Isolated Molecule Approach to the Orbital Study of Chemical Reactions. I. Bimolecular Nucleophilic Substitution

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A method of analyzing chemical interactions between two systems is presented and applied to the bimolecular nucleophilic substitution of methylfluoride by fluoride ion. In order to get a clear insight into the mechanisms of chemical interactions, the interacting system has been represented by a combination of various electron configurations of the reactants involved. The matrix elements necessary for the configuration interaction have been obtained by transforming the MO's of the isolated reactants into a set of orthogonalized functions. The change in the energy and the redistribution of the electrons due to the interaction in the reaction have been calculated by the use of the *ab initio* (STO-3G) MO's and have been divided into the Coulomb, exchange, delocalization, and polarization interactions. A comparison of the results with the results of the SCF CI calculations of the composite system has shown the utility of the method in studying weak and moderately strong interactions between two systems.

The bimolecular nucleophilic substitution (S_N2) reaction of aliphatic systems is one of the most extensively investigated reactions in organic chemistry.[1] Since Hughes and Ingold,[2] numerous experiments have attempted to study the mechanism of the reactions. It is now well-established that the attacking base approaches the substrate from the back, displacing the leaving group. Thus, the Walden inversion is characteristic of S_N2 reactions. It has been suggested that the carbon atom of a substrate under attack will take a nearly sp^2 planar structure at the transition state, although no stable intermediate has ever been trapped.

Recent developments in quantum mechanical methods of calculating the electronic structure of sizable molecules have led us to consider the detailed molecular mechanisms of organic reactions. In particular, *ab initio* MO methods have been accepted as a way of studying the basic nature of chemical reactions in recent years. Although it is unlikely, at present, that such methods can supply us with quantitatively reliable results on the magnitude of the activation energy and the geometry of transition state complex for systems with many degrees of freedom, an extensive configuration interaction with a large set of basis functions will lead to an improvement of the calculations.[3] In this respect, MO approaches to chemical reactions seem to be promising.

The perturbation theory is a convenient tool to deal with weakly interacting systems. The energy and the electron density are separated into several interaction terms and are interpreted in relation to chemical and physical concepts of molecular interaction.[4] In this paper, we will present the result of our calculation of the electron reorganization in a model S_N2 reaction. A direct evaluation of the interaction integrals and configuration energies is attempted. Our primary aim is to develop a theoretical method of studying molecular interactions, furnished both with the accuracy of *ab initio* calculations and with the accessibility of perturbation theories to the nature of chemical reactions.

Description of Chemical Interactions

In order to study the molecular mechanism of S_N2 reactions, we have chosen methylfluoride and fluoride ion as the substrate and the attacking base respectively.[5] The geometry of the reacting system was taken to be as is given in Fig. 1, after Veillard.[5c] In an early stage of the reaction, the electronic structure of the composite system can be represented by a wave function which is a linear combination of various electron configurations of the reactants involved:[4]

$$\Psi = \sum_p C_p \Psi_p . \qquad (1)$$

Some of the most important configurations are illustrated in Fig. 2. The wave functions of these electron configurations are given by the Slater determinants, as usual. The original configuration contains only the occupied MO's of the isolated reactants:

$$\Psi_0 = |a_1 \cdots a_i \cdots a_m b_1 \cdots b_k \cdots b_n \bar{a}_1 \cdots \bar{a}_i \cdots \bar{a}_m \bar{b}_1 \cdots \bar{b}_k \cdots \bar{b}_n|,$$

where a and $\bar{a}$ are the spinorbitals of methylfluoride ($m=9$) with spin α and spin β respectively, and where

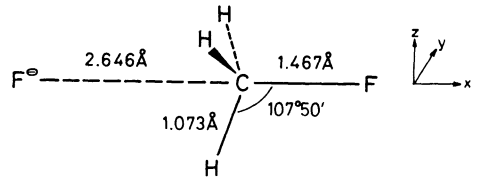

Fig. 1. A sketch of reaction model after Veillard.[5c]

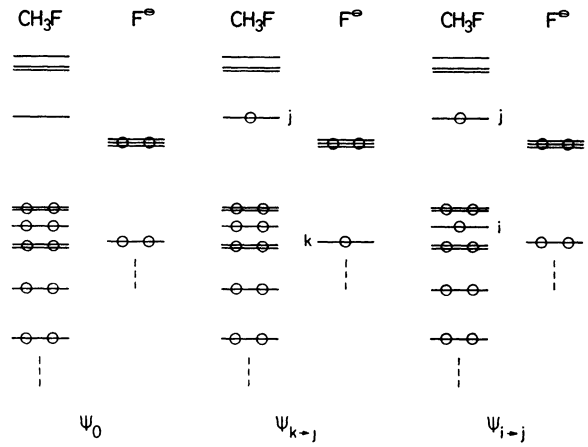

Fig. 2. An illustration of some electron configurations.

b and $\bar{b}$ are the spinorbitals of the fluoride ion ($n=5$). Similarly, we have:

$$\Psi_{k\to j} = 1/\sqrt{2}\,(|a_1\cdots a_m b_1\cdots a_j\cdots b_n\bar{a}_1\cdots\bar{a}_m\bar{b}_1\cdots\bar{b}_k\cdots\bar{b}_n| + |a_1\cdots a_m b_1\cdots b_k\cdots b_n\bar{a}_1\cdots\bar{a}_m\bar{b}_1\cdots\bar{a}_j\cdots\bar{b}_n|),$$

$$\Psi_{i\to j,i\to j} = |a_1\cdots a_j\cdots a_m b_1\cdots b_n\bar{a}_1\cdots\bar{a}_j\cdots\bar{a}_m\bar{b}_1\cdots\bar{b}_n|.$$

It should be noted here that, in general, the MO's a_i and b_k are not mutually orthogonal.

Among the various electron configurations appearing in Eq. 1, Ψ_0 is the dominant term, and the expansion coefficients, C_p, can be obtained as the solution of the simultaneous equations:

$$(\boldsymbol{H}-E\boldsymbol{S})\boldsymbol{C} = 0, \tag{2}$$

in which:

$$H_{p,q} = \int \Psi_p^* H \Psi_q \mathrm{d}\tau,$$

$$S_{p,q} = \int \Psi_p^* \Psi_q \mathrm{d}\tau.$$

The Hamiltonian operator for the interacting system is given by:

$$H = \sum_i -1/2\Delta_i + \sum_i\sum_\alpha -Z_\alpha/r_{i\alpha} + \sum_{i<j}\sum 1/r_{ij} + \sum_{\alpha<\beta}\sum Z_\alpha Z_\beta/R_{\alpha\beta}, \tag{3}$$

where the familiar notations are used.[4b] In obtaining the matrix elements in Eq. 2, it is convenient to carry out a certain transformation of the basis MO's into a set of orthogonalized orbitals and/or corresponding orbitals.[6,7] Thus, all the integrals can be calculated exactly in the framework of the method of the MO calculation employed. In the present calculation, we used an SCF LCAO MO approximation, all the necessary atomic integrals being evaluated by expanding the basis Slater atomic orbiatls in three-term Gaussian functions (STO-3G).[8,9] No polarization function was adopted.

Calculation of Matrix Elements

Here we may mention briefly the method of calculating the integrals appearing in the secular equations. First, we consider overlap integrals. A wave function, $\boldsymbol{\phi}$, is a subset of the MO's chosen from the occupied and unoccupied MO's of methylfluoride and the fluoride ion:

$$\boldsymbol{\phi} = (\phi_1\phi_2\cdots\cdots\phi_N) \qquad (N=m+n=14)$$

where the one-electron function, ϕ_i, corresponds to one of the a's or b's of the isolated reactants. In a similar manner, $\boldsymbol{\phi}'$, $\boldsymbol{\varphi}$, and $\boldsymbol{\varphi}'$ span other subsets:

$$\boldsymbol{\phi}' = (\phi_1'\phi_2'\cdots\cdots\phi_N'),$$
$$\boldsymbol{\varphi} = (\varphi_1\varphi_2\cdots\cdots\varphi_N),$$
$$\boldsymbol{\varphi}' = (\varphi_1'\varphi_2'\cdots\cdots\varphi_N').$$

Now the overlap integral between two configurations, p and q, is given by:

$$\Psi_p = |\phi_1\cdots\cdots\phi_N\bar{\phi}_1'\cdots\cdots\bar{\phi}_N'| = A(\boldsymbol{\phi}\cdot\bar{\boldsymbol{\phi}}')/N_p,$$
$$\Psi_q = |\varphi_1\cdots\cdots\varphi_N\bar{\varphi}_1'\cdots\cdots\bar{\varphi}_N'| = A(\boldsymbol{\varphi}\cdot\bar{\boldsymbol{\varphi}}')/N_q,$$
$$S_{p,q} = 1/(N_p\cdot N_q)\cdot|\boldsymbol{S}_{\phi,\varphi}|\cdot|\boldsymbol{S}_{\bar{\phi}',\bar{\varphi}'}|, \tag{4}$$

where $\boldsymbol{S}$ is an MO overlap matrix:

$$\boldsymbol{S}_{\phi,\varphi} = \int {}^+\boldsymbol{\phi}\cdot\boldsymbol{\varphi}\mathrm{d}\tau = (s_{i,j}), \tag{5}$$

$$s_{i,j} = \int \phi_i\varphi_j \mathrm{d}v.$$

When the wave functions, Ψ_p and Ψ_q are given by the linear combinations of Slater determinants, $S_{p,q}$ is the sum of the overlap integrals between the determinantal wave functions. The normalization factors, N_p, for the wave functions due to the intermolecular MO overlap are immediately derived from Eq. 4,[10]

$$\Psi_0 = 1/\sqrt{(2N)!}\cdot 1/|\boldsymbol{S}_{0,0}|\cdot A(\boldsymbol{\phi}_0\cdot\bar{\boldsymbol{\phi}}_0), \tag{6}$$

$$\Psi_{k\to j} = 1/\sqrt{(2N)!}\cdot 1/(2|\boldsymbol{S}_{0,0}|\cdot|\boldsymbol{S}_{k\to j,k\to j}| + 2|\boldsymbol{S}_{0,k\to j}|^2)^{1/2}\cdot\{A(\boldsymbol{\phi}_0\cdot\bar{\boldsymbol{\phi}}_{k\to j}) + A(\boldsymbol{\phi}_{k\to j}\cdot\bar{\boldsymbol{\phi}}_0)\}, \tag{7}$$

$$\Psi_{i\to j,i\to j} = 1/\sqrt{(2N)!}\cdot 1/|\boldsymbol{S}_{i\to j,i\to j}|\cdot A(\boldsymbol{\phi}_{i\to j}\cdot\bar{\boldsymbol{\phi}}_{i\to j}), \tag{8}$$

where:

$$\boldsymbol{S}_{0,0} = \int {}^+\boldsymbol{\phi}_0\cdot\boldsymbol{\phi}_0\mathrm{d}\tau,$$

$$\boldsymbol{S}_{0,k\to j} = \int {}^+\boldsymbol{\phi}_0\cdot\boldsymbol{\phi}_{k\to j}\mathrm{d}\tau,$$

$$\boldsymbol{S}_{i\to j,i\to j} = \int {}^+\boldsymbol{\phi}_{i\to j}\cdot\boldsymbol{\phi}_{i\to j}\mathrm{d}\tau,$$

$$\boldsymbol{\phi}_0 = (a_1\cdots a_i\cdots a_m b_1\cdots b_k\cdots b_n),$$
$$\boldsymbol{\phi}_{k\to j} = (a_1\cdots a_m b_1\cdots a_j\cdots b_n),$$
$$\boldsymbol{\phi}_{i\to j} = (a_1\cdots a_j\cdots a_m b_1\cdots b_n).$$

The corresponding electron density can be calculated by means of the following equation:

$$\rho_{p,q} = 1/(N_p\cdot N_q)\{|\boldsymbol{S}_{\bar{\phi}',\bar{\varphi}'}|\cdot(\boldsymbol{\varphi}\hat{\boldsymbol{S}}_{\phi,\varphi}{}^+\boldsymbol{\phi}) + |\boldsymbol{S}_{\phi,\varphi}|\cdot(\bar{\boldsymbol{\varphi}}'\hat{\boldsymbol{S}}_{\bar{\phi}',\bar{\varphi}'}{}^+\bar{\boldsymbol{\phi}}')\}, \tag{9}$$

where $\hat{\boldsymbol{S}}_{\phi,\varphi}$ is the minor of $\boldsymbol{S}_{\phi,\varphi}$ with respect to the particular MO's concerned, ϕ and φ.

Next let us consider the energy matrix between various electron configurations. As has been mentioned above, $\boldsymbol{\varphi}$ is not generally orthogonal to $\boldsymbol{\phi}$. Now, let us assume that $\boldsymbol{\varphi}$ can be converted into a set of orbitals, $\boldsymbol{\lambda}$, by a certain transformation, $\boldsymbol{X}$, to give rise to:

$$\boldsymbol{\lambda} = \boldsymbol{\varphi}\boldsymbol{X}, \tag{10}$$

which satisfies the condition that:

$$\boldsymbol{1} = \int {}^+\boldsymbol{\phi}\cdot\boldsymbol{\lambda}\mathrm{d}\tau. \tag{11}$$

Therefore, we obtain:

$$\boldsymbol{X} = \boldsymbol{S}_{\phi,\varphi}{}^{-1}. \tag{12}$$

The matrix element between two configurations is given by:

$$H_{p,q} = \int|\phi_1\cdots\phi_N\bar{\phi}_1'\cdots\bar{\phi}_N'|H|\varphi_1\cdots\varphi_N\bar{\varphi}_1'\cdots\bar{\varphi}_N'|\mathrm{d}\tau$$
$$= \int|\phi_1\cdots\phi_N\bar{\phi}_1'\cdots\bar{\phi}_N'|H|\lambda_1\cdots\lambda_N\bar{\lambda}_1'\cdots\bar{\lambda}_N'|\mathrm{d}\tau/|\boldsymbol{S}_{\phi,\varphi}{}^{-1}|\cdot|\boldsymbol{S}_{\bar{\phi}',\bar{\varphi}'}{}^{-1}|$$
$$= \int|\phi_1\cdots\phi_N\bar{\phi}_1'\cdots\bar{\phi}_N'|H|\lambda_1\cdots\lambda_N\bar{\lambda}_1'\cdots\bar{\lambda}_N'|\mathrm{d}\tau\cdot|\boldsymbol{S}_{\phi,\varphi}|\cdot|\boldsymbol{S}_{\bar{\phi}',\bar{\varphi}'}|. \tag{13}$$

We can define here the bond order matrix, $\boldsymbol{P}^{\alpha}$ for electrons with the α spin and $\boldsymbol{P}^{\beta}$ for electrons with the β spin:

$$\boldsymbol{P}^{\alpha}_{p,q} = (\boldsymbol{c}_{\varphi}\boldsymbol{X})^{+}\boldsymbol{c}_{\psi} = \boldsymbol{c}_{\varphi}\boldsymbol{S}_{\psi,\varphi}{}^{-1+}\boldsymbol{c}_{\psi}, \tag{14}$$

$$\boldsymbol{P}^{\beta}_{p,q} = \boldsymbol{c}_{\bar{\varphi}'}\boldsymbol{S}_{\bar{\psi}',\bar{\varphi}'}{}^{-1+}\boldsymbol{c}_{\bar{\psi}'}, \tag{15}$$

where $\boldsymbol{c}$ is the LCAO coefficient matrix of the basis AO's $\boldsymbol{\chi}$:

$$\boldsymbol{\psi} = \boldsymbol{\chi}\boldsymbol{c}_{\psi}, \tag{16}$$

$$\boldsymbol{\varphi} = \boldsymbol{\chi}\boldsymbol{c}_{\varphi}. \tag{17}$$

By the use of the partial bond order, P_{rs}, between the AO's χ_r and χ_s defined as the (r,s) element of the matrix $\boldsymbol{P}$, we obtain:

$$\begin{aligned} H_{p,q} = {} & [\sum_{r}\sum_{s}(P^{\alpha}_{rs}+P^{\beta}_{rs})(t_{rs}+v_{rs}) \\ & + \sum_{r}\sum_{s}\sum_{t}\sum_{u}(P^{\alpha}_{rs}P^{\alpha}_{tu}+P^{\beta}_{rs}P^{\beta}_{tu})/2 \\ & \cdot\{(rs|tu)-(rt|su)\} + \sum_{r}\sum_{s}\sum_{t}\sum_{u}P^{\alpha}_{rs}P^{\beta}_{tu}(rs|tu) \\ & + \sum_{\alpha<\beta}\sum Z_{\alpha}Z_{\beta}/R_{\alpha\beta}]\cdot\boldsymbol{S}_{p,q}, \end{aligned} \tag{18}$$

where:

$$t_{rs} = \int \chi_r(1)(-1/2\Delta_1)\chi_s(1)\mathrm{d}v_1,$$

$$v_{rs} = \int \chi_r(1)(\sum_{\alpha} -Z_{\alpha}/r_{1\alpha})\chi_s(1)\mathrm{d}v_1,$$

and:

$$(rs|tu) = \iint \chi_r(1)\chi_t(2)(1/r_{12})\chi_s(1)\chi_u(2)\mathrm{d}v_1\mathrm{d}v_2.$$

When the wave functions Ψ_p and Ψ_q are represented by linear combinations of the Slater determinants, the matrix element, $H_{p,q}$, is given by the sum of the integrals obtained in a similar manner.[11]

Results of Calculation

Figure 3 shows the relative spacings of the MO's of methylfluoride and the fluoride ion in an isolated state.

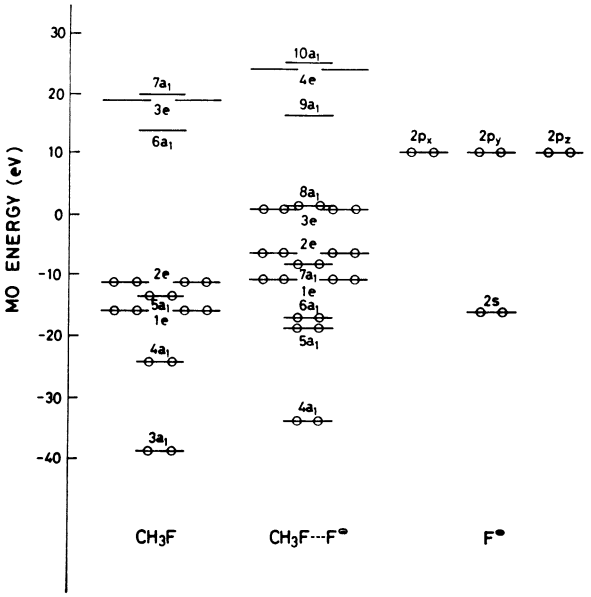

Fig. 3. Orbital diagram of interaction between methylfluoride and fluoride ion. Orbital exponents were taken after Hehre *et al.*[20]

The SCF MO levels of the composite system are also given in Fig. 3, although they are not necessary for our isolated-molecule approach to chemical interactions. They are used later in order to compare our results with the usual supermolecule calculation of the interacting system by the aid of configuration analysis. The matrix elements of Eq. 2 are given in Tables 1 and 2 with regard to some mono- and diexcited and electron-transferred configurations. It may be seen that the transferred configuration in which an electron is moved from the $2p_x$ of the fluoride ion to the LUMO of methylfluoride is located low only 4.02 eV above Ψ_0 and has a large off-diagonal element 0.80 eV. The pi-type interaction between the $2p_y$ or $2p_z$ of the fluoride ion and the $3e$ MO's of methylfluoride is found to be weaker than the sigma-type interaction. Ditransferred configurations can scarcely contribute to the stabilization of the system.

Table 1. The energies $(H_{p,p}-H_{0,0})$ of monoexcited and monotransferred configurations (upper) and diexcited and ditransferred configurations (lower) above Ψ_0 (in eV)

		j[a]		
		$6a_1$	$3e$	$7a_1$
i[a]	$5a_1$	21.474	—	26.105
		35.320	—	61.207
	$2e$	—	24.420	—
		—	63.667	—
k[a]	2s	30.880	—	36.510
		94.747	—	99.948
	$2p_x$	4.015	—	9.661
		43.448	—	48.667
	$2p_{y,z}$	—	9.215	—
		—	49.958	—

a) i and j stand for the occupied and unoccupied MO's of methylfluoride respectively, and k denotes the occupied MO's of the fluoride ion.

Table 2. The interaction integrals $(H_{0,p}-S_{0,p}H_{0,0})$ of monoexcited and monotransferred configurations (upper) and diexcited and ditransferred configurations (lower) (in eV) (The values in parentheses indicate the intramolecular portions.)

		j[a]		
		$6a_1$	$3e$	$7a_1$
i[a]	$5a_1$	1.258	—	0.035
		4.874 (4.873)	—	0.759 (0.758)
	$2e$	—	0.307	—
		—	0.852 (0.852)	—
k[a]	2s	0.336	—	0.193
		0.003	—	0.001
	$2p_x$	0.803	—	0.239
		0.013	—	0.000
	$2p_{y,z}$	—	0.351	—
		—	0.003	—

a) The same as in Table 1.

The locally diexcited configurations in methylfluoride possess large off-diagonal matrix elements with Ψ_0, although they lie very high. These integrals originate, however, principally from intramolecular electron repulsions and, hence, should be further partitioned into several terms in evaluating the intermolecular interaction energy. The values in parentheses indicate the intramolecular parts. One may see that the enhancement of diexcited configurations due to the intermolecular interaction is negligibly small in this case.[12] The large matrix element, 1.26 eV, for the monoexcited configuration, $\Psi_{5a\to 6a}$, signifies a strong polarization of methylfluoride under the influence of the electrostatic field of the fluoride ion.

The coefficients of the ground-state wave function are given approximately by:

$$C_0 = 1 - \sum_{p\neq 0}(H_{0,p}-S_{0,p}H_{0,0})S_{0,p}/(H_{0,0}-H_{p,p}) - 1/2\sum_{p\neq 0}(H_{0,p}-S_{0,p}H_{0,0})^2/(H_{0,0}-H_{p,p})^2, \quad (19)$$

$$C_p = (H_{0,p}-S_{0,p}H_{0,0})/(H_{0,0}-H_{p,p}) + \sum_{q\neq 0,p}(H_{p,q}-S_{p,q}H_{0,0}) \cdot (H_{0,q}-S_{0,q}H_{0,0})/\{(H_{0,0}-H_{p,p})\cdot(H_{0,0}-H_{q,q})\}. \quad (20)$$

They are listed in Table 3. The monotransferred configuration in which an electron is shifted from the $2p_x$ of the fluoride ion to the $6a_1$ MO of methylfluoride is found to be dominant among the various electron configurations except for Ψ_0. The electron transfer from the $2p_y$ and $2p_z$ of the fluoride ion to the $3e$ MO's of methylfluoride is not effective. The present calculation indicates that the reaction is initiated by the attack of the 2p orbitals of the anion. The participation of the 2s orbital is found to be minor at the beginning of the reaction.

The electron density of the composite system can be divided into several terms:

$$\rho = \rho(CH_3F) + \rho(F^-) + \rho_K + \rho_\Pi + \rho_D + \cdots, \quad (21)$$

where $\rho(CH_3F)$ and $\rho(F^-)$ mean the electron densities of the isolated methylfluoride and fluoride ion respectively, and where ρ_K, ρ_Π, and ρ_D represent the exchange, polarization, and delocalization interactions respectively. The polarization density covers the locally excited electron configurations, while the delocalization density consists of the electron-transferred configurations involved in Table 3. The exchange density is defined by:

$$\rho_K = \rho_{0,0} - \rho(CH_3F) - \rho(F^-). \quad (22)$$

The exchange, polarization, and delocalization densities are illustrated in Fig. 4. The exchange interaction brings about a negative difference density between the attacking anion and the substrate, since both of the reactants possess closed-shells. On the other hand, the electron delocalization from the anion to methylfluoride produces a positive density in the intermolecular region. The competition between the exchange interaction and the delocalization interaction seems to govern the appearance of the new chemical bond to be formed between the reagent and the reactant. The polarization of methylfluoride induced by the electrostatic field of the fluoride ion causes a drift of electrons from carbon to fluorine to increase the polarity of the bond to be broken.

The energy of the interacting system is divided in a similar manner[4b] for the ground-state of the interacting

Table 3. The expansion coefficients of the ground-state wave function of the interacting system obtained by perturbation calculations[b]

$C_0=0.966$		j[a] $6a_1$	$3e$	$7a_1$
i[a]	$5a_1$	0.059	—	0.001
		0.138	—	0.012
	$2e$	—	0.013	—
		—	0.013	—
k[a]	2s	0.011	—	0.005
		0.000	—	0.000
	$2p_x$	0.200	—	0.025
		0.000	—	0.000
	$2p_{y,z}$	—	0.038	—
		—	0.000	—

a) The same as in Table 1. b) Absolute values are given. The upper numbers correspond to monoexcited and monotransferred configurations, and the lower ones, to diexcited and ditransferred configurations.

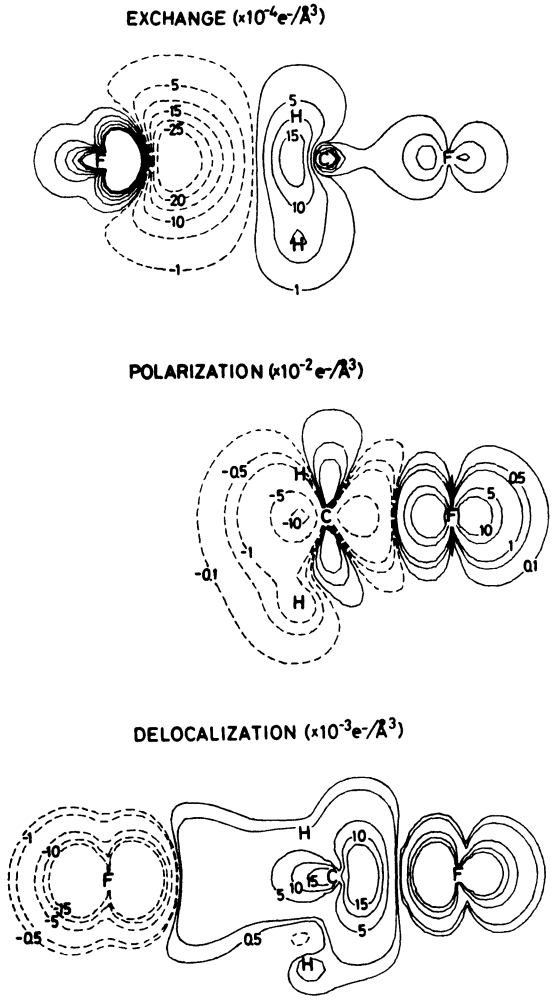

Fig. 4. Contour maps for the exchange, polarization, and delocalization densities in x-z plane at y=0.

system:

$$E_g = E(CH_3F) + E(F^-) + \varepsilon_Q + \varepsilon_K + \varepsilon_{II} + \varepsilon_D + \cdots, \quad (23)$$

where $E(CH_3F)$ and $E(F^-)$ are the energies of the isolated reactants and where ε_Q, ε_K, ε_{II}, and ε_D mean the Coulomb, exchange, polarization, and delocalization energies respectively. We have $\varepsilon_Q = -0.271$ eV, $\varepsilon_K = 0.110$ eV, $\varepsilon_{II} = -0.081$ eV, and $\varepsilon_D = -0.198$ eV for this system.

Configuration Analysis

An alternative way of calculating the coefficients in Eq. 1 is the configuration analysis of the SCF MO wave function of the interacting systems.[10,13] The given SCF wave function, Ψ, of the composite system can be expanded in terms of the various electron configurations, Ψ_p, of the reactants. Table 4 presents the result of the analysis of the wave function without CI. A comparison of the results given in Table 4 with those in Table 3 indicates that a single determinantal wave function describes the basic feature of the interaction pretty well in this case.[14] The inclusion of CI with the diexcited configurations of the composite system in which a pair of electrons are removed from an occupied MO and placed in an unoccupied MO improves the wave function appreciably, as is shown in Table 5. That is, the diexcited configurations in methylfluoride are recovered. The changes in the occupation numbers of the MO's of methylfluoride and the fluoride ion due to the interaction are given in Table 6.[15] The results confirm our conclusion that the electron delocalization from the $2p_x$ orbital of the fluoride ion to the $6a_1$ MO of methylfluoride plays the key role in the early stage of the S_N2 reaction.[16]

Table 4. The expansion coefficients of the ground-state wave function of the interacting system without CI obtained by configuration analysis[b]

$C_0 = 0.981$		j[a] $6a_1$	$3e$	$7a_1$
i[a]	$5a_1$	0.049	0	0.000
		0.001	0	0.000
	$2e$	0	0.006	0
		0	0.000	0
k[a]	2s	0.012	0	0.005
		0.000	0	0.000
	$2p_x$	0.159	0	0.021
		0.013	0	0.000
	$2p_{y,z}$	0	0.035	0
		0	0.001	0

a) The same as in Table 1. b) The same as in Table 3.

Table 5. The expansion coefficients of the ground-state wave function of the interacting system with CI obtained by configuration analysis[b]

$C_0 = 0.968$		j[a] $6a_1$	$3e$	$7a_1$
i[a]	$5a_1$	0.054	0	0.001
		0.119	0.004	0.009
	$2e$	0	0.006	0
		0.014	0.012	0.005
k[a]	2s	0.012	0	0.005
		0.002	0.000	0.002
	$2p_x$	0.159	0	0.020
		0.001	0.001	0.000
	$2p_{y,z}$	0	0.034	0
		0.000	0.000	0.000

a) The same as in Table 1. b) The same as in Table 3.

Table 6. The changes in the occupation numbers of the MO's due to the interaction

	MO	Isolated state	Interacting state
CH_3F	$4a_1$	1.997	1.997
	$1e$	1.995	1.996
	$5a_1$	1.966	1.968
	$2e$	1.999	1.999
	$6a_1$	0.036	0.064
	$3e$	0.005	0.006
	$7a_1$	0.003	0.003
F^-	2s	2.000	1.999
	$2p_x$	2.000	1.970
	$2p_{y,z}$	2.000	1.998

Discussion

As the first attempt to test the validity of our analysis, we carried out a preliminary evaluation of the expansion coefficients by the use of a perturbation formalism. The breakdown of the energy and the electron density was made tentatively by utilizing the coefficients. It may be unnecessary to say that they can be replaced by those derived from a configuration analysis of an SCF wave function of the interacting system. In this respect, the present method retains the flexibility of adapting to any degree of sophistication in the MO methods. Attempts to get information about the aspects of complicated chemical reactions by means of elaborate MO calculations seem to be getting more and more frequent in organic chemistry with the progress of computing facilities. On the other hand, the concept of orbital interaction based on rather simplified reaction models has provided us with some governing principles of chemical reactions.[17] Though qualitative in nature, the approach offers a promise of uncovering new insights into chemical reactions. In this study, we preferred a configuration interaction approach[4b] to the one-electron-orbital interaction approach,[17] because the former is expected to be capable of elucidating the characteristics of chemical interactions in a more acceptable manner both chemically and physically.

We have focused our attention mainly on the development of a method of relating the qualitative but lucid theory of molecular interactions to up-to-date computations of chemically interacting systems in a quantitative way. The numerical results presented here with regard to an S_N2 reaction do not necessarily give us novel information about the nature of the reaction. One may recognize, however, that further applications and possible refinements to fit for various kinds of reactions, involving open-shells, external perturbations,[18]

and so on, will verify the utility of our method for studying the molecular mechanisms of chemical reactions.

It has been demonstrated in this calculation that our isolated-molecule approach gives us a wave function which is comparable to the one obtained by the SCF CI calculation of the composite system. The usual SCF MO method possesses a serious drawback in that it fails to give a stable solution for weakly interacting systems. Therefore, it is necessary to employ the multiconfiguration SCF MO method in place of the single configuration SCF MO method to study weak interactions. On the contrary, our present method is quite useful in dealing with loosely bound systems, such as the early stages of chemical reactions and dissociation processes. Applications to strongly interacting systems by enlarging the basis electron configurations are in progress.

Finally, it should be noted that the destabilization of an interacting system due to the necessary distortion of the reactants in the course of the reaction must be an important source of activation energy, though the distortion is likely to take place in such a way as to promote further electron delocalization.[19] Accodingly, in order to obtain a reasonable activation energy from an MO calculation, it seems to be important to employ a basis set which is able to reproduce the energy change for a wide range of molecular deformations of the reactants.

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