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Compatibility of the Methods of Calculation and Semiempirical Parameters in the Theory of Molecules with Conjugated Bonds

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Various methods for the selection of the parameters of the model π-electron Hamiltonian are discussed, certain aspects of the interaction of π electrons with the σ skeleton are considered, and the scope of various methods for the calculation of the electronic structures of molecules and radicals wtih conjugated bonds are analysed.
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1. INTRODUCTION

The modern theory of the electronic structures of compounds with conjugated bonds employs the π-electron approximation, which has been analysed in detail in a previous review by the present authors[1]. According to this approximation, it is possible to obtain all the observed characteristics of conjugated many-electron systems if only the π electrons are considered explicity in the quantum-chemical calculation. The properties of π electrons are specified by an effective model Hamiltonian[4]:

$$H = \sum_{p,q,\eta} h_{pq} c^{+}_{p\eta} c_{q\eta} + \sum_{p,q,\eta,\rho} \gamma_{pq} c^{+}_{p\eta} c_{p\eta} c^{+}_{q\rho} c_{q\rho}, \qquad (1)$$

where $c^{+}_{p\eta}$ and $c_{p\eta}$ are the operators of the creation and annihilation of an electron with a spin η in the state with the function $\varphi_p(\mathbf{r})$ localised at an atom p, h_{pq} is the one-electron parameter for the kinetic energy and the energy of attraction of the σ skeleton, and γ_{pq} is the parameter for the Coulomb repulsion of the π-electrons at the atoms p and q.

A minimal representation of second quantisation is employed in the review: in formulating the Hamiltonian and other operators and in considering the derivation of important results obtained by Linderberg (in Section 2, a).

In the present review attention is concentrated on the problem of the consistency between the method of calculation and the calculated molecular characteristics and also the problem of consistency between the semiempirical parameters (h_{pq}, γ_{pq}, etc.) and the method of calculation. Certain problems of the interaction of π-electrons with the σ skeleton, where the question of the π-electron approximation and its possibilities becomes most acute, are likewise examined.

2. VARIOUS METHODS FOR THE DETERMINATION OF THE PARAMETERS OF THE MODEL π-ELECTRON HAMILTONIAN

We shall consider certain methods or schemes for the parametrisation of the effective model Hamiltonian which differ from the two general parametrisation schemes (Scheme 1 and Scheme 2) examined in the previous review[1]. All these schemes normally give good agreement with experiment and similar effective Hamiltonian parameters. Such are the parametrisation schemes for conjugated systems with N and O heteroatoms[2] and with amino-groups[3], and for conjugated hydrocarbons[4]. In these studies the authors altered somewhat the generally accepted values of the parameters in order to achieve a better description of the experimental data for molecules of the specified type. Calculations have been made[5] on heterocyclic conjugated molecules with N, O, and S atoms and in a subsequent study[6] fairly combersome formulae were proposed whereby all the empirical parameters of the earlier investigation[5] were reproduced with satisfactory accuracy (using Slater's $2p_z$ functions). These formulae were obtained from model physical ideas concerning the π-electron system and the σ skeleton.

This parametrisation procedure is convenient in computer calculations and is formally (but not in reality) less empirical than Scheme 1. Empirical information is contained, as in Scheme 2, in the effective charges of Slater's functions and in the special form of the formulae for the parameters[1,6].

The simple parametrisation schemes of the Pariser–Parr–Pople (PPP) method (neglect of the parameters of the Coulomb interaction between electrons in non-adjacent atoms, neglect of the relation between $\beta_{\mu\nu}$ and $R_{\mu\nu}$, etc.) have been used in calculations on polysubstituted benzenes and five-membered heterocycles with N, O, and S atoms[7], azabenzenes and azanaphthalenes[8], and substituted benzenes, pyridines, and pyrimidinones[9]. It is interesting to note that the optimal values of the same parameters of the model Hamiltonian for molecules of different homologous series differ somewhat as a rule. This is typical for a semiempirical theory.

In one of the parametrisation schemes for hydrocarbons[10,11] the benzene excitation energies (as in the old Pariser–Parr method[12]) and the benzene ionisation potential are used to determine $\gamma_{\mu\nu}$ and βCC. If the excitation energies (in terms of the ZDO approximation) depend on the differences between the $\gamma_{\mu\nu}$, then the $\gamma_{\mu\nu}$ themselves enter into the expression for the ionisation potential obtained using Koopman's theorem. As a result, somewhat unusual values of the parameters were obtained for benzene: $\beta CC = -2.4$ eV and $\gamma_{11} = 9.4$ eV[10] or $\beta CC = -2.5$ eV and $\gamma_{11} = 8.2$ eV.[11] The remaining $\gamma_{\mu\nu}$ were estimated from formulae of the Mataga–Nishimoto type[12].

We believe that it is more natural to employ a corrected Koopman's relation [see the previous review[1], formula (32)] or to compensate the inaccuracies in the Koopman's relation by introducing a special parameter ΔW_0 [see the previous review[1], Eqns. (15)–(17)], as was done in Scheme 1, particularly since the improvements introduced by the new parameters are insignificant. For example the energy of the $S \rightarrow T$ transition in anthracene is $\Delta E =$ 1.84 eV (experimental value), $\Delta E = 1.79$ eV (value obtained with the new parameters[10]), and $\Delta E = 1.66$ eV (value calculated by the PPP scheme taking into account excited configurations made up from Hückel molecular orbitals[13]).

a. The Linderberg Method for the Calculation of Resonance Integrals

The new possibilities for the creation of a unified parametrisation scheme for the effective Hamiltonian arose after the publication of Linderberg's study[14]. In order to calculate the resonance integral $\beta_{\mu\nu}$ or the parameter $h_{\mu\nu}$ in the PPP(1) Hamiltonian, Linderberg employed a familiar quantum-mechanical relation for the momentum $\mathbf{p}$ in terms of the commutation relation

$$[\mathbf{r}, H] \equiv \mathbf{r}H - H\mathbf{r},$$

the coordinates $\mathbf{r}$, and the Hamiltonian H:

$$i\hbar \frac{d\mathbf{r}}{dt} = [\mathbf{r}, H] = i\hbar \frac{\mathbf{p}}{m}, \qquad (2)$$

where H is the PPP(1) Hamiltonian, $\hbar$ the Planck constant, and m the mass of the electron. In the second quantisation representation the operators $\mathbf{r}$ and $\mathbf{p}$ can be expressed as follows in terms of the electron creation and annihilation operators:

$$\mathbf{r} = \sum_{q,\eta} \mathbf{R}_q c^+_{q\eta} c_{q\eta}, \qquad \mathbf{p} = \sum_{\nu \neq s, \eta} \mathbf{p}_{\nu s} c^+_{\nu\eta} c_{s\eta}, \qquad (3)$$

where $\mathbf{R}_q$ is the coordinate of the atom q with which the basis function $\varphi_q(\mathbf{r})$ is associated. The matrix element $\mathbf{p}_{\nu s}$ has the following form (v and s are neighbouring atoms):

$$\mathbf{p}_{\nu s} = \int \varphi_\nu(\mathbf{r})(-i\hbar\nabla)\varphi_s(\mathbf{r})\,d\mathbf{r} = \int \varphi(\mathbf{r}-\mathbf{R})(-i\hbar\nabla)\varphi(\mathbf{r})\,d\mathbf{r} = \\ = i\hbar\nabla_R \int \varphi(\mathbf{r}-\mathbf{R})\varphi(\mathbf{r})\,d\mathbf{r} = -i\hbar\nabla_R S(R). \qquad (4)$$

where $\mathbf{R} = \mathbf{R}_S - \mathbf{R}_V$ and $S(R)$ is the overlap integral between $\varphi_s(\mathbf{r})$ and $\varphi_v(\mathbf{r})$.

Using Eqns. (1), (3), and (4), we obtain from Eqn. (2) the relation between the parameter h_{vs} of the Hamiltonian and the matrix element $\mathbf{p}_{vs}$ of the momentum:

$$i\hbar\,\mathbf{p}_{vs} = h_{vs}(\mathbf{R}_v - \mathbf{R}_s),$$

or, finally, we obtain the following formula for the resonance integral:

$$h_{vs} \equiv \beta_{vs}(R) = \frac{\hbar^2}{m}\frac{1}{R}\frac{dS}{dR}, \quad R = |\mathbf{R}_v - \mathbf{R}_s|. \qquad (5)$$

The Slater functions with $Z_{eff} = 3.18$ for carbon and $Z_{eff} = 3.8$ for nitrogen as well as the Hartree–Fock functions for these atoms were used as the atomic $2p_z$ functions from which the $\varphi_s(\mathbf{r})$ functions were constructed with the aid of Lowdin's orthogonalisation procedure[15]. The results of the calculation (together with certain refinements[16]) for the benzene and ethylene bonds and the aniline CN bond are presented in Table 1. It was found that the observed βCN and βCC are close to the empirical values determined from the absorption spectra.

Linderberg's scheme for the calculation of resonance integrals has been used in calculations on a number of molecules with heteroatoms[17,18]. It was found that the results of the calculation agree well with experiment and are close to the results obtained in calculations employing the usual parametrisation schemes[19].

We believe that the derivation of relations between theoretical parameters, such as the Linderberg relation (5), constitutes a fruitful procedure for the development of the theory and for the achievement of its internal self-consistency.

We may note certain inaccuracies in the derivation of Eqn. (5), which was taken from Linderberg's paper[14]. According to this derivation, the overlap integral S is

calculated with the orthogonal functions $\varphi_p(\mathbf{r})$. Therefore the overlap integral $S = 0$ for $\varphi_s(\mathbf{r})$ and $\varphi_p(\mathbf{r})$ $(s \neq p)$, which does not prevent the derivative dS/dR from being non-zero. However, the functions $\varphi_p(\mathbf{r})$ are made up by the superposition of non-orthogonal atomic functions $\chi_i(\mathbf{r})$ of the $2p_z$ type localised at atoms i (see the previous review[1] for more detail):

$$\varphi_p(r) = \sum_i \chi_i(r)\, c_{ip}\,.$$

Table 1. The resonance integrals calculated by Linderberg's method[14] [the upper figures represent the value calculated using Slater's functions and the lower figures the values obtained with the Hartree–Fock functions for the C and N atoms. The last columns list the resonance integrals $(-\beta)$ for benzene obtained by an improved calculation using Slater's functions with different Z (Jug[16])].

Molecule	Designation of resonance integral	C-C bond			
		R, Å	$-\beta$ (R), eV	$Z = 3.18$	$Z = 2.58$
Ethylene	β_{12}	1.34	2.685 2.588		
Benzene	β_{12}	1.4	2.42 2.38	2.27	2.47
	β_{13}	2.42	0 0	−0.05	−0.02
	β_{14}	2.8	0.14 0.19	0.08	0.13
		CN bond			
Aniline	β CN	1.47	1.75 1.77		

Therefore in Eqns. (3) and in subsequent treatment $\mathbf{R_q}$ is not a coordinate of the atom q. Formally $\mathbf{R_q}$ is a diagonal matrix element, expressed as a function of $\mathbf{r}$, calculated using the functions $\varphi_q(\mathbf{r})$:

$$\mathbf{R}_q = \int \varphi_q(\mathbf{r})\, \mathbf{r}\, \varphi_q(\mathbf{r})\, d\mathbf{r}\,.$$

On the other hand, the true coordinate of the atom q, which will now be designated by $\mathbf{R}^0_q$, is equal to the diagonal matrix element expressed as a function of $\mathbf{r}$, using the functions $\chi_q(\mathbf{r})$:

$$\mathbf{R}^0_q = \int \chi_q(\mathbf{r})\, \mathbf{r} \chi_q(\mathbf{r})\, d\mathbf{r},$$

and it is readily seen that $\mathbf{R_q} \neq \mathbf{R}^0_q$. Furthermore, Eqn. (3) for the operator $\mathbf{r}$ is inaccurate also because non-zero matrix elements with the off-diagonal indices p and q, expressed in terms of the functions $\varphi_p(\mathbf{r})$, were neglected in its formulation. The exact formula for the operator $\mathbf{r}$ is

$$\mathbf{r} = \sum_{pq,\eta} \mathbf{R}_{pq} c^+_{p\eta} c_{q\eta}, \quad \mathbf{R}_{pq} = \int \varphi_p(\mathbf{r})\, \mathbf{r}\, \varphi_q(\mathbf{r})\, d\mathbf{r}.$$

These inaccuracies were corrected in subsequent studies†, but we shall not consider this problem in greater detail‡ in view of the fairly cumbersome nature of the expressions.

†In Linderberg's[20] and Jug's[21] studies.

‡Various aspects of the employment and interpretation of Eqn. (5) are discussed in a recent study[22].

Linderberg's idea, employing the fundamental relation between the coordinate and the momentum, appears to us more attractive and fruitful than direct calculation of $\beta_{\mu\nu}$ with specified functions and potentials of the Goeppert–Mayer and Sklar type (see, for example, Yoshida and Kobayashi[6] whose calculated $\beta_{\mu\nu}$ are very close to the semiempirical values). At the same time, we believe that in the future it will be necessary to compare carefully these two methods for the calculation of $\beta_{\mu\nu}$.

3. PROBLEMS OF THE INTERACTION OF π ELECTRONS WITH THE σ SKELETON

The problem of the interaction of π and σ electrons have always been of interest for the semiempirical theory of conjugated systems, since the limits of the applicability of the π-electron theory are then elucidated and the significance of the semiempirical formulae employed is discovered.

a. The Mixing of One-Electron σ and π Energy Levels in Conjugated Molecules

Studies have been published recently indicating the mixing of one-electron σ and π energy levels in conjugated systems, which seemingly constitutes evidence against the π-electron approximation. Thus analysis of experiments on the photoionisation of benzene[23,24] showed that a filled σ energy level is located in benzene between filled π levels. A similar pattern with mixing of σ and π energy levels follows also from numerous calculations on various molecules in terms of the SCF approximation, which have given rise to a lively discussion[25].

Many investigators found the reports of such mixing of σ and π levels very unexpected, because all the properties of conjugated systems, including absorption spectra, had been satisfactorily explained hitherto with the aid $\pi \rightarrow \pi^*$ transitions alone. All previous experience in the quantum chemistry of conjugated system could be reconciled with the mixing of σ and π energy levels only by postulating a weak interaction between the σ- and π-electron systems. This was in fact found to be the case.

A study of transition probabilities by the Hückel method for all the valence electrons of naphthalene and anthracene[25] showed that the transition probabilities (oscillator strengths) for the $\sigma \rightarrow \pi^*$ transitions are smaller by 3–4 orders of magnitude than for the $\pi \rightarrow \pi^*$ transitions. In $\sigma \rightarrow \pi^*$ transitions the emission is polarised perpendicular to the plane of the conjugated molecules, because only matrix elements of the type[25]

$$I = \langle \varphi_{s_i} | z | \varphi_{z_i} \rangle\,,$$

where φ_{s_i} and φ_{z_i} are $2s$ and $2p_z$ functions of the atom i, contribute to the transition moment (in terms of the one-centre approximation). The quantity $I \leqslant a_0$ (a_0 is the Bohr radius) is in fact independent of the molecular size and the number of atom i.

In $\pi \rightarrow \pi^*$ transitions the emission is polarised in the molecular plane and matrix elements of the type

$$X_i = \langle \varphi_{z_i} | x | \varphi_{z_i} \rangle, \quad Y_i = \langle \varphi_{z_i} | y | \varphi_{z_i} \rangle$$

contribute to the transition amplitude. X_i and Y_i are essentially coordinates of the atoms i, so that they are comparable to the dimensions of the conjugated molecule, exceeding appreciably the value of a_0.

There is yet another cause of the decrease of the probability of the $\sigma \rightarrow \pi^*$ transitions. When the two molecular orbitals involved in the $\sigma \rightarrow \pi^*$ transition are formulated:

$$\psi^\sigma = \sum_i c_i^\sigma \varphi_{s_i} + \text{члены с } \varphi_{x_i}, \varphi_{y_i}$$

$$\psi^\pi = \sum_i c_i^\pi \varphi_{z_i},$$

the $\sigma \rightarrow \pi^*$ transition amplitude becomes

$$\langle \psi^\sigma | z | \psi^\pi \rangle = \langle \varphi_{s_i} | z | \varphi_{z_i} \rangle \sum_i c_i^\sigma c_i^\pi = I \sum_i c_i^\sigma c_i^\pi. \quad (6)$$

It was discovered that this amplitude is small also because the coefficients c_i^σ are as a rule small for the highest occupied σ orbitals.

This analysis shows that the lines of the $\sigma \rightarrow \pi^*$ transitions must be much weaker than those of the $\pi-\pi^*$ transitions, which predominate in the experimental spectrum. The different polarisations of emission in $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ transitions may assist the observation of weak $\sigma \rightarrow \pi^*$ transitions. Furthermore, it is quite likely that ionisation from filled σ orbitals was indeed observed in the photoionisation of benzene and other molecules[23,24,26].

We may note that, for small conjugated molecules such as ethylene and formaldehyde, $\sigma \rightarrow \pi^*$ transitions (and $\pi-\sigma^*$ transitions) are just as intense as the $\pi \rightarrow \pi^*$ transitions. This also follows from Eqn. (6), since in ethylene, for example, the coefficients c_i^σ are relatively large[25].

b. Calculations on Non-planar Conjugated Systems

The interaction of σ and π electrons becomes significant when non-planar conjugated systems are considered. So far very few studies have been devoted to calculations on the electronic structures of such systems. For example, stilbene and diphenylbutadiene molecules, in which the coplanarity breaks down as a result of rotation about the central C–C bond of one part of the molecule relative to the other by an angle α, have been considered[27,28]. In the calculation by the PPP method the usual parameters were used and only the resonance integral of the central bond was multiplied by $\cos\alpha$. A good agreement has been obtained[28] with the experimental position of the first singlet energy level, while in another study[27] not even a qualitative explanation of the energy level shifts on passing to a non-planar system was obtained.

We believe that the problem of the parameters for non-planar conjugated systems cannot be solved by a simple alteration of the resonance integral for one bond. The interactions between non-bonded atoms in the molecule become significant in non-planar systems[28] and it is necessary to take into account more accurately the repulsion of the positively charged σ skeleton[29]. In non-planar systems the π-electron orbitals are no longer orthogonal with respect to the orbitals of the electrons in the σ skeleton. Therefore, in order to consider π electrons separately, as before, i.e. in order to retain the π-electron approximation, it is necessary to carry out the orthogonalisation (for example, by Löwdin's method[15]) of the π-electron orbitals in the non-planar configuration with respect to the orbitals of the new σ skeleton. Only then is it possible to understand how the effective parameters of the model π-electron Hamiltonian are changed relative to the planar case.

c. The Hyperfine Structure of the ESR Spectra and the McConnell Formula

The interaction of σ and π electrons can be readily observed by ESR (and NMR) methods, when a spin density ρ^π appears in the π-electron system. The spin density ρ^π in π-electron radicals, radical-ions, or triplet states of conjugated molecules polarises the electrons of the σ skeleton and leads to the appearance of a spin density ρ^σ in the σ-electron system. As a result of the contact interaction of ρ^σ with the magnetic moments of the nuclei in the conjugated system (when these nuclei have magnetic moments), a hyperfine structure (HFS) appears in the ESR method[30], the additional (hyperfine) splitting of the ESR Zeeman line by each magnetic nucleus is specified by the hyperfine splitting constant. In the case of hydrocarbons the HFS of the ESR spectra depends on the proton splittings a_{H_i} in the Ci–Hi bonds.

According to the theory of McConnell and Chesnut[31], the splitting a_{H_i} is proportional to the exchange integral calculated using the $2p_z$ functions (φ_{z_i}) of the atoms Ci and the functions of the ground (Φ_σ) and excited (Φ_{σ^*}) states of the electrons in the Ci–Hi bond:

$$a_{H_i} = \text{const} \cdot \langle \Phi_\sigma \varphi_{z_i} | \Phi_{\sigma^*} \varphi_{z_i} \rangle. \quad (7)$$

Making certain assumptions, the relation known as the McConnell formula was obtained from Eqn. (7):[31]

$$a_{H_i} = Q \rho_i^\pi, \quad (8)$$

where ρ_i^π is the π-electron spin density at the atom C_i linked to Hi and Q is a constant. Eqn. (8) made it possible to employ the results of the calculation of ρ_i^π in the interpretation of ESR spectra. As a result, ESR became one of the procedures for the investigation of the electronic structures of conjugated systems.

Subsequently analysis of the systematic deviations from McConnell's formula [Eqn. (8)] for hydrocarbon radical-cations and radical-anions led to a refinement of this formula[32] by the introduction of a relation between a_{H_i} and the π-electronic charge q_i of the atom Ci:

$$a_{H_i} = (Q' + Kq_i)\rho_i^\pi. \quad (9)$$

This relation, known as the Colpa–Bolton formula, was obtained from Eqn. (7) on the assumption that the charge q_i influences the σ orbital of the C–H bond[32].

Detailed analysis of the approximations leading to the McConnell formula [Eqn. (8)] showed[33] that the formula is correct only in the zeroth approximation. A more accurate formula for a_{H_i} includes both the diagonal elements of the spin density matrix $Q_{ii} = \rho_{ii}^\pi$ and the off-diagonal elements Q_{ij} ($Q_{ij} = c_i^0 c_j^{0*}$, where c_j^0 is a coefficient of the jth atomic orbital for the unpaired electron molecular orbital). This more general formula is[33]

$$a_{H_i} = -26.07 Q_{ii} - 10.40 \sum_{k\ (i\ \text{neighbours})} Q_{ik}\ (\text{gauss}). \quad (10)$$

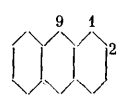
A similar formula was proposed for a_{H_i} even earlier[34].

The results of the calculation of a_{H_i} by Eqn. (10) are presented in Table 2, which shows that Eqn. (10) represents satisfactorily the changes in a_{H_i} on passing from a cation to an anion and therefore constitutes a generalisation of both the McConnell [Eqn. (8)] and Colpa–Bolton [Eqn. (9)] formulae.

Nevertheless, the McConnell and Colpa–Bolton formulae are widely used in semiempirical calculations, because

they make it possible to determine with satisfactory accuracy (to within about 10–15%) both the relative and absolute HFC constants not only for protons but also for other nuclei (^{13}C, ^{14}N, etc.)[35]. Eqns. (8) and (9) are usually treated as empirical relations with the constants Q, Q', and K.

Table 2. The hyperfine splittings a_{H_i} for the positive and negative ions of naphthalene and anthracene[33].

Molecule	Sign of ion	No. of atom	a_{H_i}, G expt.	a_{H_i}, G Eqn.(10)
	–	1	−4.90	−5.11
		2	−1.83	−1.78
	+	1	−5.54	−5.64
		2	−2.06	−1.89
	–	1	−2.74	−2.74
		2	−1.51	−1.35
		9	−5.56	−5.45
	+	1	−3.11	−2.80
		2	−1.40	−1.24
		9	−6.56	−6.68

Relations between the experimental constants $a_{H_i}^{exp}$ and $a_{H_i}^{calc}$ calculated by Eqns. (8) and (9) for a large number of π-electron radicals have been analysed[36]. The ρ_i^π were calculated by ten different methods, optimum values of the constants Q, Q', and K being selected for each method. It was found that all the methods for the calculation of ρ_i^π yield a good agreement between $a_{H_i}^{exp}$ and $a_{H_i}^{calc}$. The average discrepancies are $\leqslant 1$ G, although in a few instances they may reach 2–3 G. However, the optimum constants Q, Q', and K depend markedly on the method of calculation (Table 3).

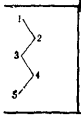
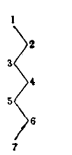
Table 3. The optimum constants Q' and K (gauss) in the Colpa–Bolton formula [Eqn. (9)] for different methods of calculating spin densities[36].

Method of calculation of spin density	Q'	K
Hückel	35.62	16.78
Hückel + CI (Ref.37)	31.50	16.86
McLachlan	25.05	18.37
UHF	20.43	10.60
UHF with annihilation of the quartet	28.50	12.66

It was also noted[36] that the optimum constants depend on the number of neighbours of the carbon atom and on the sign of its spin density. These fine features are not taken into account in the McConnell formula [Eqn. (8)]. A characteristic example is the benzyl radical, where the ratio $a_{H_2}/a_{H_4} < 1$ (in contrast to the McConnell formula), while according to all the methods of calculation employed, the ratio of the spin densities of the carbon atoms $\rho_2^\pi/\rho_4^\pi \geqslant 1$ (Table 4).

A non-empirical calculation of the electronic structure of the benzyl radical in terms of the SCF approximation taking into account all the electrons (σ and π), carried out by Kruglyak et al.[44], yielded directly the spin densities of the *ortho*- and *para*-protons. The ratio of these densities $\rho_{H_2}^\sigma/\rho_{H_4}^\sigma < 1$, in agreement with experiment, while the ratio of the spin densities in the π-electron system was still incorrect: $\rho_2^\pi/\rho_4^\pi \gtrsim 1$. The calculation showed that the $\sigma \rightarrow \pi$ interaction had an insignificant influence on the π orbitals and on the distribution of spin density in the π-electron system. It was therefore concluded that the McConnell formula is inadequate for the calculation of a_{H_i} for the benzyl radical[44].

Table 4. Spin densities calculated by different methods[38].

Radical	No. of atom	Method of calculation: SCF	SCF + singly excited configurations	full CI[c]	UHF	UHF with annihilation	Hückel	McLachlan	$\lvert a_{H_i}\rvert$ (expt.) G
	1	0.253	0.330[a]	0.413	0.553	0.387	0.333		8.99[e]
	2	0	−0.092	−0.140	−0.314	−0.096	0		2.65
	3	0.494	0.525	0.452	0.523	0.418	0.333		13.40
	7	0.791	0.706[b]	0.745	0.760	0.711	0.571	0.770	16.36[d]
	1	0	−0.095	−0.110	−0.197	−0.062	0	−0.102	—
	2	0.081	0.174	0.185	0.268	0.163	0.143	0.161	5.14
	3	0	−0.058	−0.070	−0.172	−0.054	0	−0.063	1.75
	4	0.046	0.156	0.165	0.238	0.134	0.143	0.137	6.14
	1			0.325	0.356		0.25		
	2			−0.117	−0.096		0		
	3			0.367	0.295		0.25		
	4			−0.150	−0.110		0		

[a] According to Hinchliffe[39].
[b] According to Kuprievich et al.[40].
[c] According to Amos and Burrows[41].
[d] According to Trinajstić[42].
[e] According to Nowakowski[43].

4. THE DISTRIBUTION OF SPIN DENSITY IN RADICALS

a. The Hückel Method

The application of the Hückel method makes it possible to obtain a qualitatively correct distribution of spin density in the radical[45–48]. In combination with the McConnell formula, the Hückel method permits the interpretation of fairly complex ESR spectra, which may have an unresolved HFS for a solid phase. In the interpretation of such spectra of the radicals of certain acetylene derivatives the necessity to take into account the real bond lengths in the radicals in order to obtain a correct spin density distribution was demonstrated for the first time[48]. The "bond length–bond order" formula and the linear relation between the resonance integral β and the bond length, $\beta = \beta_0 + \delta(R - R_0)$, were used for this purpose in the

Hückel approximation. It was found that the exponential relation [49]

$$\beta = \beta_0 \exp[a(R_0 - R)] \qquad (11)$$

frequently leads to an incorrect spin density distribution in radicals with long and short bonds (from 1.45 to 1.20 Å). For example in the radical $C_{(1)}H_2-C_{(2)}\equiv C_{(3)}H$ the ratio of the spin densities at the $C_{(1)}$ and $C_{(3)}$ atoms is

$$\rho_1^\pi/\rho_3^\pi = (\beta_{23}/\beta_{12})^2$$

and Eqn. (11) leads to a very high value of this ratio, in conflict with experiment [48]. The region of applicability of Eqn. (11) is limited to small changes in bond lengths, were the exponential relation barely differs from a linear relation.

For aromatic radicals, where all the $R \simeq R_0 = 1.4$ Å, the influence of differing bond lengths on the spin density distribution was not studied systematically. Nevertheless allowance for the real geometry of the radicals can alter the calculated ρ_i^π by 5–10%. This remark applies not only to the Hückel method but also to other methods in which the interaction between electrons is taken into account.

The Hückel method yields satisfactory relative values of not unduly small spin densities ρ_i^π, but fails to predict small (positive and negative) values of ρ_i^π. A negative spin density appears as a result of the repulsion of π electrons with opposed spin projections, which can accumulate at different atoms and lead to a pattern of alternating signs of the spin density at neighbouring atoms. Therfore, in order to describe such spin density distributions, it is necessary to take into account explicitly the interaction of π electrons. The changes in spin density $\Delta\rho_i^\pi$ due to inclusion of the π-electron interaction are as a rule small ($|\Delta\rho_i^\pi| < 0.1$), which accounts for the relative success of the Hückel method.

b. Methods with Different Molecular Orbitals for Different Spins. Projection of the Wave Functions on to States with a Correct Total Spin

In order to take into account the electron interactions, it is reasonable to employ the SCF method with different molecular orbitals for electrons having different spins [50–55]. In this method two electrons with opposite spins do not occupy the same molecular orbital (as in the simple SCF method) but two different molecular orbitals. As a result, an electron having one spin is largely located at one set of atoms in the molecule, while an electron having another spin is located at another set of atoms. Owing to the decrease of the Coulomb interaction energy of these electrons, the total energy of the molecule is lower than in the simple molecular orbital method [50,51]. The method using different molecular orbitals for different spins is equivalent to the method of interacting configurations and is used to calculate the electronic structures of conjugated molecules [56]. Its application to conjugated radicals provides a natural explanation of the appearance of negative spin densities in the system.

One of the variants of this method is called the unrestricted Hartree–Fock method (UHF). The wave function of the radical in the UHF method (one Slater determinant of molecular spin orbitals) consists of a superposition of functions for different spins and can be represented as follows:

$$\Phi = \sum_{S=1/2}^{N/2} a_S \Phi_{1/2}^S, \qquad (12)$$

where $\Phi_{1/2}^S$ are orthonormalised functions which are the eigenfunctions of the operator of the square of the total spin $\hat{S}^2$ with eigenvalues $S(S+1)$ and the operator of the projection of the total spin $\hat{S}_z$ with $S_z = 1/2$. In order to separate the components having the spin $S = 1/2$ (the radicals have a doublet ground state) from Eqn. (12), a fairly cumbersome spin projection operation is necessary. The application of the operator [57]

$$O_{1/2} = \prod_{k\,(\neq 1/2)}^{N/2} [k(k+1) - \hat{S}^2]$$

to function (12) eliminates all terms except $a_{1/2}\Phi_{1/2}^{1/2}$. The operator $\hat{S}^2$ for a system of N electrons is

$$\hat{S}^2 = -\frac{1}{4}N(N-4) + \sum_{i<j}^{N} P_{ij}^\eta,$$

where P_{ij}^η interchanges the spin coordinates of the electrons i and j.

In view of the complexity of the projection operation, it has been suggested [58,59] that one excludes from function (12) only the quartet component ($S = 3/2$), which apparently makes the next highest contribution to the function Φ after the component with $S = 1/2$. The quartet is annihilated by the operator

$$\hat{A} = \hat{S}^2 - 15/4.$$

The closeness of the average value of $\langle\Phi|S^2|\Phi\rangle$ to $3/4 = S(S+1)$ for $S = 1/2$ can serve as a criterion of the closeness of the function Φ to the doublet state. Usually $\langle\Phi|S^2|\Phi\rangle > 3/4$ and the annihilation of the quartet reduces the average value of $\hat{S}^2$. However, it has been shown [60] that in certain cases the mean $\hat{S}^2$ increases after the annihilation of the quartet. The observed ineffectiveness of the annihilation of the quartet depends on the choice of the parameters of the PPP Hamiltonian [60].

The UHF method and the UHF method with partial annihilation are fairly complex and the results obtained for the distribution of spin density are so far only qualitatively consistent with one another and with the results of calculations with complete allowance for the interaction of π electrons (Table 4).

In certain cases, particularly in analytical calculations for large molecules with a regular structure, another technique of projecting the wave function on to a state with a correct total spin is more convenient [61–63]. This technique employs the operator of a finite rotation in spin space by the Eulerian angles $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\gamma}$:

$$\hat{R} = \exp(-i\hat{S}_z\tilde{\alpha}) \cdot \exp(-i\hat{S}_y\tilde{\beta}) \cdot \exp(-i\hat{S}_z\tilde{\gamma}).$$

The action of the operator $\hat{R}$ on the function Φ_m^S, the eigenfunction $\hat{S}^2$, and $\hat{S}_z$ (with a spin S and its projection $S_z = m$) is defined by the formula

$$\hat{R}\Phi_m^S = \sum_{n=-S}^{S} D_{nm}^{(S)}(\tilde{\alpha}\tilde{\beta}\gamma)\,\Phi_n^S, \qquad (13)$$

where $D_{nm}^{(S)}(\tilde{\alpha}\tilde{\beta}\tilde{\gamma})$ is the Wigner D-function [64]. D-Functions possess the property of orthogonality, which is important for our problem:

$$\int_0^{2\pi} d\tilde{\alpha} \int_0^{\pi} d\tilde{\beta}\sin\tilde{\beta} \int_0^{2\pi} d\tilde{\gamma}\, D_{nm}^{(S)}(\tilde{\alpha}\tilde{\beta}\tilde{\gamma})\, D_{n'm'}^{(S')*}(\tilde{\alpha}\tilde{\beta}\tilde{\gamma}) = \frac{8\pi^2}{2S+1}\delta_{SS'}\delta_{nn'}\delta_{mm'}. \qquad (14)$$

We allow the operator $\hat{R}$ to act on the function Φ [Eqn. (12)]. Using Eqn. (13), we obtain

$$\hat{R}\Phi = \sum_{S_1=1/2}^{N/2} a_{S_1} \sum_{n=-S_1}^{S_1} D_{n1}^{(S_1)}(\tilde{\alpha}\tilde{\beta}\tilde{\gamma})\,\Phi_n^{S_1}. \qquad (15)$$

We multiply both sides of Eqn. (15) by $D^{(S)}_{S_{Z1/2}}(\tilde{\alpha}\tilde{\beta}\tilde{\gamma})$ and integrate with respect to all the angles, as in Eqn. (14); then, using Eqn. (14), we obtain

$$a_S\Phi^S_{S_z} = \frac{2S+1}{8\pi^2}\int_0^{2\pi} d\tilde{\alpha}\int_0^{\pi} d\tilde{\beta}\sin\tilde{\beta}\int_0^{2\pi} d\tilde{\gamma}D^{(S)*}_{S_z{}^1/_2}(\tilde{\alpha}\tilde{\beta}\tilde{\gamma})\hat{R}\Phi \quad . \qquad (16)$$

In order to isolate the doublet component, it is necessary to put $S = S_Z = 1/2$. In principle, Eqns. (16) can be used also in calculations on molecules employing different variants of the method with different molecular orbitals for different spins (see, for example, Refs. 61–64).

c. McLachlan's Method

Since the changes in the spin densities $\Delta\rho_i^{\pi}$ due to the inclusion of the interelectron interaction in polyatomic radicals are small compared with unity, one can employ perturbation theory in order to take into account the effect of electron interactions on the distribution of spin density. Instead of a complete solution of the SCF equations in the UHF method, McLachlan [65] employed the perturbation theory and obtained an approximate formula for the spin density. The spin density of the π electrons in the atom i is given by the formula [65]:

$$\rho_i = \rho_i^{\circ} - \lambda\sum_k \pi_{ik}\rho_k^{\circ}, \qquad (17)$$

where π_{ik} is the coefficient of the mutual polarisability of the atoms i and k, $\rho_i^{\circ} = |c_i^{\circ}|^2$ is the spin density calculated by the Hückel method (c_i° is the coefficient of the molecular orbital of the unpaired electron of the atom i in the Hückel method), and $\lambda \simeq \gamma_{11}/2|\beta| \simeq 1.2$ is an empirical constant.

There are several modern schemes based on the McLachlan method for hydrocarbons [43] which lead to a satisfactory agreement with experiment when McConnell's formula is used to calculate the hyperfine splittings.

McLachlan's method has been used successfully to calculate the proton, ^{13}C, and ^{14}N splittings in compounds with heteroatoms, In order to calculate the ^{13}C and ^{14}N splittings, McConnell's formula [Eqn. (8)] was modified by adding contributions proportional to the spin densities at the neighbouring atoms [45–47]. For example the formula

$$a_N = 23.1\rho_N - 6.3\rho_C \qquad (18)$$

is used to calculate the hyperfine splitting constant for nitrogen in the cyano-group C≡N. Similar formulae are used also for other hyperfine splittings [66]. Empirical formulae of type (18) are very similar to Eqn. (10), which constitutes a generalisation of the McConnell and Colpa–Bolton formulae for hydrocarbons: the mutual influence of atoms is taken into account in these formulae.

A paradoxical situation existed for some time: calculations of hyperfine splittings for compounds with heteroatoms by McLachlan's method [45–47] agreed better with experiment than calculations by the UHF method or the SCF method in the multi-configuration approximation [39], despite the fact that McLachlan's method is an approximation to the UHF method.

The situation became clarified after the calculation by the UHF method (with annihilation of the quartet) using the parameters of the PPP Hamiltonian which reproduced satisfactorily the excitation and ionisation energies of the corresponding molecules [66]. It was found that in this case the agreement with experiment is better than in McLachlan's method: the average deviation from the experimental values of the hyperfine splitting proved to be ±0.59 G, while in McLachlan's method the average deviation was ±0.86 G. [46,47] In this calculation [66] new values of the parameters in the formulae for the splittings were selected. The high effectiveness of the annihilation of the quartets was noted, probably by virtue of a successful choice of the PPP Hamiltonian parameters: the mean values of $\hat{S}^2$ after annihilation differed from the exact value for the doublet (0.75) only in the third decimal place [66]. This example yet again demonstrates the necessity for employing sets of parameters adjusted for consistency in semiempirical calculations.

d. Calculations with Partial and Full Configuration Interaction

Kuprievich et al. [40] calculated the spin structure of the benzyl radical by the SCF method with subsequent inclusion of singly excited, doubly excited, ect. configurations until all the configurations (404) for the ground state were included, i.e. complete account was taken of the interaction of π electrons. The results of the calculation are presented in Table 5, which shows that the spin densities calculated taking into account all possible configurations are reproduced with satisfactory accuracy (to within ≤ 10%) when account was taken of singly excited configurations only. In this connection we may note the satisfactory qualitative and quantitative agreement with experiment obtained in SCF calculation of the spin structure of radicals which include the configurations of the ground state and all singly excited configurations [37,39]. We may note that in the above studies use was made of both molecular orbitals adjusted for consistency and of Hückel molecular orbitals, which are fairly close to one another and which led to similar spin densities.

Table 5. The spin structure of the benzyl radical in terms of the configuration interaction method [40].

No. of atom	Spin densities			
	ground state (GS) and single excitations (15 configurations)	GS and single and double excitations (89 configurations)	GS and single, double, and triple excitations (239 configurations)	full configuration interaction (404 configurations)
7	0.706	0.741	0.722	0.724
1	−0.095	−0.100	−0.110	−0.112
2	0.174	0.165	0.183	0.183
3	−0.058	−0.058	−0.069	−0.070
4	0.156	0.146	0.161	0.161

Calculations taking into account all possible excited configurations (full configuration interaction) have been carried out also in other studies [41]. The spin densities calculated for certain radicals by different methods are compared in Table 4 with the values calculated allowing for the full configuration interaction.

5. CERTAIN RECENT METHODS FOR THE CALCULATION OF THE ELECTRONIC STRUCTURES OF MOLECULES OTHER THAN THE PARISER–PARR–POPLE METHOD

a. The Method of "Molecules in Molecules"

In calculations on large conjugated molecules consisting of several fragments linked by one or two bonds the method of "molecules in molecules" (MIM) has been used successfully. As a rule, the absorption spectra of such a molecule contain lines and bands characteristic of the isolated fragments. This serves as a "criterion" for the application of the MIM method.

In the MIM method one calculates initially (the electronic structures of the individual fragments (for example by the PPP method). The wave function of the entire molecule is constructed as a superposition of the product of the wave functions of the fragments, the ground and several excited states of each fragment and the state with charge transfer from one fragment to another being considered. The total number of configurations of this kind involved in the construction of the wave function is much smaller than in calculations on the molecule by the PPP method. The results of the calculation agree with experiment just as well as the complete calculation by the PPP method. This was demonstrated, for example, in the calculation on decacyclene (36 atoms), which consists of three fragments—acenaphthylene molecules (12 atoms)[67]. The general postulates of the theory of the MIM method have been described together with a brief survey of the literature by von Niessen[68].

The MIM method has been used[69] for calculations on the $S-T$ and $T-T$ transitions in aromatic molecules. In these calculations the experimental energies were used for the fragments (for the corresponding matrix elements of the Hamiltonian) instead of the energies calculated by the PPP method, as in the study of Brugmann et al.[67] This led to a satisfactory agreement with experiment. Thus use was made of the old idea put forward by Moffitt[70,71] (on which the method of "atoms of molecules" is based), who employed the experimental energies for the atoms (O, N, etc.) in calculations on the molecules (O_2, N_2, etc.).

b. The Random Phase Approximation and the Multi-configuration Interaction Method

Mestechkin[72-74] used successfully the approximation of random phases (in the semiempirical version for conjugated systems using the technique of density matrices) to calculate the electronic structures of condensed aromatic molecules[72-74]. A special parametrisation scheme was used which, as we have seen, is reasonable for various methods in the semiempirical theory. As a result, it was possible to calculate the positions of the triplet levels to within about 0.1 eV (for the lowest levels) and with a somewhat poorer accuracy for the highest levels.

In the random phase approximation configurations are taken into account in a compact form and the configurations themselves do not arise explicitly. If the same configurations were considered explicitly, then in principle the calculation would be more accurate, although it would be much more laborious and time consuming.

The condition for the applicability of the random phase approximation is the smallness of the relative changes in the π-electron density at the atom on excitation of the molecule, namely[75]

$$\Delta q_l/q_l \ll 1 \quad \text{or} \quad \Delta q_l \ll 1\,, \tag{19}$$

since the π-electron densities at atoms in conjugated molecules are $q_l \simeq 1$. The greater the charge redistribution in the molecule, i.e. the greater the Δq_i, the higher the excitation energy. Therefore the accuracy of the random phase approximation falls for high excitation energies. A similar criterion of the applicability of the random phase approximation (spin densities much less than unity) exists also for triplet excitations[75].

The random phase approximation has so far been rarely used to investigate conjugated systems[72-80]. Therefore the scope of the method has still not been fully explored.

The same remark holds also for the multi-configuration interaction method (MCI). In the MCI method the wave function of the system Φ is constructed as a superposition of several (n) configurations Φ_i (each configuration consists of a Slater determinant comprising molecular spin orbitals):

$$\Phi = \sum_{i=1}^{n} c_i \Phi_i.$$

The coefficients c_i and the coefficients of the linear combinations of molecular orbitals used to construct the Φ_i are found by a special procedure. This yields both the function of the ground state (with the coefficients c_i^0) and the functions of the n-1 excited states (with the coefficients c_i^k, $k = 1, 2, \ldots, n$-1).

The MCI method is used to calculate various molecular characteristics, including the distributions of spin densities in radicals[38]. Different versions of the MCI method have been developed by Japanese[81] and Soviet[82] investigators.

The MCI method resembles somewhat the MIM method and the random phase approximation. As in the random phase approximation, account is taken in the MCI method of the interaction of π electrons and of excited configurations, but the contributions of these configurations are calculated exactly and the number of configurations is small; as in the MIM method, the configurations are selected on the basis of simple considerations (for example, on the basis of their energies, on symmetry grounds, etc.).

c. The Method of Full Configuration Interaction

Calculations with full allowance for the interaction of π electrons, with full configuration interaction, occupy a special place in the theory of conjugated systems. If we are interested in all the energy levels and all the properties of the system, the method of full configuration interaction is equivalent to the problem of the determination of these properties. Then, using the same effective parameters of the model π-electron Hamiltonian to describe all the properties of the molecule, we can detect the inaccuracies of the π-electron approximation itself. Calculations with full configuration interaction are interesting not only as a method for the complete investigation of the system properties but mainly because such calculations reveal the scope of various approximate methods.

The method of calculation with full configuration interaction proposed by the present authors[75,83,84] is very convenient for the ZDO approximation when the PPP

Hamiltonian is used. In this method [84] the wave function Φ for the system of N electrons is expressed in the form

$$\Phi = \sum_{i=1}^{l_S^N} \psi_i(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\theta_i(\eta_1\eta_2 \ldots \eta_N),$$

where the spin functions θ_i are defined by the spin state of the system and the coordinate functions ψ_i are expressed as an expansion in products of the atomic orbitals $\varphi_n(\mathbf{r})$:

$$\psi_l = \sum_{n_1=1}^{K}\sum_{n_2=1}^{K} \ldots \sum_{n_N=1}^{K} c_l(n_1 n_2 \ldots n_N)\varphi_{n_1}(\mathbf{r}_1)\varphi_{n_2}(\mathbf{r}_2) \ldots \varphi_{n_N}(\mathbf{r}_N),$$

where K is the number of different atomic orbitals [the dimension of the basis set $\varphi_n(\mathbf{r})$]:

$$l_S^N = \frac{(2S+1)\cdot N!}{(N/2+S+1)!\,(N/2-S)!},$$

where S are the spin states.

The requirement that Φ be antisymmetric with respect to interchange of the particles (the Pauli principle) and allowance for molecular and spin symmetry decrease the number of unknown coefficients $c_i(n_1 n_2 \ldots n_N)$ and establish simple linear relations between the latter. These relations reduce the large number of coefficients $c_i(n_1 n_2 \ldots n_N)$ to a comparatively small number M of unknown coefficients which can be found from the Schrödinger equation $H\Phi = E\Phi$ or $H\psi_i = E\psi_i$, where H is the Hamiltonian of the system and E the total energy.

The required matrix $H_{\mu\nu}$ for the secular equation can be found in the simplest possible way by a sequence of simple operations [84]. The degree of this secular equation, obtained as a result of the variation of the average total energy with respect to M unknown coefficients, is equal to the number of all the configurations μ, ν, ..., possible for the given state. A characteristic feature of this method of allowance for all configurations [84] is that, owing to the ZDO approximation, the PPP Hamiltonian has the following features: (1) the off-diagonal elements $H_{\mu\nu}$ consist of simple linear combinations of resonance integrals β_{mn} or are zero; (2) the number of zero elements $H_{\mu\nu}$ is several times greater than that of the non-zero elements; (3) the diagonal elements $H_{\mu\mu}$ consist only of linear combinations of the parameters α_m and γ_{mn} and such combinations can be calculated very simply.

These characteristics of the matrix $H_{\mu\nu}$ make it possible to reduce the problem of full configuration interaction for a system of N electrons (with $N > K$) to the simpler problem of total configurational interaction for a system of $2K-N$ particles (holes). In this change from electrons to holes the off-diagonal $H_{\mu\nu}$ are not altered and the new $H_{\mu\mu}$ are calculated according to the same simple rules. For example, the full configuration interaction for thiourea $CS(NH_2)_2$ constitutes a two-electron problem involving a basis set of four molecular orbitals, while the PPP method constitutes a six-electron problem with the same basis set (two π electrons are contributed by each N atom and the C and S atoms each contribute one π electron).

The results of calculations on ethylene, the allyl radical and radical-ions, butadiene, and benzene with full configuration interaction have been compared with the experimental values and the results of calculations by the PPP method [84]. It was found that (1) the correlation energy E_{corr} (i.e. the difference between the energy of the ground state found with full configuration interaction and the energy of the ground state found by the PPP method) is given approximately by the relation

$$E_{corr.} \approx -(0.11 \div 0.13)\cdot N(\text{eV})$$

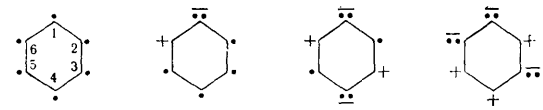
(this relation holds also for the benzyl radical [40]); (2) the optimum values of the parameters of the model Hamiltonian in the PPP method and in the method with full configuration interaction differ appreciably (Table 6). This confirms the view that the disadvantages of the approximate method are transferred to the effective parameters and the latter are therefore different for different methods.

Table 6. The excitation energies of benzene (PPP and full configuration interaction methods) [84] (eV).

Parameters	Method	Designation of energy state				
		$^1A_{1g}$	$^3B_{1u}$	$^1B_{2u}$	$^1B_{1u}$	$^1E_{1u}$
I	PPP	0 (−12.85)	3.7	4.8	5.9	6.75
	full CI	0 (−13.64)	3.35	4.1	6.2	5.07
II	PPP	0 (−15.5)	4.36	5.43	5.57	6.87
	full CI	0 (−16.17)	4.1	4.83	5.8	6.7
Experiment		—	3.7	4.8	5.9	6.76

I $\beta = -2.4$ $\gamma_{11} = 6.1$ $\gamma_{12} = 2.1$ $\gamma_{13} = 0.7$ $\gamma_{14} = 0$
II $\beta = -2.6$ $\gamma_{11} = 4.64$ $\gamma_{12} = 1.39$ $\gamma_{13} = \gamma_{14} = 0$

The covalent-ionic structure of the wave functions of benzene has also been studied [75,83,84]. Components with the coefficients $c_i(n_1 n_2 \ldots n_6)$, in which all the indices n_m are different, correspond to covalent structures in the function Φ; for unipolar structures, the coefficients have a single pair of identical indices (for example, $n_1 = n_2$); for dipolar structures, there are two pairs of indices ($n_2 = n_5$, $n_3 = n_6$), etc. Benzene structures with different polarities (with an indication of the atomic charges) are quoted below as an example:



The dots in the formulae denote π electrons. Non-zero coefficients of the type $c(123\,456)$, $c(112\,345)$, $c(124\,541)$, and $c(131\,366)$ correspond to these structures.

Table 7. Relative contributions (%) of covalent and polar (ionic) structures to the wave functions of certain benzene energy states [75,84].

Energy state, method of calculation		Type of structure			
		covalent	unipolar	dipolar	tripolar
$^1A_{1g}$	full CI	14.7	48.6	32.6	4.1
$^1A_{1g}$	Hückel method	7.9	42.7	42.4	7
$^3B_{1u}$	full CI	31.6	51.7	16.7	—

It was found that the polar structures make the main contribution to the ground state of benzene (see Table 7).

The contribution of each part of the function to the energy is approximately the same. Indeed calculation of

the energy of the ground state of benzene without vibrational structures (with polar structures alone!) increased the energy of the ground state (bond energy −16.17 eV) by only 2.3 eV. It is interesting to note that the contribution of covalent structures to certain excited states can increase [$^3B_{1u}$, the lowest benzene triplet (Table 7)] or can be rigorously equal to zero (for the $^1B_{1u}$ and $^1E_{1u}$ energy states of benzene).

Thus we conclude that structures of different polarity play different roles in the formation of different energy states. If we begin with the approximation in which structures of some kind are neglected, we shall be making different errors for different energy states. The non-uniformity of the contributions of different types of structures to different energy states and different properties can be used in calculations to reject insignificant structures.

These conclusions concerning the structure of the wave function demonstrate the lack of validity of the valence bond methods in which the role of covalent structures is overestimated.

The large contribution of polar (ionic) structures to wave functions is a consequence of the relative weakness of the Coulomb repulsion of π electrons in conjugated systems. In this connection it is interesting to note that, in the calculation on the ground state of benzene by the Hückel method (all the $\gamma_{mn} = 0$), the covalent-ionic structure of the wave function is reproduced correctly (Table 7). This is also a consequence of the relative weakness of the Coulomb interaction of π electrons and at the same time throws light on the relative success of the Hückel method in the calculation of certain properties of conjugated molecules and radicals.

d. The Hückel Method

Despite the development of various methods for calculations on conjugated systems, the simple Hückel molecular orbital method still retains its value and is frequently used. The Hückel method yields results which agree adequately with experimental data. This applies both to the properties of the ground state (bond lengths, charge densities, and spin densities) and to singlet excitation energies[9,85], ionisation potentials and electron affinities[86], and other properties of conjugated molecules[87]. The results of calculations on a large number of conjugated hydrocarbons by the Hückel method (molecular orbital coefficients and energies, bond orders, polarisabilities, etc.) have been tabulated[88,89]. Using these data for hydrocarbons the special perturbation theory of Coulson and Longuet-Higgins[88,89] greatly simplifies calculations, on the analogous molecules with heteroatoms.

Various versions of the Hückel method have been examined and analysed by Peacock[87]. Among other problems, he considered certain possibilities of improving the Hückel method based on known relations between Coulomb (α_n) and resonance (β_{mn}) integrals of the Hückel method on the one hand and the parameters of the effective PPP Hamiltonian on the other. The Hückel and PPP methods were compared in relation to a number of examples with analysis of the differences between the predictions of various molecular properties[86,87,90]. In particular, the inductive effect of π electrons can also be incorporated in the Hückel method using the so called ω technique (see, for example, Ehrenson[86]). This technique is analogous to the method whereby the inductive effect of electrons is taken into account in Scheme 2 of the PPP method (see the previous review[1]).

The Hückel method is also used to simplify calculations by the PPP method. One then employs the fact that self-consistent molecular orbitals are close to the molecular orbitals of the Hückel method. This makes it possible to use the Hückel molecular orbital method with the formal procedures of the PPP method to construct the excited configurations with subsequent determination of the excitation energies, etc. by the PPP method. Such a computational method has been used both for hydrocarbons[13] and for heterocycles[90].

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In conclusion we must mention that by no means all problems of the theory of conjugated systems have been considered here and in the previous review[1]. We may mention, for example, the theory of large conjugated systems, the theory of the reactivities of conjugated systems, and other problems which are important for the interpretation of experiments.

Examination of the vast quantum-chemical field which constitutes the semiempirical theory of conjugated systems is very difficult if only because the relevant research itself has not been completed. Therefore, in writing this review the authors frequently wished to postpone it and to undertake the development or simply the confirmation of certain aspects of the theory. If similar thoughts have also occurred to the reader, we can regard our task as fulfilled.

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