

Force in SCF theories. Second derivative of potential energy

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The analytic second derivative of a potential energy hypersurface is studied with the use of the Hellmann-Feynman theorem at the stage of the first derivative. As shown previously, the use of the $\{r, r'\}$ basis in the SCF calculation guarantees that the Hellmann-Feynman theorem is essentially satisfied. (r' is a derivative of the AO $r = \chi_r$, $r' = \partial\chi_r/\partial\mathbf{x}_r$.) In comparison with the straightforward second derivative of the SCF energy, the number of terms and the labors in calculations are much reduced in the present method. Furthermore, the added $\{r'\}$ basis improves the quality of the calculated force constant, and an intuitive physical picture is associated with the calculated second derivative, as the intuitive Hellmann-Feynman force picture is associated with the first derivative. The applications are given for the force constants of the molecules N_2 , CO, and H_2O . Some interesting features of the electron density reorganizations during vibrations are reported.

I. INTRODUCTION

The derivatives of a potential energy hypersurface, especially the first and second derivatives, are the quantities which play a central role in many fields of theoretical chemistry. In previous papers of this series,¹⁻³ we have shown that an SCF wave function is improved, by an addition of the first derivative AO's $\{r'\}$ to the "parent" set $\{r\}$, to essentially satisfy the Hellmann-Feynman (H-F) theorem. This method is based on the theorem that a sufficient condition for an SCF wave function to satisfy the H-F theorem is that the basis set includes the derivative AO $r' = \partial\chi_r/\partial\mathbf{x}_r$ for any basis $r = \chi_r$.¹⁻⁵ The validity of this method has been confirmed for closed-shell RHF,^{1,3} open-shell RHF,² and MCSCF² theories. This method satisfies the two requirements which seem to be necessary for the theory of the derivatives³; one is the numerical accuracy and reliability of the theory and the other is the conceptual utility of the theory for understanding the electronic origins of the derivatives.^{6,7} Though the energy-gradient method⁸⁻¹⁶ has already realized the first requirement, it does not fulfill the second one because of an existence of the error term which vanishes identically for a correct SCF wave function.

For an analytical calculation of the second derivative, a use of the H-F theorem at the stage of the first derivative affords some merits:

(1) The number of terms to be considered is much reduced and they are much simpler than the straightforward expressions of the second derivative of the SCF energy.^{11,17,18}

(2) The intuitive physical meaning of the H-F force is extended to the second derivative.

Though these merits have been noted by several authors,^{9,19-25} it was difficult to realize them, except for some of the simplest systems, because of a lack of a practical method to calculate a wave function which satisfies the H-F theorem. The previous studies of this series¹⁻³ have removed this obstacle.

In this paper, we give the analytic second derivative of a potential energy using the H-F theorem for the first

derivative and explain the physical meaning included. Illustrative applications are given for the molecules N_2 , CO, and H_2O and the electronic origins of the force constants are discussed. The summary of this study is given in the last section.

II. ANALYTIC SECOND DERIVATIVE OF POTENTIAL ENERGY HYPERSURFACE

The direct second derivative of the Hartree-Fock energy is written as

$$\begin{aligned} \frac{\partial^2 E}{\partial X_A \partial Y_B} = & \sum_{r,s} P_{rs} \frac{\partial^2 H_{rs}}{\partial X_A \partial Y_B} + \sum_{r,s} \frac{\partial P_{rs}}{\partial Y_B} \frac{\partial H_{rs}}{\partial X_A} + \frac{\partial^2 V_{nuc}}{\partial X_A \partial Y_B} \\ & - \sum_{r,s} D_{rs} \frac{\partial^2 S_{rs}}{\partial X_A \partial Y_B} - \sum_{r,s} \frac{\partial D_{rs}}{\partial Y_B} \frac{\partial S_{rs}}{\partial X_A} + \frac{1}{2} \sum_{rstu} P_{rs} P_{tu} \\ & \times \left[\frac{\partial^2}{\partial X_A \partial Y_B} (rt \| su) \right] + \sum_{rstu} \frac{\partial P_{rs}}{\partial Y_B} P_{tu} \left[\frac{\partial}{\partial X_A} (rt \| su) \right], \end{aligned} \quad (1)$$

where H_{rs} , S_{rs} , and P_{rs} are the core-Hamiltonian matrix, overlap matrix, and bond-order density matrix, respectively and $D_{rs} = \sum_i^{\text{occ}} \epsilon_i c_{ri} c_{si}$, with ϵ_i the orbital energy. $(rt \| su)$ is an appropriate sum of the Coulomb and exchange repulsion integrals¹¹ and V_{nuc} is the nuclear repulsion energy. On the other hand, when the Hellmann-Feynman theorem is satisfied for the first derivative, only the parts of the first three terms of Eq. (1) remain. Most of the complex terms drop out, and we obtain

$$\begin{aligned} \frac{\partial^2 E}{\partial X_A \partial Y_B} = & \frac{\partial^2 V_{nuc}}{\partial X_A \partial Y_B} + \sum_{r,s} P_{rs} \delta_{AB} Z_A \langle r | \frac{\partial}{\partial Y_A} \left(\frac{x_A}{r_A^3} \right) | s \rangle \\ & + \sum_{r,s} P_{rs} Z_A \left(\left\langle \frac{\partial r}{\partial Y_B} \left| \frac{x_A}{r_A^3} \right| s \right\rangle + \left\langle r \left| \frac{x_A}{r_A^3} \right| \frac{\partial s}{\partial Y_B} \right\rangle \right) \\ & + \sum_{r,s} \frac{\partial P_{rs}}{\partial Y_B} Z_A \langle r | \frac{x_A}{r_A^3} | s \rangle, \end{aligned} \quad (2)$$

where

$$\frac{\partial}{\partial Y_A} \left(\frac{x_A}{r_A^3} \right) = \begin{cases} (r_A^2 - 3x_A^2)/r_A^5 + \frac{4}{3} \pi \delta(A), & X_A = Y_A, \\ -3x_A y_A / r_A^5, & X_A \neq Y_A. \end{cases} \quad (3)$$

This equation is much simpler to calculate than Eq. (1), and, furthermore, a simple physical meaning is associ-

ated with each term as follows²⁰⁻²⁵: The first two terms of Eq. (2) show a change in the H-F force when only nucleus A is moved while the electron density surrounding it remains unaltered. They consist of an electric field gradient at nucleus A and a contribution from the density at the nucleus (Fermi term). The former is related to the nuclear quadrupole coupling constant as shown below. The third term includes the derivative of basis AO's and represents a change in the H-F force acting on nucleus A due to the movement of the AO's of atom B with keeping the AO coefficients unaltered.

Then, the physical meaning of the first three terms is considered to be a net effect on the H-F force when the nucleus and the AO's associated with it are moved *simultaneously* without changing their AO coefficients, namely, it represents the effect of *complete following* of the AO's during molecular vibration.^{7(b),24} The last term represents the effect of reorganization of the electron density matrix due to the nuclear motion $\partial P_{rs}/\partial Y_B$. It arises from the two sources since it is given by a sum of the two terms

$$\frac{\partial P_{rs}}{\partial Y_B} = \sum_{i,j}^{\text{occ}} c_{ri} c_{sj} S_{ij}^{(1)} + \sum_i^{\text{occ}} \sum_a^{\text{unocc}} u_{ai}^{(1)} (c_{ri} c_{sa} + c_{ra} c_{si}) . \quad (4)$$

The first term is the *renormalization* term which arises in order to keep the total wave function normalized during vibration and the second term represents the *relaxation* of the molecular charge distribution during vibration through the mixing between occupied and unoccupied orbitals. In Eq. (4), c_{ri} is the coefficient of the AO χ_r in the molecular orbital ϕ_i and $S_{ij}^{(1)}$ is given by

$$S_{ij}^{(1)} = \left\langle \frac{\partial \phi_i}{\partial Y_B} \middle| \phi_j \right\rangle + \left\langle \phi_i \middle| \frac{\partial \phi_j}{\partial Y_B} \right\rangle . \quad (5)$$

$u_{ai}^{(1)}$ gives the extent to which the occupied MO ϕ_i and the unoccupied MO ϕ_a mix through molecular vibration and is given by a solution of the coupled perturbed Hartree-Fock theory. It is a solution of the linear equation^{9,11}

$$(1 - A)B = B_0 , \quad (6)$$

where

$$\begin{aligned} B &= \{u_{ai}^{(1)}\}^T , \\ A_{(ai, bj)} &= [(ab || ij) + (aj || ib)] / (\epsilon_i - \epsilon_a) , \\ B_{0(ai)} &= Q_{ai}^{(1)} / (\epsilon_i - \epsilon_a) , \\ Q_{ai}^{(1)} &= H_{ai}^{(1)} - S_{ai}^{(1)} \epsilon_i - \sum_{k,l} S_{ki}^{(1)} (al || ik) \\ &\quad + \sum_{rstu} c_{ra} c_{si} P_{tu} \left[\frac{\partial}{\partial Y_B} (rt || su) \right] . \end{aligned} \quad (7)$$

The role of the reorganization term during a nuclear rearrangement process is generally very important. The renormalization term usually gives a positive contribution to the force constant and is one of the important origins of the electron-cloud incomplete following, which is a density origin of a stable geometry.^{7(b),26} On the other hand, the relaxation term usually gives a negative contribution to the force constant and works to lower the barrier. It is an origin of the electron-cloud preceding, which is a density origin of many nuclear rearrangement processes.^{7(b),26} The role of the relaxation term

during the course of a chemical reaction is of special interest.

It is noted that the force constant is related to the nuclear quadrupole coupling constant $(eq_A Q_A / \hbar)_{\alpha\beta}$, where q_A is given by

$$\begin{aligned} (q_A)_{xx} &= \sum_{r,s} P_{rs} \langle r | (r_A^2 - 3x_A^2) / r_A^5 | s \rangle + \frac{\partial^2 V_{\text{nuc}}}{\partial X_A^2} , \\ (q_A)_{xy} &= - \sum_{r,s} P_{rs} \langle r | 3x_A y_A / r_A^5 | s \rangle + \frac{\partial^2 V_{\text{nuc}}}{\partial X_A \partial Y_A} . \end{aligned} \quad (8)$$

With these quantities, we obtain from Eq. (2) the equation

$$\begin{aligned} \frac{\partial^2 E}{\partial X_A \partial Y_A} &= Z_A (q_A)_{xy} + \frac{4}{3} \pi \delta_{xy} \sum_{r,s} P_{rs} Z_A \langle r | \delta(A) | s \rangle \\ &\quad + \sum_{r,s} P_{rs} Z_A \left(\left\langle \frac{\partial r}{\partial Y_B} \middle| \frac{x_A}{r_A^3} \middle| s \right\rangle + \left\langle r \middle| \frac{x_A}{r_A^3} \middle| \frac{\partial s}{\partial Y_B} \right\rangle \right) \\ &\quad + \sum_{r,s} \frac{\partial P_{rs}}{\partial Y_B} Z_A \langle r | \frac{x_A}{r_A^3} | s \rangle . \end{aligned} \quad (9)$$

Based on this equation, Salem²⁰ discussed the relation between the force constant and quadrupole coupling constant of the MH molecule (M is an alkali metal or halogen).

III. APPLICATION TO N₂ AND CO

We study here the force constant of N₂ and CO. Closed-shell Hartree-Fock calculations were performed at the experimental bond length (N-N = 1.09768 Å, C-O = 1.1283 Å)²⁷ with the use of the family set $\{r, r'\}$ in which the parent set $\{r\}$ is the 4-31G set²⁸ for N₂ and [3s2p/2s] CGTO's²⁹ for CO. (Reference 3 includes the results of the H-F force for N₂ and CO with the same basis set.) It is now well established that with the use of the family set the H-F theorem is essentially satisfied.¹⁻³ The second derivative (force constant) was calculated with Eq. (2) and the derivative of the density matrix was calculated by the coupled perturbed Hartree-Fock theory [Eqs. (6) and (7)].

Table I shows the force constants of N₂ and CO and their analyses. For the force constant of the A-B molecule, we have given four expressions $-\partial F_A / \partial X_A$, $\partial F_A / \partial X_B$, $-\partial F_B / \partial X_B$, and $\partial F_B / \partial X_A$, where the X axis points from nucleus A to B. The analysis of the force constant depends on a choice of a coordinate system, though the force constant itself is free from such choice.

Mathematically, the quantities $-\partial F_A / \partial X_A$ and $\partial F_A / \partial X_B$ should be equal. In general, such a relation holds for polyatomic molecules as $\sum_B \partial F_A / \partial X_B = 0$. This equality also holds for the sum of the first three terms of Eq. (2), and for each of the renormalization and relaxation terms. Interestingly, this equality does not hold for each of the second and third terms but holds for their sum, showing a physical unity of the latter. This equality means that when the electron cloud and the nuclei are moved altogether in the x direction, nothing is changed for the F_A . On the other hand, the equality between the two sets of terms $-\partial F_A / \partial X_A$ (or $\partial F_A / \partial X_B$) and $-\partial F_B / \partial X_B$ (or $\partial F_B / \partial X_A$) depends on whether the Hellmann-Feynman forces F_A and F_B satisfy the trans-

TABLE I. Force constants of N₂ and CO and their analysis (a. u.).^a

	N ₂		CO			
	$-\frac{\partial F_{N1}}{\partial X_{N1}}$	$\frac{\partial F_{N1}}{\partial X_{N1}}$	$-\frac{\partial F_C}{\partial X_C}$	$\frac{\partial F_C}{\partial X_O}$	$-\frac{\partial F_O}{\partial X_O}$	$\frac{\partial F_O}{\partial X_C}$
Nuclear term	10,980	10,980	9,906	9,906	9,906	9,906
$Z_A \sum_{r,s} P_{rs} \left\langle r \left \frac{3x_A^2 - r_A^2}{r_A^5} \right s \right\rangle$	-20,236	...	-16,522	...	-14,454	...
$Z_A \sum_{r,s} P_{rs} \left\langle r \left -\frac{4}{3} \pi \delta(A) \right s \right\rangle$	5098,689	...	3032,572	...	9899,184	...
$Z_A \sum_{r,s} P_{rs} \left\langle r' \left \frac{x_A}{r_A^3} \right s \right\rangle^b$	-5093,035	-14,581	-3027,701	-11,651	-9897,233	-12,503
Total	-3,601	-3,601	-1,744	-1,744	-2,596	-2,596
Renormalization term	5,883	5,883	4,061	4,061	5,697	5,697
Relaxation term	-0,637	-0,637	-1,002	-1,002	-1,785	-1,785
Total	5,247	5,247	3,059	3,059	3,911	3,911
Grand total	1,645	1,645	1,315	1,315	1,315	1,315
Experimental value	1,474		1,222			
From energy gradient						
For family set	1,625		1,288			
For parent set	1,734		1,422			

^aAt the experimental geometry: N₂, 1.09768 Å; CO, 1.1283 Å; 1 a. u. = 15.569187 mdyn/Å.

^b $r' = \partial \chi_r / \partial x_B$.

lational invariance. In the present calculations of CO, these numbers are equal up to four figures since the Hellmann-Feynman theorem is essentially satisfied for the present wave function.³

From Table I, it is seen that the force constant is a sum of large canceling contributions. The nuclear term is large and always positive. For the diagonal term (i. e., $\partial F_A / \partial X_A$), the electric field gradient and the Fermi term give large contributions. Especially, the latter is very large because of the 1s contribution of C, N, and O. It increases with an increase in nuclear charge. However, this large value is almost canceled by the fourth term of Table I, which represents the H-F force on A due to the displaced AO's (inner and valence) of atom A. The net effect of the second to fourth terms of Table I is due to the AO density moving simultaneously with the nucleus (complete following). This result shows that these terms should be treated as a whole as a completely following term. The mathematical invariance given above also supports this analysis. Note that though the sum of the first four terms is equal for $-\partial F_A / \partial X_A$ and $\partial F_A / \partial X_B$, they are different between $-\partial F_A / \partial X_A$ and $-\partial F_B / \partial X_B$ when A and B are different. The sum of the first four terms is negative for N₂ and CO.

In the next two rows of the table, the reorganization terms are given. In Fig. 1, the contour map of the density reorganization $\sum_{r,s} -\partial P_{rs} / \partial R_{AB} \chi_r(\mathbf{r}) \chi_s(\mathbf{r})$ is plotted for N₂ and CO. The top shows the renormalization term, the middle the relaxation term, and the bottom the sum of them. They show the change in density when the bond

distance is shortened. For covalent diatomic molecules, the renormalization term seems always to be positive (Table I). This is understood as follows from Fig. 1: When two atoms A and B come closer, the overlap between the AO's become larger. Therefore, in order to renormalize the total density, the electrons should flow out of the A-B region. When atoms A and B are separated, the reverse flow of the electron density is expected as a renormalization effect. Thus, the density flow due to the renormalization corresponds to the electron-cloud incomplete following^{7(b),26} and gives a positive contribution to the force constant. On the other hand, in the relaxation term, the density increases in the bond region as the two atoms come closer. This behavior is the electron-cloud preceding. It works to shield the nuclear charge and stabilize the system. Then, the relaxation term gives negative contribution to the force constant. This is confirmed from Table I. Such a trend would be valid at least for diatomic molecules with covalent bonds. The bottom of Fig. 1 shows the total density differential, i. e., the sum of the renormalization and relaxation terms. It reflects mainly the contribution of the renormalization term, giving a positive contribution to the force constant. Actually, in Table I the renormalization term is larger than the relaxation term and their sum is positive.

The sum of the nuclear term, the complete following term, and the reorganization term gives the calculated force constant. It is 1.645 a. u. for N₂ and 1.315 a. u. for CO. The experimental values are 1.474 and 1.222 a. u. for N₂ and CO, respectively.²⁷ The present Hartree-Fock values are larger than the experimental

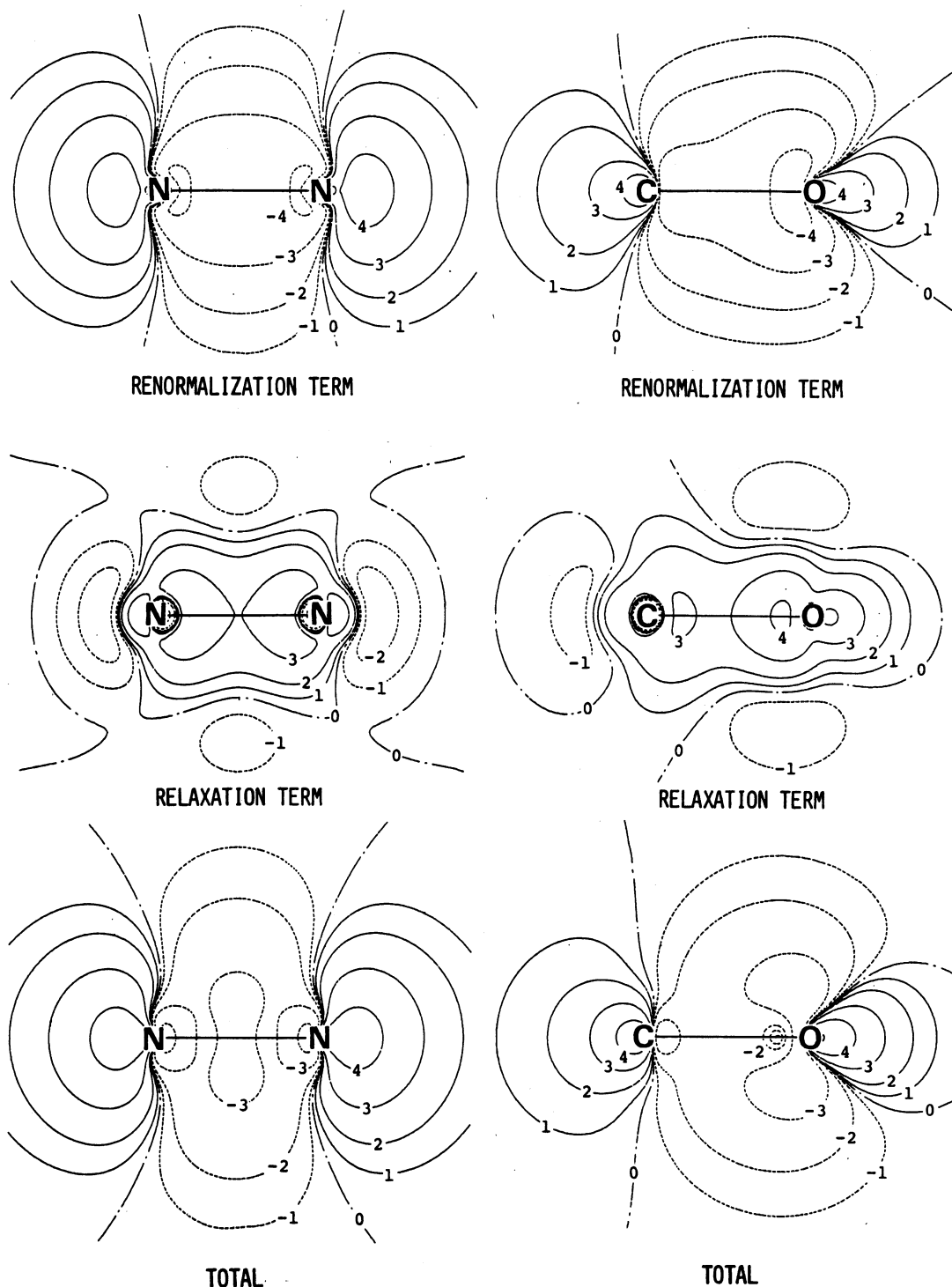


FIG. 1. Contour map of the density differential $-\sum_{r,s} \partial P_{rs} / \partial R_{AB} \chi_r(r) \chi_s(r)$ for N_2 and CO. The top shows the renormalization term, the middle the relaxation term, and the bottom the sum of them. They show the change in density when the bond distance is shortened. The real lines correspond to an increase in density, and the broken lines correspond to a decrease, with the contour values of 0, ± 1 , ± 2 , ± 3 , and ± 4 corresponding to 0, 0, ± 0.01 , ± 0.03 , ± 0.1 , and ± 0.3 a. u., respectively.

values, as in the well-known trend. In the last two rows of Table I, the values obtained by the numerical differentiation of the energy gradient is shown. The values obtained with the family set, 1.625 a.u. for N_2 and 1.288 a.u. for CO, are very close to the present results. The difference, which is less than 2%, is due to a small error in the Hellmann-Feynman force and to

the error in the numerical differentiation. The last two rows compare the force constants obtained from the family and parent sets. The difference is large and the result of the family set is closer to the experimental value. This shows that the $\{r'\}$ basis, a kind of polarization function, included in the family set is important for the force constant. Thus, the added $\{r'\}$

TABLE II. Force constants of H₂O and their analysis (a. u.).^{a,b}

	$\frac{\partial^2 E}{\partial Q_1^2}$	$\frac{\partial^2 E}{\partial Q_2^2}$
Nuclear term	3.040	-1.481
$Z_A \sum_{r,s} P_{rs} \left\langle r \left \frac{3x^2 - r^2}{r^5} \right s \right\rangle$	-2.212	-1.113
$Z_A \sum_{r,s} P_{rs} \langle r -\frac{4}{3} \pi \delta(A) s \rangle$	26.016	46.620
$Z_A \sum_{r,s} P_{rs} \left\langle r' \left \frac{x}{r^3} \right s \right\rangle$	-26.270	-46.261
Total	0.574	-0.009
Renormalization term	0.376	0.065
Relaxation term	-0.338	0.076
Total	0.038	0.141
Grand total	0.613 (3938 cm ⁻¹)	0.132 (1803 cm ⁻¹)
Experimental value	3657 cm ⁻¹	1595 cm ⁻¹

^aAt the experimental equilibrium geometry.

^b Q_1 : mostly stretching mode; $Q_1 = 0.735 (\Delta R_{OH_1} + \Delta R_{OH_2}) + 0.019 R_{OH} \Delta \theta_{HOH}$; Q_2 : mostly bending mode; $Q_2 = 0.052 (\Delta R_{OH_1} + \Delta R_{OH_2}) - 1.517 R_{OH} \Delta \theta_{HOH}$.

basis works not only to give the correct Hellmann-Feynman force but also to improve the quality of the second derivative.

IV. APPLICATION TO H₂O

H₂O is adopted here to show the result for a bending mode as well as a stretching mode. Only the totally symmetric mode is considered here. SCF calculations were carried out at the experimental geometry ($R_{OH} = 0.957 \text{ \AA}$, $\theta_{HOH} = 104.5^\circ$)³⁰ with the family set in which the parent set is the [3s2p/2s] set.^{29,31} Table II shows the force constants of the normal modes Q_1 and Q_2 , which are mostly stretching and bending modes, respectively. The coupling of the stretching and bending is shown in footnote b. Figures 2 and 3 show the contour maps of the density reorganization $\sum_{r,s} \partial P_{rs} / \partial Q \chi_r(r) \chi_s(r)$ for Q_1 and Q_2 , respectively.

First, we consider the normal mode Q_1 . Since this is mostly a stretching mode, the electronic origins have some similarities to those shown for the diatomic molecules. Actually, the sign of each contribution shown in Table II is the same as that in Table I. However, the sum of the first four terms (i.e., nuclear and complete following terms) is positive here but negative in Table I. The contribution of the reorganization term is smaller

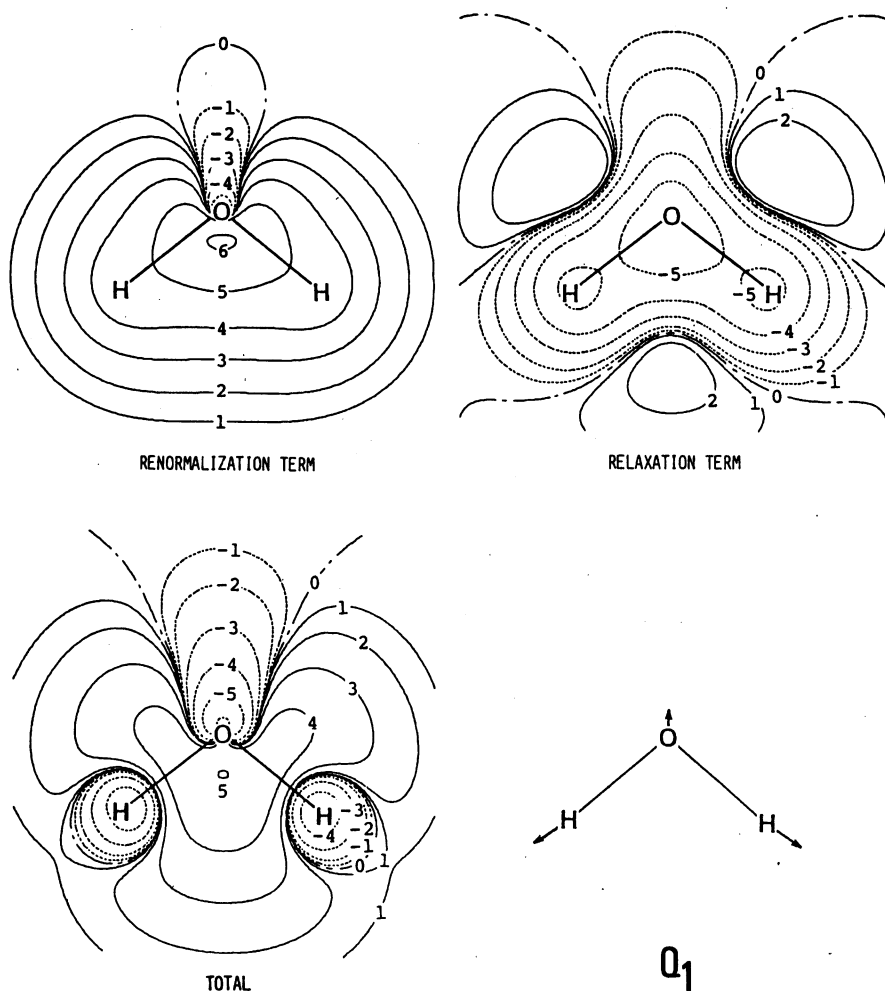


FIG. 2. Contour map of the density differential $\sum_{r,s} \partial P_{rs} / \partial Q_1 \chi_r(r) \chi_s(r)$ of H₂O for the Q_1 mode which is mostly the stretching mode. The real lines correspond to an increase in density and the broken lines correspond to a decrease, with the contour values of 0, ± 1 , ± 2 , ± 3 , ± 4 , and ± 5 corresponding to 0.0, ± 0.01 , ± 0.03 , ± 0.1 , ± 0.3 , and ± 1.0 a. u., respectively.

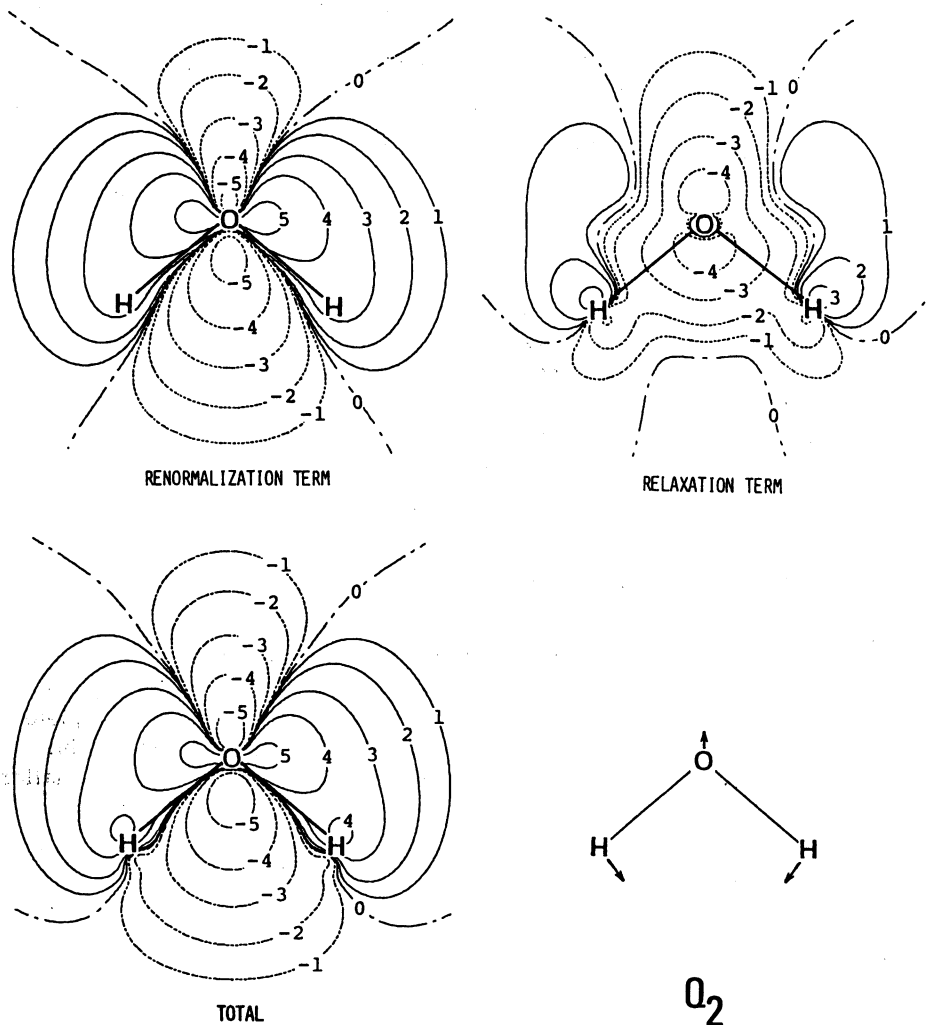


FIG. 3. Contour map of the density differential $\sum_{r,s} \partial P_{rs} / \partial Q_2 \chi_r(r) \chi_s(r)$ of H_2O for the Q_2 mode which is mostly the bending mode. The real lines correspond to an increase in density and the broken lines correspond to a decrease, with the contour values of 0, ± 1 , ± 2 , ± 3 , ± 4 , and ± 5 corresponding to 0.0, ± 0.01 , ± 0.03 , ± 0.1 , ± 0.3 , and ± 1.0 a. u., respectively.

here than in Table I. These differences seem to be general between hydride and nonhydride molecules from our several data for these two types of molecules. Actually, in the normal vibrations of H_2O , the contribution of the motion of the proton is large because of its small mass. The calculated vibrational frequency is 3938 cm^{-1} , which is 7% larger than the experimental value of 3657 cm^{-1} . An inclusion of electron correlation will reduce this difference.³²

The density reorganization shown in Fig. 2 is for the normal mode Q_1 . When the OH bond is elongated during the vibration, the overlaps between the AO's of the oxygen and protons reduce, so that in order to keep the wave function normalized the electrons should flow into the bond region. This is the origin of the renormalization term and gives a positive contribution to the force constant (Table II). The relaxation term works to reduce the electron density from the bond region and to accelerate the bond stretching. It gives a negative contribution to the force constant. In the total sum, the density increases in the bond region, giving a positive net contribution. We note that the density reorganization in the renormalization term corresponds to the electron-cloud incomplete following^{7(b)} and that in the relaxation term to the electron-cloud preceding.^{7(b)}

The net effect is the electron-cloud incomplete following.

We next consider the mode Q_2 . Since this is essentially a bending mode which has not been considered so far, some difference may be expected. In Table II, the signs of the first two terms (electric field gradient) are different from those given hitherto. The origin of the negative contribution of the nuclear term is as follows: We denote the force acting on the proton as $F(\theta)$, where θ is the HOH angle. The force constant for the normal mode Q_2 is approximately given by

$$-\lim_{\Delta\theta \rightarrow 0} \frac{[F(\theta + \Delta\theta) - F(\theta)]_{\perp}}{R_{OH} \Delta\theta},$$

where \perp denotes an element perpendicular to the bond. As expected, the interproton repulsion gives a positive contribution. Though the force due to the oxygen is always parallel to the bond, it gives an element perpendicular to the bond to the term $F(\theta + \Delta\theta) - F(\theta)$. Actually, this contribution is negative and larger than the contribution due to the interproton repulsion, since the nuclear charge Z_O is much larger than Z_H and the OH distance is smaller than the HH distance. The positive contribution of the second term in Table II (electronic term of the electric field gradient) is due to a similar reason.

The density reorganization in the bending mode is shown in the contour map of the density differential given in Fig. 3. The renormalization term shows typically a formation of an outward bent bond,^{7(b)} which is an electron-cloud incomplete following in the motion shown by the arrow. The decrease in electron density within the HOH triangle is due to an increase of the overlap in this region. The decrease in the lone pair region of oxygen is due to an increase of the lone pair density by the Q_2 motion. These changes are necessary to keep the wave function normalized. Interestingly, the relaxation term also shows an outward polarization near the proton, giving an effect similar to the renormalization term as confirmed from Table II. Since the nuclear term is negative, this positive contribution of the relaxation term may be understood as working to diminish the nuclear term.^{7(b)} The sum of the renormalization and relaxation terms shows the nature of electron-cloud incomplete following. The calculated frequency for the Q_2 mode is 1803 cm^{-1} , which is again about 12% larger than the experimental value of 1595 cm^{-1} . An inclusion of electron correlation will reduce this difference.³²

Lastly, we note that the density differential maps shown in Figs. 2 and 3 are very similar to the corresponding generalized Berlin diagrams^{7(c)} reported previously for H_2O [Figs. 3 and 4 of Ref. 7(c)]. This is true for both of the Q_1 and Q_2 modes. Further, such similarity also holds for the diatomic molecules N_2 and CO .^{7(c)} The generalized Berlin diagram defines a region-functional concept of electron density and divides a space of the electron density into accelerating and registering regions for a process under consideration. This is a generalization of the Berlin diagram for diatomic molecules.³³ The observed similarity between the density differential map and the generalized Berlin diagram implies that the density reorganization at the equilibrium geometry occurs *very effectively* in such a way to resist the nuclear displacement. Namely, the electron-cloud incomplete following occurs very effectively at the equilibrium geometry.

V. SUMMARY

The points of an argument of this paper are as follows.

(1) As shown in the previous papers,¹⁻³ the use of the $\{r, r'\}$ basis in the SCF calculations (closed and open shell SCF, MCSCF, etc.) guarantees that the Hellmann-Feynman theorem is essentially satisfied.

(2) With the use of the Hellmann-Feynman theorem at the stage of the first derivative, the number of terms and the labors in the analytic calculations of the second derivative are much reduced in comparison with the straightforward second derivative of the SCF energy.¹¹ [Compare Eqs. (1) and (2).]

(3) Since the $\{r'\}$ basis (a kind of polarization functions) is usually important for the force constant and other second derivatives, the quality of the numerical result is improved by the present method in comparison with the direct analytic second derivative of the SCF energy with only the parent $\{r\}$ basis.

(4) Intuitive physical pictures are associated *quantita-*

tively with the calculated second derivatives. With the use of the Hellmann-Feynman force picture^{6,7,26} for the first derivative, and with the use of the present picture for the second derivative, we would be able to understand more deeply the electronic origins of the important aspects and behaviors of the potential energy hypersurface.

The present method has been applied to the calculation of the force constants of the molecules N_2 , CO , and H_2O and some interesting pictures on the electronic origins of the force constant are clarified. The difference in the stretching and bending modes is discussed for H_2O . Some interesting features of the electron density reorganizations during vibrations are reported.

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