Reply to "Comment on 'Force in SCF theories' "

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Pulay[1] commented upon our accurate Hellmann–Feynman (HF) force method[2–4] from a comparison of solely a computer time with an energy gradient (EG) method.[5] What we aim in this series of studies[2–4,6,7] is a development of force concept in various fields of chemistry. Timing problem is a technical part of this approach, though it is very important to improve further this aspect.

Table I shows a timing comparison for LiH and CO with the use of the 5-21G, 4-31G, and [$3s2p$] sets as parent set $\{\chi_r\}$. The family, half-family, and half-family plus bond function sets are defined in Ref. 4. A difference is that in Ref. 4 we have added only the derivative $\partial\chi_r/\partial x$ with x along the internuclear axis, but here we have added all the derivatives $\partial\chi_r/\partial x$, $\partial\chi_r/\partial y$, and $\partial\chi_r/\partial z$.[8] The error terms Δ shown in Table I are therefore smaller than the previous results. The "standard" basis is the parent set plus single set of 1G polarization functions, which we adopted as a standard as Pulay suggested. We have used HONDOG program published by King, Dupuis, and Rys[9] without modification.

Pulay's estimate of the computational time[1] seems roughly correct at present. *If we assume* that the above "standard" set gives a wave function comparable to our family set, our method takes 3.8–8.1 times more cpu time than the EG method. However, if we use half-family or half-family plus bond function set, the cpu time is reduced by half without much affecting the magnitude of the error term; i.e., 1.7–3.8 times more cpu time than the EG method. Then, these sets would be a reasonable compromise in our approach. The argument based on the factor $N_{\mathrm{family}}/N_{\mathrm{parent}}$ is inadequate, because the added derivative basis improves the quality of the wave function and then the quality of the force (EG) itself. Comparison should be made at least between comparable basis sets. Though Pulay suggested a necessity of additional f functions, they are unnecessary from our experiences. For CO under discussion, the error terms shown in Table I are smaller than the previous results.[4,8] (When more accuracy is necessary, an addition of the bond function would be effective as discussed in Ref. 4, giving a result close to the Hartree–Fock limit.)

Furthermore, we doubt the validity of the basic assumption in the above comparison. The HF theorem is a necessary condition for an exact or correct SCF wave function to have to satisfy. Our wave function essentially satisfies this condition, but the wave function based

TABLE I. Comparison of the timing, error term, and SCF energy between the accurate Hellmann–Feynman force method and the energy gradient method.[a]

Molecule[b]		CPU time (second)					Error term (a.u.)[d]		SCF
AB	Basis set	Integral	SCF	Gradient	Total	Ratio	Δ_A	Δ_B	energy (a.u.)
LiH	5-21G parent	0.6	1.5	0.5	2.6	0.6	−0.1567	−0.0346	−7.97193
	half-family	4.7	2.6	···	7.3	1.7	−0.0077	−0.0035	−7.98010
	family	11.0	5.1	···	16.2	3.8	−0.0003	−0.0015	−7.98205
	standard[c]	1.1	1.5	1.5	4.2	1.0	−0.1333	−0.0032	−7.97699
	[$3s2p$] parent	1.2	1.8	1.2	4.3	0.6	−0.1591	−0.0356	−7.98109
	half-family	12.6	2.8	···	15.4	2.1	−0.0064	−0.0024	−7.98332
	family	28.5	8.3	···	36.8	5.0	−0.0005	−0.0004	−7.98520
	standard[c]	2.4	1.8	3.2	7.4	1.0	−0.1614	−0.0035	−7.98335
CO	4-31G parent	1.7	3.6	3.3	8.6	0.5	1.0578	−2.1585	−112.55235
	half-family	42.3	7.1	···	49.4	3.0	0.0463	−0.0936	−112.60692
	half-family plus bond function	49.5	8.2	···	57.6	3.4	0.0179	−0.0484	−112.61100
	family	112.8	23.0	···	135.8	8.1	0.0107 (0.0210)	−0.0183 (−0.0140)	−112.62353
	standard[c]	4.0	3.6	9.1	16.7	1.0	0.4516	−0.6084	−112.62865
	[$3s2p$] parent	7.0	4.0	13.6	24.7	0.5	1.0741	−2.3176	−112.68484
	half-family	141.0	12.6	···	153.6	3.3	0.0156	−0.0589	−112.73492
	half-family plus bond function	158.0	16.4	···	174.4	3.8	−0.0361	−0.0076	−112.75809
	family	315.3	60.4	···	375.7	8.1	0.0195 (0.0234)	−0.0235 (−0.0365)	−112.74943
	standard	13.3	5.8	27.3	46.4	1.0	0.3749	−0.5415	−112.75940

[a] The computation was carried out with the FACŌM M382 computer at the Data Processing Center of Kyoto University.

[b] At the equilibrium geometry; $R_{\mathrm{LiH}} = 1.595$ Å, $R_{\mathrm{CO}} = 1.1283$ Å.

[c] The standard set denotes parent set plus a single set of 1G polarization functions on each atom.

[d] Values in parentheses were calculated at $R_{\mathrm{CO}} = 0.8636$ Å.

on the standard set is far from satisfying this necessary condition as shown in Table I. Theoretically this is an obvious defect. Since the HF force depends sensitively on the error involved in the electron density distribution $\rho(r)$ through

$$\mathbf{F}_A = Z_A \int \mathbf{r}_A / r_A^3 \rho(\mathbf{r})\, d\mathbf{r} - Z_A \sum_{B(\neq A)} Z_B \mathbf{R}_{AB}/R_{AB}^3,$$

we believe that the family set gives a better density function than a conventional one. Previously, we observed that an addition of the derivative bases improves several one-electron properties.[4] It is dangerous to judge the quality of a wave function solely from its energy, because energy is insensitive to the error involved in the wave function.

When the HF theorem is satisfied for the first derivative, an analytic expression of the second derivative[10–12] becomes much simpler and more perspective than a straightforward second derivative of energy.[13] Some examples were shown for the studies of molecular vibrations and chemical reactions.[6,7] An intuitive picture was assigned to the electronic origin of the second derivatives.[14]

We believe that an intuitive and simple physical meaning associated with the HF force and its derivative (second derivative of energy) is more than offset the present demerit in the cpu time. This is certainly our motive of the studies. On the other hand, it is difficult to assign any physical meaning to the error term and the derivative of that involved in the EG approach,[14] since they vanish identically for an exact or correct SCF wave function.

The purpose of computation is definitely not only for a number, but also to get a deeper insight on the nature of the phenomena under study. The HF force concept is very valuable, especially in the present day's very computational situations, because it is valid from an SCF level to an exact limit. The concept is approximation independent so that it can give a common language to investigate and understand the electronic origin of the phenomena. Further, as given in a book recently published,[15] several predictive models in chemistry have been constructed on this ground.[16,17] Previously, the construction of such a model was rather difficult because no method was available to check the validity of the basic assumption involved in the model.[18] But now, the present method is available. Previously, we have used such methodology to construct a model of the geometry of molecules in an electric field.[19] We have used floating AO technique,[20] which is more difficult and less general than the present one, since it was before we realized the present method. The accurate HF force method is probably a method to pave the way to a development of the force concept in chemistry in combination with the modern computational chemistry.

For a correlated wave function, the utility of the HF force is an open question, because the HF theorem is not satisfied by an ordinary CI wave function (though it is satisfied by the MC-SCF wave function). However, it is clear that the calculation of the HF force is much simpler than the CI energy gradient, since the former depends only on the electron density but the latter on both the first and second order density matrices and requires a solution of the coupled Hartree–Fock equation.[21]

Lastly, one word for core polarization. Let us recall that there is a considerable body of chemistry in which core electrons play a central role, e.g., NMR, ESR, ESCA, and Mössbauer spectroscopies, etc. Core polarization is certainly a feature of an exact wave function, since the HF theorem is a necessary condition for that. It might be important for an accurate description and understanding of these phenomena (probably even of potential surfaces). On the other hand, core-electron problems can be circumvented by using an effective-core potential (ECP) approximation.[22] We have shown very recently that the present method can be combined successfully with the ECP method.[23] Such an approach would be useful for a development of force concept in organometallic and inorganic chemistry.

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[8] In Refs. 4 and 6, the derivatives were added only for the directions in which the force does not vanish identically from symmetry. (Table I of Ref. 4 gives a definition of the family set for diatomics.) For diatomic molecules, the force transverse to the bond is identically zero from symmetry, so that the AO's never float in such directions. Therefore, the derivatives are necessary only for the x axis and they form a complete family set. In the present calculations in which the HONDOG program was used without modification for timing comparison, we could not add derivatives in only one direction. The roles of $\partial\chi_r/\partial y$ and $\partial\chi_r/\partial z$ are second order. Further, by the same reason, the contraction between s and d_{xx} arising from the derivative of p_x was not done in the present calculations.

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