# *De-localization of Bond Eigenfunctions in $\pi$-Electronic Systems. II. Non-Empirical Calculation of the $\pi$-Electronic States of the trans-Butadiene Molecule*

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*trans*-Butadiene is a simple molecule, suitable for considering the $\pi$-electronic states of conjugated chain compounds consisting of homonuclear atoms.

Non-empirical treatment of *trans*-butadiene molecule was first undertaken by Parr and Mulliken(1), using the ASMO SCF method, and the wave function for the ground state and the energy levels were calculated. The method of molecular orbitals with configuration interaction has been applied to the study of the $\pi$-electronic structure of the molecule by Coulson and Jacobs(2). Then the influences of the configuration interaction procedure upon the LCAO SCF treatment was investigated by Pullman and Baudet(3).

It does not appear that treatments by the valence bond method have been undertaken. In this paper, the approximate method proposed by us in part I(4) is applied to the calculation of the $\pi$-electronic states of the *trans*-butadiene molecule. The wave functions, energy levels, electron densities, and bond orders are evaluated. These results are compared with those, obtained by the molecular orbital method.

### Classification of Resonance Structures

The skeleton of the *trans*-butadiene molecule is shown in Fig. 1. Slater $2p_\pi$-orbitals with the effective nuclear charge $Z_C=3.18$ have been assumed for the atomic orbitals of the carbon atoms. Integrals over atomic orbitals have been taken from Parr and Mulliken(1). Calculations have been carried out, considering all kinds of overlap, single exchange, and multiple exchange integrals.

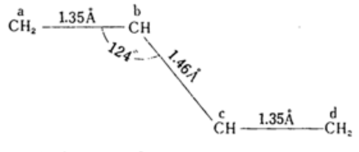

Fig. 1. Skeleton of *trans*-butadiene molecule.

Three classes of the canonical structures,

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

2) C. A. Coulson and J. Jacobs, *Proc. Roy. Soc.*, **A206**, 287 (1951).

3) A. Pullman and J. Baudet, *Compt. rend.*, **233**, 241 (1954); A. Pullman, *J. chim. phys.*, **51**, 188 (1954).

4) S. Takekiyo, This Bulletin, **35**, 355 (1962).

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

### A-Class

$$\begin{aligned}\phi_1{}^A({}^1\mathrm{A_g}) &= 0.69650\Psi_A+0.16134(\Psi_{D1}+\Psi_{D2})+0.14379(\Psi_{E1}+\Psi_{E2})\\ &\quad +0.042833(\Psi_{J1}+\Psi_{J2})+0.026672\Psi_L+0.019308\Psi_M \qquad E_1{}^A=-51.009\ \mathrm{eV.}\end{aligned}$$

$$\phi_2{}^A({}^1\mathrm{B_u}) = 0.43857(\Psi_{D1}-\Psi_{D2})+0.37715(\Psi_{E1}-\Psi_{E2})+0.23695(\Psi_{J1}-\Psi_{J2}) \qquad E_2{}^A=-39.782\ \mathrm{eV.}$$

$$\begin{aligned}\phi_3{}^A({}^1\mathrm{A_g}) &= -0.077807\Psi_A+0.47244(\Psi_{D1}+\Psi_{D2})-0.43306(\Psi_{E1}+\Psi_{E2})\\ &\quad +0.0^273967(\Psi_{J1}+\Psi_{J2})+0.17201\Psi_L-0.13351\Psi_M \qquad E_3{}^A=-38.842\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_4{}^A({}^1\mathrm{A_g}) &= 0.93567\Psi_A-0.29682(\Psi_{D1}+\Psi_{D2})-0.36520(\Psi_{E1}+\Psi_{E2})\\ &\quad -0.29357(\Psi_{J1}+\Psi_{J2})-0.12725\Psi_L-0.13294\Psi_M \qquad E_4{}^A=-35.562\ \mathrm{eV.}\end{aligned}$$

$$\phi_5{}^A({}^1\mathrm{B_u}) = 0.54520(\Psi_{D1}-\Psi_{D2})-0.57878(\Psi_{E1}-\Psi_{E2})-0.022620(\Psi_{J1}-\Psi_{J2}) \qquad E_5{}^A=-35{\cdot}463\ \mathrm{eV.}$$

$$\begin{aligned}\phi_6{}^A({}^1\mathrm{A_g}) &= -0.25850\Psi_A+0.14459(\Psi_{D1}+\Psi_{D2})+0.20197(\Psi_{E1}+\Psi_{E2})\\ &\quad -0.60574(\Psi_{J1}+\Psi_{J2})+0.48110\Psi_L+0.40945\Psi_M \qquad E_6{}^A=-27.549\ \mathrm{eV.}\end{aligned}$$

$$\phi_7{}^A({}^1\mathrm{B_u}) = 0.44326(\Psi_{D1}-\Psi_{D2})+0.45714(\Psi_{E1}-\Psi_{E2})-0.79353(\Psi_{J1}-\Psi_{J2}) \qquad E_7{}^A=-25.046\ \mathrm{eV.}$$

$$\begin{aligned}\phi_8{}^A({}^1\mathrm{A_g}) &= 0.092798\Psi_A-0.48255(\Psi_{D1}+\Psi_{D2})+0.32118(\Psi_{E1}+\Psi_{E2})\\ &\quad +0.081012(\Psi_{J1}+\Psi_{J2})+0.86399\Psi_L-0.75270\Psi_M \qquad E_8{}^A=-21.918\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_9{}^A({}^1\mathrm{A_g}) &= -0.64760\Psi_A+0.57117(\Psi_{D1}+\Psi_{D2})+0.65752(\Psi_{E1}+\Psi_{E2})\\ &\quad -0.48308(\Psi_{J1}+\Psi_{J2})-0.59975\Psi_L-0.77956\Psi_M \qquad E_9{}^A=-19.172\ \mathrm{eV.}\end{aligned}$$

### B-Class

$$\begin{aligned}\phi_1{}^B({}^1\mathrm{A_g}) &= 0.87202\Psi_B-0.028051(\Psi_{F1}+\Psi_{F2})+0.14073(\Psi_{G1}+\Psi_{G2})\\ &\quad -0.073901(\Psi_{J1}+\Psi_{J2})+0.0^215347(\Psi_{K1}+\Psi_{K2}) \qquad E_1{}^B=-47.593\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_2{}^B({}^1\mathrm{B_u}) &= 0.30402(\Psi_{F1}-\Psi_{F2})-0.57044(\Psi_{G1}-\Psi_{G2})+0.18725(\Psi_{J1}-\Psi_{J2})\\ &\quad -0.0^218986(\Psi_{K1}-\Psi_{K2}) \qquad E_2{}^B=-37.334\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_3{}^B({}^1\mathrm{A_g}) &= -0.38216\Psi_B-0.47364(\Psi_{F1}+\Psi_{F2})+0.22006(\Psi_{G1}+\Psi_{G2})\\ &\quad -0.33059(\Psi_{J1}+\Psi_{J2})-0.0^240435(\Psi_{K1}+\Psi_{K2}) \qquad E_3{}^B=-35.532\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_4{}^B({}^1\mathrm{B_u}) &= -0.31915(\Psi_{F1}-\Psi_{F2})-0.43752(\Psi_{G1}-\Psi_{G2})-0.40064(\Psi_{J1}-\Psi_{J2})\\ &\quad -0.0^271229(\Psi_{K1}-\Psi_{K2}) \qquad E_4{}^B=-34.700\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_5{}^B({}^1\mathrm{A_g}) &= 0.49807\Psi_B-0.0^269394(\Psi_{F1}+\Psi_{F2})-0.67697(\Psi_{G1}+\Psi_{G2})\\ &\quad -0.31260(\Psi_{J1}+\Psi_{J2})-0.0^237628(\Psi_{K1}+\Psi_{K2}) \qquad E_5{}^B=-34.439\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_6{}^B({}^1\mathrm{B_u}) &= 0.59232(\Psi_{F1}-\Psi_{F2})+0.12105(\Psi_{G1}-\Psi_{G2})-0.60224(\Psi_{J1}-\Psi_{J2})\\ &\quad +0.033251(\Psi_{K1}-\Psi_{K2}) \qquad E_6{}^B=-28.715\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_7{}^B({}^1\mathrm{A_g}) &= -0.32135\Psi_B+0.56549(\Psi_{F1}+\Psi_{F2})+0.25634(\Psi_{G1}+\Psi_{G2})\\ &\quad -0.58847(\Psi_{J1}+\Psi_{J2})+0.035068(\Psi_{K1}+\Psi_{K2}) \qquad E_7{}^B=-28.281\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_8{}^B({}^1\mathrm{B_u}) &= -0.28248(\Psi_{F1}-\Psi_{F2})-0.022139(\Psi_{G1}-\Psi_{G2})+0.064216(\Psi_{J1}-\Psi_{J2})\\ &\quad +0.74692(\Psi_{K1}-\Psi_{K2}) \qquad E_8{}^B=-13.440\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_9{}^B({}^1\mathrm{A_g}) &= 0.019928\Psi_B-0.28298(\Psi_{F1}+\Psi_{F2})-0.026408(\Psi_{G1}+\Psi_{G2})\\ &\quad +0.065243(\Psi_{J1}+\Psi_{J2})+0.74685(\Psi_{K1}+\Psi_{K2}) \qquad E_9{}^B=-13.438\ \mathrm{eV.}\end{aligned}$$

### C-Class

$$\begin{aligned}\phi_1{}^C({}^1\mathrm{A_g}) &= -0.98330\Psi_C+0.028834(\Psi_{H1}+\Psi_{H2})+0.0^386563(\Psi_{I1}+\Psi_{I2})\\ &\quad +0.0^345712(\Psi_{K1}+\Psi_{K2})+0.071200\Psi_L+0.065556\Psi_M \qquad E_1{}^C=-45.823\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_2{}^C({}^1\mathrm{A_g}) &= -0.082603\Psi_C+0.38780(\Psi_{H1}+\Psi_{H2})-0.51862(\Psi_{I1}+\Psi_{I2})\\ &\quad +0.033300(\Psi_{K1}+\Psi_{K2})+0.21597\Psi_L+0.090028\Psi_M \qquad E_2{}^C=-36.466\ \mathrm{eV.}\end{aligned}$$

$$\phi_3{}^C({}^1\mathrm{B_u}) = -0.43587(\Psi_{H1}-\Psi_{H2})+0.52025(\Psi_{I1}-\Psi_{I2})-0.036205(\Psi_{K1}-\Psi_{K2}) \qquad E_3{}^C=-35.808\ \mathrm{eV.}$$

$$\begin{aligned}\phi_4{}^C({}^1\mathrm{A_g}) &= -0.015013\Psi_C-0.54691(\Psi_{H1}+\Psi_{H2})-0.37571(\Psi_{I1}+\Psi_{I2})\\ &\quad +0.0^249540(\Psi_{K1}+\Psi_{K2})+0.31388\Psi_L-0.21248\Psi_M \qquad E_4{}^C=-32.938\ \mathrm{eV.}\end{aligned}$$

$$\phi_5{}^C({}^1\mathrm{B_u}) = 0.55945(\Psi_{H1}-\Psi_{H2})+0.47970(\Psi_{I1}-\Psi_{I2})-0.010689(\Psi_{K1}-\Psi_{K2}) \qquad E_5{}^C=-32.242\ \mathrm{eV.}$$

$$\begin{aligned}\phi_6{}^C({}^1\mathrm{A_g}) &= 0.16167\Psi_C+0.069125)\Psi_{H1}+\Psi_{H2})+0.29043(\Psi_{I1}+\Psi_{I2})\\ &\quad -0.019480(\Psi_{K1}+\Psi_{K2})+0.92172\Psi_L+0.15536\Psi_M \qquad E_6{}^C=-28.849\ \mathrm{eV.}\end{aligned}$$

$$\begin{aligned}\phi_7{}^C({}^1\mathrm{A_g}) &= -0.11281\Psi_C+0.22034(\Psi_{H1}+\Psi_{H2})+0.082154(\Psi_{I1}+\Psi_{I2})\\ &\quad +0.0^242028(\Psi_{K1}+\Psi_{K2})+0.10382\Psi_L-0.96407\Psi_M \qquad E_7{}^C=-28.340\ \mathrm{eV.}\end{aligned}$$

$$\phi_8{}^C({}^1\mathrm{B_u}) = -0.046027(\Psi_{H1}-\Psi_{H2})+0.064809(\Psi_{I1}-\Psi_{I2})+0.71216(\Psi_{K1}-\Psi_{K2}) \qquad E_8{}^C=-15.538\ \mathrm{eV.}$$

$$\begin{aligned}\phi_9{}^C({}^1\mathrm{Ag}) &= 0.0^224620\Psi_C-0.045969(\Psi_{H1}+\Psi_{H2})+0.065435(\Psi_{I1}++\Psi_{I2})\\ &\quad +0.70753(\Psi_{K1}+\Psi_{K2})+0.013931\Psi_L+0.0^288951\Psi_M \qquad E_9{}^C=-15.538\ \mathrm{eV.}\end{aligned}$$

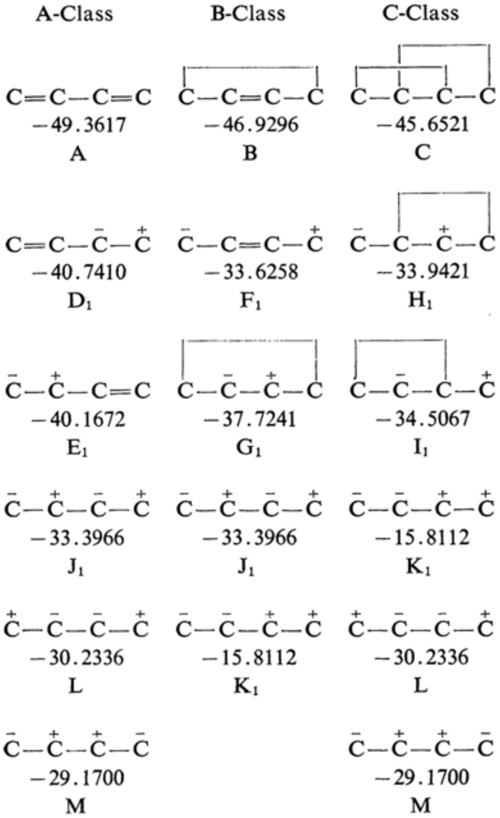


Fig. 2. Classification of resonance structures and the energy values for the structures.

$K_2$'s are given by inversion with respect to the center of molecule from $K_1$'s. Values 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.

derived from the three covalent structures, and the corresponding energy values are shown in Fig. 2.

Wave functions $\phi_i^K$'s, associated with class K, and the corresponding energy values $E_i^K$'s are shown in Table I, where $\Psi_L$ is the normalized bond eigenfunction for structure L.

Then, the probability $P_L^K$ of structure L, the $\pi$-electrons densities, and the bond orders in class K have been evaluated. Results are shown in Table II and Fig. 3.

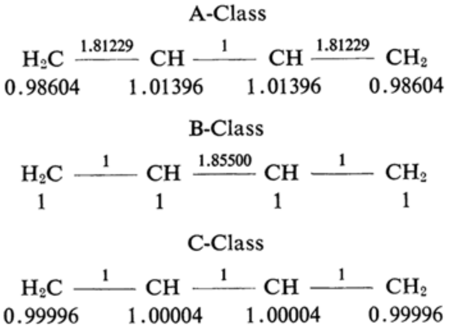


Fig. 3. $\pi$-Electron densities and bond orders in each class.

## Interaction of the Classes

Wave functions, associated with the classes, have been linearly combined, and the wave functions $\Phi_i$'s for the molecule and the corresponding energy values $E_i$'s have been calculated These results are shown in Table III.

Probabilities $P^K$'s of class K's are obtained as follows:

$$P^A=0.84750 \quad P^B=0.1243 \quad 7P^C=0.028126$$

TABLE II. PROBABILITIES OF STRUCTURES IN EACH CLASS

A-class

| A | $D_i$ | $E_i$ | $J_i$ | L | M |
|---|---|---|---|---|---|
| 0.65965 | 0.082133 | 0.070506 | 0.011625 | $0.0^{2}70777$ | $0.0^{2}47473$ |

B-class

| B | $F_i$ | $G_i$ | $J_i$ | $K_i$ |
|---|---|---|---|---|
| 0.85038 | $0.0^{2}23063$ | 0.060866 | 0.011658 | $-0.0^{4}23156$ |

C-class

| C | $H_i$ | $I_i$ | $K_i$ | L | M |
|---|---|---|---|---|---|
| 0.97770 | $0.0^{3}99973$ | $-0.0^{5}77684$ | $0.0^{5}11362$ | 0.010676 | $0.0^{2}96326$ |

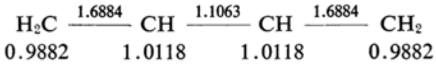
TABLE III. WAVE FUNCTIONS FOR THE MOLECULE AND THE CORRESPONDING ENERGY VALUES

| | |
|---|---|
| $\Phi_1({}^1A_g)=0.85295\phi_1{}^A+0.19279\phi_1{}^B-0.06290\phi_1{}^C$ | $E_1=-51.0989$ eV. |
| $\Phi_2({}^1A_g)=0.37406\phi_1{}^A-0.83569\phi_1{}^B-0.37448\phi_1{}^C$ | $E_2=-45.2366$ eV. |
| $\Phi_3({}^1B_u)=0.61613\phi_2{}^A+0.35938\phi_2{}^B-0.35463\phi_3{}^C$ | $E_3=-41.4287$ eV. |
| $\Phi_4({}^1B_u)=0.86007\phi_2{}^A-0.60375\phi_2{}^B+0.38005\phi_3{}^C$ | $E_4=-37.1047$ eV. |
| $\Phi_5({}^1A_g)=3.24187\phi_1{}^A-2.93339\phi_1{}^B+2.97114\phi_1{}^C$ | $E_5=-32.8775$ eV. |
| $\Phi_6({}^1B_u)=0.00758\phi_2{}^A-0.95755\phi_2{}^B-1.03260\phi_3{}^C$ | $E_6=-26.9595$ eV. |

TABLE IV. PROBABILITIES OF RESONANCE STRUCTURES

| A | B | $D_i$ | $E_i$ | $F_i$ | $G_i$ |
|---|---|---|---|---|---|
| 0.57280 | 0.11951 | 0.06961 | 0.05975 | 0.00029 | 0.00757 |
| $H_i$ | $I_i$ | $J_i$ | $K_i$ | L | M |
| 0.00003 | 0.00000 | 0.01130 | 0.00000 | 0.00630 | 0.00429 |

From these values, the probabilities $P_L$'s of structure L's, the π-electron densities, and the bond orders in the molecule have been computed. Results are shown in Table IV and Fig. 4.



$$\underset{0.9882}{H_2C} \xrightarrow{1.6884} \underset{1.0118}{CH} \xrightarrow{1.1063} \underset{1.0118}{CH} \xrightarrow{1.6884} \underset{0.9882}{CH_2}$$

Fig. 4. π-Electron densities and bond orders.

## Comparison with Other Methods

Calculations have also been performed by the Heitler-London method, including all kinds of overlap, single exchange, and multiple exchange, integrals. The results are as follows:

$$\Phi_1(^1A_g) = 0.90568\Psi_A + 0.15086\Psi_B$$

$$E_1 = -49.4312\ \text{eV.}$$

$$\Phi_2(^1A_g) = 0.81991\Psi_A - 1.21233\Psi_B$$

$$E_2 = -44.8795\ \text{eV.}$$

The probabilities of the two covalent structures are

$$P_A = 0.89875 \qquad P_B = 0.10125$$

and the π-electron densities and the bond orders are given in Fig. 5.

In Fig. 6, the energy levels, obtained above, are shown, together with the results found by the molecular orbital method.

From this figure, it can be seen that the values obtained by our approximate method agree quantitatively with those obtained by the ASMO SCF CI method[5]. The energy value for the ground state computed for the class, derived from the most stable covalent structure, is more satisfactory than that by the Heitler-London method. In the calculation due to that single class. however, it is impossible to obtain the correct order of the levels of the molecule*.

$$\underset{1}{H_2C} \xrightarrow{1.89875} \underset{1}{CH} \xrightarrow{1.10125} \underset{1}{CH} \xrightarrow{1.89875} \underset{1}{CH_2}$$

Fig. 5. π-Electron densities and bond orders (Heitler-London method).

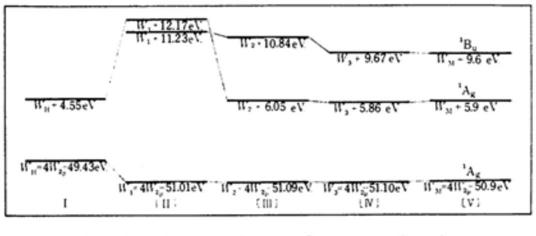


Fig. 6. Comparison of energy levels.

I, The Heitler-London method. II, A-class. III, A-, B-class interaction. IV, A-, B-, C-class interaction. V, The ASMO SCF CI method[5].

The π-electron densities obtained by the ASMO SCF CI method are:

$$D_a = D_d = 0.978 \qquad D_b = D_c = 1.022^{3)}$$

and are in good agreement with our results (Fig. 4).

One of the causes of the success of our method is that the ionic structures are always considered; this point is a difference between our method and the conventional approximate methods.

## Summary

An approximate method, proposed in Part I, has been applied to the non-empirical calculation of the π-electronic states of the *trans*-butadiene molecule. All the higher orders of overlap and exchange integrals have been considered. Slater $2p_\pi$-orbitals have been used through out. The values of the energy levels obtained are −51.099 eV. ($^1A_g$), −45.237 eV. ($^1A_g$), and −41.429 eV. ($^1B_u$). The π-electron densities for the ground state are $D_a = D_d = 0.988$, and $D_b = D_c = 1.012$. These results agree quantitatively with those evaluated by the ASMO SCF CI method.

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5) Y. Mori, ibid., **28**, 291 (1956).

* In Fig. 6, some of the levels obtained by our mothod are lower than the corresponding levels found by the ASMO SCF CI method. The cause of this appearance seems to be due to intermediate approximations in numerical calculations.