De-localization of Bond Eigenfunctions in π-Electronic Systems. IV. Non-Empirical Calculation of the π-Electronic States of the Cyclobutadiene Molecule

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In part I1) of this series an approximate method for the calculation of the π-electronic states of molecules was proposed, and in part II2), where the method was applied to the consideration of a conjugated homo-nuclear chain compound, *trans*-butadiene molecule, the quantitative agreement of the results with those obtained by the ASMO SCF CI method was obtained. Then, in part III3), that method was extended to the treatment of a hetero-nuclear system, the vinyl chloride molecule, in which a special atom possesses a lone pair of π-electrons; good results were obtained.

In this paper, the theory is applied to the calculation of the π-electronic states of a molecule, the cyclobutadiene molecule, belonging to the conjugated cyclic systems. Calculations of the probabilities of the resonance structures, the wave functions and the corresponding energy levels are made non-empirically, using the non-orthogonal atomic orbitals. The higher orders of overlap and exchange integrals are taken into account. These results are compared with the values obtained by the HLSP method.

The orthogonalized rather than the non-orthogonal (cf. Ref., part I) atomic orbitals4) are usually employed for the quantitative considerations of polyatomic molecules, since it is very difficult to consider fully the higher order permutations of the electrons5). Therefore, calculations based on the orthogonalized atomic orbitals are also attempted, and the adaptability of the approximate method in this scheme is investigated.

Classification of the Resonance Structures

Cyclobutadiene has been assumed to be a square molecule, with the neighboring carbon nuclear distance $R_{\mathrm{C-C}}=1.40\,\text{Å}$.

Core integrals have been evaluated by the method of Parr and Mulliken6), and the numerical values of the electron repulsion integrals have been taken from Craig7).

The three classes of canonical structures are given in Fig. 1, in which energies are relative to $4W_{2\mathrm{p}}$, where $W_{2\mathrm{p}}$ is the energy of a $2\mathrm{p}_\pi$-electron of a carbon atom in its valence state.

Relations between bond eigenfunctions Ψ_{L}'s and functions Ψ_i's which are the bases for

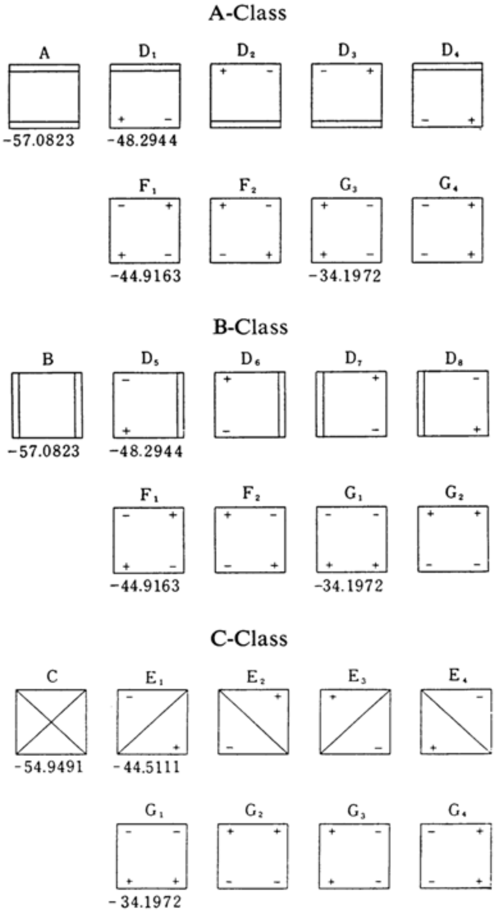

Fig. 1. Classification of resonance structures and the energies for the structures. Values are in electron volts.

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1) S. Takekiyo, This Bulletin, **35**, 355 (1962).
2) S. Takekiyo, ibid., **35**, 360 (1962).
3) S. Takekiyo, ibid., **35**, 460 (1962).
4) P. O. Löwdin, *J. Chem. Phys.*, **18**, 365 (1950); **21**, 496 (1953).
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TABLE I. WAVE FUNCTIONS ASSOCIATED WITH THE CLASSES AND THE CORRESPONDING ENERGY VALUES

Based on non-orthogonal atomic orbitals

AB-Class

$\phi_1^{AB}(^1B_{2g}) = 0.80023\Psi_9 + 0.26085\Psi_{10} - 0.011107\Psi_{11}$ $E_1^{AB} = -58.352$ eV.
$\phi_2^{AB}(^1A_{1g}) = 0.75713\Psi_1 + 0.33830\Psi_2 + 0.097642\Psi_4 + 0.0^{3}88699\Psi_5$ $E_2^{AB} = -56.182$ eV.
$\phi_3^{AB}(^1B_{1g}) = 0.83604\Psi_6 + 0.23707\Psi_8$ $E_3^{AB} = -51.950$ eV.
$\phi_4^{AB}(^1A_{1g}) = 0.75628\Psi_1 - 0.69019\Psi_2 - 0.40701\Psi_4 - 0.038294\Psi_5$ $E_4^{AB} = -47.316$ eV.
$\phi_5^{AB}(^1B_{2g}) = 1.0579\Psi_9 - 1.2077\Psi_{10} + 0.19836\Psi_{11}$ $E_5^{AB} = -40.215$ eV.
$\phi_6^{AB}(^1B_{1g}) = 0.95809\Psi_6 - 1.2493\Psi_8$ $E_6^{AB} = -35.695$ eV.
$\phi_7^{AB}(^1A_{1g}) = 0.27432\Psi_1 - 0.74924\Psi_2 + 1.0071\Psi_4 - 0.48722\Psi_5$ $E_7^{AB} = -35.170$ eV.
$\phi_8^{AB}(^1B_{2g}) = 0.41455\Psi_9 - 0.88445\Psi_{10} - 1.1124\Psi_{11}$ $E_8^{AB} = -28.912$ eV.
$\phi_9^{AB}(^1A_{1g}) = 0.34795\Psi_1 - 1.2239\Psi_2 + 0.73688\Psi_4 + 1.0501\Psi_5$ $E_9^{AB} = -26.484$ eV.

C-Class

$\phi_1^{C}(^1A_{1g}) = 0.13626\Psi_3 - 0.046463\Psi_5 + 0.97403\Psi_{12}$ $E_1^{C} = -55.268$ eV.
$\phi_2^{C}(^1B_{1g}) = \Psi_7$ $E_2^{C} = -44.354$ eV.
$\phi_3^{C}(^1A_{1g}) = 0.93597\Psi_3 + 0.27181\Psi_5 - 0.15022\Psi_{12}$ $E_3^{C} = -41.995$ eV.
$\phi_4^{C}(^1B_{2g}) = \Psi_{11}$ $E_4^{C} = -34.372$ eV.
$\phi_5^{C}(^1A_{1g}) = 0.35148\Psi_3 - 0.97158\Psi_5 - 0.22506\Psi_{12}$ $E_5^{C} = -32.558$ eV.

Based on orthogonalized atomic orbitals

AB-Class

$\bar{\phi}_1^{AB}(^1B_{2g}) = 0.82284\overline{\Psi}_9 + 0.55729\overline{\Psi}_{10} - 0.11117\overline{\Psi}_{11}$ $\overline{E}_1^{AB} = +41.877$ eV.
$\bar{\phi}_2^{AB}(^1A_{1g}) = 0.78598\overline{\Psi}_1 + 0.55209\overline{\Psi}_2 + 0.25299\overline{\Psi}_4 + 0.11590\overline{\Psi}_5$ $\overline{E}_2^{AB} = +44.029$ eV.
$\bar{\phi}_3^{AB}(^1B_{1g}) = 0.79951\overline{\Psi}_6 + 0.60066\overline{\Psi}_8$ $\overline{E}_3^{AB} = +50.622$ eV.
$\bar{\phi}_4^{AB}(^1A_{1g}) = 0.59540\overline{\Psi}_1 - 0.55874\overline{\Psi}_2 - 0.54996\overline{\Psi}_4 - 0.17564\overline{\Psi}_5$ $\overline{E}_4^{AB} = +53.231$ eV.
$\bar{\phi}_5^{AB}(^1B_{2g}) = 0.54136\overline{\Psi}_9 - 0.70925\overline{\Psi}_{10} + 0.45155\overline{\Psi}_{11}$ $\overline{E}_5^{AB} = +61.182$ eV.
$\bar{\phi}_6^{AB}(^1A_{1g}) = 0.13052\overline{\Psi}_1 - 0.40438\overline{\Psi}_2 + 0.72518\overline{\Psi}_4 - 0.53052\overline{\Psi}_5$ $\overline{E}_6^{AB} = +65.343$ eV.
$\bar{\phi}_7^{AB}(^1B_{1g}) = 0.60066\overline{\Psi}_6 - 0.79951\overline{\Psi}_8$ $\overline{E}_7^{AB} = +67.136$ eV.
$\bar{\phi}_8^{AB}(^1B_{2g}) = 0.17280\overline{\Psi}_9 - 0.43174\overline{\Psi}_{10} - 0.88529\overline{\Psi}_{11}$ $\overline{E}_8^{AB} = +72.725$ eV.
$\bar{\phi}_9^{AB}(^1A_{1g}) = 0.10348\overline{\Psi}_1 - 0.46849\overline{\Psi}_2 + 0.32811\overline{\Psi}_4 + 0.81373\overline{\Psi}_5$ $\overline{E}_9^{AB} = +73.358$ eV.

C-Class

$\bar{\phi}_1^{C}(^1A_{1g}) = 0.0^{2}24190\overline{\Psi}_3 + 0.0^{5}28596\overline{\Psi}_5 + 1.00000\overline{\Psi}_{12}$ $\overline{E}_1^{C} = +48.456$ eV.
$\bar{\phi}_2^{C}(^1B_{1g}) = \overline{\Psi}_7$ $\overline{E}_2^{C} = +58.979$ eV.
$\bar{\phi}_3^{C}(^1A_{1g}) = 0.99999\overline{\Psi}_3 + 0.0^{2}23119\overline{\Psi}_5 - 0.0^{2}24190\overline{\Psi}_{12}$ $\overline{E}_3^{C} = +58.979$ eV.
$\bar{\phi}_4^{C}(^1A_{1g}) = 0.0^{3}73113\overline{\Psi}_3 + 0.31623\overline{\Psi}_5 - 0.0^{6}86422\overline{\Psi}_{12}$ $\overline{E}_4^{C} = +69.990$ eV.
$\bar{\phi}_5^{C}(^1B_{2g}) = \overline{\Psi}_{11}$ $\overline{E}_5^{C} = +69.990$ eV.

Note: $\bar{\phi}_i^{K}$'s, $\overline{\Psi}_i$'s and $\overline{E}_i^{K}$'s are based on the orthogonalized atomic orbitals $\overline{k}(i)$'s. Values of energies $\overline{E}_i^{K}$'s are relative to $4\bar{\alpha}$, where $\bar{\alpha}$ is $\int \overline{k}(i) H_{\mathrm{core}}(i) \overline{k}(i) \mathrm{d}v_i$.

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

Based on non-orthogonal atomic orbitals

$\Phi_1(^1B_{2g}) = 0.80023\Psi_9 + 0.26085\Psi_{10} - 0.01111\Psi_{11}$ $E_1 = 4W_{2p} - 58.352$ eV.
$\Phi_2(^1A_{1g}) = 0.80081\Psi_1 + 0.28561\Psi_2 - 0.02261\Psi_3 + 0.08243\Psi_4 + 0.00846\Psi_5$ $E_2 = 4W_{2p} - 56.218$ eV.
$\Phi_3(^1B_{1g}) = 0.70008\Psi_6 + 0.24344\Psi_7 + 0.19852\Psi_8$ $E_3 = 4W_{2p} - 52.647$ eV.

Based on orthogonalized atomic orbitals

$\overline{\Phi}_1(^1B_{2g}) = 0.82284\overline{\Psi}_9 + 0.55729\overline{\Psi}_{10} - 0.11117\overline{\Psi}_{11}$ $\overline{E}_1 = 4\bar{\alpha} + 41.877$ eV.
$\overline{\Phi}_2(^1A_{1g}) = 0.74643\overline{\Psi}_1 + 0.59424\overline{\Psi}_2 + 0.00024\overline{\Psi}_3 + 0.27231\overline{\Psi}_4 + 0.12475\Psi_5$ $\overline{E}_2 = 4\bar{\alpha} + 43.991$ eV.
$\overline{\Phi}_3(^1B_{1g}) = 0.70390\overline{\Psi}_6 + 0.47420\overline{\Psi}_7 + 0.52883\overline{\Psi}_8$ $\overline{E}_3 = 4\bar{\alpha} + 47.206$ eV.

TABLE III. WAVE FUNCTIONS FOR THE MOLECULE AND THE CORRESPONDING ENERGY VALUES (the HLSP method)

Based on non-orthogonal atomic orbitals

$$\Phi_1(^1\mathrm{B}_{2g}) = 0.80023\Psi_9 + 0.26085\Psi_{10} - 0.01111\Psi_{11} \qquad E_1 = 4W_{2p} - 58.352\ \mathrm{eV.}$$
$$\Phi_2(^1\mathrm{A}_{1g}) = 0.75393\Psi_1 + 0.32697\Psi_2 - 0.11784\Psi_3 + 0.09264\Psi_4 - 0.00386\Psi_5 \qquad E_2 = 4W_{2p} - 56.363\ \mathrm{eV.}$$
$$\Phi_3(^1\mathrm{B}_{1g}) = 0.68396\Psi_6 + 0.24527\Psi_7 + 0.21925\Psi_8 \qquad E_3 = 4W_{2p} - 52.652\ \mathrm{eV.}$$

Based on orthogonalized atomic orbitals

$$\overline{\Phi}_1(^1\mathrm{B}_{2g}) = 0.82284\overline{\Psi}_9 + 0.55729\overline{\Psi}_{10} - 0.11117\overline{\Psi}_{11} \qquad \overline{E_1} = 4\overline{\alpha} + 41.877\ \mathrm{eV.}$$
$$\overline{\Phi}_2(^1\mathrm{A}_{1g}) = 0.78562\overline{\Psi}_1 + 0.55233\overline{\Psi}_2 - 0.01629\overline{\Psi}_3 + 0.25304\overline{\Psi}_4 + 0.11591\overline{\Psi}_5 \qquad \overline{E_2} = 4\overline{\alpha} + 44.025\ \mathrm{eV.}$$
$$\overline{\Phi}_3(^1\mathrm{B}_{1g}) = 0.75721\overline{\Psi}_6 + 0.49877\overline{\Psi}_7 + 0.42174\overline{\Psi}_8 \qquad \overline{E_3} = 4\overline{\alpha} + 46.939\ \mathrm{eV.}$$

the irreducible representations of the D_{4h} group, are shown in the Appendix.

A- and B-classes are incorporated to form one class, AB-class, due to the symmetry of the molecule. Wave functions for each class and the corresponding energy values are given in Table I.

Interaction of the Classes

Wave functions for the lowest energies, belonging to the same symmetry, have been picked up from the two classes, AB- and C-classes, and have been linearly combined.

The resulting wave functions for the molecule and the corresponding energy values are given in Table II.

TABLE IV. WAVE FUNCTIONS FOR THE MOLECULE AND THE CORRESPONDING ENERGY VALUES (the Heitler-London method)

Based on non-orthogonal atomic orbitals

$$\Phi_1(^1\mathrm{B}_{2g}) = \Psi_\mathrm{A} - \Psi_\mathrm{B} \qquad E_1 = 4W_{2p} - 57.653\ \mathrm{eV.}$$
$$\Phi_2(^1\mathrm{A}_{1g}) = \Psi_\mathrm{A} + \Psi_\mathrm{B} \qquad E_2 = 4W_{2p} - 54.949\ \mathrm{eV.}$$

Based on orthogonalized atomic orbitals

$$\overline{\Phi}_1(^1\mathrm{A}_{1g}) = \overline{\Psi}_\mathrm{A} + \overline{\Psi}_\mathrm{B} \qquad \overline{E_1} = 4\overline{\alpha} + 47.968\ \mathrm{eV.}$$
$$\overline{\Phi}_2(^1\mathrm{B}_{2g}) = \overline{\Psi}_\mathrm{A} - \overline{\Psi}_\mathrm{B} \qquad \overline{E_2} = 4\overline{\alpha} + 48.456\ \mathrm{eV.}$$

TABLE V. PROBABILITIES OF THE RESONANCE STRUCTURES IN EACH CLASS

Based on non-orthogonal atomic orbitals

AB-Class

A=B	D_i	F_i	G_i
0.35204	0.031682	0.021115	$0.0^{4}58862$

C-Class

C	E_i	G_i
0.96449	$0.0^{2}70862$	$0.0^{2}17902$

Based on orthogonalized atomic orbitals

AB-Class

A=B	D_i	F_i	G_i
0.30888	0.038101	0.032002	$0.0^{2}33580$

C-Class

C	E_i	G_i
0.99999	$0.0^{5}14629$	$0.0^{12}20443$

In Tables III and IV, results based on the usual HLSP method and on the Heitler-London method respectively are shown.

The probabilities of the resonance structures in the first excited $^1A_{1g}$-state have next been calculated*. The results are shown in Tables V and VI.

TABLE VI. COMPARISON OF THE PROBABILITIES OF RESONANCE STRUCTURES

Based on non-orthogonal atomic orbitals

Approximate method

A=B	D_i	E_i	F_i	G_i
0.37253	0.02670	0.00112	0.01779	0.00033

HLSP method

A=B	D_i	E_i	F_i	G_i
0.35027	0.02999	0.00542	0.01941	−0.00024

Based on orthogonalized atomic orbitals

Approximate method

A=B	D_i	E_i	F_i	G_i
0.25752	0.04093	−0.00000	0.03438	0.00361

HLSP method

A=B	D_i	E_i	F_i	G_i
0.30860	0.03813	0.00007	0.03201	0.00336

Discussion

In Fig. 2, the energy levels of the cyclobutadiene molecule, which have been found by the various methods, are shown.

From the figure, it can be noticed that the approximate method gives successful results to the calculations of the electronic states of a conjugated cyclic system, as it did to that of a conjugated chain system investigated in part II.

Good agreements of the energy levels are also seen in the case of the evaluation for only the AB-class, which originates from the most stable covalent structures. From such agreements we can expect that, for molecules with high symmetry, the quantitative calculations of the energy levels may be performed

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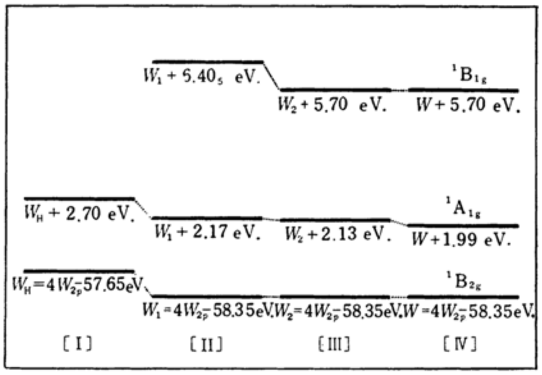
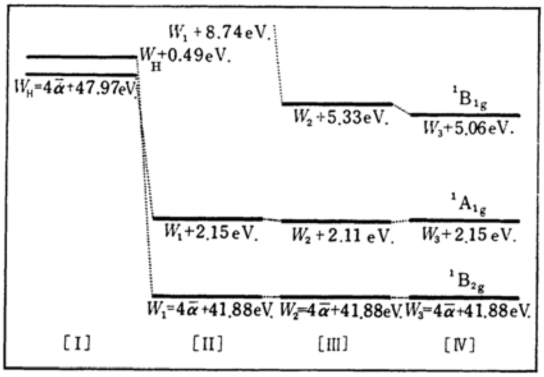
* For the ground $^1B_{2g}$-state, the approximate and the usual method are theoretically identical.



Based on non-orthogonal atomic orbitals



Based on orthogonalized atomic orbitals

Fig. 2. Comparison of energy levels.
I) Heitler-London method. II) AB-class. III) AB-, C-class interaction. IV) HLSP method (S. Takekiyo, This Bulletin, **34**, 1686 (1961)).

with a good result by a simplified process in the valence bond method.

It is recognized that, for the calculations of the energy levels, the approximate method gives quantitative agreements with the usual method, even if we use the orthogonalized instead of the non-orthogonal atomic orbitals.

Good agreements of the approximate method with the usual method are also seen for the values of the probabilities of the resonance structures (Tables V and VI).

In the cases of complex molecules, the valence bond method has, hitherto, been used only for the object of the qualitative considerations. But in view of the success in trials over parts I–IV, such deadlocks can probably be overcome to some extent by the application of our approximate method.

Summary

Calculations of the π-electronic energy levels, the wave functions, and the probabilities of the resonance structures of cyclobutadiene molecule have been made by an approximate method, proposed in part I, using the non-orthogonal Slater orbitals. Results have agreed quantitatively with the values calculated by the usual HLSP method.

Calculations have also been made using the orthogonalized atomic orbitals. Agreement of the results with those obtained by the usual method has been recognized.

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Appendix

AB-Class

$^1A_{1g}$ $\Psi_1 = (1/N_1)(\Psi_A + \Psi_B)$

$\Psi_2 = (1/N_2)(\Psi_{D1} + \Psi_{D2} + \Psi_{D3} + \Psi_{D4} + \Psi_{D5} + \Psi_{D6} + \Psi_{D7} + \Psi_{D8})$

$\Psi_4 = (1/N_4)(\Psi_{F1} + \Psi_{F2})$

$\Psi_5 = (1/N_5)(\Psi_{G1} + \Psi_{G2} + \Psi_{G3} + \Psi_{G4})$

$^1B_{1g}$ $\Psi_6 = (1/N_6)(\Psi_{D1} - \Psi_{D2} + \Psi_{D3} - \Psi_{D4} + \Psi_{D5} - \Psi_{D6} + \Psi_{D7} - \Psi_{D8})$

$\Psi_8 = (1/N_8)(\Psi_{F1} - \Psi_{F2})$

$^1B_{2g}$ $\Psi_9 = (1/N_9)(\Psi_A - \Psi_B)$

$\Psi_{10} = (1/N_{10})(\Psi_{D1} + \Psi_{D2} + \Psi_{D3} + \Psi_{D4} - \Psi_{D5} - \Psi_{D6} - \Psi_{D7} - \Psi_{D8})$

$\Psi_{11} = (1/N_{11})(\Psi_{G1} + \Psi_{G2} - \Psi_{G3} - \Psi_{G4})$

C-Class

$^1A_{1g}$ $\Psi_{12} = \Psi_C$

$\Psi_3 = (1/N_3)(\Psi_{E1} + \Psi_{E2} + \Psi_{E3} + \Psi_{E4})$

$\Psi_5 = (1/N_5)(\Psi_{G1} + \Psi_{G2} + \Psi_{G3} + \Psi_{G4})$

$^1B_{1g}$ $\Psi_7 = (1/N_7)(\Psi_{E1} - \Psi_{E2} + \Psi_{E3} - \Psi_{E4})$

$^1B_{2g}$ $\Psi_{11} = (1/N_{11})(\Psi_{G1} + \Psi_{G2} - \Psi_{G3} - \Psi_{G4})$

* $1/N_i$ is the normalizing factor.