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A Coupled Fragment Molecular Orbital Method for Interacting Systems

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Abstract: A succinct orbital description of molecular interactions is presented. This covers automatically all the orbital interactions and orbital mixings in perturbation theory and visualizes their consequences in terms of hybrid molecular orbitals which are localized in the region of interaction. These hybrid orbitals are determined within the framework of the pairing theorem so as to offer a clearer view of bond-forming processes along a reaction coordinate. Of these paired hybrid orbitals, one or a few pairs play the dominant role and they thereby define the domains of reagent and reactant that participate actively in the interaction. These hybrid molecular orbitals are suggested to give the basis of frontier orbitals.

Almost 30 years have passed since the first paper on the frontier electron theory came out.[1] By utilizing the mathematical simplicity of the primitive Hückel molecular orbital (MO) method, reactivities of polyenes and condensed aromatic systems were discussed extensively.[2] The extended Hückel,[3] CNDO,[4] and other semiempirical MO methods appearing in 1960's magnified the applicability of the theory to sizable molecules with three-dimensional frameworks.[5] The stereoselection rules[6] seem also to be explainable by means of interactions between frontier orbitals,[7] though several alternative ways of interpretation surely exist.[6,8-10]

The basic frontier orbital concept appears to have grown to an efficient tactic to understand the results of semiempirical and ab initio MO calculations, being called frequently orbital interactions and orbital mixings.[11-18] The inclusion of other MOs than the highest occupied MO and/or the lowest unoccupied MO is clearly of significance for a detailed study of the geometric changes and electron reorganization in chemically interacting systems along a reaction coordinate.[16-18] Perturbation theory has most often been utilized to elucidate how the MOs of fragments interact or intermix through interactions.[11-15] The expansion of composite MOs in terms of the fragment MOs has led, on the other hand, to a powerful method of analyzing weak and moderately strong interactions by means of electron configurations of the reagent and reactant.[19,20] It is obvious that the frontier electron theory is related closely in this respect to the theory of charge transfer developed by Mulliken.[21]

Very recently, we have proposed a novel concept of "interaction frontier orbitals".[22] By taking not only the frontier MOs but also all the relevant MOs properly into account, we intended to condense the entire consequence of delocalization interaction into a pair or, at most, a few pairs of hybrid orbitals of fragments which are localized in the region of interaction. An application to some systems demonstrated the utility of the method in elucidating the role of electron delocalization in chemical interactions.[22] In this paper, we show an extensive generalization of the method to cover the significant effects of the exchange and polarization interactions in chemical reactions. Reactive domains of molecules are illustrated.

Procedure of Calculations

To begin with we may mention orbital interactions between the fragments A and B in a composite system A–B. The MOs of the system A–B can be expanded as usual in linear combinations of the MOs of fragments:

$$\Phi_m = \sum_i^{\mathrm{A}} c_{m,i}\phi_i + \sum_k^{\mathrm{B}} c_{m,k}\psi_k \tag{1}$$

It is easy to calculate exactly the coefficients $c_{m,i}$ and $c_{m,k}$ by the use of expansion theorems or by solving linear simultaneous equations.[20]

From eq 1 we define an *intermolecular interaction matrix* **P** for some appropriate one-electron operator $\mathbf{p}(1)$;

$$\mathbf{P} = (P_{i,k}) \tag{2}$$

$$i = 1, 2, \cdots, s;\ k = 1, 2, \cdots, t$$

where s and t signify the number of relevant MOs of A and of B, respectively. In the case of the system A–B having a closed-shell electronic structure the ground state of which is described by a single determinant wave function, we get:

$$P_{i,k} = 4\sum_m^{\mathrm{occ}} c_{m,i}c_{m,k}\int \phi_i(1)\mathbf{p}(1)\psi_k(1)\,dv_1 \tag{3}$$

The modifications associated with an employment of multiconfiguration wave function and applications to open-shell systems are straightforward.

The matrix **P** is rectangular, in general, of order $s \times t$. All the occupied and unoccupied MOs of fragments are included in

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order to represent all the orbital effects, e.g., the exchange, delocalization, and polarization interactions. The product $\mathbf{P}^\dagger\mathbf{P}$ is an Hermitian matrix and gives nonnegative eigenvalues upon diagonalization;

$$\mathbf{P}^\dagger\mathbf{P}\mathbf{U} = \mathbf{U}\boldsymbol{\Gamma} \tag{4}$$

where:

$$\mathbf{U} = (U_{j,i}) \tag{5}$$

$$\boldsymbol{\Gamma} = (\gamma_i) \tag{6}$$

Assuming tentatively that $s \leq t$ and that the eigenvalues γ_i are not zero for $i = 1, 2, \cdots, s$,[23] the canonical MOs of A and those of B are converted into separate orthonormal sets of hybrid MOs by the following pairwise orbital transformations;

$$\phi'_i = \gamma_i^{-1/2} \sum_{j=1}^{s} \sum_{l=1}^{t} P_{j,l} U_{l,i} \phi_j \tag{7}$$

$$i = 1, 2, \cdots, s$$

and:

$$\psi'_k = \sum_{l=1}^{t} U_{l,k} \psi_l \tag{8}$$

$$k = 1, 2, \cdots, t$$

Note that replacement of the overlap integral matrix **S** for the matrix **P** reduces these transformations to the corresponding orbital formalism by Amos and Hall.[24] In the present case, we have to iterate the whole procedure by evaluating the matrix elements $P'_{i,k}$ for the new sets of orbitals ϕ'_i and ψ'_k to make the transformations self-consistent.[25,26]

Upon convergence the orbitals ϕ' of the fragment A and the orbitals ψ' of the fragment B yield a unique set of orbital couples in which an orbital ϕ'_i interacts only with its counterpart ψ'_i and vice versa.[27] We get, therefore:

$$\sum_{i=1}^{s} \sum_{k=1}^{t} P_{i,k} = \sum_{i=1}^{s} P'_{i,i} \tag{9}$$

The $s \times t$ orbital interactions can thus be reduced to the interactions of paired hybrid MOs of fragments, s in number. Note here that s is the smaller of the numbers of MOs in the fragments, A and B. The orbitals ϕ' are constructed only from the canonical MOs of the fragment A and the orbitals ψ' consist only of the canonical MOs of the fragment B, but they are no longer constrained by the local symmetry of fragments. They are adapted in pairs for the symmetry of the composite system.

By tracing the procedure of orbital transformations mentioned above, one may recognize that a pair of orbitals, say ϕ'_f and ψ'_f, corresponding to the largest eigenvalue γ'_f, should have the greatest amplitude in the region of mutual interaction in A and in B, respectively, with regard to each symmetry element of the composite system, provided that the one-electron operator $\mathbf{p}(1)$ was chosen adequately to represent the interaction. Other orbitals are localized naturally in other regions to determine the electronic structure of the fragments in interaction and, therefore, they will not participate significantly in the intermolecular interaction. The *interactive hybrid MOs* ϕ'_f and ψ'_f do not have to be either occupied or unoccupied. They are something in-between, depending on the type of interaction.

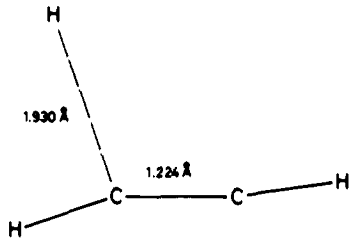

Figure 1. A sketch of reaction model for addition of hydrogen atom to acetylene.

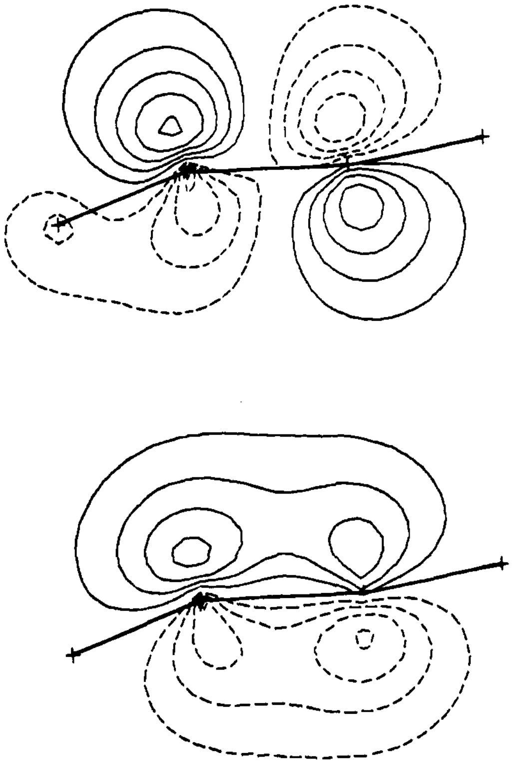

Figure 2. Interaction frontier orbitals of acetylene to interact with a hydrogen atom in the α spin part (upper) and in the β spin part (lower).

It is a general extension of the early frontier electron theory to try to locate the particular orbital(s) which shall play a dominant role in reactions. It is obvious that the frontier orbitals, as well as the interaction frontier orbitals,[22] are nothing but simplified versions of the interactive hybrid MOs, determined for minor sets of canonical MOs. When the matrix **P** spans only the occupied subset of donor orbitals and the unoccupied subset of acceptor orbitals, the orbital transformations yield the *interaction frontier orbitals*.[28] A combination of the highest occupied MO of donor and the lowest unoccupied MO of acceptor gives rise at once to the frontier MOs. In order to clarify the relation between several types of interaction MOs, we have begun our discussion above by representing the intermolecular part of the density matrix in terms of the canonical MOs of fragments. An important aspect of the interactive hybrid MOs is that they can also be derived directly from the atomic orbital density matrix of the composite system without reference to the fragment canonical MOs.[29]

Results of Calculation

Addition of hydrogen atom to acetylene provides a simple but suitable example to illustrate the foregoing argument. The reaction model shown in Figure 1 was taken from an extensive calculation by Nagase and Kern.[30] We used an ab initio UHF SCF MO

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[23] The treatment of zero eigenvalues is trivial.

[24] Amos, A. T.; Hall, G. G. *Proc. R. Soc. London, Ser. A* **1961**, *263*, 483–93. See, also: King, H. F.; Stanton, R. E.; Kim, H.; Parr, R. G. *J. Chem. Phys.* **1967**, *47*, 1936–41.

[25] The matrix element $P_{i,k}$ is not directly proportional to the overlap integral $S_{i,k}$, in general.

[26] Prime is used to distinguish the hybrid MOs from the canonical MOs.

[27] The remaining $(t - s)$ orbitals of B find no counterpart in A and, therefore, do not contribute to the intermolecular interaction.

[28] Interaction frontier orbitals were defined more rigorously in ref 22 with regard to the Hamiltonian operator of the composite interacting system. Hybrid MOs depend more or less on the choice of matrix **P**.

[29] Atomic orbitals should once be converted to some orthonormal set of orbitals within each fragment.

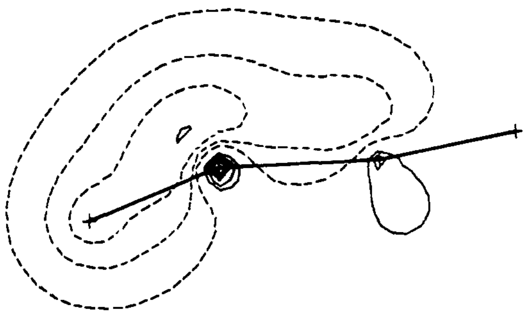

Figure 3. Hybrid MO of acetylene taking part in overlap repulsion.

method with the STO-6G basis set to calculate the electron density between the two species.[31] Without loss of generality, we assigned the odd electron with the spin α.

In Figure 2 we show the interaction frontier orbitals. Here, we took tentatively the intermolecular overlap populations[32] between the fragments as the elements of **P**.[33] Since a hydrogen atom possesses a single orbital, a single hybrid MO participates in the delocalization interaction in each spin part of acetylene. In the α spin part, electron delocalization takes place from hydrogen atom to acetylene and, therefore, the interaction frontier orbital is obtained with regard to the matrix **P** defined for the unoccupied subset of canonical MOs. The resultant orbital is given by an admixture of unoccupied MOs. In the β spin part, on the contrary, the delocalization interaction takes place between the occupied MOs of acetylene and the orbital of the hydrogen radical. The interaction frontier orbital of acetylene for β spin is defined, therefore, with respect to the occupied subset of canonical MOs of the acetylene fragment. Though the unoccupied and occupied π-type MOs of the deformed acetylene molecule are the predominant constituent of the interaction frontier orbital for the α spin part and that for the β spin part, respectively, contributions of σ-type MOs have also been taken obviously into the hybrid MO in each spin part by this procedure.

An overlap repulsion arises in the α spin part due to the interactions between the occupied MOs of the acetylene fragment and the singly occupied MO of the attacking radical.[34] By carrying out the orbital transformation within the occupied MOs of acetylene, we obtained a hybrid MO shown in Figure 3. It is seen clearly that not only the site under attack but also the bonds connecting the reaction site and the adjacent atoms take part in the overlap repulsion. Rehybridization at the reaction center to bend the molecule should reduce effectively the repulsive interaction.[18]

Figure 4 shows the interactive hybrid MOs of acetylene for the α and β spin parts. All the occupied and unoccupied canonical MOs participate in these orbitals to determine the regions of bonding and antibonding interactions with the incoming hydrogen atom. Because of a strong competition between the exchange and delocalization interactions as demonstrated by the orbitals shown in Figures 2 and 3, the interactive hybrid MO for the α spin part does not show signficant amplitude in the region of interaction.[35] The interaction between the hybrid MO and the hydrogen 1s orbital is antibonding. In the β spin part, on the other hand, the interactive hybrid MO is localized well around the site under attack to give a bonding interaction with the attacking radical. The hybrid MO contains explicitly, unlike the interaction frontier orbital given in Figure 2, the important effect of polarization to specify the domain of acetylene molecule which takes part actively in the interaction. It seems to be more favorable for a carbon–carbon π bond to donate electron density in part via unoccupied MOs, particularly the π^* MO, than to donate all the electron density directly from the π MO in order to create a new single bond between a carbon atom and an attacking reagent.

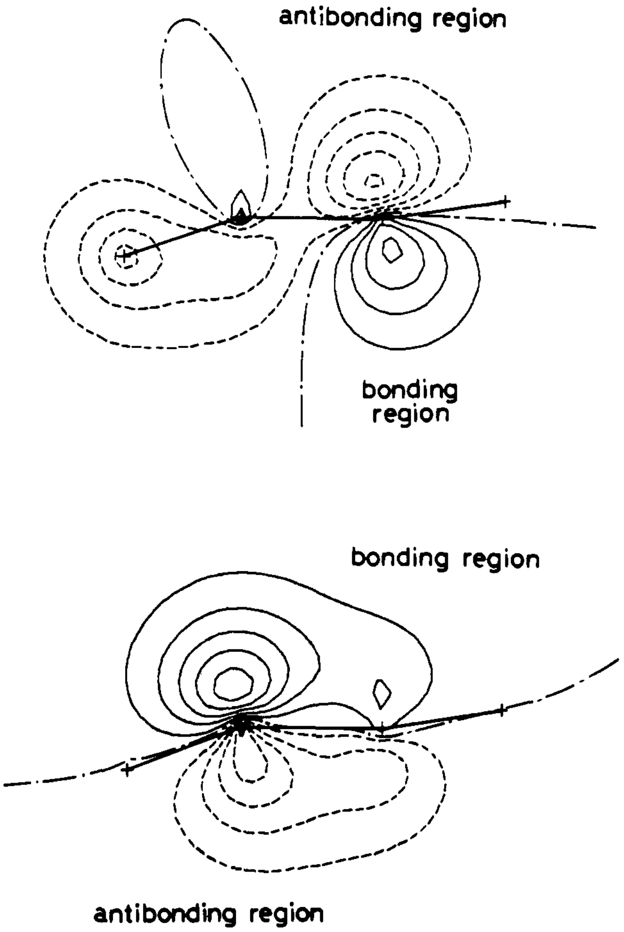

Figure 4. Interactive hybrid MOs of acetylene to interact with a hydrogen atom in the α spin part (upper) and in the β spin part (lower).

Table I. Coefficients of Canonical MOs in Interactive Hybrid MOs of Acetylene

	α spin			β spin	
MO	all MOs[a]	occupied subset[b]	unoccupied subset[c]	all MOs[a]	occupied subset[c]
σ'_1	−0.0343	−0.0437		−0.0051	−0.0060
σ'_2	−0.0501	−0.0669		−0.0105	−0.0112
σ'_3	−0.4889	−0.6771		0.0304	0.0320
σ'_4	−0.3426	−0.4708		0.0654	0.0720
σ'_5	−0.2010	−0.2774		0.0383	0.0426
π	0	0		0	0
π'	−0.3537	−0.4881		0.9538	0.9959
π'^*	0.6876		0.9991	0.2886	
π^*	0		0	0	
σ'_6	0.0383		0.0406	−0.0108	
σ'_7	−0.0019		−0.0024	0.0128	
σ'_8	0.0085		0.0141	0.0004	

[a] The hybrid MOs shown in Figure 4. [b] The hybrid MO shown in Figure 3. [c] The hybrid MOs shown in Figure 2.

The coefficients of canonical MOs in the hybrid MOs are presented in Table I. The canonical MOs of the deformed acetylene molecule having maximal amplitudes in the plane of hydrogen attack were denoted by σ' and π' to retain approximately a correlation with the σ and π MOs of linear acetylene. The signs of these canonical MOs were chosen so as to give positive overlap integrals between the fragment MOs. The π and π^* MOs which have the direction of extension perpendicular to the plane do not

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(30) Nagase, S.; Kern, C. W. *J. Am. Chem. Soc.* **1979**, *101*, 2544–49.

(31) Hehre, W. J.; Lathan, W. A.; Ditchfield, R.; Newton, M. D.; Pople, J. A. *QCPE No. 236*.

(32) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833–40.

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(34) The exchange interaction in homolytic reactions was studied in detail previously. See: Fujimoto, H.; Yamabe, S.; Minato, T.; Fukui, K. *J. Am. Chem. Soc.* **1972**, *94*, 9205–10.

(35) Note here that the interactive hybrid MO for the α spin part is not given by the 1:1 mixture of the orbitals shown in Figures 2 and 3.

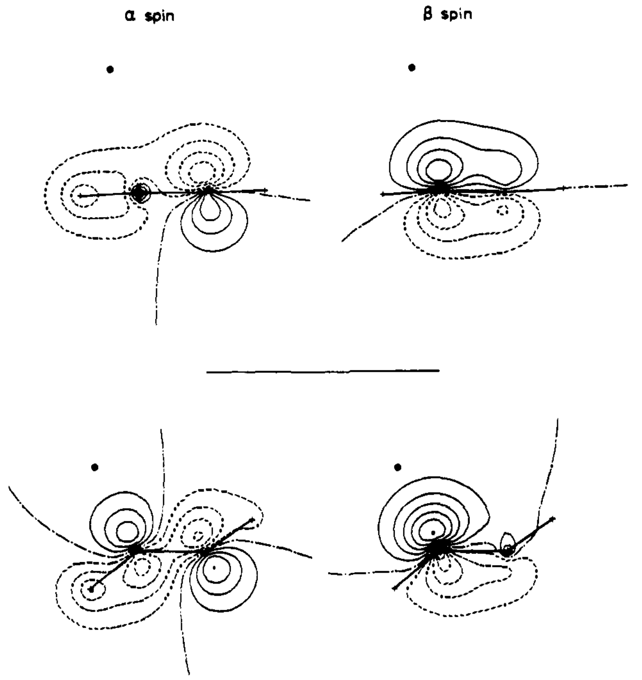

Figure 5. Interactive hybrid MOs of acetylene in the acetylene–hydrogen system located before (upper) and after (lower) the transition state. Position of the attacking hydrogen atom is marked by a dot.

interact with the 1s orbital of the attacking hydrogen radical by symmetry.

The lowest unoccupied π'^* MO is found to play an exclusively important role among the unoccupied MOs of the α spin part, while the highest occupied π' MO is seen to participate dominantly in the interaction among the occupied MOs of the β spin part, demonstrating a characteristic of reactions of small conjugated molecules. The occupied π' MO is shown to take part in the interaction in an antibonding manner in the α spin part, indicating the presence of a strong exchange repulsion. The unoccupied π'^* MO contributes to the bonding interaction from the beginning of reaction in the β spin part to construct a localized interaction orbital. A basic aspect of homolytic reactions is represented by these hybrid MOs.

This calculation suggests that addition of electrophiles to unsaturated bonds is facile, whereas addition of nucleophiles is unfavorable in accordance with a general trend observed experimentally. One may suppose, therefore, that an attacking radical should play the electron-acceptor part in homolytic additions. This is unlikely, however. Replacement of an electron-releasing group for the hydrogen which is attached to the carbon under attack, for instance, may strengthen the bonding interaction in the β spin part, but will lead concurrently to a strengthening of the overlap repulsion and a weakening of the delocalization interaction in the α spin part. The substituent does not seem to favor the addition. Introduction of an electron-withdrawing substituent will suppress the antibonding interaction and promote the bonding interaction in the α spin part, though the bonding interaction in the β spin part is weakened to some extent. It is suggested, therefore, that a π bond would play preferably an electron-acceptor part in homolytic additions, in agreement with a broad generalization of observed trends by Hefter, Hecht, and Hammond.[36] An application of the present method to addition of proton to propene has shown that a selective attack to the terminal carbon is interpreted in terms of a more efficient localization of bonding region in the vicinity of the interaction center.[37]

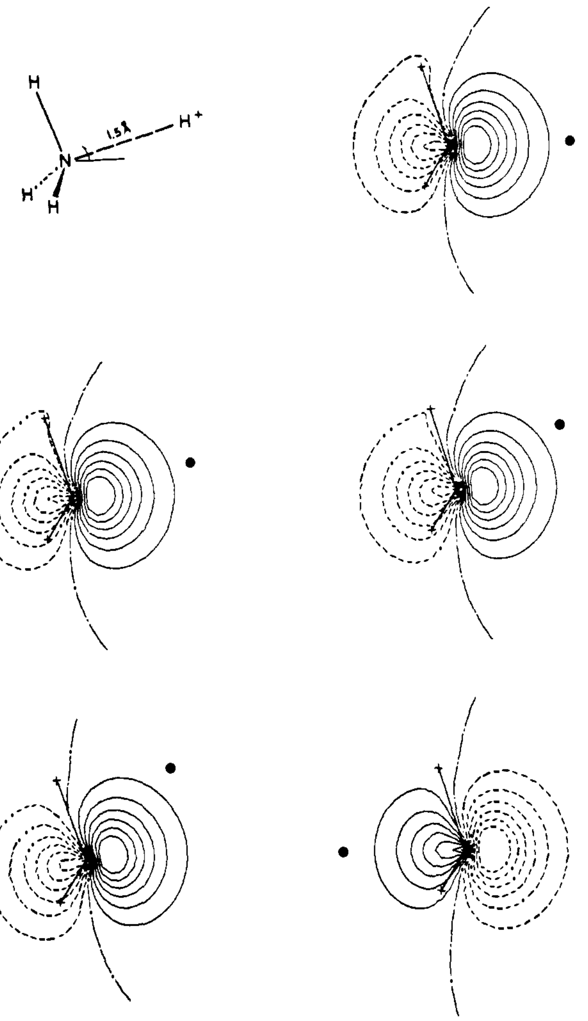

Figure 6. Interactive hybrid MO of ammonia in the ammonia–proton system. Location of proton is marked by a dot.

Figure 5 presents the interactive hybrid MOs for two models of the acetylene–hydrogen atom system, one being located before and the other being located after the transition state illustrated in Figure 1.[30] By comparing the hybrid MOs with those given in Figure 4, we can trace an evolution of reactive domains with the progress of reaction in terms of the hybrid MOs. The occupied π' MO begins to participate in the bonding interaction in the α spin part and the unoccupied π'^* MO plays an increasingly important role in the β spin part at a later stage of reaction.

Figure 6 shows the interactive hybrid MOs of ammonia calculated by placing a proton at several different positions. Since no saddle point was found within an STO-6G level study, the N–H$^+$ distance was chosen tentatively at 1.5 Å. The orbitals look very similar to the interaction frontier orbital obtained in our previous calculation.[38] The polarization interaction is not important in this case and the highest occupied canonical MO dominates the interaction with proton. The interactive hybrid MO, as well as the interaction frontier orbital, of ammonia was found to be of stronger p character than the localized molecular orbital obtained by the use of the Edmiston–Ruedenberg procedure.[39] In an isolated state of ammonia, the nitrogen 2s orbital may constitute a large portion of the lone pair to stabilize the molecule. When a proton attacks, the lone-pair orbital should rearrange itself to strengthen the ability for electron donation. The 2p component should be enhanced in the lone-pair orbital. The localized hybrid orbitals generated by the Edmiston–Ruedenberg procedure and by our method appear to each symbolize the static and dynamic aspect of lone-pair orbitals, respectively. Incidentally, the lone-pair orbital of ammonia which interacts with a proton approaching

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(36) Hefter, H. J.; Hecht, T. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 2793–7. See, also ref 34.

(37) Fujimoto, H.; Koga, N., unpublished result.

(38) See Figure 1 in ref 22. The N–H$^+$ distance was taken somewhat longer in the present calculation.

(39) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457–465.

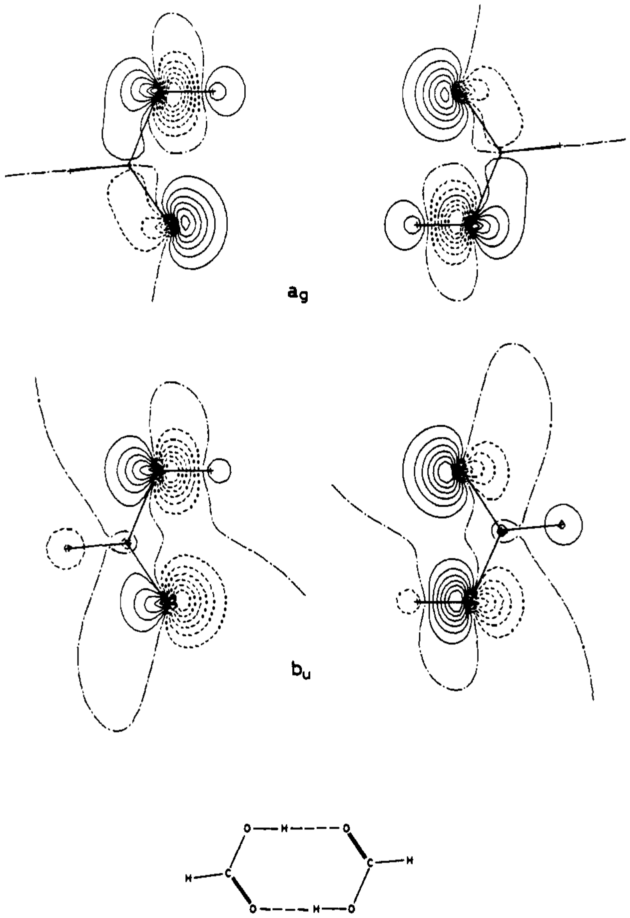

Figure 7. Two pairs of interactive hybrid MOs in formic acid dimer. Contours are shown for separated monomers.

from the backside shows a weaker p nature relative to others, suggesting that such an interaction is unfavorable.

It was shown in Figure 6 that, like the bond orbitals in stable molecules,[40,41] the hybrid MO of ammonia could hardly follow the motion of proton. When a proton was placed in a position 45° away from the symmetry axis, for example, the hybrid MO was calculated to decline only about 10°. The hybrid MOs taking part in interactions seem also to be governed rigorously by the structure of fragments, notwithstanding that these orbitals are derived only by looking at the intermolecular part of the density matrix. It is obvious that the structural constraint arises indirectly by projecting the geometry and orientation of a fragment in space on the other fragment. Thus, by virtue of the delicately arranged valence-active electron density between fragments, whole molecular frameworks participate actively in the determination of reaction pathways, even if interactions are local by nature.

In the acetylene–hydrogen atom system presented above, the interactive hybrid MO of acetylene tends to point nicely at the incoming hydrogen both in the α spin part and in the β spin part, as demonstrated in Figure 5. This signifies that the addition is a typical nonpolar reaction in which the formation of a new covalent bond is the principal driving force of the process. When the interactive hybrid MOs would deviate in the direction of its extension from the path of reagent approach, some other factors than orbital effects, most probably Coulombic attractions or repulsions, should come to play a significant role. The maximum overlap of the hybrid MOs seems to provide the simplest criterion to interpret the pathway of nonpolar reactions.

Both in the acetylene–hydrogen atom system and in the ammonia–proton system, the attacking reagent possesses a single orbital. Accordingly, all the orbital effects are condensed in a single hybrid MO of the reactant in these cases. In the majority of chemical reactions, the growth of a new bond between the particular sites of reagent and reactant is the main driving force. A single pair of hybrid MOs will suffice for describing virtually all orbital interactions, even when the attacking reagent has several orbitals. In highly symmetrical multicentric processes, however, several pairs of fragment MOs are supposed to participate in interactions. In Figure 7, we show, as an example, the interactive hybrid MOs for dimeric formic acid.

Table II. Contributions of Canonical MOs to Interactive Hybrid MOs of Formic Acid Molecule

	MO	weight %	
		a_g	b_u
occupied	σ_4	0.00	5.90
	σ_5	6.92	0.52
	σ_6	0.37	13.85
	σ_7	15.96	0.31
	σ_8	18.65	0.06
	σ_9	3.40	30.23
	σ_{10}	21.95	21.11
unoccupied	σ_{11}	23.31	20.06
	σ_{12}	8.62	6.83
	σ_{13}	0.22	0.42
	σ_{14}	0.59	0.70

We obtain two pairs of interactive hybrid MOs which contribute to the hydrogen bonding. The fragment MOs obtained are seen clearly to be adapted in pairs for the symmetry of the composite system. The overlap population between the hybrid MOs, $P'_{\mathrm{f,f}}$, was calculated to be small but positive, being 0.0474 for the $\mathrm{a_g}$ pair and 0.0367 for the $\mathrm{b_u}$ pair. The sum of occupancies in the pair of MOs is 2.728 and 2.949, indicating the existence of a pretty strong overlap repulsion which has somehow been counterbalanced by the delocalization, polarization, and other interactions.[42] This result is in line with our analysis of the interaction energy by the use of an ab initio perturbation scheme.[43] We obtained −0.0232, 0.0367, −0.0343, and −0.0014 au for the Coulomb, exchange, delocalization, and polarization interactions, respectively.[44] Constituents of the hybrid MOs are presented in Table II in which σ denotes the canonical MOs of monomeric formic acid having maximal amplitudes in the molecular plane. Incidentally, no bonding pair of hybrid MOs was found in the case of cyclic water dimer. The electrostatic interaction between water molecules was shown previously to be the most important component of the bonding force.[45]

Discussion

We may examine next some aspects of the interactive hybrid MOs. As it has thoroughly been discussed in our previous papers,[5,20] the ground state of a composite reacting system is presented by a combination of various electron configurations of the fragments, A and B:

$$\Psi = \sum_{\mathrm{p}} C_{\mathrm{p}} \Psi_{\mathrm{p}} \qquad (10)$$

Electron configurations that we should note here are the original one Ψ_0, electron-transferred ones $\Psi_{i\to l}$ ($\Psi_{k\to j}$) and $\Psi_{i\to l,i\to l}$, and locally excited ones $\Psi_{i\to j}$ ($\Psi_{k\to l}$), where i and k denote the occupied MOs of A and B, respectively, and j and l signify the unoccupied MOs of A and B, respectively. In the original configuration, the fragments retain their ground-state configurations that they possess

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(40) Nakatsuji, H. *J. Am. Chem. Soc.* **1974**, *96*, 30–37.

(41) Chipman, D. M.; Palke, W. E.; Kirtman, B. *J. Am. Chem. Soc.* **1980**, *102*, 3373–83.

(42) The interaction between a doubly occupied orbital and a singly occupied orbital is mostly destabilizing. See ref 34 and, also: Bernardi, F.; Epiotis, N. D.; Cherry, W.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1976**, *98*, 469–78.

(43) Fujimoto, H.; Kosugi, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2209–14.

(44) The delocalization interaction was found to be weak in a semiempirical perturbation calculation by Nagase and Fueno. See: Nagase, S.; Fueno, T. *Theor. Chim. Acta* **1974**, *35*, 217–30.

(45) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1977**, *99*, 1316–32.

Table III. Overlap Populations between the Hydrogen 1s Orbital and the Canonical MOs of Acetylene Molecule

acetylene MO	α spin	β spin
σ'_1	−0.0001	−0.0000
σ'_2	−0.0002	−0.0001
σ'_3	−0.0166	0.0008
σ'_4	−0.0092	0.0013
σ'_5	−0.0030	0.0004
π	0	0
π'	−0.0186	0.0381
π'^*	0.0313	0.0093
π^*	0	0
σ'_6	0.0001	−0.0001
σ'_7	−0.0000	0.0000
σ'_8	0.0000	0.0000

in an isolated state. The shift of an electron and that of a pair of electrons are distinguished from each other by the suffix $i \rightarrow l$ and the suffix $i \rightarrow l, i \rightarrow l$, respectively. Diexcited configurations $\Psi_{i \rightarrow j, i \rightarrow j}$ ($\Psi_{k \rightarrow l, k \rightarrow l}$) arise mainly from the intramolecular part and, therefore, scarcely take part in the intermolecular interaction.[43]

Besides the well-known effect of shifting the electronic charge from one fragment to the other fragment,[46] a mixing in of electron-transferred configurations possesses another important consequence, i.e., accumulation of the valence-active density in the intermolecular region.[16] For instance, the interaction between the configurations Ψ_0 and $\Psi_{i \rightarrow l}$ gives rise to the overlap density term $\phi_i(1)\psi_l(1)$. A part of electron population donated from the occupied MO ϕ_i is retained in the region between A and B through the overlap of ϕ_i with the unoccupied MO ψ_l. Similarly, the ditransferred configuration $\Psi_{i \rightarrow l, i \rightarrow l}$ yields the density term $\phi_i(1)\psi_l(1)$ by means of the interaction with the monotransferred configuration $\Psi_{i \rightarrow l}$.

The locally excited configurations contribute primarily to electron reorganization within the fragments induced by several causes.[17] They also yield overlap density terms by mixing with electron-transferred configurations. We obtain, for example, $\phi_i(1)\psi_k(1)$ from the interaction between $\Psi_{k \rightarrow l}$ and $\Psi_{i \rightarrow l}$ and $\phi_j(1)\psi_l(1)$ from the interaction between $\Psi_{i \rightarrow j}$ and $\Psi_{i \rightarrow l}$. That is, the occupied MO ψ_k of the acceptor fragment participates in the generation of the intermolecular overlap density through the interaction with the electron hole ϕ_i and the unoccupied MO ϕ_j of the donor fragment does so by promoting an electron from the occupied MO ϕ_i in the course of interactions. Thus, the intermolecular interaction matrix **P** involves the contributions of all the important electron configurations and, therefore, the interactive hybrid MOs represent important orbital effects. The hybrid MOs are given accordingly by linear combinations of the occupied and unoccupied (and, also, singly occupied) canonical MOs in each fragment with respect to each symmetry element of the composite interacting system.

Conclusion

The hybrid molecular orbitals obtained here have been found to be localized in the frontier of mutual interaction. They may deserve, therefore, to be called the original of the frontier orbitals. Then, several possibilities of modification arise, the highest occupied MO or the lowest unoccupied MO being regarded as the simplest prototype.[1] Once again, we may stress here the significant assistance of other MOs throughout the course of chemical reactions. An important consequence of mixings between the frontier MO and extrafrontier MOs is the construction of reactive domain in a particular region of the reactant. The growth of new covalent bonds begins between the reaction sites.

The hybrid MO description of interactions will offer hopefully a clearer insignt into the bond-forming processes by visualizing, in line with our chemical intuition, effects of various factors that will possibly have a great influence on reactivities of molecules and selectivities of reactions. Especially, analyses of interactions between a large molecular system and a small reagent will be much simplified, since they are represented in terms of several pairs of fragment hybrid MOs. Finally, we may notice that the present approach seems to provide a concrete application of the principle of maximum overlap by Pauling[47,48] and the overlap and orientation principle by Mulliken[49] to practical problems.

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Appendix

Table III shows the overlap populations between the 1s orbital of the attacking hydrogen radical and the canonical MOs of acetylene molecule with respect to a reaction model sketched in Figure 1. According to eq 4 we constructed a matrix of order 12×12 which was diagonalized to yield a set of new orbitals for each spin part. Then, the MOs of the composite interacting system were expanded in terms of the hydrogen 1s orbital and the new orbitals of acetylene and, thus, a new overlap population matrix was obtained in each spin part. The whole procedure of orbital transformations was repeated till a self-consistent result was generated. We got one positive eigenvalue and eleven zero eigenvalues in this case in the final matrix product. Twenty-two cycles and ten cycles of iterative calculations for the α spin part and for the β spin part, respectively, paying attention to the signs of interim orbitals to facilitate the convergence, reached our tentative self-consistency limit, $|P'_{i,k}| < 1 \times 10^{-5}$ ($i \neq k$). Total computing time used to calculate the interactive hybrid MOs for both spins was 2.1 s on a FACOM M200 at the Data Processing Center, Kyoto University. The calculation of hybrid MOs for subsets of canonical MOs was found to be much faster.

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