

Hidden potentials in classical theorems

Hiroshi Nakatsuji

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan
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Some exact equations are derived which clarify some potentials that are hidden in the classical theorems such as the Hellmann–Feynman (H–F) and the integral Hellmann–Feynman (I–H–F) theorems. The differential form of the density equation given previously includes not only the classical force operator but also the force operator associated with the quantum-mechanical potential introduced by Bohm. The latter arises essentially only from the noncommuting property of coordinates and momenta in quantum mechanics. However, after integration only the classical force term survives and results in the H–F theorem. The important role of the quantum force term is completely *hidden* in the H–F theorem. This fact would be closely related to the nondeterminicity and the classical interpretation of the H–F theorem. A similar role of the quantum potential is also shown for the I–H–F theorem. We have also investigated the origin of force density (the integrand of the H–F theorem) and isolated the roles of the generalized exchange and correlation effects which are also *hidden* in the H–F theorem.

I. INTRODUCTION

The Hellmann–Feynman (H–F)¹ and the integral Hellmann–Feynman (I–H–F)² theorems permit us to study quantum systems with semiclassical intuitions. The simplicity and visuality of the theorems are quite useful in understanding the regularities and varieties of chemical phenomena,^{3,4} as shown for example in the applications of the electrostatic force (ESF) theory to molecular structures, chemical reactions, and long-range forces.^{5,6} These theorems have also been utilized to study the characteristic behaviors of electron density which commonly occur in any nuclear rearrangement processes.^{6,7}

However, these theorems are only weak necessary conditions of the Schrödinger equation. That is, these theorems alone are insufficient to determine the electron density and the transition density included in the theorems.⁸ Previously,⁹ we have presented the variationally deterministic expressions of these theorems using the idea of Hohenberg and Kohn.¹⁰ These expressions however require the exact knowledge of the density of the reference system.⁹

Recently, I have presented a nonvariational equation, called the density equation, for the direct determination of the (reduced) density matrix.¹¹ Within the N -representable space of the density matrices the equation is connected with the Schrödinger equation by a necessary and sufficient theorem and is a self-contained equation for the density matrix.¹¹ It may therefore be considered as giving a projection of the Schrödinger equation onto the fewer particle space. Cho¹² and Cohen and Frishberg¹³ have also given a similar equation, though the implication of their equation is very different from ours.

In this paper I will derive from the density equation some exact equations which will clarify some potentials that are hidden in the classical theorems such as the H–F and I–H–F theorems. In Sec. II we will start from the density equation in the Ψ representation. For the present purpose it is more convenient than that in the density matrix representation and avoids also the unsolved N -representability problem. We will differentiate the density equation with respect to the external parameter included in the external potential. The resul-

tant equation includes not only the classical force operator but also the force operator associated with the quantum mechanical potential introduced by Bohm.¹⁴ We will discuss the role of the quantum force operator which is *hidden*, by integration, in the H–F theorem. In Sec. III we will isolate the generalized exchange and correlation effects included in the differential density equation and show that the effects are also hidden in the H–F theorem. This formulation will also clarify the origin of the force density which is the integrand of the H–F theorem. In Sec. IV we will isolate a similar role of the quantum potential which is also hidden in the I–H–F theorem. Section V gives a brief summary.

II. QUANTUM FORCE AND THE H–F THEOREM

We consider a stationary N -electron system specified by the Hamiltonian

$$H = T + V_\alpha + W \\ = \sum_i t(i) + \sum_i v_\alpha(i) + \sum_{i>j} w(i, j), \quad (1)$$

where T and $t(i)$ denote the kinetic operator, V_α and $v_\alpha(i)$ the external potential which depends on the external parameter α (e.g., atomic number Z_A and the nuclear coordinate R_A in atomic and molecular systems), and W and $w(i, j)$ the electron–electron repulsion operator. We also write the one-electron operator in Eq. (1) as $v(i)$, i.e.,

$$v(i) = t(i) + v_\alpha(i). \quad (2)$$

We define the n th order reduced density matrix by

$$\Gamma^{(n)}(1' \cdots n' | 1 \cdots n) \\ = {}_N C_n \int [\Psi^*(1' \cdots N') \Psi(1 \cdots N)]_{n+1'=n+1, \dots, N'=N} \\ \times dx_{n+1} \cdots dx_N \\ = {}_N C_n \langle \Psi', \Psi \rangle_n, \quad (3)$$

where ${}_N C_n$ is the binomial coefficient and the prime on Ψ means that it depends only on the primed coordinates, i.e., $\Psi' = \Psi(1' \cdots N')$. The coordinate $i = x_i$ represents both space r_i and spin s_i coordinates. The symbol $\langle \cdots \rangle_n$ means the integration over the last $N-n$ spin–space co-

ordinates after the primed variables are equated with the unprimed variables. With this notation the density equation is given in the Ψ representation as

$$E\langle\Psi', \Psi\rangle_n = \langle\Psi', H\Psi\rangle_n, \quad (4)$$

or in the Γ representation as

$$\int [\mathfrak{H}^{(n)}(1 \cdots n; n+1, n+2) - E] \times \Gamma^{(n+2)}(1' \cdots n+2' | 1 \cdots n+2) dx_{n+1} dx_{n+2} = 0, \quad (5)$$

where the coordinates $n+1'$ and $n+2'$ are equated to $n+1$ and $n+2$ after the operation of the reduced Hamiltonian $\mathfrak{H}^{(n)}$ given by

$$\begin{aligned} \mathfrak{H}^{(n)}(1 \cdots n; n+1, n+2) &= \sum_i^n v(i) + \sum_{i>j}^n w(i, j) \\ &+ (N-n) \left[v(n+1) + \sum_i^n w(i, n+1) \right] \\ &+ \frac{1}{2} (N-n)(N-n-1) w(n+1, n+2). \end{aligned} \quad (6)$$

It has been shown previously¹¹ that if the density matrix satisfies the density equation with $n \geq 2$, then the wavefunction connected with it by Eq. (3) will satisfy the Schrödinger equation, and *vice versa*. The density equation (5) is a self-contained equation for the density matrix so that it may be used for the direct determination of the density matrix.¹¹ The exact Γ and Ψ should also satisfy the first-order density equation with $n=1$.

Although the density equation given by Eqs. (4) and (5) depends on both spin and space variables, we can also consider the spin-independent density equation by replacing $\langle \rangle_n$ defined in Eq. (3) with $()_n$, which is defined by

$$\begin{aligned} (\cdots)_n &= \int [\cdots]_{s_1'=s_1, \cdots, s_n'=s_n, x_{n+1}'=x_{n+1}, \cdots, x_N'=x_N} \\ &\times ds_1 \cdots ds_n dx_{n+1} \cdots dx_N. \end{aligned} \quad (7)$$

In such a density equation the density matrix $\Gamma^{(n+2)}$ is spin independent. It is easily shown that the previous necessary and sufficient theorem¹¹ also holds for such a spin-independent density equation, if the Hamiltonian of the system is spin independent. The formulation given in this section is also valid for such a spin-independent case where we can replace $\langle \rangle_n$ with $()_n$.

In order to derive an equation which is closely related with the H-F theorem we differentiate the density equation with respect to the external parameter α included in the external potential V_α . From Eq. (4) we obtain

$$\frac{\partial E}{\partial \alpha} \langle\Psi', \Psi\rangle_n = \left\langle \Psi', \frac{\partial H}{\partial \alpha} \Psi \right\rangle_n + \left\langle \Psi', H \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle H' \Psi', \frac{\partial \Psi}{\partial \alpha} \right\rangle_n, \quad (8)$$

where we have used the fact that the Ψ in Eq. (4) with $n \geq 2$ should necessarily satisfy the Schrödinger equation. From Eq. (5) we obtain

$$\begin{aligned} \frac{\partial E}{\partial \alpha} \Gamma^{(n)} &= ({}_N C_n / {}_N C_{n+2}) \left\{ \int \frac{\partial \mathfrak{H}^{(n)}}{\partial \alpha} \Gamma^{(n+2)} dx_{n+1} dx_{n+2} \right. \\ &\left. + \int [\mathfrak{H}^{(n)} - E] \frac{\partial \Gamma^{(n+2)}}{\partial \alpha} dx_{n+1} dx_{n+2} \right\}, \end{aligned} \quad (9)$$

where we have omitted the coordinate dependences of Γ and $\mathfrak{H}^{(n)}$. The first and the second terms on the rhs of Eq. (9) correspond to the first and the last two terms on the rhs of Eq. (8), respectively.

For the following study Eq. (8) is more convenient than Eq. (9). It also avoids the unsolved N -representability problem. We will derive some exact equations which the exact Ψ should satisfy, though they are not sufficient for the Ψ to satisfy the Schrödinger equation. Since the H-F theorem depends only on the diagonal elements of the first-order density matrix, i. e., the electron density $\rho(1)$, we restrict ourselves to consider the diagonal density equation with $n \geq 1$, which depends only on the unprimed coordinates $1, \cdots, n$. Namely, we omit the prime on Ψ and H in Eq. (8), i. e.,

$$\frac{\partial E}{\partial \alpha} \langle\Psi, \Psi\rangle_n = \left\langle \Psi, \frac{\partial H}{\partial \alpha} \Psi \right\rangle_n + \left\langle \Psi, H \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle H \Psi, \frac{\partial \Psi}{\partial \alpha} \right\rangle_n, \quad (10)$$

where we stress that the operator applies only to the immediate right, though we have used the same notation $\langle \rangle_n$ without any ambiguity. The quantity $\langle\Psi, \Psi\rangle_n$ is connected with the diagonal density matrix by $\Gamma^{(n)}(1 \cdots n) = {}_N C_n \langle\Psi, \Psi\rangle_n$.

The differential density equation (10) has a form which is suitable for studying the hidden potentials in the H-F theorem. Inserting the Hamiltonian given by Eq. (1) we can rewrite the first term of Eq. (10) as

$$\left\langle \Psi, \frac{\partial H}{\partial \alpha} \Psi \right\rangle_n = \left\langle \Psi, \frac{\partial V_\alpha}{\partial \alpha} \Psi \right\rangle_n, \quad (11)$$

which includes only the external potential V_α , which depends on the external parameter α . Similarly, the last two terms of Eq. (10) are transformed in three equivalent forms as

$$\left\langle \Psi, H \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle H \Psi, \frac{\partial \Psi}{\partial \alpha} \right\rangle_n = \left\langle \Psi, T \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle T \Psi, \frac{\partial \Psi}{\partial \alpha} \right\rangle_n \quad (12a)$$

$$= \left\langle \Psi, T^{(n)} \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle T^{(n)} \Psi, \frac{\partial \Psi}{\partial \alpha} \right\rangle_n \quad (12b)$$

$$= -\frac{1}{2} \sum_i^n \nabla_i \left[\left\langle \Psi, \nabla_i \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle \nabla_i \Psi, \frac{\partial \Psi}{\partial \alpha} \right\rangle_n \right], \quad (12c)$$

which include only the kinetic operator. We have used the real and multiplicative property of the potential operators V_α and W . The rhs has arisen essentially only from the noncommuting property of the coordinate and momentum operators in quantum mechanics. In Eq. (12b), $T^{(n)}$ is the kinetic operator associated with the first n electrons

$$T^{(n)} = \sum_{i=1}^n t(i), \quad (13)$$

and we have used the relation

$$\left\langle \Psi, t(j) \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle t(j) \Psi, \frac{\partial \Psi}{\partial \alpha} \right\rangle_n = 0 \quad (j = n+1, \cdots, N), \quad (14)$$

which shows the Hermiticity of the kinetic operator associated with the integrated coordinate j . Since Eq. (14) might not be trivial, we have given the proof in the Appendix. In Eq. (12c) the ∇_i in front of the brace oper-

ates on all the i th coordinates ($1 \leq i \leq n$) in the brace. By such a way we easily obtain Eq. (12b) from (12c), where $T^{(n)} = \sum_i^n -\frac{1}{2}\nabla_i^2$. In this expression each term represents only the noncommuting part of the corresponding term of Eq. (12b).

The quantity given by Eq. (12) can be compactly rewritten by introducing the quantum mechanical potential defined formally by Bohm¹⁴ as

$$\begin{aligned} U_i &= \frac{i(i)\Psi}{\Psi}, \\ U^{(n)} &= \sum_i^n U_i = \frac{T^{(n)}\Psi}{\Psi}, \\ U &= \sum_i^N U_i = \frac{T\Psi}{\Psi}. \end{aligned} \quad (15)$$

This quantum (mechanical) potential has played an important role in his interpretation of quantum mechanics. He has interpreted the quantum potential as a potential produced by the " Ψ field," which obeys the Schrödinger equation as the electromagnetic field obeys Maxwell's equation.¹⁴ Each particle is acted on not only by a "classical" potential $V_\alpha + W$, but also by the quantum potential U .¹⁴ Note that the quantum operators U_i , $U^{(n)}$, and U depend on all the spin-space coordinates of the system. However, since the quantum potential applies only to the Ψ in the present paper, the Ψ in the denominator always cancels. The quantum potential is essentially a multiplicative operator as the classical potential is, since in Eq. (15) the kinetic operator applies only to the Ψ in the numerator.

Since the quantum potential is produced by the Schrödinger Ψ field,¹⁴ it should be a functional of the external parameter α , so that we may further define the force operator associated with the quantum potential by $\partial U/\partial\alpha$, as we define the force operator associated with the classical potential by $\partial V_\alpha/\partial\alpha$. Namely, we define the quantum force operator by

$$\frac{\partial U}{\partial\alpha} = \frac{1}{\Psi^2} \left\{ \Psi \left(T \frac{\partial \Psi}{\partial\alpha} \right) - (T\Psi) \frac{\partial \Psi}{\partial\alpha} \right\}, \quad (16)$$

where we have assumed Ψ to be real without loss of generality since our Hamiltonian is real. Again this definition is formal and in the present paper the quantum force operator always appears in the form $\Psi(\partial U/\partial\alpha)\Psi$, so that the Ψ^2 in the denominator of Eq. (16) cancels. Note that the quantum force operator is essentially multiplicative as the quantum potential is. The quantum force operators associated with U_i and $U^{(n)}$ of Eq. (15) are defined similarly to Eq. (16). Using these quantum force operators we may rewrite the quantity given by Eq. (12) in a compact form as

$$\begin{aligned} \left\langle \Psi, H \frac{\partial \Psi}{\partial\alpha} \right\rangle_n - \left\langle H\Psi, \frac{\partial \Psi}{\partial\alpha} \right\rangle_n &= \left\langle \Psi \frac{\partial U}{\partial\alpha} \Psi \right\rangle_n \\ &= \left\langle \Psi \frac{\partial U^{(n)}}{\partial\alpha} \Psi \right\rangle_n, \end{aligned} \quad (17)$$

where we have used the relation obtained from Eq. (14), i. e.,

$$\left\langle \Psi \frac{\partial U_j}{\partial\alpha} \Psi \right\rangle_n = 0 \quad (j = n+1, \dots, N). \quad (18)$$

Namely, the quantum force operator for the j th electron averaged over the j th coordinate in the distribution Ψ^2 vanishes identically.

Thus, using Eqs. (11) and (17) we can rewrite the differential density equation (10) as

$$\frac{\partial E}{\partial\alpha} \Gamma^{(n)}(1 \cdots n) = {}_N C_n \left\langle \Psi \left(\frac{\partial V_\alpha}{\partial\alpha} + \frac{\partial U^{(n)}}{\partial\alpha} \right) \Psi \right\rangle_n. \quad (19)$$

When $n=1$, Eq. (19) gives

$$\frac{\partial E}{\partial\alpha} \rho(1) = N \left\langle \Psi \left(\frac{\partial V_\alpha}{\partial\alpha} + \frac{\partial U_1}{\partial\alpha} \right) \Psi \right\rangle_1. \quad (20)$$

These equations include both of the force operators associated with the classical and quantum potentials. As seen from Eq. (12), the quantum force term has arisen essentially only from the noncommuting property of the coordinate and momentum operators, i. e., the Heisenberg relation $[q, p] = i\hbar$, in quantum mechanics. When $n=N$, Eq. (19) may be written in a formal form as

$$\frac{\partial E}{\partial\alpha} = \frac{\partial V_\alpha}{\partial\alpha} + \frac{\partial U}{\partial\alpha}, \quad (21)$$

which is just a differential of the Schrödinger equation $E = U + V_\alpha + W$ again in a formal form.

The differential density equations (19) and (20) are related to the H-F theorem by integration. Namely, integrating these equations over the coordinates $1, \dots, n$ we obtain

$$\frac{\partial E}{\partial\alpha} = \left\langle \Psi \frac{\partial V_\alpha}{\partial\alpha} \Psi \right\rangle = \int \frac{\partial v_\alpha(1)}{\partial\alpha} \rho(1) dr_1, \quad (22)$$

which is just the H-F theorem. The quantum force term in Eq. (19) or (20) vanishes identically after the complete integration, i. e.,

$$\left\langle \Psi \frac{\partial U^{(n)}}{\partial\alpha} \Psi \right\rangle = 0 \quad (n = 1, \dots, N), \quad (23)$$

because of the relation given by Eq. (18). Only the classical force term survives after integration and gives the H-F theorem.

The above formulation may be interpreted as isolating an important role of the quantum force term in the differential density equation. The equation gives a very stringent condition which the exact density and wavefunction should satisfy. For instance, when the system is spin independent, the symbol $\langle \rangle_n$ in Eqs. (19) and (20) can be replaced by $()_n$ defined by Eq. (7) and the densities $\Gamma^{(n)}(1 \cdots n)$ and $\rho(1)$ are then spin independent, so that we may divide Eqs. (19) and (20) by these densities. From Eq. (19) we obtain

$$\frac{\partial E}{\partial\alpha} = \left(\Psi \frac{\partial V_\alpha}{\partial\alpha} \Psi \right)_n / (\Psi\Psi)_n + \left(\Psi \frac{\partial U^{(n)}}{\partial\alpha} \Psi \right)_n / (\Psi\Psi)_n. \quad (24)$$

This expression may be called a "local force" expression from an analogy to the "local energy" expression proposed by Frost.¹⁵ Although the classical and quantum force terms on the rhs are the functions of coordinates r_1, \dots, r_n , the sum of them, i. e., the local force, should be everywhere a constant, i. e., the force $\partial E/\partial\alpha$, as a result of a balance between the two terms. This is certainly a very stringent condition. Equation (24) may

further be interpreted as being analogous to the action-reaction law in classical mechanics. The first and second terms on the rhs may be understood as representing, respectively, the normalized strengths of the classical and quantum force fields at $r_1 r_2 \cdots r_n$ exerted on electrons from the "nucleus" α . Their sum should be everywhere equal but opposite in direction to the "reaction," i. e., for force acting on the "nucleus" α , $-(\partial E/\partial \alpha)$. Similar interpretation would also be possible for Eq. (21).

However, when the differential density equations (19) and (20) are integrated over the coordinates $1, \dots, n$, such a stringent condition is completely smeared out. The quantum force term is completely hidden by such integration due to Eq. (23) and only the classical force term survives, giving rise to the H-F theorem. Thus, in the H-F theorem the quantum force term and the stringent condition between the classical and quantum force terms are completely *hidden*. This fact may be considered as a source of the facts that the H-F theorem is only a weak necessary condition (almost nondeterministic) for the exact density and that the theorem is amenable to semiclassical interpretations.

The above results are also in accordance with the results of previous studies. Balázs¹⁶ has shown that the electron density can not be a simple local function of the classical potential alone. Bader and Preston¹⁷ have studied the topological behavior of the kinetic energy density. They have shown that the diagram due to the noncommuting part of the kinetic operator is far from understandable from only classical grounds. They have analyzed its importance in the deterministic stage.

Lastly, we note that the quantum force operator has been derived from Eq. (10), which is a special case of Eq. (8) for the diagonal elements with respect to the coordinates $1' \cdots n'$ and $1 \cdots n$. In general, the last two terms of Eq. (8) or the last term of Eq. (9) include more complex terms than the quantum force term isolated in Eq. (19), though they all vanish after the complete integration. The last term of Eq. (9) gives a density-matrix representation of the quantum force term in a generalized fashion.

III. EXCHANGE AND CORRELATION EFFECTS AND ORIGIN OF FORCE DENSITY

In this section we analyze the first-order differential density equation (20) in more detail, separating out the (generalized) exchange and correlation effects. This analysis clarifies at the same time the origin of the force density $[\partial v_\alpha(1)/\partial \alpha]\rho(1)$, which is the integrand of the H-F theorem.

We first analyze the classical force term of Eq. (20). We rewrite it as

$$N \left\langle \Psi \frac{\partial V_\alpha}{\partial \alpha} \Psi \right\rangle_1 = \frac{\partial v_\alpha(1)}{\partial \alpha} \rho(1) + 2 \int \frac{\partial v_\alpha(2)}{\partial \alpha} \Gamma(12) dx_2, \quad (25)$$

where $\Gamma(12) = \Gamma^{(2)}(12)$. We then partition the second-order density matrix $\Gamma(12)$ as

$$\Gamma(12) = \frac{1}{2} \rho(1)\rho(2) - \frac{1}{2} \sum_i n_i \rho_i(1)\rho_i(2) + B(12), \quad (26)$$

which is a simple generalization of the relation existing for the Hartree-Fock density matrix. ρ_i is the density of the natural orbital χ_i , i. e., $\rho_i(1) = \chi_i^*(1)\chi_i(1)$, and n_i the occupation number of χ_i . The first term of Eq. (26) is a simple product of the electron density and is normalized to

$$\frac{1}{2} \int \rho(1)\rho(2) dx_1 dx_2 = \frac{1}{2} N^2, \quad (27)$$

which shows that this term overcounts the number of interactions. The second term eliminates such overcounting as seen from its normalization

$$\frac{1}{2} \int \sum_i n_i \rho_i(1)\rho_i(2) dx_1 dx_2 = \frac{1}{2} N. \quad (28)$$

This term has a common origin to the so-called self-interaction term. The last term $B(12)$ denotes the rest and may be understood as representing the exchange and correlation effects in a generalized sense. In accordance with this interpretation, it has the following interesting property:

$$\int B(12) dx_1 = \int B(12) dx_2 = 0, \quad (29)$$

since we have the formulas

$$\int \Gamma(12) dx_2 = \frac{N-1}{2} \rho(1), \quad (30a)$$

$$\rho(1) = \sum_i n_i \rho_i(1). \quad (30b)$$

Namely, the exchange-correlation effect $B(12)$ represents a fluctuation in the two-electron space and vanishes identically when it is projected onto the one-electron space. Inserting Eq. (26) into (25) we rewrite the classical force term as

$$N \left\langle \Psi \frac{\partial V_\alpha}{\partial \alpha} \Psi \right\rangle_1 = \frac{\partial v_\alpha}{\partial \alpha} \rho + \frac{\partial E}{\partial \alpha} \rho - \sum_i n_i \rho_i \left\langle \frac{\partial v_\alpha}{\partial \alpha} \rho_i \right\rangle + 2 \int \frac{\partial v_\alpha(2)}{\partial \alpha} B(12) dx_2, \quad (31)$$

where the term $(\partial E/\partial \alpha)\rho$ has arisen from the first term of Eq. (26) using the H-F theorem (22).

Next, we analyze the quantum force term in the first-order equation (20). From Eqs. (12) and (15) it is written as

$$\left\langle \Psi \frac{\partial U_1}{\partial \alpha} \Psi \right\rangle_1 = \left\langle \Psi, t(1) \frac{\partial \Psi}{\partial \alpha} \right\rangle_1 - \left\langle t(1) \Psi, \frac{\partial \Psi}{\partial \alpha} \right\rangle_1. \quad (32)$$

Carlson and Keller¹⁸ have shown that the wavefunction Ψ is expanded with the natural orbitals χ_i as

$$\Psi(12 \cdots N) = \frac{1}{\sqrt{N}} \sum_i \chi_i(1) \eta_i(2 \cdots N), \quad (33)$$

where η_i is the complementary function given by

$$\eta_i(2 \cdots N) = \sqrt{N} \int \chi_i^*(1) \Psi(12 \cdots N) dx_1 \quad (34)$$

and is normalized to the occupation number n_i :

$$\langle \eta_i, \eta_j \rangle = n_i \delta_{ij}. \quad (35)$$

The function $(n_i)^{-1/2} \eta_i(2 \cdots N)$ is also a natural function

which diagonalizes $\Gamma^{(N-1)}$. Using this expansion we can transform the quantum force term given by Eq. (32) as

$$N \left\langle \Psi \frac{\partial U_1}{\partial \alpha} \Psi \right\rangle_1 = \sum_i n_i \left\langle \chi_i t \frac{\partial \chi_i}{\partial \alpha} - \frac{\partial \chi_i}{\partial \alpha} t \chi_i \right\rangle + \sum_{i \neq j} \left\langle \eta_i \frac{\partial \eta_j}{\partial \alpha} \right\rangle (\chi_i t \chi_j - \chi_j t \chi_i), \quad (36)$$

where we have assumed χ_i to be real and abbreviated the coordinate 1 of χ_i and t . We now introduce the *orbital* quantum potential by

$$u_i = t \chi_i / \chi_i, \quad (37)$$

and the *orbital* quantum force by

$$\frac{\partial u_i}{\partial \alpha} = \frac{1}{\chi_i^2} \left[\chi_i \left(t \frac{\partial \chi_i}{\partial \alpha} \right) - (t \chi_i) \frac{\partial \chi_i}{\partial \alpha} \right]. \quad (38)$$

These definitions are similar to those of the quantum potential and quantum force operators given by Eqs. (15) and (16) respectively. Then, the quantum force term (36) is written in terms of the orbital quantum potential and force as

$$N \left\langle \Psi \frac{\partial U_1}{\partial \alpha} \Psi \right\rangle_1 = \sum_i n_i \rho_i \frac{\partial u_i}{\partial \alpha} + \sum_{i \neq j} \left\langle \eta_i \frac{\partial \eta_j}{\partial \alpha} \right\rangle \chi_i \chi_j (u_j - u_i). \quad (39)$$

In this equation the first term is the contribution of the orbital quantum force ($\partial u_i / \partial \alpha$) weighted by the orbital density $n_i \rho_i$. The second term represents the generalized correlation effect, since it vanishes identically in the Hartree-Fock limit. This is easily verified from Eq. (32) by replacing Ψ with the Hartree-Fock single determinant. There, the term ($\partial \Psi_{HF} / \partial \alpha$) belongs to the space spanned by the singly excited configurations from occupied to unoccupied orbitals.¹⁹

Inserting Eqs. (31) and (39) into Eq. (20) we finally obtain the first-order differential density equation in the form

$$\frac{\partial v_\alpha}{\partial \alpha} \rho = \sum_i n_i \rho_i \left\langle \frac{\partial v_\alpha}{\partial \alpha} \rho_i \right\rangle - \sum_i n_i \rho_i \frac{\partial u_i}{\partial \alpha} - 2 \int \frac{\partial v_\alpha(2)}{\partial \alpha} B(12) dx_2 - \sum_{i \neq j} \left\langle \eta_i \frac{\partial \eta_j}{\partial \alpha} \right\rangle \chi_i \chi_j (u_j - u_i). \quad (40)$$

Here, we note that the term ($\partial E / \partial \alpha$) ρ on the lhs of Eq. (20) has canceled out with the same term in Eq. (31). The term ($\partial v_\alpha / \partial \alpha$) ρ on the lhs of Eq. (40) is the integrand of the H-F theorem and may be called the *force density*. In the exact limit the force density should be equal to the sum of the terms on the rhs. The first two terms show the contributions of the orbital classical force ($\langle \partial v_\alpha / \partial \alpha \rho_i \rangle$) and the orbital quantum force ($\partial u_i / \partial \alpha$) weighted by the orbital density $n_i \rho_i$. The last two terms show the generalized exchange-correlation effects arising from the classical and quantum force terms. However, when we integrate Eq. (40) the terms coming from the quantum force term vanishes identically since

$$\left\langle \rho_i \frac{\partial u_i}{\partial \alpha} \right\rangle = 0, \quad \langle \chi_i (u_i - u_j) \chi_j \rangle = 0, \quad (41)$$

and moreover the exchange-correlation term coming from the classical potential term also vanishes identically, i. e.,

$$\int \frac{\partial v_\alpha(2)}{\partial \alpha} B(12) dx_1 dx_2 = 0, \quad (42)$$

because of Eq. (29). Only the force density and the orbital classical force term survive after integration and both reduce to the H-F force. Namely, not only the quantum force term but also the generalized exchange-correlation effects are completely *hidden* in the H-F force. Although the statement that the generalized exchange-correlation effects are hidden in the H-F force might be trivial since the H-F force depends only on the electron density of the system, the differential equation (40) shows how these hidden terms correlate with the force density in the more stringent condition than the H-F theorem.

IV. QUANTUM POTENTIAL AND THE I-H-F THEOREM

In this section we start from the following necessary condition for the Schrödinger equation: Suppose that we have two isoelectronic systems a and b . The Hamiltonians of these systems are denoted as H_a and H_b , which have the same forms as Eq. (1), and the wavefunctions are denoted as Ψ_a and Ψ_b . When they satisfy the Schrödinger equations $H_a \Psi_a = E_a \Psi_a$ and $H_b \Psi_b = E_b \Psi_b$, they necessarily satisfy the equations

$$\langle \Psi'_a, (H_b - E_b) \Psi_b \rangle_n = 0 \quad (43a)$$

and

$$\langle \Psi'_b, (H_a - E_a) \Psi_a \rangle_n = 0. \quad (43b)$$

When $a = b$ these simultaneous equations reduce to the density equation (4). We define the following difference quantities between a and b :

$$\Delta E = E_b - E_a, \quad (44a)$$

$$\Delta V = H_b - H_a = V_{bb} - V_{aa}, \quad (44b)$$

$$\Delta U^{(n)} = U_b^{(n)} - U_a^{(n)}, \quad U_a^{(n)} = \frac{T^{(n)} \Psi_a}{\Psi_a}. \quad (44c)$$

Since a and b are isoelectronic systems, the kinetic and electron repulsion operators are common to both systems. Then, the difference in the Hamiltonians are only in the external potentials V_{aa} and V_{bb} . $\Delta U^{(n)}$ is the difference in the quantum potentials.

Starting from Eq. (43) for the diagonal elements for the coordinates $1' \cdots n'$ and $1 \cdots n$, and assuming Ψ_a and Ψ_b to be real, we obtain

$$\Delta E \langle \Psi_a \Psi_b \rangle_n = \langle \Psi_a \Delta V \Psi_b \rangle_n + \langle \Psi_a, T^{(n)} \Psi_b \rangle_n - \langle \Psi_b, T^{(n)} \Psi_a \rangle_n, \quad (45a)$$

$$= \langle \Psi_a (\Delta V + \Delta U^{(n)}) \Psi_b \rangle_n, \quad (45b)$$

where we have used Eq. (A7) of the Appendix. On the lhs $\langle \Psi_a \Psi_b \rangle_n$ is the transition density matrix and the rhs is composed of both the classical and quantum potential terms as in the differential density equation (19). Equation (45) gives a stringent condition for these quantities. However, when we integrate this equation for the coordinates $1, \cdots, n$, the quantum potential term vanishes identically

$$\langle \Psi_a \Delta U^{(n)} \Psi_b \rangle = 0 \quad (46)$$

from Eq. (A7) of the Appendix. Only the classical po-

tential term survives after integration and gives

$$\Delta E = \frac{1}{S} \langle \Psi_a \Delta V \Psi_b \rangle = \int \Delta v(1) \rho_{ab}(1) dx_1, \quad (47)$$

which is just the integral Hellmann–Feynman (I–H–F) theorem,² in which S is the overlap integral $S = \langle \Psi_a \Psi_b \rangle$ and $\rho_{ab}(1)$ is the normalized transition density $\rho_{ab}(1) = (N/S) \langle \Psi_a \Psi_b \rangle_1$. This theorem gives the energy difference for the isoelectronic process $a \rightarrow b$ only with the transition density $\rho_{ab}(1)$. The above formulation shows that the role of the quantum potential difference $\Delta U^{(n)}$ in Eq. (45) is completely *hidden* in the I–H–F theorem (47). This is similar to the quantum force operator $\partial U^{(n)}/\partial \alpha$ in Eq. (19), which is hidden in the H–F theorem. As seen from Eq. (45a), the quantum potential difference $\Delta U^{(n)}$ has also arisen from the noncommuting property of the coordinate and momentum operators in quantum mechanics.

V. SUMMARY

In this paper we have derived some exact equations which clarify some potentials that are hidden in the classical theorems such as the H–F and I–H–F theorems. The differential form of the density equation has separated out an important role of the quantum force operator which has arisen essentially only from the noncommuting property of the coordinate and momentum in quantum mechanics. However, when we integrate the equation, the quantum force term vanishes identically and only the classical force term survives leading to the H–F theorem. The role of the quantum force operator is completely hidden in the H–F theorem. This fact may be closely related to the nondeterminicity and the classical interpretation of the H–F theorem. Similar role of the quantum potential has also been shown for the I–H–F theorem. We have further investigated the origin of the force density, which is the integrand of the H–F theorem, and isolated the role of the generalized exchange–correlation effects which are also hidden in the H–F theorem.

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APPENDIX

Here we prove the relation

$$\left\langle \Psi', v(j) \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle v(j') \Psi', \frac{\partial \Psi}{\partial \alpha} \right\rangle_n = 0 \quad (j = n+1, \dots, N), \quad (A1)$$

where $v(j)$ is an arbitrary one-electron operator which is Hermitian. We use the expansion formula given by Carlson and Keller¹⁸ in the form

$$\Psi(1 \dots N) = \frac{1}{\sqrt{N}} \sum_p \chi_p(j) \eta_p(1, \dots, j-1, j+1, \dots, N). \quad (A2)$$

Then, the first term of Eq. (A1) is written as

$$\left\langle \Psi', v(j) \frac{\partial \Psi}{\partial \alpha} \right\rangle_n = \frac{1}{N} \sum_p \sum_q \left(\left\langle \chi_p, v \frac{\partial \chi_q}{\partial \alpha} \right\rangle \times \langle \langle \eta'_p, \eta_q \rangle \rangle_n + \langle \chi_p, v \chi_q \rangle \langle \langle \eta'_p, \frac{\partial \eta_q}{\partial \alpha} \rangle \rangle_n \right), \quad (A3)$$

where $\langle \langle \dots \rangle \rangle_n$ is defined similarly to Eq. (3) except that the integrand in $\langle \langle \dots \rangle \rangle_n$ does not include the coordinates j' and j . Similarly, the second term of Eq. (A1) is written as

$$\left\langle v(j') \Psi', \frac{\partial \Psi}{\partial \alpha} \right\rangle_n = \frac{1}{N} \sum_p \sum_q \left(\left\langle v \chi_p, \frac{\partial \chi_q}{\partial \alpha} \right\rangle \times \langle \langle \eta'_p, \eta_q \rangle \rangle_n + \langle v \chi_p, \chi_q \rangle \langle \langle \eta'_p, \frac{\partial \eta_q}{\partial \alpha} \rangle \rangle_n \right). \quad (A4)$$

Since v is an Hermitian operator, we have

$$\langle \chi_p, v \chi_q \rangle = \langle v \chi_p, \chi_q \rangle, \quad \left\langle \chi_p, v \frac{\partial \chi_q}{\partial \alpha} \right\rangle = \left\langle v \chi_p, \frac{\partial \chi_q}{\partial \alpha} \right\rangle. \quad (A5)$$

Subtracting Eq. (A4) from (A3) and using (A5) we obtain Eq. (A1). Equation (A1) is also valid for its diagonal element

$$\left\langle \Psi, v(j) \frac{\partial \Psi}{\partial \alpha} \right\rangle_n - \left\langle v(j) \Psi, \frac{\partial \Psi}{\partial \alpha} \right\rangle_n = 0 \quad (j = n+1, \dots, N), \quad (A6)$$

which proves Eq. (14). Further, it is easy to prove the relation

$$\langle \psi', h(j, \dots, k) \varphi \rangle_n - \langle h(j', \dots, k') \psi', \varphi \rangle_n = 0 \quad (n+1 \leq j, \dots, k \leq N), \quad (A7)$$

where h is an arbitrary Hermitian operator which depends on fewer coordinates than $N-n$, and ψ and φ are two wavefunctions which are different in general. Equations (A1) and (A7) means that even in the partial integration like $\langle \dots \rangle_n$ the usual Hermiticity relation holds for the Hermitian operator which depends only on the integrated coordinates.

- ¹H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Vienna, 1937), p. 285; R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).
- ²R. G. Parr, *J. Chem. Phys.* **40**, 3726 (1964); H. Kim and R. G. Parr, *J. Chem. Phys.* **41**, 2892 (1964).
- ³B. M. Deb, *Rev. Mod. Phys.* **45**, 22 (1973), and the references cited therein.
- ⁴*The Force Concept in Chemistry*, edited by B. M. Deb (Macmillan, Bombay, in press).
- ⁵H. Nakatsuji, *J. Am. Chem. Soc.* **95**, 345, 354, 2084 (1973); H. Nakatsuji, T. Kuwata, and A. Yoshida, *ibid.* **95**, 6894 (1973); H. Nakatsuji and T. Koga, *ibid.* **96**, 6000 (1974); T. Koga and H. Nakatsuji, *Theor. Chim. Acta* **41**, 119 (1976).
- ⁶H. Nakatsuji and T. Koga, Chap. 4 of Ref. 4.
- ⁷H. Nakatsuji, *J. Am. Chem. Soc.* **96**, 24, 30 (1974).
- ⁸See, for example, R. F. W. Bader and G. A. Jones, *Can. J. Chem.* **41**, 586 (1963); *J. Chem. Phys.* **38**, 2791 (1963).
- ⁹H. Nakatsuji and R. G. Parr, *J. Chem. Phys.* **63**, 1112 (1975).
- ¹⁰P. Hohenberg and W. Kohn, *Phys. Rev. B* **136**, 864 (1964); see also S. T. Epstein and C. M. Rosenthal, *J. Chem. Phys.* **64**, 247 (1976).

- ¹¹H. Nakatsuji, *Phys. Rev. A* **14**, 41 (1976).
¹²S. Cho, *Sci. Rep. Gumma Univ.* **11**, 1 (1962).
¹³L. Cohen and C. Frishberg, *Phys. Rev. A* **13**, 927 (1976).
¹⁴D. Bohm, *Phys. Rev.* **85**, 166, 180 (1952).
¹⁵A. A. Frost, *J. Chem. Phys.* **10**, 240 (1942); A. A. Frost, R. E. Kellogg, and E. C. Curtis, *Rev. Mod. Phys.* **32**, 313 (1960); see also J. H. Bartlett, *Phys. Rev.* **98**, 1067 (1955).
¹⁶N. L. Balázs, *Phys. Rev.* **156**, 42 (1967).
¹⁷R. F. W. Bader and H. J. T. Preston, *Int. J. Quantum Chem.* **3**, 327 (1969).
¹⁸B. C. Carlson and J. M. Keller, *Phys. Rev.* **121**, 659 (1961).
¹⁹C. A. Coulson, *Mol. Phys.* **20**, 687 (1971).