

FORCE IN SCF THEORIES. COMBINATION WITH THE EFFECTIVE-CORE POTENTIAL METHOD

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The Hellmann–Feynman force method is combined with the effective-core potential (ECP) method. Based on a theorem previously reported, we have added the derivative AOs r' to the original basis r , and confirmed that the wavefunctions of the ECP method essentially satisfy the Hellmann–Feynman (HF) theorem. This makes it easier to apply an intuitive force concept quantitatively to molecular systems including heavier atoms and metals.

1. Introduction

A force acting on a nucleus in a molecular system may give important knowledge relating to the study of molecular structures and chemical reactions. Two alternative theoretical approaches have been used. One is an energy gradient (EG) method which gives an analytic gradient of the energy calculated by the RHF SCF, MC SCF or CI method [1]. The other is based on the Hellmann–Feynman (HF) theorem [2], in which the force is described with an intuitive electronic origin [3]. We have been developing the latter approach.

Previously [4], we have reported a theorem which gives a sufficient condition for a general SCF wavefunction (closed- and open-shell RHF, MC SCF, etc.) to satisfy the HF theorem. The accurate Hellmann–Feynman force method is based on this theorem and gives a systematic and practical method for using the HF force quantitatively. Further, when the HF theorem is satisfied for the first derivative of the energy, an analytic second derivative (e.g. force constant) becomes much simpler and gives more perspective than a straightforward second derivative of the SCF energy [5,6]. This approach provides the force and force constant (second derivative) which are numerically reliable and full of intuitive simplicity.

In this paper, we want to combine this force approach with the effective-core potential (ECP) or pseudo-potential approximation [7,8]. There, only

the valence electrons are treated explicitly and the core electrons are considered as giving an effective-core potential (ECP). The computational efforts are much reduced in comparison with all-electron ab initio calculations. Our aim is that a force approach will become applicable to inorganic and organometallic chemistry, and the force concept will be used there quantitatively to elucidate an electronic origin.

Calculations are given here to test the ability of the geometry optimization for sodium halides, magnesium dichloride, and hydrogen sulfide.

2. Force in the ECP method

The accurate Hellmann–Feynman force approach and its basic theorem have been summarized in some detail [4]. Here, we describe the theoretical basis in conjunction with the effective-core potential (ECP) method [8]. In the ECP method, the hamiltonian H^{ECP} includes only valence electrons explicitly and the core electrons are replaced effectively by the core potential V^{ECP} :

$$H^{\text{ECP}} = \sum_i \left[-\frac{1}{2} \nabla_i^2 - \sum_A \left(\frac{Z_A - N_A^{\text{C}}}{r_{Ai}} + V_{Ai}^{\text{ECP}} \right) \right] + \sum_{ij} \frac{1}{r_{ij}} + \sum_{A>B} \frac{(Z_A - N_A^{\text{C}})(Z_B - N_B^{\text{C}})}{R_{AB}}, \quad (1)$$

where i and j run over valence electrons and A and B

over nuclei. N_A^C is the number of core electrons on atom A . A force acting on nucleus A , F_A , is written as

$$F_A = -\langle \Psi | \partial H^{\text{ECP}} / \partial \mathbf{R}_A | \Psi \rangle - \sum_r \Delta_r \partial \mathbf{x}_r / \partial \mathbf{R}_A. \quad (2)$$

The first term is the HF force, and it contains the derivative of the effective-core potential as $\langle \Psi | \partial V^{\text{ECP}} / \partial \mathbf{R}_A | \Psi \rangle$. This term was calculated by the method reported by Kitaura et al. [9]. The second term is called the error term because it vanishes identically when the wavefunction is exact or an exact solution of the SCF equation (\mathbf{x}_r is the center of the basis (AO) χ_r). The error term is composed of the AO error Δ_r which is written as

$$\begin{aligned} \Delta_r = & \sum_s P_{rs} \left(2(r'|h + V^{\text{ECP}}|s) \right. \\ & + \sum_{t,u} P_{tu} [2(r'|s|tu) - (r'|t|su)] \\ & \left. - 4 \sum_{s,i} \epsilon_i C_{ri} C_{si} (r'|s) \right), \end{aligned} \quad (3)$$

where r' denotes the derivative of the AO χ_r , $r' = \partial \chi_r / \partial \mathbf{x}_r$. The AO error Δ_r given by eq. (3) is written, as in the all-electron theories, as

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

Eq. (4) leads to a theorem; a sufficient condition for an SCF wavefunction to satisfy the HF theorem is that the basis set includes the derivative r' for any basis r [4]. A first approximation based on this theorem is

to add only the first-derivative basis $\{r'\}$ to a conventional basis $\{r\}$. We call the original basis set the "parent" set and the basis $\{r\} + \{r'\}$ the "family" set. The validity of this approximation has been tested in detail for closed- and open-shell RHF theories and MC SCF theory [4]. Thus, the only difference in the ECP approximation from the all-electron theory is an additional calculation of the derivative of the ECP which appears in the HF force.

3. Results

Test calculations for the stretching force are performed for sodium halides. The parent set is the uncontracted (4s4p) basis for fluorine, (3s3p) basis for chlorine, bromine, and iodine [8], and the LP-41G basis for sodium [10]. The bases of halogens were modified slightly[‡] to economize our approach, i.e. to form an sp shell structure. The first derivative bases were added to the parent set to form the family set. For the bases which already have their first derivatives in the parent set, due to the shell structure, a duplicate addition is not necessary.

Table 1 shows the energy gradient, Hellmann–Feynman force and error term for sodium halides. The symbol Δ_A denotes a sum of the AO errors Δ_r on

[‡] Two outer sp gaussians of F, Br, and I [8] were modified as F(1.213, 0.364; 1.621, 0.374) → F(1.213, 0.364; 1.213, 0.364), Br(0.357, 0.130; 0.503, 0.147) → Br(0.430, 0.1385; 0.430, 0.1385), and I(0.300, 0.118; 0.336, 0.108) → I(0.318, 0.113; 0.318, 0.113), where the notation is X($\xi_s, \xi_s; \xi_p, \xi_p$).

Table 1
Energy gradient, Hellmann–Feynman force, and error term of sodium halides^{a,b} (au)

NaX	Bond length (Å)	Parent basis					Family basis				
		EG	HF force on Na	Δ_{Na}	HF force on halogen	Δ_X	EG	HF force on Na	Δ_{Na}	HF force on halogen	Δ_X
NaF	1.92594	0.0276	0.0193	0.0083	0.4298	-0.4022	0.0215	0.0151	0.0064	0.0193	0.0022
NaCl	3.0	0.0286	0.0261	0.0025	0.1506	-0.1220	0.0313	0.0283	0.0020	0.0314	-0.0001
NaBr	2.7	0.0104	0.0072	0.0032	0.1520	-0.1416	0.0145	0.0133	0.0012	0.0123	0.0022
NaI	3.0	0.0122	0.0088	0.0034	-0.1040	0.1162	0.0148	0.0140	0.0008	0.0136	0.0012

^{a)} The force is positive if it points to the other nucleus.

^{b)} Δ_A denotes a sum of the AO error Δ_r on the atom A .

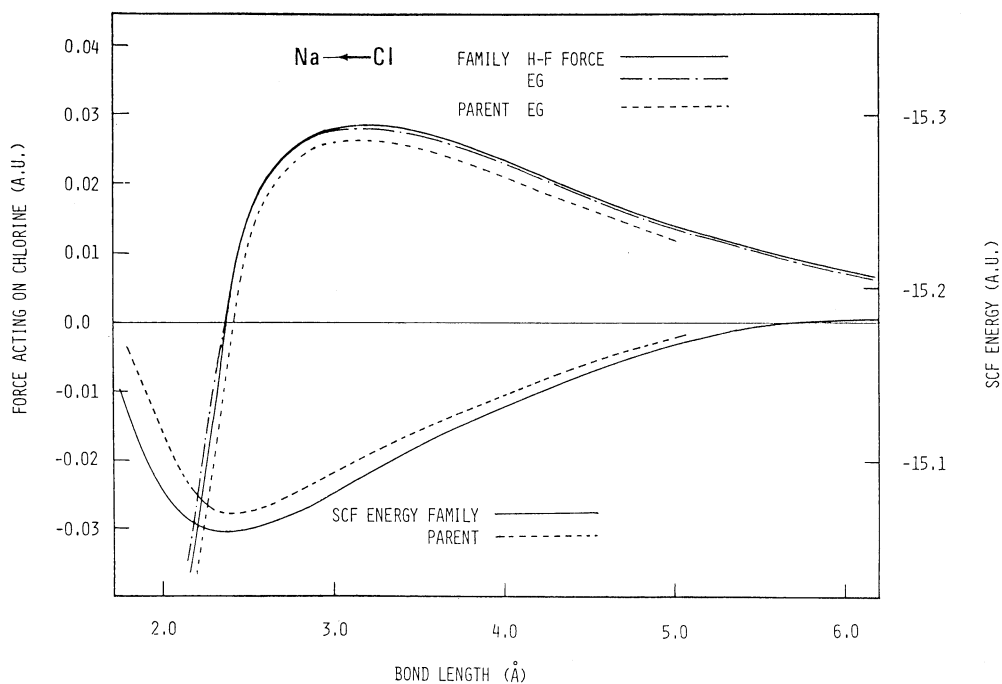


Fig. 1. Hellmann-Feynman force, energy gradient, and SCF energy of NaCl versus internuclear distance.

atom A . By addition of the derivatives r' , the error term Δ_X of halogen becomes dramatically small for all the sodium halides with light to heavy halogens. For sodium, the error term Δ_{Na} is already small in the parent set because the LP41G set forms an sp shell structure. In fig. 1, the force acting on chlorine in sodium chloride is plotted against the internuclear distance. When the family set is used, the HF force

curve agrees quite well with the EG curve; the HF theorem is essentially satisfied over a wide range of internuclear distance. Further the EG itself is also affected by addition of the derivatives (compare the EG curves of the parent and family sets). It results from an improvement of the wavefunction by addition of the first-derivative bases. For NaCl, the effect is -0.045 \AA (EG) or -0.032 \AA (HF) for the bond length and -0.11 eV for the binding energy.

Table 2
Equilibrium bond length and dissociation energy to Na + X of sodium halids

NaX	Equilibrium bond length (Å)				exp. a)	Dissociation energy (eV)		
	parent EG	family		parent		family	exp. a)	
		EG	HF force					
			Na					X
NaF	1.804	1.872	1.884	1.880	1.92549	2.55	2.70	5.33
NaCl	2.415	2.370	2.383	2.384	2.36079	2.87	2.98	4.23
NaBr	2.579	2.506	2.513	2.533	2.50230	1.64	1.90	3.47
NaI	2.802	2.736	2.741	2.760	2.71145	1.30	1.56	3.00

a) Ref. [11].

Table 3
Energy gradient, Hellmann–Feynman force, and error term of H_2S and MgCl_2 ^{a)} (au)

Term	H_2S ($\angle \text{HSH} = 140^\circ$)				MgCl_2 ($\angle \text{ClMgCl} = 150^\circ$)			
	parent		family		parent		family	
	F_S	F_H	F_S	F_H	F_{Cl}	F_{Mg}	F_{Cl}	F_{Mg}
energy gradient	0.0927	0.0685	0.0962	0.0506	-0.0046	-0.0051	-0.0048	-0.0125
Hellmann–Feynman	0.3978	0.0016	0.0963	0.0505	-0.0146	0.0021	-0.0047	-0.0126
error term	-0.3051	0.0669	-0.0001	0.0001	0.0100	-0.0072	-0.0001	0.0001

^{a)} Definition of force;

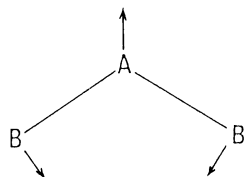


Table 2 shows the equilibrium bond length and dissociation energy of sodium halides. After the addition of the derivatives, the lengths calculated by the EG, HF forces on halogen and sodium, are essentially equivalent. The maximum difference is 0.027 Å for NaBr.

This difference is less than the effect of the derivative basis on the bond length (the maximum effect is 0.073 Å for NaBr). In the case of sodium halides, the bond length calculated with the family set is nearer the experimental value [11].

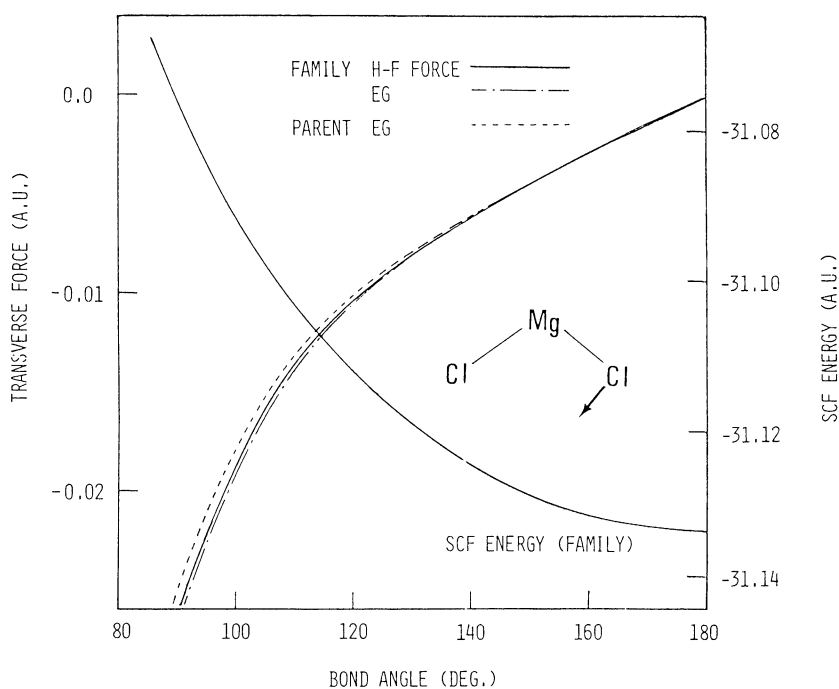


Fig. 2. Hellmann–Feynman force, energy gradient, and SCF energy of MgCl_2 along the bending mode.

The energy of the dissociation, $\text{NaX} \rightarrow \text{Na} + \text{X}$, is rather poor by the present ECP method. The maximum effect of the first-derivative bases is 0.26 eV for NaBr and NaI. Note that the dissociation limit of the present SCF calculation, shown in fig. 1, is ionic and higher than the radical fission.

Next, two triatomic molecules, magnesium dichloride and hydrogen sulfide, are adopted to test a transverse force during the bending process. The parent set is the LP-31G basis [10] for Mg, Cl and S, and [2s] basis for hydrogen [12]. The first derivatives were added to provide the family set. The bond lengths were kept fixed during the bending process (Mg-Cl = 2.18 Å [13], S-H = 1.328 Å [14]). Table 3 shows

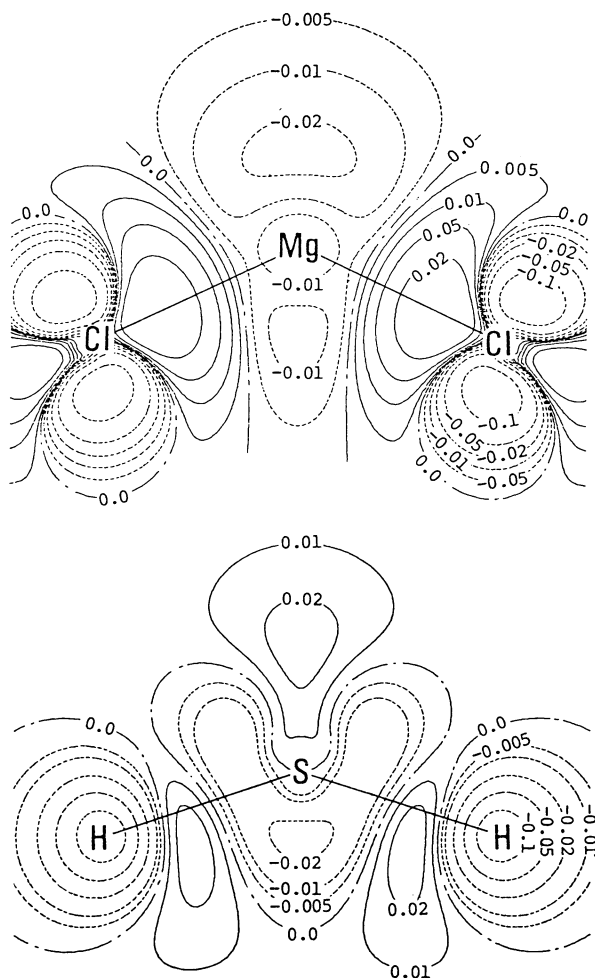


Fig. 3. Density difference map, $\Delta\rho = \rho(\text{AB}_2) - \rho(\text{A}) - \rho(\text{B}) - \rho(\text{B}')$ of MgCl_2 and SH_2 at the valence angle 130° .

Table 4
Optimized bond angle of H_2S and optimized bond length of MgCl_2

Geometrical parameter	Parent EG	Family		Exp.
		EG	HF	
$\angle \text{HSH}$ bond angle (deg) ^{a)}	95.0	93.8	93.9	92.2
Mg-Cl bond length (Å)	2.21	2.16	2.18	2.18

^{a)} The S-H length was fixed at the experimental value.

the EG, HF force, and error term. By addition of the first-derivative bases, the error term becomes negligibly small and the HF theorem is essentially satisfied. In fig. 2, the transverse force acting on the terminal chlorine of MgCl_2 is plotted against the bond angle. The HF theorem is satisfied over a wide range of bond angles. Fig. 3 is a contour map of the density difference for MgCl_2 and H_2S ; $\Delta\rho(\text{AB}_2) = \rho(\text{AB}_2) - \rho(\text{A}) - \rho(\text{B}) - \rho(\text{B}')$. In the case of MgCl_2 , which is a linear molecule, the electron density polarizes downward near the Mg and increases upward along the Mg-Cl bond. But in the case of H_2S ($\angle \text{HSH} = 140^\circ$ is larger than the equilibrium bond angle), the electron density polarizes upward near the sulfur and increases downward along the S-H bond. We can estimate the direction of the force acting on the nuclei from this polarization of density and the occurrence of the bent bond. The electron cloud incompletely follows and precedes, respectively, in the bending process and causes the HF forces to resist and accelerate the process, respectively [15]. This behavior is the same as in molecules of the first-row atoms. Table 4 shows the optimized bond angle and bond length of H_2S and MgCl_2 . The calculated geometries are improved by addition of the first-derivative bases.

The results presented in this paper are encouraging, suggesting a utility of the present force approach in combination with the ECP method. We want to pave the way for a development of the force concept in the fields of organometallic and inorganic chemistry.

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