

## Note on Stationariness of State Energies to Shifting of Hartree-Fock Orbital Energies

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ハートリー・フォック軌道エネルギーの変位に対する  
状態エネルギーの停留性について

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It is succinctly shown that the state energy up to third order is stationary to simultaneous shifting of all Hartree-Fock orbital energies by the same amount. Significance of the stationariness is discussed in the context of the Hellmann-Feynman theorem; it is pointed out that orbital energies still remain arbitrary, though relative distances between orbital energies are determinable from a variational condition on the state energy up to third order.

Hartree-Fock (HF) orbitals have physically definite nature, based on the variation principle.<sup>1,2)</sup> Of course, as is well known, the variation principle merely determines the occupied and unoccupied orbital manifolds, leaving orbitals themselves arbitrary in each of the manifolds. This orbital ambiguity is resolved with additional physical requirement or, in other words, utilized profitably to the purpose.<sup>3-10)</sup> After such determination of HF orbitals we can still vary the orbital energies, keeping the topological nature of the orbital unchanged.<sup>11)</sup> This lingering arbitrariness of orbital energies gets into shape, for example, in what is called the level-shifting technique.<sup>12-14)</sup> Now how does shifting of HF orbital energies affect perturbation-theoretical state energies?

We work within the spin unrestricted picture, calling spin orbitals merely orbitals for brevity. Occupied and unoccupied HF orbitals are labelled with the indices  $\{j, k\}$  and  $\{a, b\}$ , respectively, whereas the indices  $\{p, q, r, s\}$  are used for both. Let us denote the creation and annihilation operators for the  $p$ -th HF orbital, respectively, by  $a_p^\dagger$  and  $a_p$ . Shifting the  $p$ -th HF orbital energy by the amount  $\theta_p$ , we can write the second quantized electronic Hamiltonian in the HF orbital representation as

$$H = K + V \tag{1}$$

with

$$K = \sum_p (\varepsilon_p + \theta_p) a_p^\dagger a_p \quad (2)$$

and

$$V = \frac{1}{2} \sum_{pqrs} v_{qs}^{pr} a_p^\dagger a_r^\dagger a_s a_q - \sum_{pq} x_{pq} a_p^\dagger a_q - \sum_{jk} y_{jk} a_j^\dagger a_k - \sum_{ab} y_{ab} a_a^\dagger a_b - \sum_p \theta_p a_p^\dagger a_p, \quad (3)$$

where  $\{\varepsilon_p\}$  are HF orbital energies;  $\{v_{qs}^{pr}\}$  and  $\{x_{pq}\}$  stand for the electron repulsion and the HF potential matrix elements, respectively. We do not specify  $\{y_{jk}\}$  and  $\{y_{ab}\}$ , the matrix elements due to the orbital ambiguity resolution, but it is crucial that they have either both occupied or both unoccupied double indices.<sup>11)</sup>

Now we invoke the Rayleigh-Schrödinger perturbation expansion.<sup>15)</sup> The unperturbed Hamiltonian  $K$  has the HF state

$$|0\rangle = \prod_j a_j^\dagger |\text{vacuum}\rangle \quad (4)$$

as an eigenstate, which gives the unperturbed energy and the first order energy correction:

$$E_0 = \langle 0 | K | 0 \rangle \quad (5)$$

$$E_1 = \langle 0 | V | 0 \rangle \quad (6)$$

By the virtue of Brillouin's theorem the first order state correction contains only doubly excited configurations;

$$|1\rangle = \frac{1}{2} \sum_{jkab} c_{jk}^{ab} a_a^\dagger a_b^\dagger a_k a_j |0\rangle \quad (7)$$

with

$$c_{jk}^{ab} = v_{jk}^{ab} / (\varepsilon_j + \varepsilon_k - \varepsilon_b - \varepsilon_a + \theta_j + \theta_k - \theta_b - \theta_a). \quad (8)$$

The second and third order energy corrections are expressed

in terms of  $|0\rangle$  and  $|1\rangle$ :

$$E_2 = \langle 1 | V | 0 \rangle \quad (9)$$

$$E_3 = \langle 1 | V | 1 \rangle - E_1 s \quad (10)$$

with

$$s = \langle 1 | 1 \rangle. \quad (11)$$

Let us use the notation  $E(n)$  to indicate the state energy up to n-th order;

$$E(n) = \sum_{i=0}^n E_i. \quad (12)$$

Since

$$\frac{\partial}{\partial \theta_p} K = -\frac{\partial}{\partial \theta_p} V = a_p^\dagger a_p, \quad (13)$$

we immediately obtain

$$\frac{\partial}{\partial \theta_p} E_0 = -\frac{\partial}{\partial \theta_p} E_1 = \begin{cases} 1 & (p : \text{occupied}) \\ 0 & (p : \text{unoccupied}). \end{cases} \quad (14)$$

Hence we have

$$\frac{\partial}{\partial \theta_p} E(1) = 0. \quad (15)$$

*The state energy up to first order is stationary to any shifting of individual HF orbital energies.*

This seems rather trivial, for the Hamiltonian itself is independent of  $\{\theta_p\}$  (See eq. (27)). We can regard this stationariness, anyway, as a foundation of the level-shifting technique in the HF theory.

On the other hand, it is readily found that the partial derivatives of  $|1\rangle$  with respect to  $\{\theta_p\}$  satisfy the relation

$$\sum_p \frac{\partial}{\partial \theta_p} |1\rangle = 0, \quad (16)$$

which gives

$$\sum_p \frac{\partial}{\partial \theta_p} s = 0. \quad (17)$$

From eq. (13) we see

$$\sum_p \frac{\partial}{\partial \theta_p} V = -\sum_p a_p^\dagger a_p = -N, \quad (18)$$

$N$  being the number-of-electron operator. Using eqs. (14), (16), and (17), noting that  $|0\rangle$  and  $|1\rangle$  are both eigenstates of  $N$  with the same eigenvalue and that they are mutually orthogonal, we easily arrive at

$$\sum_p \frac{\partial}{\partial \theta_p} E_2 = \sum_p \frac{\partial}{\partial \theta_p} E_3 = 0, \quad (19)$$

which results in

$$\sum_p \frac{\partial}{\partial \theta_p} E(3) = 0 \quad (20)$$

because of eq. (15). Using the normalized state

$$|\psi\rangle = (|0\rangle + |1\rangle) / (1+s)^{1/2}, \quad (21)$$

we can write the state energy up to third order with the normalization correction as<sup>15)</sup>

$$\begin{aligned} \tilde{E}(3) &= \langle \psi | H | \psi \rangle \\ &= E_0 + E_1 + (E_2 + E_3) / (1+s), \end{aligned} \quad (22)$$

for which also we have

$$\sum_p \frac{\partial}{\partial \theta_p} \tilde{E}(3) = 0 \quad (23)$$

by means of eqs. (15), (17), and (20). Now in the equation of differentials

$$dE(3) = \sum_p \frac{\partial}{\partial \theta_p} E(3) d\theta_p \quad (24)$$

if we impose the condition

$$d\theta_p = d\theta \quad (\text{all } p) \quad (25)$$

upon  $\{d\theta_p\}$ , it follows immediately that

$$dE(3) = 0. \quad (26)$$

This stationariness of  $E(3)$  is leading implication of eq. (23): *The state energy up to third order is stationary to the shifting of all HF orbital energies as a whole.* The same holds for  $\tilde{E}(3)$ . By the way, calculating the right hand sides of eqs. (9), (10), and (11) explicitly with eqs. (3), (4), (7), and (8), we can see that  $E_2$ ,  $E_3$ , and  $s$  contain  $\{\theta_p\}$  only in the form of  $\theta_j + \theta_k - \theta_b - \theta_a$ .

Finally, it is significant and instructive to view the stationariness in the context of the Hellmann-Feynman theorem. Since  $|0\rangle$  is variationally optimized, the Hellmann-Feynman

theorem is satisfied.<sup>16)</sup> Hence, eq. (15) is to result from

$$\frac{\partial}{\partial \theta_p} E(1) = \langle 0 | \left( -\frac{\partial}{\partial \theta_p} H \right) | 0 \rangle. \quad (27)$$

Contrastively we do not have

$$\frac{\partial}{\partial \theta_p} \tilde{E}(3) = \langle \psi | \left( -\frac{\partial}{\partial \theta_p} H \right) | \psi \rangle \quad (28)$$

in general; regarding  $\{\theta_p\}$  as variation parameters, we reasonably require the variational condition<sup>11)</sup>

$$\frac{\partial}{\partial \theta_p} \tilde{E}(3) = 0, \quad (29)$$

which necessarily means the fulfillment of eq. (28), the special Hellmann–Feynman theorem for  $\{\theta_p\}$ . What is asserted by eq. (23) is then that eq. (29)'s for all  $p$ 's are not independent of each other; though relative distances between orbital energies are determinable, orbital energies still remain arbitrary.

### References

- 1) A. C. Hurley : *Introduction to the Electron Theory of Small Molecules* (Academic Press, London, 1976) Section 7. 2.
- 2) R. K. Nesbet : *Adv. Chem. Phys.* **9** (1968) 321 ; *Rev. Mod. Phys.* **33** (1961) 28.
- 3) C. Edmiston and K. Ruedenberg : *Rev. Mod. Phys.* **35** (1963) 457.
- 4) H. J. Silverstone and M.-L. Yin : *J. Chem. Phys.* **49** (1968) 2026.
- 5) S. Huzinaga and C. Arnau : *Phys. Rev. A* **1** (1970) 1285 ; *J. Chem. Phys.* **54** (1971) 1948.
- 6) E. R. Davidson : *J. Chem. Phys.* **57** (1972) 1999.
- 7) K. Morokuma and S. Iwata : *Chem. Phys. Lett.* **16** (1972) 192 ; S. Iwata and K. Morokuma : *Theor. Chim. Acta* **33** (1974) 285.
- 8) K. Hirao : *J. Chem. Phys.* **61** (1974) 3247.
- 9) E. R. Davidson and L. Z. Stenkamp : *Int. J. Quantum Chem. Symp. No. 10*, (1976) 21 ; H.-L. Hsu, E. R. Davidson, and R. M. Pitzer : *J. Chem. Phys.* **65** (1976) 609.
- 10) M. Isihara : *Bull. Chem. Soc. Jpn.* **55** (1982) 1392 ; *ibid.* **55** (1982) 2692.
- 11) M. Isihara : *Bull. Chem. Soc. Jpn.* **57** (1984) 361.
- 12) V. R. Saunders and I. H. Hillier : *Int. J. Quantum Chem.* **7** (1963) 699.
- 13) O. Matsuoka : *Mol. Phys.* **30** (1975) 1293.
- 14) R. Carbo, J. A. Hernandez, and F. Sanz : *Chem. Phys. Lett.* **47** (1977) 581.
- 15) J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein : *Adv. Quantum Chem.* **1** (1964) 255.
- 16) S. T. Epstein : *The Variation Method in Quantum Chemistry* (Academic Press, New York, 1974) Section 15.

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