# Orbital Interaction and Chemical Bonds. Polarization in Chemical Reactions

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**Abstract:** The effects of polarization in chemical reactions are studied. Applying the concept of orbital interaction, the significance of the mixing in of locally excited electron configurations in bringing about the redistribution of electrons is discussed. The electrostatic field of the approaching reagent and the orbital overlap between reagent and reactant are investigated as the possible origins of polarization, in some ionic and nonionic reactions. In polar reactions, the attacking reagent polarizes the reactant so as to reduce the electrostatic repulsion or increase the electrostatic attraction prior to bond formation. In nonpolar reactions, dominant electron-donating and -accepting interactions are accompanied by effective polarization of reactants to give the relaxation of interacting systems. It is suggested that the collaboration of the polarization interaction with the electrostatic and delocalization interactions is important in making efficient the formation and breaking of chemical bonds with the progress of chemical reactions. Some numerical results are presented to support the conclusion derived from the qualitative but lucid concept of orbital interaction.

The concept of orbital interaction has been utilized to disclose the origin of the changes in energy and in electron distribution along reaction paths in a number of chemical reactions.[2-10] By introducing a configuration interaction description to chemical reactivity theory, the interaction energy between a reagent and a reactant was partitioned into several terms, including the Coulombic, exchange, delocalization, and polarization interactions, and each of them was assigned with a chemically accessible interpretation.[11,12] Among them, the roles of the Coulombic and delocalization interactions in chemical reactions have been studied extensively.[2-10] On the effects of the polarization interaction, there have been several interesting discussions in regard to the electronic structure and the chemical reactivity of organic molecules. They are on the effect of substituent groups in conjugated systems,[13] the catalytic activities of external perturbations,[14,15] and the stereoselection through orbital mixing.[16] It seems likely that some important points still remain untouched on the roles of the polarization interaction in the theory of chemical reactions. In this paper, we will examine how the polarization of reactants can contribute to chemical reactions by bringing about the formation and breaking of chemical bonds along reaction paths.

## Chemical Interaction between Two Systems

The interaction between two systems is represented by the combination of various electron configurations.[2c,d] Some important ones in an early stage of the interaction between a donor, A, and an acceptor, B, are illustrated in Figure 1. Provided that the interaction is not strong, the dominant term is the original configuration $\Psi_0$ and the mixing in of other configurations is estimated by the use of perturbation theory. The contribution of an electron configuration $\Psi_p$ ($p \neq 0$) to the wave function is approximately given by[17]

$$C_p \simeq (H_{0,p} - S_{0,p}H_{0,0})/(H_{0,0} - H_{p,p}) + \sum_{q \neq 0,p} (H_{p,q} - S_{p,q}H_{0,0})(H_{0,q} - S_{0,q}H_{0,0})/\{(H_{0,0} - H_{p,p})(H_{0,0} - H_{q,q})\} \quad (1)$$

where familiar notations are employed.[2c,d] The coefficient $C_0$ for the configuration $\Psi_0$ is taken to be positive. The consequence of the interaction between $\Psi_0$ and the electron-transferred configuration $\Psi_{i\to l}$ has been studied extensively.[10]

The perturbation of molecules by means of a modification of the Coulomb and resonance integrals was investigated by Coulson and Longuet-Higgins to discuss the chemical reactivity of nonpolar polycyclic aromatics.[18] The reactivity index "polarizability" was defined. By invoking locally excited electron configurations in our theoretical approach to chemical interactions, we are able to examine the influence of attacking reagent on the formation and breaking of chemical bonds in an explicit manner. Although our interest is not confined to chemical reaction between nonpolar systems, the change in the electronic structure of a reactant due to the perturbation of a reagent is termed polarization (Π) in this paper.

The local reorganization of electrons is described by the aid of unoccupied orbitals. As for the system A, for example, the interaction between a locally excited configuration $\Psi_{i\to j}$ and the original configuration brings about a change in the electron distribution by introducing the intermixing product of the occupied MO $\phi_i$ and the unoccupied MO $\phi_j$[19] (see Appendix I).

$$\begin{aligned}\rho_{\Pi}^{(0,i\to j)}(1) &= C_0C_{i\to j}(\rho_{0,i\to j}(1) + \rho_{i\to j,0}(1) - 2S_{0,i\to j}\rho_{0,0}(1)) \\ &\simeq \sqrt{2}C_0C_{i\to j}(\phi_i(1)\phi_j(1) + \phi_j(1)\phi_i(1))\end{aligned} \quad (2)$$

where

$$\rho_{p,q}(1) = M\int \Psi_p{}^*(1,2,\ldots,M)\Psi_q(1,2,\ldots,M)\mathrm{d}\xi_1\mathrm{d}\tau_2\ldots\mathrm{d}\tau_M$$

The integration of the polarization density $\rho_\Pi$ over all space obviously vanishes.

As the chemical reaction between A and B is initiated, each of them is placed under the charge or dipolar field of the other, and electrons are added or removed through orbital overlap interactions. The electronic structures of A and B which are stable in an isolated state are not suitable any more for representing the reactants in interaction. Naturally, some relaxation process should take place in order to lift the strains accumulated in them.[20] The redistribution of electrons and the changes in the nuclear configuration of reactants should be brought about. In the following, we see some aspects of polarization in several polar and nonpolar chemical reactions.

## Polarization Induced by the Static Field of Attacking Reagent.

Let us examine the possible origins of the mixing in of locally excited configurations in chemical interactions between two closed-shell species. An inspection of the matrix elements between the original configuration and locally excited configurations indicates the presence of two apparently distinguishable

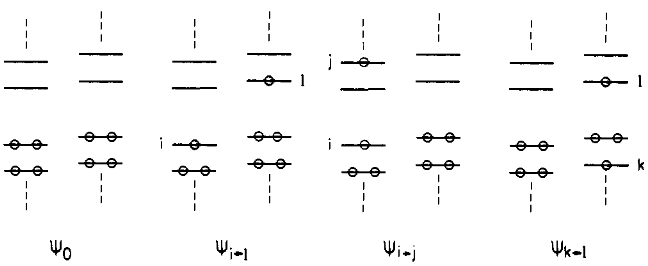

**Figure 1.** A schematic representation of some of the significant electron configurations in chemical interactions of two closed-shell systems.

effects. They are the electrostatic field of the attacking reagent and the orbital overlap interaction between the reagent and the reactant. First, we examine the polarization induced by the charge or dipolar field of the reagent, disregarding the orbital overlap term.

By the aid of the Mulliken approximation[21] and the point-charge approximations, the matrix element between $\Psi_0$ and $\Psi_{i\to j}$ is reduced to a very simple form,[11]

$$H_{0,i\to j} - S_{0,i\to j}H_{0,0} \simeq 1/\sqrt{2}\sum_{\alpha}^{\mathrm{A}}\sum_{\beta}^{\mathrm{B}}(n_{\alpha}{}^{(ij)} + n_{\alpha}{}^{(ji)})(N_{\beta} - Z_{\beta})/R_{\alpha\beta} \quad (3)$$

where $N_\beta$ is the atomic population of the atom $\beta$ of B and $n_\alpha{}^{(ij)}$ is the partial atomic population of the atom $\alpha$ of A, defined by

$$N_\beta = 2\sum_{k}^{\mathrm{occ}}\sum_{t}^{\beta}\sum_{u}^{B} c_t{}^k c_u{}^k s_{tu}$$

$$n_\alpha{}^{(ij)} = \sum_{r}^{\alpha}\sum_{s}^{A} c_r{}^i c_s{}^j s_{rs}$$

$$s_{rs} = \int \chi_r(1)\chi_s(1)\mathrm{d}v(1)$$

The MO's are given by the linear combinations of the basis atomic orbitals $\chi$, $c$'s being the coefficients. It is suggested that the appearance of the locally excited configuration of A is governed by the distribution of the net charges ($N_\beta - Z_\beta$) in B, to the first approximation ($Z$ implies the nuclear charge and $R$ signifies the internuclear distance). When the system B is an ionic system, locally excited configurations are induced strongly in the system A. Given the definite signs to the MO's $\phi_i$ and $\phi_j$, the sign of the coefficient $C_{i\to j}$ is determined by the kind, cationic or anionic, and direction of the electrostatic field provided by the system B.

In order to test the validity of the simplification and the approximations adopted above for the qualitative discussion, we developed a method of calculation which enabled us to examine the sign and magnitude of the interaction integrals in a quantitative manner.[22] We may take here the bimolecular nucleophilic substitution of methyl fluoride by fluoride ion as the first example of ionic reactions to see the effect of the electrostatic field of the reagent. The reaction model was taken after Veillard.[23] Taking the signs of the MO's of methyl fluoride and fluoride ion as shown in Figure 2, the matrix elements were calculated by the use of the ab initio (STO 3G) MO's of the reagent and the reactant.[24] They are listed in Table I, in regard to the electron configurations of interest.

The matrix element between the original configuration and the locally excited configuration ($5a_1 \to 6a_1$) is found to be even larger in magnitude than that between the original configuration and the dominant transferred configuration ($2p_x \to 6a_1$). Since the orbital overlaps between fluoride ion and methyl fluoride are still small in the reaction model, the integral for the interaction between the original configuration and the locally excited configuration is ascribed primarily to the effect of the anionic field extended by the attacking nucleophile. The positive sign of the matrix element can be interpreted easily by the use of eq 3, indicating that the positively chosen partial atomic population $n_\alpha{}^{(i,j)}$ ($i = 5a_1$ and $j = 6a_1$) of the reaction center of the substrate ($\alpha$ = carbon) is subjected to the repulsion from the excess electron of the nucleophile, i.e., $N_\beta - Z_\beta > 0$ ($\beta$ = fluoride ion).

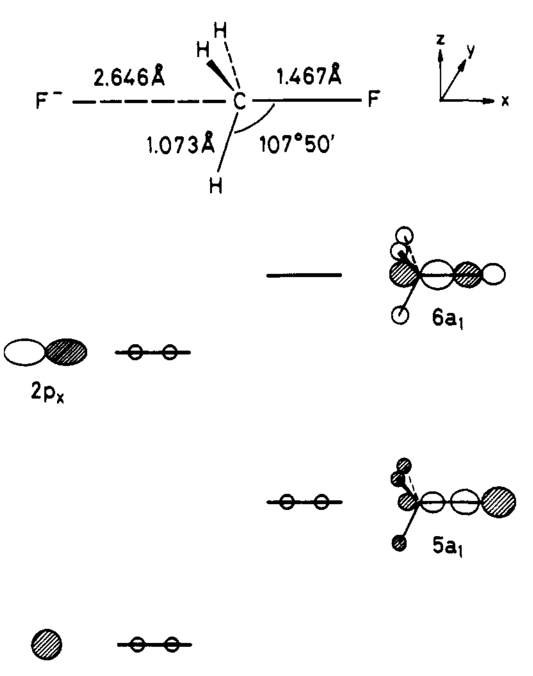

**Figure 2.** A reaction model for the bimolecular nucleophilic substitution of methyl fluoride by fluoride ion. The hatched and unhatched areas in the MO diagram symbolize the positive and negative regions of the real MO's of the isolated reactants, respectively.

**Table I.** The Matrix Elements for Some Important Electron Configurations in the Bimolecular Nucleophilic Substitution of Methyl Fluoride by Fluoride Ion (eV)

| $p$ | $H_{p,p} - H_{0,0}$ | $H_{0,p} - S_{0,p}H_{0,0}$ |
|---|---|---|
| $2s \to 6a_1$ | 30.880 | −0.336 |
| $2p_x \to 6a_1$ | 4.015 | −0.803 |
| $5a_1 \to 6a_1$ | 21.474 | 1.258 |

By substituting the matrix elements into the first term on the right-hand side of eq 1, we get the negative coefficient for the locally excited configuration ($5a_1 \to 6a_1$) which mixes in through the interaction with the original configuration. Since $C_0$ has been chosen to be positive from the outset, eq 2 indicates that the local excitation from the $5a_1$ MO to the $6a_1$ MO intermixes these MO's with negative sign. Thus, the carbon-fluorine bond of methyl fluoride is modified in such a manner as to reduce the electron population of the carbon atom and to increase the electron population of the fluorine atom, as illustrated in Figure 3. The attacking nucleophile makes the preparation for the formation of the new bond by repelling electrons away from the reaction site. Concurrently, the leaving fluorine gets ready for the departure by storing up electrons in its orbitals.

The polarization is accompanied by the weakening of the carbon-fluorine bond to be broken. Stretching of the bond leads to the lowering of the $6a_1$ MO energy and to the increase in the amplitude of the MO at the carbon atom.[8,25] These changes in the $6a_1$ MO of methyl fluoride are clearly favorable for the important electron transfer from the $2p_x$ orbital of fluoride ion. In highly polar reactions, the electrostatic interaction would be the dominant stabilization of the interacting

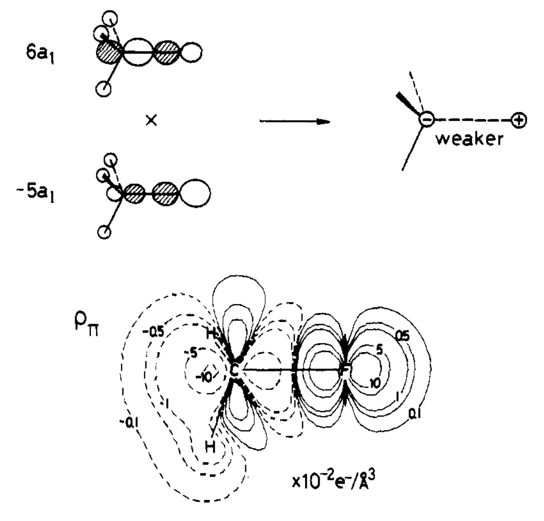

**Figure 3.** Polarization of methyl fluoride induced by the attacking fluoride ion. The signs + and − in circles indicate the increase and decrease in electron population of atoms, respectively.

system.[4] Even in polar reactions, however, the delocalization interaction plays the leading part in creating covalent bonds between the reaction sites of the reagent and reactant.[10] Here we should recognize an additional significance of the electrostatic interaction to bring about the rearrangement of the reactant skeletons. The acceleration of the delocalization interaction follows.

The second example of ionic reactions which we consider here is the ring opening of epoxide initiated by the attack of an anion.[26] Figure 4 shows the four MO's of ethylene oxide which are relevant for our present discussion. They are classified into the symmetric and antisymmetric MO's with respect to the bisecting plane. The electron transfer from the attacking anion, say hydride ion, to the unoccupied MO's 7a$_1$ and 4b$_1$ of ethylene oxide weakens both the C$_1$-O and C$_2$-O bonds equally. The local excitation from the 6a$_1$ MO to the 7a$_1$ MO induced by the electrostatic field of the anion does not distinguish the C$_1$-O bond from the C$_2$-O bond. The same is also true for the local excitation from the 3b$_1$ MO to the 4b$_1$ MO. However, when the anion attacks one of the carbons, say 1, the C$_2$-O bond must remain strong, while the C$_1$-O bond breaks.

As depicted in Figure 4 (c) and (d), the intermixing of the 6a$_1$ MO with the 4b$_1$ MO and that of the 3b$_1$ MO with the 7a$_1$ MO lead to the further weakening of the C$_1$-O bond and the strengthening of the C$_2$-O bond. Thus, the local excitation from an occupied MO to an unoccupied MO of different symmetry induced by the perturbation of reagent lifts the symmetry constraint in reactant. The electron transfer from the anion to ethylene oxide mainly increases the electron populations of the carbon atoms, since both the unoccupied MO's 7a$_1$ and 4b$_1$ possess greater amplitudes on the carbon atoms than on the oxygen. The growth of the anionic center on the oxygen atom is interpreted as the result of the electron migration from carbon 1 to oxygen achieved by the combination of the polarizations, shown in Figure 4 (a)-(d).

## Polarization Induced by Orbital Overlap

It has been shown above that ionic reagent polarizes reactant so as to facilitate the progress of reactions. A similar electron redistribution occurs in the reactant placed under the influence of the dipolar field of polar reagents.[27] The direction and magnitude of polarization are governed by the specific orientation of the reagent. In the case of a completely nonpolar reagent B, the electrostatic effect given by eq 3 vanishes.[28] Then, the orbital overlap interaction comes into play.

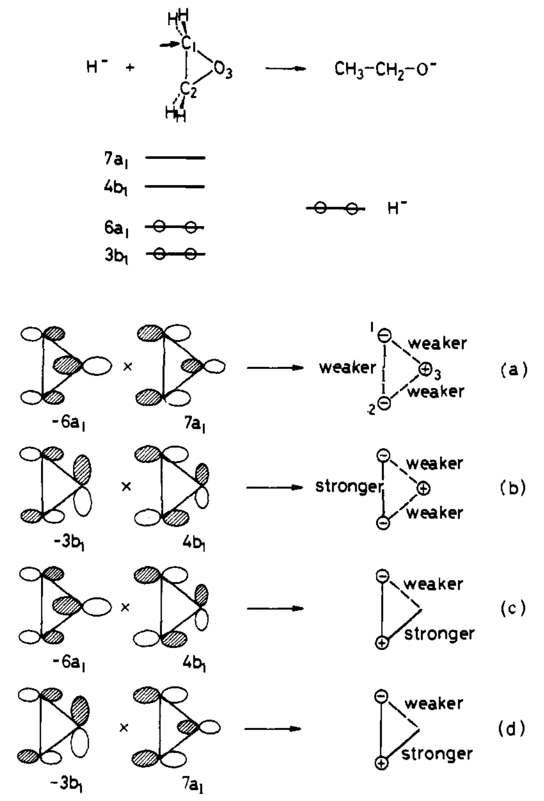

**Figure 4.** Polarization of ethylene oxide induced by the attack of an anion at carbon 1.

Let us consider first the interaction between the original configuration $\Psi_0$ and the locally excited configuration $\Psi_{i\to j}$ through orbital overlap. The overlap integral between $\Psi_0$ and $\Psi_{i\to j}$ is approximately given by $-\sqrt{2}\Sigma_k s_{ik} s_{jk}$, as depicted in Figure 5 (a). Thus, in order to induce $\Psi_{i\to j}$ effectively, there should be an occupied MO $\psi_k$ of B which overlaps strongly both with the occupied MO $\phi_i$ and with the unoccupied MO $\phi_j$ of A. When we take the signs of the MO's $\phi_i$ and $\phi_j$ as to overlap with $\psi_k$ both in-phase (or both out-of-phase), the overlap integral between $\Psi_0$ and $\Psi_{i\to j}$ is negative and, hence, the matrix element might be positive. The first term on the right-hand side of eq 1 indicates that the positive matrix element gives rise to the intermixing of $\phi_i$ and $\phi_j$ with negative sign. Therefore, if a reagent occupied MO finds out a pair of occupied and unoccupied MO's of reactant both having large overlap integrals with it, the reagent may force the reactant to polarize so as to reduce the electron density on nearby atoms. Thus, a contraction of the exclusion shell is suggested to be brought about by the polarization of reactant.

Next, we discuss the interaction between locally excited configurations and electron-transferred configurations. As shown in Figure 5 (b), the configuration $\Psi_{i\to j}$ interacts with the transferred configuration $\Psi_{i\to l}$ through the direct orbital overlap between $\phi_j$ and $\psi_l$. The overlap integral between these electron configurations is $s_{jl}$, neglecting smaller terms. On the other hand, the locally excited configuration $\Psi_{k\to l}$ is converted into the transferred configuration $\Psi_{i\to l}$ by a shift of an electron from $\phi_i$ to $\psi_k$, as indicated in Figure 5 (c). The overlap integral between these configurations is approximately given by $-s_{ik}$. It is expected, therefore, that locally excited configurations come into play not only through the overlap interaction with the original configuration but also through the interaction with electron-transferred configurations.[29] That is, as the electron transfer takes place, it demands electron rearrangements both in donor and in acceptor by invoking locally excited configurations.

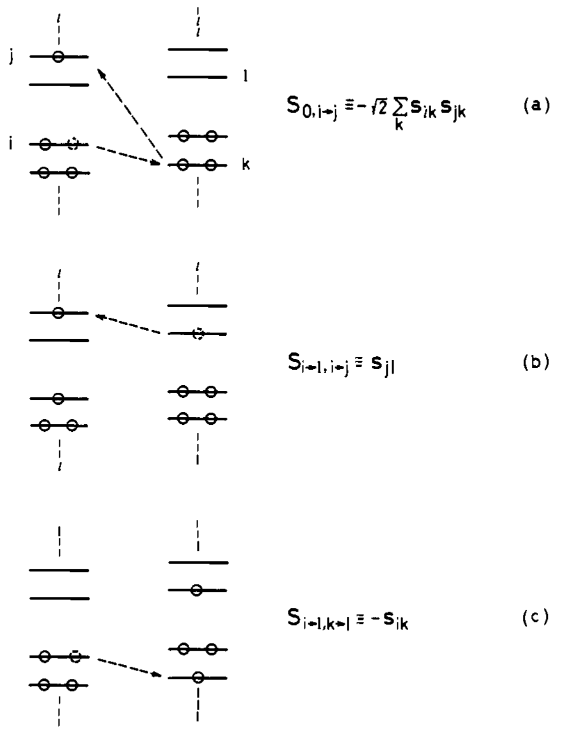

**Figure 5.** Orbital interaction of locally excited configurations with the original and electron-transferred configurations.

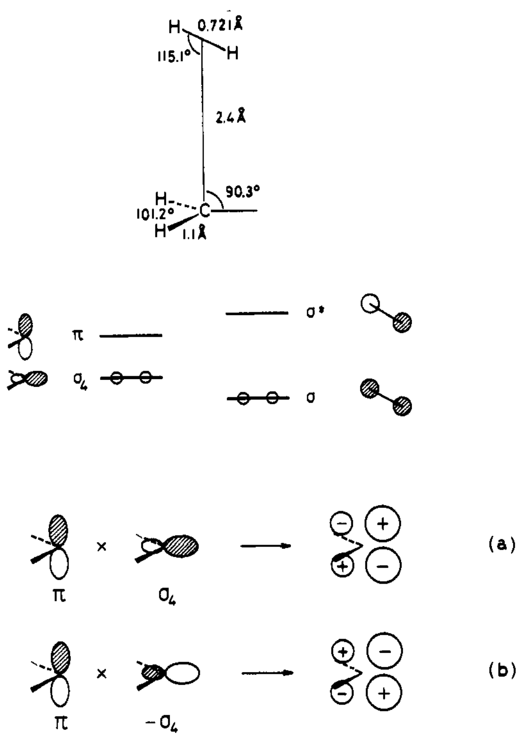

**Figure 6.** A reaction model for the non-least-motion insertion of singlet methylene to hydrogen molecule and the polarization of methylene associated with the overlap interactions. The signs + and − in circles stand for the regions of the increase and decrease in the electron density, respectively.

**Table II.** The Matrix Elements ($H_{p,q} - S_{p,q}H_{0,0}$) for Some Important Orbital Interactions in the Non-Least-Motion Insertion of Singlet Methylene into Hydrogen Molecule (eV)

| | $p$ | 0 | $\sigma_4 \to \sigma^*$ | $\sigma \to \pi$ | $\sigma_4 \to \pi$ |
|---|---|---|---|---|---|
| | 0 | 0 | | | |
| | $\sigma_4 \to \sigma^*$ | −0.7460 | 21.2226 | | |
| $q$ | $\sigma \to \pi$ | −0.8074 | −0.1345 | 15.9731 | |
| | $\sigma_4 \to \pi$ | 0.0382 | −0.4640 | 0.1387 | 2.0644 |

In order to clarify the polarization effects in chemical reactions, we have to know the mode and extent of orbital mixing and, therefore, the sign and magnitude of the matrix elements. Since the overlap integrals between the relevant configurations have been elucidated above, what we do next is to see if a certain relationship exists between the sign of the overlap integrals and the sign of the matrix elements. Let us examine the interaction integrals in a reaction of small systems, before we begin our qualitative discussion on the interaction between sizable molecules. The simplest reaction between nonpolar species taken here is the insertion of singlet methylene to hydrogen molecule. A reaction model was taken after Simonetta,[30] as shown in Figure 6. The signs of the lone-pair hybrid ($\sigma_4$) and the unoccupied p orbital ($\pi$) of methylene and the bonding ($\sigma$) and antibonding ($\sigma^*$) MO's of hydrogen were chosen in such a manner as to make all the MO overlap integrals between the two species positive. We disregard other MO's of methylene, since their contributions to the interaction have been found to be small. Table II gives the matrix elements for the important electron configurations, computed by the use of an ab initio (STO 3G) MO method.[22]

The overlap integral between the original configuration $\Psi_0$ and the transferred configuration $\Psi_{i\to l}$ is approximately given by $\sqrt{2}s_{il}$. In the case of methylene-hydrogen reaction, the interaction between the original and transferred configurations with the positive overlap integrals gives rise to the negative matrix elements, −0.7460 eV for ($\sigma_4 \to \sigma^*$) and −0.8074 eV for ($\sigma \to \pi$). Of these, ($\sigma \to \pi$) lies lower than ($\sigma_4 \to \sigma^*$) and has a stronger interaction with the original configuration. Methylene plays the part of acceptor in an early stage of the non-least-motion insertion of singlet methylene to hydrogen molecule.

The overlap integral between the locally excited configuration ($\sigma_4 \to \pi$) and the transferred one ($\sigma_4 \to \sigma^*$) is positive as depicted in Figure 5 (b) and we get the negative matrix element −0.4640 eV. On the contrary, the configuration ($\sigma_4 \to \pi$) has the negative overlap with the transferred configuration ($\sigma \to \pi$) as shown in Figure 5 (c), and the interaction between them yields the positive matrix element 0.1387 eV. By introducing the matrix elements into the second term on the right-hand side of eq 1, the mixing in of the locally excited configuration ($\sigma_4 \to \pi$) induced by the electron transfer ($\sigma_4 \to \sigma^*$) is shown to be with positive sign, and that arising from the interaction with ($\sigma \to \pi$) is calculated to be with negative sign. Figure 6 (a) and (b) illustrate schematically the spatial redistribution of electrons due to the intermixing of the $\sigma_4$ and $\pi$ MO's with positive and negative signs, respectively.

The interaction between the original configuration and the locally excited configuration ($\sigma_4 \to \pi$) yields the positive matrix element 0.0382 eV. Since the approaching hydrogen is completely nonpolar, the negative overlap indicated in Figure 5 (a) is responsible for the electron promotion. The resulting intermixing of the $\sigma_4$ and $\pi$ MO's with negative sign allows the distortion of the electron cloud to lessen the overlap repulsion between them. The numerical calculation on this small system demonstrates that the relationship, $(H_{p,q} - S_{p,q}H_{0,0})/S_{p,q} < 0$, is applicable to the interaction of the locally excited configurations with the original and dominant transferred configurations. Thus, we may be able to interpret or predict the effects of polarization by inspecting the signs of the overlap integrals (see Appendix II).

Now, we apply the concept of polarization to the Diels-Alder reaction of butadiene and ethylene. Recent calculations by the use of ab initio MO methods showed that the addition would be a concerted process.[31,32] Electron transfer takes place

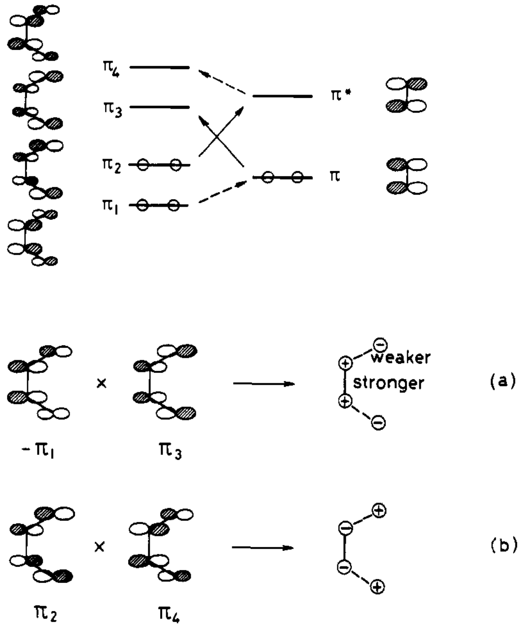

**Figure 7.** An illustration of the mode of polarization in the Diels-Alder reaction between butadiene and ethylene.

from the $\pi_2$ MO of butadiene to the $\pi^*$ MO of ethylene and from the $\pi$ MO of ethylene to the $\pi_3$ MO of butadiene, as shown in Figure 7. The locally excited configurations ($\pi_1 \rightarrow \pi_3$) and ($\pi_2 \rightarrow \pi_4$) are accountable for the polarization of $\pi$ electrons in butadiene. Neither the promotion of an electron from the $\pi_2$ MO to the $\pi_3$ MO nor that from the $\pi_1$ MO to the $\pi_4$ MO is allowed by symmetry. The mode of the orbital mixings can be elucidated in the same manner as has been done in methylene-hydrogen reaction.

Taking the signs of the MO's of ethylene and butadiene as illustrated, the local excitation from the $\pi_1$ MO to the $\pi_3$ MO mixes these MO's in the manner as shown in Figure 7 (a). Namely, the electron delocalization from the $\pi$ MO of ethylene to the $\pi_3$ MO of butadiene is accompanied by the polarization of butadiene which gives rise to the drift of electrons from the terminal carbons to the internal carbons, the weakening of the 1, 2- and 3,4-$\pi$ bonds, and the strengthening of the 2,3-$\pi$ bond. Since the donated electron from ethylene to butadiene $\pi_3$ MO populates more heavily the 1 and 4 carbons than the 2 and 3 carbons, the shift of electrons produced by the ($\pi_1 \rightarrow \pi_3$) polarization tends to minimize the change in the electron distribution. On the other hand, the local excitation from the $\pi_2$ MO to the $\pi_4$ MO induced by the electron delocalization from the $\pi_2$ MO to the $\pi^*$ MO polarizes butadiene, increasing the electron density at the reaction sites and decreasing the electron density at the adjacent carbons, as indicated in Figure 7 (b). On the donation of an electron from the $\pi_2$ MO, the 1 and 4 carbons lose a larger portion of their electron populations than the 2 and 3 carbons do. The electron rearrangement due to the ($\pi_2 \rightarrow \pi_4$) polarization makes up the deficiency in electron population at the reaction sites. The ($\pi_2 \rightarrow \pi_4$) polarization again results in the weakening of the 1,2 and 3,4-$\pi$ bonds and the strengthening of the 2,3-$\pi$ bond.

The redistribution of electron populations in butadiene due to the ($\pi_2 \rightarrow \pi_4$) polarization takes place in the opposite manner to that due to the ($\pi_1 \rightarrow \pi_3$) polarization. It is imagined, therefore, that the changes in electron populations of the carbon atoms brought about by such specific polarizations would disappear in an overall MO calculation of the interacting system. This does not mean, however, that such polarization effects can be ignored. The changes in the overlap populations of the $\pi$ bonds in butadiene which are caused by the polarizations are obviously of great significance in representing the nuclear configuration change of diene along the reaction path of the cycloaddition. In order to understand the detailed mechanism of the formation and breaking of chemical bonds in reactions, the analysis of the polarization effect is helpful.

In a study of the Diels-Alder reaction between butadiene and ethylene by the use of an ab initio MO method, Hehre, Salem, and co-workers found that the rearrangement of the butadiene skeleton would occur at a very early stage of the reaction, while the carbon-carbon bond of ethylene would still be relatively close to an olefinic bond.[31] The electron transfer from the $\pi_2$ MO of butadiene to the $\pi^*$ MO of ethylene and that from the $\pi$ MO of ethylene to the $\pi_3$ MO of butadiene weaken the 1,2- and 3,4-$\pi$ bonds and strengthen the 2,3-$\pi$ bond of butadiene.[25,33] The electron donation and acceptance, however, weaken the $\pi$ bond of ethylene as well. The polarization of ethylene by means of the promotion of an electron from the $\pi$ MO to the $\pi^*$ MO is forbidden by symmetry. On the other hand, the butadiene framework relaxes by the polarization, as mentioned above. Thus, the finding of Salem and co-workers seems to be an indication of the importance of polarization in the cycloaddition.[31,34]

One may recognize that the outcome of the electron delocalization is somewhat different from that of the polarization. The overlap populations of the 1,2 and 3,4 bonds are greater in absolute values than that of the 2,3 bond both in the $\pi_2$ MO and in the $\pi_3$ MO. Therefore, the electron donation from the $\pi_2$ MO and the electron acceptance into the $\pi_3$ MO weaken the 1,2- and 3,4-$\pi$ bonds more efficiently than they strengthen the 2,3-$\pi$ bond. On the contrary, the ($\pi_1 \rightarrow \pi_3$) and ($\pi_2 \rightarrow \pi_4$) polarizations give rise to the strengthening of the 2,3-$\pi$ bond more effectively than they bring about the weakening of the 1,2- and 3,4-$\pi$ bonds. Cooperation of the delocalization and polarization interactions yields the harmonious rearrangement of the butadiene skeleton.

In contrast to the calculations by Salem[31] and by Leroy[32] Dewar suggested that the Diels-Alder reaction between butadiene and ethylene would be a two-step process, via a biradicaloid transition state.[35] According to Salem,[31] the transition state for the pure two-step pathway is located a few kcal/mol higher than the one for the concerted pathway. In the unsymmetrical interaction, the electron transfer from the $\pi_1$ MO to the $\pi^*$ MO and that from the $\pi$ MO to the $\pi_4$ MO are allowed to take place. Then, the ground state of the system is represented by

$$\Psi = C_0\Psi_0 + C_1\Psi(\pi_2 \rightarrow \pi^*) + C_2\Psi(\pi \rightarrow \pi_3) + C_3\Psi(\pi_1 \rightarrow \pi^*) + C_4\Psi(\pi \rightarrow \pi_4) + \cdots$$

in which all the coefficients are positive. Thus, the $\pi_2$ MO mixes with the $\pi_1$ MO and the $\pi_3$ MO mixes with the $\pi_4$ MO through the delocalization interaction with the $\pi^*$ and $\pi$ MO of ethylene, respectively. The orbital mixings are represented by[10]

$$\rho_{i\rightarrow l,i'\rightarrow l}(1) - S_{i\rightarrow l,i'\rightarrow l}\,\rho_{0,0}(1) \simeq -\phi_i(1)\phi_{i'}(1) \qquad (4)$$

$$\rho_{k\rightarrow j,k\rightarrow j'}(1) - S_{k\rightarrow j,k\rightarrow j'}\,\rho_{0,0}(1) \simeq \phi_j(1)\phi_{j'}(1) \qquad (5)$$

The intermixings of the MO's reduce the overlap population of the 3,4-$\pi$ bond and increase the overlap population of the 1,2-$\pi$ bond as illustrated in Figure 8.

In order to leave the allylic conjugation from the diene framework in the hex-2-ene-1,6-diyl biradical, the 3,4 bond must be loosened, while the 1,2 bond remains $\pi$ conjugated. The delocalization interactions ($\pi_2 \rightarrow \pi^*$) and ($\pi \rightarrow \pi_3$) and the polarization interactions ($\pi_1 \rightarrow \pi_3$) and ($\pi_2 \rightarrow \pi_4$) weaken both the 1,2- and 3,4-$\pi$ bonds equally. The ($\pi_1 \rightarrow \pi_4$) and ($\pi_2 \rightarrow \pi_3$) polarizations are not of consequence. It is suggested,

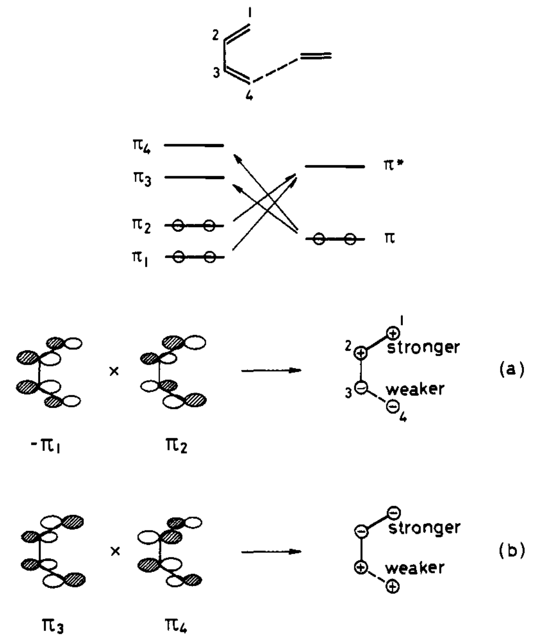

**Figure 8.** A sketch of the orbital mixings in the two-step addition of ethylene to butadiene.

therefore, that the electron transfer from the $\pi_1$ MO to the $\pi^*$ MO and that from the $\pi$ MO to the $\pi_4$ MO take place considerably in the unsymmetrical approach of ethylene to butadiene. Substituent groups, particularly the electron-releasing groups on diene and the electron-withdrawing groups on dienophile, may make the participation of the lower lying occupied MO's and of the higher lying unoccupied MO's in the orbital interaction less significant. In such cases, the two-step pathway will be very costly.

Addition of ethylene to norbornadiene provides us with another example to exhibit the polarization effect in nonpolar reactions. The electron transfer from the $\pi$ MO of ethylene to the $\pi_3$ MO of diene and the one from the $\pi_2$ MO of diene to the $\pi^*$ MO of ethylene are allowed by symmetry,[36] as shown in Figure 9. The orbital interactions result in the loosening of the double bonds of both systems and the formation of new bonds between them.

The induced local excitation in norbornadiene gives rise to the intermixing product of the $\pi_1$ and $\pi_3$ MO's with negative sign and that of the $\pi_2$ and $\pi_4$ MO's with positive sign. The charge displacement due to the ($\pi_1 \rightarrow \pi_3$) polarization counteracts the one due to the ($\pi_2 \rightarrow \pi_4$) polarization. The important consequence of the polarization is the negative $C_2$–$C_6$ overlap population and the positive $C_3$–$C_5$ overlap population. Since the formation of the three-membered ring is performed by the in-phase overlap of the orbitals of the carbons 3 and 5, the positive $C_3$–$C_5$ overlap population signifies the stabilization of the system upon the formation of the $\sigma$ bond. Namely, the polarization in norbornadiene induced by the delocalization interaction assists the formation of cyclopropane ring in homo-Diels–Alder reactions.

In the case of a reacting system which possesses an unpaired electron, electrons with different spins should migrate in different directions. For instance, Figure 10 illustrates schematically the polarization of electron spins in the addition of methyl radical to ethylene.[37-39] The $\pi$ electron with the same spin as the odd electron, say $\alpha$, migrates from the carbon under attack to the other carbon in ethylene, while the $\pi$ electron with the opposite spin $\beta$ moves toward the reaction center. The electron transfer from methyl to the $\pi^*$ MO of ethylene and that from the $\pi$ MO of ethylene to methyl do not account for the growth of the radical center on the carbon atom of ethylene

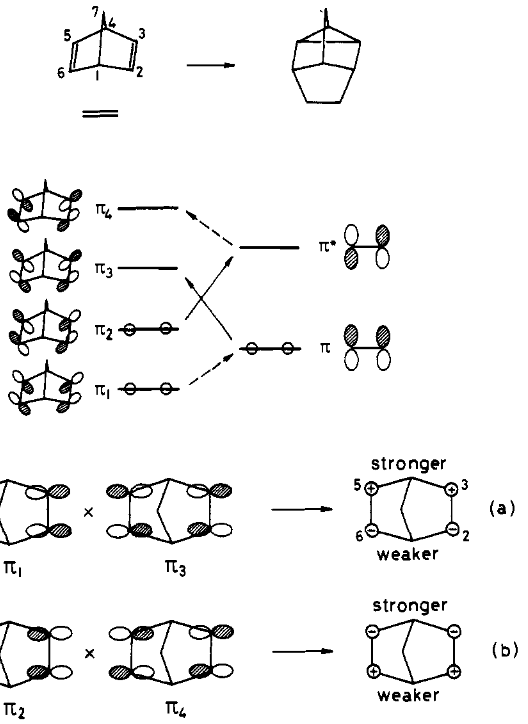

**Figure 9.** The mode of polarization in the cycloaddition between norbornadiene and ethylene.

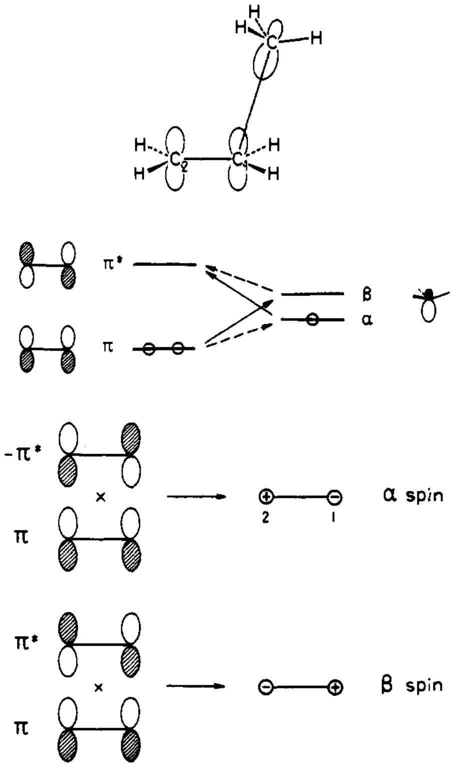

**Figure 10.** A sketch of the polarization of electron spins in the addition of methyl to ethylene.

which is next to the reaction center. The effect of polarization should be involved in MO treatments of radical reactions to represent the characteristic of chain transfer.

## Polarization Interaction and Particular Orbitals in Chemical Reactions

Let us mention briefly some general aspects of polarization effects. For simplicity, we imagine well-localized diatomic

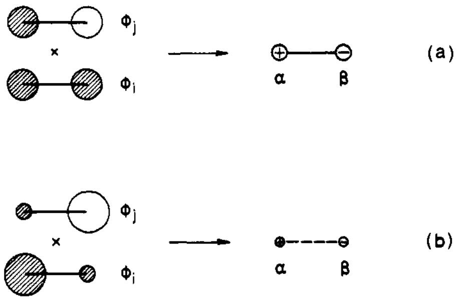

**Figure 11.** A schematic illustration of polarization in polar and nonpolar diatomic chemical bonds.

bonds between the atoms $\alpha$ and $\beta$. The occupied MO $\phi_i$ and the unoccupied MO $\phi_j$ are given by

$$\begin{aligned}\phi_i &= c_\alpha{}^i\chi_\alpha + c_\beta{}^i\chi_\beta \\ \phi_j &= c_\alpha{}^j\chi_\alpha + c_\beta{}^j\chi_\beta\end{aligned} \tag{6}$$

If we assume that the MO's $\phi_i$ and $\phi_j$ intermix each other with positive sign, the changes in the atomic densities and the bond order are given by

$$\begin{aligned}\Delta q_\alpha &= 2c_\alpha{}^i c_\alpha{}^j \\ \Delta q_\beta &= 2c_\beta{}^i c_\beta{}^j\end{aligned} \tag{7}$$

$$\Delta p_{\alpha\beta} = 2(c_\alpha{}^i c_\beta{}^j + c_\beta{}^i c_\alpha{}^j) \tag{8}$$

In the case of nonpolar bonds, the occupied and unoccupied MO's are as shown schematically in Figure 11 (a). The intermixing of these MO's brings about a charge displacement from one atom to the other atom. However, the bond is hardly loosened, because the partial bond order $c_\alpha{}^i c_\beta{}^j$ compensates for the partial bond order $c_\beta{}^i c_\alpha{}^j$. In the case of polar bonds, the main consequence of the intermixing of the MO's is the change in the bond order as shown in Figure 11 (b). The transfer of charge is not conspicuous, since one of the coefficients $c^i$ and $c^j$ is small both on the atom $\alpha$ and on the atom $\beta$.[40]

Removal of electrons from a bonding MO and addition of electrons to an antibonding MO lead to the weakening of the bond. In addition to the electron redistribution due to the intermixing of MO's given by eq 2, the local excitation $\Psi_{i\to j}$ removes an electron from the occupied MO $\phi_i$ and places an electron into the unoccupied MO $\phi_j$. The magnitude of the electron shift is $C_{i\to j}{}^2$. On the other hand, the transferred configuration $\Psi_{i\to l}$ signifies the removal of an electron from the MO $\phi_i$ of A and the addition of an electron to the unoccupied MO $\psi_l$ of B. The magnitude of the electron transfer is $C_{i\to l}{}^2$. The coefficient for the locally excited configuration $\Psi_{i\to j}$ is generally much smaller than the one for the dominant transferred configuration $\Psi_{i\to l}$. This implies that the changes in the electron occupancies of the occupied and unoccupied MO's of reagent and reactant are brought about chiefly by the delocalization interaction. The locally excited configurations contribute to the reorganization of electron distribution primarily by means of the interaction with the original configuration as has been discussed above. Namely, the absolute value of the coefficient product $C_0C_{i\to j}$ or $C_0C_{k\to l}$ may be roughly similar in magnitude to $C_{i\to l}{}^2$.[41] Then, we have a generalization of the polarization effects in chemical reactions. In nonpolar bonds, the mixing in of locally excited configuration results in a charge polarization from one atom to the other atom, while the weakening of the bond is mainly raised by the electron-transfer interaction with other systems. In polar bonds, on the contrary, the mixing in of locally excited configuration leads to a change in the bond strength, while the displacement of electronic charges is mainly caused by the electron-transfer interaction with other systems.

As exemplified above, homonuclear bonds in polyatomic systems are weakened or strengthened by the polarization interaction. It is one of the most striking features of the MO representation of chemical reactions between sizable systems that some particular MO's play the dominant roles. Specific intermixings of MO's are brought about in the course of reactions. Since individual MO's have different amplitudes on the constituent atoms, the polarization is of consequence in yielding the bond interchange even in nonpolar systems.

It has been discussed that the reaction pathway is generally governed by the particular MO's, called the "frontier" MO's.[2,42] The utility of the frontier orbital theory was supported by Houk recently.[6] The predominance of the frontier orbital interaction over the interaction between other orbitals has been attributed mainly to the small energy gap between the particular orbitals. Our present study on the details of orbital interactions has revealed another significant reason why the frontier orbitals can interpret or predict the orientation and stereoselection in a number of reactions. The electron-transfer interaction between the frontier orbitals is accompanied by an effective relaxation of reactants due to the polarization and, hence, is further promoted with the progress of chemical reactions. The high-lying occupied and low-lying unoccupied extra frontier MO's participate in the orbital interaction to collaborate with the frontier orbitals.

We traced the appearance of locally excited electron configurations to two factors. First, the electrostatic field of the attacking reagent induces the polarization of the reactant. The displacement of electronic charges is of importance in an early stage of polar reactions to reduce the static repulsion or to increase the static attraction. Second, the reagent gives rise to the redistribution of electrons in the reactant by means of orbital overlap interactions. The closed shell of reagent causes the polarization in reactant to lessen the overlap repulsion, while the electron-transfer interaction demands the electron reorganization to reduce the changes in the electron populations at the reaction sites. The changes in the overlap populations due to the polarization take place generally in favor of the rearrangement of reactant skeletons along a reaction path. The deformation of reactants enhances the delocalization interaction by modifying the shapes and levels of the MO's relevant for the interaction. Stronger delocalization interaction means stronger polarization, in turn. They accelerate each other. Now, the delocalization interaction is responsible for the formation of chemical bonds between the reaction sites of reactants. The cooperation of the polarization interaction with the electrostatic and delocalization interactions thus seems to be essential for promoting the interchange of chemical bonds in reactions.

The progress of chemical reactions is represented most distinctly by the interchange of chemical bonds. Then, the investigation of the detailed mechanisms of the formation and breaking of chemical bonds will offer a promise of disclosing new insights into the basic nature of chemical reactions. In this paper, we discussed some aspects of the polarization effect in chemical reactions on the basis of the concept of orbital interaction. We believe that the effect is of profound significance in elucidating the driving force for the rearrangements of reactant skeletons along the reaction pathways.

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## Appendix I

The wave functions for the original and locally excited configurations are given by the Slater determinants, utilizing the MO's of isolated reactants.

$$\Psi_0 = |\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_i \cdots \phi_m\bar{\phi}_m\psi_1\bar{\psi}_1 \cdots \psi_k\bar{\psi}_k \cdots \psi_n\bar{\psi}_n|$$

$$\Psi_{i\to j} = 1/\sqrt{2}\{|\phi_1\bar{\phi}_1 \cdots \phi_i\bar{\phi}_j \cdots \phi_m\bar{\phi}_m\psi_1\bar{\psi}_1 \cdots \psi_n\bar{\psi}_n| - |\phi_1\bar{\phi}_1 \cdots \bar{\phi}_i\phi_j \cdots \phi_m\bar{\phi}_m\psi_1\bar{\psi}_1 \cdots \psi_n\bar{\psi}_n|\}$$

The intermixing of these electron configurations gives the following partial electron density

$$\begin{aligned}\rho_{0,i\to j} = \sqrt{2}/(N_0 N_{i\to j}) \Big\{ &\sum_{i'}^{\text{occ}}\sum_{i''}^{\text{occ}} \phi_{i'}\phi_{i''}(D_{i',i''}(i \to j)\cdot D \\ &+ D(i \to j)\cdot D_{i',i''}) + \sum_{k}^{\text{occ}}\sum_{k'}^{\text{occ}} \psi_k\psi_{k'}(D_{m+k,m+k'}(i \to j)\cdot D \\ &+ D(i \to j)\cdot D_{m+k,m+k'}) \\ &+ 2\sum_{i'}^{\text{occ}}\sum_{k}^{\text{occ}} \phi_{i'}\psi_k(D_{i',m+k}(i \to j)\cdot D + D(i \to j)\cdot D_{i',m+k}) \\ &- \sum_{i'}^{\text{occ}} (\phi_{i'}\phi_i - \phi_{i'}\phi_j)\cdot D_{i',i}(i \to j)\cdot D \\ &- \sum_{k}^{\text{occ}} (\phi_i\psi_k - \phi_j\psi_k)\cdot D_{i,m+k}(i \to j)\cdot D \qquad (9)\end{aligned}$$

where $D$ is the determinant of the overlap integrals between the occupied MO's $\phi_i$ of A ($i = 1, 2, \ldots, m$) and the occupied MO's $\psi_k$ of B ($k = m + 1, m + 2, \ldots, m + n$).

$$D = \left|\begin{array}{c:c} 1 & (s_{i'k}) \\ \hdashline (s_{ki'}) & 1 \end{array}\right|$$

Another determinant $D(i \to j)$ is defined by replacing the elements of the $i$th row of $D$, $s_{ip}$ ($p = 1, 2, \ldots, m + n$), by $s_{jp}$. $D_{p,q}$ means the minor of the determinant $D$ in regard to the $(p,q)$ element (signs $(-1)^{p+q}$ involved). The normalization factors for the wave functions $\Psi_0$ and $\Psi_{i\to j}$ due to the intermolecular MO overlap are given by

$$N_0 = D^{-1}$$

$$N_{i\to j} = (D \cdot D(i \to j, i \to j) + D(i \to j)^2)^{-1/2}$$

where the determinant $D(i \to j, i \to j)$ is obtained by replacing the elements of the $i$th row of $D$, $s_{ip}$, by $s_{jp}$ and the elements of the $i$th column, $s_{pi}$, by $s_{pj}$ (the $(i,i)$ element is unity). Neglecting the terms including MO overlap integrals, we get eq 2.

## Appendix II

The matrix element between a locally excited configuration $\Psi_{i\to j}$ and an electron-transferred configuration $\Psi_{i\to l}$ is given by

$$\begin{aligned}H_{i\to j,i\to l} - S_{i\to j,i\to l}H_{0,0} = \Big[ &V_{Ajl} + 2\sum_{i'}^{\text{occ}} (jl|i'i') \\ &- (jl|ii) - \Big\{V_{All} + 2\sum_{i'}^{\text{occ}} (ll|i'i') - (ll|ii)\Big\}s_{jl} \\ &+ (H_{i\to l,i\to l} - H_{0,0})s_{jl}\Big] - \Big\{V_{Akl} + 2\sum_{i'}^{\text{occ}} (kl|i'i') \\ &- (kl|ii)\Big\}s_{jk} + \Big\{V_{Bij} + 2\sum_{k}^{\text{occ}}(ij|kk)\Big\}s_{il} \\ &- (ij|ii)s_{il} + \cdots \qquad (10)\end{aligned}$$

where

$$V_{Ajl} = \int \phi_j(1)\left(\sum_{\alpha}^{A} - Z_\alpha/r_{1\alpha}\right)\psi_l(1)\mathrm{d}v(1)$$

$$s_{jl} = \int \phi_j(1)\psi_l(1)\mathrm{d}v(1)$$

$$(jl|ii) = \int\int \phi_j(1)\phi_i(2)(1/r_{12})\psi_l(1)\phi_i(2)\mathrm{d}v(1)\mathrm{d}v(2)$$

The first term on the right-hand side of eq 10 comes from the direct orbital overlap between the unoccupied MO's $\phi_j$ and $\psi_l$. It involves the energy difference $(H_{i\to l,i\to l} - H_{0,0})$ multiplied by the overlap integral $s_{jl}$. The second and third terms arise from the electrostatic interaction between A and B. They have formally opposite signs. The second and third terms, therefore, enhance each other in the reactions between unlike species, e.g., between a cation and an anion, and compensate each other in the reactions of neutral and nonpolar systems. They also include overlaps between the occupied and unoccupied MO's. When the interacting system possesses a certain symmetry, some of the interaction terms will vanish owing to the orbital orthogonality.

The matrix element between a locally excited configuration $\Psi_{k\to l}$ and an electron-transferred configuration $\Psi_{i\to l}$ is given by

$$\begin{aligned}H_{k\to l,i\to l} - S_{k\to l,i\to l}H_{0,0} = -\Big[ &V_{Aik} + 2\sum_{i'}^{\text{occ}} (ik|i'i') \\ &+ (ik|ll) - (ik|ii) - \Big\{V_{Akk} + 2\sum_{i'}^{\text{occ}} (i'i'|kk) \\ &+ (kk|ll) - (ii|kk)\Big\}s_{ik} + (H_{i\to l,i\to l} - H_{0,0})s_{ik}\Big] \\ &+ 2\Big\{V_{Akl} + 2\sum_{i'}^{\text{occ}} (kl|i'i') - (kl|ii)\Big\}s_{il} + \cdots \qquad (11)\end{aligned}$$

It is seen that the magnitude of the first term depends on the overlap of the occupied MO $\phi_i$ with the occupied MO $\psi_k$. On the other hand, the second term may be proportional to the overlap between the occupied MO $\phi_i$ and the unoccupied MO $\psi_l$.

It is noteworthy that the energy difference term may be opposite in sign to the sum of the remaining terms in the brackets both in eq 10 and in eq 11. Consequently, it is not necessarily self-evident that

$$(H_{p,q} - S_{p,q}H_{0,0})/S_{p,q} < 0$$

where $p$ implies an electron-transferred configuration and $q$ stands for a locally excited configuration. As we have seen in the examples presented in the text, the effective relaxation of reactants would follow in the cases which satisfy the above relation. It is required, therefore, that the energy difference $(H_{p,p} - H_{0,0})$ be sufficiently small. This condition may make the frontier orbitals play a key role in chemical reactions.

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$$S_{p,q} = |s_{p,q}| \cdot |\overline{s}_{p,q}|$$

where

$$s_{p,q} = \int {}^\dagger\Phi_p\Phi_q d\tau \text{ and } \overline{s}_{p,q} = \int {}^\dagger\overline{\Phi}_p\overline{\Phi}_q d\tau$$

The MO's of reactants are presented in the LCAO forms

$$\Phi_p = c_p\chi,\ \overline{\Phi}_p = \overline{c}_p\overline{\chi},\ \Phi_q = c_q\chi, \text{ and } \overline{\Phi}_q = \overline{c}_q\overline{\chi}$$

By the use of the inverse of the overlap matrices $s_{p,q}$ and $\overline{s}_{p,q}$, the bond order matrices are defined by

$$P_{p,q} = c_q s_{p,q}{}^{-1\dagger} c_p \text{ and } \overline{P}_{p,q} = \overline{c}_q \overline{s}_{p,q}{}^{-1\dagger} \overline{c}_p$$

Now it is easy to calculate the integral $H_{p,q}$ weighted by the normalizing factors due to the MO overlaps by means of the transformed bond orders, in a similar way as the computation of the total electronic energy in the SCF MO theory with orthonormal one-electron functions (H. Fujimoto and N. Kosugi, *Bull. Chem. Soc. Jpn.*, **50**, 2209 (1977)).

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$$c_\alpha{}^l = c_\beta{}^i \text{ and } c_\beta{}^l = -c_\alpha{}^i$$

Then, the changes in atomic densities and bond order are given by

$$\Delta q_\alpha = 2c_\alpha{}^i c_\beta{}^l,\ \Delta q_\beta = -\Delta q_\alpha$$

$$\Delta p_{\alpha\beta} = 2\{-(c_\alpha{}^l)^2 + (c_\beta{}^i)^2\}$$

From the normalization of the MO $\phi_i$, i.e., $(c_\alpha{}^i)^2 + (c_\beta{}^i)^2 = 1$, we immediately arrive at the conclusion

$$\left.\begin{array}{l} |\Delta q|\text{: maximum} \\ |\Delta p|\text{: minimum} \end{array}\right. \quad \text{when } c_\alpha{}^i = c_\beta{}^i$$

and

$$\begin{array}{lll} |\Delta q|\text{: minimum} & \text{when,} & c_\alpha{}^i = \pm 1 \text{ and } c_\beta{}^i = 0 \\ |\Delta p|\text{: maximum} & \text{or} & c_\alpha{}^l = 0 \text{ and } c_\beta{}^i = \pm 1 \end{array}$$

(41) In the case of the bimolecular nucleophilic substitution reaction mentioned above, we obtain $C_{i\to l}{}^2 \sim 0.040$ and $C_0C_{k\to l} \sim -0.057$ where the MO's *i*, *k*, and *l* correspond to the $2p_x$ of fluoride ion and $5a_1$ and $6a_1$ MO's of methyl fluoride, respectively. A similar relation also holds in the nonpolar reaction between methylene and hydrogen.

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# Gaseous Ions. 4. MINDO/3 Calculations for Some Simple Organic Cations and for Their Hydrogen Elimination Reactions

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**Abstract:** The structures and relative energies of $CH_4{}^{+\cdot}$, $C_2H_6{}^{+\cdot}$, and the classical and nonclassical forms of the ethyl and vinyl cations are reported. The results are in agreement with recent ab initio calculations in predicting a structure of $C_{2v}$ symmetry for $CH_4{}^{+\cdot}$ and bridging structures for the ethyl and vinyl carbonium ions. The calculated activation energies for the elimination of hydrogen from these and other small cations agree with experimental estimates. The structures of the transition states for the formally forbidden 1,2-eliminations were found to be concerted but not synchronous, and to differ significantly from the transition state for the allowed 1,1-elimination of hydrogen from $C_2H_5{}^+$. The calculated frequencies of the imaginary modes for the transition states appear to be related to the observed energy distribution in the products.

Previous papers[1-3] of this series have reported a detailed MINDO/3[4] study of the $C_7H_7{}^+$ and $C_7H_8{}^+$ systems, and of the effects of various substituents on the interconversion of benzyl cation and tropylium. The results were in satisfactory agreement with the very detailed experimental evidence currently available for these systems, suggesting that MINDO/3 should prove generally useful for investigating the properties of organic ions in the gas phase. Studies[5,6] of various simple organic cations, both "classical" and "nonclassical", have, moreover, given satisfactory results, comparable with those from the rather detailed ab initio calculations of Pople et al.[7] Here we report MINDO/3 studies of two of the simplest organic cations, $CH_4{}^+$ and $C_2H_6{}^+$, and of a number of reactions involving a formal 1,2-elimination of hydrogen ($H_2$) from various cations. The heats of formation of $CH_4{}^+$ and $C_2H_6{}^+$ have, of course, been determined very precisely by photoelec-