ACCURATE HELLMANN-FEYNMAN FORCE METHOD FOR THE STUDY OF THE FIRST AND SECOND DERIVATIVES OF POTENTIAL ENERGY HYPERSURFACE

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1. INTRODUCTION

Hellmann-Feynman (H-F) theorem gives an intuitive expression of the force based on an electrostatic interaction between the electron density and nuclei.[1] This simplicity is very valuable in studying complex chemical phenomena such as molecular geometry, chemical reaction and molecular vibration.[2] A past defect of this approach was that the calculation of a wavefunction which satisfies the H-F theorem was believed to be difficult.[3]

However, we recently found a promising method of calculating a reliable H-F force.[4-7] Here, we briefly review the method starting from the underlying theorem and examine the accuracy of the calculated H-F force. We then show some recent applications of the method to geometry optimizations of the molecules in ground and excited states and of the transition state of a chemical reaction. It has also been applied to the analysis of chemical reaction parths.[8]

Further, when we use the H-F theorem, an analytic expression of the second derivative of energy becomes much simpler and more perspective than a straightforward second derivative of the energy.[7,9] We report calculations of force constants (both positive and negative) by this method and explain the electronic origins of the second derivatives.

2. THEOREM

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

$$\begin{aligned} \underset{\sim}{F}_A &= -\langle\Psi|\partial H/\partial \underset{\sim}{R}_A|\Psi\rangle - \langle\partial\Psi/\partial \underset{\sim}{R}_A|H|\Psi\rangle - \langle\Psi|H|\partial\Psi/\partial \underset{\sim}{R}_A\rangle \\ &= -\langle\Psi|\partial H/\partial \underset{\sim}{R}_A|\Psi\rangle - \sum_r \underset{\sim}{\Delta}_r \, \partial x_r/\partial \underset{\sim}{R}_A \end{aligned} \qquad (1)$$

where the first term is the H-F force and the rest is an error term which vanishes identically for a correct wavefunction. It is expressed as a sum of the AO error $\underset{\sim}{\Delta}$ associated with each basis χ_r. (In Eq. (1), $\underset{\sim}{R}_A$ is a nuclear coordinate and $\underset{\sim}{x}_r$ the center of a basis χ_r.) It is shown that the AO error is expressed as

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

where c_{ri} is a mixing coefficient of the basis χ_r in an orbital ϕ_i, and r' is a derivative $\partial\chi_r/\partial \underset{\sim}{x}_r$ of the basis $r = \chi_r$. Eq. (2) proves the following 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 closed-shell Hartree-Fock, UHF, RHF for open-shell and excited states, general MC-SCF, and some types of GVB theory. Note that if only the force acting on a nucleus A, $\underset{\sim}{F}_A$, is concerned, the derivative r' may be added only to those bases whose centers are on the nucleus A (see Eq. (1)).

3. A NEW FORCE METHOD

The above theorem gives a basis for a systematic method of improving a wavefunction so that it satisfies the Hellmann-Feynman theorem. As a first stage of such an approach, we have considered an approximation in which only the first derivative AO's {r'} are added to the "parent" AO's {r}. (The set {r, r'} is called a "family".) Then, all of the AO errors of the parent AO's vanish identically as Eq. (2) shows, but the AO errors of the added derivative AO's remain. However, if the parent basis set is already a good basis, the mixing coefficient $c_{r'i}$ of the added derivative AO's r' should be small, so that from Eq. (2) the AO error of the added AO r', $\underset{\sim}{\Delta}_{r'}$, may be neglected. This approximation has been confirmed to be very good: test calculations were performed for the closed-shell Hartree-Fock method,[4,6] open-shell RHF[5] and UHF methods, and MC-SCF method.[5] Further, it was also shown that other properties, such as dipole moment, quadrupole moment, etc., are improved at the same time.[6]