De-localization of Bond Eigenfunctions in π-Electronic Systems. I. Proposal of an Approximate Method for the Calculation of the π-Electronic States of Molecules

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If in complex π-electronic systems all kinds of linearly independent resonance structures were taken as a set of canonical structures, the calculation of the various physical quantities (for example, energy levels, π-electron densities, or bond orders) would be extremely laborious. For the sake of diminishing such difficulties, various approximate treatments have been proposed. In most of them, however, only a small number of resonance structures, which are expected to be comparatively important, have almost intuitively been taken as a set of canonical structures$^{1-3)}$.

One of these treatments is the Heitler-London method, where only the covalent structures are considered. One of the greatest defects of this method is that by this method it is impossible to explain the migration effects of the π-electrons from the substituents of mono-substituted benzenes (phenol, aniline, chlorobenzene, etc.) to the benzene nuclei$^{4)}$.

Importance of the ionic structures has been emphasized by Daudel and Daudel$^{5)}$, and a few calculations including them have been carried out$^{6)}$. But these attempts are very qualitative,

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1) L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

2) A. L. Sklar, ibid., **5**, 669 (1937).

3) D. P. Craig, *Proc. Roy. Soc.*, **A200**, 401 (1950).

4) L. Pauling and G. W. Wheland, *J. Am. Chem. Soc.*, **57**, 2086 (1935).

5) P. Daudel and R. Daudel, *J. Chem. Phys.*, **16**, 639 (1948).

6) J. A. A. Ketelaar, *Rec. trav. chim.*, **58**, 266 (1939); See also Refs. 2 and 3.

and the number of ionic structures considered is also extremely small.

Now, it is well known that the molecular orbital method and the Heitler-London method are the two extreme approximations, in which the contributions of the ionic structures are too much emphasized and too much neglected respectively. Therefore, a new approximate method is desirable one, which corresponds to the middle point of view of the two methods.

The approximate method which is proposed by us stands on this middle ground and is as follows: all the resonance structures under consideration are sorted out into a few classes, suitable functions which are the linear combinations of the bond eigenfunctions for the structures in each class are found, and the wave functions for the molecule are represented by linear combinations of them.

By this method the degree of the energy determinants is more diminished than in the straightforward method. Hence, the problem can be simplified in cases when a great number of resonance structures are included.

Since there are various manners for the classification of the resonance structures, one particular manner must be selected. The appraisal of multiple exchange integrals is however, made prior to this, since it directly relates to our manner of classification.

Appraisal of Multiple Exchange Integrals

Multiple exchange integrals, which appear by way of the computation of the π-electronic energy levels of polyatomic molecules based on the valence bond method, have hitherto been neglected[2,3]. It does not seem, moreover, that satisfactory appraisals of them have been made, in spite of the emphasis on their importance[7].

Accordingly, in this paragraph the influence of the multiple exchange integrals upon the energy matrix with respect to the bond eigenfunctions is discussed by means of illustrations

TABLE I. COMPARISON OF RESONANCE INTEGRALS*

Kind of interacting structures**	Resonance integrals	Multiple exchange integrals not included (I)	Multiple exchange integrals included (II)	Difference (II-I)
		trans-Butadiene		
N-N	(*ad* : *bc*-*ad* : *bc*)	−46.83703	−46.92960	−0.09257
	(*ab* : *cd*-*ac* : *bd*)	+25.23109	+25.26019	+0.02909
N-M	(*ab* : *cd*-*aa* : *cd*)	−18.97761	−20.85919	−1.88158
	(*ab* : *cd*-*ac* : *bb*)	+4.15071	+4.12262	−0.02809
N-D	(*ab* : *cd*-*bb* : *cc*)	−9.40144	−8.78519	+0.61624
	(*ac* : *bd*-*aa* : *dd*)	+4.71797	+4.71817	+0.00019
M-M	(*ab* : *cc*-*aa* : *bd*)	+0.63185	−1.85967	−2.49153
	(*aa* : *bd*-*aa* : *bd*)	−33.94508	−33.94215	+0.00293
M-D	(*aa* : *cd*-*bb* : *dd*)	0	−2.03915	−2.03915
	(*aa* : *bd*-*aa* : *dd*)	−2.55372	−2.55374	−0.00002
D-D	(*aa* : *cc*-*bb* : *dd*)	0	−0.46832	−0.46832
	(*aa* : *dd*-*aa* : *dd*)	−29.17000	−29.17000	−0.00000
		Cyclobutadiene		
N-N	(*ab* : *cd*-*ab* : *cd*)	−61.90093	−57.08229	+4.81863
	(*ab* : *cd*-*ac* : *bd*)	+28.76985	+25.24667	−3.52318
N-M	(*ab* : *cd*-*ab* : *cc*)	−20.51222	−19.89659	+0.61563
	(*ab* : *cd*-*aa* : *bd*)	+1.59245	+1.33355	−0.25890
N-D	(*ab* : *cd*-*aa* : *bb*)	+5.65218	+3.77742	−1.87477
	(*ac* : *bd*-*aa* : *bb*)	+3.27535	+3.91720	+0.64186
M-M	(*ab* : *cc*-*bd* : *cc*)	−15.84698	−13.36064	+2.48634
	(*ab* : *cc*-*ac* : *bb*)	+12.30104	+12.62430	+0.32326
M-D	(*ab* : *cc*-*cc* : *dd*)	−2.67620	−0.68669	+1.98951
	(*ab* : *cc*-*bb* : *dd*)	0	+0.00740	+0.00740
D-D	(*aa* : *cc*-*aa* : *bb*)	−4.59603	−3.53324	+1.06278
	(*aa* : *cc*-*bb* : *dd*)	0	+0.00492	+0.00492

* Values are in electron volts.

** N, M and D mean non-polar, mono-polar, and di-polar structures respectively.

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[7] C. A. Coulson, "Valence", Oxford University Press, Oxford (1952), p. 237.

of *trans*-butadiene and cyclobutadiene molecules.

When the numerical values of the molecular integrals are taken from Parr and Mulliken[8] for *trans*-butadiene and from Craig[9] for cyclobutadiene, the results of Table I for the resonance integrals are obtained. In the table a, b, c and d are carbon atoms and are marked in order from one end of the molecule to the other for *trans*-butadiene and clockwise beginning with the left upper atom for cyclobutadiene. $ij : kl$ $(i \neq j, k \neq l)$ is the resonance structure in which there are π-electronic covalent bonds between atoms i and j, k and l. $ii : kl$ is that in which an atom i possesses a lone pair of π-electrons. $(ij : kl - pq : rs)$ means the interaction between structures $ij : kl$ and $pq : rs$.

$$(ij : kl - pq : rs) = \int \Psi_{ij:kl} H \Psi_{pq:rs} \mathrm{d}v_1 \mathrm{d}v_2 \mathrm{d}v_3 \mathrm{d}v_4$$

were $\Psi ij_{:}kl$ is the normalized bond eigenfunction corresponding to the structure $ij : kl$, $\mathrm{d}v_i$ is the volume element for electron i, and H is the Hamiltonian operator commonly employed in considerations of π-electronic system

$$H = \sum_i H_{\mathrm{core}}(i) + (1/2) \sum_{\substack{i,j \\ i \neq j}} (c^2/r_{ij})$$

where

$$H_{\mathrm{core}}(i) = T(i) + U_{\mathrm{core}}(i)$$

$T(i)$ is the kinetic energy operator for electron i, and $U_{\mathrm{core}}(i)$ is the potential energy operator for this electron in the field of the core.

Numerical values in column 3 in Table I are results obtained by neglecting the multiple exchange integrals*. The integrals taken into account are of the following type:

$$Q_0 = \int \cdots\cdots a(1)b(2)c(3)d(4)e(5)f(6) \cdots\cdots H \cdots\cdots a(1)b(2)c(3)d(4)e(5)f(6) \cdots\cdots \mathrm{d}\tau$$

$$Q_1 = \int \cdots\cdots a(1)b(2)c(3)c(4)e(5)f(6) \cdots\cdots H \cdots\cdots a(1)b(2)c(3)c(4)e(5)f(6) \cdots\cdots \mathrm{d}\tau$$

$$Q_2 = \int \cdots\cdots a(1)b(2)b(3)d(4)d(5)f(6) \cdots\cdots H \cdots\cdots a(1)b(2)b(3)d(4)d(5)f(6) \cdots\cdots \mathrm{d}\tau$$

and the coulomb integrals Q_i's for the other higher polar structures:

$$K = \int \cdots\cdots a(1)b(2)c(3)d(4)e(5)f(6) \cdots\cdots H \cdots\cdots a(1)b(2)c(3)c(4)e(5)f(6) \cdots\cdots \mathrm{d}\tau$$

$$J_0 = \int \cdots\cdots a(1)b(2)c(3)d(4)e(5)f(6) \cdots\cdots H \cdots\cdots a(1)b(2)d(3)c(4)e(5)f(6) \cdots\cdots \mathrm{d}\tau$$

$$J_1 = \int \cdots\cdots a(1)b(2)c(3)d(4)e(5)f(6) \cdots\cdots H \cdots\cdots a(1)b(2)b(3)d(4)d(5)f(6) \cdots\cdots \mathrm{d}\tau$$

$$J_2 = \int \cdots\cdots a(1)b(2)b(3)d(4)e(5)f(6) \cdots\cdots H \cdots\cdots a(1)b(2)c(3)d(4)d(5)f(6) \cdots\cdots \mathrm{d}\tau$$

where $k(i)$ is the atomic orbital of the i-th electron on atom k and $\mathrm{d}\tau$ is the product of the volume elements for all the π-electrons.

Values in column 4 in the same table are results in which all types of integrals have been taken into account in the calculations.

In this table, only the results for the interactions of the resonance structures are shown in which the differences in the results for the approximate treatment from those for the exact one are the largest or the smallest for each kind.

Numerical values of the last column in Table I are of the same order as the penetration and coulomb-exchange integrals over atomic orbitals[8,9]. Particularly, in interactions between ionic structures and covalent structures or ionic structures, the lowest order of multiple exchange integrals L_i's appear, namely:

$$L_1 = \int \cdots a(1)b(2)c(3)d(4)e(5)f(6)g(7)h(8) \cdots H \cdots a(1)b(2)d(3)c(4)e(5)e(6)g(7)h(8) \cdots \mathrm{d}\tau$$

$$L_2 = \int \cdots a(1)b(2)c(3)d(4)e(5)f(6)g(7)h(8) \cdots H \cdots a(1)b(2)b(3)d(4)d(5)f(6)f(7)h(8) \cdots \mathrm{d}\tau$$

$$L_3 = \int \cdots a(1)b(2)c(3)c(4)e(5)f(6)g(7)h(8) \cdots H \cdots a(1)b(2)d(3)d(4)e(5)e(6)g(7)h(8) \cdots \mathrm{d}\tau$$

In the computations in which this kind of integral appears frequently, the influence of the multiple exchange integrals will be larger than that in the Heitler-London method because in the Heitler-London method the J_i' type of integrals,

$$J_0' = \int \cdots a(1)b(2)c(3)d(4)e(5)f(6)g(7)h(8) \cdots H \cdots a(1)b(2)d(3)c(4)f(5)e(6)g(7)h(8) \cdots \mathrm{d}\tau$$

$$J_1' = \int \cdots a(1)b(2)d(3)c(4)e(5)f(6)g(7)h(8) \cdots H \cdots a(1)b(2)c(3)d(4)f(5)e(6)g(7)h(8) \cdots \mathrm{d}\tau$$

appear as the lowest order multiple exchange integrals and are approximately equal to $L_i S$, where S is the overlap integral**.

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[8] R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

[9] D. P. Craig, *Proc. Roy. Soc.*, **A202**, 498 (1950).

* The use here of the term "multiple exchange integral" is not strictly correct. It is used conveniently for the higher orders of integrals, whose corresponding integrals, When the Hamiltonian operator is substituted for the unit operator, are more than the three order of overlap integrals.

** It will go without saying that the multiple exchange integrals which appear among atoms with nearer distances are more important than the non-multiple exchange integrals in the farther ones.

Use of the Orthogonalized Atomic Orbitals and Classification of Resonance Structures

From these considerations it seems that for quantitative or at least semi-quantitative computations of the π-electronic states of molecules, including the ionic structures besides the covalent ones, multiple exchange integrals must be taken into consideration.

One of the manners of classification of resonance structures which may easily be thought of is that in which covalent structures, monopolar structures, and di-polar structures, etc., are assigned to respective classes. It is, however, entirely inadequate to apply this manner to the quantitative calculations of polyatomic molecules, because in complex molecules the explicit evaluations of the multiple exchange integrals are extremely troublesome. Orthogonalized atomic orbitals(10) are, therefore, generally used to avoid this difficulty.

Actually, when only the covalent structures are assigned to a class, the integral types appearing in calculations are Q_0, J_0 and the other higher order ones. In cases when orthogonalized atomic orbitals are used, Q_0 is a mere additive term in each energy level and J_0 is generally repulsive, as can be inferred from the following expanded expression:

$$\overline{J_0}=\sum_{\substack{k\\ k\neq c,d}}\overline{\alpha}_k\overline{S}^2_{cd}+2\overline{\beta}_{cd}\overline{S}_{cd}+(1/2)\sum_{\substack{k,'\\ k\neq c,d\\ l\neq c,d,k}}(\overline{k}\overline{k}\mid\overline{l}\overline{l})\overline{S}^2_{cd}$$

$$+2\sum_{\substack{l\\ l\neq c,d}}(\overline{c}\overline{d}\mid\overline{l}\overline{l})\overline{S}_{cd}+(\overline{c}\overline{d}\mid\overline{c}\overline{d}),$$

where

$$\overline{\alpha}_k=\int\overline{k}(i)H_{\mathrm{core}}(i)\overline{k}(i)\mathrm{d}v_i$$

$$\overline{\beta}_{kl}=\int\overline{k}(i)H_{\mathrm{core}}(i)\overline{l}(i)\mathrm{d}v_i$$

$$\overline{S}_{kl}=\int\overline{k}(i)\overline{l}(i)\mathrm{d}v_i$$

$$(\overline{k}\overline{l}\mid\overline{p}\overline{q})=e^2\int(1/r_{ij})\overline{k}(i)\overline{l}(i)\overline{p}(j)\overline{q}(j)\mathrm{d}v_i\mathrm{d}v_j$$

where $\overline{k}(i)$ is the orthogonalized atomic orbital for the atomic orbital $k(i)$.

It will be understood by a procedure similar to that for $\overline{J_0}$ that the other higher order multiple exchange integrals lead to zeros.

It is ultimately deduced that, when the orthogonalized atomic orbitals are employed, the integral type, playing the most important role for the resonance effect of a molecule, is type $\overline{K}$, whose expanded expression is

$$\overline{K}=\sum_{\substack{k\\ k\neq d}}\overline{\alpha}_k\overline{S}_{cd}+\overline{\beta}_{cd}+(1/2)\sum_{\substack{k,l\\ k\neq d\\ l\neq d,k}}(\overline{k}\overline{k}\mid\overline{l}\overline{l})S_{cd}$$

$$+\sum_{\substack{l\\ l\neq d}}(\overline{c}\overline{d}\mid\overline{l}\overline{l})$$

It can be understood from the integral form of type K that, when including this type of integral in calculations, the ionic structures must always be included in each class of the classification.

From these considerations, the following manner of classification of resonance structures is proposed.

A covalent structure K and all the ionic structures, in which the two π-electrons on a certain bond in the structure K occupy the same atomic orbital on either side of the atom for the bond, are assigned to class K. Then the normalized bond eigenfunctions Ψ_L's corresponding to all the resonance structures L's belonging to this class are combined linearly, viz.,

$$\phi^K_i=\sum_L C^K_L\Psi_L$$

C^K_L is the coefficient of the bond eigenfunction Ψ_L and is determined by the variational method together with the normalization condition. ϕ^K_i is the function associated with class K, and the corresponding energy is E^K_i.

The function ϕ^K_i may be derived from the other covalent structures. Wave functions Φ_j's for the electronic states of the molecule are assumed to be linear combinations of the linearly independent ϕ^K_i's,

$$\Phi_j=\sum_K C^K_i\Phi^K_i$$

The values of the coefficients C^K_i's are, again, determined by the use of the variational method and the normalization condition. The resulting energies are denoted by E_j's.

Probabilities of Resonance Structures, π-Electron Densities and Bond Orders

Electron density and bond order have been discussed and have also been defined variously from the points of view of the molecular orbital method and the valence bond method(11). Since, however, analyses of these definitions are not our principal purpose, in this paper the contributive probabilities of resonance structures, π-electron densities, and bond orders are first defined for the straightforward HLSP valence bond method by the most conventional

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10) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950); **21**, 496 (1953).

11) L. Pauling, L. O. Brockway and J. Y. Beach, *J. Am. Chem. Soc.*, **57**, 2705 (1935); C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947); W. G. Penny, ibid., **A158**, 306 (1937); R. McWeeny, ibid., **A223**, 63 (1954).

expressions, and then a definition of them on the basis of our approximate method is made on that basis.

The Straightforward HLSP Method.—When the wave function Φ_G for the ground state of a molecule is represented by

$$\Phi_G=\sum_L C_L \Psi_L$$

where Ψ_L is the normalized bond eigenfunction for structure L and C_L is the coefficient, the probability P_L for structure L is

$$P_L=C_L\sum_J C_J\int \Psi_L \Psi_J \mathrm{d}\tau$$

and the π-electron density D_i in atom i is

$$D_i=\sum_L P_L m(i)_L$$

where $m(i)_L$ is the number of π-electrons in atom i in structure L. The bond order B_{ij} between atoms i and j is

$$B_{ij}=\sum_L P_L\,[n(ij)_L+1]$$

where $n(ij)_L$ is the number of π-electronic covalent bonds between atoms i and j in structure L.

The approximate method.—1) The probability P^K_L of structure L in class K is

$$P^K_L=C^K_L\sum_J C^K_J\int \Psi_L \Psi_J \mathrm{d}\tau$$

where C^K_L is the coefficient of the bond eigenfunction Ψ_L in the wave function ϕ^K_1 for the ground state of this class.

The π-electron density D^K_i in atom i in the ground state of class K is

$$\mathrm{D}^K_i=\sum_J P^K_J m(i)^K_J$$

where $m(i)^K_J$ is the number of π-electrons in atom i in structure J in class K. The bond order B^K_{ij} between atoms i and j in this state of class K is

$$B^K_{ij}=\sum_J P^K_J\,[n(ij)^K_J+1]$$

where $n(ij)^K_J$ is the number of π-electronic covalent bonds between atoms i and j in structure J in class K.

2) The probability P^K of the class K in the ground state of the molecule under consideration is represented by

$$P^K=C^K_1\sum_J C^J_1\int \phi^K_1 \phi^J_1 \mathrm{d}\tau$$

Therefore, the probability P_L of structure L is

$$P_L=\sum_J P^J P^J_L$$

the π-electron density D_i of atom i is

$$D_i=\sum_J P^J D^J_i$$

and the bond order B_{ij} between atoms i and j is

$$B_{ij}=\sum_J P^J B^J_{ij}$$

Survey of the Approximate Method and the Excited States

It must now be explained to what kind approach our method belongs. When a conjugated molecule is interpreted to be due to the σ-bond between parts, each of which contains a double bond, the wave functions representing the π-electronic states of this hypothetical molecule K are ϕ^K_i's in our approximation, and the energy values E^K_i's are obtained by solving the following equation:

$$H\phi^K_i=E^K_i\phi^K_i$$

Since, from the point of view of the valence bond method, the parts due to the π-bond between two non-neighboring atoms may be supposed, such hypothetical molecules K's can be found by the same number as all the π-type covalent structures conceivable for the molecule under consideration. The corresponding wave functions are ϕ^K_i's for all the class K's in our approximation. Wave functions Φ_i's for the electronic states of the entire molecule may, therefore, be represented by linear combinations of these linearly independent functions ϕ^K_i's.

Our approximate method is based on a hypothetical interpretation of the structures of molecules rather than on a mathematical approximation. In the Heitler-London method the basic functions Ψ_K's correspond to covalent structures. On the other hand, the functions ϕ^K_i's in our method mean that the π-bond between the two atoms is not the so-called "covalent bond", but is partly ionic.

For obtaining wave functions corresponding to the excited states of a molecule, number of wave functions in each class should be considered as a step in calculating the interaction of classes. It is not easy to find such wave functions however. In the practical calculations given in a later paper, therefore, an assumption will be made that the wave functions ϕ^K_i's for the lowest energies belonging to the respective symmetries in class K are employed as the wave functions associated with this class.

Our method may now also be applied successfully to computations using non-orthogonal atomic orbitals and Slater functions, as well as the orthogonalized atomic orbitals. An example based on the non-orthogonal atomic orbitals will be shown in Part II, where the energy levels evaluated by our approximaxe method are lower than the corresponding ones obtained by the Heitler-London method.

In the examples of Parts II–IV, the orthogonalization of the atomic orbitals is not made, except in cases where it is especially required. This is because, since the approximate procedure is generally made for the orthogonalization, the accuracy of the results is lower than that for calculations based on the non-orthogonal atomic orbitals, considering all the overlap and exchange integrals. Particularly for a molecule with a lower symmetry, matrix S does not commute with matrix H[10], and the procedure for the orthogonalization is more troublesome than expected.

Summary

The influence of the multiple exchange integrals in the HLSP method for the π-electronic systems has been investigated by means of the illustrations of *trans*-butadiene and cyclobutadiene molecules. Their importance for the theory, including ionic structures, has been emphasized. For avoiding difficulties in calculations due to the presence of many resonance structures in complex compounds, an approximate method has been proposed. In that method, the degree of energy determinants is diminished.

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