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An MO-Theoretical Calculation of Solvent Effect upon the $NH_3 + HF = NH_4F$ Reaction

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An *ab initio* molecular orbital calculation was done as to a reacting system, $NH_3 + HF = NH_4F$, with the inclusion of the solvent effect as the origin of dipolar field. The reactants were assumed to stay in dimers, $(NH_3)_2$ and $(HF)_2$, in advance to the reaction, and the respective partners of two reactants were regarded as point dipoles. The system was stabilized to some extent by two dipoles adopted. A study of *configuration analysis* on this system was made with and without the dipoles. Their effect was found to be favorable for proceeding of the reaction.

Key words: Reactivity – Solvent effect

1. Introduction

Solvent effect upon reaction rates and mechanisms has been of long-standing interest to both physical and organic chemists [1]. And the effect in the course of the liquid-phase reaction is microscopically understood as the interactions between reactants and solvent molecules, called *solvation*. Then the interactions have been interpreted in the theoretical word by partitioning them into several terms, such as Van der Waals force, hydrogen bonding, electrostatic force, and charge-transfer effect. Of course, which plays the major role in the reaction process among them is dependent upon the type of reactions. For example in the case of the Menschutkin reaction between alkyl halides and amines, the electrostatic term was pointed out to be of considerable importance [2].

Thus in order to clarify the manner in which the solvent effect operates, it is indispensable to seek the nature of the *interactions* systematically and elaborately.

Then it seems an attractive problem for theoretical investigations, especially in terms of the Molecular Orbital (MO) method, to analyze how the interactions in the solvation process affect the reactivity of a reagent and a substrate [3].

Here among the above mentioned several terms of the interactions between the solvent molecules and reactants, we tentatively take up only the electrostatic operation of the *polar* solvent upon the reactants by simplifying it as the origin of the dipolar field. As seen easily, this simplification holds several questionable points for grasping the whole feature of the solvent effect in consideration of the complexity of the phenomenon caused by the solvent. But at least as long as the dipole moment is the one measure of the *polar* solvent, the effect originated from the moment can be by no means neglected.

So in this work, as a first step to consider the interactions between the solvent molecules and the reactants, we focus our attention on the subject how the ability of the dipolar potential in the *polar* solvent can change the electronic structure and the reactivity of the reactants in the frame of MO method.

In the next section we will describe the way of the treatment of this additive effect on MO's. Then with and without this external field the numerical details about the MO calculation will be displayed for a model reaction, $NH_3 + HF = NH_4F$.

Finally in the light of these results, we discuss how the deformation of MO's in NH_3 and HF is brought about and how the orbital overlap interaction, which is the one criterion of the easiness of reactions, is changed by the influence.

2. Description of Method

For closed-shell molecules, the well known Roothaan's equation [4] is derived as Eq. (1).

$$\sum_s F_{rs} c_s^i = \varepsilon_i \sum_s S_{rs} c_s^i . \tag{1}$$

Here S_{rs} is the element of the overlap matrix and F_{rs} is that of the Fock matrix given as follows;

$$F_{rs} = H_{rs}^{\text{core}} + \sum_{t,u} P_{tu}[(rs|tu) - 1/2(rt|su)] , \tag{2}$$

where P_{tu} is the element of the bond order density matrix.

$$P_{tu} = 2 \sum_i^{\text{occ}} c_t^i c_u^i . \tag{3}$$

H_{rs}^{core} is that of the core Hamiltonian (kinetic plus potential energy in the field of fixed nuclei), and $(rs|tu)$ is the electronic repulsion integral;

$$(rs|tu) = \int\int \chi_r(2)\chi_s(2) e^2/r_{12} \chi_t(1)\chi_u(1) d\tau_1 d\tau_2 . \tag{4}$$

The LCAO (Linear Combination of Atomic Orbitals) coefficient, c_s^i, can be obtained by the usual iterative procedure.

Here the basis functions, χ_r and χ_t, are Slater Type Orbitals (STO) expanded in three Gaussian Type Orbitals (GTO)[1] for the easiness of calculation [7, 8]. Namely we adopt STO-3G (minimal) basis set for the evaluation of the integrals, H_{rs}^{core}, S_{rs} and $(rs|tu)$. Then we define a new matrix element, F'_{rs}.

$$F'_{rs} = F_{rs} + V_{rs} , \tag{5}$$

where V_{rs} is the matrix element of *any* one electronic operator, $\hat{V}(1)$.

$$V_{rs} = \int \chi_r(1) \hat{V}(1) \chi_s(1) d\tau_1 . \tag{6}$$

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[1] The Gaussian α exponents and the coefficients are taken from the least-squares fitting by Stewart [5].

At the same time we have used the *standard* Slater ζ exponents by Pople *et al.* [6].

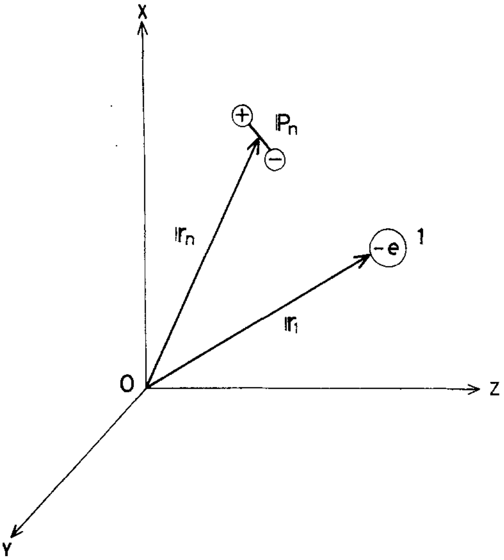


Fig. 1. The vector representation of the position of a *point* dipole $\boldsymbol{P}_n$ and an electron, 1

This operator is used so as to represent the additive external field. Of course V_{rs} will change the variational condition concerning F_{rs} and we can not predict whether Self-Consistent-Field (SCF) is obtained with respect to the new matrix element, F'_{rs}. But if the absolute value of V_{rs} is so small as to be regarded as a *perturbation*, in other words the external field is sufficiently weak, we may expect the convergence will be still gained. Here we give the following concrete formula to $\hat{V}(1)$.

$$\hat{V}(1) = \sum_{n=1}^{j} \frac{-\boldsymbol{P}_n(\boldsymbol{r}_n - \boldsymbol{r}_1)}{|\boldsymbol{r}_n - \boldsymbol{r}_1|^3}. \tag{7}$$

As well known, Eq. (7) indicates the scalar potential for one electron, 1, by the dipole moment, $\boldsymbol{P}_n (n = 1, 2, \ldots, j)$ [9]. There, $\boldsymbol{r}_n$ is the vector from the origin, O, to a dipole $\boldsymbol{P}_n$, $\boldsymbol{r}_1$ is the same with respect to electron 1 (see Fig. 1). Although $\boldsymbol{P}_n$ should be identified as a point dipole in a strict sense, the positive and the negative centers of it are divided distinctly in the representation of Fig. 1 for reader's understanding. The way to evaluate the element of V_{rs} is the same Gaussian expansion method [10] as mentioned above. Following the literature [10], V_{rs} is termed *Field Integral* (FI).

The use of Eq. (7) means that the solvent molecules are simply looked upon as the source of the dipolar field to change the electronic structure, i.e. MO's. On this point some discussion will be held later.

As for the procedure to deal with the orbital overlap interaction between two reactants, we have derived the equation in another paper [11] available here, so we hope readers would refer to it about the details.

Briefly speaking of the method, the state of the whole reacting system expressed by Ψ is divided into some states with various types of orbital interactions as shown below;

$$\begin{aligned}\Psi = C_0\Psi_0 &+ \sum_{i}^{\text{occ}}\sum_{l}^{\text{uno}} C_{i\to l}\Psi_{i\to l} + \sum_{k}^{\text{occ}}\sum_{j}^{\text{uno}} C_{k\to j}\Psi_{k\to j} \\ &+ \sum_{i}^{\text{occ}}\sum_{j}^{\text{uno}} C_{i\to j}\Psi_{i\to j} + \sum_{k}^{\text{occ}}\sum_{l}^{\text{uno}} C_{k\to l}\Psi_{k\to l} + \cdots .\end{aligned} \tag{8}$$

There, Ψ_0 is the adiabatic interacting state without any jumping of electrons, and $\Psi_{i\to l}$ means a charge-transferred state from the i-th occupied MO to the l-th unoccupied one, and the others are similar charge-transferred or excited states. Furthermore the coefficients, C_0, $C_{i\to l}$ and $C_{k\to l}, \ldots$, can be obtained by the usual configuration analysis [11–13].

In this work these quantities play an important role for our discussion.

3. Numerical Results of Calculation

A few years ago Clementi presented an extensive *ab initio* calculation [14, 15] for a reacting system, $NH_3 + HCl = NH_4Cl$, and then he detected the stabilization energy and the charge transferred in a variety of distances between the nitrogen atom in NH_3 and the hydrogen atom in HCl. We here adopt a similar reaction model, $NH_3 + HF = NH_4F$.

Then we must mention the motive for this adoption; the respective reactants, NH_3 and HF, can not exist solely before the reaction occurs, and they are thought to form the complexes, called *hydrogen bonding* such as the dimer of ammonia [16] and the zigzag polymer of hydrogen fluoride [17].

With respect to the molecules taken here, Kollman and Allen looked for the reasonable geometries of $(NH_3)_2$ and $(HF)_2$ [18, 19] to predict both dimers gain their stableness in the *linear* structure (see Fig. 2).

Fig. 2. The most stable linear structure of $(NH_3)_2$ and $(HF)_2$ by Kollman and Allen [18, 19]

As a result of taking circumstances into consideration, the reactants in the reaction, $NH_3 + HF = NH_4F$, will accept the influence by their partners, provided that the reactants had no associates in the original state except the *partners*.

Hereupon the reasons for the employment of the system, $NH_3 + HF = NH_4F$, are summarized in the following;

1. The system has a reaction path clearly grasped by the information from above mentioned Clementi's result [14, 15] or the overlap and orientation principle by Mulliken [20].

2. By assuming the reactant has only one *fellow* respectively at the beginning of the reaction, we can take into account the effect of their partners as the origin of scalar potential of two dipoles in a first approximation, reflecting that $(NH_3)_2$ and $(HF)_2$ are not so strongly bound [18, 19].

In Fig. 3 the reacting model is sketched.

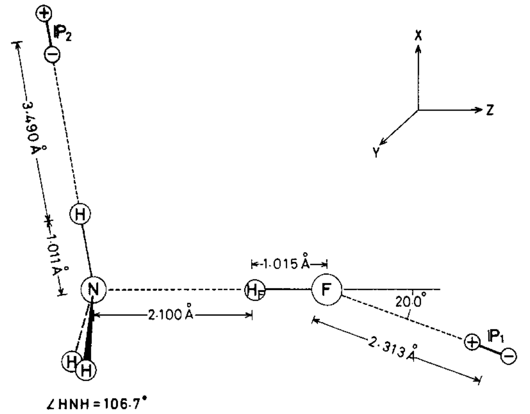


Fig. 3. The reacting model taken in this calculation. The position of $\boldsymbol{P}_1$ and $\boldsymbol{P}_2$ was taught by the work of Kollman and Allen. $\boldsymbol{P}_1$ corresponds to HF and $\boldsymbol{P}_2$ to NH_3 in Fig. 2

We used the experimental values for the moment ($|\boldsymbol{P}_1| = 1.82$ debye [21], $|\boldsymbol{P}_2| = 1.48$ debye [22]).

The geometry of ammonia is taken also from the experimental result [23]. The distance, R(N–F), is arbitrarily taken 3.115 Å, and $R(N\text{–}H_F)$ is determined by the optimization with respect to the whole system in CNDO/2 method [24] excluding the two dipoles.

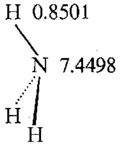
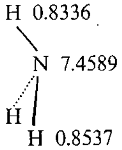
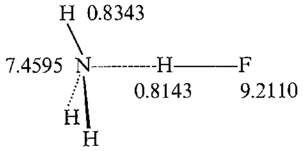
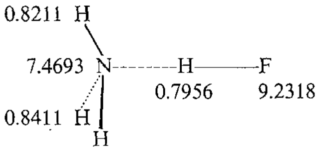
This system involving dipoles has a C_s symmetry as to x–z plane, while it has C_{3v} symmetry when they are absent.

In Table 1 the results of MO calculation are given. Here we show the difference by F'_{rs} and F_{rs} according to whether V_{rs} is contained or not. E_K and E_T mean kinetic and total energy in atomic units (a.u.). In the evaluation of MO's by F'_{rs} they always undergo the two dipoles simultaneously. But actually the other partners of the reactants, that is $\boldsymbol{P}_1$ for NH_3 and $\boldsymbol{P}_2$ for HF, give no serious effect upon MO's owing to the remarkable sensitivity to the distance, $|\boldsymbol{r}_n - \boldsymbol{r}_1|$, of $\hat{V}(1)$ in Eq. (7).

Then the comparison of (I) with (II) in Table 1 indicates the effect by $\boldsymbol{P}_1$ to prompt the tendency of the charge redistribution ($H^{\delta+}$—$F^{\delta-}$). This is because the nearer cationic center of $\boldsymbol{P}_1$ to fluorine atom attracts the charge density of HF (see Fig. 3).

As for the lowest unoccupied (LU) MO of HF, having a node along the direction of the sigma bond, the spatial extension on the contrary increases on the side of the hydrogen atom (H_F). At the same time HF molecule is a little stabilized thanks to the operation of the nearer cationic center of $\boldsymbol{P}_1$. On the other hand

Table 1. The results of MO calculation

No.	System	Dipoles?	Atom population	E_T (a.u.)	$(-E_K/E_T)$
(I)	HF	F_{rs}	H——F 0.8407 9.1593	− 98.5540	0.9940
(II)	HF	F'_{rs}	H——F 0.8199 9.1801	− 98.5672	
(III)	NH_3	F_{rs}	 H 0.8501 N 7.4498 H H	− 55.4450	0.9969
(IV)	NH_3	F'_{rs}	 H 0.8336 N 7.4589 H H 0.8537	− 55.4808	
(V)	NH_4F	F_{rs}	 H 0.8343 7.4595 N------H——F 0.8143 9.2110 H H	− 154.0094	0.9957
(VI)	NH_4F	F'_{rs}	 0.8211 H 7.4693 N------H——F 0.7956 9.2318 0.8411 H H	− 154.0601	

NH_3 in (III) experiences the migration of charge density from the hydrogen in x–z plane to both nitrogen atom and the residual two hydrogens by virtue of $\boldsymbol{P}_2$ as shown in (IV). And the highest occupied (HO) MO of NH_3, which is mainly composed of the lone pair on the nitrogen, undergoes a destabilization and the growth of the lone pair to a minor extent.

At a glance the more stabilized total energy in (IV) than in (III) may seem strange, reflecting that NH_3 is linked to the nearer anionic center in $\boldsymbol{P}_2$ and that electronic repulsion energy may increase. However the *classical* attractive energy between the anionic center of $\boldsymbol{P}_2$ and the positive nuclear charge on the hydrogen atom in x–z plane mainly overcomes the above painful condition. As a whole a small stabilization is gained also in NH_3.

From the inspection of these deviations of the quantities by the external field, we can expect the growth of the overlapping between HOMO of NH_3 and LUMO of HF, as will be shown directly by the coefficients in Eq. (8) later.

We can obtain the similar information from the comparison in (V) and (VI) both on the calculation in terms of the whole reacting system, the latter more stabilized.

Referring to (III) and (V), we should notice the decrease of the charge density on the three hydrogens of NH_3 part as a new bond ($N \cdots H_F$) is formed. It is meaningful that toward the product, $NH_4^+F^-$, the cationic component on NH_3 is first redistributed on three hydrogen atoms, shown also by Kollman and Allen [18]. The stabilization energy (ΔE) of the system in Fig 3, $\Delta E = E_T(NH_3) + E_T(HF) - E_T(NH_4F)$, are 6.5 kcal/mole in F_{rs} and 7.6 kcal/mole in F'_{rs} respectively, compared with 11.7 kcal/mole in their most stable geometry of NH_4F by Kollman and Allen.

4. The Interaction Mode of MO's

By applying the solution in Eq. (1) to a variety of the systems in Table 1, the CI (Configuration Interaction) representation of the reacting system in the form of Eq. (8) is achieved, shown below;

$$\begin{aligned} F_{rs} &: \Psi = 0.9787\,\Psi_0 + 0.0976\,\Psi_{\mathrm{HO}\to\mathrm{LU}} + 0.0048\,\Psi_{\substack{\mathrm{HO}\to\mathrm{LU}\\ \mathrm{HO}\to\mathrm{LU}}} + 0.0242\,\Psi_{\sigma\to\sigma^*} + \cdots \\ F'_{rs} &: \Psi' = 0.9772\,\Psi'_0 + 0.1029\,\Psi'_{\mathrm{HO}\to\mathrm{LU}} + 0.0054\,\Psi'_{\substack{\mathrm{HO}\to\mathrm{LU}\\ \mathrm{HO}\to\mathrm{LU}}} + 0.0238\,\Psi'_{\sigma\to\sigma^*} + \cdots, \end{aligned} \tag{9}$$

where F'_{rs} or F_{rs} corresponds to the presence or the absence of two dipoles. In this paper we use the prime for the caution of the existence of them.

Ψ_0 and Ψ'_0 denote the adiabatic interacting state without inclusion of *any* configurations different from the original one.

The coefficients attached to Ψ_0 and Ψ'_0, the overwhelming values compared with others, show that at the reacting point adopted here the original configuration without any jumping of electrons retains its majority yet. The comparison of these two coefficients gives us the knowledge of the effective operation of two point dipoles to decrease the weight of this state and to make electrons active in favor for the progress of the reaction.

Furthermore $\Psi_{\mathrm{HO}\to\mathrm{LU}}$ and $\Psi_{\substack{\mathrm{HO}\to\mathrm{LU}\\ \mathrm{HO}\to\mathrm{LU}}}$ stand for one- and two-electron transferred states from HOMO of NH_3 to LUMO of HF. These configurations do their part in increasing the weight of the ionic character of the reacting system and accelerating the formation of a new bond [25].

Here the existence of two dipoles is found to support these *invasions* of electrons into the unoccupied MO's of the other reactant. $\Psi_{\sigma\to\sigma^*}$ means one electron excited state from the third occupied MO (3σ) (in order of increasing orbital energies) to the LUMO ($1\sigma^*$) in HF. The reason for the reduction of the coefficients (0.0242→0.0238) is as follows; namely two dipoles act more remarkably on the isolated reactant, HF, than the reacting whole system, with the result of the proper charge redistribution beforehand because of the dipolar field. Therefore the contribution of the excited state to polarize electronic densities is not so necessary as in the case without dipoles.

Other states, such as tri-transferred and di-excited ones, are omitted in the above expression owing to their negligible smallness. Viewing these results as to Ψ and Ψ', we may say the two dipoles play their role to prompt the tendency to decrease the contribution of the original state, Ψ_0, along the reaction path.

Here from another standpoint this insistence will be understood more clearly. That is, as displayed in Table 2, the configuration analysis presents some vivid feature[2] in the sense of organic chemistry.

Table 2. The weights of some electronic structures

Structures	F_{rs} (in %)	F'_{rs} (in %)
$(NH_3 \cdot HF)$	97.3540	97.1504
$(NH_3^- \cdot HF^+)$	0.0071	0.0054
$(NH_3^+ \cdot HF^-)$	2.4705	2.6742
$(NH_3 \cdot HF^*)$	0.0901	0.0873
$(NH_3^* \cdot HF)$	0.0141	0.0163
$(NH_3^{--} \cdot HF^{++})$	0.0000	0.0000
$(NH_3^{++} \cdot HF^{--})$	0.0836	0.0969
$(NH_3^{+-} \cdot HF^{-+})$	0.0001	0.0000
$(NH_3^* \cdot HF^*)$	0.0000	0.0000
Total	99.9487	99.9434

There the evaluation by the use of the method was done as to both models with and without two dipoles, denoted by F'_{rs} and F_{rs} in the same way as before. Hereupon $(NH_3 \cdot HF)$ means the covalent structure. $(NH_3^+ \cdot NF^-)$ is an ionic structure with one electron moving from NH_3 to HF, and $(NH_3^- \cdot HF^+)$ holds the reverse relation. $(NH_3^* \cdot HF)$ is the one electron excited state in NH_3, and $(NH_3 \cdot HF^*)$ is the same in HF. $(NH_3^{+-} \cdot HF^{-+})$ means two electron transferred ionic structure mutually between two entities. For other structures in Table 2, the analogy is available. From the tabulated results the favorable effect of dipoles upon the proceeding of the reaction can be observed, particulary in that the weight of $(NH_3^+ \cdot HF^-)$ and $(NH_3^{++} \cdot HF^{--})$ is made larger. $(NH_3 \cdot HF^*)$ contains the above mentioned $\Psi_{\sigma \to \sigma^*}$ state. Summing up the tabulated values with respect to the two cases, F_{rs} and F'_{rs}, we can get the totals which are almost 100% in both cases, indicated in the bottom of the Table. This gives the ground for demonstrating the adequacy regarding the employment of only the tabulated electronic structures in representing the whole state, Ψ and Ψ'.

Next in Table 3, the overlap bond population between the nitrogen atom in NH_3 and the hydrogen atom in HF (H_F) is given in the partitioned form as regards to four different types of the orbital interaction. There, "Exchange type" corresponds to the population produced by the overlap between both occupied orbitals of the two reactants in their beginning, and this term yields antibonding population as shown in the table. However this tendency is weakened by the inclusion

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[2] The involvement of overlap integrals makes somewhat intricate the actual calculation. The derivation of the equation used here will be noted elsewhere by one of the authors (S.K.).

Table 3. The atomic bond population between N and H_F

Types	F_{rs}	F'_{rs}
Exchange type	−0.0225	−0.0216
CT type	0.0365	0.0387
Back CT type	−0.0002	−0.0001
Both unocc	−0.0000	−0.0000
Total	0.0138	0.0169

of dipoles to some extent. "CT type" is the population originated from the charge transfer interaction between the occupied orbitals in NH_3 and the unoccupied ones in HF.

This mode presents the considerable quantity to the bond formation with the larger value in F'_{rs} than F_{rs}. Thus the importance of the charge transfer interaction can be confirmed in the standpoint of the analysis of the new bond formation [26].

Other types, "Back CT type" which means the donation from HF to NH_3 and "Both unocc" which denotes the orbital interaction between both unoccupied ones of two, are found to play a minor role in the bond formation.

As a whole the dipolar field helps to form a new bond also. Configuration analysis offers another interesting quantity termed *Occupancy of* MO's [11]. When the interaction between two molecules is absent, their MO's are filled with *two* electrons respectively. But the occurrence of the electron migration or the excitation by the interaction somewhat changes this number, that is, the *old* occupied orbitals lose the portion of the number, and the *old* unoccupied ones gain the electronic density a little.

Table 4. Occupancy of MO's in the interacting state

$1\sigma^*$	0.0264	0.0285
$\bar{\pi}$	2.0000	2.0000
π	2.0000	2.0000
3σ	1.9988	1.9989
2σ	2.0000	2.0000
1σ	2.0000	2.0000
MO's of HF	F_{rs}	F'_{rs}
$2e_2$	0.0001	0.0001
$2e_1$	0.0001	0.0001
$4a_1$	0.0001	0.0001
$3a_1$	1.9749	1.9729
$1e_2$	1.9999	1.9999
$1e_1$	1.9999	1.9999
$2a_1$	1.9997	1.9997
$1a_1$	2.0000	2.0000
MO's of NH_3	F_{rs}	F'_{rs}

Table 4 displays these rearrangements in MO's owing to the active electrons, where these notations of the respective MO's are defined in the case without two dipoles (F_{rs}) [3].

There the notable change can be found in $1\sigma^*$ of HF and $3a_1$ in NH_3. These are both, in a greater part, due to the particular orbital interactions, that is, $\Psi_{\mathrm{HO}\to\mathrm{LU}}$ and $\Psi_{\substack{\mathrm{HO}\to\mathrm{LU}\\ \mathrm{HO}\to\mathrm{LU}}}$. The decrease in 3σ of HF is mainly owing to the appearance of $\Psi_{\sigma\to\sigma^*}$ in Eq. (9). Comparison of F_{rs} with F'_{rs} again demonstrates the efficient operation of the two dipoles upon the inclination to change the original occupancy more and more.

5. Conclusive Discussion

In this report we have described a method to inform the MO's of the solvent effect as if it could be reduced to that of some dipole moments. We have here only *two* dipoles tentatively as the source of the potential which are the partners of two reactants. And the two dipoles, $\boldsymbol{P}_1$ and $\boldsymbol{P}_2$, in Fig. 3 are the simplified products in $(HF)_2$ and $(NH_3)_2$ by the use of the result by Kollman and Allen. Of course if we had no knowledge about the report, we could not determine the position and the direction of $\boldsymbol{P}_1$ and $\boldsymbol{P}_2$, i.e. the *partners* after the simplification. In other words, it is a too crude abstraction to take only the dipole-electron interaction into account in the dimer systems in Fig. 2. That is, even if the reactants had only one fellow to interact with each other, more detailed informations are necessary for the description of the *interaction.* Then the first step to improve the condition in the frame of this method seems to adopt the operator $\hat{V}(1)$ in Eq. (6) of another type as well as the dipolar potential, already set forth in this work. In this respect the circumstances are not so troublesome for us, and now with the utilization of other operators a new calculation is in progress concerning a typical SN_2 reaction. But in spite of these improvements the enough accuracy will not be gained yet as far as the *statical* treatment for many solvent molecules is not considered. This procedure will be included in the future.

Viewing the above mentioned weak point of this calculation on $NH_3+HF=NH_4F$ in a quantative sense, here again we would like to insist our situation that we do not intend to seek *accurate* properties as to the interacting mode from the energetic standpoint, but to show the analytical and concrete representation about the phenomenon of the interactions, called *solvation.*

Lastly the results of this work are summarized as follows; *if the two reactants in a reaction,* $NH_3+HF=NH_4F$, *originally exist in their dimers,* $(NH_3)_2$ *and* $(HF)_2$, *and furthermore the influence of the respective partners of the reactants are sufficiently weak to be regarded as if it could be simply approximated to that of the dipolar field, the effect of the partners works favorably for proceeding of the reaction.*

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[3] The two dipoles lower the symmetry of the whole system from C_{3v} to C_s with respect to x–z plane, mentioned before (see Fig. 3). Therefore as for the state including them (F'_{rs}), these notations can not be applied. But the deviation is so small that a new notation for C_s symmetry is not prepared in Table 4.

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