Non-Empirical Calculation of the π-Electronic Structure of Cyclobutadiene Molecule by Valence Bond Method

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Non-empirical calculation of the energy levels of the cyclobutadiene molecule was first made by Craig[1] from the point of view of molecular orbital method and later a calculation by valence bond method was performed, by McWeeny[2-4] using orthogonalized atomic orbitals[5].

In the calculation by Craig a complete basis of antisymmetric molecular orbital configurations was taken into considerations and, on the other hand, in the working of McWeeny a complete set of canonical structures was included. Energy levels in both of the methods, therefore, should arrive at a complete agreement theoretically*. But it was pointed out by Shida and Kuri[6] that the numerical value 11.1289 eV. of molecular integral γ_{22} in the paper of Craig should be corrected to 10.5586 eV. The difference between these two values may have some effects on the energy levels.

In this paper, therefore, the calculation of the π-electronic energy levels and the wave functions of the molecule is made by valence bond method, including the complete set of canonical structures and considering all kinds of overlap, single exchange, and multiple exchange integrals. The results are compared with those due to ASMO CI calculation.

Calculations are also made in the way of the orthogonalization of atomic orbitals, and Slater functions, and thus the magnitude of the ionic character of the molecule is found. The results are discussed in comparison with those due to the non-orthogonal orbitals.

Calculation

Cyclobutadiene was assumed to be a square molecule in which the bond distance between two neighboring carbon atoms is 1.40 Å. Slater $2p_\pi$-orbitals were used for the atomic orbitals of the four carbon atoms, with the screening constant $Z_C=3.18$. π-Electron repulsive integrals were taken from Craig[1] and penetration and core integrals were calculated directly by the present author according to the method of Parr and Mulliken[7]. The canonical structures and the corresponding energies are shown in Fig. 1.

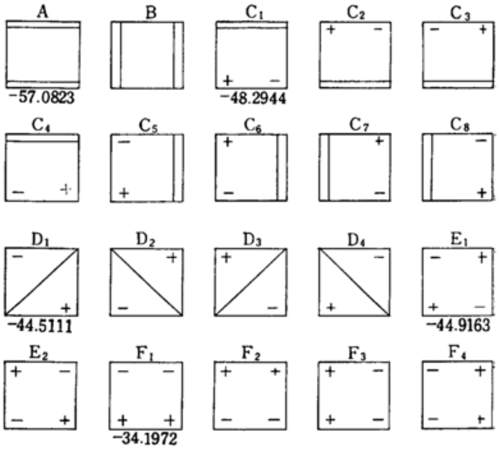

Fig. 1. Canonical structures and the energy values for the structures. (Energies are in electron volts and are relative to $4W_{2p}$, where W_{2p} is the energy of a $2p_\pi$-electron of a carbon atom in its valence state.)

Bases Ψ_i's for irreducible representations of the group, to which the molecule belongs, are given in Table I, where N_i is the normalization constant and Ψ_K is the normalized bond eigenfunction for structure K.

In our approximation the Hamiltonian operator H is expressed in the form

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

where

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

$T(i)$ 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.

Calculated wave functions Φ_i's for the molecule and the corresponding energy values E_i's

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1) D. P. Craig, *Proc. Roy. Soc.*, **A202**, 498 (1950).

2) R. McWeeny, ibid., **A223**, 63 (1954).

3) R. McWeeny, ibid., **A223**, 306 (1954).

4) R. McWeeny, ibid., **A227**, 288 (1955).

5) P.-O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1951); P.-O. Löwdin, ibid., **21**, 496 (1953).

* Agreement of the results in both of the methods has been reported by McWeeny[4].

6) S. Shida and Z. Kuri, *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*), **76**, 322 (1955).

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

TABLE I. RELATIONS BETWEEN BOND EIGENFUNCTIONS AND BASES

$$
{}^1\mathrm{A}_{1g}\ \begin{cases}
\Psi_1=(1/N_1)(\Psi_A+\Psi_B)\\
\Psi_2=(1/N_2)(\Psi_{C1}+\Psi_{C2}+\Psi_{C3}+\Psi_{C4}+\Psi_{C5}+\Psi_{C6}+\Psi_{C7}+\Psi_{C8})\\
\Psi_3=(1/N_3)(\Psi_{D1}+\Psi_{D2}+\Psi_{D3}+\Psi_{D4})\\
\Psi_4=(1/N_4)(\Psi_{E1}+\Psi_{E2})\\
\Psi_5=(1/N_5)(\Psi_{F1}+\Psi_{F2}+\Psi_{F3}+\Psi_{F4})
\end{cases}
$$

$$
{}^1\mathrm{B}_{1g}\ \begin{cases}
\Psi_6=(1/N_6)(\Psi_{C1}-\Psi_{C2}+\Psi_{C3}-\Psi_{C4}+\Psi_{C5}-\Psi_{C6}+\Psi_{C7}-\Psi_{C8})\\
\Psi_7=(1/N_7)(\Psi_{D1}-\Psi_{D2}+\Psi_{D3}-\Psi_{D4})\\
\Psi_8=(1/N_8)(\Psi_{E1}-\Psi_{E2})
\end{cases}
$$

$$
{}^1\mathrm{B}_{2g}\ \begin{cases}
\Psi_9=(1/N_9)(\Psi_A-\Psi_B)\\
\Psi_{10}=(1/N_{10})(\Psi_{C1}+\Psi_{C2}+\Psi_{C3}+\Psi_{C4}-\Psi_{C5}-\Psi_{C6}-\Psi_{C7}-\Psi_{C8})\\
\Psi_{11}=(1/N_{11})(\Psi_{F1}+\Psi_{F2}-\Psi_{F3}-\Psi_{F4})
\end{cases}
$$

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

Based on non-orthogonal atomic orbitals	
$\Phi_1({}^1\mathrm{B}_{2g})=0.80023\Psi_9+0.26085\Psi_{10}-0.01111\Psi_{11}$	$E_1=4W_{2p}-58.3517$ eV.
$\Phi_2({}^1\mathrm{A}_{1g})=0.75393\Psi_1+0.32697\Psi_2-0.11784\Psi_3+0.09264\Psi_4-0.00386\Psi_5$	$E_2=4W_{2p}-56.3627$ eV.
$\Phi_3({}^1\mathrm{B}_{1g})=0.68396\Psi_6+0.24527\Psi_7+0.21925\Psi_8$	$E_3=4W_{2p}-52.6519$ eV.
Based on orthogonalized atomic orbitals	
$\bar{\Phi}_1({}^1\mathrm{B}_{2g})=0.82284\bar{\Psi}_9+0.55729\bar{\Psi}_{10}-0.11117\bar{\Psi}_{11}$	$\bar{E}_1=4\bar{\alpha}+41.8774$ eV.
$\bar{\Phi}_2({}^1\mathrm{A}_{1g})=0.78562\bar{\Psi}_1+0.55233\bar{\Psi}_2-0.01629\bar{\Psi}_3+0.25304\bar{\Psi}_4+0.11591\bar{\Psi}_5$	$\bar{E}_2=4\bar{\alpha}+44.0248$ eV.
$\bar{\Phi}_3({}^1\mathrm{B}_{1g})=0.75721\bar{\Psi}_6+0.49877\bar{\Psi}_7+0.42174\bar{\Psi}_8$	$\bar{E}_3=4\bar{\alpha}+46.9387$ eV.

are given in Table II. In the table, $\bar{\Phi}_i$'s are the wave functions for the molecule, obtained in the way of the orthogonalization of the atomic orbitals, $\bar{E}_i$'s are the corresponding energy values, and $\bar{\alpha}$ is as follows:

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

where $\bar{k}(i)$ is the orthogonalized expression of atomic orbital $k(i)$ of electron i on atom k and $\mathrm{d}v_i$ is the volume element of this electron.

Ionic Character

Now, ionic characters, evaluated on the basis of non-orthogonal atomic orbitals are generally different from the values, obtained in their orthogonalized representation[5),*1].

Probabilities P_K's of structure K's in both of the ground ${}^1\mathrm{B}_{2g}$ state and the first excited ${}^1\mathrm{A}_{1g}$ state were calculated from the following expression and the results are shown in Table III.

$$P_K=C_K\sum_L C_L\int\Psi_K\Psi_L\,\mathrm{d}\tau$$

where C_K is the coefficient of normalized bond eigenfunction Ψ_K in $\Phi_1({}^1\mathrm{B}_{2g})$ or $\Phi_2({}^1\mathrm{A}_{1g})$ and $\mathrm{d}\tau$ is the product of the volume element for all the π-electrons.

TABLE III. PROBABILITIES OF STRUCTURES

Based on non-orthogonal atomic orbitals

$A=B$	C_i	D_i	E_i	F_i
Ground ${}^1\mathrm{B}_{2g}$-state				
0.3924	0.0265	0.0008	0	0
First excite ${}^1\mathrm{A}_{1g}$-state				
0.3503	0.0300	0.0054	0.0194	−0.0002

Based on orthogonalized atomic orbital

$A=B$	C_i	D_i	E_i	F_i
Ground ${}^1\mathrm{B}_{2g}$-states				
0.3385	0.0388	0.00309	0	0
First excited ${}^1\mathrm{A}_{1g}$-state				
0.3086	0.0381	0.0001	0.0320	0.0034

From these results, ionic characters are

$$
{}^1\mathrm{B}_{2g}\ \text{state}\ \begin{cases}
21.517\% & \text{based on } k(i)\\
32.293\% & \text{based on } \bar{k}(i)
\end{cases}
$$

$$
{}^1\mathrm{A}_{1g}\ \text{state}\ \begin{cases}
29.946\% & \text{based on } k(i)\\
38.280\% & \text{based on } \bar{k}(i)
\end{cases}
$$

In the ${}^1\mathrm{B}_{2g}$ and ${}^1\mathrm{A}_{1g}$ states the ionic characters based on $\bar{k}(i)$ are larger than on $k(i)$ by 10.776% and 8.334%, respectively.

Bond orders B_{ij}'s between neighboring two carbon atoms i and j were evaluated by formula

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

where n_{ij}^K is the number of the π-electronic

[*1] It does not appear that considerations of such discrepancies for π-electronic systems have been made.

covalent bonds between carbon atoms i and j in structure K. The results are

$$
{}^1\mathrm{B}_{2g}\ \text{state}\ \begin{cases} 1.445 & \text{based on } k(i) \\ 1.416 & \text{based on } \bar{k}(i) \end{cases}
$$

$$
{}^1\mathrm{A}_{1g}\ \text{state}\ \begin{cases} 1.410 & \text{based on } k(i) \\ 1.385 & \text{based on } \bar{k}(i) \end{cases}
$$

Double bond characters based on $k(i)$ are larger by 2.92% and 2.52% than these based on $\bar{k}(i)$ the ${}^1\mathrm{B}_{2g}$ and ${}^1\mathrm{A}_{1g}$ states, respectively.

Discussion

Energy levels of the molecule, calculated by various methods, are shown diagrammatically in Fig. 2.

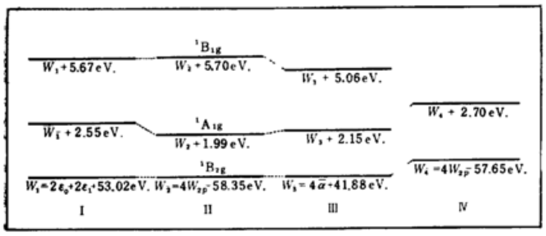

Fig. 2. Comparison of energy levels.

I. ASMOCI method[1]. II. VB method (based on non-orthogonal atomic orbitals). III. VB method (based on orthogonalized atomic orbitals). IV. Heitler-London method.

The ${}^1\mathrm{A}_{1g}$ level evaluated by the present author (II) is lower by 0.56 eV. relatively than that of Craig. But influences of the difference in the values of the molecular integral on the other levels hardly appear at all[*2].

One of the causes for the discrepancies of the ionic characters in the two ways is that, in the cases of the use of the orthogonalized atomic orbitals, exchange integrals which appear in the interactions of covalent structures give generally repulsive forces.

Actually, in the case of an exchange integral $\bar{J}$,

$$
\bar{J}=\int\cdots\cdots\bar{a}(1)\bar{b}(2)\bar{c}(3)\bar{d}(4)\cdots\cdots H
$$

$$
\cdots\cdots\bar{a}(1)\bar{c}(2)\bar{b}(3)\bar{d}(4)\cdots\cdots\mathrm{d}\tau
$$

is expanded as follows and $\bar{J}$ is, therefore, equal to $(\bar{b}\bar{c}|\bar{b}\bar{c})$.

$$
\bar{J}=\sum_{\substack{k\\ k\neq b,\,c}}\bar{\alpha}_k\bar{S}_{bc}{}^2+2\bar{\beta}_{bc}\bar{S}_{bc}
$$

$$
+(1/2)\sum_{\substack{k,\,l\\ k\neq b,\,c\\ l\neq b,\,c,\,k}}(\bar{k}\bar{k}|\bar{l}\bar{l})\bar{S}_{bc}{}^2
$$

$$
+2\sum_{\substack{k\\ k\neq b,\,c}}(\bar{k}\bar{k}|\bar{b}\bar{c})\bar{S}_{bc}+(\bar{b}\bar{c}|\bar{b}\bar{c})
$$

where

$$
\bar{\alpha}_k=\int\bar{k}(i)H_{\mathrm{core}}(i)\bar{k}(i)\mathrm{d}v_i{}^{*3}
$$

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

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

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

From similar analyses multiple exchange integrals lead to zeros. In the use of the orthogonalized atomic orbitals, therefore, the weight of the covalent structures appears generally smaller than in the use of the non-orthogonal orbitals.

Accordingly, when π-electron densities or bond orders etc. are considered as the measure of chemical reactivities, it will be necessary for attention to be given to the discrepancies of these values in the two ways.

Summary

π-Electronic energy levels, probalities of the resonance structures, and bond orders of cyclobutdiene molecule have been calculated by the valence bond method on the bases of two ways, one is based on non-orthogonal atomic orbitals and the other on their orthogonalization. Calculated ionic characters are 21.517% (ground ${}^1\mathrm{B}_{2g}$ state), 29.946% (first excited ${}^1\mathrm{A}_{1g}$ state) in the former and 32.293%, 38.280% in the latter. Bond orders between neighboring carbon atoms are 1.445, 1.410 and 1.416, 1.385 respectively.

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[*2] Relative differences of levels between II and III in Fig. 2 seem to be due to the approximate orthogonalization of atomic orbitals[4,5].

[*3] Since atoms except carbon are generally included in π-electronic system, $\bar{\alpha}_k$ is here to be distinguished from $\bar{\alpha}$ in the previous paragraph.