A Deduction of the Hellmann-Feynman Theorem

Chen Feng[1] · Cheng Wei[1] · Bao-long Fang[1] · Hong-yi Fan[2]

Abstract

In this paper we present a deduction of the Hellmann-Feynman (HF) theorem for the lowest eigenenergy $E_0(\lambda)$ of a Hamiltonian $H(\lambda)$, that is : its second-order derivative with respect to he parameter λ, $\frac{\partial^2 E_0}{\partial \lambda^2}$, is always less than the expectation value of $\frac{\partial^2 H(\lambda)}{\partial \lambda^2}$ in the ground state. We also point out that the above deduction does not hold for the FH theorem in ensemble average. The electric polarizability of molecules is studied by the deduction of the HF theorem

Keywords Hellmann-Feynman (HF) theorem · Eigenenergy $E_0(\lambda)$ · Hamiltonian $H(\lambda)$ · The expectation value

1 Introduction

In theoretical quantum physics and quantum chemistry the Hellmann-Feynman (HF) theorem [1, 2] has been widely used for calculating various observables [3–6]. The Hellmann-Feynman theorem states that when a system's Hamiltonian, which depends upon a real parameter λ, possesses its energy eigenvector $|\alpha_n\rangle$, $H|E_n\rangle = E_n|E_n\rangle$ with $\langle E_n|E_n\rangle = 1$, then

$$\frac{\partial E_n(\lambda)}{\partial \lambda} = \frac{\partial \langle E_n|H(\lambda)|E_n\rangle}{\partial \lambda} = \left\langle E_n \left| \frac{\partial H}{\partial \lambda} \right| E_n \right\rangle, \quad (1)$$

Applying the HF theorem to multi-electron-neuclon interaction one can derive the electrostatic theorem [5]. By noticing that the HF theorem only deals with the first-order derivative of the average energy (or $H(\lambda)$) with respect to λ, an interesting question thus naturally arises: is there any physical rule or physical meaning which can be exposed by performing

✉ Chen Feng
  chenfeng@hfuu.edu.cn

1 Department of Mathematics and Physics, Hefei University, Hefei, Anhui 230022, China

2 Department of Material Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

the second-order derivative of $E(\lambda)$ with respect to the parameter λ? This question has some physical background, for instance, the electric polarizability, denoted as α in this paper, of a molecule is a measure of its ability to respond to an electric field and acquires an electric dipole moment, $\vec{\mu} = \sum_i q_i \vec{r}_i$, where q_i is the charge of the particle i at the location $\vec{r}_i$. The effect caused by an electric field $\vec{\varepsilon}$, applied in the x-direction with electric field strength ε, which is assumed uniform over the molecule, is described by

$$H = H_0 - \vec{\mu} \cdot \vec{\varepsilon} = H_0 - \mu_x \varepsilon, \ \mu_x = qX, \tag{2}$$

where H_0 denotes the Hamiltonian of a molecule in the absence of the field, which is usually taken as

$$H_0 = \frac{P^2}{2m} + \frac{m\omega^2}{2} X^2. \tag{3}$$

In the context of quamtum mechanics, the expectation value of the electric dipole moment operator μ_x in the presence of the electric field is the sum of a permanent dipole moment μ_{0x} and the contribution induced by the field, so we can expand

$$\langle \mu_x \rangle = \mu_{0x} + \alpha_{xx}\varepsilon + O\left(\varepsilon^2\right) + \cdots, \tag{4}$$

where α_{xx} is named the polarizability in the x-direction [6]. For obtaining the polarizability, one may use the HF theorem such that the variation of the energy E_n with respect to the electric field strength ε is given by

$$\frac{dE_n}{d\varepsilon} = \langle \psi_n | \frac{\partial H}{\partial \varepsilon} | \psi_n \rangle = - \langle \psi_n | \mu_x | \psi_n \rangle, \ H | \psi_n \rangle = E_n | \psi_n \rangle. \tag{5}$$

On the other hand, the energy E_n of the molecule in the presence of the electric field can be Taylor-expanded relative to its energy $E_n(0)$ in the absence of the field

$$E_n = E_n(0) + \left(\frac{dE_n}{d\varepsilon}\right)_0 \varepsilon + \frac{1}{2}\left(\frac{d^2E_n}{d\varepsilon^2}\right)_0 \varepsilon^2 + \frac{1}{3!}\left(\frac{d^3E_n}{d\varepsilon^3}\right)_0 \varepsilon^3 + \cdots \tag{6}$$

the subscript 0 implies that the derivative is evaluated at $\varepsilon = 0$. Substituting (6) into (4) yields

$$-\frac{dE_n}{d\varepsilon} = \langle \psi_n | \mu_x | \psi_n \rangle = -\left(\frac{dE_n}{d\varepsilon}\right)_0 - \left(\frac{d^2E_n}{d\varepsilon^2}\right)_0 \varepsilon - \frac{1}{2}\left(\frac{d^3E_n}{d\varepsilon^3}\right)_0 \varepsilon^2 - \cdots, \tag{7}$$

Then comparing (7) with (5) one can identify

$$\mu_{0x} = -\left(\frac{dE_n}{d\varepsilon}\right)_0, \qquad \alpha_{xx} = -\left(\frac{d^2E_n}{d\varepsilon^2}\right)_0, \qquad \cdots \tag{8}$$

thus for obtaining α_{xx} we need to enlarge the scope of usual FH theorem to the case about the second-order derivative $\frac{d^2E_n}{d\varepsilon^2}$ and explore its relation to $\frac{d^2H}{d\varepsilon^2}$. In the following we shall analyse it and will obtain a deduction of the usual FH theorem, that is:

For the lowest eigenenergy $E_0(\lambda)$, its second-order derivative with respect to parameter λ is always less than the expectation value of $\frac{\partial^2 H(\lambda)}{\partial \lambda^2}$ in the ground state.

In Ref. [7] Fan and Chen has developed the HF theorem for pure state to mixed state case, we shall also point out that the above deduction does not hold for the FH theorem in ensemble avarage case.

2 Deduction of the FH Theorem

Writing the eigenvalue equation of H as $(H - E_n)|E_n\rangle \equiv G_n|E_n\rangle = 0$,

$$(H - E_n) \equiv G_n. \tag{9}$$

by considering that this equation holds for any variation of λ, we have

$$\frac{\partial G_n}{\partial \lambda}|E_n\rangle + G_n \frac{\partial}{\partial \lambda}|E_n\rangle = 0, \tag{10}$$

From the hermitian of the Hamiltonian operator H, it follows

$$\langle E_n|\frac{\partial G_n}{\partial \lambda} + \frac{\partial \langle E_n|}{\partial \lambda}G_n = 0. \tag{11}$$

Then

$$\left(\langle E_n|\frac{\partial G_n}{\partial \lambda}\right)\frac{\partial}{\partial \lambda}|E_n\rangle = \left(-\frac{\partial \langle E_n|}{\partial \lambda}G_n\right)\frac{\partial}{\partial \lambda}|E_n\rangle. \tag{12}$$

Doing the second-order derivative with respect to λ for (10) leads to

$$\frac{\partial^2 G_n}{\partial \lambda^2}|E_n\rangle + 2\frac{\partial G_n}{\partial \lambda}\frac{\partial}{\partial \lambda}|E_n\rangle + G_n\frac{\partial^2}{\partial \lambda^2}|E_n\rangle = 0, \tag{13}$$

then taking inner product with $\langle E_n|$ we have

$$\langle E_n|\frac{\partial^2 G_n}{\partial \lambda^2}|E_n\rangle + 2\langle E_n|\frac{\partial G_n}{\partial \lambda}\frac{\partial}{\partial \lambda}|E_n\rangle + \langle E_n|G_n\frac{\partial^2}{\partial \lambda^2}|E_n\rangle = 0. \tag{14}$$

After taking $\langle E_n|G_n = 0$ into account, (14) becomes to

$$\langle E_n|\frac{\partial^2 G_n}{\partial \lambda^2}|E_n\rangle = -2\langle E_n|\frac{\partial G_n}{\partial \lambda}\frac{\partial}{\partial \lambda}|E_n\rangle \tag{15}$$

then from (12) we have

$$\langle E_n|\frac{\partial^2 G_n}{\partial \lambda^2}|E_n\rangle = 2\left(\frac{\partial \langle E_n|}{\partial \lambda}\right)G_n\frac{\partial}{\partial \lambda}|E_n\rangle \tag{16}$$

or

$$\frac{\partial^2 E_n}{\partial \lambda^2} = \langle E_n|\frac{\partial^2 H}{\partial \lambda^2}|E_n\rangle - 2\left(\frac{\partial \langle E_n|}{\partial \lambda}\right)(H - E_n)\left(\frac{\partial |E_n\rangle}{\partial \lambda}\right), \tag{17}$$

which is sharply in contrast to (1), i.e., while one has $\frac{\partial E_n(\lambda)}{\partial \lambda} = \langle E_n|\frac{\partial H}{\partial \lambda}|E_n\rangle$, one should know $\frac{\partial^2 E_n(\lambda)}{\partial \lambda^2} \neq \langle E_n|\frac{\partial^2 H}{\partial \lambda^2}|E_n\rangle$. By setting

$$|\psi\rangle_n = \frac{\partial}{\partial \lambda}|E_n\rangle, \tag{18}$$

we see

$$\frac{\partial^2 E_n}{\partial \lambda^2} = \langle E_n|\frac{\partial^2 H}{\partial \lambda^2}|E_n\rangle - 2\,_n\langle\psi|(H - E_n)|\psi\rangle_n. \tag{19}$$

In particular, if E_n is the ground state energy E_0, then the value $_0\langle\psi|H|\psi\rangle_0 - E_0 = \left(\frac{\partial}{\partial \lambda}\langle E_0|\right)H\left(\frac{\partial}{\partial \lambda}|E_0\rangle\right) - E_0 \geqslant 0$, is always positive, so

$$\frac{\partial^2 E_0}{\partial \lambda^2} = \langle E_0|\frac{\partial^2 H}{\partial \lambda^2}|E_0\rangle - 2\,_0\langle\psi|(H - E_0)|\psi\rangle_0 \leqslant \langle E_0|\frac{\partial^2 H}{\partial \lambda^2}|E_0\rangle, \tag{20}$$

this states that for the lowest energy E_0, its second-order derivative with respect to λ, $\frac{\partial^2 E_0}{\partial \lambda^2}$, is always less than the expectation value of $\frac{\partial^2 H}{\partial \lambda^2}$ in the ground state, this is the deduction of the Hellmann-Feynman theorem.

For example, for a harmonic oscillator $H_0 = \frac{P^2}{2m} + \frac{m\omega^2}{2}X^2$, in its ground state $|0\rangle$ with the energy $E_0 = \hbar\omega$, we do have

$$\left\langle 0 \left| \frac{\partial^2 H_0}{\partial\omega^2} \right| 0 \right\rangle = \left\langle 0 \left| mX^2 \right| 0 \right\rangle = \frac{m}{2} \left\langle 0 \left| \left(a + a^\dagger\right)^2 \right| 0 \right\rangle \frac{\hbar}{m\omega} = \frac{\hbar}{2\omega} \geq \frac{\partial^2 E_0}{\partial\omega^2} = 0, \quad (21)$$

where $X = \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^\dagger\right)$, and noticing $P = i\sqrt{\frac{m\omega\hbar}{2}}\left(a^\dagger - a\right)$ we also have

$$\left\langle 0 \left| \frac{\partial^2 H_0}{\partial m^2} \right| 0 \right\rangle = \left\langle 0 \left| \frac{P^2}{m^3} \right| 0 \right\rangle = \frac{-\omega\hbar}{2m^2} \left\langle 0 \left| \left(a - a^\dagger\right)^2 \right| 0 \right\rangle = \frac{\omega\hbar}{2m^2} \geq \frac{\partial^2 E_0}{\partial m^2} = 0, \quad (22)$$

satisfying (20). We now apply (20) to studying the Electric polarizability of a molecule described by the Hamiltonian in (2), we have

$$\left\langle \frac{\partial H}{\partial\varepsilon} \right\rangle_n = \langle -qX \rangle_n = \frac{\partial E_n(\varepsilon)}{\partial\varepsilon}. \quad (23)$$

Supposing that the bound eigenstate of $H = H_0 - \mu_x\varepsilon$ is $|n\rangle$ (not H_0's eigenstate), from $[X, P] = i\hbar$, we have

$$0 = \left\langle n \left| \frac{1}{i\hbar}[P, H] \right| n \right\rangle = \left\langle n \left| \left(q\varepsilon - m\omega^2 X\right) \right| n \right\rangle. \quad (24)$$

It follows

$$\langle n | X | n \rangle = \frac{q\varepsilon}{m\omega^2}, \quad (25)$$

and

$$\frac{\partial E_n(\varepsilon)}{\partial\varepsilon} = -\frac{q^2\varepsilon}{m\omega^2}, \quad (26)$$

which is independent of n, so we can write

$$E(\varepsilon) = -\frac{q^2\varepsilon^2}{2m\omega^2}, \quad (27)$$

As a result of (8), the polarizability is

$$\alpha_{xx} = -\left(\frac{d^2 E}{d\varepsilon^2}\right)_0 = \frac{q^2}{m\omega^2}. \quad (28)$$

We now check if (28) agrees with (20), comparing with (20) we see indeed

$$\frac{d^2 E}{d\varepsilon^2} = \frac{-q^2}{m\omega^2} \leqslant \left\langle E_0 \left| \frac{\partial^2 H}{\partial\varepsilon^2} \right| E_0 \right\rangle = 0, \quad (29)$$

since $\frac{\partial^2 H}{\partial\varepsilon^2} = 0$. Further, from (20) we also obtain

$$\frac{-q^2}{m\omega^2} = -2\,_n\langle\psi|(H - E_n)|\psi\rangle_n, \quad |\psi\rangle_n = \frac{\partial}{\partial\varepsilon}|E_n\rangle \quad (30)$$

Since the Hamiltonian in (2) can be rewritten as

$$H = H_0 - \mu_x\varepsilon = \frac{P^2}{2m} + \frac{m\omega^2}{2}X^2 - \varepsilon qX = \omega a^\dagger a - \varepsilon q\sqrt{\frac{\hbar}{2m\omega}}\frac{a^\dagger + a}{\sqrt{2}},$$

its eigenstate $|E_n\rangle$ is a coherent state. If $|\psi\rangle_n$ is normalizable, $_n\langle\psi|\psi\rangle_n = c$, we have the expectation value of H in $|\psi\rangle_n$

$$_n\langle\psi|H|\psi\rangle_n = \frac{q^2}{2m\omega^2} + cE_n. \quad (31)$$

3 Some Discussions

We now consider two moleculars with mutual interaction in electric field described by the Hamiltonian

$$H_2 = \sum_{i=1}^{2} \left(\frac{P_i^2}{2m} + \frac{m\omega^2}{2} X_i^2 \right) - \varepsilon q \left(X_1 + X_2 \right) - \lambda X_1 X_2 \tag{32}$$

We calculate for the eigenvector of H_2

$$\langle \psi_n | X_1 | \psi_n \rangle = \frac{1}{i\hbar} \langle \psi_n | [P_1, H_2] | \psi_n \rangle = \left\langle \psi_n \left| \left(\varepsilon q - m\omega^2 X_1 + \lambda X_2 \right) \right| \psi_n \right\rangle$$

$$\langle \psi_n | X_2 | \psi_n \rangle = \frac{1}{i\hbar} \langle \psi_n | [P_2, H_2] | \psi_n \rangle = \left\langle \psi_n \left| \left(\varepsilon q - m\omega^2 X_2 + \lambda X_1 \right) \right| \psi_n \right\rangle \tag{33}$$

noting

$$\langle \psi_n | [P_i, H_2] | \psi_n \rangle = 0, \ i = 1, 2 \tag{34}$$

so

$$\langle \psi_n | \left(X_1 + X_2 \right) | \psi_n \rangle = \frac{2q\varepsilon}{m\omega^2 - \lambda} \tag{35}$$

Thus the variation of the energy E_n with respect to the electric field strength ε is

$$\frac{dE_n}{d\varepsilon} = - \langle \psi_n | q \left(X_1 + X_2 \right) | \psi_n \rangle = - \frac{2q^2 \varepsilon}{m\omega^2 - \lambda} \tag{36}$$

which is not related to n, and the polarizability is

$$\alpha_{xx} = - \left(\frac{d^2 E}{d\varepsilon^2} \right)_0 = \frac{2q^2}{m\omega^2 - \lambda} \tag{37}$$

hence we see when two moleculars has inner interaction, its polarizability in electric field becomes to $\frac{2q^2}{m\omega^2 - \lambda}$. Moreover, when $m\omega^2 > \lambda$, we do have

$$\frac{d^2 E_0}{d\varepsilon^2} = - \frac{2q^2}{m\omega^2 - \lambda} \leqslant \langle E_0 | \frac{\partial^2 H_2}{\partial \varepsilon^2} | E_0 \rangle = 0, \tag{38}$$

which conforms to the deduction of Hellmann-Feynman theorem.

By noticing that the usual Hellmann-Feynman theorem is about the pure state average $\langle \psi_n | \frac{\partial H}{\partial \lambda} | \psi_n \rangle$, Fan and Chen developed it to the case of ensemble average (denoted by $\langle \ \rangle_e$) and derived the generalized Hellmann-Feynman (GFHT) in Refs. [7–11]

$$\frac{d}{d\lambda} \langle H \rangle_e \equiv \frac{d\bar{E}}{d\lambda} = \left\langle \left(1 + \beta \bar{E} - \beta H \right) \frac{\partial H}{\partial \lambda} \right\rangle_e \tag{39}$$

where $\langle H \rangle_e \equiv \bar{E}$ indicates the ensemble average, $\beta = 1/KT$, K is the Boltzmann constant. When H is β−independent, (39) becomes to [7]

$$\frac{d}{d\lambda} \langle H (\lambda) \rangle_e = \left(1 + \beta \frac{\partial}{\partial \beta} \right) \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_e = \frac{\partial}{\partial \beta} \left[\beta \left\langle \frac{\partial H}{\partial \lambda} \right\rangle_e \right]. \tag{40}$$

However, we do not have a general conclusion that $\frac{\partial^2 E_n}{\partial \lambda^2} \leqslant \langle E_n | \frac{\partial^2 H}{\partial \lambda^2} | E_n \rangle$ for all n, so the above deduction does not hold for the ensemble avarage.

For example, when

$$H' = \begin{pmatrix} 0 & \lambda \\ \lambda & 1 \end{pmatrix}, \tag{41}$$

so

$$\frac{\partial^2 H'}{\partial \lambda^2} = 0, \; \langle E_n | \frac{\partial^2 H'}{\partial \lambda^2} | E_n \rangle \equiv 0 \tag{42}$$

On the other hand, H' eigenvalues are

$$E_0 = \frac{1 - \sqrt{1 + 4\lambda^2}}{2}, \; E_1 = \frac{1 + \sqrt{1 + 4\lambda^2}}{2} \tag{43}$$

it follows

$$\frac{\partial^2 E_0}{\partial \lambda^2} = -\frac{4\lambda^2}{\left(1 + 4\lambda^2\right)^{3/2}} < 0, \tag{44}$$

which obeys the deduction of FH theorem, however, for E_1 we can calculate

$$\frac{\partial^2 E_1}{\partial \lambda^2} = \frac{4\lambda^2}{\left(1 + 4\lambda^2\right)^{3/2}} > 0 \tag{45}$$

which does not obey the deduction of FH theorem.

In summary, we have presented the deduction of the Hellmann-Feynman (HF) theorem for the lowest eigenenergy $E_0(\lambda)$ of a Hamiltonian $H(\lambda)$, that is : its second-order derivative with respect to he parameter λ, $\frac{\partial^2 E_0}{\partial \lambda^2}$, is always less than the expectation value of $\frac{\partial^2 H(\lambda)}{\partial \lambda^2}$ in the ground state. The electric polarizability of molecules is studied by the deduction of the HF theorem.

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