The Hellmann-Feynman Theorem and Brillouin's Theorem in the Hartree-Fock Approximation

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ハートリー・フォック近似における ヘルマン・ファインマンの定理とブリュアンの定理

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It is shown that the fulfillment of the Hellmann-Feynman theorem in the Hartree-Fock approximation is an obvious consequence rather than a proposition to be proved through Brillouin's theorem. Moreover it is pointed out that, within the molecular orbital picture, the general fulfillment of the Hellmann-Feynman theorem leads us naturally to the one-particle hypervirial theorem, which is reducible to Brillouin's theorem for the single configurational case and conditionally reducible to the generalized Brillouin's theorem for the multiconfigurational case.

So far quite a number of papers have been devoted to the "intimate" relation between the Hellmann-Feynman theorem (HFT)[1,2] and Brillouin's theorem (BT)[3–5] or to derivations of the HFT under the Hartree-Fock (HF) approximation.[6–13] Most of them are, of course, not incorrect, but often include superfluous discussions as repeatedly pointed out by Epstein.[2,14] Suitably and sufficiently, he has emphasized the simplicity and generality of Hurley's theorem,[15] which does not seem to be widely appreciated. In this note, giving a transpicuous description of the problem, we would like to clarify the situation for the HF approximation, which seems more or less helpful in understanding the nature of the HFT and to have some pedagogical value.

Let us take the Hamiltonian $H(\sigma)$ dependent on a real parameter σ. The energy expectation value $E(\sigma)$ for the approximate state $\Phi(\sigma)$, which is not necessarily normalized, is given by

$$E(\sigma)=\langle\Phi(\sigma)|H(\sigma)|\Phi(\sigma)\rangle/\langle\Phi(\sigma)|\Phi(\sigma)\rangle, \tag{1}$$

from which we can immediately obtain

$$\dot{E}=(\langle\Phi|\dot{H}|\Phi\rangle+\langle\dot{\Phi}|(H-E)|\Phi\rangle+\langle\Phi|(H-E)|\dot{\Phi}\rangle)/\langle\Phi|\Phi\rangle. \tag{2}$$

Hereafter the dot is used to indicate the differentiation with respect to σ and the symbol (σ), "a function of σ", is often omitted for brevity. The fulfillment of the HFT for σ

$$\dot{E}=\langle\Phi|\dot{H}|\Phi\rangle/\langle\Phi|\Phi\rangle \tag{3}$$

is ascribed to the condition that

$$\langle\dot{\Phi}|(H-E)|\Phi\rangle+\langle\Phi|(H-E)|\dot{\Phi}\rangle=0. \tag{4}$$

On the other hand, with the variation $|\delta\Phi\rangle$ we may put the variation principle into[16)]

$$\langle\Phi|(H-E)|\delta\Phi\rangle=0. \tag{5}$$

Various variational approximations are characterized by specifying the space of the trial function, or equivalently that of the variation. Thus, if $|\delta\Phi\rangle$ runs over $\lambda|\dot{\Phi}\rangle$ with an infinitesimal number λ, that is, if $\lambda|\dot{\Phi}\rangle$ is a possible $|\delta\Phi\rangle$ in a variational approximation, then the HFT holds under that approximation. This is an obvious consequence requiring no kind of derivations. Epstein has neatly showed that *when the set of trial functions is invariant to changes in* σ, $|\dot{\Phi}\rangle$ *is a possible* $|\delta\Phi\rangle$ *and the HFT for* σ *will be satisfied.*[2)] Because this is in its essentials due to Hurley,[15)] it has been named Hurley's theorem.

Now let us denote the creation and annihilation operators for the one-particle quantum state ξ, respectively, by $a_\xi^\dagger$ and a_ξ. Taking a complete set of one-particle quantum state $\{\xi\}$, we can write the Hamiltonian which consists of one- and two-particle operators and depends parametrically on σ as

$$H(\sigma)=\sum_{\xi\eta}h_{\xi\eta}(\sigma)a_\xi^\dagger a_\eta+\frac{1}{2}\sum_{\xi\eta\theta\gamma}v_{\eta\gamma}^{\xi\theta}(\sigma)a_\xi^\dagger a_\theta^\dagger a_\gamma a_\eta. \tag{6}$$

Here it should be noted that the σ-dependence of the Hamiltonian comes only from that of the matrix elements, $\{h_{\xi\eta}\}$ and $\{v_{\eta\gamma}^{\xi\theta}\}$. To let the Hamiltonian be hermitian we assume that

$$h_{\xi\eta}(\sigma)=h_{\eta\xi}^*(\sigma) \tag{7}$$

and

$$v_{\eta\gamma}^{\xi\theta}(\sigma)=v_{\xi\theta}^{\eta\gamma*}(\sigma). \tag{8}$$

Introducing a relevant hermitian one-particle operator

$$X(\sigma)=\sum_{\xi\eta}x_{\xi\eta}(\sigma)a_\xi^\dagger a_\eta, \tag{9}$$

solving the eigenvalue problem

$$\sum_\eta(h_{\xi\eta}(\sigma)+x_{\xi\eta}(\sigma))u_{\eta j}(\sigma)=u_{\xi j}(\sigma)\varepsilon_j(\sigma), \tag{10}$$

we obtain the molecular orbitals $\{j, k,\cdots\}$; the Hamiltonian (6) can be written in the molecular orbital representation as

$$H(\sigma)=\sum_j\varepsilon_j(\sigma)a_j^\dagger(\sigma)a_j(\sigma)-\sum_{jk}x_{jk}(\sigma)a_j^\dagger(\sigma)a_k(\sigma)+\frac{1}{2}\sum_{jklm}v_{km}^{jl}(\sigma)a_j^\dagger(\sigma)a_l^\dagger(\sigma)a_m(\sigma)a_k(\sigma), \tag{11}$$

where

$$a_j^\dagger(\sigma)=\sum_\xi a_\xi^\dagger u_{\xi j}(\sigma), \tag{12}$$

$$x_{jk}(\sigma)=\sum_{\xi\eta}u_{\xi j}^*(\sigma)x_{\xi\eta}(\sigma)u_{\eta k}(\sigma), \tag{13}$$

and so on. Since $\{h_{\xi\eta}\}$ and $\{x_{\xi\eta}\}$ are hermitian, we can assume the unitarity of $\{u_{\xi j}\}$;

$$\sum_{\xi} u^*_{\xi j}(\sigma)\, u_{\xi k}(\sigma) = \delta_{jk}. \tag{14}$$

The single determinant state specified by a set L of the occupied orbitals

$$|L(\sigma)\rangle = \prod_{j \in L} a^\dagger_j(\sigma)|\text{vacuum}\rangle \tag{15}$$

is an eigenstate of

$$K(\sigma) = \sum_j \varepsilon_j(\sigma)\, a^\dagger_j(\sigma)\, a_j(\sigma). \tag{16}$$

Because $\{a^\dagger_\xi\}$ is independent of σ, we have

$$\dot{a}^\dagger_j = \sum_\xi a^\dagger_\xi \dot{u}_{\xi j}, \tag{17}$$

which is rewritten by means of the reverse transformation of eq. (12),

$$a^\dagger_\xi = \sum_j u^*_{\xi j}(\sigma)\, a^\dagger_j(\sigma), \tag{18}$$

as

$$\dot{a}^\dagger_j = \sum_k \zeta_{jk}(\sigma)\, a^\dagger_k(\sigma) \tag{19}$$

with

$$\zeta_{jk}(\sigma) = \sum_\xi \dot{u}_{\xi j} u^*_{\xi k}(\sigma). \tag{20}$$

Note that $\{\zeta_{jk}\}$ is antihermitian ;

$$\zeta_{jk}(\sigma) = -\zeta^*_{kj}(\sigma), \tag{21}$$

as is easily seen from the unitarity of $\{u_{\xi j}\}$. Using eq. (19), we obtain

$$|\dot{L}\rangle = \sum_{jk} \zeta_{jk} a^\dagger_k a_j |L\rangle. \tag{22}$$

First consider the single configurational case. The variation in eq. (5) for the HF approximation is to be constructed by varying $\{a^\dagger_j, a_j\}$ as

$$\begin{cases} a^\dagger_j \rightarrow a^\dagger_j + \sum_k \lambda_{jk} a^\dagger_k \\ a_j \rightarrow a_j + \sum_k \lambda^*_{jk} a_k, \end{cases} \tag{23}$$

where an arbitrary infinitesimal matrix $\{\lambda_{jk}\}$ must be antihermitian to preserve the anticommutation relations between the creation and annihilation operators. Immediately it follows that

$$|\delta\Phi\rangle = \sum_{jk} \lambda_{jk} a^\dagger_k a_j |L\rangle, \tag{24}$$

whereas we know eq. (22) ;

$$|\dot{\Phi}\rangle = \sum_{jk} \zeta_{jk} a^\dagger_k a_j |L\rangle. \tag{25}$$

Obviously $\lambda|\dot{\Phi}\rangle$ is a possible $|\delta\Phi\rangle$; the fulfillment of the HFT is trivial rather than derived from BT, a particular restatement completely equivalent to the variation principle with regard to the single configurational case.[3]

Next consider the multiconfigurational case, where the trial function is a linear combination of some $|L\rangle$'s ;

$$|\Phi(\sigma)\rangle=\sum_L C_L(\sigma)|L(\sigma)\rangle. \tag{26}$$

Since

$$\begin{aligned}\sum_L C_L|\delta L\rangle&=\sum_L C_L\sum_{jk}\lambda_{jk}a_k^\dagger a_j|L\rangle\\&=\sum_{jk}\lambda_{jk}a_k^\dagger a_j|\Phi\rangle,\end{aligned} \tag{27}$$

the variation in eq. (5) for the multiconfigurational HF approximation takes the form as

$$|\delta\Phi\rangle=\sum_L \delta C_L|L\rangle+\sum_{jk}\lambda_{jk}a_k^\dagger a_j|\Phi\rangle. \tag{28}$$

On the other hand, it is readily found that

$$|\dot\Phi\rangle=\sum_L \dot C_L|L\rangle+\sum_{jk}\zeta_{jk}a_k^\dagger a_j|\Phi\rangle. \tag{29}$$

Hence $\lambda|\dot\Phi\rangle$ is again a possible $|\delta\Phi\rangle$ and again the fulfillment of the HFT is trivial. What is called the generalized BT[5] is, by itself, not equivalent to the variational principle under the multiconfigurational approximation. It seems, however, unnecessary to invoke the generalized BT in examining the fulfillment of the HFT in the multiconfigurational HF approximation.

As far as the HF approximation is concerned, it is very obvious or rather trivial for the HFT to hold, as we see in the above. However, the story should be thought to be confined to the HF limit,[17] for we assume the complete basis expansion at the beginning. The use of an incomplete basis, which is practically almost the case, requires another consideration, of course.[17,18]

It is never futile to see what the condition (4) asserts in the molecular orbital picture. For the single configurational case, we have

$$\sum_{jk}\zeta_{jk}^*\langle L|a_j^\dagger a_k(H-E)|L\rangle+\sum_{jk}\zeta_{jk}\langle L|(H-E)a_k^\dagger a_j|L\rangle=0, \tag{30}$$

which is rewritten, by virtue of the antihermiticity of $\{\zeta_{jk}\}$, compactly as

$$\sum_{jk}\zeta_{jk}\langle L|[H,\ a_k^\dagger a_j]|L\rangle=0. \tag{31}$$

Within the molecular orbital picture defined by eqs. (9), (10), and (15), the "general" fulfillment of the HFT leads us naturally to the one-particle hypervirial theorem ;[19]

$$\langle L|[H,\ a_k^\dagger a_j]|L\rangle=0 \qquad (\text{any } j,\ k), \tag{32}$$

which gives BT by deleting the trivially satisfied relations. For the multiconfigurational case, if the Ritz variation method is assumed for determining the mixing coefficients $\{C_L\}$, that is, if

$$\sum_M\langle L|H|M\rangle C_M=C_L E, \tag{33}$$

then similarly to the single configurational case we obtain

$$\sum_{jk} \zeta_{jk} \langle \Phi | [H, a_k^\dagger a_j] | \Phi \rangle = 0. \tag{34}$$

Moreover, if we can assume that $\{u_{\xi j}\}$ are real, then $\{\zeta_{jk}\}$ is a real antisymmetric matrix. Therefore, instead of eq. (34), we have

$$\sum_{j<k} \zeta_{jk} \langle \Phi | [H, a_k^\dagger a_j - a_j^\dagger a_k] | \Phi \rangle = 0. \tag{35}$$

Thus the "real" one-particle hypervirial theorem

$$\langle \Phi | [H, a_k^\dagger a_j - a_j^\dagger a_k] | \Phi \rangle = 0 \tag{36}$$

is fundamental, but it is really rewritten as

$$\mathrm{Re}(\langle \Phi | H (a_k^\dagger a_j - a_j^\dagger a_k) | \Phi \rangle) = 0. \tag{37}$$

The relevant reality restriction gives the generalized BT.

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