De-localization of Bond Eigenfunctions in π-Electronic Systems. III. Non-Empirical Calculation of the π-Electronic States of the Vinyl Chloride Molecule

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In previous papers⁽¹⁾ an approximate method, in which all the ionic structures are taken into consideration, was applied to the calculation of the π-electronic states of a conjugated homo-nuclear chain compound, and the quantitative agreement of the results with those obtained by the ASMO SCF CI method was achieved.

On the other hand, if that approximate method is applied, in the same way as in part II, to a consideration of the π-electronic states of monosubstituted benzenes, such as chlorobenzene or phenol molecules, almost meaningless results will be obtained. This is because by that method the ionic structures in such molecules, which are obtained by moving one or both of the lone pair of π-electrons in the atom adjacent to the benzene ring in the covalent structure into the ring, are not derived from any covalent structure conceivable at all with respect to those molecules.

In order to apply the approximate method to such molecules, therefore, special treatment will be required.

In this paper, the method is developed in order to be applied to the vinyl chloride molecule, from which chlorobenzene is derived by substituting the benzene nucleus for the vinyl radical. Electronic states of the molecule are calculated, and the results are compared with those obtained by the HLSP standard method.

Derivation of Three Classes of Canonical Structures

A conjugated double bond molecule, having the same number (four) of π-electrons as the vinyl chloride molecule, is supposed, and all the covalent structures conceivable with respect to this molecule are set up (Ref. Fig. 1.).

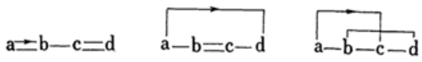

Fig. 1. Resonance structures of the conjugated molecule, consisting of four π-electrons and four atoms.

Then the π-electron, belonging to atom a in each structure, is made to move towards the atom in the direction of the arrow head, and ion a^+ is made to shift to an infinite distance (Ref. Fig. 2.).

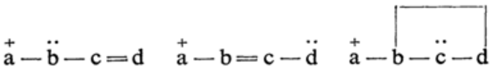

Fig. 2

Atoms b, c and d being substituted for chlorine, carbon and carbon atoms respectively, the resultant structures are the basic forms for the three classes of canonical structures; each class is obtained as in Fig. 3.

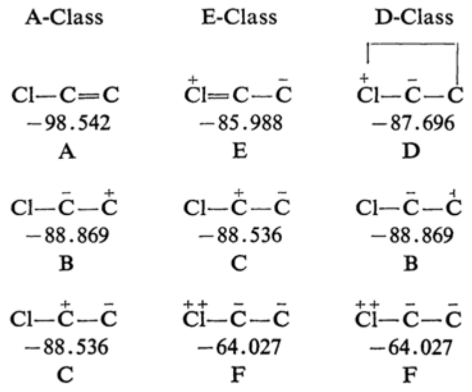

Fig. 3. Three classes of canonical structures and the energy values for the structures. Values are in electron volts.

The skeleton of the molecule is shown in Fig. 4. Slater $2p_\pi$- and $3p_\pi$-orbitals, with $Z_C=3.18$, $Z_{Cl}=6.099$ respectively, have been assumed for the carbon and the chlorine atoms. Numerical values of integrals over the atomic orbitals have been taken from Simonetta et al.⁽²⁾

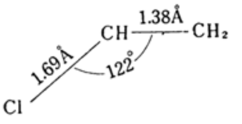

Fig. 4. Skeleton of vinyl chloride molecule.

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1) S. Takekiyo, This Bulletin, 35, 355 (1962); 35, 360, (1962).

2) M. Simonetta, G. Favini and S. Carra, *Mol. Phys.*, 1, 181 (1958).

TABLE I. WAVE FUNCTIONS ASSOCIATED WITH CLASSES AND THE CORRESPONDING ENERGY VALUES

A-Class	
$\phi_1^A = 0.78468\Psi_A + 0.23865\Psi_B + 0.22923\Psi_C$	$E_1^A = -100.304$ eV.
$\phi_2^A = 0.026821\Psi_A - 0.75119\Psi_B + 0.71540\Psi_C$	$E_2^A = -86.005$ eV.
$\phi_3^A = 0.84357\Psi_A - 0.73278\Psi_B - 0.77065\Psi_C$	$E_3^A = -80.335$ eV.
E-Class	
$\phi_1^E = 0.73693\Psi_C + 0.51843\Psi_E + 0.034910\Psi_F$	$E_1^E = -91.061$ eV.
$\phi_2^E = 0.71522\Psi_C - 0.85513\Psi_E - 0.099032\Psi_F$	$E_2^E = -81.517$ eV.
$\phi_3^E = 0.072333\Psi_C - 0.34638\Psi_E + 1.0230\Psi_F$	$E_3^E = -61.593$ eV.
D-Class	
$\phi_1^D = 0.81035\Psi_B + 0.55853\Psi_D + 0.024643\Psi_F$	$E_1^D = -89.891$ eV.
$\phi_2^D = 0.58685\Psi_B - 0.82679\Psi_D - 0.041893\Psi_F$	$E_2^D = -86.628$ eV.
$\phi_3^D = 0.0^{2}51618\Psi_B - 0.081459\Psi_D + 0.99936\Psi_F$	$E_3^D = -63.870$ eV.

All kinds of overlap, single exchange, and multiple exchange integrals have been considered.

Wave functions ϕ_i^K's for class K's and the corresponding energy values E_i^K's are given in Table I, where Ψ_L is the normalized bond eigenfunction for structure L.

Probabilities of the structures, π-electron densities, and bond orders for each class are shown in Table II and Fig. 5 respectively.

TABLE II. PROBABILITIES OF STRUCTURES IN EACH CLASS

	A-Class	
A	B	C
0.74923	0.12893	0.12183
	E-Class	
C	E	F
0.63234	0.36154	$0.0^{2}61249$
	D-Class	
B	D	F
0.67160	0.32733	$0.0^{2}10717$

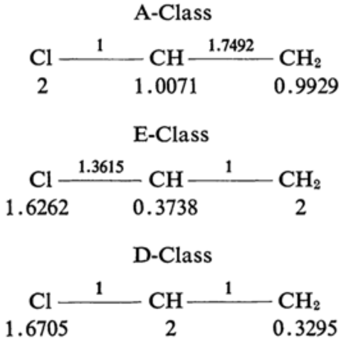

Fig. 5. π-Electron densities and bond orders in each class.

Electronic States of the Molecule

Wave functions for the lowest energy values in the respective classes have been combined linearly, and the wave functions Φ_i's for the molecule and the corresponding enery values E_i's have been calculated. The results are shown in Table III.

Then the probabilities of the structures, the π-electron densities, and the bond orders in the ground state of the molecule have been calculated from the results of Table II and Fig. 5. The results are shown in Table IV and Fig. 6, together with those obtained by the exact method.

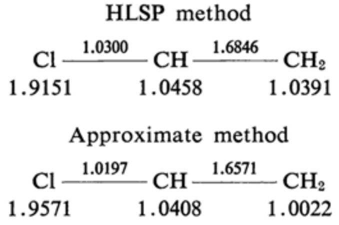

Fig. 6. Comparison of π-electron densities and bond orders.

Discussion

The value of the energy level for the ground state of the molecule, obtained by the exact HLSP method[3], is -100.91 eV. The difference of this value from the one obtained by the approximate method (Table III) is 0.35 eV., so the approximate method constitutes a good approach.

On the other hand, the excitation energy from the ground state to the first excited state is 11.41 eV. in the HLSP method. The approximate method, in which 12.98 eV. is obtained as in Table III, does not show a good agreement.

Finally, the wave function for the ground state has been transformed to represent the bond eigenfunctions explicitly. The result is:

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[3] S. Takekiyo, This Bulletin, 34, 1466 (1961).

TABLE III. WAVE FUNCTIONS FOR THE MOLECULE AND THE CORRESPONDING ENERGY VALUES

$\Phi_1 = 0.88437\phi_1^A + 0.10501\phi_1^E + 0.11540\phi_1^D$	$E_1 = -100.5590$ eV.
$\Phi_2 = 0.51913\phi_1^A - 1.10164\phi_1^E + 0.09376\phi_1^D$	$E_2 = -87.5810$ eV.
$\Phi_3 = 0.80471\phi_1^A - 0.19716\phi_1^E - 1.17076\phi_1^D$	$E_3 = -83.8402$ eV.

TABLE IV. COMPARISON OF THE PROBABILITIES OF RESONANCE STRUCTURES

HLSP method

A	B	C	D	E	F
0.68460	0.11099	0.11979	0.05429	0.03000	0.00033

Approximate method

A	B	C	D	E	F
0.65709	0.15915	0.14124	0.02245	0.01966	0.00041

$$\Phi_1 = 0.6939\Psi_A + 0.3046\Psi_B + 0.2801\Psi_C + 0.0644\Psi_D + 0.0544\Psi_E + 0.0065\Psi_F$$

while the result obtained by the HLSP method is

$$\Phi_G = 0.7359\Psi_A + 0.2184\Psi_B + 0.2213\Psi_C + 0.1616\Psi_D + 0.1152\Psi_E + 0.0067\Psi_F$$

From these results, it can be noticed that the migration percentage of the π-electrons in the chlorine atom to the vinyl radical in the approximate method is smaller than that in the other method.

One of the causes for such unsatisfactory results seems to be the neglect of the lower excited states in each class, which are at energy states close to the corresponding ground state, in the interaction of the classes (Ref. Table I).

Summary

The π-electronic energy levels, wave functions, π-electron densities, and bond orders of the vinyl chloride molecule have been calculated by the approximate method proposed in part I. Slater orbitals have been employed for the atomic orbitals of the carbon and chlorine atoms. All kinds of overlap, single exchange, and multiple exchange integrals have been considered. The calculated values of the energies for the ground state and the first excited state are -100.56 and -87.58 eV. The values obtained by the HLSP method are -100.91 and -89.50 eV. π-Electron densities are Cl $= 1.957$, C (in the center of the molecule) $= 1.041$, and C (in the edge of the molecule) $= 1.002$. These values, based on the HLSP method, are 1.915, 1.046 and 1.039 respectively. Bond orders between the neighboring carbon and chlorine atoms are 1.02 and 1.03 in the respective methods.

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