FORCE IN SCF THEORIES. MC SCF AND OPEN-SHELL RHF THEORIES

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Received 18 February 1981

A theorem reported for Hartree–Fock SCF theory is shown to be valid for general MC SCF and open-shell RHF theories – a sufficient condition for these wavefunctions to satisfy the Hellmann–Feynman theorem is that the basis set includes the derivative AO $\partial\chi_r/\partial x_r$ for any basis χ_r. The new force approach is applicable to wider fields including electronic processes in chemical reactions. Test calculations are given for some simple systems.

1. Introduction

Derivatives of the potential energy hypersurface of a molecular system are of fundamental importance in many aspects of theoretical chemistry. The Hellmann–Feynman theorem [1] gives a viewpoint on the electronic origins of the force. However, since most conventional wavefunctions do not give reliable Hellmann–Feynman (H–F) forces, the direct analytic derivative of the energy (energy gradient) has been used for numerical purposes *. It is necessary to develop a systematic method for improving the wavefunction so that it satisfies the Hellmann–Feynman theorem.

In a previous paper [2], we have given a theorem which gives a sufficient condition for the Hartree–Fock SCF wavefunction to satisfy the Hellmann–Feynman theorem. It provides a basis for a new systematic force approach which was shown to be very encouraging. In this paper we show that the same basic theorem is also valid for general MC SCF theories [3–5] and RHF theories for open-shell and excited states [5,6]. Some type of GVB theory [7] is also included. This fact means that the new force approach is applicable to wider fields including chemical reactions and open-shell and excited states with these SCF theories as a tool. Test calculations are given for methylene (open-shell RHF) and the hydrogen molecule (MC SCF) at several nuclear configurations.

* See references cited in ref. [2].

2. Theorem

A force acting on nucleus A, $\boldsymbol{F}_A$ is written as

$$\boldsymbol{F}_A = -\langle\Psi|\partial H/\partial \boldsymbol{R}_A|\Psi\rangle - \sum_r \boldsymbol{\Delta}_r\, \partial \boldsymbol{x}_r/\partial \boldsymbol{R}_A, \qquad (1)$$

where the first term is the H–F force and the second term is an error term composed of an AO error $\boldsymbol{\Delta}_r$ of a basis χ_r. ($\boldsymbol{R}_A$ is nuclear coordinate and $\boldsymbol{x}_r$ the center of the basis χ_r.) We show that the AO error is expressed as

$$\boldsymbol{\Delta}_r = 2\sum_i c_{ri} \quad \text{(SCF requirement projected on } |r'\rangle), \qquad (2)$$

where c_{ri} is a mixing coefficient of the basis χ_r in an orbital ϕ_i, and r' is the derivative $\partial\chi_r/\partial x_r$ of the basis $r = \chi_r$. Eq. (2) proves the theorem: *a sufficient condition for a general SCF wavefunction to satisfy the Hellmann–Feynman theorem is that the basis set includes the derivative r′ for any basis r. The basis set {r, r′, r″, ...} is such a basis. If the basis is recurrent in the sense* $r = r^{(n)}$, *then the number of elements can be finite.* This theorem is valid for general SCF theories including Hartree–Fock, UHF, RHF for open-shell and excited states, general MC SCF, and some type of GVB theory. Note that if only the force acting on a nucleus A, $\boldsymbol{F}_A$ is concerned, the derivative r' may be limited only to those bases whose centers are on nucleus A.

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3. Force in general MC SCF and open-shell RHF theories

We give the proof of the theorem stated in the above section for general MC SCF theory. RHF theory for open-shell and excited states, GVB theory, etc. are included as special cases.

A general MC SCF wavefunction may be expressed as

$$\Psi = \sum_K A_K \Phi_K, \tag{3}$$

where Φ_K is a Slater determinant composed of the orbitals $\{\phi_i\}$. They are expanded by a basis set $\{\chi_r\}$ as

$$\phi_i = \sum_r c_{ri}\chi_r . \tag{4}$$

The basis $\{\chi_r\}$ usually includes several (non-linear) parameters $\{\alpha_p\}$ in which our special concern is the center $\boldsymbol{x}_r$ of the AO χ_r. The wavefunction Ψ thus includes (variational) parameters A_K, c_{ri}, and α_p. The normality and orthonormality conditions for Ψ and ϕ_i give, respectively,

$$\sum_K A_K^2 = 1, \quad \mathbf{c}^+\mathbf{S}\mathbf{c} = 1, \tag{5}$$

where $S_{rs} = (\chi_r|\chi_s)$. We consider the MC SCF theory in its most general form [3] and write the energy as

$$\mathcal{E}(\boldsymbol{R}_A; A_K, c_{ri}, \alpha_p)$$

$$= \langle\Psi(A_K, c_{ri}, \alpha_p)|H(\boldsymbol{R}_A)|\Psi(A_K, c_{ri}, \alpha_p)\rangle \tag{6a}$$

$$= \sum_{ij}\gamma_{ij}(\phi_i|h|\phi_j) + \frac{1}{2}\sum_{ijkl}\Gamma_{ij,kl}(\phi_i\phi_j|\phi_k\phi_l) \tag{6b}$$

$$= \sum_{ij}\gamma_{ij}\sum_{rs}c_{ri}c_{sj}(r|h|s)$$

$$+ \frac{1}{2}\sum_{ijkl}\Gamma_{ij,kl}\sum_{rstu}c_{ri}c_{sj}c_{tk}c_{ul}(rs|tu), \tag{6c}$$

where $(rs|tu) = (\chi_r(1)\chi_s(1)|1/r_{12}|\chi_t(2)\chi_u(2))$ and $\{\boldsymbol{R}_A\}$ are a set of nuclear coordinates. γ_{ij} and $\Gamma_{ij,kl}$ are the first- and second-order density matrices in the orbital representation

$$\gamma_{ij} = \langle\Psi|a_i^+a_j|\Psi\rangle, \quad \Gamma_{ij,kl} = \langle\Psi|a_i^+a_k^+a_la_j|\Psi\rangle. \tag{7}$$

They depend only on the form of the MC SCF wavefunction and the coefficients $\{A_K\}$. In eq. (7), a_i^+ (a_i) is a creation (annihilation) operator associated with the orbital ϕ_i. For simplicity we assume our wavefunction Ψ and orbitals $\{\phi_i\}$ to be real, so that

$$\gamma_{ij} = \gamma_{ji}, \quad \Gamma_{ij,kl} = \Gamma_{ji,lk} = \Gamma_{kl,ij} = \Gamma_{lk,ji}. \tag{8}$$

The MC SCF wavefunction thus defined is very general. It includes the wavefunction for both ground and excited states [3–5, 8,9]. It also includes the full CI wavefunction as an extreme.

We apply the variational principle to the three parameters A_K, c_{ri}, and α_p. With the method of lagrangian multipliers, the function to be made stable is

$$\mathcal{L} = \mathcal{E} - \eta\left[\sum_L A_L^2 - 1\right] - \mathrm{Tr}[\boldsymbol{\varepsilon}(\mathbf{c}^+\mathbf{S}\mathbf{c} - \mathbf{1})], \tag{9}$$

where η and $\boldsymbol{\varepsilon}$ are multipliers ($\epsilon_{ij} = \epsilon_{ji}^*$). Optimization of A_K and c_{ri} gives

$$\partial\mathcal{E}/\partial A_K = 2\eta A_K \tag{10}$$

and

$$\partial\mathcal{E}/\partial c_{ri} = 2(\mathbf{S}\mathbf{c}\boldsymbol{\varepsilon})_{ri}, \tag{11}$$

respectively. Similarly, optimization of α_p gives

$$\partial\mathcal{E}/\partial\alpha_p = \mathrm{Tr}[\boldsymbol{\varepsilon}\mathbf{c}^+(\partial\mathbf{S}/\partial\alpha_p)\mathbf{c}]. \tag{12}$$

When the MC SCF wavefunction is completely variational, it satisfies eqs. (10)–(12). However, ordinary MC SCF wavefunctions do satisfy eqs. (10) and (11), but seldom eq. (12). Therefore, we do *not* assume eq. (12) in the present formulation.

It is convenient to rewrite eq. (11) in a more familiar form. Using eq. (6), we obtain [3]

$$\sum_{sj}[(r|F_{ij}|s) - \epsilon_{ji}(r|s)]\,c_{sj} = 0, \tag{13}$$

where

$$(r|F_{ij}|s) = \gamma_{ij}(r|h|s)$$

$$+ \sum_{kl}\Gamma_{ij,kl}\sum_{tu}c_{tk}c_{ul}(rs|tu). \tag{14}$$

This is a well-known MC SCF equation.

We now calculate the first derivative of the MC SCF energy with respect to the parameter λ. It was derived in more detail by Pulay [10]. We obtain from eq. (6a)

$$\partial E/\partial\lambda = \langle\Psi|\partial H/\partial\lambda|\Psi\rangle + \sum_K \frac{\partial \mathcal{E}}{\partial A_K}\frac{\partial A_K}{\partial\lambda} + \sum_{ri}\frac{\partial \mathcal{E}}{\partial c_{ri}}\frac{\partial c_{ri}}{\partial\lambda} + \sum_p \frac{\partial \mathcal{E}}{\partial\alpha_p}\frac{\partial\alpha_p}{\partial\lambda}. \quad (15)$$

The first term is the Hellmann–Feynman term. The second term is easily shown to vanish identically from eqs. (5) and (10). From the second relation of eq. (5) we also have the condition

$$\frac{\partial \mathbf{c}^+}{\partial\lambda}\mathbf{S}\mathbf{c} + \mathbf{c}^+\mathbf{S}\frac{\partial \mathbf{c}}{\partial\lambda} + \mathbf{c}^+\left[\sum_p \frac{\partial \mathbf{S}}{\partial\alpha_p}\frac{\partial\alpha_p}{\partial\lambda}\right]\mathbf{c} = 0. \quad (16)$$

Using eqs. (11) and (16), we can rewrite eq. (15) as

$$\partial E/\partial\lambda = \langle\Psi|\partial H/\partial\lambda|\Psi\rangle + \sum_p [\partial \mathcal{E}/\partial\alpha_p - \mathrm{Tr}(\mathbf{c}\boldsymbol{\varepsilon}\mathbf{c}^+\partial\mathbf{S}/\partial\alpha_p)]\,\partial\alpha_p/\partial\lambda. \quad (17)$$

Referring to eq. (11), we see that the second term of eq. (17) vanishes identically (i.e. the Hellmann–Feynman theorem holds) when the MC SCF wavefunction is optimized with respect to the remaining parameters $\{\alpha_p\}$. This term is therefore due entirely to the non-variational errors included in the wavefunction. We refer to this term as the *error term* accordingly.

Now we limit ourselves to consider the force acting on the nucleus A,

$$\boldsymbol{F}_\mathrm{A} = -\partial E/\partial \boldsymbol{R}_\mathrm{A}. \quad (18)$$

Then, in the set of parameters $\{\alpha_p\}$, we have only to consider the center $\boldsymbol{x}_r$ of the AO χ_r which belongs to nucleus A. The other parameters may be fixed or optimized [11]. Eq. (17) then becomes

$$\partial E/\partial \boldsymbol{R}_\mathrm{A} = \langle\Psi|\partial H/\partial \boldsymbol{R}_\mathrm{A}|\Psi\rangle + \sum_r \boldsymbol{\Delta}_r \partial \boldsymbol{x}_r/\partial \boldsymbol{R}_\mathrm{A}, \quad (19)$$

where

$$\boldsymbol{\Delta}_r = \partial \mathcal{E}/\partial \boldsymbol{x}_r - \mathrm{Tr}(\mathbf{c}\boldsymbol{\varepsilon}\mathbf{c}^+\partial\mathbf{S}/\partial \boldsymbol{x}_r). \quad (20)$$

The error term is the sum of the AO contribution $\boldsymbol{\Delta}_r$ which we call the *AO error*. Inserting $\mathcal{E}$ of the present theory [eq. (6)] and using eq. (8), we obtain

$$\boldsymbol{\Delta}_r = 2\sum_i c_{ri}\Big[\sum_j \gamma_{ij}\sum_s c_{sj}(r'|h|s) + \sum_{jkl}\Gamma_{ij,kl}\sum_{stu} c_{sj}c_{tk}c_{ul}(r's|tu) - \sum_j \epsilon_{ji}\sum_s c_{js}(r'|s)\Big], \quad (21)$$

where r' is the derivative of the AO χ_r, $r' = \partial\chi_r/\partial \boldsymbol{x}_r$. From the definition of the Fock matrix given by eq. (14), the AO error can further be rewritten as

$$\boldsymbol{\Delta}_r = 2\sum_i c_{ri} \times \Big[\sum_{sj}[(r'|F_{ij}|s) - \epsilon_{ji}(r'|s)]\,c_{sj}\Big], \quad (22)$$

which has the form of eq. (2). When the basis set $\{\chi_r\}$ includes not only χ_r but also its derivative r', the MC SCF solution satisfies [see eq. (13)]

$$\sum_{sj}[(r'|F_{ij}|s) - \epsilon_{ji}(r'|s)]\,c_{sj} = 0, \quad (23)$$

and therefore the AO error $\boldsymbol{\Delta}_r$ vanishes identically,

$$\boldsymbol{\Delta}_r = 0. \quad (24)$$

Thus, the theorem has been proven.

The above proof of the theorem is very general and applies also to the RHF theories for open-shell and excited states [5,6] and more specific MC SCF theories such as paired excitation MC SCF theory [5,12,13] and GVB theory [7]. These theories are specified by the non-zero elements of γ_{ij} and $\Gamma_{ij,kl}$ in the energy expression (6) as

$$\gamma_{ii} = f_i, \quad \Gamma_{ij,ij} = a_{ij}, \quad \Gamma_{ij,ji} = b_{ij}. \quad (25)$$

The energy expression then becomes in a familiar form

$$\mathcal{E} = \sum_i f_i(i|h|i) + \frac{1}{2}\sum_{ij}(a_{ij}J_{ij} + b_{ij}K_{ij}), \quad (26)$$

where $J_{ij} = (ii|jj)$ and $K_{ij} = (ij|ij)$. The Fock equation,

Table 1
Energy gradient, Hellmann–Feynman force, and error term before and after addition of first derivative AOs on the protons of triplet and singlet CH_2 at ∠HCH = 150° [a]

	Triplet		Singlet	
	parent [b]	family [b]	parent	family
energy gradient	−0.0153	−0.0143	−0.0283	−0.0278
Hellmann–Feynman force	−0.0059	−0.0139	−0.0202	−0.0268
error term	−0.0094	−0.0004	−0.0081	−0.0010

[a] The transverse force acting on the proton is given in atomic units.
[b] Parent denotes 4-31G basis and family denotes 4-31G basis plus first-derivative bases on hydrogen.

(13) and (14), the force and AO error, eqs. (19)–(22), and the theorem, eqs. (23) and (24), are also simplified with the use of eqs. (25) and (26).

4. A new force approach

The above theorem gives a systematic method of improving a wavefunction so that it satisfies the Hellmann–Feynman theorem. We may expect that the other properties are improved at the same time. As a first stage of such an approach, we consider an approximation in which only the first derivative AOs $\{r'\}$ are added to the "parent" AOs $\{r\}$. (The set $\{r,r'\}$ is called a "family".) Then, all of the AO errors of the parent AOs vanish identically as eq. (2) shows, but the AO errors of the added derivative AOs remain. However, if the parent basis set is already a good basis, the mixing coefficient $c_{r'i}$ of the added derivative AOs r' should be small, so that from eq. (2) the AO error of the added AO r', $\Delta_{r'}$, may be neglected. This approximation was shown to be very good in the Hartree–Fock case [2]. Here, we test this method for open-shell RHF and MC SCF theories. We have calculated singlet and triplet states of methylene by the closed- and open-shell RHF theories, respectively, and the hydrogen molecule by the MC SCF theory.

Table 1 and fig. 1 show the results for methylene. The transverse force acting on a proton is shown against the HCH angle. The 4-31G basis [14] was used as parent AOs and the first derivative AOs were added only to hydrogens. The CH length was kept fixed for both states at 1.11 Å which is the observed value for the singlet

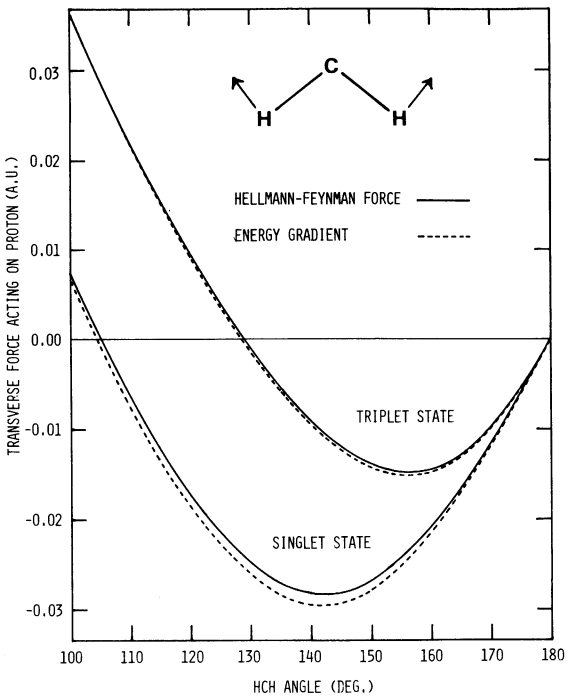

Fig. 1. Energy gradient and Hellmann–Feynman force versus HCH angle for the singlet and triplet states of methylene.

state [15]. For the triplet state, it is 1.078 Å [16]. From table 1 it is seen that the error term decreases rapidly by the addition of the first derivative AOs. The effect is larger for the triplet state than for the singlet state. After the addition of the first derivative AOs, the Hellmann–Feynman theorem is satisfied to a good approximation. The change in the energy gradient by

Table 2
Energy gradient, Hellmann–Feynman force, and error term before and after addition of the first-derivative AOs for the hydrogen molecule (au)

	Hartree–Fock				MC SCF (GVB)			
	R = 1.4011		R = 2.0		R = 1.4011		R = 2.0	
	parent [a]	family [a]	parent	family	parent	family	parent	family
energy	−1.12477	−1.12836	−1.08511	−1.08856	−1.14440	−1.14688	−1.11664	−1.11842
energy gradient	−0.0047	−0.0039	0.1015	0.1016	−0.0212	−0.0194	0.0780	0.0789
Hellmann–Feynman force	−0.0736	−0.0002	0.0410	0.1028	−0.0767	−0.0163	0.0347	0.0797
error term	0.0689	−0.0037	0.0605	−0.0012	0.0556	−0.0031	0.0433	−0.0008

[a] Parent denotes [2s] CGTO and family denotes [2s] CGTO plus their first derivatives.

the addition of the first derivative AOs is due to the improvement of the wavefuntion. It is small in this case since the first derivative AOs were added only to the AOs of the hydrogens. Fig. 1 shows that the error term is consistently small over the wide range of the HCH angle. For the triplet state, the equilibrium angle was calculated to be 128.8° by the H–F force and 128.4° by the energy gradient. The experimental value is 136° [16]. For the singlet state, the corresponding value is 105.2° by the H–F force and 104.7° by the energy

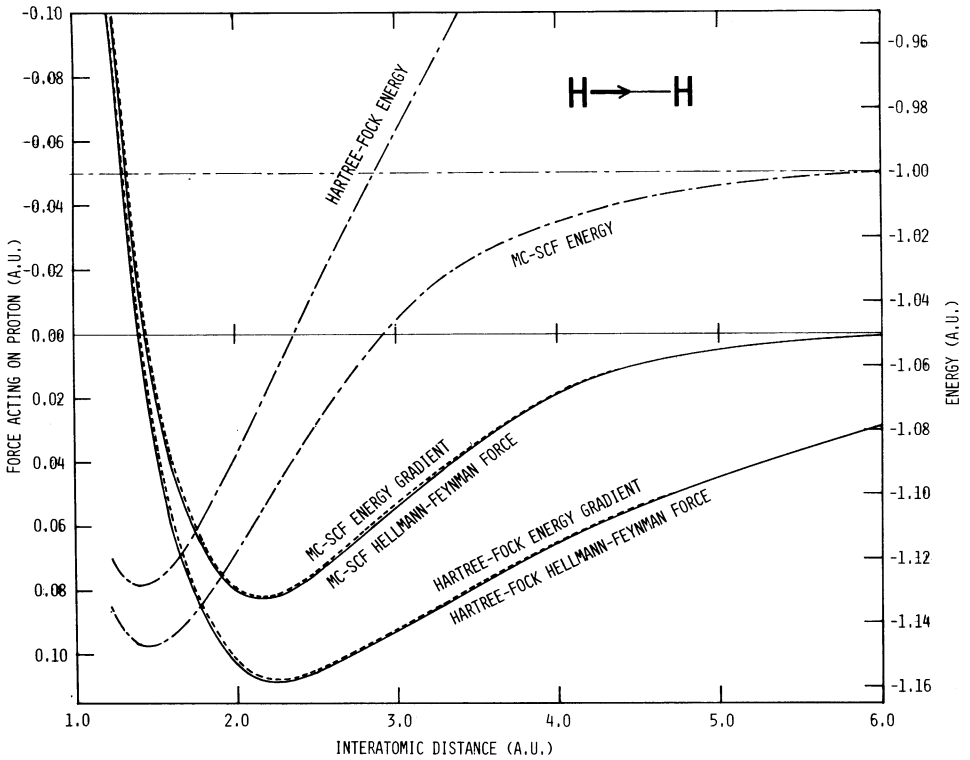

Fig. 2. Energy gradient, Hellmann–Feynman force, and energy versus interatomic distance for the hydrogen molecule.

gradient. The experimental value is 102.4° [15]. These results show a practical utility of the present method for geometry predictions.

Table 2 and fig. 2 show the results for the hydrogen molecule. The double-shell CGTO of Dunning [16] with the scale factor 1.0 was used as parent AOs and the first derivative AOs were added. The MC SCF calculation was performed for the two configurations $A_0|\sigma\sigma| + A_1|\sigma^*\sigma^*|$, which is also equivalent with the GVB wavefunction [17]. This system is well known for which the MC SCF type correction is very important for a proper description of the dissociation [18]. The energy gradient for the MC SCF wavefunction was calculated analytically [10,19]. Table 2 shows the Hartree–Fock and MC SCF results. By the addition of the first derivative AOs (family basis), the error term decreases dramatically, the orders being almost the same for both Hartree–Fock and MC SCF theories. For the family basis, the error term is negligibly small. In fig. 2 we have plotted the Hartree–Fock and MC SCF results obtained with the family basis over a wide range of interatomic distances. The energy gradient and Hellmann–Feynman force curves almost superpose each other. The Hellmann–Feynman theorem is essentially satisfied over the wide range of interatomic distances up to the dissociation limit. Though the Hartree–Fock theory itself breaks down in the range $R > 2.5$ au, the smallness of the error term is kept. Table 3 shows the bond length and vibrational frequency obtained from the energy gradient and Hellmann–Feynman force. At both Hartree–Fock and MC SCF levels, the quantities obtained from the energy gradient and Hellmann–Feynman force agree with each other.

Table 3
Bond length and vibrational frequency of H_2 obtained from the energy gradient and Hellmann–Feynman force

	Bond length R (au)	Vibrational frequency ω_e (cm^{-1})
Hartree–Fock		
energy gradient	1.411	4592
Hellmann–Feynman force	1.402	4613
MC SCF		
energy gradient	1.453	4282
Hellmann–Feynman force	1.445	4236
exp.	1.401	4401

Thus, the results of the test calculations for the open-shell RHF and MC SCF theories are very encouraging, as in the previous Hartree–Fock case [2]. After the addition of the first derivative AOs, the Hellmann–Feynman force gives essentially the same results as the energy-gradient method. Then, we can save time for calculations of the energy gradient. The present result means further that the utility of the new force approach is extended to important fields including electronic processes in chemical reactions and in open-shell and excited states with the use of the MC SCF and open-shell RHF theories. Intuitive pictures of the Hellmann–Feynman force [20] will be used quantitatively to clarify the electronic origins of these processes.

Acknowledgement

The authors thank Profesor T. Yonezawa for interest and support for this study, and Mr. K. Kanda for useful discussions. This study was supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science, and Culture.

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