

Force in SCF theories. Test of the new method

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A new force method reported previously, which may be called the (r, r') method, is tested for several di- and triatomic molecules, CO, N₂, LiF, H₂O, and HNO, with the use of several basis sets. It is shown that by the addition of the first derivatives of the basis set, the Hellmann–Feynman (H–F) theorem is essentially satisfied. The present force method is shown to be useful for calculations of equilibrium geometries and force constants. The basis set of double zeta accuracy such as 4-31G, 6-31G, and [3s 2p/2s] sets are well suited for the present method. The STO-3G set seems to be less suitable. Further it is shown that by the present method the other one-electron properties are improved at the same time. We have discussed the features of the present method as compared with the energy gradient method.

I. INTRODUCTION

Derivatives of potential energy hypersurfaces are the quantities of central importance in many fields of chemistry. Molecular geometries of stable and excited species, molecular vibrations, chemical reactions, and their dynamics are all phenomena developed on this hypersurface. Thus, for the theory of potential derivatives we need at least two characteristics. 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. These properties are important for a development of chemical theories of quantitative and predictive ability.

So far, two methods have been used for the derivative studies: one uses the direct (analytic) gradient of the SCF¹⁻⁵ and MC-SCF^{3,6} energies and the other uses the Hellmann–Feynman (H–F) theorem.⁸⁻¹¹ However, in their present situations, both of these theories do not satisfy the above two requirements. The two methods are connected by

$$\frac{\partial E}{\partial \mathbf{R}_A} = \langle \Psi | \frac{\partial H}{\partial \mathbf{R}_A} | \Psi \rangle + \sum_r \Delta_r \frac{\partial \chi_r}{\partial \mathbf{R}_A}, \quad (1)$$

where Δ_r is given in the SCF theory by

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

In these equations, \mathbf{R}_A denotes the position of the nucleus A , \mathbf{x}_r the center of the AO χ_r , r' the derivative of the AO χ_r , $\partial \chi_r / \partial \mathbf{x}_r$, P_{rs} the bond-order density matrix, and $D_{rs} = \sum_i^{\text{occ}} 2 \epsilon_i c_{ri} c_{si}$ with ϵ_i the orbital energy. In Eq. (1), the left-hand side is the energy gradient, the first term on the right-hand side is the Hellmann–Feynman (H–F) force, and the second term then shows the difference of the two methods. Though this term vanishes identically for exact and stable wave functions^{11,12} (therefore, we refer it as error term), it is disappointingly large for most approximate wave functions. Thus, though the energy gradient is correct to second order in the error included in the wave function, as the energy itself is, it is difficult to assign physical meaning to the respective terms. Especially, any physical meanings cannot be assigned to the error term, since they, if any,

should sum up to zero at exact limit. On the other hand, the H–F force permits us a very intuitive electrostatic concept since it is written as

$$\langle \Psi | \frac{\partial H}{\partial \mathbf{R}_A} | \Psi \rangle = - \int (Z_A r_{A1} / r_{A1}^3) \rho(\mathbf{r}_1) d\mathbf{r}_1 + \sum_{B \neq A} Z_A Z_B \mathbf{R}_{AB} / R_{AB}^3. \quad (3)$$

The first term represents an electrostatic interaction of the nuclear charge with the electronic charge distribution $\rho(\mathbf{r}_1)$ surrounding it, and the second term is an inter-nuclear repulsion. However, so long as the error term is large, the H–F term itself is unreliable, since it includes a large first-order error which should be cancelled out by the error term.

Thus, in order to obtain a method which meets the above two requirements, we have to search for a practical method of improving the wave function so that it satisfies the H–F theorem. It is clear that the problem lies in the nature of the basis set, since SCF theories in general with *complete* basis set satisfy the H–F theorem.¹² Thus, one way is to search for a basis set which is “complete” at least with respect to the H–F force. Another way is, as shown by Hurley,¹¹ to “float” and optimize the positions of the bases. It corresponds to treating the electronic coordinates as variables free from the nuclear coordinates, as they should be. We have reported several calculations with floating orbitals for geometries and chemical reactions of simple systems.^{13,14} However, the underlying multidimensional optimization will become impractical for large system.

In a previous paper, we have reported another systematic method for obtaining a stable wave function.^{15,16} The method belongs to the first approach mentioned in the above paragraph. It was shown that the AO contribution to the error term Δ_r (then we refer to it as AO error) is expressed in general as¹⁶

$$\Delta_r = 2 \sum_i c_{ri} \{ \text{SCF requirement projected on } |r'\rangle \}, \quad (4)$$

where c_{ri} is a mixing coefficient of the basis χ_r in an orbital ϕ_i and r' is the derivative $\partial \chi_r / \partial \mathbf{x}_r$ of the basis $r = \chi_r$. Equation (4) is valid for SCF theories in gen-

eral, including closed- and open-shell RHF theories, UHF theory, and MC-SCF theory. Specifically, for the closed-shell RHF theory, Δ_r given by Eq. (3) is rewritten as¹⁵

$$\Delta_r = 4 \sum_i c_{r,i} \left[\sum_s (F_{r',s} - \epsilon_i S_{r',s}) c_{s,i} \right], \quad (5)$$

where $F_{r',s} = \langle r' | F | s \rangle$ and $S_{r',s} = \langle r' | s \rangle$. Therefore, if the basis set includes r' as well as r , Δ_r should vanish identically:

$$\Delta_r = 0. \quad (6)$$

Thus, the *theorem* follows^{15,16} a sufficient condition for an SCF wave function to satisfy the H-F theorem is that the basis set includes the derivative AO r' for any basis r . The basis set $\{r, r', r'', \dots\}$ is such basis. Similar recognition seems to be obtained by Hall¹² and recently by Habitz and Votava¹⁷ in a different way. This theorem gives a unique and systematic way of improving the wave function, so that it satisfies the H-F theorem. We may expect that the other properties are also improved at the same time as will be shown below.

As a first stage of this approach, we have tested an approximation in which only the first derivative AO's $\{r'\}$ are added to the "parent" AO's $\{r\}$.^{15,16} (The set $\{r, r'\}$ is called "family".) This method may be called (r, r') method. There, all of the AO errors of the parent AO's vanish identically as Eq. (6) shows, but the AO errors of the added derivative AO's remain and are given by (in the closed-shell RHF case):

$$\Delta_{r'} = 4 \sum_i c_{r',i} \left[\sum_s (F_{r'',s} - \epsilon_i S_{r'',s}) c_{s,i} \right], \quad (7)$$

where r'' denotes the second derivative AO. However, if the parent basis set is already a good basis, the mixing coefficients $c_{r',i}$ of the added derivative AO's r' should be small, and then from Eq. (7) the remaining error $\Delta_{r'}$ is expected to be small. Previously, we have tested this idea for LiH, BH,¹⁵ and CH₂(¹A₁) by closed-shell RHF method, CH₂(³B₁) by open-shell RHF method, and H₂ by the two-configuration MC-SCF method.¹⁶ In all of these cases, the error term decreased dramatically by the addition of the first derivative AO's. This was shown to be true in wide range of nuclear coordinates. The remaining error terms were small enough to be neglected practically for calculations of equilibrium geometries and force constants.

The above method is related to the method of floating wave functions¹¹⁻¹⁵ as follows. The AO $\chi_r(\mathbf{x})$ may be expanded around the position \mathbf{x}_0 as

$$\chi_r(\mathbf{x}) = \chi_r(\mathbf{x}_0) + (\partial \chi_r / \partial \mathbf{x})_{\mathbf{x}_0} (\mathbf{x} - \mathbf{x}_0) + \dots, \quad (8)$$

where \mathbf{x}_0 is usually the position of the nucleus to which χ_r belongs. Thus, the derivative AO's give the freedom of "floating" to the parent AO. They are literally the *polarization* functions. The present method usually gives lower energy than the floating method since the basis set space is wider in the former than in the latter.

In this paper, we further test the validity of the new method for di- and triatomic molecules using several kinds of basis set as parent AO's. By the previous^{15,16}

and present studies, we examine diatomic molecules including all of the first-row atoms except for beryllium. We examine the utility of this method for calculations of bond length, bond angle, and the corresponding force constants. The molecules studied here are CO, N₂, LiF, H₂O, and HNO. We also test the quality of the basis set to be used as parent set. The basis sets studied here are [3s2p/2s] CGTO set of Huzinaga¹⁸ and Dunning,¹⁹ 4-31G²⁰ and 6-31G²¹ sets of Pople *et al.* (for Li 5-21G set),²² and the STO-3G set with standard exponent.²³ We further show that the present method improves the other one-electron properties at the same time.

In the next section we summarize the calculational method. The result for diatomic molecule is given in Sec. III. The CO molecule is studied in detail with various basis sets. In Sec. IV we apply the present method for geometry optimization of triatomic molecules. The improvements in the other one-electron properties are shown in Sec. V. In the last section we discuss the features of the present method as compared with the conventional energy gradient method.

II. CALCULATIONAL METHOD

We calculate the wave functions of CO, N₂, LiF, H₂O, and HNO by the closed-shell Hartree-Fock-Roothaan SCF method²⁴ using the parent and family sets. For the Gaussian basis,

$$\chi_r = \sum_i^n d_i (x - x_r)^L (y - y_r)^M (z - z_r)^N \exp(-\alpha_i |\mathbf{r} - \mathbf{r}_r|^2), \quad (9)$$

the first derivative AO is given by

$$\begin{aligned} \frac{\partial \chi_r}{\partial x_r} = & \sum_i^n d_i \cdot 2\alpha_i (x - x_r)^{L+1} (y - y_r)^M (z - z_r)^N \\ & \times \exp(-\alpha_i |\mathbf{r} - \mathbf{r}_r|^2) - \sum_i^n d_i \cdot L(x - x_r)^{L-1} \\ & \times (y - y_r)^M (z - z_r)^N \exp(-\alpha_i |\mathbf{r} - \mathbf{r}_r|^2), \end{aligned} \quad (10)$$

the exponent α_i being the same for both parent and first derivative AO's; they compose a so-called *shell structure*.^{23,25,26} This property may be valuable computationally because of the existing powerful algorithms for fast evaluation of the integrals.^{25,26} In Table I, we have given an example of the first derivative AO's for the 4-31G set of nitrogen. It is seen that in the first derivative AO's of the contracted basis, the weights of the inner Gaussians increase relative to those of the outer Gaussians. The (*sp*) shell in the *N*-31G parent set becomes (*spd*) shell in the family set. For the basis of a single Gaussian element, the derivative of the *s* AO gives the *p* AO which already exists in the parent set (*sp* shell structure). Therefore, we can save an addition of such *p* AO's in the family set. Further, the AO error of this *s* AO is zero even in the parent set (see, e.g., Table III). Though the derivative of *p_x* AO with $\partial/\partial x$ gives *d_{xx}* and *s* AO's contracted together in a fixed relative coefficients, we can add them freely without imposing such constraint, obtaining usually better results since the dimension of SCF calculation increases by one. In the present calculations, the molecules CO,

TABLE I. Family set for the 4-31G set of nitrogen.

Exponent	parent AO's		first derivative AO's			
	l	coefficient	l	coefficient	l	coefficient
671.279 5		0.017 598 2		0.117 359 1		
101.201 7		0.122 846 2		0.318 090 8		
22.699 97	s	0.433 782 1	p_x	0.531 960 9		
6.040 609		0.561 418 2		0.355 158 6		
12.645 24		-0.117 489 3		-0.417 822 4		
2.981 719	s	-0.213 994 0	p_x	-0.369 542 9		
0.849 431 8		1.174 502 0		1.082 549 8		
0.235 281 3	s	1.0	p_x	1.0		
12.645 24		0.064 020 3		0.196 508 6		0.176 487 0
2.981 719	p_x	0.311 202 6	$\sqrt{3} * d_{xx}$	0.463 849 0	$-2 * s$	0.416 589 0
0.849 431 8		0.752 748 2		0.598 844 4		0.537 830 2
0.235 281 3	p_x	1.0	$\sqrt{3} * d_{xx}$	1.0	$-2 * s$	1.0
12.645 24		0.064 020 3		0.196 508 6		
2.981 719	p_y	0.311 202 6	d_{xy}	0.463 849 0		
0.849 431 8		0.752 748 2		0.598 844 4		
0.235 281 3	p_y	1.0	d_{xy}	1.0		

N_2 , LiF, and H_2O were calculated with such constraint and HNO without such constraint.

In order to compare with the H-F force, we have calculated two kinds of energy gradient; the energy gradient before and after addition of the first derivative AO's. Between the two kinds of energy gradient, that of the parent set is the one which is used frequently in the literature. The energy gradient of the family set is better theoretically than that of the parent set, since the basis set space is wider for the former than for the latter. The difference in these two kinds of energy gradient is usually *not* small. We will show that when we use the family set, the H-F theorem is essentially satisfied, i. e., the H-F force is very close to the energy gradient of the *family* set.

III. RESULTS FOR DIATOMIC MOLECULES

Most extensive tests of basis sets are done for CO. N_2 and LiF are chosen as typical covalent and ionic molecules, respectively.

A. CO

Table II shows the AO errors, H-F force, energy gradient, and SCF energy of CO before and after addition of the first derivative AO's. The basis sets are the Huzinaga-Dunning's [3s2p] and related sets. The bond length is 0.8636 Å (equilibrium length is 1.1283 Å).²⁷ The first column shows the results for the parent set alone. The second column shows the results obtained with the family set. There, the AO errors of the parent set vanish identically as Eq. (6) shows and the AO errors shown in this column are the sums of the AO errors of the added derivative AO's. In the parent set, the AO errors are large especially for $s1$, $s2$, $p1\sigma$, and $p1\pi$ AO's. However, by the addition of the first derivative AO's, the AO errors decrease dramatically. The total errors of the forces acting on the carbon and oxy-

gen decrease from 1.301 and -2.855 a. u. to 0.045 and -0.056 a. u., respectively. Then in the family set the H-F force is in good agreement with the energy gradient. Further, the smallness of the total error in the family set is not due to a cancellation: the AO errors of carbon are all positive and those of oxygen all negative. (The implication of these AO errors are clarified later.) By the addition of the first derivative AO's, the energy gradient changes from 1.899 to 1.665 a. u. The difference (0.235 a. u.) is an order of magnitude larger than the error term (~ 0.05) of the family set. The sum of the H-F forces acting on C and O does not vanish and is 0.012 a. u., which is an error for the translational invariance.²⁸ This is however practically very small. The SCF energy lowering due to the addition of the first derivative AO's is 0.120 a. u., which is the same order of magnitude as those obtained by the addition of the conventional polarization functions.²⁹

In Fig. 1, the force acting on carbon is plotted against the internuclear distance. It is seen that the H-F force and the energy gradient obtained with the family set agree quite well with each other over the wide range of the internuclear distance; i. e., the H-F theorem is essentially satisfied. The distance at which the force vanishes is the calculated equilibrium distance. It is 1.13 Å by the H-F force and 1.11 Å by the energy gradient. The experimental value is 1.128 Å (see Table IV). The energy gradient obtained with the parent set, which is the one conventionally used, gives 1.14 Å. In this case, the H-F force result is closest to the experimental value. The difference of the two broken lines of Fig. 1 shows the effect of the derivative AO's on the energy gradient.

In Table II the AO errors of the family set are all positive for carbon and all negative for oxygen. Since the AO errors show "virtual" forces acting on the AO's, this implies that the AO's should be floated inside of the bond

TABLE II. AO error, Hellmann-Feynman force, energy gradient, and SCF energy of CO for the parent, family, and related sets based on the $[3s2p]$ set (a. u.).^a

Atom	Parent	Family	Family with bond functions	Half family	Half family with bond functions
C					
AO error					
s1	0.4943	0.0062	-0.0040	0.0038	-0.0080
s2	-0.0932	0.0052	-0.0005	0.0022	-0.0003
s3	0.0012	0.0002	0.0002	0.0015	0.0010
p1 σ	0.3816	0.0117	0.0094	0.0157	0.0111
p2 σ	0.0023	0.0003	0.0006	0.0007	0.0
p1 π	0.2574	0.0104	-0.0065	0.0078	-0.0077
p2 π	-0.0001	0.0002	0.0001	0.0001	0.0003
Total error	1.3007	0.0446	-0.0074	0.0395	-0.0113
H-F force	-3.1998	-1.7094	-1.7007	-1.7345	-1.7242
Energy gradient	-1.8990	-1.6648	-1.7080	-1.6950	-1.7355
O					
AO error					
s1	-0.7986	-0.0079	0.0020	-0.0102	0.0038
s2	0.0167	0.0	0.0053	0.0124	0.0208
s3	-0.0096	-0.0008	-0.0029	-0.0026	-0.0015
p1 σ	-0.7835	-0.0248	-0.0181	-0.0285	-0.0202
p2 σ	-0.0036	-0.0002	-0.0001	-0.0013	-0.0009
p1 π	-0.6379	-0.0102	0.0030	-0.0101	0.0035
p2 π	-0.0005	-0.0014	-0.0007	0.0035	0.0024
Bond functions	0.0	...	0.0
p σ	-0.0002	...	-0.0027
p π	-0.0026	...	-0.0041
Total error	-2.8553	-0.0565	-0.0144	-0.0431	0.0021
H-F force	4.7543	1.7213	1.7224	1.7381	1.7334
Energy gradient	1.8990	1.6648	1.7080	1.6950	1.7355
SCF energy	-112.3278	-112.4480	-112.4703	-112.4341	-112.4604

^aThe CO length is 0.8636 Å (experimental equilibrium length, 1.1283 Å). The CO is on the σ axis in the direction from C to O.

in the viewpoint of the floating wave function.^{13,14} We expect that the addition of "bond" function would have an effect similar to floating the AO's inside. The third column

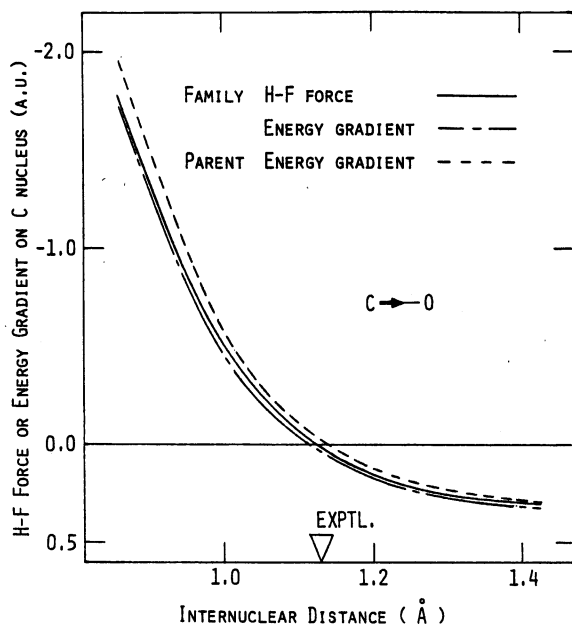


FIG. 1. Energy gradient and Hellmann-Feynman force acting on C vs internuclear distance for CO. The basis sets are the parent and family sets of the $[3s2p]$ set.

of Table II shows the result of an addition of the bond functions to the family set. They are s and p type single GTO's centered at the midpoint of the bond with the exponent 1.0. The AO errors certainly become smaller and their signs become random (both positive and negative). The total errors are considerably smaller than those of the simple family set. In Fig. 2, the forces acting on carbon are plotted against the internuclear distance. The H-F force shows better agreement with the corresponding energy gradient in comparison with Fig. 1. It is seen that the bond function works to shorten the bond length (see also Table IV).

Next we explain the results of "half family" set. In the first column of Table II, the AO errors of the parent set are large only for the s_1 , s_2 , $p1\sigma$, and $p1\pi$ AO's. So, we have considered an approximation in which the first derivative AO's are added only to these AO's of carbon and oxygen. Such basis set are referred to as half family set and the results are shown in the fourth column of Table II. It is seen that the idea is successful: i. e., the AO errors are small and comparable to those of the full family set (second column). This approximation should be useful so long as only some AO errors are known to be large in the parent set. In cases where the weights of the AO errors may change in the processes under study (e. g., chemical reaction), the use of the full family set is recommended. The last column of Table II shows the results of adding the bond functions to the half family set. The error term again

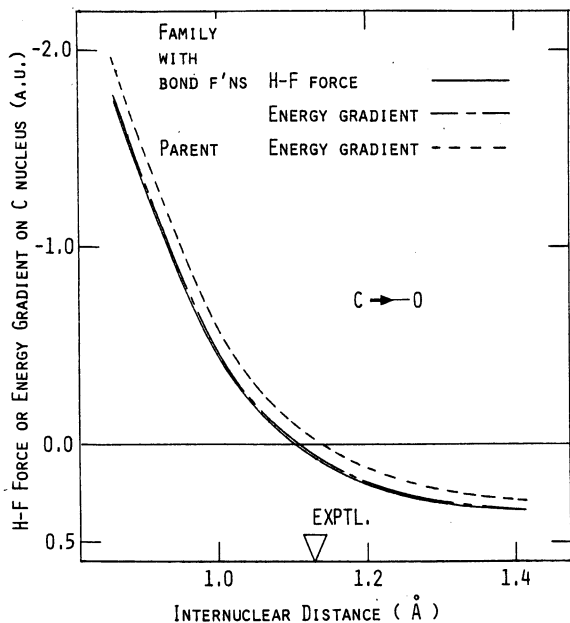


FIG. 2. Energy gradient and Hellmann-Feynman force acting on C vs internuclear distance for CO. The basis sets are the $[3s2p]$ parent set and its family set plus bond functions.

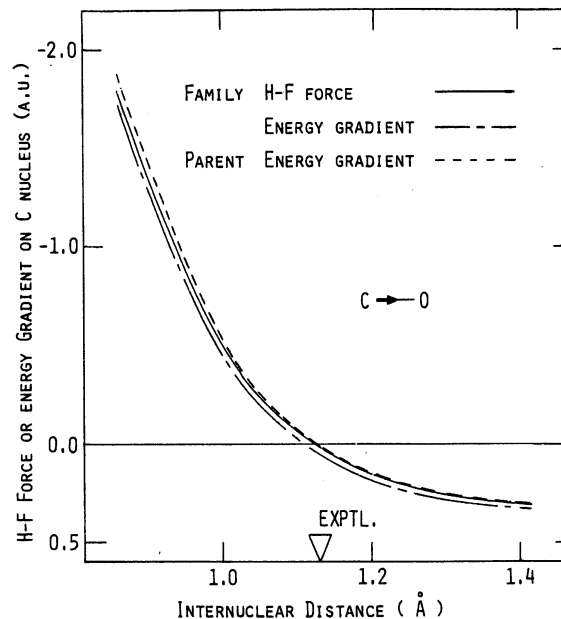


FIG. 3. Energy gradient and Hellmann-Feynman force acting on C vs internuclear distance for CO. The basis sets are the parent and family sets of the 4-31G set.

becomes very small.

Table III shows the results obtained for the 4-31G and 6-31G sets of Pople *et al.* The addition of the first derivative AO's decreases largely the error terms. The results are similar to and as good as the case of the

$[3s2p]$ set shown in Table II. Here the AO error of the $s3$ AO is zero even for the parent set because of the "shell" structure of these basis sets. In Fig. 3, the energy gradient and the H-F force obtained with the 4-31G set are compared over wide range of internuclear distance. Again the error term is consistently small in this

TABLE III. AO error, Hellmann-Feynman force, energy gradient, and SCF energy of CO for the parent and family sets based on the 4-31G, 6-31G, and STO-3G sets (a. u.).^a

Atom	4-31G		6-31G		STO-3G	
	Parent	Family	Parent	Family	Parent	Family
C	AO error					
s1	0.4024	0.0152	0.4845	0.0167	1.0218	-0.0253
s2	-0.0637	0.0001	-0.0651	0.0006	0.0704	0.0208
s3	0.0	0.0	0.0	0.0
p1σ	0.3146	0.0202	0.3247	0.0209	0.0983	0.0156
p2σ	-0.0014	-0.0007	-0.0018	-0.0002
p1π	0.2613	0.0111	-0.2605	0.0109	0.2251	-0.0168
p2π	0.0014	0.0001	0.0008	0.0002
Total error	1.1772	0.0570	1.2648	0.0603	1.6407	0.1581
H-F force	-2.9864	-1.7315	-3.0911	-1.7376	-1.8392	-1.9295
Energy gradient	-1.8092	-1.6745	-1.8264	-1.6773	-2.1985	-1.7714
O	AO error					
s1	-0.5015	-0.0285	-0.6770	-0.0306	-1.1947	-0.1365
s2	0.0095	0.0022	0.0089	0.0038	-0.0751	0.0268
s3	0.0	0.0	0.0	0.0
p1σ	-0.7346	-0.0244	-0.7565	-0.0236	-1.2004	-0.0265
p2σ	0.0004	-0.0003	-0.0007	0.0014
p1π	-0.5997	-0.0088	-0.6086	-0.0086	-0.6467	0.0376
p2π	-0.0280	0.0013	-0.0209	0.0009
Total error	-2.4814	-0.0661	-2.6844	-0.0642	-3.7636	-0.0612
H-F force	4.2906	1.7406	4.5108	1.7415	5.9621	1.8326
Energy gradient	1.8092	1.6745	1.8264	1.6773	2.1985	1.7714
SCF energy	-112.2208	-112.3146	-112.3305	-112.4251	-110.7968	-111.0792

^aThe CO length is 0.8636 Å (experimental equilibrium length, 1.1283 Å). The CO is on the σ axis in the direction from C to O.

TABLE IV. Bond length and force constant of CO calculated by various forces (bond length in Å, force constant in mdyn/Å).^{a,b}

Basis set	Property	Energy gradient	H-F force on carbon	H-F force on oxygen
[3s2p]				
Parent	bond length	1.138
	force constant	22.15
Family	bond length	1.114	1.124	1.127
	force constant	20.05	20.47	20.32
Family with bond functions	bond length	1.108	1.105	1.109
	force constant	20.66	20.50	20.63
Half family	bond length	1.113	1.124	1.136
	force constant	20.27	20.50	19.74
Half family with bond functions	bond length	1.108	1.105	1.114
	force constant	20.99	20.76	20.24
4-31G				
Parent	bond length	1.128
	force constant	21.37
Family	bond length	1.112	1.125	1.129
	force constant	20.30	20.74	20.92
6-31G				
Parent	bond length	1.131
	force constant	21.44
Family	bond length	1.113	1.127	1.131
	force constant	20.28	20.73	20.89
STO-3G				
Parent	bond length	1.146
	force constant	27.03
Family	bond length	1.093	1.124	1.099
	force constant	22.61	23.95	22.82

^aExperimental value (Ref. 27): bond length, 1.128 Å; force constant, 19.02 mdyn/Å.

^bThe force constant was calculated at the experimental bond length.

range as was seen for the [3s2p] set. The curves for the 6-31G set were also very similar. Computationally, the 4-31G and 6-31G sets are more advantageous than the [3s2p] set because the number of the primitive Gaussians are small.

Table III also gives the results of the STO-3G basis. In this case the energy lowering obtained by the addition of the derivative AO's is as large as 0.282 a. u., suggesting that the added AO's are used not only as polarization functions but also to improve totally the crudeness of the parent set itself. The individual AO errors are larger than those for the basis set of double zeta accuracy, though the total error may become small as a result of cancellation. (In the double zeta case, the smallness of the total error is not due to the cancellation.) We then think that the STO-3G basis is too crude to be used as a parent set, if we limit ourselves to add only the first derivative AO's. The second derivative AO's may be necessary.

Table IV summarizes the bond length and force constant of CO calculated by the H-F force and energy gradient obtained by various basis sets. The experimental value is 1.128 Å for the bond length and 19.02 mdyn/Å for the force constant. It is seen that with the family set the H-F force gives essentially the same results as the corresponding energy gradient. This is

true for the [3s2p], 4-31G, and 6-31G sets and also for some modified family sets of [3s2p] set. For the STO-3G basis, the difference is relatively large. From the results of the energy gradient, it is seen that the addition of the first derivative AO's works to shorten the bond length and decrease the force constant. This trend was observed by Bell³⁰ for the bond length when the basis set was improved toward the Hartree-Fock limit. The force constant becomes closer to the experimental value. The results of the H-F force are between the energy gradient results of the parent and family sets, though they are closer to the latter as they should be. This is true for both bond length and force constant. Though the H-F forces acting on carbon and oxygen give different results due to a small error in the translational invariance, the difference is less than 1% for both the bond length and force constant when the family set is used. (Though different values may be obtained by the use of different coordinates, the differences are within this range.) The STO-3G results are again exceptions (the differences in bond length and force constant are about 2% and 9%, respectively). These errors are smaller than the differences in the energy gradient obtained by the parent and family sets. Thus, the results of Table IV show the utility of the present method for the calculations of bond length and force constant.

TABLE V. AO error, Hellmann-Feynman force, energy gradient, and SCF energy of N_2 for the parent and family sets based on the $[3s2p]$ and 4-31G sets (a. u.).^a

Atom	$[3s2p]$		4-31G	
	Parent	Family	Parent	Family
N				
AO error				
s1	0.6229	0.0075	0.6486	0.0208
s2	0.0408	0.0015	0.0490	0.0079
s3	0.0012	-0.0001	0.0	0.0
p1 σ	0.3311	0.0067	0.3604	0.0025
p2 σ	0.0004	0.0001	0.0089	0.0005
p1 π	0.2019	0.0030	0.1854	0.0016
p2 π	0.0114	0.0006	0.0290	0.0010
Total error	1.4230	0.0228	1.4956	0.0370
H-F force	-1.0440	0.3912	-1.1007	0.3883
Energy gradient	0.3791	0.4140	0.3949	0.4253
SCF energy	-108.7521	-108.7863	-108.6108	-108.6525

^aThe bond length is 1.362 Å (equilibrium distance, 1.098 Å). The N nucleus given in the table lies on the left-hand side along σ axis.

B. N_2 and LiF

The results of N_2 and LiF parallel those of CO. We have chosen N_2 and LiF as typical covalent and ionic molecules, respectively.

Table V shows for N_2 the effects of the first derivative AO's on the AO errors, H-F force and energy gradient. It is seen that the addition of the first derivative AO's largely decreases the error terms. The total errors of the family set are 1.6% and 2.5% of those of the parent set for the $[3s2p]$ and 4-31G sets, respectively. The smallness of the total errors is *not* due to a cancellation, since the constituent AO errors are positive. The SCF energy is lowered by 0.034 and 0.042 a. u. by the addition of the first derivative AO's to the $[3s2p]$ and 4-31G sets, respectively.

Figure 4 shows the H-F force and energy gradient of N_2 plotted against the internuclear distance. They were obtained by the 4-31G set. The closeness of the curves for the H-F force and energy gradient of the family set shows that the Hellmann-Feynman theorem is essentially satisfied. As will be seen in Table VII, the bond lengths calculated by the energy gradient and H-F force are 1.072 and 1.086 Å, respectively. The experimental value is 1.098 Å.²⁷

Table VI shows the results for LiF. Again, the addition of the first derivative AO's reduces effectively the error term. In the parent set, the AO error of Li is large only for the innermost s1 AO, but that of F is large for all the AO's. This reflects the ionic character Li^+F^- of this molecule. In the family set, however,

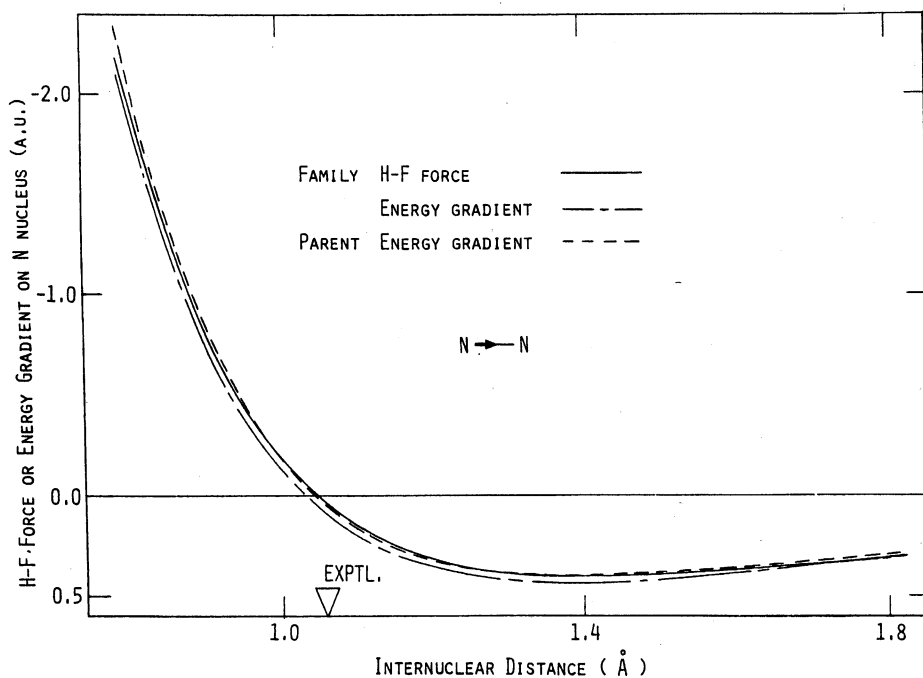


FIG. 4. Energy gradient and Hellmann-Feynman force acting on N vs internuclear distance for N_2 . The basis sets are the parent and family sets of the 4-31G set.

TABLE VI. AO error, Hellmann-Feynman force, energy gradient, and SCF energy of LiF for the parent and family sets based on the $[3s2p]$ and 4-31G, 5-21G sets (a. u.).^a

Atom	$[3s2p]$		5-21G(Li), 4-31G(F)	
	Parent	Family	Parent	Family
Li	AO error			
s1	-0.1552	-0.0006	-0.1235	-0.0003
s2	-0.0028	0.0008	0.0002	0.0001
s3	0.0001	0.0001	0.0	0.0
p1 σ	0.0003	-0.0001	-0.0070	0.0001
p2 σ	0.0003	0.0001	0.0076	0.0016
p1 π	0.0030	0.0005	0.0055	0.0010
p2 π	0.0	0.0001	0.0010	0.0023
Total error	-0.1514	0.0015	-0.1096	0.0079
H-F force	0.1922	0.0452	0.1625	0.0473
Energy gradient	0.0408	0.0467	0.0529	0.0552
F	AO error			
s1	-0.3222	-0.0015	-0.2974	-0.0060
s2	-0.0219	-0.0001	-0.0121	-0.0009
s3	-0.0039	0.0004	0.0	0.0
p1 σ	-0.1837	-0.0019	-0.1718	-0.0011
p2 σ	-0.0327	-0.0010	-0.0439	-0.0020
p1 π	-0.1261	0.0001	-0.1104	0.0003
p2 π	-0.0215	-0.0003	-0.0347	-0.0008
Total error	-0.8594	-0.0046	-0.8154	-0.0111
H-F force	0.8186	-0.0420	0.7625	-0.0441
Energy gradient	-0.0408	-0.0467	-0.0529	-0.0552
SCF energy	-106.9471	-106.9592	-106.8056	-106.8316

^aThe bond length is 1.828 Å (equilibrium distance, 1.564 Å). The LiF is on the σ axis in the direction from Li to F.

all of the AO errors become very small. For the 5-21G, 4-31G sets, the AO errors of the s3 AO's of Li and F vanish even in the parent set because of the shall structure of this set. The SCF energy lowering is 0.012 and 0.026 a. u. for $[3s2p]$ and 5-21G, 4-31G sets, respectively.

Figure 5 shows the plots of the H-F force and energy gradient vs internuclear distance for LiF. The basis set is the $[3s2p]$ set. The H-F force and energy gradient of the family set agree quite well, showing that the Hellmann-Feynman theorem is satisfied in a practical sense. In this case the effect of the first derivative

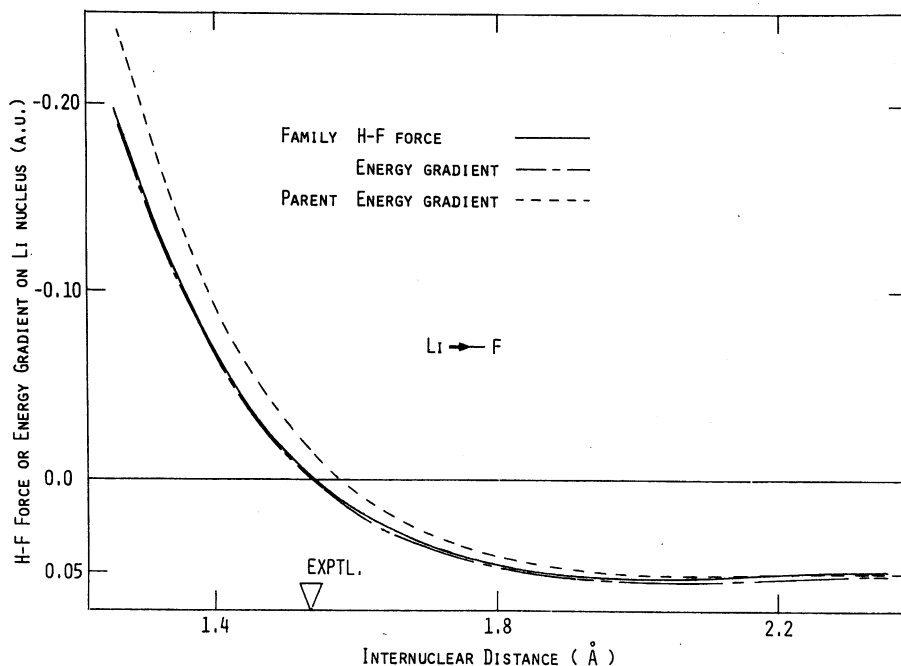


FIG. 5. Energy gradient and Hellmann-Feynman force acting on Li vs internuclear distance for LiF. The basis sets are the parent and family sets of the $[3s2p]$ set.

TABLE VII. Bond length and force constant of N₂ and LiF calculated by different forces (bond length in Å, force constant in mdyn/Å).^a

Basis set	Property	N ₂			LiF			
		Energy gradient	H-F force on N	Exptl ^b	Energy gradient	H-F force on Li	H-F force on F	Exptl ^b
[3s2p]								
Parent	bond length	1.100	...	1.098	1.606	1.564
	force constant	28.15	...	22.95	3.239	2.502
Family	bond length	1.074	1.084	1.098	1.566	1.570	1.583	1.564
	force constant	25.25	25.50	22.95	2.731	2.717	2.775	2.502
4-31G(N, F), 5-21G(Li)								
Parent	bond length	1.085	...	1.098	1.540	1.564
	force constant	26.99	...	22.95	2.749	2.502
Family	bond length	1.072	1.086	1.098	1.540	1.558	1.580	1.564
	force constant	25.29	25.61	22.95	2.693	2.681	2.763	2.502

^aThe force constant was calculated at the experimental bond length.^bReference 27.

AO's on the energy gradient is relatively large.

Table VII shows the bond length and force constant of N₂ and LiF calculated by different forces. With the use of the family set, the H-F force gives essentially the same results as the energy gradient method. Though the H-F forces acting on Li and F of LiF give different results due to the translational error, the difference is very small in a practical point of view. The results of Table VII are parallel to those of Table IV obtained for CO. We conclude from these results that the present force method is useful for calculations of bond length and force constants.

IV. APPLICATION TO TRIATOMIC MOLECULES

In this section we test the present method for the geometry optimization of triatomic molecules. Since

the present method has been shown to be useful for calculations of bond length and its force constant, a main purpose of this section is to test it for calculations of bond angle and its force constant. We calculate various forces for H₂O and HNO with the use of the [3s2p/2s] set and the 4-31G set, respectively.

Table VIII shows the error term, H-F force, and energy gradient calculated for the force acting on the terminal nuclei of HNO. The results obtained for H₂O are omitted for brevity. F_{\perp} and F_{\parallel} denote the transverse force and the force parallel to the bond, respectively. Again, the addition of the first derivative AO's reduces largely the error term in both F_{\perp} and F_{\parallel} . The error term in F_{\perp} is an order of magnitude smaller than that in F_{\parallel} . This is true not only for the force acting on proton but also for the force acting on oxygen. The smallness

TABLE VIII. Error term, Hellmann-Feynman force, energy gradient, and SCF energy of HNO for the parent and family sets based on the 4-31G set (a. u.).^{a, b}

			$\theta = 108.6^{\circ}$ ^c		$\theta = 140^{\circ}$	
			Parent	Family	Parent	Family
H	F_{\perp}	error term	-0.0041	-0.0002	-0.0315	-0.0007
		H-F force	0.0088	-0.0010	-0.0289	-0.0643
		energy gradient	0.0048	-0.0013	-0.0603	-0.0650
H	F_{\parallel}	error term	-0.1077	-0.0035	-0.0932	-0.0035
		H-F force	0.0825	-0.0231	0.0592	-0.0273
		energy gradient	-0.0252	-0.0267	-0.0340	-0.0308
O	F_{\perp}	error term	-0.1483	-0.0009	-0.2622	-0.0014
		H-F force	-0.1525	-0.0002	0.2093	-0.0556
		energy gradient	0.0042	-0.0011	-0.0529	-0.0570
O	F_{\parallel}	error term	-2.1635	-0.0300	-2.0752	-0.0303
		H-F force	2.1381	-0.0369	2.1118	-0.0475
		energy gradient	-0.0257	-0.0668	-0.0365	-0.0778
SCF energy			-129.5778	-129.6495	-129.5410	-129.6074

^aThe bond lengths were kept fixed at the experimental values ($R_{\text{HN}} = 1.063$ Å, $R_{\text{NO}} = 1.212$ Å) Reference 30.^b F_{\perp} is the transverse force in the direction of increasing the bond angle. F_{\parallel} is the force parallel to the bond in the direction of increasing the bond length.^cThe experimental equilibrium angle.

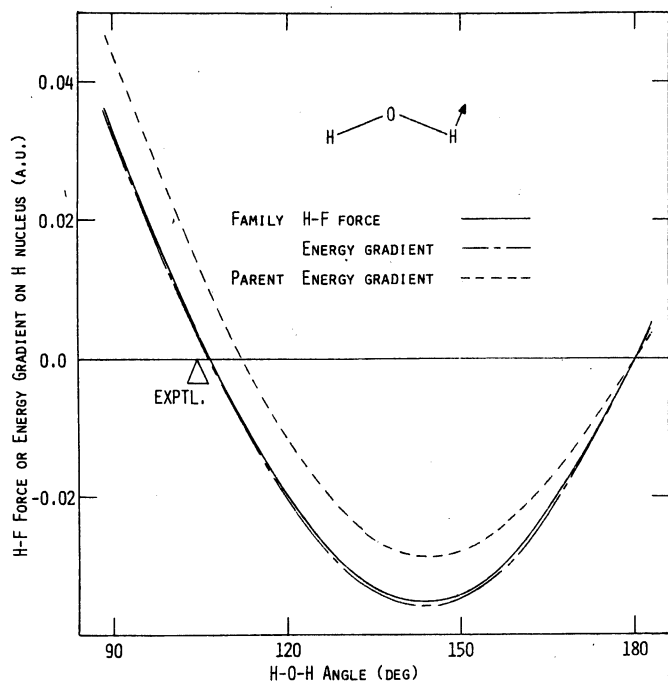


FIG. 6. Hellmann–Feynman force and energy gradient for the transverse force acting on the terminal proton of H_2O vs the bond angle. The basis sets are the parent and family sets of the $[3s2p/2s]$ set.

of the error term for F_1 is important since the force constant for the angular vibration is smaller than that for the stretching mode.

Figure 6 shows the plot of the transverse force acting on the terminal proton of H_2O against the bond angle. The H–F force and the energy gradient obtained from the family set agree very well, showing that the H–F theorem is almost satisfied. The difference between the forces obtained from the parent and family sets shows the effect of the derivative AO's on the predicted geometry. It is large for the angular geometry of H_2O ; the bond angles calculated from the parent and family sets are 112.5° and 107.0° , respectively (Table IX). The experimental value is 104.5° .³¹

Figure 7 shows the transverse forces acting on the terminal nuclei of HNO vs the bond angle. The bond

lengths were fixed at the experimental value.³¹ Figures 7(a) and 7(b) are for the forces acting on the proton and oxygen, respectively. In both cases, the curves for the H–F force and the energy gradient obtained with the family set almost superpose each other showing that the H–F theorem is almost satisfied. The addition of the first derivative AO's improves the predicted value of the bond angle. The forces acting on H and O vanish at almost the same angle, as they should do so.

Table IX summarizes the geometries of H_2O and HNO optimized by different forces. The geometries obtained from the H–F force and the energy gradient of the family set are essentially the same, showing the validity of the present method. Since the present H–F forces still have small errors in the translational and rotational invariance, we have to specify the coordinate (or the forces) used for geometry optimization. The forces we have used are F_{H_1} and F_{H_2} for H_2O and F_{O_1} , F_{H_1} , and $\frac{1}{2}(F_{\text{O}_1} + F_{\text{H}_1})$ for HNO. Different choices may cause small differences though they are negligible in the present case because the errors for the invariance are very small. (The translational forces at equilibrium geometries of H_2O and HNO are 0.004 and 0.009 a. u., respectively.) The bond lengths calculated from the family set are shorter than those calculated from the parent set. For the bond angle the effect of electron correlation is known to make it longer.³⁰ For the bond angle the effect of the first derivative AO's is large and important; the results of the family set are closer to the experimental values. The trend in the present results is in accord with the general trend reported by Bell.³⁰ We conclude from this table that the present method is useful for optimizations of both bond lengths and bond angles.

V. IMPROVEMENT IN THE OTHER ONE-ELECTRON PROPERTIES

Now it is concluded that the SCF wave function is improved by the addition of the first derivative AO's to essentially satisfy the H–F theorem. Here we show that the present method improves not only the H–F forces but also other one-electron properties such as dipole moment, quadrupole moment, nuclear quadrupole coupling tensors, etc. Needless to say, in the conventional energy gradient method we have no such improve-

TABLE IX. Force-optimized geometries of H_2O and HNO for the parent and family sets based on the $[3s2p/2s]$ and 4-31G sets, respectively. (Bond length in Å, bond angle in degrees.)

	H_2O		HNO		
	$R(\text{O}-\text{H})$	$\angle \text{HOH}$	$R(\text{N}-\text{O})$	$R(\text{N}-\text{H})$	$\angle \text{HNO}$
Parent					
energy gradient	0.9514	112.5	1.197	1.026	110.7
Family					
energy gradient	0.9455	107.0	1.176	1.029	109.2
H–F force	0.9488	107.0	1.193	1.029	108.8
Exptl ^a	0.957	104.5	1.212	1.063	108.6

^aReference 31.

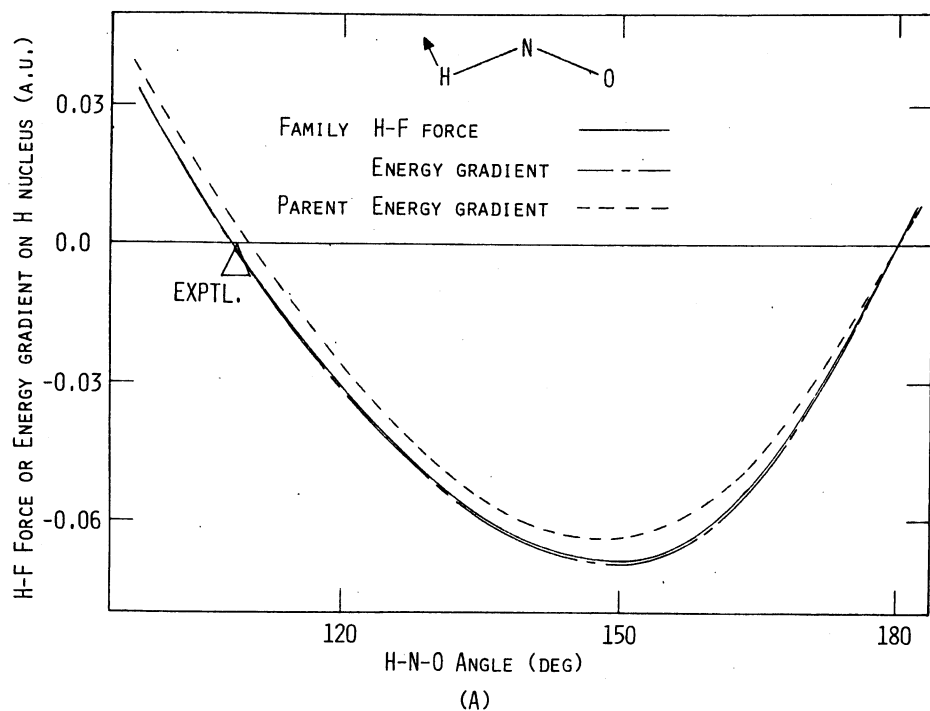
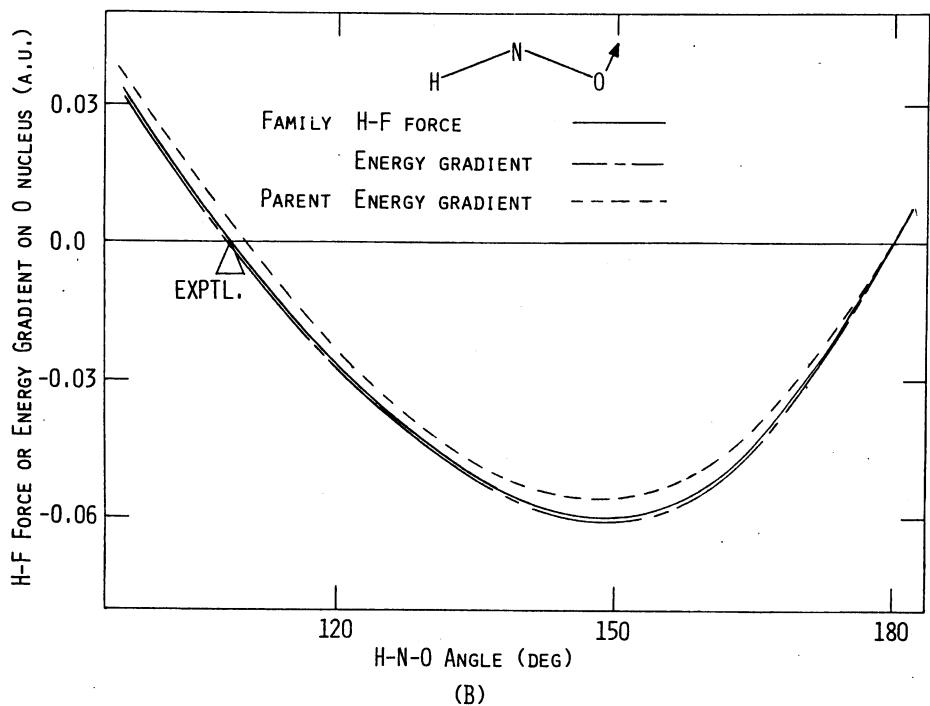


FIG. 7. Hellmann-Feynman force and energy gradient for the transverse force acting on the terminal proton (A) and oxygen (B) of HNO vs the bond angle. The basis sets are the parent and family sets of the 4-31G set.



ments. Table X shows some one-electron properties of CO, N₂, LiF, H₂O, and HNO calculated with the parent and family sets. The [3s2p/2s] sets are used for CO, N₂, LiF, and H₂O, and 4-31G set for HNO. The results of near-Hartree-Fock wave functions are cited for comparison. (For HNO they are the results of MRD-CI.)³²

Dipole moment is rather sensitive to an addition of the first derivative AO's and for all the molecules studied here the dipole moment is improved considerably in the family set. The CO molecule is famous for that even the Hartree-Fock limit cannot predict correct sign of the

dipole moment.³³ The correlation effect is known to be very important. The present value obtained with the family set (0.2476 D) is close to the Hartree-Fock limit (0.261 D).³³ For HNO both of the μ_y and μ_x components are improved in the family set.

Quadrupole moment is also sensitive to the addition of the first derivative AO's. The operator is $\theta_{xx} = \frac{1}{2}(3z^2 - r^2)$. For CO, N₂, and H₂O, we have the experimental values. The result of the family set is closer to the experimental value and to the near-Hartree-Fock results. For the θ_{xx} component of H₂O, the experimen-

TABLE X. One-electron properties of CO, N₂, LiF, H₂O, and HNO.^{a,b}

Property	Parent	Family	Other calculation (near Hartree-Fock)	Exptl.	
Dipole moment (Debye unit)					
CO	0.4260	0.2476	0.261 ^c	-0.1222 ^j	
LiF	6.787	6.391		6.2839 ^j	
H ₂ O	2.682	2.034	1.995 ^d	1.8473 ^d	
HNO					
μ_y	1.36	1.10	1.10 ^e	1.01 ^e	
μ_x	1.94	1.51	1.46 ^e	1.33 ^e	
$ \mu $	2.37	1.87	1.83 ^e	1.67 ^e	
Quadrupole moment (Buckingham unit)					
CO	θ_{xx}	-3.077	-2.356	-2.089 ^f	-2.5, -2.0 ^j
N ₂	θ_{xx}	-2.435	-1.561	-1.335 ^g	-1.4 ^j
LiF	θ_{xx}	5.575	6.042		
H ₂ O	θ_{xx}	-2.283	-2.444	-2.524 ^d	-2.50 ^d
	θ_{yy}	2.467	2.530	2.619 ^d	2.63 ^d
	θ_{zz}	-0.184	-0.086	-0.095 ^d	-0.13 ^d
HNO	θ_{xx}	1.007	0.561		
	θ_{yy}	2.484	2.224		
	θ_{zz}	-3.490	-2.784		
Nuclear quadrupole coupling tensor (MHz)					
CO	¹⁷ O (eqQ/h) _{xx}	1.91	3.47	3.93 ^f	4.48 ^f
N ₂	¹⁴ N (eqQ/h) _{xx}	4.16	5.82	6.38 ^g	
LiF	⁶ Li (eqQ/h) _{xx}	0.004 749	0.010 159	0.007 541 ^{h,i}	0.007 3 ⁱ
H ₂ O	D (eqQ/h) _{aa}	0.380 10	0.347 66	0.341 27 ^d	0.307 95 ^d
	(eqQ/h) _{bb}	-0.168 13	-0.156 77	-0.147 31 ^d	-0.133 13 ^d
	(eqQ/h) _{xx}	-0.211 97	-0.190 88	-0.193 96 ^d	-0.174 78 ^d
	¹⁷ O (eqQ/h) _{xx}	12.51	11.60	11.58 ^d	10.17 ^d
	(eqQ/h) _{yy}	-11.05	-11.03	-10.37 ^d	-8.89 ^d
	(eqQ/h) _{zz}	-1.46	-0.57	-1.21 ^d	-1.28 ^d
HNO	D (eqQ/h) _{xx}	0.131 36	0.111 09		
	(eqQ/h) _{aa}	0.131 11	0.122 69		
	(eqQ/h) _{bb}	-0.262 46	-0.233 79		
	¹⁴ N (eqQ/h) _{xx}	-6.26	-7.27		
	(eqQ/h) _{aa}	7.35	8.04		
	(eqQ/h) _{bb}	-1.09	-0.78		
	¹⁷ O (eqQ/h) _{xx}	14.83	16.77		
	(eqQ/h) _{aa}	-20.80	-22.36		
	(eqQ/h) _{bb}	5.97	5.59		

^a[3s2p/2s] set of Dunning and Hay¹⁹ is used for the parent set of CO, N₂, LiF, and H₂O and 4-31G set of Pople *et al.* for HNO.

^bCO, N₂, and LiF are on the z axis. H₂O is in the yz plane, with z as the principal axis of symmetry. HNO is in the yz plane, with y being parallel to the N-O bond. The a and b axes are defined as the principal axes for the nuclear quadrupole coupling tensor.

^cReference 33.

^dB. J. Rosenberg and I. Shavitt, *J. Chem. Phys.* **63**, 2162 (1975); B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *ibid.* **65**, 4072 (1976).

^eResults of MRD-CI. Reference 32.

^fD. B. Neumann and J. W. Moskowitz, *J. Chem. Phys.* **50**, 2216 (1969).

^gReference 29.

^hA. D. McLean and M. Yoshimine, *IBM J. Res. Develop.* **12**, 206 (1968).

ⁱP. Pyykkö and J. Linderberg, *Chem. Phys. Lett.* **5**, 34 (1970).

^jReference 27.

tal value is just median between those calculated with the parent and family sets. For HNO, the differences between the results of the parent and family sets are large but we do not know the experimental values to the best of our knowledge.

Quadrupole coupling tensor at the nucleus A is also a quantity which is sensitive to the present improvement of the wave function. This is natural because the opera-

tors, $q_{xx} = (3z_A^2 - r_A^2)/r_A^5$, etc., are the derivatives of the H-F force operator. Table X shows that the family set gives better agreement with experiment and with the near-Hartree-Fock result than the parent set except for the zz component of the ¹⁷O quadrupole coupling tensor.

We have also calculated diamagnetic shielding tensor, diamagnetic susceptibility, second moment, and

charge density at the nucleus. These quantities were less sensitive to the addition of the derivative AO 's than the quantities shown in Table X.

From Table X it is concluded that by the present method the wave function is improved not only to essentially satisfy the H-F theorem but also to give better one-electron properties. Since the H-F force is sensitive to electron distributions, the present method improves molecular electron distributions and hence the various one-electron properties are improved at the same time.

VI. CONCLUDING REMARKS

The results of the present study, together with those reported previously,^{15,16} establish the utility of the present force method. It gives H-F forces which are as reliable as energy gradients. By the present method of improvement, the wave function essentially satisfies the H-F theorem. Further, the other one-electron properties are improved at the same time. We have shown that the present method is useful for calculations of equilibrium geometries and force constants of several di- and triatomic molecules. We have also shown that the basis set of double zeta accuracy such as 4-31G, 6-31G, and [3s2p/2s] sets are well suited for the present method. The STO-3G set seems to be less suitable. In a previous paper,¹⁶ we have shown with a few examples that the same approach is also valid for open-shell SCF (RHF and UHF) theories and for general MC-SCF theories.

The features of the present method as compared with the energy gradient method are as follows:

(1) In the energy gradient method, the derivative AO 's are evaluated after SCF process to calculate the error term, which is a time consuming process. In the present method, they are added to the basis set of the SCF calculations and are used to improve the wave function. Since the H-F theorem is essentially satisfied by the present method, we need not to calculate the error term: we can save computational time at this stage, though we use time for improving the wave function in the SCF process.

(2) The gradient method includes the integrals of the types $(r'|h|s)$ and $(r'|s|tu)$ alone in which the derivative AO appears only once. In the present method, however, the integrals of the types $(r'|h|s')$, $(r'|s'|tu)$, $(r'|s'|t'u)$, and $(r'|s'|t'u')$ are also involved in the SCF calculations. Therefore, the present method is more time consuming than the gradient method, if the same algorithm is used. However, since the AO 's r and r' form a so-called *shell-structure* and appear in a same program, the existing algorithm²⁵ for fast evaluation of integrals would be useful to reduce computational time.

(3) Though the dimension of the SCF calculation increases in the present method, the *quality* of the resultant force is improved. Further, the other one-electron properties such as dipole moment, quadrupole moment, nuclear quadrupole coupling tensor, etc., are improved at the same time. The so-called "polarization" functions need not be added to the parent set, because the

derivative AO is just a kind of polarization function.

(4) The conventional SCF program is enough for the present calculations if it includes d orbitals as well as s and p orbitals. For the energy gradient method, a program for calculations of the error term is necessary. Calculation of the H-F force is trivial anyway.

(5) An intuitive concept of the Hellmann-Feynman theorem is associated quantitatively to the results of the present method. The conceptual utility of the Hellmann-Feynman force has well been developed in wide fields of chemistry.⁸⁻¹⁰ The present method paves a way to a *quantitative* use of the force concept for deeper understandings of the electronic origins of the derivatives. In the energy gradient method, however, it is difficult to assign physical meaning to the error term involved.

(6) The present method gives further a merit in the study of second derivatives. Use of the H-F theorem in the first derivative greatly reduces the terms to be calculated in the second derivative studies.¹ Most of the complex terms in a direct evaluation of the second derivative⁵ do not arise in the present approach. This further gives us a method to clarify and understand the electronic origin of the second derivatives.

Recently Habitz and Votava¹⁷ reported a similar method to improve the H-F force. They proposed to add some effectively chosen polarization functions in order to reduce the number of the basis functions. Though their approach is interesting, their method of choosing the polarization function seems to be ambiguous. Due to our experiences,³⁴ a set of polarization functions useful for a molecule is not necessarily effective for calculations of different molecules. Our method is however unique and should be effective for any molecules in wide range of nuclear configurations.

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