Non-empirical Study of the π-Electronic Structure of Vinyl Chloride Molecule by Valence Bond Method

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(Received October 21, 1960)

In the year 1956, a semi-empirical consideration of conjugation in vinyl chloride molecule with molecular orbital method was performed by Goldstein[1] and recently the self-consistent field calculations of the π-electronic energy levels and the wave functions for the ground state have been carried out non-empirically by Simonetta and others[2].

On the other hand, it seems that no considerations by valence bond method have ever been made, except a semi-empirical calculation of the double bond character due to the resonance of the C–Cl bond in the molecule[3].

In this paper, the HLSP method[4] is applied to the non-empirical calculation of the π-electronic energy levels and other electronic properties of the molecule and the results are compared with those obtained by the method of LCAO self-consistent field.

Energy Levels and Wave Functions

The skeleton of the molecule is shown in Fig. 1.

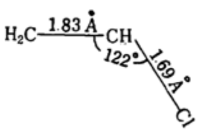

Fig. 1. Skeleton of vinyl chloride molecule.

For the carbon atoms and the chlorine atom, Slater $2p_\pi$- and $3p_\pi$-orbitals with $Z_C=3.18$, $Z_{Cl}=6.099$ have been assumed.

The approximate Hamiltonian operator H employed here is

$$H=\sum_i [T(i)+U_{\text{core}}(i)]+(1/2)\sum_{\substack{i,\ j\\ i\neq j}}(e^2/r_{ij})$$

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

Numerical values of integrals over atomic orbitals have been taken from Simonetta and others[2].

All the π-type resonance structures, whose corresponding bond eigenfunctions are linearly independent, and the energy values for these structures are shown in Fig. 2.

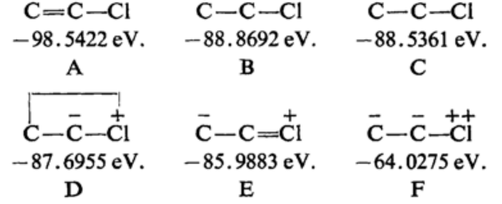

Fig. 2. Canonical structures and the energy values for the structures.

In the calculations all kinds of overlap and exchange integrals have been considered.

Wave functions for the molecule and the corresponding energy values are shown in Table I, where Φ_i is the wave function, corresponding to the energy E_i, and Ψ_K is the normalized bond eigenfunction for structure K.

TABLE I. WAVE FUNCTIONS FOR THE MOLECULE AND THE ENERGY VALUES

$$\Phi_1=0.73595\Psi_A+0.21845\Psi_B+0.22127\Psi_C+0.16156\Psi_D+0.11523\Psi_E+0.00667\Psi_F$$
$$E_1=-100.91\text{ eV.}$$

$$\Phi_2=0.09265\Psi_A-0.01220\Psi_B-0.29470\Psi_C-0.31017\Psi_D+1.09225\Psi_E-0.30640\Psi_F$$
$$E_2=-89.50\text{ eV.}$$

$$\Phi_3=0.09583\Psi_A-0.57177\Psi_B+0.71265\Psi_C-0.49640\Psi_D-0.04121\Psi_E+0.00000\Psi_F$$
$$E_3=-85.50\text{ eV.}$$

$$\Phi_4=0.04141\Psi_A-0.05625\Psi_B-0.01469\Psi_C+0.02055\Psi_D-0.03334\Psi_E-0.00362\Psi_F$$
$$E_4=-82.37\text{ eV.}$$

$$\Phi_5=0.61285\Psi_A-0.31888\Psi_B-0.78240\Psi_C-0.52176\Psi_D+0.70541\Psi_E+0.11148\Psi_F$$
$$E_5=-76.41\text{ eV.}$$

$$\Phi_6=0.03309\Psi_A-0.00686\Psi_B-0.09569\Psi_C-0.07927\Psi_D+0.38669\Psi_E-1.02578\Psi_F$$
$$E_6=-61.47\text{ eV.}$$

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Probabilities of Resonance Structures, Charge Densities, and Bond Orders

Probability P_K for structure K has been calculated by the most popular expression

$$P_K=C_K\sum_L C_L\int \Psi_K\Psi_L d\tau$$

where C_K is the coefficient of bond eigenfunction Ψ_K in the wave function for the ground state of the molecule and $d\tau$ is the product of the volume elements for the four π-electrons. The results are as follows:

$$P_A=0.6846 \qquad P_B=0.1110 \qquad P_C=0.1198$$

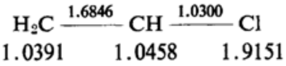
$$P_D=0.0543 \qquad P_E=0.0300 \qquad P_F=0.0003$$

Then π-electron density D_i for atom i and bond order B_{ij} between atoms i and j have been evaluated by the following equations:

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

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

where m_i^K is the number of π-electrons on atom i in structure K and n_{ij}^K is the number of the covalent π-bonds between atoms i and j in structure K. These results are shown in Fig. 3.



$$\underset{1.0391}{H_2C}\overset{1.6846}{\overline{\qquad}}\underset{1.0458}{CH}\overset{1.0300}{\overline{\qquad}}\underset{1.9151}{Cl}$$

Fig. 3. π-Electron densities and bond orders.

Discussion

The transition energy between the ground state and the first excited state is 11.41 eV. (Table I) The value, calculated by the method of LCAO self-consistent field, is

$$E_{V23}-E_N=11.1842 \text{ eV.}^{2)}$$

The numerical difference between the two methods seems to be due to the neglect of the self-consistent procedure for the calculation of the excited state in the latter.

The formula of Pauling and others[5] has been used to evaluate the C–C and the neighboring C–Cl bond lengths from the semi-empirical values of bond radii[6]; and the results are as follows:

$$R_{C-C}=1.358\,\text{Å} \qquad R_{C-Cl}=1.744\,\text{Å}$$

The values, obtained by Simonetta and others, are $R_{C-C}=1.448$ Å and $R_{C-Cl}=1.73$ Å[2], and the experimental values are 1.38 and 1.69 Å respectively[7].

The positive charge on the chlorine atom is evaluated as $2-1.9151=0.0849$ and the interpreted value from observation is 0.06[8].

The ionic character of the molecule, calculated from the values of the probabilities, is 31.54%.

Summary

π-electronic energy levels, probabilities of the resonance structures, π-electron densities, and the bond orders of the vinyl chloride molecule have been calculated non-empirically by the standard valence bond method, based on a complete set of the π-type resonance structures. Slater $2p_\pi$- and $3p_\pi$-orbitals have been assumed for the carbon and chlorine atoms and all the multiple exchange integrals have been considered. The calculated transition energy between the ground state and the first excited state is 11.41 eV., the ionic character is 31.54%, and the positive charge on the chlorine atom is 0.0849 (experimental value is 0.06.).

The author wishes to express his sincere thanks to Professor Kyosuke Omori, Kyushu University, for many helpful criticisms and suggestions. Thanks are also due to Professor Saburo Nagakura, the University of Tokyo, for his advice and valuable assistance.

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