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The Structure of the Electronic Excitation of Molecules in Quantum-chemical Models

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Methods for the analysis of the excited states of molecules and their electronic distribution are examined. The advantages of using procedures based on transition density matrices are noted. The application of the delocalisation numbers of the transition, reflecting the multiconfiguration nature of the electronically excited state, the excitation localisation numbers, providing a quantitative measure of the localisation of the transition in a particular molecular fragment, the interfragment charge transfer numbers, the atomic excitation energy indices, indicating the fraction of the molecular excitation energy which can be assigned to a given atom, etc., all of which have been introduced recently, are discussed. The structural-chemical factors favouring the isolation of the excitation of a single fragment are considered.
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I. INTRODUCTION

The theoretical and applied aspects of molecular spectroscopy have been closely related for a long time to quantum-chemical studies on the excited states of molecules. The role of theory in the interpretation of spectroscopic experiments, which are so common in modern physicochemical research techniques, still remains important. The experimental difficulties in the direct estimation of the parameters of the electronic structure, which determine the real behaviour of molecular systems, are not the only explanation. In this field many fundamental concepts follow naturally primarily from the theory which permits, in principle, the understanding of all the details of the behaviour of the electron shell in any of its states and sometimes even in states which are not observed.

Such claims do not imply in any way that all the fundamental problems of the theory of molecules have already been solved. The obstacles to the determination of detailed electronic-nuclear wave functions are generally known. However, intensive use of approximate quantum-chemical models has undoubtedly played a positive role in the understanding of the excited state by workers in the field of spectroscopy as a tangible feature with a specified internal structure, which can be inferred from the corresponding wave function. The latter is usually represented by a fairly complex set of the coefficient $c_{\mu i}$ of the expansion of the molecular orbitals, the coefficients d_{pi} of the configurational interaction, etc. Unfortunately, the abundance of numerical data frequently conceals from the investigator the very structure for the investigation of which the entire computation has been undertaken. Furthermore, the idea of the delocalisation of electrons, which is natural for quantum mechanics as a whole, at one time in the past made it impossible for chemists to see the familiar autonomy of the fragments of complex molecules. In this connection, many theoreticians attempted, while retaining the quantum-chemical rules of construction, to interpret excited and other electronic molecular states in terms of the more readily understood terms of localisation, charge transfer, etc.[1-6] However, in this field, which is so important for the understanding of the nature of the electronic spectra of complex molecules, rigorously proved criteria or quantitative characteristics had not been developed until recently. In the present review an attempt is made to consider the tendency, established in recent years, to carry out such analysis on the basis of a structural-chemical interpretation of the excited states of molecules.

II. THE INTERACTION OF THE CONFIGURATIONS AND THE TRANSITION OPERATORS IN THE THEORY OF ELECTRONIC SPECTRA

The methods used hitherto in calculations on large organic molecules and in the interpretation of their spectroscopic properties have been discussed in detail in monographs[7-12] and in a review[13]. Here we shall consider only comparatively new methods of calculation using the transition density matrix, which will prove to be the main instrument in the version of the analysis of the excited states to which we shall give preference.

The wave function $|\Phi>$ of the ground state of the molecule must be constructed with obligatory allowance for the electron–electron interaction. In the Hartree–Fock model, which has served as a standard hitherto, this is achieved by representing $|\Phi>$ in terms of a determinant of occupied molecular spin-orbitals $|\phi_1>, \ldots |\phi_i>, \ldots |\phi_N>$. Then, according to the Brillouin theorem[14], any determinant $|\Phi_{i\to p}>$, obtained from $|\Phi>$ by replacing a self-consistent spin-orbital $|\phi_i>$ by a vacant spin-orbital $|\phi_p>$, has zero matrix elements of the Hamiltonian H with the ground state $|\Phi>$:

$$\langle\Phi|H|\Phi_{i\to p}\rangle=0; \quad p=N+1, \ldots, M, \tag{1}$$

where M is the dimension of the spin-orbital basis set. Consequently the set of all the functions $|\Phi_{i\to p}>$ can be regarded as a basis set of N electronic functions on which the space of all possible excited states $|\Phi_*>$ has been superimposed

and, by virtue of Eqn.(1), the fulfilment of the natural condition of "excitation" is guaranteed for the latter:

$$\langle\Phi|H|\Phi_*\rangle=0. \quad (2)$$

After finding the self-consistent orbitals of the ground state, it is easy to achieve a configurational mixing of the type

$$|\Phi_*\rangle=\sum_{i=1}^{N}\sum_{p=N+1}^{M} d_{pi}|\Phi_{i\to p}\rangle, \quad (3)$$

which yields an approximation to the excited state made consistent with the Hartree–Fock description of the ground state $|\Phi\rangle$. The configurational coefficients d_{pi} as well as the excitation energy λ are then found from the secular equations for the configurational interaction matrix $||\langle\Phi_{i\to p}|H|\Phi_{j\to q}\rangle||$. This model of the excited state will be called the Tamm–Dancoff model, as is usually done in modern investigations of molecular theory (see, for example, Refs. 15–17) and the theory of the nucleus[18]. The semiempirical version of this model for π-electron systems is associated with the familiar studies by Pariser, Parr, and Pople and is also referred to as the PPP model, which has been discussed in detail[7,11,13].

PPP calculations on the electronic states of organic molecules are widely used at the present time, which is also due to the relative simplicity of the relevant computer programs[19,20]. Subsequently, in many instances, particularly for triplet energy states, attempts have been made to improve the results of the calculation by including higher doubly excited $|\Phi_{\substack{i\to p\\ j\to q}}\rangle$ configurations,[21–23] and even triply excited configurations[24].

New approaches based on the application of the transition density matrix have been used[25–29]. An equation for the Hermitian transition density matrix D in terms of the Tamm–Dancoff approximation, convenient for computational purposes, has been formulated[26]. Its spin-orbital generalisation can be represented[29] with the aid of the operator modulus of the Fock operator f and a projected antisymmetrised potential of the Coulombic interaction of the electrons g^A (12):

$$u(12)=\rho(1)\rho_\ominus(2)g^A(12)\rho_\ominus(1)\rho(2)+\rho_\ominus(1)\rho(2)g^A(12)\rho(1)\rho_\ominus(2), \quad (4)$$

where $\rho=\sum_{i=1}^{N}|\phi_i\rangle\langle\phi_i|$ is the density matrix of the ground Hartree–Fock state $|\Phi\rangle$, and $\rho_\ominus=\sum_{p=N+1}^{M}|\phi_p\rangle\langle\phi_p|=1-\rho$ is a matrix projected on to vacant one-electron states. The superoperator $\hat{\Pi}$, which generates another operator by acting on an operator D in accordance with the rule

$$\hat{\Pi}(D)=D\cdot|f|+|f|\cdot D+2\operatorname{Sp}_{(2)}u(12)D(2), \quad (5)$$

is introduced by means of these quantities.

The fundamental equation of the Tamm–Dancoff model can then be formulated in terms of the equations for the eigenvalues of the superoperator $\hat{\Pi}$, each eigenvector of which plays the role of a transitional matrix D of an excited state. The eigenvalue of the superoperator $\hat{\Pi}$ is the excitation energy λ:

$$\hat{\Pi}(D)=\lambda D. \quad (6)$$

The transition matrix D permits a representation of the type

$$D=\sum_{i=1}^{N}\sum_{p=N+1}^{M}(d_{pi}|\varphi_p\rangle\langle\varphi_i|+d_{pi}^{*}|\varphi_i\rangle\langle\varphi_p|), \quad (7)$$

where d_{pi} can be regarded as the configurational coefficients of the excited state $|\Phi_*\rangle$ of the type of Eqn.(3).

In the construction of $|\Phi_*\rangle$ condition (2) is not the only possible requirement, particularly since the approximation to the ground state $|\Phi\rangle$ does not as a rule satisfy the exact Schrödinger equation. For example, in the method based on the equations of motion without an explicit construction of a wave function for the ground state more accurate than the Hartree–Fock function it is possible to take into account, particularly in the calculation of the oscillator strengths, the correlation effects in the excited states which are not included in the Tamm–Dancoff method[30]. However, the lack of explicit wave functions or correct density matrices corresponding to them precludes in this instance a well-founded analysis of the excited states. Another approach to the construction of $|\Phi_*\rangle$ can be devised on the basis of a self-consistent perturbation theory, various aspects of which have been discussed[11,29,31].

The general relations of the quantum-mechanical perturbation theory contain the so-called energy denominators, which in the case of a perturbation of the ground state have the values of the excitation energies. Indeed, for the first correction $|\delta\Phi\rangle$ to the wave function $|\Phi\rangle$ arising from the perturbation δH, one can write (E is the energy of the system and I a unit operator)

$$(H-E)|\delta\Phi\rangle=-(I-|\Phi\rangle\langle\Phi|)\delta H|\Phi\rangle. \quad (8)$$

Here $H-E$ is the excitation operator with the eigenvalues $\lambda=E_*-E$. After reducing formula (8) to one-electron quantities, the operator $H-E$ is transformed into the superoperator $\hat{\Lambda}$ and the correction $|\delta\Phi\rangle$ is replaced by the one-electron transition operator corresponding to the N-electron Hermitian operator $|\delta\Phi\rangle\langle\Phi|+|\Phi\rangle\langle\delta\Phi|$.

The explicit form of the superoperator $\hat{\Lambda}$ for singlet states has been obtained[26]. Its relation with the random phase approximation, which constitutes a special case of the method of equations of motion, has been discussed[32,33]: on this basis, the theory of spin perturbations has been developed[34] and a perturbation theory has been devised for open shells in the unrestricted Hartree–Fock method[35]. The spin–orbital definition of $\hat{\Lambda}$ is similar in form to the formulation of the superoperator $\hat{\Pi}(5)$, but the potential $u(12)$ is now replaced by the half-sum $\frac{1}{2}[u(12)+v(12)]$, where $v(12)$ is a correlation operator describing particle–hole pair interactions of the electrons in the $|\phi_p\rangle$ and $|\phi_i\rangle$ states:

$$v(12)=\rho(1)\rho(2)g^A(12)\rho_\ominus(1)\rho_\ominus(2)+\rho_\ominus(1)\rho_\ominus(2)g^A(12)\rho(1)\rho(2).$$

The operator $v(12)$ is encountered in calculations on the correlation interaction, since it is in fact responsible for the mixing of $|\Phi\rangle$ with the doubly excited configurations, for the superposition of $|\Phi_*\rangle(3)$ on $|\Phi_{\substack{i\to p\\ j\to q\\ k\to r}}\rangle$, etc.[29,36] The presence of an additional term of this kind in the expression for $\hat{\Lambda}$ therefore indicates an indirect, average allowance for the correlations in relation to the Tamm–Dancoff approximation, although the number of variational parameters (the coefficients d_{pi}) is the same in the two instances. At the same time, for the functions $|\Phi_*\rangle$, constructed with the aid of $\hat{\Lambda}$, the explicit wave function parameter remains in the form of the same operator D, which carries all the necessary information about the excited state, constituting a superposition of singly excited configurations (3). As a result of this, the analysis of $|\Phi_*\rangle$ for the $\hat{\Pi}$ and $\hat{\Lambda}$ versions can be carried out in the same way.

The $\hat{\Lambda}$ matrix had previously been introduced in a different form by Thoules[37] in connection with the introduction into the self-consistent field theory of the concept of stable and unstable solutions which do and do not require respectively a local minimum in the Hartree–Fock energy E. A stable

solution arises only for a rigorously positive quadratic form made up of local second derivatives of E with respect to the parameters for small deviations from the self-consistent solution. The matrix of this quadratic form, which corresponds to the variational derivative $\delta^2 E/\delta\rho^2$, is the same as the supermatrix $\hat{\Lambda}$, and its eigenvalues λ, which appear as energy denominators in the perturbation theory, are therefore at the same time stability numbers of some kind for the Hartree–Fock model.

It has been suggested that in the case of closed electron shells the stability numbers for spin-free distortions of $|\Phi>$ be identified[26] with the singlet excitation energies and that in the case of triplet states the Tamm–Dancoff description be retained, which can be justified to some extent by taking into account the tendency not to change the spin properties of a triplet wave function[29]. However, it is easy to find all the spectroscopic series (singlet–singlet, triplet–triplet, transitions, etc.) solely with the aid of stability numbers, adopting in each case the lowest state of the specified multiplicity as the ground state for the given series.

Such calculations can be most simply carried out with the aid of the unrestricted Hartree–Fock method, as suggested by the present author and Umanskii[35,38]. For example, with the same parametrisation, it is possible to calculate satisfactorily the singlet–singlet transitions in many aromatic molecules with the aid of singlet stability numbers; the energy of the $S_0 \to T_0$ transition can be found from the difference between the total energy of S_0 and the energy of the T_0 state calculated by the unrestricted method (the unrestricted method yields as a rule the same value for S_0 as the restricted method), while the energy of the triplet–triplet absorption is identified with the triplet spin-free stability numbers of the self-consistent state T_0 (see Table 1).

Table 1. The Hartree–Fock stability numbers corresponding to the singlet and triplet transitions (in eV).

Compound	$^1A_{1g}^- \to {}^1B_{3u}^-$	$^1A_{1g}^- \to {}^1B_{2u}^+$	$^1A_{1g}^- \to {}^3B_{2u}^+$	$^3B_{2u}^+ \to {}^3B_{1g}^-$	$^3B_{2u}^+ \to {}^3A_{1g}$
Naphthalene	3.90 (4.0)	4.48 (4.4)	2.87 (2.6)	3.18 (3.1)	4.11
Anthracene	3.44 (3.5)	3.45 (3.3)	1.82 (1.8)	2.83 (2.9)	4.09
Pyrene	3.25 (3.4)	3.57 (3.6)	2.04 (2.1)	2.43 (2.4)	3.27 (3.0)
Perylene	3.56 (3.4)	3.06 (2.8)	1.64	2.51 (2.6)	2.91 (4.4)

Note. The experimental data are given in brackets[8,11].

III. THE CONFIGURATIONAL–ORBITAL ANALYSIS OF EXCITED STATES. THE SPECIAL ROLE OF NATURAL ORBITALS

We shall now turn to the main problem discussed in this review—the analysis of excited states described by the standard superposition (3) of singly excited configurations. In the majority of studies involving specific calculations on excited states the largest configurational coefficients d_{pi}, from which one can infer the degree of configurational interaction[39–41], are usually quoted. This type of representation of the excited state is in certain respects (for example, as regards the cumbersome nature of the formulation) inapt and non-universal.

A form of the representation of Φ_*, which is independent of the explicit form of the occupied and vacant orbitals employed, can be regarded as universal in the given instance. In fact, these orbitals can be chosen quite arbitrarily not only as canonical molecular orbitals, i.e. as the eigenvectors of a single-particle Hamiltonian (the Fock operator f), but also as the eigenvectors of any other operator which commutes with the density matrix of the ground state ρ. This implies that the occupied orbitals $|\phi_i>$ can be mixed with one another in an arbitrary fashion but their orthonormalisation must be retained (i.e. unitary transformations are carried out). The vacant orbitals $|\phi_p>$ can also be subjected to a unitary transformation to the same extent. It is important that such transformations of the orbital set do not cause an overall alteration of the excited state Φ_*, but the configuration coefficients d_{pi} and the individual configurations $\Phi_{i\to p}$ are then considerably distorted. Consequently the coefficients d_{pi} do not yield an invariant description of the structure of the excited state (3) in the general case.

It is natural to attempt to isolate from all possible sets $\{d_{pi}\}$ an optimum set, which has the fewest members among all those permissible. The maximum number of configurations $\Phi_{i\to p}$, when all d_{pi} are non-zero (the least desirable situation from our point of view), can be found readily: it is equal to the product of the number of occupied orbitals N and the number of vacant orbitals $M-N$. As a rule the number of spin–orbital basis functions M is equal to or almost equal to twice the number of electrons $2N$. With increase in the size of the molecule, i.e. with increase of N, the maximum possible number of configurations $N(M-N) \cong N^2$ therefore increases in accordance with a quadratic law. It is found that there always exists a set of orbitals which the number of configurations is significantly smaller than and does not exceed the number of electrons in the system, i.e. varies linearly with N. It has been shown[42] that the most compact set of this kind is the set of natural spin–orbitals of the excited state Φ_*.

In the general case the natural orbitals of a certain state are the eigenvectors of a one-particle density matrix ρ_1 of this state[11]. In terms of the Hartree–Fock approximation, $\rho_1 = \rho$, so that the spin–orbitals $|\phi_i>$ are natural for any set of occupied molecular orbitals. The Tamm–Dancoff approximation (3) is characterised, in accordance with the work of Luzanov[17] and Mestechkin and Gutyrya[27], by a density matrix ρ_1^* of the type

$$\rho_1^* = \rho + D^2(\rho_\ominus - \rho). \tag{9}$$

The definition of the matrix D in form (7) makes it possible to find the identity $D\rho = \rho_\ominus D$, whence it follows, taking into account $\rho^2 = \rho$, that the occupied and vacant orbitals can be selected from the very beginning in the form of natural orbitals of the excited state investigated, because

$$\rho_1^*\rho = \rho\rho_1^*.$$

The natural orbitals are at the same time the eigenvectors of the matrix D^2.

This type of natural orbital will be designated by $|\phi_\alpha>$, if it is occupied in the ground state Φ, i.e. $\rho = \sum_{\alpha=1}^{N} |\phi_\alpha><\phi_\alpha|$ and by $|\phi_{N+\alpha}>$ if the natural orbital is populated only in the excited state. The matrix D then assumes the following form in terms of the basis set of the natural orbitals introduced[42]:

$$D = \sum_{\alpha=1}^{N} d_\alpha (|\varphi_\alpha\rangle\langle\varphi_{N+\alpha}| + |\varphi_{N+\alpha}\rangle\langle\varphi_\alpha|), \tag{10}$$

where the quantities d_α are the new configurational coefficients in the expansion of Φ_* in terms of (natural) configurations:

$$|\Phi_*\rangle = \sum_{\alpha=1}^{N} d_\alpha |\Phi_{\alpha\to N+\alpha}\rangle. \tag{11}$$

Here $\Phi_{\alpha\to N+\alpha}$ is formed as a result of the substitution of the natural occupied spin orbital $|\phi_\alpha\rangle$ in the main determinant Φ by the vacant orbital $|\phi_{N+\alpha}\rangle$. It follows from Eqns.(10) and (11) that the number of natural configurations never exceeds the number of electrons N; the transition to natural orbitals therefore sharply reduces the number of excited configurations and significantly simplifies the analysis of Φ_*, which can now be concentrated on only N values of d_α and not on N^2 coefficients d_{pi}. This reduction of the number of configurations (without a change in the overall wave function Φ_*) is clearly illustrated by the scheme of transitions in Fig.1.

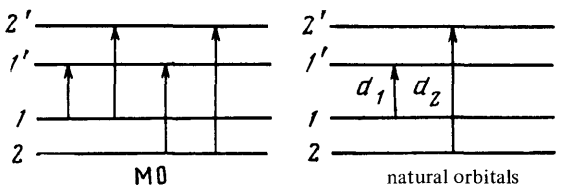


Figure 1. Decrease of the number of configurations on passing to natural orbitals of the excited state.

Fig.1 shows that, in the representation of the natural orbitals, all the cross-configurations $1\to 2'$, $2\to 1'$, etc. are missing; the excitation is described by the set of only the "diagonal" one-electron transitions $1\to 1'$, $2\to 2'$, etc. with the amplitudes d_1, d_2, etc. The numbers d_1, ..., d_α, ..., d_N are obtained from the matrix of the old configuration coefficients $d=||d_{pi}||$ by a kind of diagonalisation of this generally rectangular matrix, so that the number of non-zero terms of expansion (11) is equal to the rank $r\leq N$ of the matrix d:

$$|\Phi_*\rangle=\sum_{\alpha=1}^{r} d_\alpha|\Phi_{\alpha\to N+\alpha}\rangle. \qquad (12)$$

The number r is also an invariant characteristic of the matrix d, which remains constant in all the transformations of the basis set. In certain simple cases the rank of the matrix d is easily calculated and can yield direct information about the true nature of the configuration interaction.

As an example of this kind, we shall consider an excited state in which all the configurations $\Phi_{i\to p}$ are represented with the same weighting factor determined by the normalisation:

$$|\Phi_*\rangle=\frac{1}{\sqrt{N(M-N)}}\sum_{i;p}|\Phi_{i\to p}\rangle. \qquad (13)$$

It would appear that this is the extreme case of the maximum possible configuration interaction. Subject to condition (13), the matrix d assumes the following form:

$$d=[N(M-N)]^{-1/2}\begin{Vmatrix} 1 & 1 & \dots & 1\\ 1 & 1 & \dots & 1\\ . & . & \dots & .\\ . & . & \dots & .\\ 1 & 1 & \dots & 1 \end{Vmatrix}.$$

Evidently its rank is unity. Consequently the outwardly widest superposition (13), with the aid of which the idea of the delocalisation of transitions has been illustrated[43], can be reduced to only one determinant by a unitary transformation of vacant orbitals and orbitals occupied to different extents!

In this connection it is desirable to have a simple numerical characteristic which would indicate the number of significant configurations which cannot be reduced by any transformations. The average rank $\bar{r}$ of the matrix d, in which each natural configuration $\Phi_{\alpha\to N+\alpha}$ is included in proportion to its weighting factor d_α^2, can be used as such a quantity. An explicit expression for the average rank has been obtained[28,44]:

$$\bar{r}=1/\mathrm{Sp}\,(d^+d)^2=2/\mathrm{Sp}D^4, \qquad (14)$$

and a series of simple inequalities for Sp D^4 guarantees that the number $\bar{r}$ is between unity and the usual rank r of the matrix of configurational coefficients:

$$1\leqslant\bar{r}\leqslant r. \qquad (15)$$

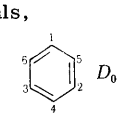
The natural nature of inequality (15) justifies the term "average rank" for the quantity defined by Eqn.(14). With the aid of Eqn.(14), it is easy to calculate the average rank of state (13) and to show that in this case $\bar{r}=1$.

On passing to configurations with a regular spin symmetry, the matrix D is replaced by the spin-free matrix D_0 and the average rank is always proportionally doubled as a result of the spin multiplier $(|\alpha(1)\beta(2)\rangle\pm|\beta(1)\alpha(2)\rangle)/\sqrt{2}$ used in the construction of the singlet and triplet configurations. It is therefore convenient to introduce the spin-free rank κ, which has been called[44] the delocalisation number, defined by the relations

$$\varkappa=1/\mathrm{Sp}\,D^4={}^1/_2\,\mathrm{Sp}\,D_0^4,\quad 1\leqslant\varkappa\leqslant r_0, \qquad (16)$$

where r_0 is the rank of the matrix of the corresponding spin-free configurational coefficients, which does not exceed the number of spin-free occupied or vacant molecular orbitals.

We shall calculate, for example, the delocalisation number of the excited state B_{1u} of the π-electron shell of the benzene molecule, where, in accordance with the study of Mestechkin and Gutyrya[27], we have in terms of the basis set of atomic orbitals,



$$D_0(B_{1u})=\begin{Vmatrix}\Delta & 0\\ 0 & \Lambda\end{Vmatrix},\quad \Delta=[6(y^2+1)]^{1/2}\begin{Vmatrix} y & 1 & 1\\ 1 & y & 1\\ 1 & 1 & y\end{Vmatrix}. \qquad (17)$$

Here the first block refers to the set of atoms in the 1-, 2-, and 3-positions and the second refers to the remaining atoms; y is the parameter of the configurational mixing equal to -2 for the Hückel solution, to -1.620 for the singlet, and to -2.818 for the triplet. Calculation by Eqn.(16) yields

$$\varkappa=3(y^2+2)^2/(y^4+12y^2+8y+6). \qquad (17')$$

Table 2. The delocalisation numbers of the transitions corresponding to the α-, p-, and β-absorption bands.

Molecule	α	p	p'	β	Molecule	α	p	p'	β
Naphthalene	2.09	1.34	1.68	2.01	Perylene	2.11	1.13	5.15	2.84
$(\text{Naphthalene})^{2+}$	1.51	1.19	1.57	1.56	Aniline	1.61	1.38	1.82	2.00
Anthracene	2.17	1.19	1.66	2.02	Benzonitrile	1.97	1.42	1.85	2.00
$(\text{Anthracene})^{2+}$	1.50	1.12	2.36	1.57	*p*-Aminobenzonitrile	1.86	1.21	2.14	1.82

For the Hückel solution, we obtain the natural value $\kappa=2$ and, when account is taken of the electronic interaction, we have $\kappa(^1B_{1u})=2.04$ and $\kappa(^3B_{1u})=2.94$. As a result of symmetry, all the remaining π-transitions in the benzene

molecule correspond strictly to two configurations, since the matrix relation $D_0^2 = 4D_0^4$ holds for them. Taking y to infinity in Eqn.(17'), we obtain the maximum possible delocalisation number $\kappa = 3$ for Eqn.(17).

The delocalisation numbers for the lowest transitions in a series of conjugated hydrocarbons have been found[44] (Table 2). Table 2 permits the following conclusions. All the lowest transitions involve a small number of configurations, the number of natural configurations not exceeding five. In uncharged systems the p band (the B_{2u}^{+} state) corresponds as a rule to virtually only one configuration, while the α and β bands (the $B_{3u}^{\mp}$ states) correspond to at least two configurations. This is consistent with the familiar qualitative picture of the transitions used for alternant systems[45] (Fig.2).

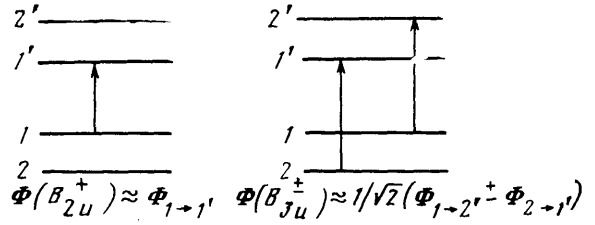


Figure 2. The principal one-electron transitions involved in the formation of the lowest excited states of alternant hydrocarbons.

For ions and substituted aromatic hydrocarbons, the alternant property disappears and the degree of delocalisation of these states diminishes. Table 2 also shows that the second transitions involve a higher degree of delocalisation compared with the first transitions of the same symmetry, i.e. the expansion of the set of configurations has a greater effect on the second and higher transitions than on the first.

One should note that the delocalisation numbers characterise not only the multiconfiguration nature of the excited state but also the degree of deviation of the excited state from the ground state. Indeed, the sum of squares of the changes in the charges and bond orders on excitation, which is the same as the quantity $\mathrm{Sp}\,(\rho_1^* - \rho)^2 = \mathrm{Sp}\,D^4 = 1/\kappa$, can serve as a characteristic of this deviation. Therefore, the higher the delocalisation number κ, the smaller the overall changes undergone by the molecular system as a result of the given excitation. In particular, those spectroscopic properties which are caused by changes in the electron density at the atoms (dipole moment, the influence of the substituent, etc.) should have the greatest influence on transitions with low delocalisation numbers. From this follows, for example (in conformity with the available experimental data[46]), a higher sensitivity to chemical substitution of the virtually one-configuration p bands than that of the two-configuration α and β bands. These factors can apparently also account for the greater polarisability of the excited p states, observed in the calculations[47], compared with the α states of aromatic hydrocarbons.

IV. THE METHOD OF EXCITATION LOCALISATION NUMBERS

While the degree of delocalisation of the transition is more in the nature of an "internal" than a purely theoretical characteristic necessary for the complete understanding of the structure of the wave function of the excited molecule, the localisation of the electronic transition plays a direct role in the interpretation of spectroscopic and certain other physicochemical experiments. The possibility of a real localisation of the excitation at individual fragments of the molecule is closely related to the additivity of a series of molecular properties described by the usual perturbation theory.

Suppose that the excitation is each time sufficiently localised at a particular group of atoms A. Then a certain observed property of the molecule, modelled as a second-order effect of the perturbation theory (polarisability, diamagnetic susceptibility, etc.)

$$E^{(2)} = \sum_a (1/\lambda_a) \cdot |\langle \Phi | \delta H | \Phi_*^{(a)} \rangle|^2,$$

can be represented by the sum of the contributions in terms of the fragments into which the molecule has been subdivided and in which each excitation $\Phi_*^{(a)}$ is significantly concentrated.

From the standpoint of the molecular orbital theory, it is to be expected that both occupied and vacant orbitals will in this case also be localised at individual atoms and bonds, which necessarily leads to the localisation of all possible transitions. Such localisation of orbitals is indeed possible but by no means obligatory. It can occur, as a rule, in saturated systems and this feature has been demonstrated by Lennard–Jones and coworkers for saturated hydrocarbons with a high degree of symmetry, while in the general case it has been demonstrated by Ruedenberg and coworkers[4] (see also Bazilevskii[48]).

However, in conjugated systems the additivity of properties of the type $E^{(2)}$ does not obtain, which indicates the impossibility of identifying all transitions with local transitions. This means that the localisation of the π orbitals is less extensive and the interaction of approximately localised orbitals cannot be neglected[4,5,13]. Therefore in the case of π systems it is difficult to expect the concentration of excitation at individual bonds. Nevertheless, in many instances large molecular fragments can be responsible for particular transitions. This factor has been frequently noted by spectroscopists[12,49–52] and required a theoretical interpretation. A logical quantum-chemical analysis must therefore extract directly from calculated data information about the localisation of transitions characterised by a readily calculable quantity. Until recently such a characteristic was not available and investigators usually confined themselves to a qualitative observation of the local nature of the transitions on the basis of the form of the molecular orbitals, provided that these orbitals had been localised beforehand (to the extent that this is possible)[53,54], or on the basis of the charges and bond orders, etc.[40,55]

The abandonment of the traditional orbital analysis and its replacement by the study of the transition density matrix D enabled Luzanov et al.[42] to put forward a logical quantitative characteristic of the localisation. We shall consider in greater detail the fundamental ideas of the above study[42] and the subsequent investigations[56–60]. As usual, we shall adopt the sum of squares of the moduli of the expansion coefficients $c_{\mu i}$ of the orbital $|\phi_i\rangle$ in terms of the atomic orbitals $|\chi_\mu\rangle$, referring to the fragment A investigated, as a measure of the degree of localisation of the molecular orbital. This quantity will be formulated thus:

$$L_A(\varphi_i) = \sum_{\mu \in A} c_{\mu i}^2, \qquad (18)$$

assuming for simplicity that all the quantities are real.

If we are dealing with a one-electron transition of the type $\Phi_{i\to p}$, then the localisation of the excitation of the fragment A can be naturally regarded as equally legitimately associated

with the localisation of both the occupied orbital $|\phi_i>$ and the vacant orbital $|\phi_p>$, i.e.

$$L_A\{\Phi_{i\to p}\} = \frac{1}{2}(L_A(\varphi_i) + L_A(\varphi_p)). \quad (19)$$

The coefficient 1/2 was introduced so that the sum of L_A and L_B, where B is the remainder of the molecule, was unity. The localisation number L_A introduced in this way represents the degree of involvement of the fragment A in the resultant excitation. If the molecule has been divided into a number of fragments larger than two, then a set of localisation numbers $\{L_A\}$, corresponding to the number of fragments, appears; these are also limited by the natural normalisation condition

$$\sum_A L_A = 1, \quad 0 \leqslant L_A \leqslant 1, \quad (20)$$

where the sum with respect to A is the sum with respect to all the fragments into which the molecule has been subdivided. In the limiting subdivision of the molecule into atoms, atomic localisation numbers L_μ arise, which we shall also refer to as the excitation indices. It is evident that

$$L_B = \sum_{\mu\in A} L_\mu. \quad (21)$$

The scheme described is in principle fairly natural and is in fact convenient for the analysis of one-configuration excited states.

We shall now consider the possible ways of extending it to the case of multiconfiguration excited state of type (3). A generalisation of the numbers L_A, which would take into account, with the aid of Eqn.(19), each configuration $\Phi_{i\to p}$ in proportion to its weighting factor d^2_{pi}, becomes immediately apparent, namely

$$L_A\{\Phi_*\} = \sum_{i,p} d^2_{pi} L_A\{\Phi_{i\to p}\}. \quad (22)$$

However, the numbers defined by Eqn.(22) suffer from a significant defect—they are not invariant relative to the transformation of the basis set of occupied and individually vacant molecular orbitals†. It is possible to eliminate this ambiguity by changing Eqn.(22) to the basis set of natural orbitals, which at the same time significantly simplifies Eqn.(22):

$$L_A = \sum_{\alpha=1}^{r} d^2_\alpha L_A\{\Phi_{\alpha\to N+\alpha}\}. \quad (22')$$

Using the explicit form [Eqn.(10)] of the Hermitian transition density operator D in terms of the natural basis set, we find an alternative form of Eqn.(22):

$$L_A = \sum_{\mu\in A} \langle\chi_\mu| D_0^2 |\chi_\mu\rangle. \quad (23)$$

Eqn.(23) does indeed exhibit the required invariance, because the transition operator D is, like the matrix ρ for the ground state, a fundamental invariant of the excited state (3). The requirement that L_A should be positive and the normalising condition (20) are satisfied automatically, because the matrix D_0^2 has been defined as a non-negative quantity and the normalisation of Φ_* yields $\mathrm{Sp}\, D_0^2 = 1$.

† Numbers of the type defined by Eqn.(22) have been introduced by Ohta et al.[61] to describe the localisation of the transition.

If each atom supplies several orbitals of different types (π, σ, etc.) to the valence shell, then the summation in Eqn. (23) must be carried out with respect to all the valence orbitals of the atoms of the fragment A. Accordingly, in calculating the excitation index of the atom L_μ, it is necessary to sum the elements D_0^2 for all the orbitals of each atom.

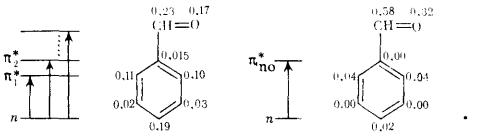
The choice of the quantity defined by Eqn.(23) as a measure of localisation was proposed by Luzanov et al.[42] on the grounds of other considerations. Namely, the localisation of the excitation was described in terms of the operator modulus of the change in the density matrix on excitation:

$$|\Delta\rho| = |\rho_1^* - \rho| = [(\rho_1^* - \rho)^2]^{1/2}, \quad (24)$$

which is exactly identical with the D^2 matrix in the Tamm–Dancoff model. The numbers L_A therefore automatically take into account the changes in both the charges and bond orders on excitation. In this connection, we may note that the employment in estimating the degree of localisation of the transition of only one of the above components, for example, only the changes in the charges, is not justified and the new quantity introduced on this basis[59] is not well founded.

With the aid of the quantities L_A in the form defined by Eqn.(22'), one observes immediately the fundamental role of the natural orbitals also in the localisation problem. Suppose that the excitation is almost fully localised at the fragment A, i.e. $L_A \cong 1$. Then, by virtue of the normalisation property $\Sigma d^2_\alpha = 1$, we must have $L_A\{\Phi_{\alpha\to N+\alpha}\} \cong 1$. Consequently $L_A(\phi_\alpha) = L_A(\phi_{N+\alpha}) \cong 1$; in other words, if the excitation is localised at a certain fragment, then the natural orbitals of the excited state are also localised at this fragment[42]. The natural orbitals as it were draw the excited electron cloud precisely to those sections of the molecule where the given excitation is largely concentrated. As regards the Hartree–Fock molecular orbitals, this claim is generally speaking invalid, so that the analysis of the degree of localisation of molecular orbitals can yield a distorted idea about the true nature of the distribution of the excitation.

A higher degree of localisation of natural orbitals compared with the molecular orbitals is manifested particularly clearly for the $n\pi^*$-states, where, as a consequence of the usual smearing of the n orbitals, the molecular orbital method cannot explain the experimental localisation of the excitation in the sections of the molecule adjoining the heteroatom which has an unshared electron pair[12,49]. The localisation numbers, defined by Eqn.(18), of the lowest vacant π_1^* molecular orbital and the natural orbital π_{no}^*, to which the electron of the unshared pair is transferred on excitation, are given below:



The numbers were taken from Luzanov and Pedash[60]. Evidently the degree of localisation of the natural orbital at the carbonyl group is a factor of two greater than the corresponding quantity for the π_1^* molecular orbital and reaches 90%. The use of the quantity defined by Eqn.(23) for carbonyl compounds made it possible[60] to estimate quantitatively the degree of localisation of the $n\pi^*$ excitation at C=O, which was found to diminish in a series of aromatic compounds investigated with increase in the size of the π system and amounted to $L_{C=O} = 0.88$–0.95. The decrease of the degree of localisation of the $n\pi^*$ transitions involving the carbonyl group as the conjugated system expands had been observed experimentally in a previous study[62].

It is significant that the determination of the numbers L_A from Eqn.(23) as well as the determination of the delocalisation numbers defined by Eqn.(16) do not require a special construction of natural states. It is sufficient to construct from the known configurational coefficients d_{pi} and the LCAO-MO coefficient $c_{\mu i}$ a matrix D_0 in terms of the atomic basis set, the elements of which can be identified with the quantities (n is the number of occupied molecular orbitals and m is the number of atomic orbitals)

$$D^0_{\mu\nu} = \frac{1}{\sqrt{2}} \sum_{i=1}^{n} \sum_{p=n+1}^{m} d_{pi} (c_{\mu p} c_{\nu i} + c_{i\mu} c_{\nu p}). \quad (25)$$

Then one determines the atomic (orbital) excitation indices from the formula

$$L_\mu = \sum_{\nu=1}^{m} [D^0_{\mu\nu}]^2 \quad (26)$$

and hence also the localisation numbers defined by Eqn.(21). In the methods for the calculation of the electronic spectra of molecules with the aid of the superoperators $\hat{\Lambda}$ or $\hat{\Pi}$ discussed in Section II, the matrix D_0 is usually calculated immediately in terms of the atomic basis set simultaneously with λ, so that the computational stage (25) becomes superfluous.

V. ISOLATION OF TRANSITIONS AT INDIVIDUAL FRAGMENTS AND MOLECULAR STRUCTURE

The relative simplicity of the calculation of the localisation numbers L_A and the clarity which they introduce into the interpretation of the electronically excited states permitted the analysis of the localisation of excitations for many molecular structures of an arbitrary degree of complexity[56-58,63]. With the aid of these calculations, it is natural to consider certain structural-chemical features, the presence of which favours the preferential concentration of excitation at an individual molecular fragment. Experimental studies, which stimulated such investigations, have been discussed in detail[12,49-52].

Numerous calculations have confirmed the natural hypothesis that a significant factor in the localisation of excitation at an individual section of the molecule is the asymmetry of the molecular structure. Indeed, for a combined system A+B, the type Λ excitation operator is described by the block supermatrix $||\Lambda_{AB,CD}||$, the diagonal blocks $\Lambda_{AA,AA}$ and $\Lambda_{BB,BB}$ of which characterise the excitation of the fragments A and B respectively and the blocks $\Lambda_{AB,AB}$ and $\Lambda_{BA,BA}$ characterise states with charge transfer from A to B and conversely, while the non-diagonal blocks $\Lambda_{AA,AB}$, etc. include the interaction between them. In the case of a weak interaction between the fragments, the approximate solutions (11) can be represented approximately by transitional matrices of three types generated by the corresponding diagonal blocks Λ:

$$\left\| \begin{matrix} D_A & 0 \\ 0 & 0 \end{matrix} \right\|, \left\| \begin{matrix} 0 & 0 \\ 0 & D_B \end{matrix} \right\|, \left\| \begin{matrix} 0 & D_{AB} \\ D^+_{AB} & 0 \end{matrix} \right\|. \quad (27)$$

As a result of this, we have either $L_A \cong 1$, or $L_B \cong 1$, or even $L_A \cong L_B \cong 1/2$ [see Eqn.(23)].

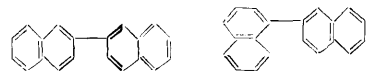
The first two cases correspond to the concentration of excitation alternately first in one and then in another fragment, while the third corresponds to excitation throughout the molecule, the first two solutions of Eqn.(27) being valid only when the fragments are non-equivalent, i.e. when the A+B system is asymmetric. On the other hand, if B is a copy of A and the symmetry of the system is not below C_2, then solutions which have the correct symmetry are

$$\frac{1}{\sqrt{2}} \left\| \begin{matrix} D_A & 0 \\ 0 & D_B \end{matrix} \right\|,$$

which evidently leads to a uniform localisation $L_A = L_B = 1/2$. Asymmetry is in fact the physically well-founded structural factor which distinguishes the so-called crossing conjugated systems where investigators sought, not without justification, quasi-autonomous excitation regions[51,52]. We may note that formally the same causes are responsible for the appearance of localised excitations in a molecular crystal, where the absorption bands of individual molecules are observed instead of exciton bands, but in the solid the asymmetry factors are the local deformation of the crystal, the presence of impurities, and defects, etc.[64]

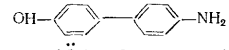
Proceeding now to specific illustrations, we shall consider initially the excited states of the styrene molecule Ph–CH=CH_2. According to estimates in the literature[56,58], one may claim that the first transition involves mainly the phenyl group, since $L_{Ph} = 0.92$, while the second transition involves the molecule as a whole ($L_{Ph} = 0.64$). The same interpretation follows also from experimental data which have been discussed in detail in a monograph[50]#.

An apt example of the structure containing two equivalent fragments which can be joined symmetrically and asymmetrically is provided by the binaphthyl system Nh–Nh:



(28)

Evidently, for all transitions in the first molecule $L_{Nh_1} = L_{Nh_2} = 1/2$, while in the second it is most likely that $L_{Nh_1} = L_{Nh_2}$. Specific calculations showed that, in the first excited state of the asymmetric 1,2'-binaphthyl, we have $L_{Nh_1} = 0.63$, i.e. there is an almost uniform distribution of excitation, the second transition involves mainly the β-naphthyl group ($L_{Nh_1} = 0.16$), and, finally, the third transition is almost entirely concentrated in the first fragment ($L_{Nh_1} = 0.94$). Thus, in this example all three situations illustrated in formula (27) are clearly manifested. Another asymmetric structure is that of α-phenylnaphthalene, the values of L_{Ph} for the first three electronic excitations of which are respectively 7, 15, and 88%. Finally, in the compound

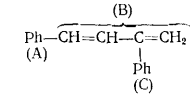


(29)

even a slight asymmetry (Ö is almost equivalent to N̈) leads to a sharp non-equivalence of the fragments in the first excited state (α-band)—95% of the entire excitation has been "collected" in the aniline fragment. These examples could be continued.

However, for asymmetry to have an effect in the direction indicated, it is necessary that the fragment should be weakly coupled, which obtains when the fragments are joined in the "minimal" manner, i.e. by only one bond (on dissociation of this bond, the molecule breaks up into at least two components). In the theory of graphs, such structures are assigned to graphs with edge connectivity 1 (graphs with a bridge). All the systems mentioned here belong to this type. In such systems the requirement that the interaction between the fragments is negligible compared with the overall interaction within the fragments, essential for the autonomy of the fragments[6], is readily fulfilled.

The 1,3-diphenylbutadiene molecule, where it is natural to distinguish three sections

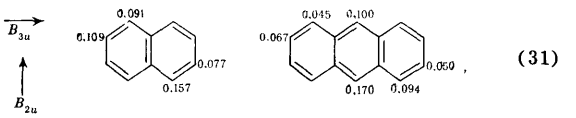


(30)

In contrast to the second band, the first band is hardly displaced following chemical substitution in –CH=CH_2.

has a remarkable structure as regards the non-equivalence of the fragments. The π-electronic excitation for the first two singlet transitions is very highly localised at the A+B fragment ($L_{A+B}=0.959$ and 0.999 respectively), while the next two transitions are localised at the B+C fragment (0.997 and 0.892). These data were obtained by Luzanov et al.,[42] while those for the keto-derivative of compound (30), called a chalcone, were obtained by Sukhorukov et al.[59] Example (30) illustrates an additional structural-chemical factor favouring localisation—the presence in the π-system of a branch associated with the bridges of the graph, which in chemistry is sometimes referred to as cross-conjugation.

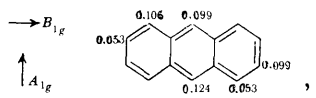
When the edge connectivity of the graph exceeds unity, rigidly bound systems of the type of condensed hydrocarbons are produced. Even when the fragments are differentiated within such molecules, the strong interaction between them via two or more carbon–carbon bonds significantly weakens the autonomy of the fragments on excitation. Nevertheless some non-uniformity is manifested in the distribution of excitation at the level of individual atoms. It has been shown[57] that under these conditions it is convenient to employ atomic excitation indices L_μ for the analysis of localisation. For example, in naphthalene and anthracene the following excitation index diagrams correspond to the two lowest energy transitions:



(31)

where the numbers in the upper half refer to the α band and those in the lower half refer to the *p* band, the arrow indicating the direction of polarisation of the transition. Comparison of the 1- and 2-positions of these molecules shows that the difference between the polarisations of the transitions of the α band (in the direction of the long molecular axis) and the *p* band (in the direction of the short axis) leads to the accumulation of excitation in the direction of polarisation.

However, for *T*–*T* transitions this tendency is non-obligatory. For example, it has been reported[38] that the $^3B_{2u}\rightarrow{}^3B_{1g}$ (in the direction of the long axis) and $^3B_{2u}\rightarrow{}^3A_{1g}$ (in the direction of the short axis) transitions in anthracene can be represented by the following localisation diagram:



(32)

which shows that, despite the opposed polarisations of the bands, the excitation is localised in the direction of the short axis.

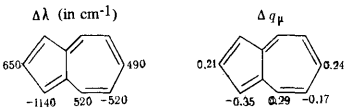
It has been suggested[57] that the excitation indices L_μ in alternant systems be used to estimate the spectral shifts $(\Delta\lambda)_\mu$ following the introduction of weak substituents X in the μ-position:

$$(\Delta\lambda)_\mu = K_X L_\mu. \qquad (33)$$

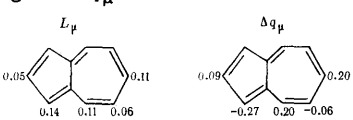
The spectroscopic substituent constant K_X was fitted on the basis of data for the corresponding benzene derivatives, where by virtue of symmetry $L_\mu = 1/6$. Conversely, it is possible to find by Eqn.(33) empirical localisation indices from the values of L_μ in an arbitrary alternant molecule and the previously determined substituent constants. For the naphthalene α band, the empirical $\bar{L}_\mu$ are $\bar{L}_1 = 0.081$ and $\bar{L}_2 = 0.108$, while for the phosphorescent $^1A_{1g}\rightarrow{}^3B_{2u}$ transition we have $\bar{L}_1 = 0.125$ and $\bar{L}_2 = 0.040$. These figures agree satisfactorily with the calculated values (0.091 and 0.109 for the α band and 0.174 and 0.072 for the $^2A_{1g}\rightarrow{}^3B_{2u}$ transition).

Thus we can assume that diagrams of types (31) and (32) make it possible to specify the substituent positions which are most sensitive as regards spectral shift. In the singlet case [formula (31)] one can therefore expect that the introduction of a substituent in the direction of the polarisation of the transition displaces the energy of this transition to a greater extent than the energy of the perpendicularly polarised transition. This rule, based on experimental observations, has been discussed[12,65] and has been extended to a triplet–triplet transition[65]. Diagram (32) shows, however, that this conclusion is by no means entirely general.

The influence of the insertion of a substituent X in the μ-position in non-alternant molecules can be estimated merely with the aid of the first correction to the excitation energy $\lambda_\mu^{(1)}$. Successive calculation of $\lambda_\mu^{(1)}$ shows that one of the main contributions to $\lambda_\mu^{(1)}$ is the term $\Delta q_\mu\cdot(\Delta\alpha)_X$, where Δq_μ is the change in the charge on the atom μ on excitation and $(\Delta\alpha)_X$ is the change in the Coulombic integral under the influence of the substituent X. In systems with a non-uniform distribution of charge both bathochromic and hypsochromic shifts can therefore arise[46]. For example, according to Godfrey and Murrell[66], reliable values of $(\Delta\lambda)_\mu$ for the first excited state of azulene are available and are satisfactorily correlated with the calculated Δq_μ[66]:



A similar correlation between Δq_μ and the values of $\lambda_\mu^{(1)}$ calculated exactly from the formulae of Luzanov et al.,[67] on the one hand, and the $(\Delta\lambda)_\mu$ for aromatic aza-hydrocarbons, on the other, have been discussed by Vysotskii[68]. In this case the excitation indices yield a distribution of excitation from which it is possible to infer only approximately the most reactive positions of the substituents in a given molecule without specifying the direction, which is apparently determined by the sign of Δq_μ[56]:



Excitation indices have found an unusual application in the qualitative description of the intercombination transition $S_1\rightsquigarrow T_0$. In the large molecules of aromatic hydrocarbons the symmetries of the fluorescent and phosphorescent states are the same. The spin–orbital coupling between these states, involving the cooperation of specific molecular vibrations, leads to the radiationless transition $S_1\rightsquigarrow T_0$, which is the main fluorescence quenching process in aromatic molecules. An exact calculation of the probability of this process is extremely difficult. In order to be able to draw qualitative inferences, it has been suggested[38] that one introduce the excitation overlap structure factor $\mathcal{P}$, which is defined as the product of the excitation indices $L_\mu(S_0\rightarrow S_1)$ of the fluorescent state S_1 and the excitation indices $L_\mu(S_0\rightarrow T_0)$ of the phosphorescent state T_0 as the quenching agent S_1:

$$\mathcal{P} = \sum_\mu L_\mu(S_0\rightarrow S_1)\,L_\mu(S_0\rightarrow T_0), \qquad (34)$$

where the summation is carried out with respect to all the atoms of the test system.

The factor $\mathcal{P}$ clearly reflects the likely assumption that the spin–orbital coupling of the states S_1 and T_0 is stronger the greater the degree of involvement of each atom μ simultaneously in the fluorescent and phosphorescent states. The greater the factor $\mathcal{P}$, the greater the probability of the

transition, and the lower the fluorescence quantum yield Φ_f. For molecules of a similar structural type, one may therefore hope for a correlation between $\mathscr{P}$ and the reciprocals of the quantum yields $1/\Phi_f$. In the class of condensed aromatic systems such correlation does in fact occur[69]:

Compound	Tetracene	Anthracene	Pyrene	Perylene
$\mathscr{P}$	0.271	0.121	0.091	0.088
$1/\Phi_f^{69}$	0.58	0.38	0.17	0.13

In the case of a uniform distribution of excitations we have $\mathscr{P}=1/m$, in conformity with Eqn.(34), where m is the number of atoms in the molecule. If such uniformity did actually obtain, then, with increase of the size of the system, the probability of the transition would fall and the fluorescence quantum yield would increase. The non-uniformity of the distribution over the atoms in the excited state is in fact responsible for the greater overlap of the excitations and the lower yield Φ_f in tetracene (18 carbon atoms) than in the anthracene molecule with 14 carbon atoms. The data for polyphenyls show that $\mathscr{P}$ is close to $1/m$, since the decrease of $\mathscr{P}$ for these compounds is almost proportional to the increase of the number of rings.

VI. ANALYSIS OF CHARGE TRANSFER IN THE METHOD OF TRANSITION OPERATORS

In the discussion of the localisation of excitation in weakly coupled systems two significantly non-equivalent possibilities, reflected in Eqn.(27), were indicated: either the excitation is localised exclusively at the fragment A or B or there is excitation throughout the molecule, in which electrons, as it were, oscillate between different parts (A and B) of the molecule. Excited states of the latter type have come to be called charge-transfer states. The transition to such an excited state is as a rule characterised by a more pronounced redistribution of electron density and by a marked increase of the dipole moment (relative to the ground state) and hence by distinct solvatochromic effects, which in fact makes them attractive for spectroscopic investigation[70-72].

Charge-transfer states can be realised in a virtually "pure" form in excimers and charge-transfer complexes, whence both the terminology and the methods of identification have been taken[73]. Intramolecular charge-transfer is rarely fairly complete and the need to estimate the relative contributions of charge-transfer states led in its time to the development of special computational methods differing from the standard Pariser–Parr model. We have in mind primarily the so-called "molecule in molecule" method, which was initially developed by Longuet-Higgins and Murrell[1,66] and has found numerous adherents up to very recent times[2,74-77]. The essential feature of the method is that, having specified a certain subdivision of the molecule into fragments A, B, ..., C and using the orbitals for the individual fragments, one constructs the wave functions for the combined A + B + ... + C system. The basis set of N-electron functions employed in this procedure consists of products, antisymmetrised with the aid of the antisymmetrisation operator $\mathscr{A}$, comprising mainly the ground configuration $\Psi_0=\mathscr{A}\Phi_A\Phi_B\ldots\Phi_C$, where Φ_A denotes the determinant made up of the occupied molecular orbitals in the ground state in the fragment A and of different types of locally excited molecular orbitals:

$$\Psi_A^*=\mathscr{A}\Phi_A^*\Phi_B\ldots\Phi_C,\ \ldots,\ \Phi_C^*=\mathscr{A}\Phi_A\Phi_B\ldots\Phi_C^*, \qquad (35)$$

where the wave function of each fragment of the entire molecule is replaced by a singly excited configuration or a superposition of such configurations Φ_A^* made up of the molecular orbitals of only this fragment. In addition, all possible charge-transfer configurations are introduced:

$$\Psi_{A\to B}=\mathscr{A}\Phi_A^+\Phi_B^-\ldots\Phi_C,\ \ldots,\ \Phi_{C\to A}=\mathscr{A}\Phi_A^-\Phi_B\ldots\Phi_C^+, \qquad (36)$$

in which the occupied molecular orbital of one fragment is replaced by the vacant molecular orbital of another fragment.

In the basis set of the functions Ψ_0, $\{\Psi_A^*\}$, $\{\Psi_{A\to B}\}$ set up in this way one diagonalises the overall Hamiltonian of the molecule $H_{A+B+\ldots+C}$, the eigenvectors of which are identified (on the basis of the increase of the energy) with the resultant ground and excited states of the entire system. Since the molecular orbitals of the fragments are not self-consistent for the combined system, the resultant ground state comprises the locally excited states Ψ_A and charge-transfer states of the type $\Psi_{A\to B}$, apart from the ground configuration Ψ_0. Accordingly the excited states of the entire system include a contribution from the ground configuration Ψ_0. This factor leads to some inconsistency of the "molecule in molecule" method for the analysis of the structure of excited states in terms of the localisation of charge-transfer useful to the investigator.

In the method of Baba et al.[3] one begins with the Pariser–Parr wave functions of the excited states obtained from self-consistent molecular orbitals by the usual method of configuration interaction (see Section II). However, the contribution of charge-transfer states is estimated by a procedure similar to that in the "molecule in molecule" method. Namely, having selected for each fragment specific reference molecular orbitals, for example, the self-consistent molecular orbitals of these fragments, the coefficients of expansion of the functions Φ_* of type (3) for excited states in terms of the basis set $\Psi_0\{\Psi_A,\Psi_{A\to B}\}$ are found by linear transformations of the self-consistent molecular orbitals of the entire system into the reference molecular orbitals of the fragments. Thus the given method of analysis does not eliminate the difficulties in interpretation associated with the method of Murrell and Longuet-Higgins.

As a typical example of studies on electronic states in terms of this approach, we shall consider data for the ground and the lowest excited $\pi\pi^*$-states of the aniline molecule[78]. Charge-transfer states $\Psi_{NH_2\to Ph}$ with an overall contribution of 11.8%, reflecting the electron-donating function of the amino-group when it is incorporated in the overall π-system, are "imposed" on the ground state of this molecule. In the first $\pi\pi^*$-excited state the contribution of the above states increases to 28.5%. In the second excited state the contribution of $\Psi_{NH_2\to Ph}$ reaches 37.4%, but the ground configuration Ψ_0 with a 6% contribution also appears. As a result, it is difficult to understand how these figures reflect the charge transfer proper on excitation, this being a consequence of the lack of self-consistency of the reference molecular orbitals of the individual fragments in relation to the entire system made up of the given fragments. It is therefore difficult to compare such contributions even for different excited states of the same molecule. Apart from the cumbersome nature of the methods described, the contributions obtained are not invariant, because they depend on the form of the reference molecular orbitals of the fragments.

We may also note studies[53,54] where a set of orbitals localised at atoms and bonds is used in the construction and analysis of the Tamm–Dancoff excited state (3). However, the approximate nature of the localisation of the molecular orbitals, found by the Ruedenberg method or some other procedure, permits only qualitative inferences, which, owing to the lack of numerical characteristics, also hinder a comparative analysis of the excitations.

We shall now show how the problem of charge transfer is solved in the method of localisation numbers described in Section V. In order to extract the maximum amount of

information, it is necessary to employ in this case, instead of the Hermitian transition density matrix D, the overall one-electron matrix τ of the transition, which can be readily expressed in terms of D, and the density matrix ρ of the ground state, namely

$$\tau = D\rho. \tag{37}$$

The excited state (3) can then be represented as the result of the action of the operator (37) on the Hartree–Fock ground state Φ for each electron i:

$$|\Phi_*\rangle = \sum_{i=1}^{N} \tau(i)|\Phi\rangle.$$

The matrix elements $\tau_{\mu\nu}$ of the operator τ in terms of the atomic basis set can therefore be regarded as amplitudes of the electron transfer from the atom ν to the atom μ. Proceeding further to the spin-free quantities τ_0 and, putting, as before, $(\tau_0)_{\mu\nu} = \tau_{\mu\nu}$, we assume that the probability of a jump of the excited electron from the atom μ to the atom ν is characterised by the number

$$l_{\mu\to\nu} = 2\tau^2_{\nu\mu}. \tag{38}$$

If we are interested in the probability $l_{A\to B}$ of the electron transfer on excitation from the fragment A to the fragment B, it is necessary to carry out a summation of the probability defined by Eqn.(38) with respect to the corresponding atoms (orbitals):

$$l_{A\to B} = \sum_{\mu\in A}\sum_{\nu\in B} l_{\mu\to\nu}. \tag{39}$$

The positive quantities defined by Eqns.(38) and (39) will be called the *charge-transfer numbers*[79,80]. On the other hand, if A = B, then Eqn.(39) is converted into the partial localisation number:

$$l_A = 2\sum_{\mu,\nu\in A} \tau^2_{\mu\nu}, \tag{40}$$

which describes the probability that the excited electron is located in the fragment A, i.e. the probability of its local excitation. In particular, for the local excitation of the atom μ we have $l_\mu = 2\tau^2_{\mu\mu} = [(D_0)_{\mu\mu}]^2$.

There exists a simple relation, established with the aid of Eqn.(37), between the charge-transfer numbers defined by Eqns.(39) and (40) and the localisation numbers defined by Eqn.(23) and introduced previously:

$$L_A = l_A + {}^1/_2(l_{A\to B} + l_{B\to A}), \tag{41}$$

where B is a component of the overall molecule A + B in addition to A. If the molecule has been divided into a large number of fragments A + B + ... + C, then

$$L_A = l_A + {}^1/_2(l_{A\to B} + l_{B\to A} + \cdots + l_{A\to C} + l_{C\to A}). \tag{42}$$

Thus the overall localisation of the excitation in a certain fragment consists of the local excitation of the fragment proper (the number l_A), the charge transfer from the given fragment to all the remaining fragments, and the reverse transfer from all the remaining fragments to the given fragment. This conclusion is quite natural, because charge-transfer states involving simultaneously two fragments cause a rearrangement, on excitation, of the electron shells of the fragments and make a specific contribution, like local excitations, to the overall distribution of the excitation in the molecule.

An important feature of this approach is the fact that the introduction of the transfer numbers defined by Eqn.(39) eliminates the discrepancy, noted previously, between the charge transfer arising following the appearance of states of the type $\Psi_{A\to B}$ and the observed charge transfer (the change in electron density Δq_A in the fragment or the dipole moment of the molecule on excitation). Eqns.(9) and (37) permit the claim that the following relation is valid for the molecule A + B:

$$\Delta q_A = l_{B\to A} - l_{A\to B}, \tag{43}$$

while for the system A + B + ... + C we have

$$\Delta q_A = \sum_{B\neq A} (l_{B\to A} - l_{A\to B}). \tag{44}$$

Eqn.(43) implies that an increase of electron density in the fragment A takes place only at the expense of states involving charge transfer from the remainder of the molecule to the fragment A, while states with electron transfer from A to the remainder of the molecule merely decrease Δq_A. In other words, the transfer numbers $l_{A\to B}$ and $l_{B\to A}$ represent a kind of virtual charges of opposite sign, which are induced in the fragments following the excitation of the neutral molecule.

Thus Δq_A is a difference characteristic of the charge transfer and in the general case it can therefore yield only indirect evidence concerning the "charge transfer" nature of the excited state. Only in the case of an absolutely strong donor or acceptor does one of the components of Eqn.(43) disappear ($l_{B\to A}$ for the donor and $l_{A\to B}$ for the acceptor) and Δq_A is equal to the contribution of the charge states ($l_{A\to B}$ or $l_{B\to A}$).

In alternant systems $\Delta q_A = 0$ for any fragment, since, in conformity with the parity theorem, the excitation of such systems does not cause any changes in the charge density[27]. Hence follows also the finding that the charge-transfer numbers associated with transfer in opposite directions ($l_{A\to B}$ and $l_{B\to A}$) are the same. The contribution of the charged states of alternant molecules can therefore be characterised by the overall quantity $l_{AB} = 2l_{A\to B}$, and in the general case we have

$$l_{AB} = l_{A\to B} + l_{B\to A}. \tag{45}$$

A method based on the employment of only the transition matrix D has been proposed[80] for the estimation of the overall charge transfer defined by Eqn.(45). The results of the calculation of l_{AB} by the two methods usually yields similar values.

We may note that, by analogy with the theory of excitons, locally excited states ($l_{AB} \cong 0$) can be naturally referred to also as small-radius excitations while charge-excitations involving the entire molecule ($l_{AB} \cong 1$) can be called large-radius excitations.

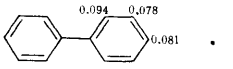
We shall now consider the results of the calculation of the charge-transfer numbers for specific hydrocarbon systems. For the α-, p-, and β-bands of biphenyl, these quantities have the following values:

Band	α	p	β
l_{Ph}, %	43	31	5
$l_{Ph,\,Ph}$, %	14	38	90

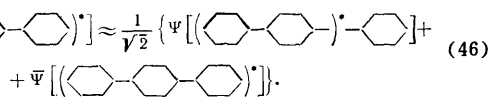
Evidently the α-band is caused by the small-radius excitation and can be identified with the benzene absorption band[81], in the p-band the contributions of the charged and locally excited states are comparable, while the large-radius excitation and hence the strongest linkage between the fragments correspond to the β-band. Naturally the asymmetric introduction of substituents into biphenyl leads to the removal of "degeneracy with respect to localisation" for the α-band and this results in the isolation of this excitation in one of the benzene rings; as a consequence of the strong interaction between the rings, the excitation involving the molecule as a whole persists for the p- and β-bands. The example of the 4-amino-4'-hydroxybiphenyl molecule [formula (29)] examined in Section V is fully consistent with this interpretation.

The similarity of the biphenyl α-band to the benzene band is manifested by the fact that the atomic localisation indices L_μ can be inferred fairly accurately from the values of L_μ

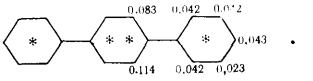
for the corresponding band in the benzene spectrum, where all the L_μ are 1/6 by virtue of symmetry. Then, having superimposed two diagrams of the benzene molecule and having renormalised the resulting numbers to unity, we find that all the L_μ should be close to $1/12 \cong 0.083$. Direct quantum-chemical calculation yields a diagram close to this uniform picture:



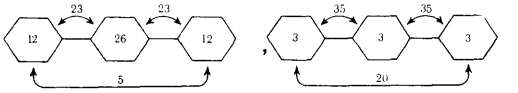
In terphenyl the α-band is also of the benzene type, but the central and lateral rings are not equivalent, since the excitation can be regarded as the result of alternate benzene-type excitation of two biphenyl fragments, or more precisely



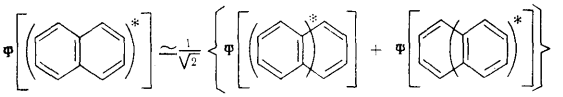
The central ring therefore contributes to the resultant excitation twice as much as the side rings, which can be represented by means of a scheme in which the indices L_μ, arising in this description, are indicated on top and the values calculated by Eqn.(25) are given below:



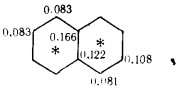
In the spectrum of the same molecule the p- and β-absorption bands are characterised by charge-transfer number diagrams similar to those for biphenyl:



The existence of a benzene-type α absorption band in the spectra of polyacenes indicates the possibility of a structural-chemical description of the corresponding excitation similar to that in formula (46). However, owing to topological features of such systems (marked edge connectivity), their molecules cannot be subdivided into a set of non-intersecting purely benzene-type fragments. Alternate excitation of superimposed benzene rings therefore corresponds to the α-band. For example, in naphthalene we have

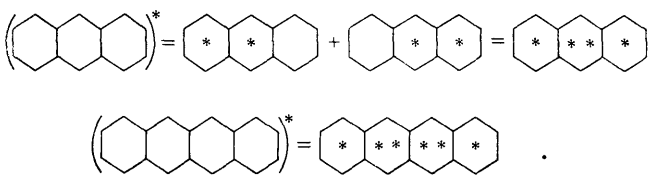


which gives rise to a diagram of L_μ indices of the type



where the numbers below are empirical values estimated by Luzanov and Umanskii[57].

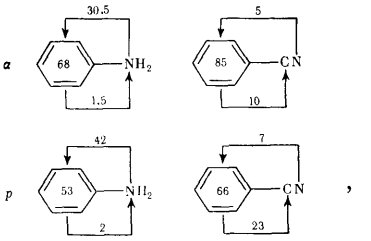
In higher polyacenes benzene-type absorption arises as a result of the alternate benzene-type excitation of the naphthalene fragment migrating throughout the molecule. For anthracene and tetracene, this has the following implication:



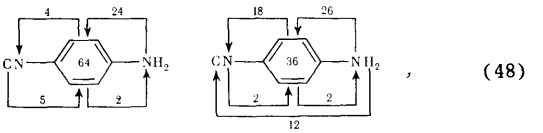
Thus, despite the rigid connectivity, in condensed hydrocarbons benzene-type absorption is also of a local type and therefore constitutes a small-radius excitation.

The study of the charge-transfer numbers in non-alternant molecules due to the charged states which lead to the observed physical effects, because $l_{A\to B} \neq l_{B\to A}$ is of special interest.

As an illustration, we shall consider the results of the calculation of the α- and p-bands of benzene derivatives. For aniline and benzonitrile, the charge-transfer number diagrams have the following form:



while for p-aminobenzonitrile we have



The absence in some of them of an arrow from A to B implies that the corresponding charge-transfer number $l_{A\to B} = 0$.

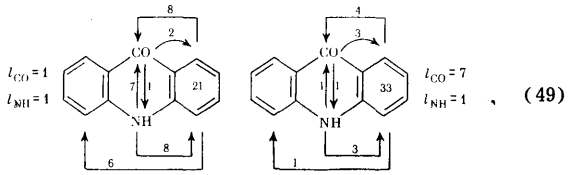
It is noteworthy that the charge transfer at right angles to the polarisation vector of the transition is smaller than in the case where the fragments between which charge transfer takes place are located on a line parallel to the polarisation vector. The α-bands therefore correspond to a less polar transition than the p-bands (cf. the numbers κ in Section II). In the same case, when the fragments are linear in a molecule with a symmetry of C_{2v} and higher, the charge-transfer number for a band polarised at right angles to the line of the fragments become rigorously equal to zero owing to symmetry factors, for example, in the case of $l_{NH_2 \rightleftharpoons CN}$ for p-aminobenzonitrile.

The case of p-aminobenzonitrile is of additional interest, because this compound contains electron-donating and electron-accepting groups simultaneously. As a consequence of symmetry factors, the long-wavelength band reflects the situation where there is no charge transfer whatever between the donor and the acceptor, while in the case of the p-band, which is identified as the charge-transfer band for molecules of this kind, the degree of charge transfer between the acceptor and the donor is smaller than the degree of charge transfer from the amino-group to the phenyl group and from the phenyl group to the nitrile group. However, since the change in the charge on CN following excitation is 0.28 and that on NH_2 is approximately −0.36, it may turn out that the charge is mainly transferred directly from the donor to the acceptor. Furthermore, diagram (48) shows that only one-third of the entire charge Δq_{NH_2} is removed in this way. The assignment of the corresponding band as one associated with charge transfer between the donor and the acceptor is therefore somewhat arbitrary, although the polar nature of such transitions, which are large-radius transitions, is significantly greater than that of the more localised small-radius transitions giving rise to α-bands. Additional illustrations have been published elsewhere[79].

Valuable information about the local nature of the transition can be obtained by considering the fine structure of molecular spectra[12]. Since electronic excitation is from the zero-point vibrational level of the ground state to the vibrational

levels of the excited state, the absorption spectra should exhibit progressions associated with the frequencies of the vibrational spectrum of the excited molecule and their intensity should be proportional to the square of the overlap of the vibrational functions of the ground and excited states. As a result of the concentration of the excitation in a certain molecular fragment, progressions generated by the characteristic vibrations of the given fragment in the excited state are the most intense. In the luminescence spectra one then observes the vibrational frequencies of the fragment in the ground state (corresponding to the infrared spectrum), because emission usually takes place as a result of the transition from the zero-point vibrational level of the excited molecule to the vibrational levels of the ground state.

We shall therefore consider the excitation diagrams for acridone, the spectrum of which has been studied in detail[82]. In the first excited singlet and triplet states the partial localisation and charge-transfer numbers yield the following distribution of excitations:



(49)

The degree of polarity of the singlet transition, treated as the sum of all the charge-transfer numbers $l_{AB}(A \neq B)$ is more than 50%. In the lowest triplet state, many of the properties of which are closer to those of the ground state than to the corresponding excited singlet state, the degree of polarity is smaller (26%). The vibrational structure of the phosphorescence spectrum makes it possible to determine the characteristic frequencies in the infrared spectrum of the benzene ring and the carbonyl group; in the latter they are not dominant (in contrast to $n\pi^*$-phosphorescence). Diagram (49) agrees with these observations—the local numbers for the benzene rings (0.33) prove to be much greater than for the carbonyl group (0.07).

We may note that the relation between the charge-transfer numbers and the fine structure of the band in the electronic spectrum is not unambiguous. However, one can assume that the individuality of the fragments under the conditions of pronounced charge transfer between them is lost, so that, other conditions being equal, the manifestation of the vibrational structure of the excited fragments is hindered.

The intensity of the corresponding transition is related to the polar nature of the excited state. Strictly speaking, theory does not predict a parallel variation of the degree of charge transfer and one can claim that, if $l_{AB}=1$, i.e. there is complete charge transfer, then the intensity of the π-band becomes zero. Complete charge transfer does not usually occur and the intensity of the transition is influenced by the topology of the molecule, its size, vibronic effects, intermolecular interaction, etc. In the systems considered above charge-transfer bands arose for transitions polarised in the direction of the long molecular axis. Their intensity is therefore greater than that of the α-bands polarised at right angles and related genetically to transitions of purely benzenoid systems, which are prohibited by the alternant properties.

For short-radius excitations, it is possible to establish in many instances definite relations between the parameters of the molecular shape and the intensity of the transition[83].

In conclusion we shall state an analogue of formula (22′) for charge-transfer numbers, namely, in terms of the basis set of natural orbitals, we have[80] $\tau=\Sigma\mu_\alpha^{1/2}\times|\phi_{N+\alpha}\rangle\langle\phi_\alpha|$; consequently, the charge-transfer numbers defined by Eqn.(39) can be expressed in terms of localisation orbitals defined by Eqn.(19):

$$l_{A\to B}=\sum_{\alpha=1}^{r}\mu_\alpha L_A(\varphi_\alpha)\cdot L_B(\varphi_{N+\alpha}).$$

This representation does not hold in terms of the basis set of canonical molecular orbitals, although attempts had been made earlier to use the corresponding quantities in order to estimate the degree of charge transfer[61].

VII. DISTRIBUTION OF EXCITATION ENERGY AMONG THE STRUCTURAL ELEMENTS OF THE MOLECULE

We shall now attempt to elucidate in what way selective localisation of excitation is related to changes in the properties of the molecule in the electronic transition. Apparently marked isolation of excitation in a single fragment implies that all the changes in the molecular characteristic $\mathscr{X}$ on excitation are associated precisely with this fragment, i.e. the corresponding physical quantity $\Delta\mathscr{X}=\mathscr{X}_*-\mathscr{X}$ is, as it were, localised in a given limited region of the molecule. In this connection the study of the spatial distribution of excitation energy assumes particular interest.

There is much experimental evidence for the possibility of the preferential concentration of the transition energy $\lambda=E_*-E$ at individual bonds or in other structural elements of the molecules[9]. In particular, the photochemical instability of the fragment is attributed to the localisation in the latter of a considerable proportion of the excitation energy[84].

The first attempts to explain what should be understood in terms of the spatial distribution of the electronic energy were made by Tatevskii[85]. However, the method of analogies which he used did not enable him to obtain any specific results, since the distribution of energy proved to be simply proportional to the electron density. This conclusion should have been surprising, since the energy of the system is determined not only by the one-particle density matrix, but also by the two-particle density, which averages the Coulombic interaction between the electrons in the calculation of E.

It must be emphasised that in the steady state the quantum-mechanical system possesses the total energy E observed in direct experiments as a unique quantity and the assignment to an isolated region of the molecule of a proportion of the energy localised in this region constitutes a non-trivial procedure with a controversial physical interpretation[86].

Strictly speaking steady states in which one could observe simultaneously with E also a local energy $\mathscr{E}(\mathbf{r})$ concentrated at a point $\mathbf{r}$ do not exist in the general case in quantum mechanics. However, in principle the operator corresponding to the required energy density $\mathscr{E}(\mathbf{r})$ can be set up on the basis of rules developed in the quantum field theory, where such an operator is known as the density of the Hamiltonian $\mathscr{H}(\mathbf{r})$.[87] Then, by calculating the average value of $\mathscr{H}(\mathbf{r})$ for the states of the system under investigation, we thereby obtain the required information about the spatial distribution of the energy in this state. The applied aspects of this approach[88] become evident if one takes into account the fact that regions with a low energy density (as a negative quantity) are most likely to exhibit the highest reactivity and the concentration of excitation energy (as a positive quantity) in the vicinity of specific atoms in the molecule indicates an increased photochemical reactivity of these atoms.

In order to calculate $\mathscr{E}(\mathbf{r})$, we should determine the density of the Hamiltonian as a Hermitian operator $\mathscr{H}(\mathbf{r})$, having the following form in terms of atomic units[87]:

$$\mathscr{H}(\mathbf{r})=\tfrac{1}{2}\nabla\psi^+(\mathbf{r})\cdot\nabla\psi(\mathbf{r})+U(\mathbf{r})\psi^+(\mathbf{r})\psi(\mathbf{r})+\tfrac{1}{2}\int\psi^+(\mathbf{r})\psi^+(\mathbf{r}')g(\mathbf{r},\mathbf{r}')\psi(\mathbf{r}')\psi(\mathbf{r})\,d\mathbf{r}',$$

where $\Psi^+(\mathbf{r})$ and $\Psi(\mathbf{r})$ are the electron generation and annihilation operators, the function $U(\mathbf{r})$ describes a one-particle interaction potential, and the function $g(\mathbf{r},\mathbf{r}')$ describes a two-particle interaction potential. In conformity with the approach adopted here, the required energy density $\mathscr{E}(\mathbf{r})$ is obtained by averaging $\mathscr{H}(\mathbf{r})$ with respect to the state investigated $|\Phi>$ in terms of a secondary quantisation representation:

$$\mathscr{E}(\mathbf{r}) = \langle\Phi|\mathscr{H}(\mathbf{r})|\Phi\rangle,$$

The total energy of the system E is obtained by integration with respect to the entire configurational space:

$$E = \int \mathscr{E}(\mathbf{r})\, d^3\mathbf{r}.$$

After introducing the spin-free single-particle density matrix $P(\mathbf{r}|\mathbf{r}')$ and the two-particle density matrix $R(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1',\mathbf{r}_2')$,

$$P(\mathbf{r}|\mathbf{r}') = \langle\Phi|\psi^+(\mathbf{r})\psi(\mathbf{r}')|\Phi\rangle, \tag{50}$$

$$R(\mathbf{r}_1,\mathbf{r}_2|\mathbf{r}_1',\mathbf{r}_2') = \langle\Phi|\psi^+(\mathbf{r}_1)\psi^+(\mathbf{r}_2)\psi(\mathbf{r}_2')\psi(\mathbf{r}_1')|\Phi\rangle,$$

we find a more detailed expression for the density:

$$\mathscr{E}(\mathbf{r}) = \left[\left(\tfrac{1}{2}\frac{\partial}{\partial\mathbf{r}}\frac{\partial}{\partial\mathbf{r}'} + U(\mathbf{r})\right)P(\mathbf{r}|\mathbf{r}')\right]_{\mathbf{r}=\mathbf{r}'} + \int g(\mathbf{r},\mathbf{r}')R(\mathbf{r},\mathbf{r}'|\mathbf{r},\mathbf{r}')\,d^3\mathbf{r}'. \tag{51}$$

In the special case of a system of non-interacting particles, only the first term remains in Eqn.(51) and, when a one-particle system is investigated, we have

$$\mathscr{E}(\mathbf{r}) = \tfrac{1}{2}|\nabla\varphi(\mathbf{r})|^2 + U(\mathbf{r})|\varphi(\mathbf{r})|^2,$$

where $\varphi(\mathbf{r})$ is the wave function of the particle. Even in this simple case $\mathscr{E}(\mathbf{r})$ differs from the electron density $E|\varphi|^2$ by the momentum $\frac{1}{2}(\varphi^*p^2\varphi - |p\varphi|^2)$, where $\mathbf{p}$ is the momentum operator.

We shall now turn to the details of the general formula (51) for a one-determinant description of the ground state of the molecule in terms of the Hartree–Fock approximation. For this purpose we express Eqn.(51) in a more convenient form by introducing the Hermitian energy density operator $\hat{\mathscr{E}}$ in the specified state $|\Phi>$ described by the overall density matrices of type (50) with the spin variables ρ_1 and ρ_2:

$$\hat{\mathscr{E}} = \tfrac{1}{2}([h,\rho_1]_+ - 1/2[\mathbf{p},[\mathbf{p},\rho_1]_-]_- + \underset{(2)}{\mathrm{Sp}}[g(1,2),\rho_2(1,2)]_+),$$

where the one-particle Hamiltonian $h = \frac{1}{2}\mathbf{p}^2 + U$ has been introduced. It can be readily shown that the diagonal elements $\hat{\mathscr{E}}$ in the coordinate representation $<\mathbf{r}|\hat{\mathscr{E}}|\mathbf{r}'>$ coincide exactly with the energy density (51) and $\mathrm{Sp}\,\hat{\mathscr{E}} = E$. In terms of the Hartree–Fock approximation, $\rho_1 = \rho \equiv \sum_{i=1}^{N}|i\times i|$, where $|i>$ is the population of the spin-orbital of the ground state and the two-particle density $\rho_2(1,2)$ is given by an antisymmetrised direct product: $\rho_2(1,2) = A_2\rho(1)\rho(2)$. Hence we find immediately the structure of the energy density operator in terms of the self-consistent field approximation:

$$\hat{\mathscr{E}} = \tfrac{1}{4}([f+h,\rho]_+ - [\mathbf{p},[\mathbf{p},\rho]_-]_-), \tag{52}$$

where $f = h + 2G(\rho)$ is the Fock operator of the many-electron system investigated and $G(X) \equiv \underset{(2)}{\mathrm{Sp}}A_2 g(1,2)X(2)$.

The distribution of energy among the structural elements of the molecule, primarily atoms and bonds, rather than the local density $\mathscr{E}(\mathbf{r})$ is of direct interest for quantum-chemical purposes. The corresponding index can be determined by integrating $\mathscr{E}(\mathbf{r})$ in the region A investigated and leads to the replacement of $\mathscr{E}(\mathbf{r})$ by the quantities $\mathscr{E}_\mu = <\chi_\mu|\hat{\mathscr{E}}|\chi_\mu>$ in terms of the basis set of the atomic orbitals χ_μ, and $\mathscr{E}_A = \sum_{\mu\in A}\mathscr{E}_\mu$.

We shall now consider the special cases $\mathscr{E}_\mu$ in terms of the self-consistent field approximation [formula (52)]. Firstly, for neutral states of alternant hydrocarbons, one can show that, in terms of the π-approximation, the contributions of momentum to $\mathscr{E}_\mu$ become zero whatever the multiplicity of the electronic energy state. Furthermore, neglect of the inter-electron interaction in an alternant molecule is known to result in the Hückel model, for which we obtain, taking into account $\hat{\mathscr{E}} = h\rho = \rho h$, the following index of the localisation of energy§ at the atom μ, expressed in terms of the spin-free bond orders $P_{\mu\nu}$: $\mathscr{E}_\mu = \beta\sum_\sigma P_{\mu\sigma}$, where σ represents only centres adjoining μ. This is clearly none other than the free valence index of the atom to within constant terms. Thus the energetic indices $\mathscr{E}_\mu$ extend the reactivity index to the case of the Hartree–Fock description of arbitrary molecular systems.

In the light of the foregoing, it is not difficult to find the excitation energy density $\lambda(\mathbf{r})$, which we defined naturally as the difference between the densities in the ground $\mathscr{E}(\mathbf{r})$ and excited $\mathscr{E}_*(\mathbf{r}) = <\Phi_*|\mathscr{H}(\mathbf{r})|\Phi_*>$ states. We shall adopt the superposition of all the singly excited configurations, for which the density matrices have been obtained[17], as a fairly adequate approximation for the excited state Φ_* in relation to the Hartree–Fock ground state Φ. The final result of the calculation of $\lambda(\mathbf{r}) = \mathscr{E}_*(\mathbf{r}) - \mathscr{E}(\mathbf{r})$ leads to the following excitation localisation operator:

$$\hat{\lambda} = -\tfrac{1}{4}([f+h,D^2Y]_+ + [G(DY),DY]_+ - [G(D),D]_- + 2[G(D^2Y),\rho]_+ - [\mathbf{p},[\mathbf{p},D^2Y]_-]_-),$$

the diagonal elements of which are the same as $\lambda(\mathbf{r})$ in terms of the coordinate representation, while combinations of the matrix elements in terms of the atomic basis set of type $\mathscr{E}_A$ are the same as the indices of excitation at atoms and bonds. In the stability matrix method we have a similar expression but without the second anticommutator ($Y \equiv 2\rho - I$).

As for the ground state, in the case of neutral alternant systems in the π-electron approximation the momentum contributions to the diagonal elements $\hat{\lambda}$ in terms of the atomic orbital basis set disappear. If we then again resort to the Hückel model, then the spin-free operator $\hat{\lambda}_0$ reduces merely to a single anticommutator, which can be readily transformed into a product:

$$\hat{\lambda}_0 = -[h, D_0^2Y_0]_+ = -2hD_0^2Y_0,$$

where the subscript 0 indicates a spin-free quantity here and henceforth.

We shall consider in the same systems a one-electron transition from the $|i>$ orbital to the corresponding, in terms of alternant symmetry, vacant orbital $|i'>$, i.e. $D_0 = (|i><i'| + |i'><i|)/\sqrt{2}$, and, on the basis of the theory of parity, the one-electron energy is $\mathscr{E}_i = -\mathscr{E}_{i'}$. It is then easy to observe that $\hat{\lambda}_0(i\to i') = 2|\mathscr{E}_i|D_0^2$ and if we now introduce the energy localisation operator as the operator $\hat{\lambda}_0$ normalised with respect to unity and the corresponding localisation indices

$$\hat{L}_0 = 1/\lambda\hat{\lambda}_0, \quad L_A^{\mathscr{E}} = \sum_{\mu\in A}\langle\chi_\mu|\hat{L}_0|\chi_\mu\rangle,$$

we observe in this instance ($\lambda = 2|\mathscr{E}_i|$) the identity of $\hat{L}_0$ and the matrix D_0^2.

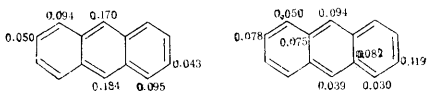
Consequently the energetic localisation indices $L_A^{\mathscr{E}}$ for the diagonal transitions $i\to i'$ in terms of the Hückel approximation are identical with the localisation numbers L_A described

§ The Hückel energy indices (without momentum contributions) have been introduced[99] on the basis of intuitive considerations.

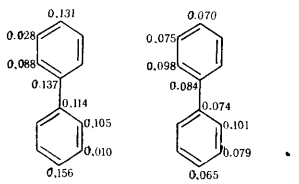
above. The inclusion of electronic interaction in terms of a self-consistent scheme for alternant systems causes an insignificant deviation of L_A^{ε} from L_A. However, in systems with an inhomogeneous charge distribution the excitation indices calculated from the operator $\hat{L}_0$ differ appreciably from the quantities defined by Eqn.(23).

For non-alternant systems, one fundamental difference between these operators is clearly manifested. In contrast to D_0^2 and despite the evident normalising property $\mathrm{Sp}\,\hat{L}_0 = 1$, the operator $\hat{L}_0$ is not in the general case defined as a non-negative quantity and its diagonal elements are therefore not definite. The possible negative sign of $\langle\chi_\mu|\hat{L}_0|\chi_\mu\rangle$ can, however, be interpreted as evidence for the existence of regions in the molecule which are not loosened on excitation but are actually stabilised to an even greater extent than in the ground state. This factor makes the localisation indices obtained from the energetic criterion particularly informative as regards the photochemical aspect.

The localisation numbers L_A (above) and the energetic indices L_A^{ε} (below) are given below for the p- and β-bands of anthracene

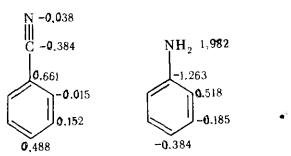


and biphenyl



The above diagrams show that, on excitation to the $^1B_{2u}$ state, the transition energy is distributed fairly non-uniformly among the atoms in the molecule, being concentrated in the 9- and 10-positions in anthracene (approximately 40% of the overall value of λ) and in the 4- and 4'-positions in biphenyl (>30% of λ). Data for the photodimerisation of anthracene and the Diels–Alder photoaddition[89] show that the atoms in the 9- and 10-positions are indeed photochemically active in anthracene.

An example of excitations for which positive and negative values of L_A^{ε} are possible is provided by the intense long-wavelength transitions (p-bands) in non-alternant molecules—benzonitrile and aniline:



The negative values of L_A^{ε} for the CN group indicate the photochemical stability of the latter. At the same time, the ring carbon atom closest to CN is greatly destabilised ($L_C^{\varepsilon} = 0.66$) and the chemical reactions in the excited state should therefore involve primarily this atom. In fact there is a tendency towards the photoaddition of trimethylethylene to benzonitrile in precisely this position[89]. On the other hand, in aniline the outer NH_2 group is the most active section of the excited molecule and this feature promotes the experimentally observed photoabstraction of hydrogen from the aniline NH_2.[90] The different signs of L_μ^{ε} in these molecules are consistent with the opposite directions of the charge transfer in them.

The uniform distribution of the excitation involving the molecule as a whole leads to smaller energetic localisation indices than for excitation isolated in a fragment and hence excited molecules which are photochemically more stable. In asymmetric systems the charge-transfer states are of this kind, as stated in Section V. In excited charge-transfer systems the photochemical stability is therefore higher than for local excitations[91].

The data presented in this review permit the formulation in a specific form of the quantum-chemical aspects of the concept of the "structure of electronic excitation".

The "internal" structure of the wave function Φ_* describing the excited state, namely the existence of the most important invariant elements of Φ_* of the type of independent singly excited configurations, the determination of orbitals which impart to Φ_* the simplest form, etc., was studied in the first place. The search for such invariant elements inevitably leads to natural orbitals of the excited state which are reconstructed anew for each electronic transition from the usual self-consistent molecular orbitals of the ground state. Analysis of model (3) yielded an important and somewhat unexpected conclusion—the greater the number of natural independent configurations in Φ_*, the smaller the changes undergone by the molecule as a whole on electronic excitation. This assertion shows how the internal structure determines the characteristic features of the external excitation structure in model (3). Our analysis of the external structure was concentrated on the study of the distribution of excitation in the direct structural-chemical sense (in atoms, bonds, whole fragments, etc.), on the elucidation of the physicochemical consequences of the selective localisation of excitation in fragments, on the determination of the relation between the localisation of excitation and charge transfer, etc.

The localisation numbers L_A and l_A, the charge-transfer numbers $l_{A\to B}$, and the energetic excitation indices L_μ^{ε} are all quantities arising in the method of transition density operators, which have demonstrated, in our view, a certain elegance and clarity in the interpretation of the external excitation structure mentioned above, which is important primarily for applied purposes.

The range of problems in the solution of which excitation indices defined by Eqns.(23) and (26) are used continues to be extended. An attempt has been made to apply the excitation localisation numbers in the analysis of data on the photoisomerisation of stilbene derivatives[92]. Studies have been made on the use of the indices L_A and l_{AB} for new classes of molecules[93–96]. Different analytical methods for excited states have been compared[97] and definite advantages of localisation numbers introduced by Luzanov and coworkers[42,80], compared with similar numbers introduced by other workers[59,61], have been pointed out.

Further efforts to generalise the above numerical characteristics of the wave function Φ_* (more accurate than in the initial model), adopted in this review (superposition of all singly excited configurations), therefore merit attention. One of the versions of such generalisation has been discussed by the present author in a paper[80], where it was suggested that the generalised matrix $\tilde{D}^2$ be constructed by analogy with Eqn.(34) using the normalised operator modulus of the change in the one-particle density matrix $|\rho_1^* - \rho_1|$ on transition from the ground state, not necessarily of the Hartree–Fock type, to an excited state, which does not necessarily reduce to approximation (3).

The internal excitation structure could be studied in a manner similar to the entropic analysis of wave functions considered by Bochvar et al.[98] In terms of the applied aspect, the application of the method of excitation indices[42,79] to non-conjugated molecules is not of interest solely as regards the

π-electron model, which has been used in all the computational studies quoted in this review. Such are apparently the likely prospects for the development of the methods of description of the electronic excitation structure of molecules discussed here.

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