

Orbital Interaction and Chemical Bonds. The Role of Antisymmetric Orbitals in Cyclic Additions

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Abstract: A partitioning analysis of the electron density of chemically interacting systems clarifies the roles of the localization, Coulombic, exchange, delocalization, and polarization interactions in creating the intermolecular chemical bonds between the reaction sites of reactants and in weakening the bonds between the reaction sites and the adjacent atoms along a reaction path. Several conditions necessary to make easy the mutual approach of reaction sites of reactants are derived and applied to some symmetry-allowed and symmetry-forbidden processes. A significant difference between the consequence of the orbital interaction of two antisymmetric MO's and that of two symmetric MO's is suggested in regard to the formation of chemical bonds in concerted cyclic additions. The effects of orbital mixing and rehybridization are also discussed.

The concept of the orbital interaction provides us with a simple but a reliable way of discussing mechanisms of chemical reactions.¹⁻⁸ The origins of the orientation and stereoselection in a variety of chemical reactions have been elucidated by studying the orbital interaction between reagent and reactant in terms of a convenient quantum mechanical method, molecular orbitals (MO). The magnitude of the electron densities at the reaction sites in the reactant MO's, particularly in the highest occupied (HO) MO of donor and in the lowest unoccupied (LU) MO of acceptor, and the symmetries of these frontier MO's have been shown to possess a prominent significance in determining the extent of the stabilization of interacting systems.¹ The energy of an interacting system thus obtained, however, does not necessarily give us detailed information about the local properties of the interaction, unless we carry out an adequate breakdown of the energy.^{9,10} Chemical bonds are apparently local in nature.¹¹ Specificity of chemical reactions is really defined by chemical bonds being formed and being broken between the reaction sites in the course of chemical reactions. The distinction between single-centric additions and multi-centric additions (cycloaddition) can be made by comparing the number of new bonds that appear and the number of old bonds that disappear on going from the reactant to the product.¹²

Here it may be worthy of carrying out an analysis of chemical bonds to study the origin of intermolecular bond formation and the associated reorganization of the electron distribution in molecular interactions. In this paper, we will develop a general view on this problem utilizing the concept of the orbital interaction. Then, our analysis will be applied to some cyclic interactions in a qualitative manner to see the consequences of the orbital interaction between two symmetric MO's and that between two antisymmetric MO's in connection with the formation of chemical bonds in these processes.

Orbital Interaction

Let us consider a chemical interaction between two closed shell systems, say A and B. For simplicity, the wave function of the interacting system, A-B, is first approximated by a linear combination of two electronic configurations,¹

$$\Psi = C_0\Psi_0 + C_{i \rightarrow l}\Psi_{i \rightarrow l} \quad (1)$$

where Ψ_0 is the original configuration in which A and B interact with each other retaining their electron configurations in an isolated state and $\Psi_{i \rightarrow l}$ stands for the transfer of an electron from the occupied MO ϕ_i of the donor, say A, to the unoccupied MO ψ_l of the acceptor B. Since the wave function is normalized under the condition that

$$1 = C_0^2 + 2C_0C_{i \rightarrow l}S_{0,i \rightarrow l} + C_{i \rightarrow l}^2 \quad (2)$$

the electron density of the system is given by

$$\rho(1) = \rho_{0,0}(1) + 2C_0C_{i \rightarrow l}(\rho_{0,i \rightarrow l}(1) - S_{0,i \rightarrow l}\rho_{0,0}(1)) + C_{i \rightarrow l}^2(\rho_{i \rightarrow l,i \rightarrow l}(1) - \rho_{0,0}(1)) \quad (3)$$

where

$$\rho_{p,q}(1) = M \int \Psi_p^*(1,2, \dots, M)\Psi_q(1,2, \dots, M) \times d\xi_1 d\tau_2 \dots d\tau_M \\ S_{p,q} = 1/M \int \rho_{p,q}(1) dv(1)$$

The integration in the definition of $\rho_{p,q}(1)$ is carried out over the spin coordinate of electron 1 and over the spin and space coordinates of electrons 2 to M (M signifies the total number of electrons of the system). The wave functions are represented by the Slater determinants, as usual. Then, we have

$$\rho(1) \cong \rho_{0,0}(1) + 2\sqrt{2}C_0C_{i \rightarrow l}(\phi_i(1)\psi_l(1) - s_{il}\phi_i(1)^2) + C_{i \rightarrow l}^2(\psi_l(1)^2 - \phi_i(1)^2) \quad (4)$$

where

$$s_{il} = \int \phi_i(1)\psi_l(1) dv(1)$$

The MO's ϕ_i and ψ_l are given by the linear combinations of the basis atomic orbitals (AO) χ :

$$\phi_i(1) = \sum_r^A c_r^i \chi_r(1) \text{ and } \psi_l(1) = \sum_t^B c_t^l \chi_t(1)$$

The first term on the right-hand side of eq 4 is partitioned into three density terms,

$$\rho_{0,0}(1) = \rho_A(1) + \rho_B(1) + \rho_K(1) \quad (5)$$

where ρ_A and ρ_B are the electron densities of isolated reactants A and B, and ρ_K is defined as the exchange density. They are given by

$$\rho_A(1) = 2 \sum_i^{\text{occ}} \phi_i(1)^2 = 2 \sum_i^{\text{occ}} \sum_r^A \sum_s^A c_r^i c_s^i \chi_r(1)\chi_s(1)$$

$$\rho_B(1) = 2 \sum_k^{\text{occ}} \psi_k(1)^2 = 2 \sum_k^{\text{occ}} \sum_t^B \sum_u^B c_t^k c_u^k \chi_t(1)\chi_u(1)$$

and

$$\rho_K(1) \cong 2 \sum_i^{\text{occ}} \left\{ \sum_k^{\text{occ}} (s_{ik}\phi_i(1)^2 - \phi_i(1)\psi_k(1))s_{ik} \right\} + 2 \sum_k^{\text{occ}} \left\{ \sum_i^{\text{occ}} (s_{ik}\psi_k(1)^2 - \psi_k(1)\phi_i(1))s_{ik} \right\} \quad (6)$$

It is seen that the exchange interaction between two closed shells causes a change in the electron distribution, introducing a negative electron density between reactants. The amount of

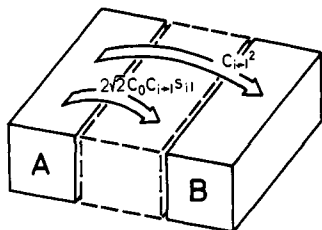


Figure 1. A schematic representation of the electron delocalization associated with electron transfer from A to B.

electrons expelled by the repulsion from the intermolecular region sums up to $\sim 4\sum_i \sum_k S_{ik}^2$, one-half of which is accommodated in A and the other half in B. The exchange density, as well as the second and the third terms in eq 3, vanish upon integration over all space, because they represent the redistribution of electrons of isolated reactants to promote or suppress the occurrence of chemical reactions, depending on the systems.

Chemical Bonds

The second and the third terms on the right-hand side of eq 4 stand for the distortion of the electron density distribution due to the delocalization interaction (D), appearing through the mixing of the electron-transferred configuration into the wave-function of the interacting system. It should be noted here that the donor MO ϕ_i loses electrons in two apparently distinctive ways as illustrated in Figure 1. Electrons of the magnitude of $C_{i \rightarrow l}^2$ are directly transferred from the MO ϕ_i of A to the MO ψ_l of B. In addition, the MO ϕ_i donates electrons into the intermolecular region between A and B through the overlapping between ϕ_i and ψ_l . The amount of electrons moving around the intermolecular region is approximately $2\sqrt{2}C_0C_{i \rightarrow l}S_{il}$. Namely, a fraction of electrons released from the donor MO is used to construct intermolecular chemical bonds.

Here we adopt a basic assumption that *both of the reactants should change their nuclear configurations in such a way as to make the principal interaction between the reaction sites stronger in chemical reactions*, as is schematically shown in Figure 2.¹³ A small displacement of a reaction site of A, say α , in the direction to the reaction sites of B is denoted by $\Delta\mathbf{x}_\alpha$, and that of a reaction site of B, say β , toward the reaction sites of A is denoted by $\Delta\mathbf{x}_\beta$. Then, the energy change of the system may be given by

$$\Delta W = \sum_{\gamma} (\partial W(\bar{x})/\partial \mathbf{x}_{\gamma}) \Delta \mathbf{x}_{\gamma} \quad (7)$$

where \bar{x} indicates the nuclear coordinates of the system collectively. Applying the Hellmann–Feynman theorem to the present problem, the energy derivative with respect to a coordinate \mathbf{x}_{γ} is given by¹⁴

$$\partial W(\bar{x})/\partial \mathbf{x}_{\gamma} = \int \rho(1)(\partial V(1)/\partial \mathbf{x}_{\gamma}) dv(1) + \sum_{\lambda \neq \gamma} \partial V_{\gamma\lambda}/\partial \mathbf{x}_{\gamma} \quad (8)$$

where $V(1)$ is the nucleus–electron attractive potential and $V_{\gamma\lambda}$ is the nucleus–nucleus repulsive potential in the Hamiltonian operator of the interacting system. The negative of the energy gradient gives the force imposed on the nucleus in the molecular potential field. Chemical reactivity and reaction path are obviously controlled by the forces, because they govern the motions of the nuclei in the interaction.^{15,16} We assume here that every atom has only one AO participating in the interaction. This is the case when we discuss the chemical reactivities of conjugated systems on the basis of the π -electron

approximation. The important role of σ – π mixing will be discussed later.

From the delocalization interaction, we have two components of the energy gradient with respect to the displacement of the nucleus α ,

$$(\partial W(\bar{x})/\partial \mathbf{x}_{\alpha})_D \cong 2\sqrt{2}C_0C_{i \rightarrow l}(-\mathbf{F}_{\alpha})_{0,i \rightarrow l} + C_{i \rightarrow l}^2(-\mathbf{F}_{\alpha})_{i \rightarrow l,i \rightarrow l} \quad (9)$$

By the use of the Mulliken approximation¹⁷ and the point-charge approximation employed in one of our previous papers,^{1k} we obtain

$$(-\mathbf{F}_{\alpha})_{0,i \rightarrow l} \cong \sum_l^B c_r^i c_l^l s_{rl} (r|\partial V/\partial \mathbf{x}_{\alpha}|l)/s_{rl} - s_{il} \sum_{s \neq r}^A p_{rs}^{(i)} s_{rs} \{2(r|\partial V/\partial \mathbf{x}_{\alpha}|s)/s_{rs} - (s|\partial V/\partial \mathbf{x}_{\alpha}|s)\} + \sum_{\alpha' \neq \alpha}^A n_{\alpha'}^{(i)} Z_{\alpha} s_{il} \mathbf{R}_{\alpha\alpha'}/R_{\alpha\alpha'}^3 \quad (10)$$

$$(-\mathbf{F}_{\alpha})_{i \rightarrow l,i \rightarrow l} \cong -\sum_{\beta}^B Z_{\alpha} n_{\beta}^{(l)} \mathbf{R}_{\alpha\beta}/R_{\alpha\beta}^3 - \sum_{s \neq r}^A p_{rs}^{(i)} s_{rs} \times \{2(r|\partial V/\partial \mathbf{x}_{\alpha}|s)/s_{rs} - (s|\partial V/\partial \mathbf{x}_{\alpha}|s)\} + \sum_{\alpha' \neq \alpha}^A n_{\alpha'}^{(i)} Z_{\alpha} \mathbf{R}_{\alpha\alpha'}/R_{\alpha\alpha'}^3 \quad (11)$$

in which

$$(s|\partial V/\partial \mathbf{x}_{\alpha}|t) = \int \chi_s(1)\partial V(1)/\partial \mathbf{x}_{\alpha}\chi_t(1) dv(1) \\ s_{rs} = \int \chi_r(1)\chi_s(1) dv(1) \\ n_{\gamma}^{(i)} = \sum_s^{\gamma} \sum_{s'}^{\text{all}} c_s^i c_{s'}^i s_{ss'}, \quad p_{rs}^{(i)} = c_r^i c_s^i$$

and Z_{α} is the nuclear charge of α , $R_{\alpha\beta}$ is the internuclear distance, and the origin of the vector $\mathbf{R}_{\alpha\beta}$ is taken at the nucleus α . All the intermolecular three-center integrals were tentatively disregarded in eq 10.^{1k}

From these equations, we find out several conditions which are necessary to make easier the formation of intermolecular chemical bonds between the reaction sites. The first term on the right-hand side of eq 10 comes from the direct overlap of the MO's ϕ_i and ψ_l . The integral $(r|\partial V/\partial \mathbf{x}_{\alpha}|t)$ divided by the overlap integral s_{rl} between the AO χ_r of the reaction site α and the AO χ_l of the reaction site β has a definite sign, being negative for the displacement of the nucleus α toward the reaction sites of B (the overlap between the reaction sites is assumed to be not zero). Accordingly, the sign of the first term depends on the sign of the intermolecular partial overlap population between the sites, $\sim 2\sqrt{2}C_0C_{i \rightarrow l}c_r^i c_l^l s_{rl}$, which is created by the electron delocalization interaction between the MO's ϕ_i and ψ_l . In order to make the reaction favorable, the total energy gradient along a reaction path to reach the transition state should be as small as possible. It is required, therefore, that *the partial overlap population between the reaction site of A and that of B should be positive (bonding) and large*. Namely, the reaction site of donor should have a large amplitude in the electron-donating MO ϕ_i and that of acceptor should have a large amplitude in the electron-accepting MO ψ_l . The overlap integral s_{rl} controls the spatial direction of the mutual approach of reagent and reactant. The second and the third terms are ascribed to the donation of an electron from ϕ_i . The partial loss of electrons from the MO leads to a weakening of the binding force on the nucleus α from the remaining atoms of A. The value in the braces will be positive when the reaction site α gets released from other atoms. Since $C_0C_{i \rightarrow l}S_{il}$ is positive for the ground state of the interacting system, *the partial overlap populations, $p_{rs}^{(i)}s_{rs}$, between the AO χ_r of the reaction site α and the AO's χ_s of*

the remaining atoms of A should be positive and large in the donor MO ϕ_i . In other words, the reaction site α should be loosened efficiently from other atoms of A through the electron donation in order to be ready for the bond formation with the reaction sites of B. The third term indicates that the static attraction between the atom α and another atom, say α' , in A is reduced by the removal of an electron from ϕ_i to an extent proportional to the partial atomic population $n_{\alpha'}^{(i)}$ of the atom. Here the second term on the right-hand side of eq 10 may be regarded as indicating a change in the through-bond (orbital overlap) attraction or repulsion, while the third term may be interpreted as representing a change in the through-space attraction.

The first term on the right-hand side of eq 11 corresponds to the attraction onto the nucleus α from the portion of electrons donated from ϕ_i and accepted in ψ_l . Because the attraction energy increases as α approaches to β , the partial atomic population $n_{\beta}^{(l)}$ of the reaction site β of B should be large in the acceptor MO ψ_l to reduce the gradient. The second and the third terms of eq 11 possess the same meanings as the corresponding terms in eq 10.

In regard to the displacement of the nucleus β of B, we have

$$(\partial W(\bar{x})/\partial \mathbf{x}_{\beta})_D \cong 2\sqrt{2}C_0C_{i \rightarrow l}(-\mathbf{F}_{\beta})_{0,i \rightarrow l} + C_{i \rightarrow l}^2(-\mathbf{F}_{\beta})_{i \rightarrow l,i \rightarrow l} \quad (12)$$

where

$$(-\mathbf{F}_{\beta})_{0,i \rightarrow l} \cong \sum_r c_r^i c_l^l s_{rl} (r|\partial V/\partial \mathbf{x}_{\beta}|l)/s_{rl} + s_{il} \sum_{\alpha} Z_{\beta} n_{\alpha}^{(i)} \mathbf{R}_{\beta\alpha}/R_{\beta\alpha}^3 \quad (13)$$

$$(-\mathbf{F}_{\beta})_{i \rightarrow l,i \rightarrow l} \cong \sum_{l \neq u}^B p_{lu}^{(l)} s_{lu} \times \{2(t|\partial V/\partial \mathbf{x}_{\beta}|u)/s_{tu} - (u|\partial V/\partial \mathbf{x}_{\beta}|u)\} - \sum_{\beta' \neq \beta}^B Z_{\beta} n_{\beta'}^{(l)} \mathbf{R}_{\beta\beta'}/R_{\beta\beta'}^3 + \sum_{\alpha} Z_{\beta} n_{\alpha}^{(i)} \mathbf{R}_{\beta\alpha}/R_{\beta\alpha}^3 \quad (14)$$

Equation 13 gives the force due to the electron delocalization from the MO ϕ_i to the intermolecular region. In order that the donated portion of electrons is utilized effectively for the intermolecular bond formation, the first term on the right-hand side of eq 13 should be strongly attractive. This again leads to the same condition as the one derived from eq 10 that the partial overlap population between the reaction sites of A and B produced by the orbital interaction of ϕ_i with ψ_l should be large and positive, because the potential gradient integral divided by the overlap integral s_{rl} is negative for the displacement of the nucleus β toward A. The second term in eq 13 implies a decrease in the static attraction on β from A by losing a fraction of electrons from ϕ_i . The first term obviously exceeds the second one in the intermolecular bond formation.

The first term on the right-hand side of eq 14 stands for a change in the attraction through the orbital overlap between the AO χ_l of the site β and the AO's χ_u of the remaining atoms of B due to the acceptance of an electron in the unoccupied level ψ_l . The sum of the integrals in the braces is positive for such a motion of the reaction site β as is depicted in Figure 2. Accordingly, we obtain here an additional condition to reduce the potential gradient that the partial overlap population, $p_{lu}^{(l)} s_{lu}$, between the reaction site and other atoms should be large (in absolute value) and negative in ψ_l . This indicates that the reaction site should be freed from the remaining part of the molecule in the direction to the reaction sites of the other system by diminishing the intramolecular binding force on receiving electrons. From eq 11 and 14, the AO χ_l of the site β is requested to have a large valence-inactive population, $(c_l^l)^2$.

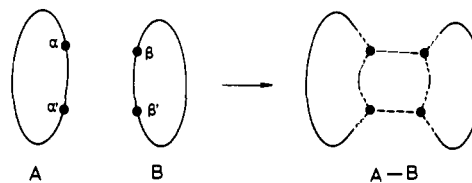


Figure 2. Deformation of reactants in chemical interaction between A and B accompanied by bond interchange. The reaction sites of one system approach the reaction sites of the other system and, at the same time, are freed from the adjacent atoms in the same system.

and, at the same time, strongly antibonding valence-active populations, $p_{lu}^{(l)} s_{lu}$, with the AO's of other atoms in the acceptor MO ψ_l .^{18,19} The second and the third terms in eq 14 represent the increase in the electrostatic binding force from the atoms of B and the decrease in that from the atoms of A caused by the shift of an electron from ϕ_i to ψ_l .

The density $\rho_{0,0}$ gives three components of the energy gradient, the Coulomb (Q), the localization (L), and the exchange (K) interactions, with respect to the displacement of the nucleus α ,²⁰

$$(\partial W(x)/\partial \mathbf{x}_{\alpha})_{0,0} = (-\mathbf{F}_{\alpha})_Q + (-\mathbf{F}_{\alpha})_L + (-\mathbf{F}_{\alpha})_K \quad (15)$$

where

$$(-\mathbf{F}_{\alpha})_Q = \int \rho_B(1)(\partial V(1)/\partial \mathbf{x}_{\alpha}) d\nu(1) + \sum_{\beta}^B \partial V_{\alpha\beta}/\partial \mathbf{x}_{\alpha} \cong -Z_{\alpha} \sum_{\beta}^B (N_{\beta} - Z_{\beta}) \mathbf{R}_{\alpha\beta}/R_{\alpha\beta}^3 \quad (16)$$

$$(-\mathbf{F}_{\alpha})_L = \int \rho_A(1)(\partial V(1)/\partial \mathbf{x}_{\alpha}) d\nu(1) + \sum_{\alpha' \neq \alpha}^A \partial V_{\alpha\alpha'}/\partial \mathbf{x}_{\alpha} \cong \sum_{s \neq r} p_{rs} s_{rs} \{2(r|\partial V/\partial \mathbf{x}_{\alpha}|s)/s_{rs} - (s|\partial V/\partial \mathbf{x}_{\alpha}|s)\} - Z_{\alpha} \sum_{\alpha' \neq \alpha}^A (N_{\alpha'} - Z_{\alpha'}) \mathbf{R}_{\alpha\alpha'}/R_{\alpha\alpha'}^3 \quad (17)$$

and

$$(-\mathbf{F}_{\alpha})_K = \int \rho_K(1)(\partial V(1)/\partial \mathbf{x}_{\alpha}) d\nu(1) \quad (18)$$

The atomic population N_{α} and the bond order p_{rs} are defined by

$$N_{\alpha} = 2 \sum_i^{\text{occ}} n_{\alpha}^{(i)}, \quad p_{rs} = 2 \sum_i^{\text{occ}} p_{rs}^{(i)}$$

The force vector $(\mathbf{F}_{\alpha})_Q$ is the sum of the nucleus–electron attractions and the nucleus–nucleus repulsions onto the atom α , arising from B. By the use of the point-charge approximation,^{1k} it is reduced to an electrostatic attraction between the nucleus α and the net charges of the atoms in B.

On the other hand, $(\mathbf{F}_{\alpha})_L$ gives the force element originating inside of A which may prevent the displacement of the nucleus α , accompanied by a destabilization.²¹ Other atoms in A exert two kinds of binding forces on the nucleus α . Of these, the dominant term in neutral species is the first term arising from the chemical bonds through orbital overlap. Accordingly, in order to make easier the displacement of the nucleus α toward the reaction sites of B, the sum of the atomic orbital bond populations, $p_{rs} s_{rs}$, with the adjacent atoms should be smaller in an isolated state. Here we recall the reactivity index “free valence” which claims a larger reactivity of a position possessing a smaller sum of the bond orders with the adjacent atoms in a conjugated system.²² The localization approach, on the other hand, proposes that the destabilization caused by a hypothetical isolation of a reaction site from the remaining part of a molecule governs the chemical reactivity.²³ These approaches to chemical reactivity theory are evidently covered

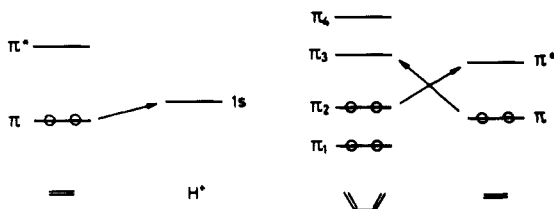


Figure 3. Orbital interaction in the Diels–Alder reaction of butadiene and ethylene and in protonated ethylene.

by the present analysis. A comparison of the condition that the reaction site should have strong bonding property with the adjacent atoms in the electron-donating MO ϕ_i as mentioned above with the one derived here from $(F_{\alpha})_L$ suggests that the reaction site should be linked to the remaining atoms of the molecule mainly in high-lying occupied MO's, because they have stronger capabilities of electron donation than lower ones. This, together with the condition that a reaction site should have a large amplitude in the relevant MO's, makes the internal double bonds of conjugated chains less reactive than the terminal ones. The localization of the reaction site from the remaining part of the molecule obviously needs a certain amount of energy and, hence, will be an important origin of the activation energy. It should be noted here, however, that the isolation of reaction sites generally leads to an elevation of the key MO in the donor and to a lowering of the key MO in the acceptor, accompanied by the increase in the partial electron density at the sites in these MO's.²⁴ Consequently, the localization of active sites is supposed to be inevitable in order to accelerate the formation of intermolecular chemical bonds through the enhancement of the delocalization interaction.

The force components $(F_{\alpha})_Q$ and $(F_{\alpha})_L$ contain respectively the intermolecular and intramolecular electrostatic attractions between the nucleus of the reaction site and the net charges of other atoms, involving the reaction site of the other system. Accordingly, the attempt to interpret the chemical reactivity of organic molecules by means of the electrostatic energy is apparently included in the present study.²⁵ The electrostatic interaction will be significant in the reactions of polar species in general.^{1k,3}

The exchange interaction may have an opposite effect to the delocalization interaction, causing a decrease of the electron density in the intermolecular region.²⁶ Therefore, the interaction provides the largest repulsive force for the chemical interactions between two nonpolar closed shell systems. As shown in eq 6, it depends on the overlap integrals between the occupied MO's of reactants and makes unfavorable the approach of them in such a way as to produce a strong interference among the occupied MO's, possessing large amplitudes at the interaction centers. The least-motion approaches of symmetry-forbidden reactions are unlikely, in general, because of the strong exchange repulsion between the HOMO's of reactants.²⁷ The stabilization through the delocalization interaction in the early stage, followed by a pseudoexcitation²⁸ and/or by a molecular promotion,²⁹ makes the reactions take place preferentially along non-least-motion reaction paths.

Cyclic Additions and Antisymmetric Orbitals

The discussion presented above is completely general and may be applicable to any kind of molecular interactions between two closed shells. Modification of the analysis to fit for photochemical reactions and homolytic reactions is straightforward. In the following, the orbital interactions in some cyclic additions will be examined by the use of the frontier orbital method at first, because the validity of the approximation has been demonstrated in classifying cyclic additions into two fundamental classes, i.e., "symmetry allowed" and "symmetry

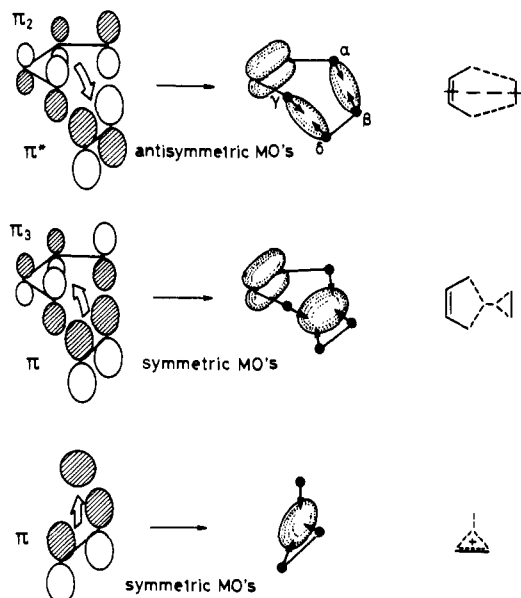


Figure 4. A sketch of orbital overlap interaction and resulting electron reorganization. Arrows on the black spots indicate qualitatively the forces exerted on nuclei from the overlap density.

forbidden".^{1,2,5} It is evident that the employment of the approximation is not essential to our analysis of chemical bonds given above. The present procedure can be extended easily to multi-configuration systems. Significance of other MO's than the frontier MO's will be studied later.

Let us first compare the Diels–Alder addition of ethylene to butadiene with the protonation of ethylene.³⁰ The major orbital interactions are schematically illustrated in Figure 3. The static interaction cannot play a dominant role in both of the cases because at least one of the reactants is nonpolar. The exchange interaction is not important in protonated ethylene, one of the systems, proton, having no electron to exchange in the original electron configuration. The interaction may also be of a minor importance in the Diels–Alder reaction since the π MO of ethylene can exchange electrons only with the π_1 MO of butadiene. The π_2 MO, having large amplitudes at the reaction sites, does not overlap with the π MO of ethylene and, therefore, the addition may not be hindered strongly by the exchange repulsion. The 1 and 4 positions of butadiene obviously satisfy the conditions for the reaction sites deduced above, both possessing the largest partial density either in the HOMO or the LUMO and being strongly bonding in the HOMO and antibonding in the LUMO with the adjacent atoms. The carbon atoms of ethylene are mutually bonding in the HOMO and antibonding in the LUMO in agreement with the propositions given above.

The dominant electron delocalization interaction in protonated ethylene is the one between the π MO of ethylene and the $1s$ AO of proton. Both of these orbitals are symmetric with respect to the reflection on the bisecting plane, and the associated change in the electron distribution will be as is illustrated in Figure 4. Proton is bonded to both of the carbons of ethylene. In the case of the Diels–Alder reaction of butadiene and ethylene, we have two major electron donating–accepting interactions, one being between the π MO of ethylene and the π_3 MO of butadiene and the other being between the π_2 MO of butadiene and the π^* MO of ethylene. As shown in Figure 4, the former leads to an accumulation of the electron density in the central part of the intermolecular region as is the case of protonation to ethylene, because the relevant MO's are symmetric with respect to the symmetry plane. Namely, the orbital interaction between the two symmetric MO's brings positive

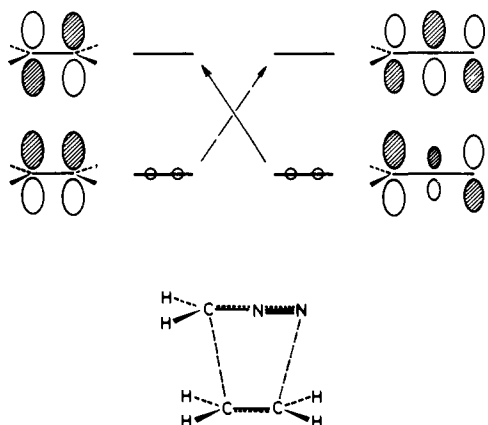


Figure 5. Orbital interaction in the 1,3-dipolar cycloaddition of diazomethane and ethylene.

overlap population both for the bonded pair of atoms, say α and β , and for the nonbonded pair of atoms, say α and δ . On the other hand, the latter orbital interaction excludes the intermolecular valence-active electron density from the central part of the intermolecular region and makes electrons stay more in the regions between the reaction sites of ethylene and those of butadiene where new chemical bonds should appear. This characteristic rearrangement of the electron distribution is obviously due to the antisymmetric properties of the MO's, giving negative overlap populations between the carbons α and δ and between the carbons β and γ . In order to have the fixed framework of cyclohexene, one of the terminal carbons of butadiene α must be linked to one of the carbon atoms of ethylene β , and the other terminal carbon of butadiene γ must be tied to the other carbon of ethylene δ . In other words, the carbon α must have a strong attraction only from the carbon β and the interaction between the carbon α and the carbon δ should be antibonding (nonbonding) or slightly bonding. Similarly, the carbon γ should have a strongly attractive force solely from the carbon δ . The orbital interaction between the antisymmetric MO's eliminates the bonding property from the nonbonded pairs of atoms.

It is now clear that the interactions of two antisymmetric MO's of conjugated systems are of primary importance in making possible the concerted formation of two bonds in cyclic additions. This conclusion seems to interpret the well-established experimental findings that the electron-releasing groups on diene and the electron-withdrawing groups on dienophile accelerate the occurrence of the Diels–Alder reactions.³¹ A dominant interaction between two symmetric MO's presumably stands for a complex formation in the course of cyclic additions.

Equation 3 indicates that the electron density responsible for the intermolecular bond formation is supplied from the donor orbital. Accordingly, donor loses its electrons more rapidly than acceptor receives. The donation of electrons from the occupied MO's and the acceptance of electrons into the unoccupied MO's cause a deformation of the molecule.^{11,32} For an instance, the removal of an electron from the π MO and the addition of an electron to the π^* MO of ethylene completely destroys the π bond of the molecule. In the case of butadiene, donation of an electron from the π_2 MO and acceptance of an electron into the π_3 MO weaken the 1,2 and 3,4 π bonds and strengthen the 2,3 π bond, but the original double bonds still retain π characters. This leads to a supposition that the larger conjugated chain should play the part of electron donor in order to bring about harmonious displacements of nuclei in both reactants along a reaction path. The postulate provides us with an additional possible reasoning why the delocalization in-

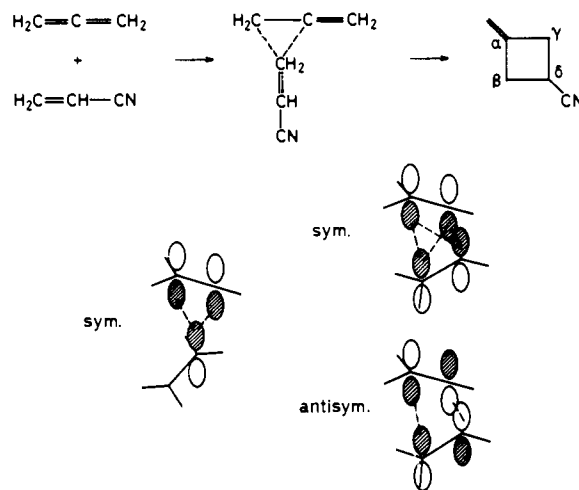


Figure 6. Orbital interaction in the addition of allene to acrylonitrile along a non-least-motion path.

teraction between the HOMO of diene and the LUMO of dienophile should be dominant.

Our recent calculation on the 1,3-dipolar cycloaddition of diazomethane to ethylene showed clearly that the electron donation from the HOMO of the 1,3-dipole to the LUMO of the dipolarophile should play a key role in the reaction models for concerted addition,³³ as shown in Figure 5. These MO's are classified as antisymmetric in an approximate sense, though specific symmetry cannot be assigned to characterize the interaction. The electron delocalization from the HOMO of the dipolarophile to the LUMO of the 1,3-dipole is weak in this particular example because of the nodal property of the LUMO of diazomethane. The calculation also suggested a greater influence of the exchange interaction than the Coulombic interaction on the selection of the reaction path.

The examples mentioned above, i.e., the Diels–Alder reaction, protonation to a double bond, and 1,3-dipolar cycloaddition, belong to a class of cyclic interactions which is considered to be “symmetry allowed” in the Woodward–Hoffmann sense.⁵ Next, we may refer to an example of another class of cyclic additions, i.e., “symmetry-forbidden” processes.⁵ We proposed previously that symmetry-forbidden [$2_s + 2_s$] cyclic additions of a good donor to a good acceptor should be initiated by a three-centered interaction between the two p AO's of donor and one of the p AO's of acceptor, followed by a rotation of the acceptor to give the final product.³⁴ Thus, we could explain the stereoselectivity observed in experiments. Figure 6 shows a sketch of the orbital interactions pertinent to a reaction course of the addition of allene to acrylonitrile. The first stage of the reaction is characterized by the orbital interaction between two locally symmetric MO's, just like that of a π complex. In the second stage of forming a cyclobutane, the interaction between the LUMO's of the addends comes to play a role, as well as the interaction between the HOMO's. Such an introduction of important LUMO–LUMO interaction and HOMO–HOMO interaction was supported by a numerical calculation and was reasoned as an outcome of pseudoexcitation in one of our recent papers.²⁸

The interaction between the LUMO's of the donor and acceptor olefins brings about negative partial overlap populations between the nonbonded pairs of atoms, i.e., between the carbons α and δ , and between the carbons β and γ , owing to the nodal properties of the MO's. The cooperation of the orbital interaction between antisymmetric MO's with that between symmetric MO's is found again to play a crucial role in generating the two apparently separated chemical bonds of the cyclic addition product. Our calculation to simulate the second

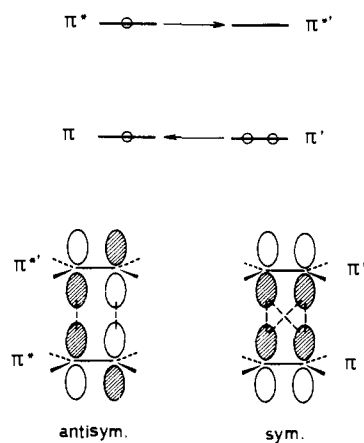


Figure 7. Orbital interaction in a cyclic addition of olefins in the first singlet excited state.

stage of the cyclic addition showed a greater contribution of the LUMO–LUMO interaction than the HOMO–HOMO interaction to the overlap populations representing the appearance of the bonds in a certain region of the path.²⁸ Prohibition of bonding interaction between two antisymmetric MO's and that between two symmetric MO's, at the initial stage, forces the reaction to take place probably as a two-stage process.

If one of the reactants is promoted to the lowest singlet excited state in a $[2_s + 2_s]$ cyclic addition of olefins, the reaction will be not only allowed but also possibly concerted as shown in Figure 7. A necessary condition to endow the reaction with a fully concerted nature seems to be that the energy gap between the π^* MO (the higher lying singly occupied MO) of the excited part and the LUMO $\pi^{*'}$ of the counterpart should not be large in comparison with that between the π MO (the lower lying singly occupied MO) and the HOMO π' .

Recently, Sustmann discussed the Diels–Alder reactions in which the electron transfer from the HOMO of dienophile to the LUMO of diene is stronger than the electron transfer from the HOMO of diene to the LUMO of dienophile.³⁵ The donor–acceptor relationship in 1,3-dipolar cycloadditions was also beautifully connected with the observed regioselectivity by Sustmann³⁶ and Houk.³⁷ They suggested that the interaction between the HOMO of dipolarophile and the LUMO of 1,3-dipole would be most important in some 1,3-dipolar cycloadditions. With the electron-transferred configuration participating in the electronic structure of the interacting system, the unoccupied MO of A and the occupied MO of B will be modified by the electron rearrangement through the principal electron delocalization from A to B. Here we have

$$-\Delta I_{Bk} \cong C_{i \rightarrow l}^2 \{(kk|ll) - (kk|ii)\} + 2\sqrt{2}C_0 C_{i \rightarrow l} \{(kk|il) - s_{il}(kk|ii)\} > 0 \quad (19)$$

$$-\Delta E_{Aj} \cong C_{i \rightarrow l}^2 \{(jj|ll) - (jj|ii)\} + 2\sqrt{2}C_0 C_{i \rightarrow l} \{(jj|il) - s_{ij}(jj|ii)\} < 0 \quad (20)$$

where ΔI_{Bk} is the change in the ionization potential of the occupied MO ψ_k of B, ΔE_{Aj} is the change in the electron affinity of A with respect to the unoccupied MO ϕ_j , and $(ij|kl)$ implies an electron repulsion integral

$$(ij|kl) = \int \int \phi_i(1)\psi_k(2)(1/r_{12})\phi_j(1)\psi_l(2) dv(1) dv(2)$$

Equations 19 and 20 indicate that the ionization potential of the MO ψ_k of acceptor B is reduced and the electron affinity of the MO ϕ_j of donor A is enhanced in case of the electron delocalization from A to B. Consequently, the preceding electron transfer from donor to acceptor will facilitate the reverse electron transfer from acceptor to donor. Antisymmetric MO's

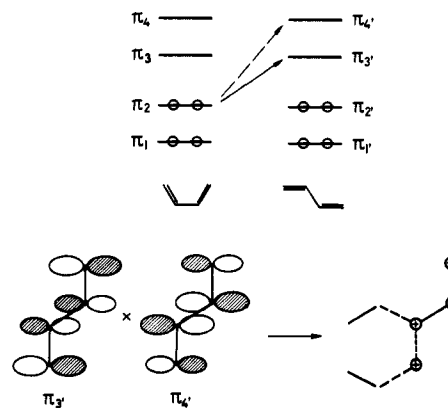


Figure 8. Orbital mixing in the dienophile of butadiene dimerization. The signs + and – in circles imply increase and decrease in the atomic populations, respectively.

presumably take their part even in the cyclic additions in which the orbital interaction between symmetric MO's looks by far most important at first sight.

Orbital Mixing and Polarization

In a number of the Diels–Alder reactions, dienophile is not a simple olefin but has substituent groups in conjugation with the double bond.³⁸ Here we may mention briefly the important role of orbital mixing, contributing in part to the electron reorganization and to the changes in the nuclear configuration of reactants.³⁹ It seems to be rather accidental to have the case in which the electronic structure of the interacting system can be described sufficiently by only two-electron configurations as eq 1. Locally excited configurations and various electron-transferred configurations participate in the ground-state wave function, in addition to the original and the principal electron-transferred configurations.^{1,40}

In the case of the Diels–Alder type dimerization of butadiene, we may have:

$$\Psi = C_0\Psi_0 + C_1\Psi(\pi_2 \rightarrow \pi_3') + C_2\Psi(\pi_2 \rightarrow \pi_4') + C_3\Psi(\pi_2 \rightarrow \pi_3) + C_4\Psi(\pi_1 \rightarrow \pi_3) + C_5\Psi(\pi_1 \rightarrow \pi_3) + C_6\Psi(\pi_2 \rightarrow \pi_4) + \dots \quad (21)$$

The mixing of the π_4' MO into the π_3' MO in the dienophile part through the orbital overlap interactions with the π_2 MO of the diene part makes the 1,2 π bond weaker and the 3,4 π bond stronger, with a migration of electrons from the non-reactive double bond to the reaction sites, as shown in Figure 8. The intermixing of unoccupied MO's does not have any physical meaning until electrons are transferred from the occupied MO's of the other system. Henceforth, this kind of orbital transformation may be called "orbital mixing through delocalization".⁴¹ Similarly, two occupied MO's of dienophile, π_1' and π_2' , may mix with each other through the delocalization interaction with the unoccupied MO's of the diene part. On the other hand, introduction of the locally excited configuration of diene in which an electron is promoted from π_1 to π_3 will weaken the 1,2 and 3,4 π bonds and strengthen the 2,3 π bond, since the π_3 MO overlaps in-phase and the π_1 MO out-of-phase with the HOMO of dienophile in the composite system. The promotion of an electron from the π_2 MO to the π_4 MO induced by the interaction leads to the same bond interchange of diene as the π_1 – π_3 orbital mixing. We may term such an orbital participation as "orbital mixing through polarization", because occupied MO's take in unoccupied MO's under the influence of the other system.⁴²

In the discussion given above, we took only one AO on each atom which is relevant in chemical interactions with other

systems. This is obviously an oversimplified approximation. Every reaction site has more than one AO, in general, to be responsible for the formation and weakening of chemical bonds in reactions. Of these, the role of s AO's must be emphasized in relation to the rehybridization at the reaction centers. Our calculation on some three-membered ring systems⁴³ has shown that the mixing of the π^* MO into an occupied σ MO (b_{3u}) of an ethylenic fragment brings about a redistribution of electrons in such a manner as to make the carbon-hydrogen bonds of the fragment bend in the direction away from the attacking reagent. The mode of the orbital mixing and the associated rehybridization are illustrated in Figure 9, in regard to the Diels-Alder reaction of ethylene and butadiene. This is a kind of orbital mixing through polarization. The bending of the carbon-hydrogen bonds at the reaction centers leads to the breakage of the σ - π separability⁴⁴ and, consequently, the 2s AO of a carbon comes to participate in the frontier MO's so as to make

$$c_{2s}^f c_{2p}^f (2s | \partial V / \partial x_\beta | 2p) < 0 \quad (22)$$

at the reaction site β which will contribute to a reduction of the potential gradient, in addition to the terms in eq 14. A similar relation may hold in regard to the reaction sites of diene. This σ - π orbital mixing may accelerate further rehybridization at the reaction centers and may facilitate the intermolecular bond formation.⁴⁵

Finally, we may refer to the structure of the transition state of the Diels-Alder reactions. We discussed the role of antisymmetric MO's in the preceding section on the assumption that the addition would take place in a quasicconcerted fashion, though the transition state need not be symmetric in a strict sense.⁴⁶ When the delocalization interaction is not effective and the exchange repulsion is large in a cyclic addition, the reaction will take place via a biradicaloid transition state. The exchange repulsion, however, is supposed to be not so large in the cyclic addition of butadiene to ethylene as to make the reacting system step out of the symmetric interaction, because the HOMO of diene does not overlap with the HOMO of dienophile. Meanwhile, the MINDO/3 calculation by Dewar and his co-workers suggested that the Diels-Alder reaction between butadiene and ethylene would be a two-stage process.⁴⁷ We find something arbitrary in the calculation in regard to the choice of the origins of measuring the intermolecular separation.⁴⁸ It should be noted that we took butadiene and ethylene in this study only as a prototype of the Diels-Alder reactions to investigate the basic nature of the cyclic additions. The mechanism of the reaction is likely to be influenced seriously by the property of substituents.

It has been shown above that the orbitals must possess certain properties to be able to play the leading part in molecular interactions. Examination of various chemical interactions has shown that the frontier MO's meet the demands, in most cases.⁴⁹ Recently, Houk noticed the applicability of the frontier orbital theory, reserving a possibility of refinement through inclusion of extrafrontier interactions and steric and Coulombic effects.⁵⁰ The significance of the Coulombic interaction was suggested also by Klopman.³ The present analysis of chemical bond formation in reactions involves the effect, though the electrostatic interaction does not seem to be important in the examples treated here. The discussion on orbital mixing and rehybridization as well as our previous studies on the related subjects^{39,41,43} suggest that the extrafrontier orbitals can contribute to chemical interactions primarily through an intermixing with the frontier MO's. The major role of the frontier MO's may be recognized as follows. Coupling of the HOMO (LUMO) of reagent and the LUMO (HOMO) of reactant will provide the interacting system with a powerful driving force.¹ On the other hand, bumping of the HOMO of

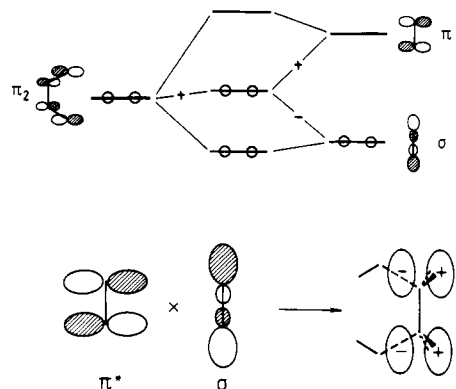


Figure 9. σ - π interaction accompanied by rehybridization. The signs + and - in the orbital interaction diagram mean the in-phase and out-of-phase orbital mixing, respectively, and + and - in ellipses symbolize the region of increase and decrease in the electron densities, respectively.

reagent into the HOMO of reactant will compel the interaction to suffer from a strong suppression. A way to relieve the system from the disadvantage may be to promote electron(s) from the HOMO to the LUMO either in reagent or in reactant by adequate means. The frontier orbitals will also participate in guiding the distortion of reagent and reactant along a reaction path, in cooperation with other orbitals. Investigation of the possible origins of the formation and breaking of chemical bonds seems to be promising in disclosing molecular mechanisms of chemical reactions.

Acknowledgment. This work was supported in part by a Grant-in-Aid from the Ministry of Education. We are grateful to Professor Kenichi Fukui for his lasting encouragement.

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$$\Delta\epsilon_{A_i} \cong \sum_r \sum_s^A p_{rs}^{(i)} \Delta s_{rs} (\Delta h_{rs} / \Delta s_{rs} - \epsilon_{A_i})$$

$$\Delta\epsilon_{B_l} \cong \sum_t \sum_u^B p_{tu}^{(l)} \Delta s_{tu} (\Delta h_{tu} / \Delta s_{tu} - \epsilon_{B_l})$$

If we adopt the extended Huckel approximation (R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963)) for the resonance integral h_{rs} , we have

$$\Delta h_{rs} / \Delta s_{rs} = K/2(h_{rr} + h_{ss})$$

The Coulomb integral h_{rr} of the carbon 2p AO is ca. -11.4 eV and K is taken to be 1.75. Accordingly, we have $(\Delta h_{rs} / \Delta s_{rs} - \epsilon) < 0$ for high-lying occupied MO's (e.g., the π MO of ethylene is located at ca. -13 eV) and unoccupied MO's. Stretching of a bonding orbital ($p_{rs} \Delta s_{rs} < 0$) leads to an elevation of the MO level and that of antibonding orbital ($p_{tu} \Delta s_{tu} > 0$) results in a lowering of the MO level. See also ref 1.

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