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The Hellmann-Feynman Theorem Applied to Long-Range Forces

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The relations between the Hellmann-Feynman forces in laboratory fixed (*L*-) and relative (*R*-) coordinate systems are clarified. In the usual *L*-coordinate system, the force is interpreted as force on nucleus, while in the *R*-coordinate system, it means force on whole particles consisting of the electrons and nuclei of each interacting subsystem. From a perturbation theoretical viewpoint, the concept of the force on whole particles correctly corresponds to the perturbation energy and is superior to the force on the nucleus.

Key words: Hellmann-Feynman theorem – Long-range forces – Perturbation theory

1. Introduction

The energetic method and the force method are the two basic approaches to physical and chemical phenomena. When one uses the electrostatic Hellmann-Feynman (H-F) theorem [1, 2] instead of taking the derivative of the calculated energies, one obtains very intuitive physical pictures which are entirely different from the conventional energetic theories [3]. This physical simplicity has been fully used previously in the development of the electrostatic force (ESF) theory for molecular structures, chemical reactions, and long-range forces [4, 5].

In comparison with the energetic theories, the force approach has a deficiency in that the calculated H-F forces are more sensitive to inaccuracies of the wavefunctions used [6, 7]. The energetic theory and the H-F force theory give identical results only when the wavefunction used in the calculation satisfies the stable condition of Hall [8]. The exact wavefunction, Hartree-Fock wavefunction, the floating wavefunction of Hurley [9], etc. have such properties [6, 10]. The fully reliable force calculations are therefore still limited at present.

For long-range interactions between two atoms, where the exact or nearly exact wavefunctions of lower orders can be obtained by perturbation theory, the force approach has given accurate and yet intuitive results [5, 11]. The ESF theory has shown that the origin of the long-range forces between two atoms are the atomic dipole (AD) and the extended gross charge (EGC) forces [5]. These force concepts are quite different from the energetic theories and more general in that the basic concepts are common to other important fields such as molecular structures and chemical reactions [4].

Although the previous H-F force calculations have been done using laboratory fixed (L-) coordinate system [5, 11], it is also possible to use relative (R-) coordinate system for the study of the long-range H-F forces. In the L-coordinate system, all the electrons and nuclei of the interacting system are measured independently from a common origin, but in the R-coordinate system, the electrons and nuclei of *each* interacting subsystem are measured from the origin fixed on *each* subsystem. The latter can be defined unambiguously only when the electron exchange between subsystems can be neglected, i.e., only for long-range interactions. Yaris [12] emphasized the advantage of the R-coordinate system from the perturbation theoretical viewpoint and gave results different from those of Salem and Wilson [7] who used the L-coordinate system. Steiner [13] reexamined the long-range H-F force study of the H_2 system due to Hirschfelder and Eliason [11]. He called the force in the L-coordinate system *force on nucleus* and that in the R-coordinate system *force on atom* and showed some important relations between these forces.

In this paper, we study the relations of the forces in the L- and R-coordinate systems in a more general fashion. We will show that the force in the R-coordinate system, which we call *force on whole particles*, is superior to the force in the L-coordinate system from the perturbation theoretical point of view. The force on whole particles is the concept which corresponds exactly to the conventional energetic perturbation theory and especially, the force on whole particles correct up to order $2n+1$ can be obtained only from the knowledge of the wavefunction to order n. This means that the H-F force approach is *not necessarily* inferior to the energetic approach at least for long-range interactions. The force in the L-coordinate system does not have such properties. Several new concepts associated with the force on whole particles and the differences from the previous ESF treatment [5] will be discussed. The results will be applied to three illustrative examples, long-range interactions in $H(1s)$–H^+, $H(1s)$–$H(1s)$, and NH_3–H^+ systems.

2. Force on Whole Particles

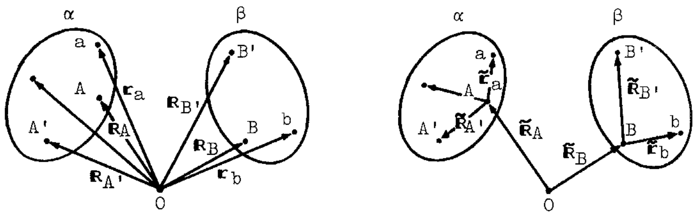
We consider the long-range force between two subsystems α and β at a distance large enough for electron exchange between them to be negligible. The subsystem α (e.g., atom or molecule) is assumed to include sets of electrons $\{a\}$ and nuclei $\{A\}$. The positions of electrons and nuclei are denoted respectively by $\mathbf{r}$ and $\mathbf{R}$ in the L-coordinate system and by $\tilde{\mathbf{r}}$ and $\tilde{\mathbf{R}}$ in the R-coordinate system. The present analysis is restricted for simplicity to the case of two subsystems, but the discussion is the same for the case of many subsystems.

2.1. Force Operators

The Hamiltonian for the total system, $\mathscr{H}$, can be divided as

$$\mathscr{H}=\mathscr{H}_0+\mathscr{H}_1, \tag{1}$$

where $\mathscr{H}_0$ is the unperturbed Hamiltonian for the isolated subsystems with the eigenfunction $|0\rangle$ and $\mathscr{H}_1$ the Coulombic interactions between all the charges in the subsystem α and in the subsystem β.



(a) Laboratory fixed (L-) coordinate system

(b) Relative (R-) coordinate system

Fig. 1. Coordinate systems

In the usual discussion of forces, the force operator for the nucleus A is expressed using the L-coordinate system as

$$\mathcal{F}_A = -(\partial\mathcal{H}/\partial\mathbf{R}_A) = -(\partial\mathcal{H}_0/\partial\mathbf{R}_A) - (\partial\mathcal{H}_1/\partial\mathbf{R}_A). \tag{2}$$

For the long-range interactions between two atoms, we have shown previously that the operators $-(\partial\mathcal{H}_0/\partial\mathbf{R}_A)$ and $-(\partial\mathcal{H}_1/\partial\mathbf{R}_A)$ are the AD and EGC force operators, respectively. The former gives the AD force due to the polarization of the electron cloud of the atom A and the latter gives the EGC force which represents the semi-classical electrostatic interactions between the two atoms [5]. The AD and EGC force operators are the zeroth- and first-order operators with respect to the perturbation.

In a perturbative sense, the differential operator in the L-coordinate system, $(\partial/\partial\mathbf{R}_A)$, in Eq.(2) does not satisfy the prerequisite of perturbation theory. Since $\mathcal{H}_0$ and $|0\rangle$ for the isolated system should be independent of the nuclear position, the differentials of $\mathcal{H}_0$ and $|0\rangle$ should vanish identically, but $(\partial\mathcal{H}_0/\partial\mathbf{R}_A)$ and $(\partial|0\rangle/\partial\mathbf{R}_A)$ do not. As shown later, the operator in the R-coordinate system, $(\partial/\partial\tilde{\mathbf{R}}_A)$, satisfies this prerequisite.

Fig. 1 illustrates and compares the L- and R-coordinate systems. In the L-coordinate system all the positions of the electrons and nuclei are measured independently from the fixed origin O, while in the R-coordinate system they are measured from the relative origin A except for the nucleus A.

$$\begin{aligned}&\tilde{\mathbf{R}}_A = \mathbf{R}_A,\\&\tilde{\mathbf{R}}_{A'} = \mathbf{R}_{A'} - \tilde{\mathbf{R}}_A \ (A' = A', A'', \ldots),\\&\tilde{\mathbf{r}}_a = \mathbf{r}_a - \tilde{\mathbf{R}}_A \ (a = a, a', \ldots).\end{aligned} \tag{3}$$

Since $\partial\mathbf{R}_A/\partial\tilde{\mathbf{R}}_A = \partial\mathbf{R}_{A'}/\partial\tilde{\mathbf{R}}_A = \cdots = \partial\mathbf{r}_a/\partial\tilde{\mathbf{R}}_A = \cdots = 1$, the differential operators in the L- and R-coordinate systems are connected by the following important relation.

$$(\partial G/\partial\tilde{\mathbf{R}}_A) = \sum_A (\partial G/\partial\mathbf{R}_A) + \sum_a (\partial G/\partial\mathbf{r}_a), \tag{4}$$

where G is an arbitrary function of positions of electrons and nuclei. On the l.h.s. of Eq.(4), G is represented in the R-coordinate system, while on the r.h.s., it is represented in the L-coordinate system, according to the transformation (3). In the R-coordinate system, the derivative of $\mathcal{H}_0$ vanishes,

$$(\partial\mathcal{H}_0/\partial\tilde{\mathbf{R}}_A) = 0, \tag{5}$$

i.e., the force operator in the R-coordinate system satisfies the prerequisite of perturbation theory. From Eqs.(4) and (5), we get

$$-(\partial\mathscr{H}_1/\partial\tilde{\mathbf{R}}_A) = -\sum_A (\partial\mathscr{H}/\partial\mathbf{R}_A) - \sum_a (\partial\mathscr{H}/\partial\mathbf{r}_a), \qquad (6)$$

where $\mathscr{H}$ on the r.h.s. of Eq.(6) can be replaced by $\mathscr{H}_1$. In Eq.(6), the first term of the r.h.s. is the sum of the force operators on *all the nuclei* $\{A\}$ of the subsystem α. The second term is interpreted as the sum of the force operators on *all the electrons* $\{a\}$ of the subsystem α. Therefore, the force operator in the R-coordinate system, $-(\partial\mathscr{H}_1/\partial\tilde{\mathbf{R}}_A)$, is understood as the force operator on *whole particles* of the subsystem α. We designate it as $\mathscr{F}_\alpha$.

$$\mathscr{F}_\alpha = -(\partial\mathscr{H}_1/\partial\tilde{\mathbf{R}}_A). \qquad (7)$$

The force on "atom" previously introduced by Steiner [13] for the long-range interaction of two hydrogen atoms corresponds to the special case. In contrast, the force operator in the L-coordinate system, $\mathscr{F}_A$ of Eq.(2), may be called force operator on *nucleus*.

In the R-coordinate representation,

$$0 = \sum_A (\partial\mathscr{H}_0/\partial\mathbf{R}_A) + \sum_a (\partial\mathscr{H}_0/\partial\mathbf{r}_a), \qquad (8)$$

from Eqs.(4) and (5), and this means that the sum of internal forces is zero for an isolated subsystem.

2.2. Forces

By the H-F theorem [1, 2], the *force on nucleus A* is given as

$$\begin{aligned}\mathbf{F}_A &= \langle\Psi| -(\partial\mathscr{H}/\partial\mathbf{R}_A)|\Psi\rangle \\ &= \langle\Psi| -(\partial\mathscr{H}_0/\partial\mathbf{R}_A)|\Psi\rangle + \langle\Psi| -(\partial\mathscr{H}_1/\partial\mathbf{R}_A)|\Psi\rangle, \qquad (9)\end{aligned}$$

where $|\Psi\rangle$ is the exact wavefunction of the total system. The *force on whole particles* in the subsystem α is defined as

$$\begin{aligned}\mathbf{F}_\alpha &= \langle\Psi| -(\partial\mathscr{H}/\partial\tilde{\mathbf{R}}_A)|\Psi\rangle \\ &= \langle\Psi| -(\partial\mathscr{H}_1/\partial\tilde{\mathbf{R}}_A)|\Psi\rangle. \qquad (10)\end{aligned}$$

From Eq.(6), $\mathbf{F}_\alpha$ is the sum of the forces on the nuclei $\{A\}$ and on the electrons $\{a\}$. However, the forces on the electrons $\{a\}$ vanish identically for *exact* wavefunctions[1].

$$\mathbf{F}_a = \langle\Psi| -(\partial\mathscr{H}/\partial\mathbf{r}_a)|\Psi\rangle = 0. \qquad (11)$$

Then,

$$\mathbf{F}_\alpha = \sum_A \mathbf{F}_A. \qquad (12)$$

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[1] The partial differentiation of the electronic Schrödinger equation $\mathscr{H}|\Psi\rangle = |\Psi\rangle E$ with respect to $\mathbf{r}_a$ and the operation of $\langle\Psi|$ yield $\langle\Psi|\partial\mathscr{H}/\partial\mathbf{r}_a|\Psi\rangle = \partial E/\partial\mathbf{r}_a = 0$. Eq.(11) does not hold when we replace $\mathscr{H}$ with $\mathscr{H}_1$ (compare with the r.h.s. of Eq.(14)).

For exact wavefunctions, the force on whole particles thus reduces to the sum of the forces on the nuclei $\{A\}$ in the subsystem α. The forces on electrons make no contribution to the force on whole particles. If we interpret this fact, it may be said that the electrons in the exact wavefunction "lie" in the "equilibrium position". However, if we employ an approximate wavefunction, the force on electron will not vanish. Then, $\mathbf{F}_a$ may give a kind of criterion for the accuracy of the wavefunction.

2.3. *Comparison with the Concept in the L-Coordinate System*

In a previous paper [5], where the L-coordinate system was used, we have shown that the AD and EGC forces are the origins of the long-range forces between two atoms. In the R-coordinate system, the concept of the AD force disappears since $(\partial\mathscr{H}_0/\partial\tilde{\mathbf{R}}_A)=0$, and instead a new force concept arises. From Eq.(4), we obtain

$$-(\partial\mathscr{H}_1/\partial\tilde{\mathbf{R}}_A)=-\sum_A(\partial\mathscr{H}_1/\partial\mathbf{R}_A)-\sum_a(\partial\mathscr{H}_1/\partial\mathbf{r}_a). \tag{13}$$

The first term represents the EGC force operator in the ESF theory [5]. The second term is a new operator which represents the force that the electrons $\{a\}$ of the subsystem α receive due to the long-range interaction with the subsystem β. Inserting Eq.(8) into Eq.(11), we obtain

$$\langle\Psi|-\sum_A(\partial\mathscr{H}_0/\partial\mathbf{R}_A)|\Psi\rangle=\langle\Psi|-\sum_a(\partial\mathscr{H}_1/\partial\mathbf{r}_a)|\Psi\rangle, \tag{14}$$

for the *exact* wavefunction^1. In the diatomic case, the l.h.s. represents the AD force, and then the new force operator gives an equivalent value with the AD force. If we call the first term of Eq.(13) the *nuclear* EGC force, the second term may be called *electronic* EGC force. As seen in the following sections, we have no need to calculate the electronic EGC force separately. Its calculation will be complicated because it includes the derivative of the electron-electron repulsion term. Moreover, since the R-coordinate system can be defined only for the long-range interactions, the present theoretical concepts are limited only to the long-range forces. This is a defect of the present treatment in comparison with the wide applicability of the ESF theory [4, 5].

3. Perturbation Theory for the Force on Whole Particles

In this section, we will show generally that the force on whole particles in the R-coordinate system is superior to the force on nucleus in the L-coordinate system in a perturbative sense. First, we summarize the results of the conventional energetic perturbation theory [14] in order to compare with the subsequent results. When the total Hamiltonian $\mathscr{H}$ is separated as in Eq.(1), the total wavefunction $|\Psi\rangle$ and the energy can be expanded as $|\Psi\rangle=\sum_{k=0}^{\infty}|k\rangle$ and $E=\sum_{k=0}^{\infty}E_k$, where the unperturbed and nth-order wavefunctions satisfy

$$\begin{aligned}&(\mathscr{H}_0-E_0)|0\rangle=0,\\&(\mathscr{H}_0-E_0)|n\rangle+\mathscr{H}_1|n-1\rangle=\sum_{k=1}^{n}|n-k\rangle E_k,\ n=1,2,\ldots,\end{aligned}\tag{15}$$

and the perturbation energies are expressed as

$$\begin{aligned}&E_1=\langle 0|\mathscr{H}_1|0\rangle,\\&E_n=\langle 0|\mathscr{H}_1|n-1\rangle-\sum_{k=1}^{n-1}\langle 0|n-k\rangle E_k,\ n=2,3,\ldots\end{aligned}\tag{16}$$

If $\mathscr{H}_1$ is Hermitian, the energy correct to order $2n+1$ can be obtained from the wavefunctions only to order n.

$$\left\{\begin{aligned}&E_{2n}=\langle n-1|\mathscr{H}_1|n\rangle-\sum_{k=1}^{n}E_k\sum_{j=0}^{k-1}\langle n+j-k|n-j\rangle,\\&E_{2n+1}=\langle n|\mathscr{H}_1|n\rangle-\sum_{k=1}^{n}E_k\sum_{j=0}^{k-1}\langle n+1+j-k|n-j\rangle,\ n=1,2,\ldots\end{aligned}\right.\tag{17}$$

The normalization condition we used is $\langle\Psi|\Psi\rangle=1$, i.e.,

$$\sum_{k=0}^{n}\langle k|n-k\rangle=0,\ n=1,2,\ldots\tag{18}$$

The nth-order forces on *nucleus* and on *whole particles* are obtained from Eqs.(9) and (10) as

$$\mathbf{F}_A^n=\sum_{k=0}^{n}\langle k|-(\partial\mathscr{H}_0/\partial\mathbf{R}_A)|n-k\rangle+\sum_{k=0}^{n-1}\langle k|-(\partial\mathscr{H}_1/\partial\mathbf{R}_A)|n-k-1\rangle,\tag{19}$$

$$\mathbf{F}_\alpha^n=\sum_{k=0}^{n-1}\langle k|-(\partial\mathscr{H}_1/\partial\tilde{\mathbf{R}}_A)|n-k-1\rangle,\ n=1,2,\ldots\tag{20}$$

These equations show that the force on nucleus correct to order n, $\mathbf{F}_A^n$, requires the wavefunctions up to order n, while the force on whole particles, $\mathbf{F}_\alpha^n$, requires the wavefunctions up to order $n-1$. This simplification for the force on whole particles comes from the relation $(\partial\mathscr{H}_0/\partial\tilde{\mathbf{R}}_A)=0$.

In a previous study of the long-range force of the H–H$^+$ system, we have pointed out that although the nth-order force on H$^+$ is obtained by the wavefunction to order $n-1$, the nth-order force on the nucleus of the hydrogen atom H requires the wavefunction to order n [5]. The reason for this difference is that the force on H$^+$ corresponds to the force on whole particles, but the force on the nucleus of H does not. If we consider the force on hydrogen *atom* instead of the force on the *nucleus* of H, the nth-order force is determined by the wavefunctions to order $n-1$, as expected.

In the following paragraphs, we prove that the force on whole particles is equal to the derivative of the perturbation energy (16) and moreover that the wavefunction to order n determines the force on whole particles to order $2n+1$.

This proof can be applied to all expectation values of $\partial\mathscr{H}/\partial\lambda$ which satisfy the condition $\partial\mathscr{H}_0/\partial\lambda=0$.

From the normalization condition (18), we obtain after some modification,

$$\sum_{k=0}^{n}\{\langle n-k|k'\rangle-\langle k|(n-k)'\rangle\}=0. \tag{21}$$

Hereafter, prime means the derivative with negative sign, $-(\partial/\partial\tilde{\mathbf{R}}_A)$. Differentiation of Eq.(15) yields

$$(\mathscr{H}_0-E_0)|n'\rangle=-\mathscr{H}_1|(n-1)'\rangle-\mathscr{H}_1'|n-1\rangle+\left\{\sum_{k=1}^{n}|n-k\rangle E_k\right\}'. \tag{22}$$

Operation of $\langle m|$ and cancellation of the term $(\mathscr{H}_0-E_0)$ using the conjugate form of Eq.(15) give

$$\langle m+1|\mathscr{H}_1'|n-1\rangle=\langle m|\mathscr{H}_1|n'\rangle-\langle m+1|\mathscr{H}_1|(n-1)'\rangle-C_{m,n}, \tag{23}$$

where

$$C_{m,n}=\sum_{k+1}^{m+1}E_k\langle m-k+1|n'\rangle-\sum_{k=1}^{n}\{E_k\langle m+1|(n-k)'\rangle+E_k'\langle m+1|n-k\rangle\}. \tag{24}$$

Substituting each term of Eq.(20) with Eq.(23), we get

$$\mathbf{F}_\alpha^n=\langle 0|\mathscr{H}_1'|n-1\rangle+\langle 0|\mathscr{H}_1|(n-1)'\rangle-\sum_{j=0}^{n-2}C_{j,n-j-1}, \tag{25}$$

where

$$\sum_{j=0}^{n-2}C_{j,n-j-1}=\sum_{j=1}^{n-1}\left\{\left(\sum_{k=1}^{j}E_k\langle j-k|(n-j)'\rangle-\sum_{k=1}^{n-j}E_k\langle j|(n-k-j)'\rangle\right)\right.$$
$$\left.+\sum_{k=1}^{n-j}E_k'\langle j|n-k-j\rangle\right\} \tag{26a}$$

In Eq.(26a), reversing the order of the summation j in the first term and interchanging the summations j and k, we obtain

$$\sum_{j=0}^{n-2}C_{j,n-j-1}=\sum_{k=1}^{n-1}E_k\sum_{j=1}^{n-k}(\langle n-k-j|j'\rangle-\langle j|(n-k-j)'\rangle)-\sum_{k=1}^{n-1}E_k'\sum_{j=1}^{n-k}\langle j|n-k-j\rangle. \tag{26b}$$

Using Eqs.(18) and (21), we get

$$\sum_{j=0}^{n-2}C_{j,n-j-1}=\sum_{k=1}^{n-1}E_k\langle 0|(n-k)'\rangle+\sum_{k=1}^{n-1}E_k'\langle 0|n-k\rangle=\sum_{k=1}^{n-1}\langle 0|\{|n-k\rangle E_k\}', \tag{26c}$$

and therefore

$$\mathbf{F}_\alpha^n=\langle 0|\mathscr{H}_1'|n-1\rangle+\langle 0|\mathscr{H}_1|(n-1)'\rangle-\sum_{k=1}^{n-1}\langle 0|\{|n-k\rangle E_k\}'. \tag{27}$$

Expression (27) is nothing but the derivative of the energy expression (16).

$$\mathbf{F}_\alpha^n = E_n', \; n = 1, 2, \ldots \tag{28}$$

Combination of Eqs.(17) and (28) gives *2n*th- and *(2n+1)*th-order expression for the force on whole particles.

$$\begin{cases} \mathbf{F}_\alpha^{2n} = \langle (n-1)' | \mathscr{H}_1 | n \rangle + \langle n-1 | \mathscr{H}_1' | n \rangle + \langle n-1 | \mathscr{H}_1 | n' \rangle - \\ \qquad \qquad \displaystyle\sum_{k=1}^{n} \sum_{j=0}^{k-1} \{ E_k \langle n+j-k | n-j \rangle \}', \\ \mathbf{F}_\alpha^{2n+1} = \langle n' | \mathscr{H}_1 | n \rangle + \langle n | \mathscr{H}_1' | n \rangle + \langle n | \mathscr{H}_1 | n' \rangle - \displaystyle\sum_{k=1}^{n} \sum_{j=0}^{k-1} \{ E_k \langle n+1+j-k | n-j \rangle \}', \\ \qquad \qquad n = 1, 2, \ldots \end{cases} \tag{29}$$

Now, we have proven the foregoing statements. Eq.(28) shows that the *n*th-order force on whole particles is identical with the derivative of the *n*th-order perturbation energy. Eq.(29) shows that the wavefunctions (and their derivatives) to order n determine the *(2n+1)*th-order long-range force, just as they do for the perturbation energy. This holds only for the force on whole particles, not for the force on nucleus. When we discuss the long-range force between two atoms with a large separation R, where the multipole expansion is used in the perturbation Hamiltonian, $-(\partial/\partial\tilde{\mathbf{R}}_A)$ becomes $\partial/\partial R$ and the derivatives of wavefunctions and perturbation Hamiltonian are obtained quite easily. Salem and Wilson concluded in general that the H-F approach (force on nucleus) seems to be a much "weaker" method of calculation than the energetics [7]. However, their conclusion does not apply to the calculation of long-range forces, because there we can always introduce the concept of the force on whole particles in the R-coordinate system. Thus, the force method is as useful as the energetic one at least for the long-range forces.

4. Applications

In this section, we calculate the leading terms of the long-range forces for H(1s)–H^+, H(1s)–H(1s), and NH_3–H^+ systems. Calculation of the force on whole particles, instead of the force on nucleus, overcomes the computational difficulty in the previous works [5, 11]. Indeed, the zeroth- and first-order wavefunctions determine the force on whole particles (*atom*) up to the third-order in the first two examples. Thus, equivalence of the force and energetic treatments is confirmed. In the last example, the NH_3–H^+ system, we estimate the forces on N and H nuclei in the NH_3 molecule using the concept of force on *molecule*.

4.1. Long-Range Force for the H(*1s*) *and* H^+ *System*

In our previous work [5], the leading term of the long-range force of this system was calculated using the L-coordinate system in three different ways, i.e., two no-resonance treatments and a resonance one. All of these calculations gave

Table 1. Leading terms of the long-range forces, F^1, F^2, and F^3, between a hydrogen atom and a proton (a.u.)

	F^1	F^2	F^3
Previous work[a]	0	$9R^{-5}$	—
Present work[b]	0	$9R^{-5}$	$1491/4R^{-8}$
Energy derivative[c]	0	$9R^{-5}$	$1491/4R^{-8}$

[a] Ref. 5. The force on the *nucleus* of a hydrogen atom is given. The second-order wavefunction is used for the calculation of F^2.

[b] The force on hydrogen *atom* is given. The zeroth-and first-order wavefunctions determine all of the F^1, F^2, and F^3.

[c] Refs. [15] and [16] of the text.

identical results. Here, we show only no resonance treatment, since the other calculations can be carried out similarly.

The forces on whole particles up to the third-order are written from Eq.(29) as

$$\begin{cases} F_\alpha^1 = \langle 0|\mathscr{H}_1'|0\rangle, \\ F_\alpha^2 = \langle 0|\mathscr{H}_1'|1\rangle + \langle 1|\mathscr{H}_1'|0\rangle, \\ F_\alpha^3 = \langle 1'|\mathscr{H}_1|1\rangle + \langle 1|\mathscr{H}_1'|1\rangle + \langle 1|\mathscr{H}_1|1'\rangle - F_\alpha^1\langle 1|1\rangle - E_1\{\langle 1|1\rangle\}', \end{cases} \tag{30}$$

which include only the zeroth- and first-order wavefunctions. In Eq.(30), prime means $\partial/\partial R$ and R is the internuclear distance. The zeroth-order wavefunction and the perturbation Hamiltonian are written as

$$|0\rangle = (1s) = \pi^{-1/2}\exp(-\tilde{r}), \tag{31}$$

$$\mathscr{H}_1 = -r'^{-1} + R^{-1} = -\sum_{k=2}^{\infty} R^{-k}\tilde{r}^{k-1}P_{k-1}(\cos\theta), \tag{32}$$

where $P_k(\cos\theta)$ is the Legendre polynomial and θ is the angle between $\tilde{\mathbf{r}}$ and $\mathbf{R}$. The first-order wavefunction was obtained as [5, 15]

$$|1\rangle = \pi^{-1/2}\exp(-\tilde{r})\sum_{k=2}^{\infty} R^{-k}(\tilde{r}^k/k + \tilde{r}^{k-1}/(k-1))P_{k-1}(\cos\theta). \tag{33}$$

Using Eqs.(31)–(33), we get the leading terms of F_{H}^1, F_{H}^2, and F_{H}^3. The results are shown in Table 1. They agree with those obtained from the energetic method. Although our previous result of F^2 was calculated using the second-order wavefunction, all of the present values were evaluated only from the zeroth- and first-order wavefunctions. This is indeed a great simplification.

4.2. Long-Range Force between Two Hydrogen Atoms

The perturbation Hamiltonian of this system is written as

$$\mathscr{H}_1 = -r_{a2}^{-1} - r_{b1}^{-1} + r_{12}^{-1} + R^{-1} = \sum_{k=3}^{\infty} V_k R^{-k}. \tag{34}$$

General formula for V_k has been given by Hirschfelder and Löwdin [17].

Using the expansion (34), the leading terms of the force on hydrogen *atom* up to third order are given by Eq.(30) as

$$\begin{cases} F_{\mathrm{H}}^{1} = \sum\limits_{k=3}^{\infty} \langle 0|(V_k R^{-k})'|0\rangle = \sum\limits_{k=3}^{\infty} -kR^{-1}\langle 0|V_k R^{-k}|0\rangle, \\ F_{\mathrm{H}}^{2} = 2\langle 0|(V_3 R^{-3})'|1\rangle = -6R^{-1}\langle 0|V_3 R^{-3}|1\rangle, \\ F_{\mathrm{H}}^{3} = 2\langle 1|V_5 R^{-5}|1'\rangle + \langle 1|(V_5 R^{-5})'|1\rangle = -11R^{-1}\langle 1|V_5 R^{-5}|1\rangle, \end{cases} \tag{35}$$

where we have considered only the term proportional to R^{-3} for the first-order wavefunction and therefore, $|1'\rangle$ is $-3R^{-1}|1\rangle$. On the other hand, the leading terms of the interaction *energies* up to third order have been calculated as [17, 18]

$$\begin{cases} E_1 = \sum\limits_{k=3}^{\infty} \langle 0|V_k R^{-k}|0\rangle = \sum\limits_{k=3}^{\infty} E_{1,k} = 0;\ E_{1,k} = 0, \\ E_2 = \langle 0|V_3 R^{-3}|1\rangle = -6.499026R^{-6}, \\ E_3 = \langle 1|V_5 R^{-5}|1\rangle = -3986R^{-11}. \end{cases} \tag{36}$$

Noticing that the integrals appearing in these energy calculations are identical with those in the force calculations, we get from Eqs.(35) and (36)

$$\begin{cases} F_{\mathrm{H}}^{1} = \sum\limits_{k=3}^{\infty} -kR^{-1}E_{1,k} = 0, \\ F_{\mathrm{H}}^{2} = -6R^{-1}E_2 = 38.994156R^{-7}, \\ F_{\mathrm{H}}^{3} = -11R^{-1}E_3 = 43846R^{-12}. \end{cases} \tag{37}$$

Since E_2 and E_3 depend respectively on R^{-6} and R^{-11}, the force results shown in Eq.(37) are just equivalent with the energy results shown in Eq.(36). Hirschfelder and Eliason [11] obtained using the first- and second-order wavefunctions the F^2 value of $39.001R^{-7}$ as the force on hydrogen *nucleus*, while we obtained using *only* the first-order wavefunction *not only* the best F^2 value $38.994156R^{-7}$ *but also* the F^3 value as the force on hydrogen *atom*. This comparison clearly shows the advantage of the present force treatment, although both should give equivalent results as shown by Eq.(12).

4.3. Long-Range Force between NH_3 *and Proton*

This is a good example to illustrate the relations of the forces on nuclei, the forces on whole particles, and the energy derivatives. We assume that the proton is situated on the symmetry axis (z-axis) of the ammonia molecule with a large distance R (Fig. 2).

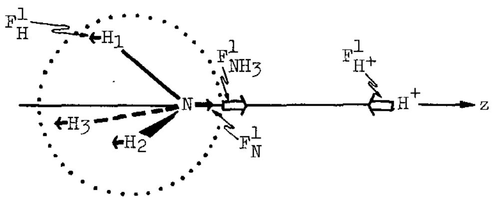

Fig. 2. Long-range forces in NH_3–H^+ system

The first-order energy of the system has been obtained as

$$E_1 = -0.58R^{-2} - 0.744R^{-3} + O(R^{-4}), \tag{38}$$

from the experimental results [19]. This interaction energy gives information about the external force acting on the NH_3 molecule as a unit, but never gives information about the internal forces in the NH_3 molecule which are induced by the interaction with the proton.

In the present force theory, the first-order forces along the axis are written from Eq.(12) as

$$\begin{cases} F^1_{NH_3} = F^1_N + 3F^1_H, \\ F^1_{NH_3} = -F^1_{H^+} = \partial E_1/\partial R. \end{cases} \tag{39}$$

Namely, the force on the NH_3 molecule is connected with the forces on the N nucleus and on the three H nuclei in the molecule. The forces on the nuclei, F^1_N and F^1_H, are written as

$$\begin{cases} F^1_N = Z_N\{2\langle 0|\sum_a z_{Na}/r_{Na}^3|1\rangle - Z_{H^+}R^{-2}\}, \\ F^1_H = Z_H\{2\langle 0|\sum_a z_{Ha}/r_{Ha}^3|1\rangle - Z_{H^+}R^{-2}\}, \end{cases} \tag{40}$$

where Z is the nuclear charge and the wavefunctions are assumed to be real. Direct calculations of the integrals in Eq.(40) are troublesome and unpractical. Instead, combining Eqs.(38–40), we get

$$\begin{cases} F^1_N = (k+3)^{-1}\{3Z_{H^+}(kZ_H - Z_N)R^{-2} + 1.16kR^{-3} + 2.232kR^{-4} + O(R^{-5})\}, \\ F^1_H = (k+3)^{-1}\{Z_{H^+}(Z_N - kZ_H)R^{-2} + 1.16R^{-3} + 2.232R^{-4} + O(R^{-5})\}, \end{cases} \tag{41}$$

where k means the ratio of the two integrals.

$$k = Z_N\langle 0|\sum_a z_{Na}/r_{Na}^3|1\rangle / Z_H\langle 0|\sum_a z_{Ha}/r_{Ha}^3|1\rangle. \tag{42}$$

The leading terms proportional to R^{-2} in Eq.(41) are the charge-charge interactions between the proton and the shielded N and H nuclei. These terms are purely the internal forces and disappear as the whole molecule. The coefficients of R^{-2} indicate that if $k > Z_N/Z_H$ the forces on the nucleus N and on the nucleus H are attractive and repulsive, respectively, and if $k < Z_N/Z_H$ the situation is in the opposite way. Since at a large separation Coulombic force dominates and the gross charges on the N and H nuclei in a free NH_3 molecule are negative and positive, respectively, we expect $k > Z_N/Z_H$, and therefore the ammonia molecule will approach the proton with closing its umbrella (Fig. 2). Note that this expectation will be valid only when the electron exchange between NH_3 and H^+ is negligible. When the electron transfer from lone-pair orbital of NH_3 to H^+ becomes appreciable, the AD force on the N nucleus will transform to the exchange (EC) force between N and H^+, and therefore the umbrella-opening will occur at this stage (see Ref. 4, Paper 1)[2]. As expected, the HNH angle in NH_4^+ is 109.5° in comparison with 106.6° in NH_3 [20].

5. Summary

In this report, we have studied the Hellmann-Feynman force approach to long-range interactions. The meaning and the perturbation theoretical properties of the H-F theorem depend critically on the choice of the coordinate system, and the relations between forces in the L- and R-coordinate systems are clarified. In the L-coordinate system, the force is interpreted as the *force on nucleus*, while in the R-coordinate system, the force has the meaning of the *force on whole particles*. Here, the whole particles mean all the electrons and nuclei of the interacting subsystem. For *exact* wavefunctions, the force on whole particles reduces to the sum of the forces acting on all the *nuclei* of the subsystem. Since $(\partial\mathscr{H}_0/\partial\tilde{\mathbf{R}}_A)=0$ in the R-coordinate system, the force on whole particles comes entirely from the derivative of the interaction Hamiltonian. When we partition the force in the R-coordinate system, a new force concept which may be called *electronic* EGC force arises and exactly substitutes, for diatomic cases, the AD force in the L-coordinate system [5]. The concept of the EGC force is preserved and may be called *nuclear* EGC force.

The fact $(\partial\mathscr{H}_0/\partial\tilde{\mathbf{R}}_A)=0$ means that the force operator in the R-coordinate system satisfies the prerequisite of the perturbation theory that the zeroth-order state should be completely non-interacting. This fact greatly simplifies the perturbation theoretical calculation of the force on whole particles. The following important relations have been proved generally. (1) The nth-order force on whole particles is equal to the derivative of the nth-order perturbation energy. (2) The wavefunctions (and their derivatives) up to order n determine the force on whole particles to order $2n+1$ (however, the wavefunctions to order n determine the force on nucleus only to order n). Especially, relation (2) means that the force approach is not necessarily inferior to, but as useful as the energetic approach to the long-range forces. The computational difficulty of the H-F force pointed out previously vanishes as shown in the first two examples. Thus, the apparent perturbation theoretical contradiction between force and energetic treatments vanishes in the R-coordinate system, although the definition of the R-coordinate system is limited to the long-range interactions. In the last example, the property of the force on whole particles is applied to estimate the long-range forces acting on the constituent nuclei in an interacting molecule.

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[2] Similar behavior was found for the S_{N2} reactions $F^- + CH_3F \rightarrow CH_3F + F^-$, etc. (Dedieu, A., Veillard, A.: J. Am. Chem. Soc. **94**, 6730 (1972)).

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