.

Then

$$S^{-1/2} = (I + S')^{-1/2} = I - \frac{1}{2}S' + \frac{3}{8}S'S' - \ldots .$$

In computer calculations it is necessary to proceed in a different way. Initially S is diagonalised with the aid of a standard program, which yields S_{diag} and the transformation matrix $V(\tilde{V} = V^{-1})$:

$$S_{\text{diag}} = V^{-1}SV.$$

Suppose that S_{diag} is of the form

$$S_{\text{diag}} = \begin{pmatrix} a & & & 0 \\ & b & & \\ & & f & \\ 0 & & & \ddots \end{pmatrix}.$$

Then it is easy to show that (a, b, f, ... are positive numbers)

$$S_{\text{diag}}^{1/2} = \begin{pmatrix} \sqrt{a} & & & 0 \\ & \sqrt{b} & & \\ & & \sqrt{f} & \\ 0 & & & \ddots \end{pmatrix}, \quad S_{\text{diag}}^{-1/2} = \begin{pmatrix} \frac{1}{\sqrt{a}} & & & 0 \\ & \frac{1}{\sqrt{b}} & & \\ & & \frac{1}{\sqrt{f}} & \\ 0 & & & \ddots \end{pmatrix}.$$

After calculating $S^{-1/2}$ in terms of the diagonal representation, we return to the non-diagonal representation with the aid of the matrix V and obtain the required expression for $S^{-1/2}$:

$$S^{-1/2} = VS_{\text{diag}}^{-1/2}V^{-1}.$$

In the diagonalisation of the matrix $\bar{H}$ we also find the coefficient matrix $\bar{C} = S^{1/2}C$. Hence we obtain $C = S^{-1/2}\bar{C}$.

We now express the wave function ψ in terms of $\bar{C}$:

$$\psi = \chi C = \chi S^{-1/2}S^{1/2}C = \lambda\bar{C},$$

where

$$\lambda = \chi S^{-1/2},$$

so that we arrive at a new orthogonalised basis set $\lambda = \{\lambda_1, \lambda_2, \ldots\}$. In fact

$$\lambda^+\lambda = S^{-1/2}\chi^+\chi S^{-1/2} = S^{-1/2}SS^{-1/2} = I.$$

We may also note that $\bar{H}$ is the matrix of the operator $\hat{H}$ in the basis set λ: $\bar{H} = \lambda^+H\lambda$. The functions λ_p are our required basis functions $\varphi_p(\mathbf{r})$ and the functions χ_i are the initial $2p_z$ functions.

1. The Effective Model Hamiltonian for π-electrons

The effective π-electron Hamiltonian can be formulated in terms of secondary quantisation:

$$H = \sum_{p,q,\eta} H_{pq}c_{p\eta}^+c_{q\eta} + \sum_{pqrt}\sum_{\rho\eta}\langle pq\,|\,rt\rangle c_{p\eta}^+c_{q\eta}c_{r\rho}^+c_{t\rho}. \qquad (1)$$

Any π-electron can be located in one of the basis states $\varphi_p(\mathbf{r})$ with projection of the spin η on the specified axis ($\eta = \pm 1/2$). The operators $c_{p\eta}^+(c_{p\eta})$ are called the operators of the generation (annihilation) of the π-electron in this state. These operators satisfy the transposition relations

$$c_{p\eta}^+c_{p'\eta'} + c_{p'\eta'}c_{p\eta}^+ = \delta_{pp'}\delta_{\eta\eta'},$$

$$c_{p\eta}c_{p'\eta'} + c_{p'\eta'}c_{p\eta} = c_{p\eta}^+c_{p'\eta'}^+ + c_{p'\eta'}^+c_{p\eta}^+ = 0.$$

The secondary quantisation representation makes it possible to avoid cumbersome steps involving Slater determinants made up of spin-orbitals. The Slater determinants, which ensure that the Pauli principle is observed for the wavefunction in terms of the coordinate representation are replaced by products of the operators $c_{p\eta}^+$, which operate in a special space. The Pauli principle (the antisymmetry of the wavefunction on transposition of two particles) holds automatically by virtue of the transposition relations for the operators $c_{p\eta}^+$ and $c_{p\eta}$.

We shall now consider briefly the essential feature of secondary quantisation in order to lift the "veil of incomprehensibility" from this concept, which is increasingly used in the literature on quantum chemistry. Secondary quantisation is introduced in quantum chemistry essentially when a one-electron wavefunction (molecular orbital) is expanded in terms of a basis set made up of atomic functions (the LCAO-MO approximation):

$$\psi(\mathbf{r}) = \sum_p c_p\varphi_p(\mathbf{r}).$$

One may say that the quantum-mechanical state $\psi(\mathbf{r})$ is yet again ("secondarily") "quantised" with respect to the states $\varphi_p(\mathbf{r})$. It is then possible to employ a matrix representation [all the operators are matrices with respect to the basis set $\varphi_p(\mathbf{r})$ with the wave functions expressed in the form of Slater determinants made up of the spin-orbitals $\varphi_p(\mathbf{r})\eta$] ($\eta$ is a spin function) or one can employ the secondary quantisation "representation" introduced by V. A. Fok (W. A. Fock), in which one again employs matrices made up of operators with respect to the basis set $\varphi_p(\mathbf{r})$ in which the expansion coefficients c_p are now regarded as operators, This makes it possible to employ simpler computational procedures without Slater determinants.

In the present review the secondary quantisation representation will be rarely used, mainly for the formulation of the Hamiltonian and other operators. Attention will be concentrated on the analysis of the matrix elements which are usually parametrised in semiempirical theories and which should be calculated, in accordance with general rules, in terms of the orthogonalised basis set $\varphi_p(\mathbf{r})$.

The parameters of Hamiltonian (1)

$$H_{pq} \text{ and } \langle pq\,|\,rt\rangle \qquad (2)$$

correspond to the one-particle and two-particle terms in the π-electron Hamiltonian in the coordinate representation

$$H_\pi = \sum_i \hat{H}(\mathbf{r}_i) + \sum_{i<j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \qquad (3)$$

Here $\hat{H}(\mathbf{r}_i)$ is the one-particle operator of the ith λ-electron, describing its kinetic energy and attraction to the σ-skeleton. The second term in Eqn. (3) is the two-particle operator of the Coulombic repulsion of π-electrons. The hamiltonians (1) and (3) are formally linked by relations of the type

$$H_{pq} = \int \varphi_p^*(\mathbf{r}_i)\,\hat{H}(\mathbf{r}_i)\,\varphi_q(\mathbf{r}_i)\,d\mathbf{r}_i,$$

$$\langle pq\,|\,rt\rangle = \iint \frac{\varphi_p^*(\mathbf{r}_1)\,\varphi_q(\mathbf{r}_1)\,\varphi_r^*(\mathbf{r}_2)\,\varphi_t(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\,d\mathbf{r}_1\,d\mathbf{r}_2. \qquad (4)$$

These relations usually serve as a basis for the determination of the parameters (2).

As a result of the slight delocalisation of the functions $\varphi_p(\mathbf{r})$, the parameters (2) or (4) depend not only on the atomic indices indicated in formulae (2) or (4) but also on the indices for other atoms. Analysis of Eqns. (4) carried out by Fischer-Hjalmars[6] made it possible to

localise in the parameters (2) and (4) the contributions due to atoms with other indices, for example indices differing from p, q, r, and t. Such separation makes it possible to develop ideas on the mechanism of the mutual influence of atoms and to understand the changes in parameters on passing from one molecule to another. These ideas are important because the correct values of the parameters (2) cannot as yet be calculated theoretically. These parameters are determined from a comparison with experimental data and Eqns. (4) make it possible to reduce to a minimum the elements of arbitrary choice in the selection of the empirical values of the parameters.

The fundamental formulae relating the matrix elements in the orthogonal (φ_p) and non-orthogonal, atomic (χ_p) basis sets are obtained with the aid of the relation

$$\varphi = \chi S^{-1/2},$$

with which we are already familiar, and the series expansion of the matrix $S^{-1/2}$, which was also discussed above. Namely it was found that

$$H_{pq}^{(\varphi)} = H_{pq}^{(\chi)} + O(S^3) \ (p \text{ and } q \text{ are adjacent}),$$

$$H_{pq}^{(\varphi)} = O(S^3) \ (p \text{ and } q \text{ are not adjacent}),$$

$$H_{pp}^{(\varphi)} = H_{pp}^{(\chi)} - \sum_q S_{pq} H_{pq}^{(\chi)} + O(S^3),$$

(q are adjacent to p),

$$\langle pq \,|\, rs \rangle^{(\varphi)} = \delta_{pq}\delta_{rs} \langle pp \,|\, rr \rangle^{(\chi)} + O(S^3) .$$

In these formulae the left-hand side represents the matrix element in the basis set φ_p and the right-hand side represents the element in the basis set χ_p; the symbol $O(S^3)$ denotes terms of the order of S_{ij}^3 or a higher power of S_{ij}—the overlap integral for neighbouring atoms. These formulae are used below in a discussion of the difference between spectroscopic and thermochemical parameters (Section III, 2) and partly in devising one of the parametrisation schemes (Section IV, 1). The diagonal matrix elements $H_{pp}^{(\varphi)}$ and $H_{pp}^{(\chi)}$ differ by terms of the order of S_{pq}^2 (q are neighbours of p). These differences have been shown by M. V. Bazilevskii (see Section III, 2) to be important in the calculation of heats of formation and in the construction of potential energy surfaces.

2. The Pariser–Parr–Pople (PPP) Approximation and Method

Goeppert-Mayer and Sklar[7] calculated all the parameters (4) for benzene with the aid of Slater $2p_z$ functions and refined the concept of the σ-skeleton, having proposed special formulae for the parameters H_{pq}. As a result, a qualitatively correct description of the absorption spectrum of benzene was obtained in terms of the self-consistent field (SCF) approximation[7]. This was a major success of the theory and indicated the validity of the π-electron approximation.

Subsequently Pariser, Parr, and Pople[8] proposed other rules for the determination of the parameters (2) using partly the approximation of Geoppert-Mayer and Sklar for the σ-skeleton. The most significant feature in the new rules was the rejection of formulae of type (4) for the calculation of the parameters (2), which were now determined empirically. Next the approximation of zero differential overlapping (ZDO) was introduced which greatly reduced the number of non-zero parameters in the Hamiltonian. In the ZDO approximation $H_{pq} \neq 0$ only for neighbouring p and q or for $p = q$; $H_{pq} = 0$ for the other p and q and $\langle pq \,|\, rt \rangle = \langle pp \,|\, tt \rangle \delta_{pq}\delta_{rt}$. For the orthogonal functions $\varphi_p(r)$ the ZDO approximation is reasonable, since all the rejected integrals are indeed small.

In calculations on the ground state, the LCAO-MO SCF approximation was used[9]. For example, the ground state of benzene was described by a single Slater determinant of molecular spin-orbitals or by a single configuration. Pariser et al.[8] showed that in the description of excited states of conjugated molecules it is necessary to employ a superposition of all singly excited configurations and not just one excited configuration, as in the method of Goeppert-Mayer and Sklar. Because of the high symmetry of benzene (D_{6h}), it was possible to obtain simple formulae for the energies of the first electronic transitions in terms of combinations of the parameters $H_{p,\,p+1} = \beta$§ and $\langle pp \,|\, qq \rangle = \gamma_{pq}$. These energies are given by formulae of the type[8]

$$\begin{aligned}
\Delta E(^1B_{2u}) &= -2\beta + \tfrac{1}{6}(\gamma_{12} - 3\gamma_{13} + 2\gamma_{14}),\\
\Delta E(^1B_{1u}) &= -2\beta + \tfrac{1}{6}(2\gamma_{11} - 5\gamma_{12} + 7\gamma_{13} - 4\gamma_{14}),\\
\Delta E(^1E_{1u}) &= -2\beta + \tfrac{1}{6}(\gamma_{11} + 4\gamma_{12} - 4\gamma_{13} - \gamma_{14}),\\
\Delta E(^3B_{1u}) &= -2\beta + \tfrac{1}{6}(-2\gamma_{11} + 3\gamma_{12} - \gamma_{13}) \text{ etc.}
\end{aligned} \tag{5}$$

Simple formulae were also obtained for the energies of ethylene. Comparison of these energies with experimental data (absorption spectra) led to numerical values of the parameters for these molecules and to the formulation of a system of rules for the determination of the parameters of other molecules, including molecules with heteroatoms[8]. The entire system of concepts concerning the parametrisation of the π-electron Hamiltonian and the degree of approximation in calculations on the states of the system (one configuration for the ground state and superposition of singly excited configurations for the excited state) has been called the "Pariser–Parr–Pople approximation" (the PPP approximation or method).

In most cases the theory of the electronic structure of conjugated systems in terms of the π-electron approximation uses the PPP Hamiltonian

$$H = \sum_{p,q,\eta} h_{pq} c_{p\eta}^{+} c_{q\eta} + \sum_{p,q} \sum_{\eta,\rho} \gamma_{pq} c_{p\eta}^{+} c_{p\eta} c_{q\rho}^{+} c_{q\rho} . \tag{6}$$

The methods for the calculation of molecular properties using Hamiltonian (6) can differ from the PPP method by the procedures employed in the estimation of the parameters. In calculations on conjugated systems one uses nowadays methods which differ in the extent to which account is taken of the π-electron interaction, from the Hückel approximation in which all the parameters $\gamma_{pq} = 0$ up to different versions of the many-configuration approximation using several or all possible configurations.

3. The Information Contained in the Effective Parameters of the Model π-electron Hamiltonian

The PPP Hamiltonian (6) is a model or effective π-electron Hamiltonian. Having postulated that all the properties of a conjugated molecule are described by π-electrons alone, we have greatly simplified the problem of the calculation of molecular properties. If all the electrons in the molecule were considered, we would have found that σ-electrons and atomic orbitals other than those of the $2p_z$ type have a relatively small influence on the

§ The $2p_z$ atomic orbitals are numbered consecutively around the ring formed by carbon atoms.

properties of the π-electron system. Nevertheless these electrons and orbitals make a finite contribution to the observed properties. Therefore the semiempirical theory can yield the observed values when π-electrons alone are considered explicitly only in the case where the parameters of Hamiltonian (6) take into account the neglected electrons and states.

As a result the parameters of the Hamiltonian differ somewhat from the values calculated by Eqns. (4). These differences can be reduced to a minimum by a special choice of the functions $\varphi_p(\mathbf{r})$. However, some differences always remain. This is a consequence (or manifestation) of many-electron correlations.

The contribution of σ-electrons to the π-electron Hamiltonian has been examined by Fischer[10] for a simple model of a conjugated molecule. The effect of the neglected electrons and atomic orbitals on the effective Hamiltonian has been considered by Freed[11]. The problem of the calculation of the parameters of the effective π-electron Hamiltonian by more accurate formulae than Eqns. (4) (taking into account the effects of electronic correlation and the influence of the σ-skeleton), which was raised in these investigations[10,11], remains very complex and has still not been solved. However, it is known that equations of type (4), based on physical intuition, yield in the main the correct idea about the parameters of the effective Hamiltonian [when a successful choice of the functions $\varphi_p(\mathbf{r})$] is made. Since these parameters can be determined from a comparison with experiment, it is always possible to estimate the accuracy of formulae of type (4). Analyses of this kind have been carried out[12,13].

The unreal nature of the π-electron Hamiltonian is enhanced by the fact that, in terms of the ZDO approximation, a number of parameters are neglected. There are simplified versions of the PPP method with short-range action of π-electrons[14,15], in which only the parameters γ_{pp} and $\gamma_{pp\pm1}$ remain (for electrons at the same atom and at adjacent atoms) (see also Ovchinnikov[16]). In this case it is hardly possible to calculate these parameters, which are determined only by an empirical procedure.

Yet another aspect of the unreal nature of the Hamiltonian is associated with the degree of its approximation used in the calculation of the observed properties. If the electronic transition energies are calculated in terms of the PPP approximation, then one set of the Hamiltonian parameters must be used to recover the experimental values. If a calculation involving a larger number of configurations than in the PPP method is carried out, then the parameters which reproduce the experimental values differ from those of the first set. Clearly it is impossible to take into account these differences and to estimate the changes in the parameters. Nevertheless this is difficult to tolerate and for this reason several schemes have been proposed for the calculation of the parameters (mainly for the PPP method), which are partly based on equations of type (4); to some extent simple formulae for the interpolation of empirical values of the parameters are also employed. Parameters which correctly reproduce the experimental electronic transition energies, ionisation potentials, etc. are obtained as a result. This approach is characteristic of a semiempirical theory, in contrast to *ab initio* calculations based solely on formulae of type (4).

Yet another aspect of the problem of the separation of σ- and π-electrons and the derivation of the model Hamiltonian has been examined from the standpoint of summetry in terms of the SCF approximation for σ- and π-electrons[17]. It was found that the solutions (molecular orbitals) can be divided into symmetrical and antisymmetrical with respect to the reflection operation in the molecular plane. The SCF equations in terms of the LCAO-MO approximation (the Roothaan equations[9]) are divided into two systems of equations: for σ-electrons (symmetric solutions) and for π-electrons (antisymmetric solutions). These systems of equations are related (by the Coulombic interaction of σ- and π-electrons) and must be solved together. If only π-electrons are considered, the effect of σ-electrons may be taken into account by choosing effective parameters[17].

Calculations of this kind are made at present for specific molecules (the LCAO-MO SCF approximation for all valence σ-electrons and π-electrons). In calculations of this kind the effect of the σ-skeleton on the π-electron system and the nature of different degrees of the σ-electron approximation are elucidated[18,19]. So far such calculations are fairly crude because a parametrisation scheme has not been developed. This applies also to *ab initio* calculations. The latter are at present performed using equations of type (4) and specified functions $\varphi_p(\mathbf{r})$. In this sense such calculations resemble semiempirical calculations, since the functions $\varphi_p(\mathbf{r})$ are specified with the aid of certain constants. So far the *ab initio* calculations are crude and have a low predictive power. One may hope that, by varying the initial functions $\varphi_p(\mathbf{r})$, it will be possible to improve their accuracy. Moreover, we believe that in the distant future the *ab initio* calculations will reach the accuracy of the semiempirical theory.

The conclusions drawn from studies where σ- and π-electrons are considered jointly in terms of the SCF approximation are so far only qualitative. An improvement of the accuracy of such calculations will make it possible, in principle, to correct the π-electron approximation from the outside, from the standpoint of a more complete calculation.

In the present review we shall not consider the qualitative conclusions of modern *ab initio* calculations, since this would significantly increase its size. Moreover, we believe that the results of these calculations merit a separate and more detailed discussion. Much attention will be devoted to problems of the interaction of π-electrons with the σ-skeleton in the authors' next review "Adjustment of the Methods of Calculation and Semiempirical Parameters for Consistency in the Theory of Molecules with Conjugated Bonds", where an attempt will be made to keep the treatment within the framework of the π-electron approximation. Such tactics in relation to *ab initio* calculations are also dictated by the fact that so far we can only indicate the causes of a number of difficulties in the semiempirical theory, but complete recipes for overcoming the difficulties of the π-electron theory cannot as yet be proposed on the basis of modern *ab initio* calculations. The point is that such calculations for molecules are carried out in terms of a limited atomic orbital basis set (filled atomic orbitals are as a rule employed as the basis set). Correlation contributions, which, for example, have been found to be fairly significant in atoms (this was demonstrated in atomic calculations with a greatly extended basis set) are thereby neglected. On the other hand, in semiempirical calculations using a limited atomic orbital basis set these correlation contributions are largely included in the parameters. Therefore the role of modern *ab initio* calculations, carried out in terms of a restricted atomic orbital basis set, in proving the validity of the semiempirical molecular theory is so far limited.

III. THE PROPERTIES OF THE GROUND STATE OF CONJUGATED MOLECULES

1. The Geometrical Structure of Molecules (Bond Lengths and Angles)

An important characteristic of a conjugated molecule is its geometrical structure, bond lengths, and bond angles. The "bond length–bond order formula"[20]

$$R_{\mu\nu} = R_0 - bP_{\mu\nu} \qquad (7)$$

is usually employed to calculate bond lengths. Here $R_{\mu\nu}$ is the length of the $\mu\nu$ bond, $P_{\mu\nu}$ the π-electron order of the $\mu\nu$ bond, and R_0 and b are constants determined from a comparison with experiment. It has been found that Eqn. (7) is not an independent empirical relation, since its constants are expressed in terms of parameters describing the electronic structure of the molecule[21].

The presence of π-electrons leads to a slight change in bond lengths (by $\delta R_{\mu\nu}$) and angles (by $\delta\varphi_l$) compared with the lengths $R^0_{\mu\nu}$ and angles φ^0_l which would be observed in a hypothetical molecule without π-electrons. If the molecule does not contain heteroatoms, then usually all the $\varphi^0_l = 120°$ and all the $R^0_{\mu\nu} = R_0$ (for example, in benzene). We thus begin with the hypothesis of an ideal structure of the σ-skeleton and assume that all the distortions of this ideal structure are due to π-electrons. The σ-skeleton is regarded as elastic (characterised by force constants) and the total energy E is equal to the sum of the energies of the σ-skeleton (E_σ) and of the π-electrons (E_π): $E = E_\sigma + E_\pi$.

In terms of the Hückel approximation in the molecular orbital method, the molecular energy of alternant hydrocarbons is[21]

$$E = E^0_\sigma + \underset{n}{\sum}\alpha_n + 2\underset{l}{\sum}\beta_l P_l + \underset{l}{\sum}\frac{k_{1l}\delta R_l^2}{2} + \underset{l}{\sum}\frac{k_{2l}R_0^2\delta\varphi_l^2}{2}, \qquad (8)$$

(w.r.t. atoms; w.r.t. bonds; w.r.t. bonds; w.r.t. angles)

where P_i is the bond order between adjacent atoms and β_i is the corresponding resonance integral; the last two terms in Eqn. (8) are due to the distortion of the initial σ-skeleton having the energy E^0_σ, k_{1i} and k_{2l} being the force constants for the lengths R_i and angles φ_l respectively.

The resonance integral β_i can be conveniently represented by an expansion in terms of the deviation δR_i from the equilibrium length R_0 in the ideal σ-skeleton:

$$\beta_l = \beta^0_l + \beta'_l\delta R_l + \beta''_l\frac{\delta R_l^2}{2}, \qquad (9)$$

where β'_i and β''_i are the first and second derivatives of $\beta_i(R)$ with respect to the distance R calculated at the point $R = R_0$.

By varying the total energy E with respect to independent δR_i and $\delta\varphi_l$, we obtain the values of δR_i and $\delta\varphi_l$ for which this energy is a minimum. The number of independent δR_i and $\delta\varphi_l$ for a planar molecule with N conjugated atoms is $2N - 3$. The observed values of δR_i and $\delta\varphi_l$ depend in a complex manner on the bond orders. On substituting these expressions in the formula for E [(Eqn. 8)], we obtain the total energy E as a function of the coefficients of the molecular orbitals c^k_n. By varying E with respect to c^{k*}_n, we obtain non-linear equations for c^k_n (the bond orders P_i are quadratic functions of c^k_n and E is a non-linear function of P_i). These non-linear equations are solved for c^k_n with the aid of a procedure whereby adjustment for self-consistency is made.

If the molecule does not contain rings, all the $\delta\varphi_l$ are independent and variation with respect to them yields $\delta\varphi_l = 0$ (the angles are not distorted). By varying with respect to δR_i, we obtain:

$$\delta R_l = -\frac{2\beta'_l}{k_{1l} + 2\beta''_l P_l}P_l. \qquad (10)$$

The equation for c^k_n is

$$0 = 2(\alpha_n - E^k)c^k_n + 2\frac{\partial}{\partial c^{k*}_n}\left(\sum_i \beta_i P_i\right) + \frac{\partial}{\partial c^{k*}_n}\left(\sum_i \frac{k_{1l}\delta R_i^2}{2}\right).$$

If $\beta_i'^2/k_{1i}|\beta_i| \ll 1$, the terms non-linear in c^k_n in this equation may be neglected and the bond orders P_i can be determined from the equation with undistorted bond lengths. As a result, we arrive at a "bond length–bond order" formula[21]:

$$R_l = R_0 - \frac{2\beta'_l}{k_{1l} + 2\beta''_l P_l}P_l. \qquad (11)$$

If the distortions of the angles and terms of the order of P_i^2 are neglected, the formula is found to apply also to molecules containing rings.

To determine the angles, terms corresponding to the interaction of π-electrons at non-adjacent atoms must be included in the formula for the energy. We may note that a successful albeit unique example of the calculation of angles by the above general method has been achieved for the naphthalene molecule[21]. It was found that approximately half the contribution to the angular distortion $\delta\varphi_l$ comes from the bond length distortion δR_i.

In the calculation of the π-electron energy of the molecule one can employ methods which include the interaction of the electrons. In terms of the PPP approximation, it is easy to show that the "bond length–bond order" formula is

$$R_{\mu\nu} = R_0 - \frac{2\beta'_{\mu\nu}P_{\mu\nu} + \gamma'_{\mu\nu}\left[(P_{\mu\mu} - N_\mu)(P_{\nu\nu} - N_\nu) - \frac{P^2_{\mu\nu}}{2}\right]}{\kappa_{1\mu\nu} + 2\beta''_{\mu\nu}P_{\mu\nu} + (\text{terms with } \gamma''_{\mu\nu})}, \qquad (12)$$

where N_μ and N_ν are the numbers of electrons introduced by the atoms μ and ν to the overall π-electron system and $\gamma'_{\mu\nu}$ and $\gamma''_{\mu\nu}$ are derivatives of $\gamma_{\mu\nu}(R)$ with respect to R at the point $R = R_0$. In alternant hydrocarbons $N_\mu = N_\nu = P_{\mu\mu} = P_{\nu\nu} = 1$. $P_{\mu\mu} - N_\mu$ is equal to the charge of the atom μ. Comparison of Eqn. (12) with Eqn. (11) of the Hückel method for alternant hydrocarbons shows that the entire difference has been reduced to the following change of parameters:

$$\beta_{\mu\nu}(\text{Hückel MO method}) \to \beta_{\mu\nu}(\text{PPP method}) - \tfrac{1}{4}\gamma_{\mu\nu}P_{\mu\nu}.$$

Thus the parameters in the formula for the bond length depend significantly on the parametrisation scheme for $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$.

The linear "bond length–bond order" relation [Eqn. (7)] usually describes satisfactorily the experimental bond lengths in conjugated molecules not only of hydrocarbons but also of compounds with the heteroatoms N, O, F, and S.[22,23] The average accuracy of the determination of bond lengths by Eqn. (7) is of the order of 0.01–0.02 Å (see, for example, Table 1). The causes of the individual discrepancies are the approximate nature of equations of type (7), the hypothesis that σ-bonds are additive, etc.

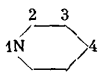
2. Heats of Formation of Conjugated Molecules

Another important characteristic of conjugated molecules is the heat of formation $-\Delta H$. The modern scheme for the calculation of this quantity was proposed by Dewar[22,23]. The formula

$$-\Delta H = n_H E_{CH} + \sum E^{\sigma}_{CC}(R) - E_{\pi} \qquad (13)$$

is used to calculate the heat of formation of a conjugated hydrocarbon. Its first term is the dissociation energy of all the C—H bonds (there are n_H such bonds in the molecule), the second term represents the dissociation energy of all the C—C σ-bonds, and the third term represents the π-electron energy with a minus sign. The usual hypothesis of the additivity of the energies of the σ-bonds and of σ- and π-energies was used here, as in Eqn. (8). The dissociation energy E_{CH} of C—H bonds is an empirical term. The C—C σ-bond energy $E^{\sigma}_{CC}(R)$ is described by a Morse function with empirical parameters. The π-electron energy E_{π} was calculated in terms of the LCAO-MO SCF approximation using the PPP Hamiltonian and $R_{\mu\nu}$, necessary for the calculation of $E^{\sigma}_{CC}(R_{\mu\nu})$, was evaluated with the aid of the empirical relation (7).

Table 1. The bond lengths in certain conjugated molecules[23].

Molecule	Bond	Bond length, Å	
		calc.	expt.
	12	1.333	1.334
	23	1.348	1.388
	12	1.338	1.340
	23	1.396	1.395
	34	1.397	1.395
	12	1.381	1.371
	23	1.347	1.354
	34	1.459	1.440

The parameters of the PPP Hamiltonian used by Dewar to calculate heats of formation[22,23] were approximately the same as in the calculation of absorption spectra. The resonance integral $\beta_{\mu\nu}$ was an exception. The values of $\beta_{\mu\nu}$ were determined by Dewar from the thermochemical conditions and exceeded by a factor of 1.3—1.4 the values used in the calculation of absorption spectra¶. This inconsistency of the parameters indicated a defect of the theory, although the agreement with experiments was very good[23] (Table 2).

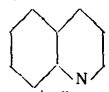
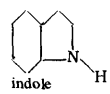
In Bazilevsky's studies[24,25] this theoretical difficulty was overcome. On the basis of the study by Fischer-Hjalmars[6], it was shown that it is possible to retain the spectroscopic values of $\beta_{\mu\nu}$, provided that in derivation of the model Hamiltonian all the terms which arise naturally on transformation from $2p_z$ functions to the orthogonal functions $\varphi_p(\mathbf{r})$ are retained. These additional terms, which are usually neglected†, make a new contribution to the total energy, which is[25]

$$\widetilde{\Delta E} = \sum K_{\mu\nu} S^2_{\mu\nu} + O(S^3),$$

where $K_{\mu\nu}$ are coefficients which depend on the molecule and $S_{\mu\nu}$ is the overlap integral of the $2p_z$ functions of the atoms μ and ν. The addition of $\widetilde{\Delta E}$ leads to the so called exchange repulsion of atoms and molecules. This exchange repulsion is well known, for example, in studies on the interaction of two helium atoms, non-bonded hydrogen atoms, etc., which was examined for the first time for non-polar conjugated systems by Bazilevsky, who proposed a simple formula for $\widetilde{\Delta E}$ containing a single empirical parameter[24], retaining $S_{\mu\nu}$ only for adjacent atoms μ and ν:

$$\widetilde{\Delta E} = \gamma \sum_{\substack{\mu\nu \\ \text{(adjacent)}}} S^2_{\mu\nu} \quad (\gamma > 0).$$

Table 2. The energies of formation of certain conjugated molecules[23].

Molecule	Energy of formation $-\Delta H$, eV	
	calc.	expt.
 pyridine	51.87	51.79
 quinoline	85.322	85.18
 pyrazine	46.272	46.44
 pyridazine	45.741	45.59
 indole	78.438	78.06

The validity of this approximation for $\widetilde{\Delta E}$ was confirmed by the satisfactory agreement of the heats of formation with experiment (Table 3). This computational scheme can be improved by employing a more accurate formula for $\widetilde{\Delta E}$.[25]

As a result, the π-electron energy of the conjugated molecule becomes[24]

$$E_{\pi} = E_{\pi}\{\beta^{\text{spectr.}}\} + \gamma \sum_{\substack{\mu\nu \\ \text{(adjacent)}}} S^2_{\mu\nu}.$$

Here the first term is the π-electron energy calculated using spectroscopic values of the resonance integral $\beta^{\text{spectr.}}$. If $S_{\mu\nu}$ is calculated using Slater $2p_z$ functions,

$$\varphi_{2p_z}(\mathbf{r}) = \frac{Z^{5/2}}{4\sqrt{2\pi}} r \cos\theta \, e^{-\frac{Zr}{2}} \quad (Z = 3.18), \qquad (14)$$

then γ = 8.7 eV.[24] This value of γ was determined by comparing $-\Delta H$ calculated by Eqn. (13) with the experimental value and depends both on the parameters of the σ-bond and on Z.

We may note that in calculations of absorption spectra there was no need for the additional exchange term $\widetilde{\Delta E}$, since it is the same for the ground and excited states (the changes in molecular geometry on excitation are usually small and are as a rule disregarded). However, this

¶ For the C—C bond length R = 1.4 Å, the spectroscopic value of the resonance integral is $\beta \simeq -2.4$ eV.

† These additional terms arise on passing to an orthogonal basis set using the formulae derived towards the end of Section II, 1.

additional term ΔE is significant in calculations on chemical reactions of conjugated systems, since terms proportional to $S^2_{\mu\nu}$ are significant in the energy of molecular interaction. Specifically exchange repulsion leads to a potential barrier and a positive activation energy for such reactions[25].

Table 3. The energies of formation of certain conjugated hydrocarbons calculated using a modified PPP method[24].

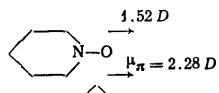
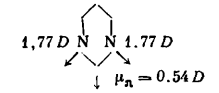
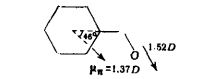
Molecule	Heat of formation $-\Delta H$, eV		Molecule	Heat of formation $-\Delta H$, eV	
	calc.	expt.		calc.	expt.
Ethylene	22.9	22.9	Phenanthrene	123.1	123.2
trans-Butadiene	41.6	41.6	Pyrene	137.4	137.5
Benzene	56.9	56.7	Naphthacene	155.7	156.0
Styrene	75.3	75.0	1,2-Benzanthracene	156.2	156.0
Naphthalene	90.0	89.9	Chrysene	156.5	156.5
Anthracene	122.6	122.5	Triphenylene	156.8	156.5

3. Dipole Moments

One of the difficult problems in quantum mechanics of molecules is the calculation of dipole moments, since such calculations require the knowledge of the wavefunction of all the electrons in the molecule. Brown and Coller[26] made a preliminary assessment of the many years of efforts to calculate the dipole moments of conjugated hydrocarbons containing N and O heteroatoms. It is suggested that σ- and π-electrons contribute to the overall dipole moment $\vec{\mu}$:

$$\vec{\mu} = \vec{\mu}_\sigma + \vec{\mu}_\pi.$$

Table 4. The dipole moments of certain conjugated hydrocarbon molecules with the N and O heteroatoms[26].

Molecule	Magnitude and directions of the σ- and π-contributions (μ_σ and μ_π) to the dipole moment	Overall dipole moment, D	
		calc.	expt.
Pyridine-*N*-oxide		3.8	4.24
Pyrimidine		2.32	2.0
Benzaldehyde		2.87	2.80

The component $\vec{\mu}_\pi$ is calculated from the distribution of π-electrons among the atoms in the molecule and the contribution to $\vec{\mu}_\sigma$ comes (by hypothesis) only from the lone electron pair localised in the sp^2 hybrid orbitals (belonging to the σ-skeleton) of the N and O atoms. These contributions of the lone electron pairs of the N and O atoms are respectively

$$\mu_N = 1.77\,D, \quad \mu_O = 1.52\,D.$$

The wavefunction χ_n of the sp^2 hybrid orbital of the lone pair is

$$\chi_n = \chi_{2s} + \theta\chi_{2p_\sigma}.$$

The contribution to $\vec{\mu}_\sigma$ is proportional to θ and in its calculation using Slater functions is given by[26]

$$\mu_n = 14.68\,\theta/Z\,(1+\theta^2)\,(D),$$

where Z is the effective Slater charge. Generally speaking, μ_n depends on the angles in the molecules (θ also depends strongly on these angles), but Brown and Coller[26] used for simplicity an estimate of μ_n from the sp^2 hybrid orbitals of neutral N and O atoms. This led to the values of μ_N and μ_O indicated above.

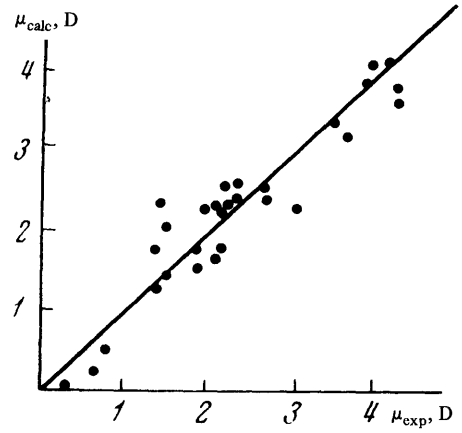


Figure 2. Correlation between the calculated (μ_{calc}) and experimental (μ_{exp}) dipole moments according to Brown and Coller[26].

To calculate $\vec{\mu}_\pi$, Brown and Coller[26] used a self-consistent method with a variable π-electronegativity. This method resembles that in Section IV, 2, but, in contrast to the latter, it does not take into account the redistribution of σ-charges in the molecule. This redistribution has an appreciable influence on the electronic excitation energies in molecules with heteroatoms (see Section IV, 2 below). However, Brown and Coller[26] neglected the contribution of σ-charges to the dipole moment.

The results of the calculation of $\vec{\mu}$ for certain molecules are presented in Table 4 together with experimental data. Fig. 2 illustrates the correlation between the experimental and calculated dipole moments. The overall accuracy of the prediction of the dipole moments of compounds with N and O heteroatoms proved to be to within about 0.4 D. This is probably all that can be expected of a theory with such rough allowance for the contribution by the σ-skeleton to $\vec{\mu}$. Table 4 shows that this contribution is very significant.

IV. CALCULATIONS ON EXCITED STATES OF CONJUGATED MOLECULES AND TWO MAIN SCHEMES FOR THE DETERMINATION OF THE EFFECTIVE PARAMETERS OF THE MODEL π-ELECTRON HAMILTONIAN

The theory of conjugated systems was developed initially and was improved by studying the properties of conjugated hydrocarbons. One of the greatest achievements in recent years has been the inclusion of calculations on systems with heteroatoms in the general scheme. This was done after a careful study of the entire parametrisation technique. As a result, several computational schemes were devised, differing in the methods used to introduce empirical information into the model Hamiltonian.

We shall consider in detail two modern parametrisation schemes for the model π-electron Hamiltonian. In one of these the parameters are introduced approximately as in the initial version of Pariser and Parr, i.e. they are calibrated against a series of simple molecules by comparing the calculated and experimental excitation and ionisation energies. This scheme is being developed by Scandinavian workers[6,27-36]. We shall call it "Scheme 1". In the second scheme ("Scheme 2") $2p_z$ functions [these are usually Slater functions defined in Eqn. (14) with different effective charges] and certain other quantities are parametrised. All the parameters are specified as before, which makes Scheme 2 less empirical than Scheme 1. Nevertheless all the parameters of Scheme 2 have been chosen empirically in the course of prolonged studies on molecular spectra using intermediate hypothesis and assumptions. Calculations on excited states by Scheme 2 have been carried out, for example, by Hammond[37], who also quotes all the references relevant to Scheme 2.

1. Scheme 1

Scheme 1 [27-36] is devised as follows. In the first place the ZDO approximation, which is natural for orthogonalised basis functions $\varphi_p(\mathbf{r})$ is used: the overlap integrals

$$S_{\mu\nu} = \delta_{\mu\nu},$$

the non-zero integrals of the skeleton

$$H_{\mu\mu} \equiv \alpha_\mu \text{ (definition) and } H_{\mu\nu} = \beta_{\mu\nu} \text{ for adjacent } \mu \text{ and } \nu;$$

and finally

$$\langle \mu\tau \mid \rho\nu \rangle = \gamma_{\mu\nu}\delta_{\mu\tau}\delta_{\nu\rho}, \quad \gamma_{\mu\nu} = \langle \mu\mu \mid \nu\nu \rangle.$$

Thus the PPP Hamiltonian [Eqn. (6)] is used.

The parameters of the skeleton are specified as follows.

$$\alpha_\mu = W_\mu - \sum_{\nu(\neq\mu)} \gamma_{\mu\nu}, \tag{15}$$

where the first term is the energy of the attraction of a π-electron of the atom μ to its positively charged ionic residue (W_μ is approximately equal to the ionisation potential of the atom μ with a minus sign) and the second term represents the energy of the attraction of a π-electron of the atom μ to the ionic residues of other atoms; the approximation for the integral $U(\nu:\mu\mu)$ for the attraction of a π-electron of the atom μ to the positively charged ionic residue of the atom ν, which is usual in the PPP method, was employed here:

$$U(\nu:\mu\mu) \simeq \gamma_{\mu\nu}.$$

Furthermore,

$$W_\mu = W_0 + \sum_{\substack{\nu \\ \text{(adjacent } \mu)}} \Delta W_\mu(R_{\mu\nu}). \tag{16}$$

Eqn. (16) takes into account the influence of neighbouring carbon atoms on the ionisation potential of the atom μ. The contributions to $H_{\mu\mu}$ by other atoms are a consequence of the orthogonalisation of the $2p_z$ functions, as shown by Fischer-Hjalmars[6]. Under these conditions, the main contribution comes from neighbouring atoms, which is reflected in Eqn. (16). If there are no neighbouring atoms, the sum in Eqn. (16) is missing and $W_\mu = W_0$. Therefore the ionisation potential of the CH_3 radical with a minus sign is chosen as the value of W_0(W_0 = -9.84 eV).

The contributions to W_μ by adjacent atoms depend on distance according to the formula

$$\Delta W_\mu(R_{\mu\nu}) = \Delta W_0 + \delta(R_{\mu\nu} - R_0). \tag{17}$$

Here (and subsequently) it is assumed that the functions of $R_{\mu\nu}$ can be represented by expansions in terms of the deviations ($R_{\mu\nu} - R_0$) from the standard line R_0 = 1.397 Å (the C–C bond length in benzene‡). In view of the smallness of these deviations (usually $|R_{\mu\nu} - R_0| \leqslant 0.2$ Å), one need retain only two terms of the expansion. It was found that ΔW_0 = 0.09 eV and δ = 8.63 eV Å^{-1}. The values of these and the remaining parameters were determined by a least squares fit of the ionisation potentials and electronic transition energies in the CH_3 radical and in the C_2H_4 (ethylene), C_6H_6 (benzene), and C_4H_8 (butadiene) molecules.

A formula of type (17) was proposed also for the resonance integral:

$$\beta_{\mu\nu} = \beta_0 + \delta_\beta \cdot (R_{\mu\nu} - R_0) \text{ (adjacent } \mu \text{ and } \nu) \tag{18}$$

β_0 = -2.43 eV and $\delta\beta$ = 3.1 eV Å^{-1}.

The following formulae have been proposed for the parameters of the Coulombic repulsion of π-electrons:

$$\begin{aligned} \gamma_{\mu\mu} &= 11.97 \text{ eV} \\ \gamma_{\mu\nu} &= \gamma_0 + \delta_\gamma(R_{\mu\nu} - R_0) \text{ (adjacent } \mu \text{ and } \nu) \end{aligned} \tag{19}$$

γ_0 = 6.95 eV and δ_γ = -4.65 eV Å^{-1}; for non-adjacent μ and ν, we have

$$\gamma_{\mu\nu} = \gamma_{\mu\mu}[\gamma_{\mu\mu} R_{\mu\nu} + \exp(-\gamma_{\mu\mu} \cdot R_{\mu\nu})]^{-1}. \tag{20}$$

In terms of the ZDO approximation, the electronic transition energies depend only on differences between type I Coulombic integrals [see Eqn. (6) and Refs. 8 and 14–16]:

$$\gamma_{11} - \gamma_{1p}, \ \gamma_{12} - \gamma_{1p}, \ \gamma_{13} - \gamma_{1p}, \ \ldots$$

or between type II integrals

$$\gamma_{11} - \gamma_{12}, \ \gamma_{12} - \gamma_{13}, \ \gamma_{13} - \gamma_{14}, \ \ldots$$

(Here γ_{1p} denotes the Coulombic integral for the most remote atoms in the molecule). As a result, for small molecules it is important to know how $\gamma_{\mu\nu}$ depends on the distance between adjacent atoms, while the variation for larger distances $R_{\mu\nu}$ is less important. This is reflected in Eqns. (19) and (20) and explains certain arbitrary features in the selection of the formula for $\gamma_{\mu\nu}$ with non-adjacent μ and ν.

If the variation of the theoretical parameters with interatomic distances is known, it is possible to obtain formulae for bond lengths and angles, as noted above, and also to

‡ A similar method for the introduction of parameters of functions, which depend on the bond length, was used in our earlier studies[21,38].

calculate the vibration frequencies of conjugated molecules. Thus semiempirical parameters must be calibrated so as to reproduce satisfactorily both the electronic spectra and the geometrical characteristics of the conjugated molecules. We approached the choice of the parameters in the Hückel method from these general standpoints: the force constants of the σ-skeleton and the variation of the resonance integral with bond length were determined, which led to six very satisfactory frequencies of the in-plane vibrations of benzene[38] and to the correct coefficient in the "bond length–bond order" formula[21].

The problem of a similar adjustment for consistency between empirical parameters and experimental data, based on optical and infrared spectra and geometrical structures of conjugated molecules, has not so far been solved for the PPP Hamiltonian. Although the problem of the in-plane vibrations of benzene has been solved in terms of the PPP approximation[39-42], only three frequencies were considered, which hinders the calibration of the parameters. A similar situation arises in the adjustment of the parameters for consistency with the geometrical structure. When the parameters of Scheme 1 for $\beta(R)$ and $\gamma(R)$ [Eqns. (18) and (19)] and the elastic constant of the σ-skeleton k_1 = 47.6 eV Å^{-2} are used[39], we find that in the formula for conjugated hydrocarbons

$$R_{\mu\nu} = R_0 - bP_{\mu\nu} \qquad (7)$$

the parameter b = 0.162 (for $P_{\mu\nu}$ = 2/3 in the case of benzene) according to Eqn. (12), instead of the value b = 0.18 used in Scheme 1.[20]

As in Dewar's studies[22,23], empirical formulae of type (7) with the parameters R_0 and b, which depended on the type of adjacent atoms, were used to calculate the bond lengths in conjugated molecules with heteroatoms[29-36]. The results obtained for these bond lengths agreed with experiment to within the same limit (about 0.01–0.02 Å) as in Dewar's work[23].

In the calculation of electronic excitation energies for molecules with heteroatoms (N, O, S, etc.) the same parametrisation method was used as for hydrocarbons: equations of type (16)–(20), in which the corresponding constants were fitted by least squares to experimental ionisation potentials and electronic transition energies in a number of simple molecules containing one of the heteroatoms, were employed for the parameters of the Hamiltonian. Thus the computational scheme was extended to the large classes of molecules with heteroatoms[29-36].

Recently the authors of Scheme 1 have tended to reduce the total number of empirical parameters, because each heteroatom introduces several parameters into the calculation. It was noted[43] that the dependence of the resonance integral on the distance between the atoms C and X (X = C, N, O, or F) may be described satisfactorily by two types of relations, which are usually employed in different parametrisation schemes:

$$\beta = \beta_0 + \delta(R - R_0) \qquad (21)$$

and

$$\beta = k\,S, \qquad (22)$$

where S is the overlap integral calculated using the Slater functions (14) for the $2p_z$ functions of the atoms C and X with the corresponding values of $Z_{eff} = 2\zeta$. For all the CX bonds, δ = 3.05 eV Å^{-1}, R_0 = 1.397 Å, β_0 = −2.42 eV, and k = −8.98 eV were adopted. The values of ζ for different atoms together with the values of β for R = 1.34 Å, calculated by Eqns. (21) and (22), are presented in Table 5, which shows a close similarity between the parameters of Scheme 1 and Scheme 2, where, as will be shown below, the resonance integral is calculated by a formula of type (22) and the ζ values are close to those in Table 5.

Table 5. Resonance integrals calculated in different ways[43].

X	βCX, eV		$\zeta = Z_{eff}/2$	X	βCX, eV		$\zeta = Z_{eff}/2$
	Eqn.(21)	Eqn.(22)			Eqn.(21)	Eqn.(22)	
C	−2.59	−2.65	1.56	O	−1.80	−1.61	2.22
N	−2.25	−2.06	1.92	F	−1.30	−1.29	2.55

The general scheme for calculations on molecules is of the usual type for the PPP method. Initially calculations are made on the ground state by the LCAO-MO SCF method, the molecular orbital coefficients and bond orders are found, and the bond lengths are calculated. Next linear combinations of singly excited molecular configurations are set up on the basis of molecular orbitals of the ground state. The coefficients of the configurations, which define the wavefunction of the excited state, are found together with the excitation energies from the minimum in the average molecular energy calculated using the PPP Hamiltonian for the nuclear configuration of the ground state. According to Koopmans' theorem, the ionisation potential is assumed equal to the energy of the highest occupied molecular orbital with the sign reversed[9].

The results of calculations in accordance with Scheme 1 [29-36] will be discussed below after examining a further parametrisation scheme.

2. Scheme 2

Hammond[37] carried out calculations on a large number of conjugated molecules within the framework of a single approach (Fig. 3). We shall now consider the parametrisation scheme adopted (Scheme 2).

The Fock equation is

$$F\chi = \varepsilon\chi, \qquad (23)$$

where ϵ are the orbital energies of the molecular orbitals, χ is the column–vector of atomic function coefficients, and F is the Fock matrix with the following elements:

$$F_{pp} = H_{pp} + N_p\gamma_{pp} - \frac{1}{2}P_{pp}\gamma_{pp} + \sum_q (P_{qq} - N_q)\gamma_{pq},$$
$$F_{pq} = H_{pq} - \frac{1}{2}P_{pq}\gamma_{pq}\ . \qquad (24)$$

Here $H_{pp} = -I_p$ when the atom p contributes one electron to the π-electron system and N_p = 1 and $H_{pp} = -I_p - \gamma_{pp}$ when N_p = 2; the non-diagonal elements H_{pq} are non-zero for all p and q:

$$H_{pq} = \text{const} \cdot \frac{H_{pp} + H_{qq}}{1 + S_{pq}} \cdot S_{pq}\ , \qquad (25)$$

where const. = 0.56 [from the condition H_{pp+1}(benzene) = −2.45 eV]. The overlap integrals S_{pq} are calculated from the Slater functions (14). The values of ζ_p, I_p, and γ_{pp} are listed in Table 6.

As already mentioned, formula (25) is similar in form to formula (22) and the Slater exponents $\zeta_p = Z_p/2$ listed in Tables 5 and 6 are also similar. This similarity is not fortuitous, since both parametrisation schemes (Schemes 1 and 2) are based on the same experimental data.

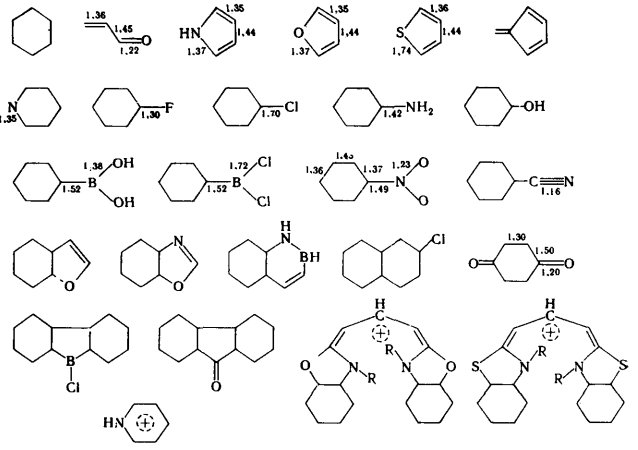


Figure 3. The molecules and ions for which calculations were made by Hammond[37] with parametrisation according to Scheme 2. The bond lengths (in Å) used in the calculation are indicated.

The following formulae were adopted for the parameters of the Coulombic repulsion of electrons in Scheme 2:

$$\gamma_{pq} = \frac{14.397}{a_{pq} + R_{pq}}, \quad a_{pq} = \frac{28.794}{\gamma_{pp} + \gamma_{qq}} \quad . \tag{26}$$

It is found that γ_{pq} for adjacent hydrogen atoms is smaller by 1.6 eV according to this scheme than according to Scheme 1. These differences are probably compensated when a special procedure is used to take into account the polarisation of the σ-skeleton and the mutual influence of σ- and π-electrons as well as the changes in other parameters.

In calculations on systems with heteroatoms an important factor is the correct allowance for effects associated with the mutual influence of atoms. This influence via the σ-skeleton has been taken into account in Scheme 2 with the aid of the concept of the atomic electronegativities ω_p of the σ-bond orbitals. The fraction of σ-electron n_p in the atom p due to the presence of the σ-bond with the atom q can be expressed in terms of ω_p and ω_q:

$$n_p = \frac{2\omega_p}{\omega_p + \omega_q}. \tag{27}$$

In each σ-bond pq there are two σ-electrons:

$$n_p + n_q = 2.$$

As a result of the influence of neighbouring atoms, the effective Slater charge Z^0_p of an isolated atom p is replaced by Z'_p according to the formula

$$Z'_p = Z^0_p + 0.35 \sum_{\substack{q \\ \text{(adjacent } p\text{)}}} \left(\frac{2\omega_q}{\omega_p + \omega_q} - 1\right)\left(\frac{1.41}{R_{pq}}\right)^2. \tag{28}$$

where 0.35 is the Slater screening constant and the multiplier $(1.41/R_{pq})^2$ characterises the rate of decrease of the inductive effect with distance, becoming unity when R_{pq} = 1.41 Å. If all the atoms are the same (all $\omega_p = \omega_q$), then the Slater functions (14) have the same $Z'_p = Z^0_p$ and the mutual influence of atoms is taken account only via the π-electron system in the usual way.

Table 6. The atomic parameters used in calculations on conjugated molecules by Scheme 2.[37]

Atom p	N_p	$Z^0_p = 2\zeta_p$	I^0_p, eV	γ^0_{pp}, eV	ω_p
B	0; 1	2.25; 2.60	8.33	6.91	1.96
C	1	3.25	11.16	11.13	2.75
N	1; 2	3.90; 4.25	14.12	12.34	4.13
O	1; 2	4.55 4.90	17.7	15.23	5.54
F	2	5.55	20.86	17.36	3.90
S	2	5.80	12.7	9.94	3.46
Cl	2	6.45	15.03	11.30	2.95

As a result of the σ-inductive effect, I^0_p and γ^0_{pp} of isolated atoms are replaced by I'_p and γ'_{pp} according to the following formulae:

$$I'_p = I^0_p - 0.324\,[(Z^0_p)^2 - (Z'_p)^2] - 6.03\,(Z^0_p - Z'_p),$$
$$\gamma'_{pp} = \gamma^0_{pp}\,(Z'_p/Z^0_p). \tag{29}$$

Z'_p, I'_p, and γ'_{pp} are the initial values for the first π-electron calculation: Eqn. (23) is solved with the above parameters. After determining the bond order matrix P_{pq}, allowance is made for the π-inductive effect, according to which the effective charge becomes

$$Z'_p = Z_p - 0.35\,(P_{pp} - 1). \tag{30}$$

The quantities I''_p and γ''_{pp} for the next π-electron calculation (using Z''_p) are evaluated by Eqn. (29), etc. Several iterations are performed until the successive P_{pq} agree to within the required accuracy.

This scheme for taking into account inductive effects involves a logical inconsistency, which, however, may be concealed by the special selection of parameters. This inconsistency was noted earlier[44,45] in relation to the Hückel method with parameters which depend on P_{pq}. As noted by Bagatur'yants[46], the point is that, by minimising the total average energy and by deriving the Fock equation, we should take into account the dependence of the parameters γ_{pp} and I_p on bond orders already at this stage. Otherwise the iterative procedure does not lead to a minimum in the total energy. The complete scheme for taking into account the changes in parameters when P_{pq} is altered, developed by Karlsson[47] for the PPP approximation, is free from this disadvantage but is very cumbersome and has not so far been used.

The excitation energies for each molecule were calculated taking into account 10 singly excited configurations for the given configuration of the nuclei: the experimental bond lengths and angles or their values for fragments of known molecules were used. The variation of several bond lengths in a series of molecules had little effect on the calculated excitation or ionisation energies, which were also determined using Koopmans' theorem. The results of the calculations of the excitation energies and

ionisation potentials are compared with experiment in Fig. 4. The average deviation of the calculated excitation energies and ionisation potentials from the experimental values proved to be 0.1—0.2 eV and about 0.4 eV respectively. The satisfactory overall agreement between the theory and experiment can be accounted for by the logic of the fundamental postulates of the theory and the exact choice of parameters. Since the same conclusions and estimates are valid for the results of calculations with the parameters of Scheme 1, these results will not be quoted. We shall only note that in calculations with the parameters of Scheme 1 the excitation energies agree better with experiment than the ionisation potentials.

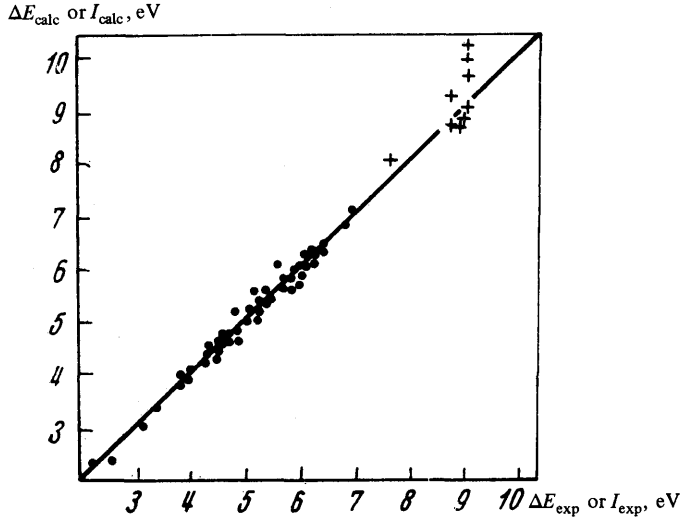


Figure 4. Correlation between the calculated and experimental excitation energies (ΔE) and ionisation potentials (I) for the molecules shown in Fig. 3. The calculated values are plotted against the experimental values[37]: ●—ΔE; +—I.

V. THE DIFFICULTIES OF THE THEORY IN THE CALCULATION OF THE INDIVIDUAL PROPERTIES OF EXCITED STATES

1. Ionisation Potentials

Large discrepancies between theory and experiment for ionisation potentials, reaching 1 eV, are characteristic of the π-electron approximation and are related to the approximate nature of Koopmans' relation:

$$I = -\varepsilon^{\pi}_{h.occ} \qquad (31)$$

where I is the ionisation potential and $\epsilon^{\pi}_{h.occ}$ the energy of the highest occupied molecular orbital. Roothaan[9] showed that Koopmans' theorem [Eqn. (31)] is valid in the LCAO-MO SCF approximation. The reasons for the large discrepancies with experiment are as follows: (1) the change in the molecular orbital energies ϵ_i on passing from the molecule to the ion is neglected; (2) the correlation contributions to the energies of the ground states of the molecule and the ion are neglected. Thus in the derivation of Eqn. (31) it was assumed that all the molecular orbital energies $\epsilon_i^{(o)} = \epsilon_i^{(+)}$, where the superscripts o and + refer to the neutral molecule and the cation respectively. Moreover, the approximate nature of the method of calculation itself (LCAO-MO SCF) has an effect. In it the ground state energy is calculated in terms of the single-configuration approximation, which implies neglect of the π-electron correlation energies, the latter being taken into account to some extent by the choice of the parameters of the effective Hamiltonian.

The calculation of the ionisation potentials of a number of conjugated molecules showed[48] that, as a rule, the calculated I_{calc} exceed the experimental values I_{exp} and the differences between them depend on the choice of parameters. Furthermore, it has been shown[48] that the agreement with experiment can actually be impaired if doubly excited configurations are included in the calculation for the same values of the parameters. This is because the parameters of the effective Hamiltonian must depend on the method of calculation: in the parameters of the SCF method correlation effects are to some extent taken into account and when these effects are taken into account explicitly other parameters must be used.

Table 7. The calculated (I_{calc}) and experimental [I^{el}_{expt} (electron impact) and I^{ph}_{expt} (photoionisation)] ionisation potentials[50].

Molecule	I_{calc}	I^{el}_{exp}	I^{ph*}_{exp}	Molecule	I_{calc}	I^{el}_{exp}	I^{ph*}_{exp}
Benzene	(9.56)	9.56	9.25	Benzaldehyde	9.87	9.82	9.50
Ethylene	10.39	10.62	—	Pyridine	9.65	9.70	9.30
trans-Butadiene	9.3	9.3	—	Quinoline	8.69	—	8.62
Aniline	8.78	8.32	7.7	*p*-Benzoquinone	9.76	—	9.96
Phenol	9.21	9.16	8.7				

*According to Potapov[51].

It has been shown[49,50] that the agreement between I_{calc} and I_{exp} is improved (Table 7) when Koopmans' relation with the correction

$$I_{calc} = -\varepsilon^{\pi}_{h.occ} - \Delta \qquad (\Delta \simeq 1\,eV) \qquad (32)$$

is employed.

In order to understand the reasons for this correction, we shall consider the results of the calculations on urazole and pyrrole and their anions and cations in terms of the SCF approximation with all the σ- and π-electrons[18]. It was found that a change in the number of π-electrons in the system alters the effective potential of the σ-skeleton for the π-electrons. This leads to a decrease of all the molecular orbital energies when the number of π-electrons is reduced:

$$\varepsilon_i^{(-)} > \varepsilon_i^{(*)} > \varepsilon_i^{(+)}. \qquad (33)$$

In order to make some allowance for this change in molecular orbital energies, it is necessary to introduce a positive correction Δ. We may note that a similar formula has been proposed[52] for the electron affinity E_A:

$$E_A = -\varepsilon^{\pi}_{l.free} - \Sigma \qquad (\Sigma \simeq 2-3\ эв) \qquad (34)$$

where $\epsilon^{\pi}_{\text{l.free}}$ is the energy of the lowest unoccupied molecular orbital of the conjugated molecule and a positive sign of Σ follows from Eqn. (33). The corrections Δ and Σ can eliminate only the average systematic error, leaving an inaccuracy of about 0.5 eV. This inaccuracy is characteristic of calculations of ionisation potentials using Koopmans' relations (31) and (32).

2. Energies of Triplet States

As stated above, the energies of electronic singlet excited states can be calculated with a high accuracy (to within 0.1—0.2 eV). The same satisfactory accuracy is characteristic of calculations using other parametrisation schemes[15,49,53-61]. The situation is less satisfactory for calculations of the energies of triplet levels. This is probably why the authors of Schemes 1 and 2 did not calculate the energies of triplet states and it has actually been suggested[62] that the parameters be altered in calculations on such states.

Table 8. The energies of the triplet states of benzene (eV) (relative to the ground state)[63].

Symmetry of level	Calc.	Expt.
$^3B_{1u}$	3.37	3.66
$^3E_{1u}$	4.85	4.65
$^3B_{2u}$	5.33	5.76
$^3E_{2g}$	6.31	6.56
$^3E_{2g}$	8.70	8.55

In fact the best agreement between theory and experiment for the energies of the triplet states of benzene has been achieved[63] with parameters which are not optimal for the calculation of the singlet energy levels (Table 8). Furthermore, the discrepancies between the calculated and experimental energies of triplet states can reach 1 eV.[56-58] Finally in the calculation of the energies of the $T-T$ transitions for a large number of aromatic molecules[64,65] it was found that a satisfactory agreement between theory and experiment (to within about 0.1—0.2 eV on average) is achieved only when all the calculated transition energies are reduced by 0.4 eV. This adjusting constant was determined from the $T-T$ transition in naphthalene.

The decrease of accuracy in the calculation of the energies of triplet states is associated with the different effects of the σ-skeleton on the singlet and triplet energy levels. In order to understand the reason for this, we shall consider the wavefunctions $\Psi_{S=0}$ and $\Psi_{S=1}$ for the singlet and triplet molecular states. These functions will be expressed as sums of products of the wavefunctions of π-electrons ($\Psi^{\pi}_{S_\pi}$) and σ-electrons ($\Psi^{\sigma}_{S_\sigma}$) with different spin multiplicities:

$$\Psi_{S=0} = N_0(\Psi^{\sigma}_{S_\sigma=0}\Psi^{\pi}_{S_\pi=0} + C_0\,\Psi^{\sigma}_{S_\sigma=1}\Psi^{\pi}_{S_\pi=1} + \ldots),$$

$$\Psi_{S=1} = N_1(\Psi^{\sigma}_{S_\sigma=0}\Psi^{\pi}_{S_\pi=1} + C_1\,\Psi^{\sigma}_{S_\pi=1}\Psi^{\pi}_{S_\pi=0} + \ldots),$$

where the coefficients C_0 and C_1 characterise the contributions of the excited states of the σ-skeleton to the singlet and triplet states of all the electrons in the molecule and N_0 and N_1 are normalising factors. In terms of the π-electron approximation, $C_0 = C_1 = \ldots = 0$ and $\Psi_{S=0} \to \Psi^{\pi}_{S_\pi=0}$ and $\Psi_{S=1} \to \Psi^{\pi}_{S_\pi=1}$. The coefficients C_0 and C_1 are inversely proportional to the differences between the energies corresponding to the first two terms in the singlet and triplet functions $\Psi_{S=0}$ and $\Psi_{S=1}$. This difference is greater for the singlet function than for the triplet function, namely

$$(E^{\sigma}_{S=1} + E^{\pi}_{S=1}) - (E^{\sigma}_{S=0} + E^{\pi}_{S=1}) > (E^{\sigma}_{S=1} + E^{\pi}_{S=0}) - (E^{\sigma}_{S=0} + E^{\pi}_{S=1})$$

owing to the self-evident inequality $E^{\pi}_{S=1} > E^{\pi}_{S=0}$. Therefore the admixture of the second term is smaller for the singlet than for the triplet,

$$|C_0|^2 < |C_1|^2,$$

which indicates a greater influence of the σ-skeleton on triplet states.

As already mentioned, the effect of the σ-skeleton is taken into account in principle by an empirical choice of the parameters of the effective Hamiltonian. Owing to the different contributions of the σ-skeleton to the singlet and triplet states, the optimal values of the parameters for the calculation of the energies of the singlet and triplet levels should differ, as has actually been observed in a number of calculations[62,63].

We may also note that, in the calculation of excitation energies (singlet and triplet), it is generally speaking necessary to take into account fully the electron interactions. If the treatment is limited to singly excited configurations, it is found that different energy levels are calculated with different accuracies, because the contributions of the neglected configurations (doubly excited, etc.) will be different for different excited states. In this connection there has been a notable failure in the calculation of transition energies between excited singlet and triplet levels of a number of molecules[66]. Another reason for this failure is associated with the increase of error in the calculation of the transition energies between excited states: when the average accuracy in the determination of the energies of excited singlet states is 0.1—0.2 eV, larger deviations are possible, being on average doubled for energy differences, i.e. for transition energies.

3. Transition Probabilities (Oscillator Strengths)

Yet another weak point in the theory is the calculation of transition probabilities (oscillator strengths) for electronic excitations of conjugated molecules. We have analysed the results of studies by a Scandinavian group of investigators[27-36], who employed the parameters of Scheme 1 and failed to find any correlation between the calculated (f_{calc}) and experimental (f_{exp}) oscillator strengths for a large number of electronic transitions. In the plot of f_{calc} against f_{exp} (Fig. 5) most of the points are distributed between two straight lines: $f_{\text{calc}} = 3f_{\text{exp}}$ and $f_{\text{calc}} = \frac{1}{3}f_{\text{exp}}$. Thus values of f_{exp} differing by a factor of 10 can correspond to the same f_{calc}. For this reason, in the majority of later studies the f_{calc} are not compared with f_{exp} but with $\lg\epsilon$, ϵ being the extinction coefficient at the corresponding maximum in the experimental absorption spectrum. The parallel variation of f_{calc} and $\lg\epsilon$ for the spectral maxima is regarded as constituting satisfactory agreement.

In the calculation of oscillator strengths one usually employs an approximation without a specific atomic orbital basis set. Suppose that ψ_0 and ψ_a are the wavefunctions

of the ground and excited states respectively and suppose that ψ_a represents a superposition of the singly excited configurations $\Phi_{i\to k}$:

$$\psi_a = \sum_{i,k} A^a_{i\to k}\Phi_{i\to k},$$

where $\Phi_{i\to k}$ is the wave function of the configuration formed from the configuration of the ground state by the transfer of an electron from the ith to the kth molecular orbital and $A^a_{i\to k}$ is a coefficient defining the contribution of this configuration to the excited state. Then the oscillator strength for the transition to the singlet state can be calculated from the formula:

$$f_{0a} = \frac{2m}{3\hbar^2 e^2}\Delta E_{0a}\vec{\mu}^2_{0a},$$

(e is the charge of the electron, m its mass, h the Planck constant, and ΔE_{0a} the excitation energy), where

$$\vec{\mu}_{0a} = \langle\psi_0|\vec{\mu}|\psi_a\rangle = e\sqrt{2}\sum_{i,k} A^a_{i\to k}\sum_\nu c^*_{\nu i}c_{\nu k}\mathbf{R}_\nu.$$

In this equation $\mathbf{R}_\nu$ is the coordinate of the atom ν, and $c_{\nu i}$ and $c_{\nu k}$ are the coefficients of the basis function $\varphi_\nu(\mathbf{r})$ in the LCAO—the expansions of the ith and kth molecular orbitals respectively.

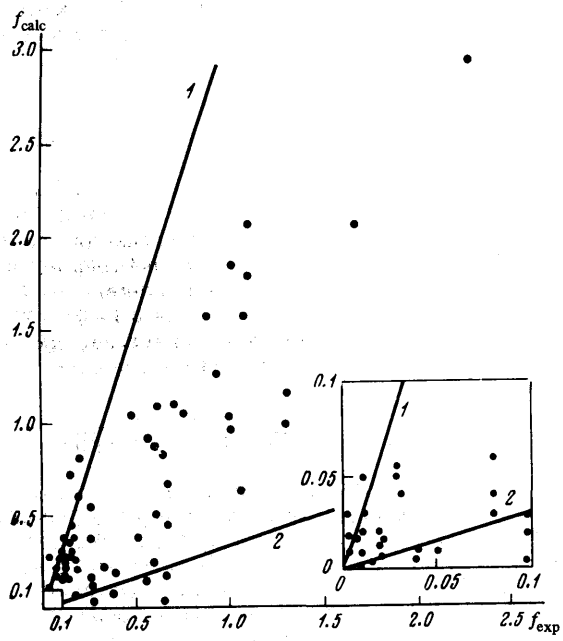


Figure 5. Correlation between the calculated (f_{calc}) and experimental (f_{exp}) oscillator strengths for 86 allowed electronic transitions in conjugated molecules according to the literature[27-36]. The section with $f < 0.1$ is shown separately on an enlarged scale: 1) $f_{calc} = 3f_{exp}$ line; 2) $f_{calc} = \frac{1}{3}f_{exp}$ line.

In the calculation of $\vec{\mu}_{0a}$ the dipole length operator

$$\vec{\mu} = e\sum_i \mathbf{r}_i$$

(summation with respect to all the electrons) was used, and in the matrix element μ_{0a} only the terms diagonal with respect to the atomic orbital indices were retained:

$$\int \varphi_p(\mathbf{r})\,\mathbf{r}\,\varphi_\nu(\mathbf{r})\,d\mathbf{r} \simeq \delta_{p\nu}\,\mathbf{R}_\nu.$$

In this formula the approximate equality $\varphi_p(\mathbf{r}) \simeq \chi_p(\mathbf{r})$, where $\chi_p(\mathbf{r})$ is the atomic orbital of the pth atom, was used. In fact (see Section II above) the orthogonal basis functions $\varphi_p(\mathbf{r})$ represent superpositions of the atomic functions $\chi_i(\mathbf{r})$, so that this approximation neglects all terms with the overlap integrals of the atomic function $\chi_i(\mathbf{r})$. As a result, the dependence of the oscillator strengths on the type of atomic functions is lost.

The development of experimental methods for the investigation of excited singlet and triplet molecular states and the important role of these states in the elementary steps of chemical and photochemical reactions should stimulate the development and improvement of theories of electronic transitions. In the calculation of transition probabilities (oscillator strengths) it is apparently necessary to describe very accurately the real (ground and excited) states of the system: account must be taken of changes in the geometry (bond length) of the molecules in the excited state and of the vibrations of the nuclei.

We shall now consider a series of studies[67-69] in which the effect of temperature on the probability of the electronic excitation and ionisation of complex molecules was investigated. As a result, a criterion was obtained for the determination of the true ionisation potential from the ionisation curve (the variation of the ion current with the energies of the photons which dislodge an electron from the molecule). This criterion is suitable for the determination of the position of the line of 0—0 transitions in the absorption spectra of complex conjugated molecules with unresolved vibrational structure and has in fact been used for this purpose[70].

The extent to which the interelectron interaction is taken into account is also of definite importance in the calculation of oscillator strengths. Thus the inclusion of doubly excited configurations in the calculation altered f_{calc} severalfold[56-58]. However, whereas in some studies[56,57] these changes improved the agreement with experiment, in one investigation[58], for other types of molecules, the agreement with experiment was impaired to such an extent that the results of the calculation were not even quoted.

Certain possible ways of improving the theory of oscillator strength have been analysed in a series of studies[71-73]. In the first of these[71] it was suggested that the gradient operator instead of the dipole length operator should be used in the calculation of f. The oscillator stengths calculated by the two procedures are

$$f_1 = \frac{2}{3}|M|^2\Delta,\quad f_2 = \frac{2}{3\Delta}|G|^2,$$

where

$$M = \left\langle\psi_0\left|\sum_i \mathbf{r}_i\right|\psi_A\right\rangle a_0^{-1},\quad \Delta = (E_A - E_0)\cdot\frac{a_0}{e^2},$$

(a_0 is the Bohr radius and e the electronic charge) and

$$G = \left\langle\psi_0\left|\sum_i \nabla_i\right|\psi_A\right\rangle a_0.$$

For the exact wavefunctions of the initial (ψ_0) and final (ψ_A) states with the energies E_0 and E_A, the equality $f_1 = f_2$ should hold. This equality does not hold for approximate variational functions involved in the theory of conjugated systems. It has been found[71-73] that, for benzene, ethylene, polyenes, and polyacenes, we always have

$f_1 > f_2$ and $f_1 > f_{exp}$. As a result, the use of f_2 instead of f_1 improved the agreement with experiment (Table 9). This agreement is fortuitous, since as a rule $f_2 < f_{exp}$ and the differences between f_2 and f_{exp} are also not small.

The reasons for the unsatisfactory situation in the theory as regards the calculation of oscillator strengths have been discussed[74,75]. It was suggested that the failures are caused by the employment of a finite basis set of atomic functions and the neglect of correlation effects in the wavefunctions (this disagrees with the results of studies[56-58] where an effect of doubly excited configurations on f_{calc} was noted). In this connection it is suggested that the approximation of random phases, which combines the simplicity of molecular orbital methods with allowance for correlation effects, be used. The random phase approximation has already been employed in the calculation of oscillator strengths[76-79]. However, in one study[76] a satisfactory parallel variation of f_{calc} with $\lg \epsilon$ was merely noted and in others[77-79] no comparison with experiment was made.

Table 9. The calculated (f_1 and f_2) and experimental (f_{exp}) oscillator strengths for certain allowed transitions in a number of molecules[71-73].

Molecule	f_1	f_2	f_{exp}	Molecule	f_1	f_2	f_{exp}
ylene	0.597	0.272	0.29	Hexatriene	2.312	0.446	~0.7
Benzene	2.369	0.945	0.88	Naphthalene	0.53	0.18	0.11
Butadiene	1.423	0.35	0.55		2.10	0.87	1.2
				Anthracene	2.77	1.21	1.6

Analysis of the solutions of certain model problems[74,75] has shown that in most cases $f_1 > f_{exact}$ and $f_2 < f_{exact}$. However, for different types of transitions, a wide variety (as regards sign and magnitude) of deviations of f_1 and f_2 from f_{exact} may be encountered. As mentioned by Dancz and Harris[75], there exists an infinite set of operators, apart from the dipole length and velocity operators, which yield the same oscillator strength f_{exact} in calculations using exact functions. In calculation with variational functions, which are not solutions of the Schrödinger equation, all these operators yield different f_{calc}: $f_1 \neq f_2 \neq \ldots \neq f_{exact}$. We believe that, in order to overcome this difficulty in a theory in which the matrix elements of operators and not wavefunctions are used, it is necessary to make sure that the matrix elements are chosen in accordance with commutative relations for the operators. For example, operators for the momentum $\hat{p} = i\hbar(\partial/\partial\bar{r})$ and the coordinate $\bar{r}$ satisfy definite commutative relations and therefore the choice of the parameters p_{mn} and r_{mn} must not conflict with these relations. With this choice of parameters, it is possible to minimise the inaccuracies associated with the employment of variational functions on a limited atomic orbital basis set. Interesting possibilities for a correct choice of parameters p_{mn} and r_{mn}, which are used in calculation of f_2 and f_1, were demonstrated by Linderberg[80]. We believe that the approach to the problem of oscillator strengths from such general standpoints will make it possible to develop a scheme (which is not at present available) for the determination of parameters, including consistently calculated oscillator strengths and other characteristics of molecular systems.

REFERENCES

1. J. Lennard-Jones and J. A. Pople, Disc. Faraday Soc., 10, 9 (1951).
2. A. A. Ovchinnikov et al., Uspekhi Fiz. Nauk, 108, 81 (1972).
3. J. Koutecky, J. Chem. Phys., 44, 3702 (1966).
4. T. Shida and W. Hamill, J. Chem. Phys., 44, 4372 (1966).
5. P. O. Löwdin, J. Chem. Phys., 18, 365 (1950).
6. I. Fischer-Hjalmars, J. Chem. Phys., 42, 1962 (1965).
7. M. Goeppert-Mayer and A. Sklar, J. Chem. Phys., 6, 645 (1938).
8. R. Parr, "Quantum Theory of Molecular Electronic Structure", Benjamin Press, New York, 1963.
9. C. Roothaan, Revs. Mod. Phys., 23, 69 (1951).
10. S. Fischer, Int. J. Quant. Chem., 3S, 651 (1970).
11. K. Freed, Chem. Phys. Letters, 15, 331 (1972).
12. I. Fischer-Hjalmars, Symposium, "Sovremennaya Kvantovaya Khimiya" (Modern Quantum Chemistry) (Translated into Russian), Izd. Mir, Moscow, 1968, Vol. 1, p. 206.
13. O. Sinanoglu and M. Orloff, Symposium, "Sovremennaya Kvantovaya Khimiya" (Modern Quantum Chemistry) (Translated into Russian), Izd. Mir, Moscow, 1968, Vol. 1, p. 222.
14. E. Weltin, J. Weber, and E. Heilbronner, Theoret. chim. Acta, 2, 114 (1964).
15. G. Favini, I. Vandoni, and M. Simonetta, Theoret. chim. Acta, 3, 45, 418 (1965).
16. A. A. Ovchinnikov, Doctoral Thesis, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1970.
17. M. Gessel, Teor. Eksper. Khim., 5, 397 (1969).
18. W. Kramling and E. Wagner, Theoret. chim. Acta, 15, 43 (1969).
19. Yu. A. Kruglyak, H. Preuss, and R. Janoschek, Zhur. Strukt. Khim., 12, 689 (1971).
20. C. Coulson and A. Golebievski, Proc. Phys. Soc., 78, 1314 (1961).
21. I. A. Misurkin and A. A. Ovchinnikov, Zhur. Strukt. Khim., 5, 888 (1965).
22. J. Dewar and C. de Llano, J. Amer. Chem. Soc., 91, 789 (1970).
23. J. Dewar and T. Morita, J. Amer. Chem. Soc., 91, 796 (1970).
24. M. Basilevsky, Theoret. chim. Acta, 13, 409 (1969).
25. M. Basilevsky and V. Tikhomirov, "23rd Intern. Congress of Pure and Applied Chemistry", Vol. 1, p. 109, Butterworths, London, 1971.
26. R. Brown and B. Coller, Theoret. chim. Acta, 7, 259 (1967).
27. B. Roos and P. Skancke, Acta chem. Scand., 21, 233 (1967).
28. B. Roos, Acta chem. Scand., 21, 2318 (1967).
29. I. Fischer-Hjalmars and M. Sundbom, Acta chem. Scand., 22, 607 (1968).
30. B. Grabe, Acta chem. Scand., 22, 2237 (1968).
31. H. Jensen and P. Skancke, Acta chem. Scand., 22, 2899 (1968).
32. G. Höjer, Acta chem. Scand., 23, 2589 (1969).
33. A. Skancke and P. Skancke, Acta chem. Scand., 24, 23 (1970).
34. O. Gropen and P. Skancke, Acta chem. Scand., 24, 1768 (1970).
35. P. Seybold and I. Fischer-Hjalmars, Acta chem. Scand., 24, 1373 (1970).

36. M. Sundbom, Acta chem. Scand., 25, 487 (1971).
37. H. Hammond, Theoret. chim. Acta, 18, 239 (1970).
38. I. A. Misurkin and A. A. Ovchinnikov, Optika i Spektrosk., 16, 238 (1964).
39. S. de Bruijn and J. Colpa, Mol. Phys., 18, 213 (1970).
40. C. Tric, Mol. Phys., 15, 205 (1968).
41. S. de Bruijn, Theoret. chim. Acta, 18, 34 (1970).
42. V. I. Lutoshkin, P. A. Kotorlenko, and Yu. A. Kruglyak, Teor. Eksper. Khim., 8, 542 (1972).
43. E.-M. Farbrot and P. Skancke, Acta chem. Scand., 24, 2652 (1970).
44. F. Harris, J. Chem. Phys., 48, 4027 (1968).
45. K. Jug, J. Chem. Phys., 51, 2779 (1969).
46. A. A. Bagatur'yants, Teor. Eksper. Khim., 7, 88 (1971).
47. G. Karlsson, Int. J. Quant. Chem., 4, 289 (1970).
48. G. Wagniere, Theoret. chim. Acta, 9, 312 (1968).
49. K. Nishimoto and L. Fòrster, Theoret. chim. Acta, 4, 155 (1966).
50. Z. Yoshida and T. Kobayashi, J. Chem. Phys., 54, 4538 (1971).
51. V. K. Potapov, Doctoral Thesis, Karpov Physicochemical Institute, Moscow, 1972.
52. T. Kunii and H. Kuroda, Theoret. chim. Acta, 11, 97 (1968).
53. Z. Yoshida and T. Kobayashi, Theoret. chim. Acta, 19, 377 (1970).
54. Z. Yoshida and T. Kobayashi, Theoret. chim. Acta, 20, 216 (1971).
55. M. Klessinger, Theoret. chim. Acta, 5, 251 (1966).
56. G. Pukanic, D. Forshey, et al., Theoret. chim. Acta, 9, 38 (1967).
57. D. Forshey and G. Pukanic, Theoret. chim. Acta, 9, 288 (1968).
58. G. Pukanic and D. Forshey, Theoret. chim. Acta, 10, 240 (1968).
59. J. Fabian and G. Troeger, Teor. Eksper. Khim., 7, 171 (1971).
60. M. Berndt and J. Kwiatkowski, Theoret. chim. Acta, 17, 35 (1970).
61. K. Nishimoto et al., Theoret. chim. Acta, 14, 80 (1969).
62. J. Pancir and R. Zahradnik, Theoret. chim. Acta, 14, 426 (1969).
63. A. Sannigrahi, Int. J. Quant. Chem., 5, 265 (1971).
64. M. Orloff, J. Chem. Phys., 47, 235 (1967).
65. J. Brinen and M. Orloff, J. Chem. Phys., 51, 527 (1969).
66. D. Lavalette, C. Tetreau, and J. Langelaar, Chem. Phys. Letters, 9, 319 (1971).
67. A. A. Ovchinnikov, Optika i Spektrosk., 26, 696 (1969).
68. V. A. Vlaskov and A. A. Ovchinnikov, Optika i Spektrosk., 27, 748 (1969).
69. V. A. Vlaskov, A. A. Ovchinnikov, and V. M. Komarov, Optika i Spektrosk., 29, 1008 (1970).
70. V. M. Komarov and V. G. Plotnikov, Optika i Spektrosk., 33, 867 (1972).
71. D. Chong, Mol. Phys., 14, 275 (1968).
62. C. Yue and D. Chong, Mol. Phys., 14, 487 (1968).
73. A. McHugh and M. Gouterman, Theoret. chim. Acta, 13, 249 (1969).
74. R. Harris, J. Chem. Phys., 50, 3947 (1969).
75. J. Dancz and R. Harris, J. Chem. Phys., 52, 5261 (1970).
76. W. Little and H. Gutfreund, J. Chem. Phys., 50, 4478 (1970).
77. M. Mestechkin and L. Gutyrya, Optika i Spektrosk., 26, 159 (1969).
78. M. Mestechkin, L. Gutyrya, and V. Poltavets, Optika i Spektrosk., 28, 454 (1970).
79. V. Poltavets and M. Mestechkin, Optika i Spektrosk., 30, 1022 (1971).
80. J. Linderberg, Chem. Phys. Letters, 1, 39 (1967).

Karpov Physical Chemical
Institute, Moscow