

## FORCE IN SCF THEORIES

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A new force approach is reported in which we improve the wavefunction so that the Hellmann–Feynman theorem is satisfied. A sufficient condition for the Hellmann–Feynman theorem to be satisfied is that the basis set includes AO derivatives  $\partial\chi_r/\partial x_r$  for any basis  $\chi_r$ . Here we test a procedure in which only the first derivative AOs are added to the “parent” AOs. The results are very encouraging.

### 1. Introduction

Knowledge on the derivatives (especially first and second derivatives) of the potential energy hypersurface and the electronic origins of them is of fundamental importance in studies of molecular geometries (stable and transient), vibrations, chemical reactions and dynamics. Two approaches have been developed for derivative studies: one uses the direct analytic gradient of the SCF [1–4], MC SCF [3,5,6], or CI [7–9] energy, and the other uses the Hellmann–Feynman (H–F) theorem [10]. Though the difference between these two expressions for the force vanishes identically for exact and stable [11] wavefunctions (therefore we refer it as an error term), it was disappointingly large for most approximate wavefunctions, except for floating wavefunctions [12–14]. However, we prove a theorem which shows that there is a unique and systematic way of improving the SCF and MC SCF wavefunctions so that they satisfy the Hellmann–Feynman theorem. Based on this theorem, we propose an approximate method and test it for LiH and BH at several internuclear distances. Our method is theoretically orthodox: we aim to improve the wavefunction so that it satisfies the Hellmann–Feynman theorem. The *quality* of the resultant force and other properties should be improved at the same time because of the improvement in the wavefunction. Further, the intuitive picture of the Hellmann–Feynman force [15,16] is associated with the results ob-

tained. It may give a basis for understanding and predicting similar phenomena. Computationally, the time for the force calculation is negligible, though we use time for improving the wavefunction.

### 2. Force in SCF theory

In the Hartree–Fock–Roothaan SCF theory [17], the MOs  $\phi_i$  in the single determinant

$$\Psi = \|\phi_1\bar{\phi}_1 \dots \phi_n\bar{\phi}_n\| \quad (1)$$

are linearly expanded in a set of basis functions  $\{\chi_r\}$ ,

$$\phi_i = \sum_r c_{ri}\chi_r, \quad (2)$$

and the linear coefficients  $\{c_{ri}\}$  are determined variationally through the SCF equation

$$\sum_s (F_{rs} - \epsilon_i S_{rs}) c_{si} = 0, \quad (3)$$

where  $F_{rs}$  is the Fock matrix given by

$$F_{rs} = (r|h|s) + \sum_{t,u} P_{tu} [(rs|tu) - \frac{1}{2}(rt|su)], \quad (4)$$

$$P_{tu} = \sum_i^{\text{occ}} 2c_{ti}c_{ui}, \quad (5)$$

in standard notation. (Though we use the notation for the closed-shell RHF theory, the following formula-

tions are also valid, with slight modification, for the UHF theory. For extensions to restricted open-shell and MC SCF theories, see a forthcoming paper [18].)

The SCF energy may be written as  $\mathcal{E}(R_A, x_r) = \langle \Psi(x_r) | H(R_A) | \Psi(x_r) \rangle$  where  $\{R_A\}$  are the nuclear coordinates and  $\{x_r\}$  a set of (non-linear) parameters involved in the wavefunction. For the present purpose, the  $\{x_r\}$  are restricted, without loss of generality, to the centers of the constituent AOs  $\{\chi_r\}$  [13]. The force acting on nucleus  $A$  is written as [3]

$$F_A = -\langle \Psi | \partial H / \partial R_A | \Psi \rangle - \sum_r \Delta_r \partial x_r / \partial R_A, \quad (6)$$

where

$$\Delta_r = \sum_s P_{rs} \left[ 2(r' | h | s) + \sum_{t,u} P_{tu} [2(r' s | tu) - (r' t | su)] \right] - 2 \sum_s D_{rs}(r' | s) \quad (7)$$

under the orthonormality of the MOs.  $r'$  denotes the derivative of the AO  $r$ ,  $\partial \chi_r / \partial x_r$  and  $D_{rs}$  is given by

$$D_{rs} = 2 \sum_i^{\text{occ}} \epsilon_i c_{ri} c_{si}. \quad (8)$$

In eq. (6), the first term is the H-F force and the second term, which is  $-2 \langle \Psi | H | \partial \Psi / \partial R_A \rangle$ , is denoted as the error term since it arises entirely from errors included in the wavefunction  $\Psi$  used. It is the sum of the AO contribution  $\Delta_r$  which we call AO error\*.

In the analytic calculation of the energy gradient [2-4], the two terms of eq. (6) are calculated explicitly. When the error term is not small, such a method gives a reliable numerical result since the energy is correct to second order in the error included in the wavefunction: the error term in eq. (6) cancels the (first-order) error included in the H-F force. In the gradient program, however, the most complex and time-consuming part is due to the calculation of the error term. The calculation of the H-F force is straightforward.

The point of the present paper is to show that there is a unique and systematic way of improving the wavefunction so that the AO error  $\Delta_r$  given by eq. (7)

\* In the calculations with a floating wavefunction [14], the AO error  $\Delta_r$  of the AO  $\chi_r$  is made zero.

vanishes identically. With the use of the Fock matrix given by eq. (4) it is easy to rewrite the AO error as

$$\Delta_r = 4 \sum_i c_{ri} \sum_s (F_{r's} - \epsilon_i S_{r's}) c_{si}, \quad (9)$$

where  $F_{r's} = (r' | F | s)$  and  $S_{r's} = (r' | s)$ . When the basis set  $\{\chi_r\}$  includes not only the AO  $r$  but also its derivative  $r'$ , the SCF solution satisfies

$$\sum_s (F_{r's} - \epsilon_i S_{r's}) c_{si} = 0, \quad (10)$$

so that the error associated with the AO  $r$  vanishes identically:

$$\Delta_r = 0. \quad (11)$$

On the other hand, when the basis set does not include  $r'$ , eq. (9) implies that the error term is just the sum of the SCF errors due to the absence of the basis  $r'$ ,  $\sum_s (F_{r's} - \epsilon_i S_{r's}) c_{si}$ , multiplied with the coefficient  $c_{ri}$  of the "parent" AO  $r$ .

Some implications of the theorem are as follows:

(1) A sufficient condition for the H-F theorem to be satisfied is that the basis set includes  $r'$  for any element  $r$ . The basis set  $\{r, r', r'', \dots\}$  is such a basis. If the basis is recurrent in the sense,  $r = r^{(n)}$ , then the number of elements can be finite.

(2) We may want to terminate the sequence,  $r, r', \dots$  at some stage, say at  $r'$ . Then all of the AO errors of the "parent" AOs  $\{r\}$  vanish identically, but the AO errors of the added derivative AOs  $\{r'\}$  remain and are given by

$$4 \sum_i c_{r'i} \sum_s (F_{r''s} - \epsilon_i S_{r''s}) c_{si}. \quad (12)$$

However, if we start from the "parent" AOs which are already reasonably good, the mixing coefficient  $c_{r'i}$  of the added derivative AOs  $r'$  should be small so that the error term may be neglected. In the next section we examine the validity of such an approximation.

The addition of the derivative AOs may be viewed differently. We already have mentioned that the floating wavefunction satisfies the H-F theorem, if the centers  $x$  of the constituent AOs  $\chi_r(x)$  are determined variationally [12-14]. Such a floating AO may be expanded around the position  $x_0$ , which is usually the position of the nucleus to which  $\chi_r$  belongs, i.e.,

$$\chi_r(x) = \chi_r(x_0) + (\partial \chi_r / \partial x)_{x_0} (x - x_0) + \dots \quad (13)$$

Table 1  
AO error, H-F force, energy gradient, and SCF energy before and after addition of first-derivative AOs for LiH and BH a)

Li/B	LiH (3.015 au)		LiH (4.015 au)		BH (2.329 au)		BH (2.800 au)		
	[3s2p/2s]	[3s2p/2s] plus first-derivative AOs	[3s2p/2s]	[3s2p/2s] plus first-derivative AOs	[3s2p/2s]	[3s2p/2s] plus first-derivative AOs	[3s2p/2s]	[3s2p/2s] plus first-derivative AOs	
Li	AO error								
	1s	-0.1615	-0.0011	-0.1252	-0.0002	0.2569	0.0023	0.2596	0.0019
	2s	-0.0045	0.0006	-0.0012	-0.0001	0.0087	-0.0011	0.0125	-0.0001
	3s	-0.0001	0.0001	0.0	0.0001	0.0015	-0.0004	0.0011	0.0002
	1p	0.0069	-0.0003	0.0050	0.0	0.1158	0.0017	0.0931	0.0014
	2p	0.0001	0.0	0.0007	0.0002	0.0011	-0.0001	0.0015	0.0
	total error	-0.1591	-0.0007	-0.1207	0.0	0.3841	0.0024	0.3678	0.0035
	H-F force	0.1540	-0.0004	0.1516	0.0306	-0.3881	-0.0011	-0.3158	0.0525
	energy gradient	-0.0050	-0.0011	0.0310	0.0306	-0.0040	0.0013	0.0520	0.0560
	H	AO error							
1s		-0.0294	0.0	-0.0153	0.0002	-0.0828	-0.0014	-0.0634	-0.0010
2s		-0.0062	-0.0006	-0.0035	-0.0004	0.0009	0.0001	-0.0064	-0.0009
total error		-0.0356	-0.0006	-0.0188	-0.0002	-0.0820	-0.0013	-0.0698	-0.0018
H-F force		0.0406	0.0017	-0.0122	-0.0304	0.0860	0.0	0.0178	-0.0542
energy gradient		0.0050	0.0011	-0.0310	-0.0306	0.0040	-0.0013	-0.0520	-0.0560
SCF energy	-7.9811	-7.9851	-7.9851	-7.9653	-25.1137	-25.1242	-25.0995	-25.1080	

a) After the addition of the derivative AOs, the AO errors of the "parent" AOs vanish identically. The values given are those of the derivative AOs.

The addition of the derivative AO thus gives the freedom of "floating" to the parent AO,  $\chi_r$ . However, an important difference between the floating and present methods lies in the width of the basis set space. The present method gives lower energy than the floating method even if we restrict ourselves only to first derivative AOs. The order of the energy lowering is similar to that obtained by the addition of so-called "polarization" functions [19]. For a gaussian basis, the functional form of the derivative AO is just that of the polarization function, namely, the derivative  $\partial/\partial x$  of  $s$ ,  $p_x$ ,  $p_y$ , etc. AOs gives  $p_x$ ,  $s + d_{x^2}$ ,  $d_{xy}$ , etc. AOs, respectively, with the same exponent  $\ddagger$ .

### 3. Test calculation for LiH and BH

Test calculations were performed for LiH and BH at several internuclear distances. The Li or B nucleus was put at the origin and the H nucleus at positive displacement along the  $z$  axis. The (9s5p/4s) primitive sets of Huzinaga [20] contracted to [3s2p/2s] sets by Dunning and Hay [19] were used as the "parent" AOs and their first-derivative AOs were added. Table 1 gives the AO errors, H-F force, and the sum of them

<sup>‡</sup> The "polarization" is shown to be most effective when two AOs have the same exponent.

(energy gradient) obtained before and after addition of the first derivative AOs. It also gives the SCF energies. Before the addition, large AO errors are seen for the 1s AOs of Li and H of LiH, and for the 1s and 1p AOs of B and the 1s AO of H of BH. The H-F force is unreliable at this stage in comparison with the energy gradient. After the addition, however, the AO errors of the parent AOs vanish identically as eq. (11) shows. The values given in table 1 are the AO errors of the added derivative AOs. It is seen that the AO errors become dramatically small. For LiH the total errors are zero up to three places of decimals and for BH up to two places. The calculated H-F force is therefore in good agreement with the energy gradient obtained *after* the addition.

In figs. 1 and 2, the forces acting on the Li and B nuclei of LiH and BH are plotted against the internuclear distances. It is seen that after the addition of the derivative AOs, the H-F force and the energy gradient agree quite well (i.e., the error term is negligibly small) over a wide range of internuclear distances. For the H-F forces acting on the H nuclei of LiH and BH, the error terms were so small that the curves for the H-F force and the energy gradient (after the addition) superpose almost completely. Further, the energy gradient itself is seen to be affected by the addition of derivative AOs. This difference is due to

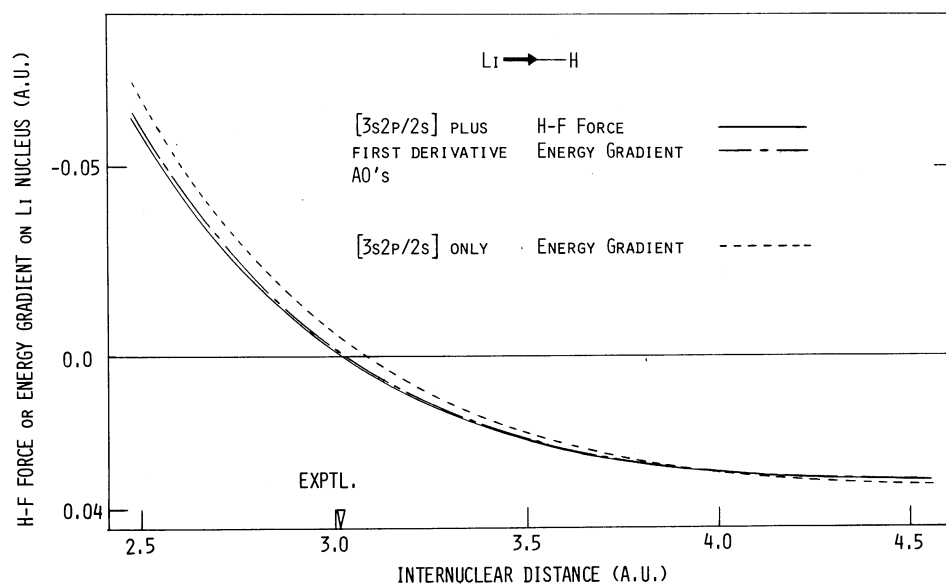


Fig. 1. Energy gradient and Hellmann-Feynman force acting on Li versus internuclear distances for LiH.

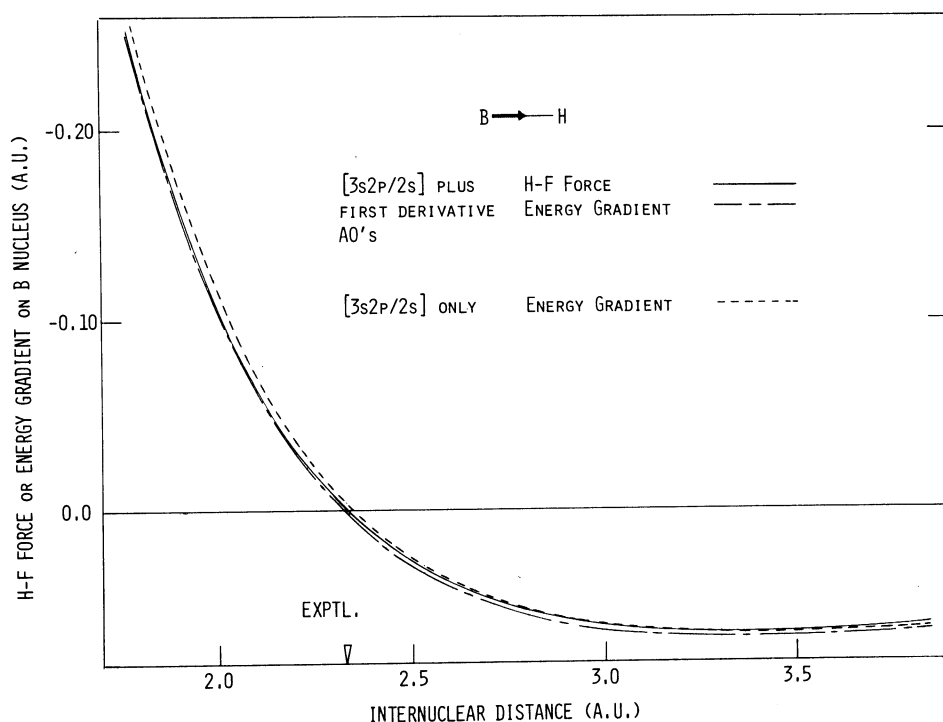


Fig. 2. Energy gradient and Hellmann–Feynman force acting on B versus internuclear distances for BH.

the improvement of the wavefunction. It is larger than the order of magnitude of the error term obtained after the addition.

Table 2 summarizes the bond lengths and force constants of LiH and BH calculated from different forces and compares them with experimental values [21]. It is seen that these properties are improved by the addition of the derivative AOs. After the addition,

the energy gradient and the H–F force give essentially the same results. Therefore, at this stage, we can use the H–F force instead of the energy gradient: the time for calculations of the error term can be saved. It is interesting to analyze the intuitive concept of the H–F theorem along the reaction path and the vibrational mode.

Table 2  
Bond lengths and force constants of LiH and BH

Molecule	Property	[3s2p/2s] energy gradient	[3s2p/2s] plus first-derivative AOs			Exp. a)
			energy gradient	H–F force on Li or B	H–F force on H	
LiH	bond length (au)	3.084	3.031	3.021	3.039	3.015
	force constant (mdyn/Å)	1.069	1.080	1.079	1.065	1.025
BH	bond length (au)	2.348	2.323	2.334	2.329	2.329
	force constant (mdyn/Å)	3.148	3.244	3.108	3.197	3.046

a) From ref. [21].

#### 4. Concluding remarks

In this paper we have shown that there is a unique and systematic way of improving the SCF wavefunction so that it satisfies the Hellmann–Feynman theorem. When the basis set includes the derivative AO  $r'$  for any element  $r$ , the SCF wavefunction strictly satisfies the H–F theorem. Based on this fact, we have examined here the approximate method in which only the first derivative AOs are added to the parent AOs, which are [3s2p/2s] sets of Huzinaga–Dunning [19,20], for LiH and BH. Over a wide range of internuclear distances, the error term became so small that the H–F theorem was essentially satisfied. This was confirmed also through calculations of equilibrium bond lengths and force constants. Further, the quality of the force itself was shown to be improved at the same time by the present improvement of the wavefunction.

In the conventional energy gradient procedure, the derivative AOs are calculated *after* the SCF process, as seen in eq. (7). The calculation of this error term is a time-consuming process and requires a special program [4,22,23]. In the present approach, however, the derivative AOs are added to the basis set *before* SCF as a basis expansion. No special programming is required. The added AOs work to improve the wavefunction as polarization functions, and the AO errors of the parent AOs vanish identically. Though the time for SCF calculation increases with this improvement, the calculation of the error term seems to be unnecessary at least for the basis set of the present quality. Since the calculation of the H–F force is straightforward, we can save time at this stage. Further, the intuitive force concept based on the H–F theorem may be used quantitatively. It is interesting to apply it to various chemical processes [24,25]. Since the set of parent AO and its derivatives  $r, r', r'',$  etc. forms a so-called shell structure, the algorithms for fast evaluation of integrals would be useful [26,27]. Lastly, we note that the present theorem is valid also for general MC SCF wavefunctions and general open-shell orbital theories. The proof will be given in a forthcoming paper.

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is the POLYATOM system [28] with the addition of a gradient part coded by Mr. S. Kanayama, whom the authors acknowledge. Calculations were carried out with the M-200 computers at the Data Processing Center of Kyoto University and at the Institute for Molecular Science. This work was supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, and Culture.

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