Non-Empirical Calculation of the π-Electronic States of Vinyl Chloride Molecule by Valence Bond Method

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In the year 1956, a semi-empirical treatment of vinyl chloride molecule with molecular orbital method has been performed by Goldstein[1] and recently self-consistent field calculation of the π-elctronic energy levels and the wave functions for the ground state has been carried out by Simonetta, Favini, and Carra[2]. On the other hand, it dues not appear that considerations on the basis of valence bond method have been made, except a semi-empirical treatment by Ketelaar[3].

In this paper the standard valence bond method is applied to the non-empirical calculations of the π-electronic states of vinyl chloride molecule and the results are compared with the values, obtained by LCAO self-consistent field calculations.

Orbital Energies

Internuclear distances and bond angle of the molecule are shown in Fig.1 and
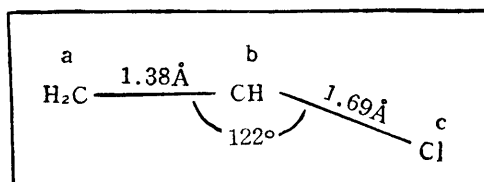

Fig. 1. Skeleton of vinyl chloride molecule.

Slater 2P- and 3P-functions are assumed for the carbon atoms and the chlorine atom, with $Z_C = 3.18$ and $Z_{cl} = 6.099$. Numerical values of integrals over atomic orbitals were taken from the paper of Simonetta and others[2].

All kinds of resonance structues, in which the corresponding bond eigenfunctions are independent mutually, and the numerical values of the energies for

1) J. H. Goldstein, *J. Chem. Phys.*, **24**, 507 (1956).

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

3) J. A. A. Ketelaar, *Rec. Trav. Chim.*, **58**,266 (1939).

structures, found by our calculations, are given in Fig. 2.

$$C\!\!=\!\!C\!\!-\!\!Cl \qquad \overset{+}{C}\!\!-\!\!\overset{-}{C}\!\!-\!\!Cl \qquad \overset{-}{C}\!\!-\!\!\overset{+}{C}\!\!-\!\!Cl$$

$$-98.5422 \text{ eV.} \qquad -88.8692 \text{ eV.} \qquad -88.5361 \text{ eV.}$$

A B C

$$C\!\!-\!\!\overset{-}{C}\!\!-\!\!\overset{+}{Cl} \qquad C\!\!-\!\!\overset{-}{C}\!\!=\!\!\overset{+}{Cl} \qquad \overset{-}{C}\!\!-\!\!\overset{-}{C}\!\!-\!\!\overset{+}{Cl}$$

$$-87.6955 \text{ eV.} \qquad -85.9883 \text{ eV.} \qquad -64.0275 \text{ eV}$$

D E F

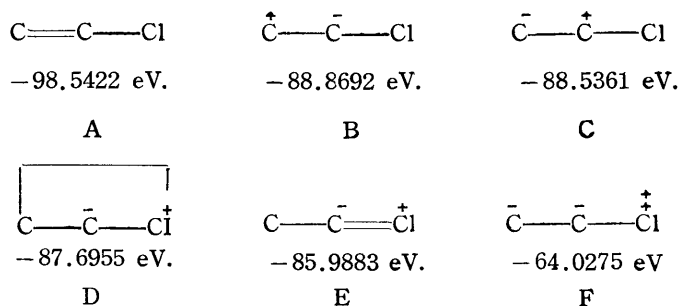Fig. 2. Canonical structures and the energies for the structues.

For the evaluations of matrix elements, required to find energy levels, all kinds of overlap, single exchange, and multiple exchange integrals have been taken into considerations. Wave functions for the molecule and the values of the corresponding energies, obtained after solving secular determinants, are shown in Table I, where Φ_i is the molecular orbital corresponding to orbital energy E_i and Φ_K is the normalized bond eigenfunction for structure K.

TABLE I. MOLECULAR ORBITALS AND THE VALUES OF THE CORRESPONDING ORBITAL ENERGIES

$$\Phi_1 = 0.73595\Phi_A + 0.21845\Phi_B + 0.22127\Phi_C + 0.16156\Phi_D + 0.11523\Phi_E$$
$$+ 0.00667\Phi_F \qquad\qquad E_1 = 100.91 \text{ eV.}$$

$$\Phi_2 = 0.09265\Phi_A - 0.01220\Phi_B - 0.29470\Phi_C - 0.31017\Phi_D + 1.09225\Phi_E$$
$$- 0.30640\Phi_F \qquad\qquad E_2 = -89.50 \text{ eV.}$$

$$\Phi_3 = 0.09583\Phi_A - 0.57177\Phi_B + 0.71265\Phi_C - 0.49640\Phi_D - 0.04121\Phi_E$$
$$+ 0.00000\Phi_F \qquad\qquad E_3 = -85.50 \text{ eV.}$$

$$\Phi_4 = 0.04141\Phi_A - 0.05625\Phi_B - 0.01469\Phi_C + 0.02055\Phi_D - 0.03334\Phi_E$$
$$- 0.00362\Phi_F \qquad\qquad E_4 = -82.37 \text{ eV.}$$

$$\Phi_5 = 0.61285\Phi_A - 0.31888\Phi_B - 0.78240\Phi_C - 0.52176\Phi_D + 0.70541\Phi_E$$
$$+ 0.11148\Phi_F \qquad\qquad E_5 = -76.41 \text{ eV.}$$

$$\Phi_6 = 0.03309\Phi_A - 0.00686\Phi_B - 0.09569\Phi_C - 0.07927\Phi_D + 0.38669\Phi_E$$
$$- 1.02578\Phi_F \qquad\qquad E_6 = -61.47 \text{ eV.}$$

Contribution of Structures to the Resonance,

Charge Densities, anb Bond Orders

probabilities of structures contributive to the resonance phenomenon, which are the basis of calculating electron densities and bond orders, were evaluated by the most popular form

$$P_K = C_K \sum_L C_L \int \Phi_K \Phi_L d\tau,$$

where P_K is the probability of structure K and C_K is the coefficient of normalized bond eigenfunction Φ_K for the ground state of the molecule. These results are given in Table II.

TABLE II. PROBABILITIES OF RESONANCE STRUCTURES IN
THE GROUND STATE

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

Then the π-electron densities and the bond orders were evaluated by the following equations, including the probabilities mentioned above,

$$D_i = \sum_K P_K m_i^K$$

$$B_{ij} = \sum_K P_K (n_{ij}^K + 1),$$

where D_i is the π-electron density of atom i, m_i^K is the number of π-electrons on atom i in structure K, B_{ij} is the bond order between atoms i and j, and n_{ij}^K is the number of the double bonds between atows i and j in structure K, respectively. These numerical values are shown in Fig. 3.

$$
\begin{array}{ccc}
& 1.6846 & 1.0300 \\
\text{H}_2\text{C}\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\text{CH}\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\text{Cl} \\
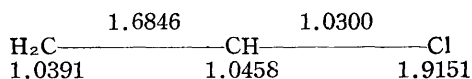1.0391 & 1.0458 & 1.9151
\end{array}
$$

Fig. 3 π-electron densities and bond orders.

Discussion

π-electronic energy levels, calculated from the orbital energies obtained in Table I, are

$$E_G = -100.91 \text{ eV.,} \qquad E_1 = E_G + 11.41 \text{ eV.,} \qquad E_2 = E_G + 15.41 \text{ eV.,}$$

$$E_3 = E_G + 18.54 \text{ eV.,} \qquad E_4 = E_G + 24.50 \text{ eV.,} \qquad E_5 = E_G + 39.44 \text{ eV.}$$

on the other side, the value of the transition energy between the ground state and the first excited state, evaluated by the method of LCAO self-consistent field is

$$E_{V23} - E_N = 11.1842 \text{ eV.}[2]$$

The difference of this-theoretical values in both of methods seems to be due to the neglect of the self-consistent field process for the calculation of the excited state in the molecular orbital method.

From the bond orders, calculated in the foregoing paragraph, the lengths of the C$-$C bond and the neighbouring C$-$Cl bond were evaluated by an application of the formula given by Pauling, Brockway, and Beach[4], as follows.

$$R_{C-C} = 1.542 - \frac{0.212 \times 3 \times 1.6846}{2 \times 1.6846 + 1} = 1.297 \text{ Å}$$

$$R_{C-Cl} = 1.761 - \frac{0.206 \times 3 \times 1.0300}{2 \times 1.0300 + 1} = 1.553 \text{ Å}.$$

On the other side, the values, obtained from the molecular orbital calculations by Simonetta and others, are

$$C-C = 1.448 \text{ Å}, \qquad C-Cl = 1.73 \text{ Å}$$

and the experimental values are 1.38 Å and 1.69 Å, respectively. Since in the valence bond calculations the bond order between the chlorine atom and the carbon atom of the edge has not entered into the evaluations and yet the representations for the bond lengths are rather qualitative than quantitative, these extents of differences will be unavoidable.

Now, the values of π-electron densities in the valence bond method, which have already been found in the foregoing paragraph, can be compared with the results of the molecular orbital calculations by the formulas of Goldstein[1] slightly modified,

$$D_i = q_i + (1/2) \sum_{j(\neq i)} n_{ij},$$

The values of π-electron densities, evaluated in this manner, are

$$D_a = 1.053 \qquad D_b = 1.041 \qquad D_c = 1.90761$$

and are in good agreements with the values (Fig. 3) in our method, in spite of

4) L. Pauling, L. O. Brockway, and J. Y. Beach, *J. Am. Chem. Soc.*, **57**, 2705 (1935).

L. Pauling and L. O. Brockway,

ibid., **59**, 1223 (1937).

the difference of the definitions in the two methods.

The positive charge on the chlorine atom is evaluated as $2-1.9151=0.0849$. This value gives the better agreement with the experimental value 0.06, than the result $2-1.90761=0.09239$ in the molecular orbital method*.

Summary

π-electronic energy levels, probabilities of the resonance structures, π-electron densities, and bond orders of vinyl chloride molecule have been calculated non-empirically by the standard valence bond method. All kinds of the resonance structures, in which the corresponding bond eigenfunctions are independent mutually, have been taken into considerations. Slater 2P- and 3P-functions have been assumed to be the atomic orbitals of carbon and chlorine atoms and all kinds of overlap, single exchange, and multiple exchange integrals have been taken into accounts. Results have been compared with the values by the treatment of LCAO self-consistent field.

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* This comparison for the positive charges may not have a great significance since many assumptions have entereed into the calculation processes in both of methods.