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An *ab initio* MO Study of the Hydrogen Bond in NH_3•HF

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The structure and properties of the hydrogen bond have been of long-standing interest to both theoretical and experimental chemists.[1] Especially by the use of the molecular orbital (MO) method, many studies have been carried out of relatively simple systems including, for example, the O—H···O, N—H···N, N—H···F bonds.[2]

Among the systems, a mixed dimer, NH_3···HF, is regarded as a strong complex, compared with such other dimers as $(NH_3)_2$ and $(HF)_2$. The several geometries of the complex were extensively studied by Kollman and Allen,[3] who found the *linear* structure to be the most stable one.

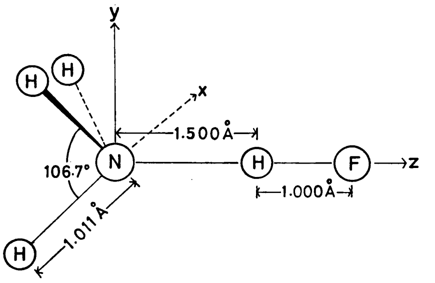

Fig. 1. The geometry of the NH_3·HF complex taken in this calculation from Ref. 3.

We thought it would be an interesting subject to detect the nature of the *strong* N···H bond in Fig. 1, taken from the results of Ref. 3. In order to analyze this in the frame of the MO method, we have used the technique which regards the MO's of NH_4F as the product of the orbital mixing of the MO's of NH_3 with those of HF.[4,5] In other words, the occupied MO's of the NH_4F system (Ψ_g, $g=1, 2, \cdots, 10$) are approximated as linear combinations of occupied MO's (a_i, $i=1, 2, \cdots, 5$ in NH_3 and b_k, $k=1, 2, \cdots, 5$ in HF) and unoccupied MO's (a_j, $j=6, 7, 8$ in NH_3 and b_l, $l=6$) of its two subsystems:

$$\Psi_g=\sum_{i=1}^{5}C_i{}^{(g)}a_i+\sum_{j=6}^{8}C_j{}^{(g)}a_j+\sum_{k=1}^{5}C_{k+8}^{(g)}b_k+C_{l+8}^{(g)}b_l \qquad (1)$$

The MO's used here are constructed by means of the minimal-basis set of Slater-type Orbitals (STO's) expanded into *three* Gaussian-type Orbitals (GTO's).[6,7] Then, all the integrals of STO's necessary for composing the Fock matrix can easily be evaluated by this expansion.

In Table 1 the calculated results of the MO's are shown in relation to the equilibrium geometry in Fig. 1, except that the configuration of NH_3 is taken from the experimental one.[8]

($-E_K/E_T$) shows satisfactory optimization with respect to the exponents of STO's[9] adopted here (Virial Theorem).

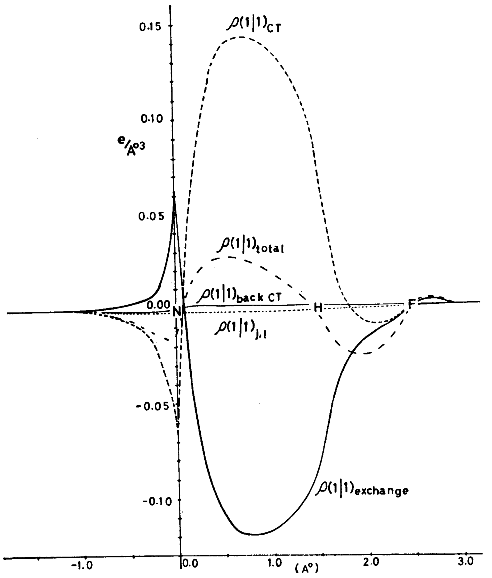

Fig. 2. The profile of the *intermolecular* charge density between NH_3 and HF.

By the use of the calculated MO's, the charge density in the *intermolecular* part as regards the two monomers (N···H region) can be obtained in the frame of the above-mentioned technique. In Fig. 2 the profile of the intermolecular charge density ($\rho(1|1)_{\text{total}}$), cut n x-y plane, is depicted in the following partitioned form:

$$\rho(1|1)_{\text{total}}=\rho(1|1)_{\text{exchange}}+\rho(1|1)_{\text{CT}}+\rho(1|1)_{\text{back CT}}+\rho(1|1)_{j,l} \qquad (2)$$

$$\rho(1|1)_{\text{cxchange}}=2\sum_{g=1}^{10}\Big[\sum_{i=1}^{5}\sum_{k=1}^{5}C_i{}^{(g)}C_{k+8}^{(g)}\{a_i(1)b_k(1)+b_k(1)a_i(1)\}\Big] \qquad (3)$$

$$\rho(1|1)_{\text{CT}}=2\sum_{g=1}^{10}\Big[\sum_{i=1}^{5}C_i{}^{(g)}C_{l+8}^{(g)}\{a_i(1)b_l(1)+b_l(1)a_i(1)\}\Big] \qquad (4)$$

$$\rho(1|1)_{\text{back CT}}=2\sum_{g=1}^{10}\Big[\sum_{k=1}^{5}\sum_{j=6}^{8}C_{k+8}^{(g)}C_j{}^{(g)}\{a_j(1)b_k(1)+b_k(1)a_j(1)\}\Big] \qquad (5)$$

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Table 1. The results of MO calculation[a)]

NH$_3$			HF			NH$_4$F		
a_i	1a$_1$	-15.3058	b_k	1a$_1$	-25.8878	Ψ_g	1a$_1$	-25.6837
	2a$_1$	-1.1050		2a$_1$	-1.4523		2a$_1$	-15.3799
	1e	-0.5680		3a$_1$	-0.5560		3a$_1$	-1.3270
	3a$_1$	-0.3651		1e	-0.4555		4a$_1$	-1.1657
a_j	4a$_1$	0.6607	b_l	4a	0.5520		1e	-0.6260
	2e	0.7151					5a$_1$	-0.5540
							6a$_1$	-0.3363
							2e	-0.3193
							7a$_1$	0.6080
							3e	0.6560
							8a$_1$	0.8199
$E_K=55.2705$ $E_T=-55.4450$ $(-E_K/E_T)=0.9969$			$E_K=97.9823$ $E_T=-98.5556$ $(-E_K/E_T)=0.9942$			$E_K=153.6836$ $E_T=-154.0059$ $(-E_K/E_T)=0.9979$		

a) E_K means the kinetic energy, and E_T the total energy. The exponents of STO's are the *standard* values by Pople *et al.* in Ref. 9. The signs of MO's (a$_1$ and e) are termed according to the irreducible representation of C_{3V} symmetry at the whole system. Energies are in atomic unit.

$$\rho(1|1)_{j,l} = 2\sum_{g=1}^{10}[\sum_{j=6}^{8}C_j{}^{(g)}C_{l+8}^{(g)}\{a_j(1)b_l(1)+b_l(1)a_j(1)\}] \quad (6)$$

First, in this figure $\rho(1|1)_{\text{exchange}}$ shows a negative component which is unfavorable for the bond formation and is originated from the orbital interaction between the occupied orbitals in NH$_3$ and the occupied orbitals in HF. The operation of this orbital interaction essentially corresponds to the *exchange* repulsion force, shown in the example of the helium molecule.

On the other hand, $\rho(1|1)_{\text{CT}}$ stands for the density caused by the charge-transfer (CT) interaction between the occupied orbitals in NH$_3$ and the unoccupied orbitals in HF; it has enough density to strengthen the N···H bond. The mixing of the highest occupied (HO) MO, *i.e.*, 3a$_1$ in NH$_3$, with the lowest unoccupied (LU) one, *i.e.*, 4a$_1$ in HF, is found to contribute remarkably to this available density for the N···H bond (96.31% of $\int\rho(1|1)_{\text{CT}}dv_1$).

The residual two terms in Eq. (2), $\rho(1|1)_{\text{back CT}}$ and $\rho(1|1)_{j,l}$, have no serious effect on the intermolecular charge density:

$$|\rho(1|1)_{\text{back CT}}|<0.0016\ \text{e/Å}^3,\quad |\rho(1|1)_{j,l}|<0.0003\ \text{e/Å}^3 \quad (7)$$

Here, the former corresponds to the density by the *back donation* from HF to NH$_3$, and the latter is the density coming from the orbital interaction between both originally unoccupied MO's in NH$_3$ and HF.

Thus, we come to the conclusion, apart from the electrostatic effect here, that among the several modes of orbital interaction, the particular HOMO–LUMO interaction supplies the considerable charge density in the intermolecular N···H region which overcomes the negative exchange density and results in the stabilization of the complex system.

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