Electronic Configuration Analysis of Molecular Deformations

Takashi Okada, Shigeru Nagase, Kizashi Yamaguchi, and Takayuki Fueno
Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560

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A procedure is described which enables to trace the variations of electronic configuration of molecular systems undergoing structural deformation. The mapping operator proposed by Trindle is used to derive a reference set of molecular orbitals which is suitable to the analysis of the wave functions for deformed molecules. The method has been applied to the twisting of ethylene as well as the electrocyclic reactions of butadiene. The results corroborate Bader's symmetry requirement for the electronic excitations accompanying nuclear displacements.

The method of configuration analysis[1] has made it possible to disclose the electronic-structural features of a transient molecular system in comparison with a pertinent reference system. In this method, any configuration Ψ_σ^{P} of a given system P is expressed as a linear combination of configurations $\Psi_\lambda^{\mathrm{Q}}$ which are constructed of the molecular orbitals (MO) for the reference system Q:

$$\Psi_\sigma^{\mathrm{P}} = \sum_\lambda l_{\sigma\lambda}\Psi_\lambda^{\mathrm{Q}} \tag{1}$$

The coefficients $l_{\sigma\lambda}$ are evaluated through calculations of appropriate minor determinants of the matrix $\boldsymbol{B}$ such that

$$\boldsymbol{\phi}^{\mathrm{P}} = \boldsymbol{\phi}^{\mathrm{Q}}\boldsymbol{B} \tag{2}$$

where the row vactor $\boldsymbol{\phi}$ represents a set of orthonormal MO's for each system. The matrix $\boldsymbol{B}$ can be expressed as

$$\boldsymbol{B} = (\boldsymbol{C}^{\mathrm{Q}})^\dagger\boldsymbol{C}^{\mathrm{P}} \tag{3}$$

where $\boldsymbol{C}^{\mathrm{P}}$ and $\boldsymbol{C}^{\mathrm{Q}}$ denote the relevant LCAO matrices for $\boldsymbol{\phi}^{\mathrm{P}}$ and $\boldsymbol{\phi}^{\mathrm{Q}}$, respectively.

The foregoing procedure may be applied to the interpretations of nuclear displacement processes such as molecular vibrations and chemical reactions. However, the method as it stands is based on the assumption that the AO basis set χ has the same implication for both systems P and Q. Consider two equivalent wave functions expressed in different coordinate systems. These functions can be identified with each other by means of configuration analysis, only if the two coordinate systems are superposed by translation alone. That is to say, the invariance for the rotation of coordinate systems does not hold in this method of configuration analysis. Therefore, there appears a difficulty in its applications to the processes accompanied by molecular deformations. In such cases, different meanings must be given to the AO basis sets χ^{P} and χ^{Q}, on which the MO's ϕ_i^{P} and ϕ_i^{Q} are to be based, respectively.

To cope with the situation delineated above, it is advantageous to introduce the mapping procedure which has been proposed by Trindle.[2-4] By making use of the mapping operator which projects the MO's ϕ_i^{Q} defined in the χ^{Q} space onto the χ^{P} space, we obtain a set of mapped orbitals ϕ_i^{R}:

$$\boldsymbol{\phi}^{\mathrm{R}} = \boldsymbol{\phi}^{\mathrm{Q}}\boldsymbol{R} \tag{4}$$

where $\boldsymbol{R}$ is the mapping operator in the matrix representation. Use of the mapped orbitals as reference orbitals renders the configuration analysis meaningful.[5] Thus, the configurations mixed in this way correspond only to the charge reorganization during the nuclear displacement. The weight of the ground configuration so calculated for the ground electronic state is equivalent to the state overlap which Trindle defined in his mapping analysis as a criterion of the orbital-symmetry allowedness of thermal reactions.[2]

It should be noted that an analogous multi-configurational representation has been proposed by Trindle and Collins in their energy-based mapping analysis.[4] Practically, however, their method could hardly be applied to problems involving a large number of configurations. There one would inevitably encounter with too numerous degrees of freedom to determine simultaneously the mapping operator and the configurational mixing coefficients with confidence.

Applications and Discussion

To illustrate the use of the present method we here apply it to two processes, the twisting of ethylene and the ring-closure of butadiene to cyclobutene. The molecular geometries were all taken from the literature.[6] Use was made of the CNDO/2 wave functions[7] in a single-determinant approximation. The mapping operators were obtained by the original overlap-based formalism.[2]

(A) Twisting of Ethylene. We have examined the wave function of a twisted ethylene molecule, for which the dihedral angle between the two $\mathrm{CH_2}$ planes is assumed to be 45°. The SCF MO's calculated for the planar ethylene were projected onto the AO basis set of the twisted ethylene. The mapped orbitals $\boldsymbol{\phi}^{\mathrm{R}}$ thus obtained are used as the reference orbitals in the configuration analysis. Given in Table 1 are the absolute values of the configurational coefficients which are larger than 0.01. Each excited singlet configuration is designated by the pair of occupied and unoccupied MO's which are specified according to the irreducible representations of the $\mathrm{D_{2h}}$ point group. The symmetries of configurations are indicated in the second column.

As Table 1 shows, the coefficients for the excited configurations are relatively small, indicating that the

Table 1. Absolute values of the configurational coefficients for the twisting of ethylene[a)]

Configuration	Symmetry	Coefficient
Ground	$\mathrm{A_g}$	0.998
$1\mathrm{b_{1u}} \rightarrow 2\mathrm{b_{1g}}^*$	$\mathrm{A_u}$	0.039
$1\mathrm{b_{2u}} \rightarrow 1\mathrm{b_{2g}}^*$	$\mathrm{A_u}$	0.039
$1\mathrm{b_{1g}} \rightarrow 2\mathrm{b_{1g}}^*$	$\mathrm{A_g}$	0.010

a) At the twisting angle of 45°.

charge distribution in ethylene suffers relaxation only slightly if the nuclear motion takes place. The effect of charge redistribution on the height of rotational barrier is, therefore, expected to be small.

More important in Table 1 is the trend that, aside from the totally symmetric excited configuration, the ground configuration mixes only with those configurations of the A_u symmetry. The twisting motion of ethylene also possesses the A_u symmetry. Thus, the excited configurations to be mixed, if slightly, with the ground configuration upon nuclear displacement have the same symmetry as the normal coordinate which is responsible for the displacement. The results are in agreement with the generalization first put forth by Bader.[8)]

(B) Ring-closure of Butadiene. Two stereochemical courses, conrotatory and disrotatory, are investigated. Since butadiene (*s-cis*) possesses the C_{2v} symmetry, the corresponding representations will be used throughout this section. Thus, the conrotatory and disrotatory reaction modes may be characterized by the A_2 and B_2 representations, respectively. Two intermediate structures I and II as well as the product structure F have been examined for each reaction. The distance between the terminal carbon atoms was assumed to change linearly with the CH_2 rotation angles θ in the course of reaction. The structures I and II correspond to $\theta=50$ and 80°, respectively.

The results of calculations are shown in Tables 2 and 3, where the absolute values of the coefficients for dominantly contributing configurations only are listed. It can be seen here also that Bader's rule is fulfilled. That is, except for the A_1 configurations, only the excited configurations having the A_2 and B_2 symmetries are mixed with the ground configuration in the conrotatory(A_2) and disrotatory(B_2) reactions, respectively.

Comparison of Table 2 with Table 3 shows that the two stereochemical courses have quite contrasting features. Thus, in the conrotatory reaction (Table 2) the configurational coefficients change continuously throughout, whereas in the disrotatory reaction mode (Table 3) there is no composite configuration at all that is common to structures I and II. In the former reaction, therefore, the nuclear motion is accompanied by a smooth development in relaxation in charge distribution, thus rendering the molecular deformation energetically favorable. The discontinuity of the configurational mixing in the latter reaction is obviously due to the interchange between the highest occupied and lowest unoccupied MO's in the course of reaction, a characteristic which inheres in orbital-symmetry forbidden reactions.

TABLE 2. ABSOLUTE VALUES OF THE CONFIGURATIONAL COEFFICIENTS FOR THE CONROTATORY RING-CLOSURE OF BUTADIENE

Configuration	Symmetry	Coefficient[a)]		
		I	II	F
Gound	A_1	0.904	0.441	0.374
$1b_2 \to 2b_2^*$	A_1	0.205	0.396	0.380
$1a_2 \to 2a_2^*$	A_1	0.155	0.352	0.364
$1b_2 \to 6b_1^*$	A_2	0.127	0.122	0.094
$3b_1 \to 2b_2^*$	A_2	0.127	0.133	0.093
$1a_2 \to 6a_1^*$	A_2	0.087	0.114	0.092
$(1b_2, 1a_2) \to (2b_2^*, 2a_2^*)$	A_1	0.035	0.317	0.370
$(1b_2, 1b_2) \to (2b_2^*, 2b_2^*)$	A_1	0.023	0.178	0.193
$(1a_2, 1a_2) \to (2a_2^*, 2a_2^*)$	A_1	0.013	0.141	0.177
$(1b_2, 1a_2) \to (2b_2^*, 6a_1^*)$	A_2	0.020	0.102	0.093
$(1b_2, 1a_2) \to (2a_2^*, 6b_1^*)$	A_2	0.022	0.097	0.091
$(3b_1, 1a_2) \to (2b_2^*, 2a_2^*)$	A_2	0.022	0.106	0.090

a) I, intermediate I for which $\theta=50°$; II, intermediate II for which $\theta=80°$; F, product (cyclobutene).

TABLE 3. ABSOLUTE VALUES OF THE CONFIGURATIONAL COEFFICIENTS FOR THE DISROTATORY RING-CLOSURE OF BUTADIENE

Configuration	Symmetry	Coefficient[a)]		
		I	II	P
Ground	A_1	0.975	—	—
$5a_1 \to 2b_2^*$	B_2	0.099	—	—
$3a_1 \to 2b_2^*$	B_2	0.092	—	—
$3b_1 \to 6b_1^*$	A_1	0.067	—	—
$2a_1 \to 2b_2^*$	B_2	0.065	—	—
$1a_2 \to 9b_1^*$	B_2	0.053	—	—
$(1a_2, 1a_2) \to (2b_2^*, 2b_2^*)$	A_1	—	0.796	0.838
$(1a_2, 1a_2) \to (2b_2^*, 9a_1^*)$	B_2	—	0.015	0.265
$(1a_2, 1a_2) \to (2b_2^*, 6a_1^*)$	B_2	—	0.300	0.238
$(4b_1, 1a_2) \to (2b_2^*, 2b_2^*)$	B_2	—	0.102	0.131
$(3b_1, 1a_2) \to (2b_2^*, 2b_2^*)$	B_2	—	0.325	0.126
$(1a_2, 1a_2) \to (2b_2^*, 8a_1^*)$	B_2	—	0.099	0.090

a) I, intermediate I for which $\theta=50°$; II, intermediate II for which $\theta=80°$; P, product (cyclobutene).

As can be seen from Tables 2 and 3, the mixing of the excited A_1 configurations is especially small in the disrotatory reaction. In this reaction, therefore, the electronic relaxation due to the approach of the terminal CH_2 groups, which should be characterized as a motion with the A_1 symmetry, must be by far less efficient than in the conrotatory reaction. This may be taken as an indication that the steric course of ring closure is governed by the ease of the approaching motion of the two CH_2 groups rather than the ease of thier rotational motions. The interpretation is compatible with the potential energy surfaces calculated by van der Lugt and Oosterhoff[10)] for the two steric courses of reaction.

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