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An MO Study on the Hydrogen Bond System of H_2O-HF

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An LCAO MO SCF calculation has been carried out on H_2O–HF system with a minimal STO-3G basis set, with respect to three assumed models, *i.e.* SIGMA, PI, and BIFURCATED models. A configuration analysis of the wave function has shown that charge-transferred electron configurations weakly mix into the original electron configuration in the SIGMA and PI models, while the contribution of charge-transferred configurations is negligibly small in the BIFURCATED model. The SIGMA model has been found to be most stable mainly due to the Coulombic attraction energy between the two species. The intermolecular electron density between the two interacting systems has been investigated by means of a concept of orbital interaction, leading to a conclusion that the mixing-in of the occupied MO's of H_2O with the unoccupied MO's of HF contributes slightly to the hydrogen bond in the SIGMA and PI models.

Over the last two decades, hydrogen bonding has been of increasing interest to both experimental and theoretical chemists.[1—14] Recent *ab initio* calculations by the use of LCAO MO SCF methods on several hydrogen-bonding systems have given satisfactory results in explaining the physical and chemical properties of those systems, such as the stable geometries, hydrogen-bonding energy and charge-transfer along the bond formation.[15—26] In these studies, the quantities which describe the hydrogen bonding are usually defined as the differences between those of a composite system and those of the isolated systems. Then, we should note that the resultant differences are far smaller than the corresponding quantities of normal chemical bonds. Therefore, they may depend, to some extent, upon the basis set adopted to construct the MO's. Morokuma and Winick pointed out, however, the addition of p-type functions to hydrogen and of d-type functions to oxygen in the calculation of water dimer would yield an excess stabilization, unless the MO's of monomers were of the Hartree-Fock limit.[17] Hence, we should be careful about the inclusion of the polarization functions.

Apart from these works on the Hartree-Fock level, there have been several theoretical ways to approach hydrogen-bonding. For instance, Coulson and Danielsson studied the hydrogen bond in water dimer on the basis of the valence-bond theory.[27] These theories could present chemically graspable pictures of hydrogen bond between a proton donor (A–H) and a proton acceptor (B). Although these approaches are only qualitative in comparison with the works performed by accurate MO calculations a partitioning of the interaction energies,[28—36] and the calculation of the weights of various electron configurations[37] will supply us some valuable information for an understanding of the basic feature of hydrogen bond.

Here, we take a simple hydrogen-bonding system composed of H_2O and HF[19] and analyze the wave function of the system, calculated by an *ab initio* MO method, into several important electron configurations by the aid of a configuration analysis procedure.[38—40]

Results of Calculation

The SCF MO's, ϕ_i, were constructed by linear combinations of the basis atomic orbitals (AO), χ_r,[41]

$$\phi_i = \sum_r c_r{}^i \chi_r$$

In this work, we employed the minimal set of the Slater type orbitals (STO's), which were expanded into three Gaussian type orbitals (GTO's).[42,43] In this STO-3G expansion, the values of the exponents (α_m) and the coefficients (d_m) of the GTO were taken after Stewart.[44]

$$\chi_r = \mathrm{STO}(\zeta) = \sum_{m=1}^{3} d_m \mathrm{GTO}(\alpha_m)$$

The exponents of the STO's, ζ, were taken to be the optimized values in regard to the two monomers, H_2O and HF, obtained by Hehre, Stewart, and Pople.[45] They are given in Table 1.

TABLE 1. THE EXPONENTS ζ OF THE STO's

Molecule	Type of STO	Value
HF	H_{1s}	1.33 (1.00)[a]
	F_{1s}	8.65 (8.70)
	F_{2s} F_{2p}	2.55 (2.60)
H_2O	H_{1s}	1.28 (1.00)
	O_{1s}	7.66 (7.70)
	O_{2s} O_{2p}	2.25 (2.275)

a) Calculated by the Slater rule as a reference.

As for the hydrogen-bonding system, we considered three different geometries, SIGMA, PI, and BIFURCATED, as illustrated in Fig. 1. The geometrical parameters are given in Fig. 1 with respect to the SIGMA model. In the three models of H_2O–HF, the distance from the oxygen atom of H_2O to the fluorine atom of HF, R(O–F), was taken to be 2.72 Å. It may be natural here to suppose that the O–H and H–F bond distances will vary, depending on the type of interaction. Therefore, the most stable geometry of the hydrogen-bonding system will be determined by a delicate balance between the stabilization due to the intermolecular interaction and the destabilization due to the deformation of the two species from the most stable geometries in an isolated state. Accordingly, our assumption of the fixed nuclei of H_2O and HF in interacting states might involve an un-

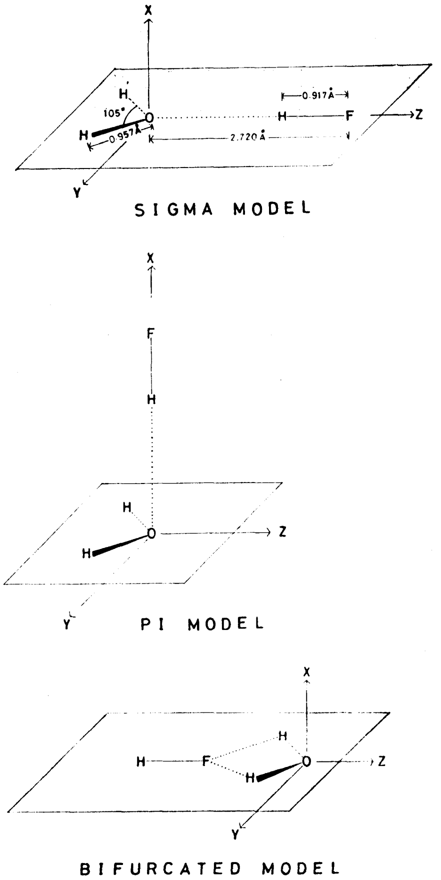


Fig. 1. The assumed models of hydrogen bonding in H_2O and HF.

certainty in studying this weakly interacting system. However, the deformations of the interacting species are usually small[19] and we hope that an approach based on an isolated molecule approximation would provide us some chemically important information on hydrogen bond.

Under the assumption mentioned above, the energy of hydrogen bond may be defined as,

$$E = E_T(H_2O\text{-}HF) - E_T(H_2O) - E_T(HF)$$

where $E_T(X)$ is the total energy of the system X (the electronic energy plus the nuclear repulsion in the fixed nuclei).

The results of the MO calculation on H_2O, HF, and H_2O–HF systems are given in Table 2. The calculation of $(-V/2T)$ (V is the potential energy and T is the kinetic energy) indicates that the assumption of the same ζ values for the composite system as those for the isolated species is not so poor. So, it seems likely that ζ's are not so sensitive to the change in the electron distribution arising from hydrogen bond formation.

The atomic populations on the three hydrogen-bonding systems calculated here show that the amount of charge transferred from H_2O to HF (ΔQ) is 0.029 in SIGMA, 0.038 in PI and −0.004 in BIFURCATED respectively. In the last model with the negative value of ΔQ, HF serves as an electron donor and H_2O as an electron acceptor. Among the three models, the PI model gives the largest ΔQ. This seems to come from the fact that the PI model contains the most effective charge-transfer interaction. This point will be discussed later in detail.

Examining $E_T(H_2O\text{–}HF)$, we see that the SIGMA model is most stable among the three models, in agreement with the result of Kollman and Allen (the linear structure in their notation).[19]

As shown in Table 2, the SIGMA model has a larger dipole moment (3.69 D) than the sum of the moments of the monomers (3.15D=1.39D+1.76D). The increase in the dipole moment comes mainly from

TABLE 2. RESULTS OF MO CALCULATION ON HF, H_2O AND $H_2O \cdot HF$ AT THE OPTIMIZED ζ OF STO-3G.
The values in the parenthesis are by other MO works or experimental (exptl.) ones.

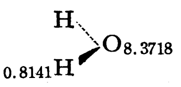
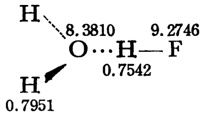
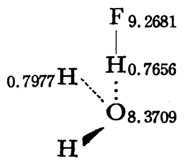
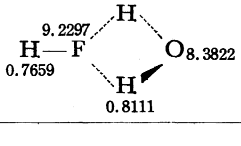
Molecule	Total energy E_T(a.u.)	Test of virial theorem $(-V/2T)$	Atomic population	Dipole moment (D)	The orbital energy of the HOMO (eV)
HF	−98.5577 (−98.5274)[45] (−100.0708)[46]	1.0019	H——F 0.7768 9.2232	1.39 (1.82)[48] exptl.	−12.11 (15.77)[50]
H_2O	−74.9515 (−75.7050)[17] (−76.0594)[47]	1.0006		1.76 (1.85)[49] exptl.	−10.27 (12.59)[51]
$H_2O \cdot HF$ SIGMA model	−173.5210 (−175.9840)[19]	1.0011		3.69	
$H_2O \cdot HF$ PI model	−173.5173	1.0011		2.60	
$H_2O \cdot HF$ BIFURCATED model	−173.5124	1.0013		3.27	

Table 3. The weights of some electronic structures of the three H_2O–HF hydrogen bond models

Electronic structures	Weights (%) SIGMA model	PI model	BIFURCATED model
$H_2O \cdot HF$	96.8740	96.5512	99.4809
$H_2O^- \cdot HF^+$	0.0636	0.0038	0.4701
$H_2O^+ \cdot HF^-$	2.8572	3.2888	0.0355
$H_2O \cdot HF^*$	0.0922	0.0584	0.0059
$H_2O^* \cdot HF$	0.0272	0.0364	0.0045
$H_2O^{-2} \cdot HF^{+2}$	0.0000	0.0000	0.0004
$H_2O^{+2} \cdot HF^{-2}$	0.0114	0.0145	0.0000
$H_2O^{+-} \cdot HF^{-+}$	0.0011	0.0001	0.0001
$H_2O^* \cdot HF^*$	0.0001	0.0000	0.0000
Total	99.9268	99.9532	99.9975

the charge-transfer from H_2O to HF. The enhancement of the moment, however, would also arise from the polarization interaction between the two monomers.

Configuration Analysis

The result of the configuration analysis of the wave function of the composite system in terms of the electron configurations of the two isolated species is given in Table 3. There, the first electronic structure ($H_2O \cdot HF$) stands for the original electron configuration without any electron shifting. In addition to this dominant configuration, several important charge-transferred and locally excited terms are presented. Here, ($H_2O^- \cdot HF^+$) indicates mono-transferred configurations with one electron migrated from HF to H_2O, and ($H_2O^* \cdot HF$) locally mono-excited configurations in H_2O. The other terms in Table 3 may be understood in a similar way.52) In these three models, the total weight covered by only these rather simple electron configurations is very close to 100%. This suggests that the other configurations omitted in Table 3, *i.e.* highly-transferred and highly-excited configurations can be neglected without a serious loss of accuracy.

As for the SIGMA and the PI models, the mono-transferred term ($H_2O^+ \cdot HF^-$) plays an important role, with the larger weight in the PI model (3.29%) than in the SIGMA model (2.86%). This superiority of the PI model to the SIGMA model in ($H_2O^+ \cdot HF^-$) arises from the more efficient charge-transfer interaction in the former than in the latter, as has been expected from the calculation of ΔQ. The next important term in these models is ($H_2O \cdot HF^*$), having a larger weight in the SIGMA model (0.09%) than in the PI model (0.06%). Considering the contributions of various electron configurations, we can approximately describe the electronic structure of H_2O–HF solely by the two terms, ($H_2O \cdot HF$) and ($H_2O^+ \cdot HF^-$).53) This calculation seems to support our insistence mentioned before

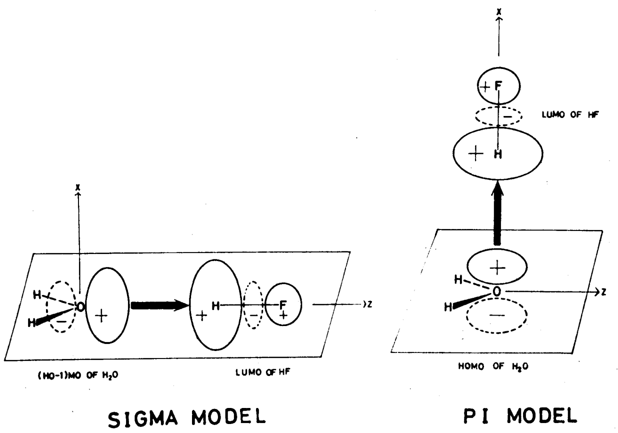


Fig. 2. A schematic representation of the dominant orbital interaction in the SIGMA and the PI models.

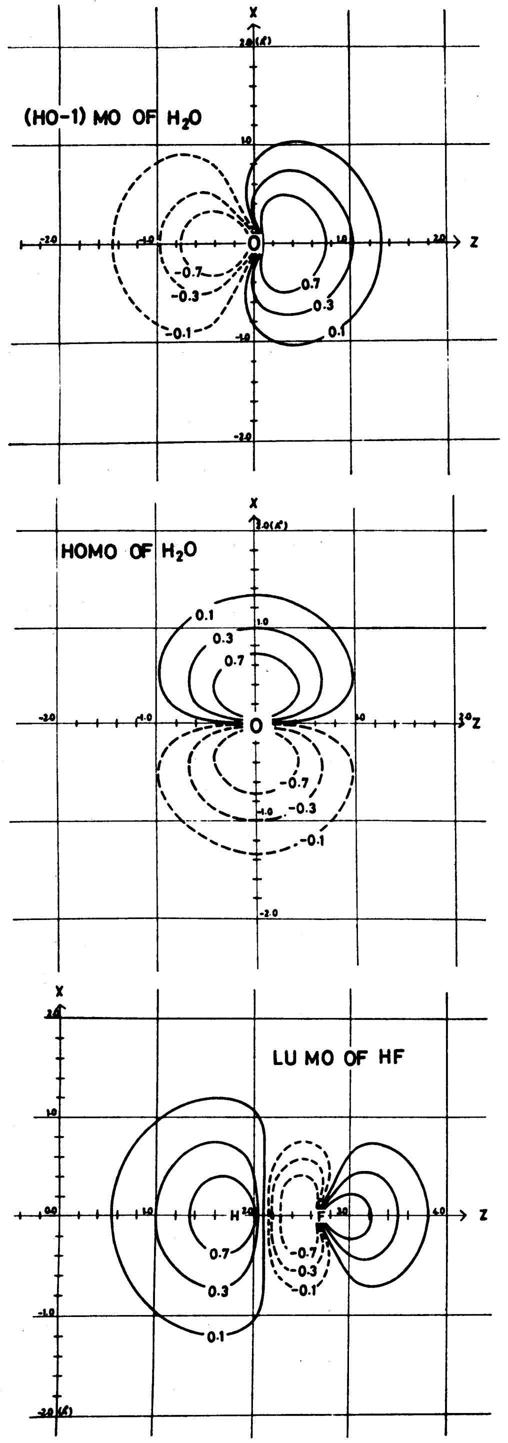


Fig. 3. The contour diagrams of HO and (HO−1) MO's of H_2O and the LUMO of HF.

that this simple hydrogen-bonding system can be regarded as an electrostatic and exchange model with a minor charge-transfer effect.

In order to examine this point a little more in detail, we evaluated the Coulomb interaction energy (E_Q) and the delocalization energy (E_D) with respect to the SIGMA and the PI models, obtaining E_Q(SIGMA) = -0.398 eV, E_Q(PI) = -0.325 eV, E_D(SIGMA) = -0.027 eV, and E_D(PI) = -0.034 eV.[54] This calculation indicates that the SIGMA model is more stabilized than the PI model through the electrostatic interaction, although the delocalization interaction is stronger in the PI model than in the SIGMA model as has been expected from the configuration analysis of the wave function. Figure 2 illustrates schematically the dominant charge-transfer interaction in the SIGMA and the PI models. The shapes of the highest occupied (HO) MO and the next highest occupied (HO-1)MO of H_2O and the lowest unoccupied (LU) MO (taken real) are shown in Fig. 3.

In the BIFURCATED model, the extremely large weight of the original configuration (99.48%) allows us one-term approximation by ($H_2O\cdot HF$). In this model, HF is an electron donor and H_2O serves as an acceptor with ($H_2O^-\cdot HF^+$)=0.47% and ($H_2O^+\cdot HF^-$)=0.04% in accordance with the calculation of ΔQ. The delocalization energy of the BIFURCATED model was found to be as small as -0.002 eV.

Chemical Binding between H_2O and HF

In the above, we found that relative orientation of H_2O and HF is mostly determined by the Coulombic and exchange interactions. However, if the hydrogen-bonding is purely electrostatic, the increase of the electron density in the region between H_2O and HF would not be yielded. The result of the present calculation, on the contrary, shows the considerable increase in the density in the intermolecular region. In order to detect the origin of this change in the electron distribution, we partition the total intermolecular electron density which is termed here $\rho(1|1)_{\text{total}}$ into the following four terms.[55,56]

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

$$\rho(1|1)_{\text{exchange}} = 2\sum_{g=1}^{10}\sum_{i=1}^{5}\sum_{k=1}^{5}C_i^{(g)}C_{k+7}^{(g)}\{a_i(1)b_k(1)+b_k(1)a_i(1)\}$$

$$\rho(1|1)_{\text{CT}} = 2\sum_{g=1}^{10}\sum_{i=1}^{5}C_i^{(g)}C_{l+7}^{(g)}\{a_i(1)b_l(1)+b_l(1)a_i(1)\} \quad (l=6)$$

$$\rho(1|1)_{\text{back CT}} = 2\sum_{g=1}^{10}\sum_{k=1}^{5}\sum_{j=6}^{7}C_j^{(g)}C_{k+7}^{(g)}\{a_j(1)b_k(1)+b_k(1)a_j(1)\}$$

$$\rho(1|1)_{j,l} = 2\sum_{g=1}^{10}\sum_{j=6}^{7}C_j^{(g)}C_{l+7}^{(g)}\{a_j(1)b_l(1)+b_l(1)a_j(1)\} \quad (l=6)$$

In the above equations, a_i and a_j stand for the occupied and unoccupied MO's of H_2O, and b_k and b_l (l=6) are the occupied and unoccupied MO's of HF. The expansion coefficients, $C_i^{(g)}$, are defined in the following way.

$$\phi_g = \sum_{i=1}^{5}C_i^{(g)}a_i + \sum_{j=6}^{7}C_j^{(g)}a_j + \sum_{k=1}^{5}C_{k+7}^{(g)}b_k + C_{l+7}^{(g)}b_l$$

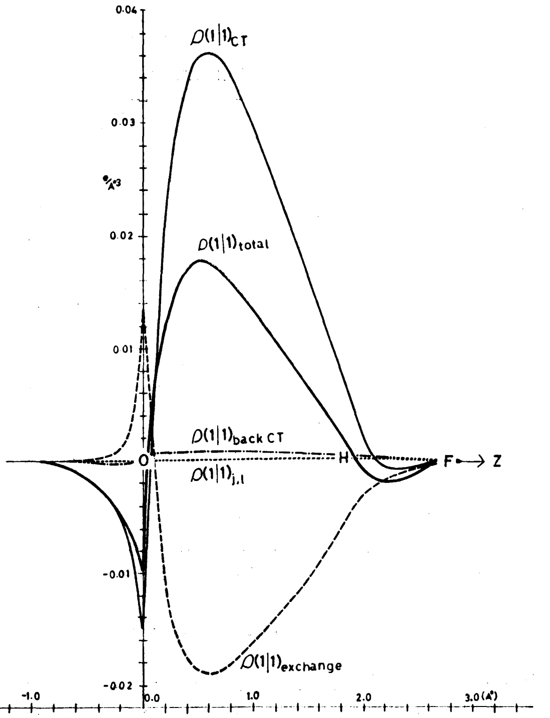


Fig. 4. The intermolecular densities in the SIGMA model.

We must mention here that the partitioning of $\rho(1|1)$ and the classification of the terms are made in an approximate sense. The density $\rho(1|1)_{\text{exchange}}$ is the intermolecular density accumulated between H_2O and HF through the overlapping of a_i with b_k (both of them are occupied MO's), $\rho(1|1)_{\text{CT}}$ comes from the interaction between the occupied MO's of H_2O and the unoccupied MO of HF, and $\rho(1|1)_{\text{back CT}}$ is due to the interaction between the unoccupied MO's of H_2O and the occupied MO's of HF. The density $\rho(1|1)_{j,l}$ stands for the density change in the intermolecular region through the overlapping of the unoccupied MO's of the two monomers. The sum $\rho(1|1)_{\text{total}}$ of these partitioned electron densities creates the usual intermolecular bond-order density. In Fig. 4, the profile of the contour map of these components with respect to the SIGMA model is illustrated. We see the change in the intermolecular electron density is composed almost exclusively of $\rho(1|1)_{\text{exchange}}$ and $\rho(1|1)_{\text{CT}}$.

$$\rho(1|1)_{\text{back CT}} < 0.0009 \text{ e/Å}^3$$

$$\rho(1|1)_{j,l} < 0.0001 \text{ e/Å}^3$$

The electron density $\rho(1|1)_{\text{exchange}}$ is negative, contributing to $\rho(1|1)_{\text{total}}$ in an antibonding way. On the contrary, $\rho(1|1)_{\text{CT}}$ presents a positive electron density in the intermolecular region, and it overcomes the negative $\rho(1|1)_{\text{exchange}}$ yielding the positive $\rho(1|1)_{\text{total}}$. This $\rho(1|1)_{\text{CT}}$ comes almost solely from the mixing of the ionic configuration ($H_2O^+\cdot HF^-$) into the original electron configuration. Therefore, the charge-transfer interaction, though small as a whole, has an important role to enforce the hydrogen bond, in addition to the purely electrostatic interaction between the two monomers. Among the terms appearing in $\rho(1|1)_{\text{CT}}$, the charge-transfer interaction between the

(HO$-$1) MO of H_2O and the LUMO of HF shown in Fig. 2 contributes dominantly to the electronic structure of the SIGMA model.

By means of a highly accurate MO calculation, Kollman and Allen showed that $\rho(1|1)_{\text{total}}$ was negative.[19)] It seems likely that the bond-order density (or the Mulliken overlap population[57)]) depends on the basis set. However, no matter whether $\rho(1|1)_{\text{total}}$ is positive or negative, $\rho(1|1)_{\text{exchange}}$ and $\rho(1|1)_{\text{CT}}$ will play their characteristic roles as mentioned above to weaken or reinforce the intermolecular chemical binding.

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