ELECTROSTATIC FORCE STUDY WITH FLOATING WAVEFUNCTION.
SHAPE OF THE H_2O MOLECULE

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A simpler way of obtaining a floating wavefunction which satisfies the Hellmann–Feynman theorem is applied to elucidate quantitatively the force and density origin of the molecular shape of H_2O. It is confirmed that the previous concept of the electrostatic force theory correctly grasps the origin of molecular geometry.

1. Introduction

The electrostatic theorem due to Hellmann and Feynman (H–F) [1] gives a completely different concept of studying chemical phenomena from the conventional energetic ones ‡. It is characterized by its marked simplicity and visuality and has been applied successfully to various fields of chemistry [2–13]. In the H–F theorem the variable is only the electron density $\rho(r)$, so that it implies that the various chemical phenomena are governed by the (dynamic) behaviour of electron density during nuclear rearrangement processes [8,11,13]. Such behaviour can be divided into two categories, i.e., the electron cloud preceding and the electron cloud incomplete following which respectively accelerates and resists the process [11]. This concept constitutes a guiding principle for the nuclear rearrangement processes on the basis of the behaviour of the electron density during the processes [10,11]. Based on a combined picture of such force and density aspects of the H–F theorem, we have developed previously the electrostatic force (ESF) theory [9–11] and shown that the theory is quite useful to systematize a variety of molecular geometries and related phenomena. Deb and his co-workers [12,13] have also given a different force approach for molecular geometry on the basis of the HOMO (highest occupied molecular orbital) postulate.

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‡ An exhaustive review of the force concept in chemistry has been given in ref. [2] and will appear in ref. [3].

On the other hand, a problem which arises in the quantitative calculation of the H–F force is the accuracy of the calculated H–F force. It is well-known that the H–F force is quite sensitive to inaccuracies of the wavefunctions used. Namely, most of the existing wavefunctions (except for the floating spherical gaussian orbital (FSGO) wavefunction [14]) have not been variationally adjusted according to the criterion of the H–F theorem and include some arbitrary errors on which the H–F force depends sensitively. As shown by Hurley [15–17] and Hall [18], such arbitary errors can be removed completely by applying the variational principle to such arbitrary factors. Here, we adopt the method of floating atomic orbitals (FAO's) proposed by Hurley. We will show that a simpler way of floating is sufficient if the H–F force acting on a particular nucleus in a system is of interest.

Thus, for the present wavefunction the H–F theorem holds, so that we can utilize the simple and visual force concepts developed previously with accuracies which are the same as those of the conventional energetics, i.e., within the accuracy correct up to second order in the error included in the wavefunction [19]. We aim by such a study to verify the previous concepts of the ESF theory, and moreover to recover a sufficient reliability of the force theoretic approaches.

2. Floating atomic orbitals

Hurley [15–17] has shown that the H–F theorem

is satisfied for the wavefunction composed of "floating" atomic orbitals, if the centers of the FAO's are determined variationally. Following his analysis, we write the energy functional of the system as

$$\mathcal{E}(\alpha_i, \lambda_i) = \langle \Psi(\lambda_i) | H(\alpha_i) | \Psi(\lambda_i) \rangle, \qquad (1)$$

where α_i denotes a set of external parameters included in the hamiltonian (e.g. nuclear coordinates R_A, R_B, ..., nuclear charge $Z_A, Z_B, ...$) and λ_i a set of variational parameters included in the normalized wavefunction Ψ. In the conventional MO calculations, λ_i is composed of a set of orbital exponents ζ_i, LCAO expansion coefficients C_i, centers of the AO's, $r_A, r'_A, ..., r_B, r'_B$, ...[*]. Since the parameters λ_i should depend on α_i, i.e., $\lambda_i(\alpha_i)$, the force acting on a nucleus A, F_A is calculated as

$$F_A = -\frac{\partial \mathcal{E}(\alpha_i, \lambda_i)}{\partial R_A} - \sum_i{}' \frac{\partial \mathcal{E}(\alpha_i, \lambda_i)}{\partial \lambda_i} \frac{\partial \lambda_i}{\partial R_A}, \qquad (2)$$

where the first term represents the H–F force and the second term, which depends upon the variational parameters λ_i, represents the error for the H–F theorem. If the wavefunction in (1) is completely variational, i.e., $\partial \mathcal{E}/\partial \lambda_i = 0$ for all λ_i, the error term in (2) vanishes identically and the H–F theorem holds. This is what Hurley [17] and Hall [18] called "floating" and "stable" wavefunctions, respectively. However, if we are interested only in the force F_A acting on a special nucleus A, a simpler wavefunction is admissible. Namely, if the orbital exponent ζ_i is fixed independent of the nuclear coordinate R_A, then $\partial \zeta_i/\partial R_A = 0$, so that the error term $(\partial \mathcal{E}/\partial \zeta_i)\partial \zeta_i/\partial R_A$ in (2) vanishes identically. The same is true for the centers $r_B, r'_B, ...$ of the AO's belonging to atoms B other than A (B ≠ A). For the AO's belonging to atom A, such an approximation is obviously wrong (i.e., even though the H–F theorem is satisfied, the value would be physically wrong). Then, we have to determine variationally the centers r_A, r'_A, ... of the AO's belonging to the atom A so that $\partial \mathcal{E}/\partial r_A = \partial \mathcal{E}/\partial r'_A = ... = 0$ [**]. Since the LCAO coefficients

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[*] We assume that these basis AO's are not complete as usual. If they are complete, the following floating procedure is unnecessary.

[**] If r_A is fixed on the nucleus A, i.e., $r_A = R_A$, as in the conventional LCAO MO calculations, the term $\partial r_A/\partial R_A = 1$ and the term $\partial \mathcal{E}/\partial R_A$ is non-zero in general so that the H–F theorem is not satisfied.

C_i are also determined variationally, $\partial \mathcal{E}/\partial C_i = 0$. Thus, it is concluded that in order to obtain reliable H–F forces F_A which satisfy the H–F theorem, it is sufficient that only the centers of the AO's belonging to atom A be determined variationally. The other AO's may be fixed onto their nuclei. This is a large simplification especially for complex systems. If we want all the forces F_A, F_B, etc. to satisfy the H–F theorem, we have to float all of the basis AO's simultaneously and determine their centers variationally.

3. Shape of H_2O molecule

Some force theoretic approaches [9–13] have already been developed to elucidate the force and density origins of molecular geometries. In any approaches the geometry of H_2O has been of key importance. It has been shown previously [9–11] that the origin of the shapes of AH_2 and AH_3 molecules is the preceding and/or the incomplete following of the electron cloud during the bending process from the linear or planar form. The preceded (or incompletely followed) electron cloud pulls the nuclei in the bending (or linearizing) direction and such forces are mostly represented by the atomic dipole (AD) force and the exchange (EC) force [9–11]. Here, we want to study quantitatively such a force and density origin of molecular geometry using H_2O as an example.

In this communication, we restrict ourselves to study only the transverse forces acting on the *terminal* protons, $F_{H\perp}$, at various bending angles, since this markedly simplifies the floating procedure as explained in the preceding section. The SCF MO calculations have been performed with the use of the minimal STO-3G bases with the standard exponents reported by Hehre et al. [20]. We have used a modified version of the GAUSSIAN 70 program. The O–H bond length was fixed at 0.990 Å which is the distance optimized by the STO-3G calculations [21]. The experimental bond length is 0.957 Å [21]. We have floated only the 1s AO's on the terminal hydrogens and the other AO's on oxygen, which are 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ AO's, were fixed onto oxygen. This is certainly a great simplification. Thus, the present wavefunction satisfies the H–F theorem for the force acting on the protons, F_H.

Table 1 summarizes the centers of the $1s_H$ FAO's and the effects of floating on the SCF energy and the

Table 1
Center of the $1s_H$ FAO and the effects of floating on the SCF energy, E and the H–F force, $F_{H\perp}$

		θ (deg)				
		0	15	30	40 (eq.)	55
FAO center (Å)	X	0.028	0.023	0.021	0.023	0.024
	Y	0.0	0.029	0.021	0.013	0.003
	R	0.028	0.037	0.029	0.026	0.024
$-10^3 \, \Delta E$ (au)		2.7	5.8	4.5	3.2	2.8
$10^2 \, F_{H\perp}$ (au) floating wavefunction						
total H–F		0.0	6.9	4.2	−0.1	−10.2
error		0.0	0.3	0.2	0.0	0.0
AD		0.0	4.6	3.9	2.6	0.6
EC (H–O)		0.0	4.1	2.6	0.0	−5.2
EC (H− −H)		0.0	0.0	−0.4	−0.9	−1.9
EGC		0.0	−1.7	−1.8	−1.8	−3.8
$10^2 \, F_{H\perp}$ (au) non-floating wavefunction						
total H–F		0.0	0.8	−0.8	−3.4	−10.9
error		0.0	6.3	5.5	3.3	0.7
AD		0.0	0.0	0.0	0.0	0.0
EC (H–O)		0.0	4.7	3.1	0.3	−4.9
EC (H− −H)		0.0	−0.3	−0.6	−1.0	−1.8
EGC		0.0	−3.6	−3.3	−2.8	−4.2

H–F force $F_{H\perp}$. Fig. 1 defines several quantities. The FAO center always lies within the HOH triangle and the distance R is about 0.03 Å which is the same order as found for H_2 by Shull and Ebbing [22]. It is about 3% of the OH distance. Although the distance X is insensitive to the bending angle θ, the distance Y, which is positive for H_2O, is sensitive to the angle θ. As seen later, this behaviour of the FAO is in accordance with the behaviour of the electron cloud during the bending process.

The stabilization energy obtained by floating is 0.003 −0.006 au (2–4 kcal/mol), which is quite small in comparison with those obtained by other ways of improving the wavefunction. This is probably due to the fact that the floating of the AO's reduces the density near the
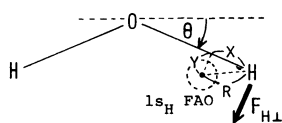

Fig. 1. Definitions of the bending coordinate θ, the center of the $1s_H$ FAO, and the transverse force acting on protons $F_{H\perp}$.

nuclei (in STO language, removes the "cusp" from the nuclear positions, though the STO-3G basis does not have such cusp), as discussed earlier by Shull and Ebbing [22]. Generally speaking, the larger the distance R, the larger the stabilization energy.

Despite the trifling effects on the SCF energy, the H–F force is affected considerably by the floating. Though the error for the H–F theorem is large for the non-floating wavefunction, it is essentially zero for the floating wavefunction (the small non-zero values are the numerical errors in the determination of the FAO centers). These errors, which are given by the second term of (2) or by $-\langle \partial\Psi/\partial R_A | H | \Psi \rangle - \langle \Psi | H | \partial\Psi/\partial R_A \rangle$, have been obtained by directly calculating the differential of the wavefunction $\partial\Psi/\partial R_A$ [23]. The equilibrium bending angle calculated from the H–F force is $\theta = 25.0°$ ($\angle$ HOH = 130.0°) with the non-floating wavefunction but it is $\theta = 40.0°$ ($\angle$HOH = 100.0°) with the floating wavefunction. The latter is just equal to the STO-3G geometry [21]. The experimental angle is $\theta = 37.8°$ ($\angle$HOH = 104.5°) [21].

Referring to the decomposition of the H–F force

into the AD, EC, and extended gross charge (EGC)
forces [9,10] shown in table 1, we see that the effect
of floating is largest for the AD force. It improves most
of the errors in the non-floating H–F force. For the
non-floating wavefunction the AD force is always zero
since our basis AO's do not include polarization func-
tions on hydrogens. When floated, the $1s_H$ AO density
pulls the proton in the direction of floating, so that the
distance Y and the AD force are parallel. The second
largest effect of floating is seen for the EGC force, i.e.,
the inward floating of the $1s_H$ AO's increases the shield-
ing of the inter-proton repulsion. The EC forces are al-
most non-affected by the floating as expected from the
order of the floating distance.

Fig. 2 shows the reorganization of electron density
during the bending process from the linear form. These
figures were prepared in order to study the behaviour
of the electron cloud in the O–H region on the right
hand side. When the molecule is bent by $15°$ from the
linear form, the electron density increases below the
O–H axis and decreases above the O–H axis. Namely,
the movement of the electron cloud in the O–H region
precedes the bending movement of the O–H axis in the
direction of the bending coordinate θ. The electron
cloud preceding forwards pulls the proton in the bend-
ing direction so that the bending process is accelerated.
Therefore, the stable geometry of H_2O is expected to
be bent in agreement with the experiment. When the
molecule reaches the equilibrium angle ($\theta = 40°$), such
preceding behaviour almost vanishes. The electron
cloud in the O–H region is almost symmetric with re-
spect to the O–H axis. A slight inwards displacement
of the electron cloud is found by detailed examination.
This is the (inward) bent bond which is necessary to
cancel the inter-proton repulsion [11]. When the mol-
ecule is bent further to $\theta = 55°$, the behaviour of the
electron density is just the reverse to that found at $\theta =
15°$. Namely, the electron cloud in the O–H region fol-
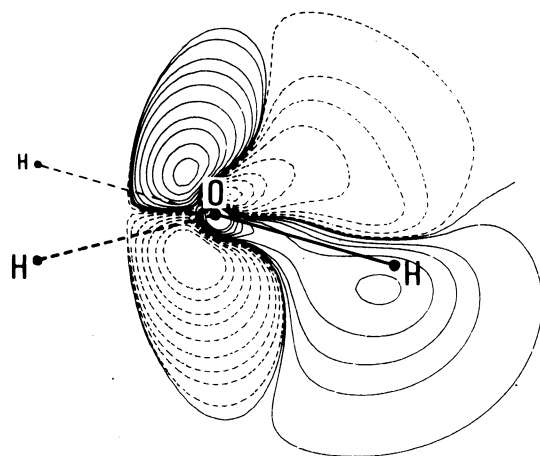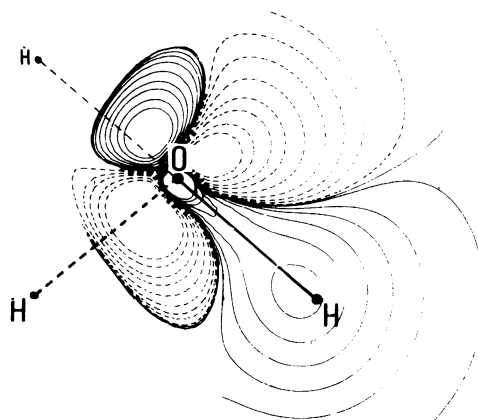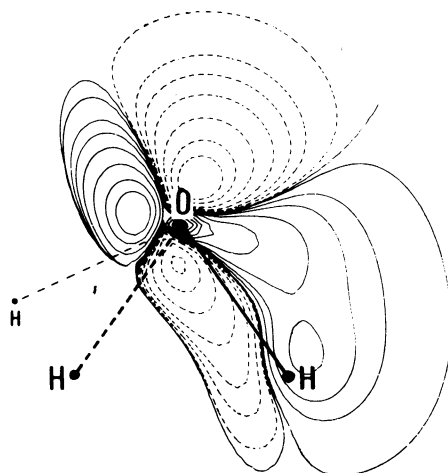lows incompletely the bending movement of the O–H

Fig. 2. Reorganization of electron density in the O–H region
on the right hand side during the bending process from the
linear form. (a) $\Delta\rho(15°) = \rho(15°) - \rho(0°)$, (b) $\Delta\rho(40°) = \rho(40°)$
$- \rho(0°)$, (c) $\Delta\rho(55°) = \rho(55°) - \rho(40°)$. In subtracting the
reference density, the O–H axes on the right hand side were
superposed. Contours are at 0.0, ±0.001, ±0.005, ±0.01, ±0.02,
±0.04, ±0.07, ±0.1, ±0.15, and ±0.2 au (solid lines ≥ 0,
dashed lines < 0).

(A) ELECTRON CLOUD PRECEDING AT $\theta = 15°$

(B) BENT BOND AT EQUILIBRIUM ANGLE, $\theta = 40°$

(C) ELECTRON CLOUD INCOMPLETE FOLLOWING AT
$\theta = 55°$

axis. The electron cloud, following backwards the O—H axis, pulls the proton in the reverse direction to θ, so that the bending process is resisted and the molecule is restored again to the equilibrium geometry. Thus, the density origin of the bent geometry of H_2O is the electron cloud preceding in the region $0° < \theta < \theta_{eq}$ ($40°$) and the electron cloud incomplete following in the region $\theta > \theta_{eq}$. This is in accordance with and reconfirms the results of the previous study [11].

In order to see quantitatively how the density behaviour shown in fig. 2 works to determine the stable geometry, we have plotted in fig. 3 the transverse force $F_{H\perp}$ and its analysis against the bending angle θ. The dashed line shows the SCF energy curve. By virtue of floating, the calculated equilibrium angle ($\theta = 40°$) is the same from both the energetics and the H—F force. In accordance with fig. 2a, the bending is facilitated by the AD and EC(H—O) forces which represent the electron cloud preceding in the atomic region near H and in the H—O overlap region, respectively. In the region $\theta > \theta_{eq}$, the electron cloud incomplete following found in fig. 2c manifests itself in the EC(H—O) force and occurs in the H—O overlap region. It is the main origin of

the restoring force in the region $\theta > \theta_{eq}$. The AD force contributes to the restoring force by diminishing its bending role. The EGC force, which represents the interaction between the shielded protons, and the EC(H——H) force, which represents the exchange repulsion between the terminal hydrogens, also work to resist the bending. It is interesting to note that the EC(H—O) curve crosses the zero line at almost equilibrium angle. Such behaviour is also found for NH_3 and CH_3^+, as will be reported elsewhere.

The direct integration of the H—F force curves shown in fig. 3 gives the energy curves which *directly* reflect the dynamic behaviour of the electron density shown in fig. 2. In other words, the energy change of a system can be calculated only from the knowledge of the one-electron density $\rho(1)$ *without* knowing the off-diagonal first-order density matrix $\rho(1|1')$ and the second-order density matrix $\Gamma(1,2)$ [24]. This procedure is essentially the same as the one given by Wilson [25]. Moreover, for the present floating wavefunction the numerical accuracy of this procedure is the same as that of the conventional energetics *which requires* in general the knowledge of $\rho(1)$, $\rho(1|1')$, and $\Gamma(1,2)$.

Fig. 4 shows the results of such direct integration. It partitions the energy change along the bending process into the force theoretic terms which directly reflect
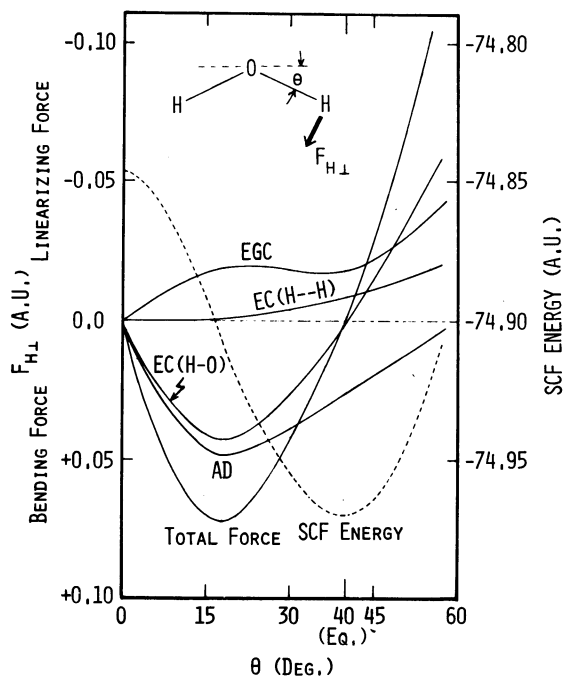

Fig. 3. The transverse force $F_{H\perp}$ and the SCF energy versus the bending angle θ for H_2O.
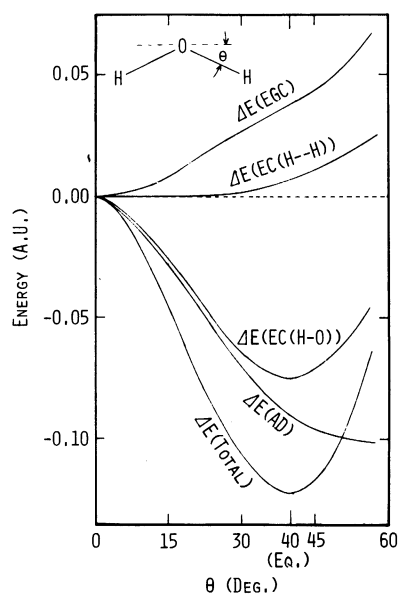

Fig. 4. Energy decomposition into the force theoretic terms for H_2O.

the dynamic behaviour of the electron density as explained in the previous paragraphs. It is seen that the ΔE(total) curve in fig. 4 agrees well with the SCF energy curve shown in fig. 3 by virtue of floating. The electron cloud preceding in the atomic and overlap regions manifests itself in the ΔE(AD) and ΔE(EC(H—O)) curves in the region $0° < \theta < \theta_{eq}$ and works to stabilize the system. The electron cloud incomplete following manifests itself in the ΔE(EC(H—O)) curve in the region $\theta > \theta_{eq}$ and works to destabilize the system by bending. Again, the parallelism between the ΔE(total) curve and the ΔE(EC(H—O)) curve is remarkable.

4. Conclusion

We have shown a simpler way of floating, i.e., in order to obtain a reliable H—F force F_A which satisfies the H—F theorem, it is sufficient that only the centers of the AO's belonging to atom A be determined variationally. The other AO's may be fixed on their nuclei. This is a large simplification especially for complex systems. We have also shown that the simple and visual concepts of the force theory developed previously are valid even with the floating wavefunction and confirmed quantitatively that the previous concepts of the ESF theory correctly grasp the origin of molecular geometry.

Acknowledgement

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