

Exchange-correlation energy functional and virial theorem in the extended constrained-search theory

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The coupling-constant expression and virial relation for the exchange-correlation energy functional of the extended-constrained search theory [M. Higuchi and K. Higuchi, *Phys. Rev. B* **69**, 035113 (2004)] are derived. These provide the guideline for developing and testing the approximate form of the exchange-correlation energy functional.

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I. INTRODUCTION

Recently we have proposed the extended constrained-search (ECS) theory in which arbitrary physical quantities can be chosen as basic variables in addition to the electron density.^{1,2} The validity of this theory has been confirmed by revisiting on the basis of it the spin-density functional theory (SDFT), the current-density functional theory (CDFT), the LDA+U method, and the Hartree-Fock-Kohn-Sham scheme.^{1,2} The ECS theory has two advantages over the conventional density functional theory (DFT), as stated in preceding papers.^{1,2} One is that the ground-state values of quantities which are characteristic of the system can be reproduced directly by means of the Kohn-Sham orbitals if they are chosen as basic variables. Another is that the approximate form of the exchange-correlation energy functional may be given in a more effective form than the conventional DFT.³⁻⁶

However, in order to perform the actual energy-band calculation within the ECS theory, a tractable form of the exchange-correlation energy functional is indispensable, i.e., some approximation has to be made on the exchange-correlation energy functional. Generally, there exist two strategies for developing such an approximate functional. One is to devise the approximate form on the basis of the coupling-constant expression for the exchange-correlation energy functional. The examples are the average-density approximation⁷⁻¹⁰ and weighted-density approximation.⁸⁻¹² Another is to utilize some exact relations which should be satisfied for the exchange-correlation energy functional. Virial theorem and scaling relations have been first discussed by Löwdin.¹³ In the DFT, virial and scaling relations are utilized in devising the density-moment expansion of density functionals such as the exchange and correlation energy functionals.¹⁴⁻¹⁸

In Sec. II, we shall give the exact expression for the exchange-correlation energy functional by means of the coupling-constant integration technique. In Sec. III, an exact relation for the exchange-correlation energy functional is derived with the aid of the virial theorem of the ECS theory. Both expressions are expected to be a good starting point

toward the development of the approximate form of the ECS exchange-correlation energy functional.

II. COUPLING-CONSTANT EXPRESSION FOR THE EXCHANGE-CORRELATION ENERGY FUNCTIONAL

In this section, the coupling-constant integration technique is applied to the ECS theory so as to derive the exact expression for the exchange-correlation energy functional. The starting point is the Hamiltonian,

$$\hat{H} = \hat{T} + \hat{W} + \hat{V}, \quad (1)$$

where \hat{T} , \hat{W} , and \hat{V} are operators of the kinetic energy, electron-electron interaction, and external potential energy, respectively. In the ECS theory,^{1,2} we can choose the arbitrary physical quantities as basic variables in addition to the electron density $\rho(\mathbf{r})$. Here, suppose that the basic variable chosen is denoted by $\mathbf{X}(\mathbf{r})$. The exchange-correlation energy functional is defined by¹

$$E_{xc}[\rho, \mathbf{X}] = F[\rho, \mathbf{X}] - T_s[\rho, \mathbf{X}] - U[\rho] \quad (2)$$

with

$$F[\rho, \mathbf{X}] = \text{Min}_{\Psi \rightarrow (\rho, \mathbf{X})} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle, \quad (3)$$

$$T_s[\rho, \mathbf{X}] = \text{Min}_{\Phi \rightarrow (\rho, \mathbf{X})} \langle \Phi | \hat{T} | \Phi \rangle, \quad (4)$$

$$U[\rho] = \frac{e^2}{2} \iint \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'. \quad (5)$$

In Eq. (3) (Eq. (4)), the minimizing is performed among anisymmetric wave functions Ψ (single Slater determinants Φ) which yield the prescribed $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$.

Let us consider the following new functional:

$$F_\lambda[\rho, \mathbf{X}] = \text{Min}_{\Psi \rightarrow (\rho, \mathbf{X})} \langle \Psi | \hat{T} + \lambda \hat{W} | \Psi \rangle \\ = \langle \Psi_\lambda[\rho, \mathbf{X}] | \hat{T} + \lambda \hat{W} | \Psi_\lambda[\rho, \mathbf{X}] \rangle, \quad (6)$$

where λ is the parameter which scales up or down the magnitude of the electron-electron interaction, and $\Psi_\lambda[\rho, \mathbf{X}]$ means the function that gives the minimum expectation value of $\hat{T} + \lambda \hat{W}$ among the antisymmetric wave functions that yield $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$. If λ is unity, $F_\lambda[\rho, \mathbf{X}]$ coincides with Eq. (3), i.e., $F_1[\rho, \mathbf{X}] = F[\rho, \mathbf{X}]$. On the other hand if λ is zero, then we shall denote it as $\tilde{T}_s[\rho, \mathbf{X}]$, i.e., $\tilde{T}_s[\rho, \mathbf{X}] := F_0[\rho, \mathbf{X}] = \text{Min}_{\Psi \rightarrow (\rho, \mathbf{X})} \langle \Psi | \hat{T} | \Psi \rangle$. For the later discussion, we define $\tilde{E}_{xc}[\rho, \mathbf{X}]$ as

$$\tilde{E}_{xc}[\rho, \mathbf{X}] := F[\rho, \mathbf{X}] - \tilde{T}_s[\rho, \mathbf{X}] - U[\rho] \\ = \int_0^1 d\lambda \frac{\partial F_\lambda[\rho, \mathbf{X}]}{\partial \lambda} - U[\rho]. \quad (7)$$

Next let us consider the case that $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$ are noninteracting v -representable, that is to say, $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$ are constructed from the ground state of the noninteracting Hamiltonian $\hat{T} + \hat{V}_s$, where \hat{V}_s stands for some external potential energy. Then, an important relation

$$\tilde{T}_s[\rho, \mathbf{X}] = T_s[\rho, \mathbf{X}] \quad (8)$$

is found. As will be shown in the following, the proof is similar to the usual constrained-search formulation.¹⁹ The functional $\tilde{T}_s[\rho, \mathbf{X}]$ is decomposed by some potential \hat{V}_s as follows:

$$\text{Min}_{\Psi \rightarrow (\rho, \mathbf{X})} \langle \Psi | \hat{T} | \Psi \rangle = \text{Min}_{\Psi \rightarrow (\rho, \mathbf{X})} \langle \Psi | \hat{T} + \hat{V}_s | \Psi \rangle - \int \rho(\mathbf{r}) v_s(\mathbf{r}) d\mathbf{r}, \quad (9)$$

where $\hat{V}_s = \sum_i v_s(\mathbf{r}_i)$. Let \hat{V}_s be the potential for which $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$ are noninteracting ground-state values. Such \hat{V}_s is nothing other than the potential which have already appeared in Ref. 1, i.e.,

$$\hat{V}_s = \sum_i \left\{ \lambda[\rho, \mathbf{X}](\mathbf{r}_i) + \int \boldsymbol{\mu}[\rho, \mathbf{X}](\mathbf{r}') \cdot \hat{\mathbf{x}}(\mathbf{r}', \mathbf{r}_i) d\mathbf{r}' \right\}, \quad (10)$$

where $\hat{\mathbf{X}}(\mathbf{r}) = \sum_i \hat{\mathbf{x}}(\mathbf{r}, \mathbf{r}_i)$. In Eq. (10) $\lambda[\rho, \mathbf{X}](\mathbf{r})$ and $\boldsymbol{\mu}[\rho, \mathbf{X}](\mathbf{r})$ are determined so that the prescribed $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$ are reproduced from the single Slater determinant which consists of N lowest eigenstates of the canonical form of Eq. (3.7) in Ref. 1. In this case the minimizing wave function of Eq. (9) exactly coincides with the ground state of $\hat{T} + \hat{V}_s$ and is given by the single Slater determinant. Consequently, Eq. (8) holds.

Noninteracting v -representability is equivalent to the assumption that basic variables can be reproduced from the single Slater determinant which is constructed from N lowest

eigenstates. This assumption has been used in most of actual calculations of DFT, and has empirically provided the reasonable results as compared with the experiments. Therefore, we shall adopt this assumption in the ECS theory. It will be mentioned again in Sec. IV.

$\tilde{E}_{xc}[\rho, \mathbf{X}]$ is equal to $E_{xc}[\rho, \mathbf{X}]$ due to Eq. (8), so that we need to evaluate $\partial F_\lambda[\rho, \mathbf{X}]/\partial \lambda$ in Eq. (7). Let us start with the constrained-search of Eq. (6). Define $\Omega[\Psi, \Psi^*]$ by

$$\Omega[\Psi, \Psi^*] = \langle \Psi | \hat{T} + \lambda \hat{W} | \Psi \rangle + \int v_\lambda(\mathbf{r}) \{ \langle \Psi | \hat{\rho}(\mathbf{r}) | \Psi \rangle - \rho(\mathbf{r}) \} d\mathbf{r} \\ + \int \mathbf{a}_\lambda(\mathbf{r}) \cdot \{ \langle \Psi | \hat{\mathbf{X}}(\mathbf{r}) | \Psi \rangle - \mathbf{X}(\mathbf{r}) \} d\mathbf{r} \\ + E_\lambda \{ N - \langle \Psi | \Psi \rangle \}, \quad (11)$$

where $v_\lambda(\mathbf{r})$ and $\mathbf{a}_\lambda(\mathbf{r})$ are the Lagrange multiplier functions for the conditions that the minimizing wave function, respectively, yield $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$, and E_λ the Lagrange multiplier for the condition that the minimizing wave function is normalized. Then, minimizing condition $\delta\Omega/\delta\Psi^* = 0$ yields

$$\hat{H}_\lambda | \Psi_\lambda[\rho, \mathbf{X}] \rangle = E_\lambda | \Psi_\lambda[\rho, \mathbf{X}] \rangle, \quad (12)$$

where

$$\hat{H}_\lambda = \hat{T} + \lambda \hat{W} + \int v_\lambda(\mathbf{r}) \hat{\rho}(\mathbf{r}) d\mathbf{r} + \int \mathbf{a}_\lambda(\mathbf{r}) \cdot \hat{\mathbf{X}}(\mathbf{r}) d\mathbf{r}. \quad (13)$$

With the aid of the Hellmann–Feynman theorem, we have

$$\frac{\partial E_\lambda}{\partial \lambda} = \langle \Psi_\lambda[\rho, \mathbf{X}] | \frac{\partial \hat{H}_\lambda}{\partial \lambda} | \Psi_\lambda[\rho, \mathbf{X}] \rangle \\ = \langle \Psi_\lambda[\rho, \mathbf{X}] | \hat{W} | \Psi_\lambda[\rho, \mathbf{X}] \rangle + \int \frac{\partial v_\lambda(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) d\mathbf{r} \\ + \int \frac{\partial \mathbf{a}_\lambda(\mathbf{r})}{\partial \lambda} \cdot \mathbf{X}(\mathbf{r}) d\mathbf{r}. \quad (14)$$

On the other hand, if one uses

$$E_\lambda = F_\lambda[\rho, \mathbf{X}] + \int v_\lambda(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + \int \mathbf{a}_\lambda(\mathbf{r}) \cdot \mathbf{X}(\mathbf{r}) d\mathbf{r}, \quad (15)$$

then

$$\frac{\partial E_\lambda}{\partial \lambda} = \frac{\partial F_\lambda[\rho, \mathbf{X}]}{\partial \lambda} + \int \frac{\partial v_\lambda(\mathbf{r})}{\partial \lambda} \rho(\mathbf{r}) d\mathbf{r} + \int \frac{\partial \mathbf{a}_\lambda(\mathbf{r})}{\partial \lambda} \cdot \mathbf{X}(\mathbf{r}) d\mathbf{r}. \quad (16)$$

Comparing Eq. (14) with Eq. (16) leads to

$$\frac{\partial F_\lambda[\rho, \mathbf{X}]}{\partial \lambda} = \langle \Psi_\lambda[\rho, \mathbf{X}] | \hat{W} | \Psi_\lambda[\rho, \mathbf{X}] \rangle. \quad (17)$$

Substituting Eq. (17) into Eq. (7), we finally get the coupling-constant expression for the exchange-correlation energy functional:

$$E_{xc}[\rho, \mathbf{X}] = \frac{e^2}{2} \int \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \{ \bar{g}(\mathbf{r}, \mathbf{r}'; [\rho, \mathbf{X}]) - 1 \}, \quad (18)$$

where the coupling-constant-averaged pair correlation function $\bar{g}(\mathbf{r}, \mathbf{r}'; [\rho, \mathbf{X}])$ is defined as

$$\begin{aligned} \bar{g}(\mathbf{r}, \mathbf{r}'; [\rho, \mathbf{X}]) &= \int_0^1 d\lambda \frac{\langle \Psi_\lambda[\rho, \mathbf{X}] | \hat{\rho}(\mathbf{r})\hat{\rho}(\mathbf{r}') | \Psi_\lambda[\rho, \mathbf{X}] \rangle - \delta(\mathbf{r} - \mathbf{r}')\rho(\mathbf{r})}{\rho(\mathbf{r})\rho(\mathbf{r}')}. \end{aligned} \quad (19)$$

The expression (18) is quite analogous to that of the conventional DFT. If the basic variable is an electron density alone, it corresponds to the expression of the conventional DFT.²⁰ If the spin density or the paramagnetic current density is chosen as $\mathbf{X}(\mathbf{r})$, then Eq. (18) is identical with the coupling-constant expression of the SDFT (Ref. 21) or CDFT,²² respectively.

III. VIRIAL RELATIONS

A. Virial relation in the real system of the ECS theory

Let us consider the ground-state wave function $\Psi_G(\mathbf{r}_1, \dots, \mathbf{r}_N)$ for an extended system. Suppose that $\Psi_G(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is periodic in the coordinates of electrons with period L , and is normalized to unity in the cube of side L (volume $L^3 =: \Omega$). The scaled wave function is defined as

$$\Psi_G^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N) := \zeta^{3N/2} \Psi_G(\zeta \mathbf{r}_1, \dots, \zeta \mathbf{r}_N), \quad (20)$$

where ζ is the scaling factor and takes a positive value. The normalization constant in Eq. (20) is determined so that the probability of finding the electron somewhere in the cube of side $\zeta^{-1}L$ is unity (volume $L^3/\zeta^3 =: \Omega_\zeta$). The details are shown in Appendix A. The Rayleigh–Ritz variational principle ensures that

$$\lim_{\zeta \rightarrow 1} \frac{d}{d\zeta} \langle \Psi_G^\zeta | \hat{T} + \hat{W} + \hat{V} | \Psi_G^\zeta \rangle_{\Omega_\zeta} = 0, \quad (21)$$

where the subscript of the angular bracket means that integrals are performed over the volume Ω_ζ . By using Eq. (20) and the transformation of the integration variables, the expectation value of \hat{T} is calculated as

$$\begin{aligned} &\langle \Psi_G^\zeta | \hat{T} | \Psi_G^\zeta \rangle_{\Omega_\zeta} \\ &= \int_{\Omega_\zeta} \cdots \int_{\Omega_\zeta} \Psi_G^\zeta(\mathbf{r}'_1, \dots, \mathbf{r}'_N)^* \hat{T} \Psi_G^\zeta(\mathbf{r}'_1, \dots, \mathbf{r}'_N) d\mathbf{r}'_1 \cdots d\mathbf{r}'_N \\ &= \zeta^2 \langle \Psi_G | \hat{T} | \Psi_G \rangle_\Omega. \end{aligned} \quad (22)$$

Then, we obtain

$$\lim_{\zeta \rightarrow 1} \frac{d}{d\zeta} \langle \Psi_G^\zeta | \hat{T} | \Psi_G^\zeta \rangle_{\Omega_\zeta} = 2 \langle \Psi_G | \hat{T} | \Psi_G \rangle_\Omega. \quad (23)$$

In the same way as the above derivation, we have

$$\begin{aligned} \lim_{\zeta \rightarrow 1} \frac{d}{d\zeta} \langle \Psi_G^\zeta | \hat{W} | \Psi_G^\zeta \rangle_{\Omega_\zeta} &= \lim_{\zeta \rightarrow 1} \frac{d}{d\zeta} \langle \zeta \langle \Psi_G | \hat{W} | \Psi_G \rangle_\Omega \rangle \\ &= \langle \Psi_G | \hat{W} | \Psi_G \rangle_\Omega, \end{aligned} \quad (24)$$

$$\begin{aligned} \lim_{\zeta \rightarrow 1} \frac{d}{d\zeta} \langle \Psi_G^\zeta | \hat{V} | \Psi_G^\zeta \rangle_{\Omega_\zeta} &= \lim_{\zeta \rightarrow 1} \frac{d}{d\zeta} \int_\Omega \rho_0(\mathbf{r}) v_{\text{ext}}(\mathbf{r}/\zeta) d\mathbf{r} \\ &= - \int_\Omega \rho_0(\mathbf{r}) \mathbf{r} \cdot \{ \nabla v_{\text{ext}}(\mathbf{r}) \} d\mathbf{r}, \end{aligned} \quad (25)$$

where $\rho_0(\mathbf{r})$ is the ground-state value of the electron density, and $\hat{V} = \sum_i v_{\text{ext}}(\mathbf{r}_i)$. In the derivation of Eq. (25), we use the following relation:

$$\lim_{\zeta \rightarrow 1} \frac{d v_{\text{ext}}(\mathbf{r}/\zeta)}{d\zeta} = - \mathbf{r} \cdot \nabla v_{\text{ext}}(\mathbf{r}). \quad (26)$$

Substituting Eqs. (23), (24), and (25) into Eq. (21), we get

$$2 \langle \Psi_G | \hat{T} | \Psi_G \rangle_\Omega + \langle \Psi_G | \hat{W} | \Psi_G \rangle_\Omega - \int_\Omega \rho_0(\mathbf{r}) \mathbf{r} \cdot \{ \nabla v_{\text{ext}}(\mathbf{r}) \} d\mathbf{r} = 0. \quad (27)$$

Although it coincides with the virial relation for the isolated system,^{23,24} Eq. (27) holds for the extended system on which the periodic boundary condition is imposed.

In the ECS theory,^{1,2} the energy functional is given by

$$\begin{aligned} E[\rho, \mathbf{X}] &= F[\rho, \mathbf{X}] + \int_\Omega \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r} \\ &= T[\rho, \mathbf{X}] + W[\rho, \mathbf{X}] + \int_\Omega \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}, \end{aligned} \quad (28)$$

where $T[\rho, \mathbf{X}]$ and $W[\rho, \mathbf{X}]$ are, respectively, defined as the expectation values of \hat{T} and \hat{W} with respect to the minimizing wave function of Eq. (3). According to the variational principle of the ECS theory, $E[\rho, \mathbf{X}]$ takes the minimum value for the correct ground-state values of basic variables, $\rho_0(\mathbf{r})$ and $\mathbf{X}_0(\mathbf{r})$.¹ We get

$$\frac{\delta}{\delta \rho(\mathbf{r})} (T[\rho, \mathbf{X}] + W[\rho, \mathbf{X}])_{\rho=\rho_0, \mathbf{X}=\mathbf{X}_0} + v_{\text{ext}}(\mathbf{r}) = 0, \quad (29)$$

$$\frac{\delta}{\delta \mathbf{X}(\mathbf{r})} (T[\rho, \mathbf{X}] + W[\rho, \mathbf{X}])_{\rho=\rho_0, \mathbf{X}=\mathbf{X}_0} = 0. \quad (30)$$

The ECS theory also ensures that the minimizing wave function for $\rho_0(\mathbf{r})$ and $\mathbf{X}_0(\mathbf{r})$ is identical with $\Psi_G(\mathbf{r}_1, \dots, \mathbf{r}_N)$.¹ Therefore, Eq. (27) can be rewritten as

$$2T[\rho_0, \mathbf{X}_0] + W[\rho_0, \mathbf{X}_0] - \int_\Omega \rho_0(\mathbf{r}) \mathbf{r} \cdot \nabla v_{\text{ext}}(\mathbf{r}) d\mathbf{r} = 0. \quad (31)$$

Substituting Eq. (29) into Eq. (31), we have

$$2T[\rho_0, \mathbf{X}_0] + W[\rho_0, \mathbf{X}_0] + \int_{\Omega} \rho_0(\mathbf{r}) \mathbf{r} \cdot \nabla \left\{ \frac{\delta}{\delta \rho(\mathbf{r})} (T[\rho, \mathbf{X}] + W[\rho, \mathbf{X}]) \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} d\mathbf{r} = 0. \quad (32)$$

Equation (31) or (32) is the virial relation in the real system of the ECS theory. Of course, these relations are applicable to the extended system.

B. Virial relation in the reference system of the ECS theory

Next we shall derive the property of the kinetic energy functional $T_s[\rho_0, \mathbf{X}_0]$ in the reference system. Suppose that the minimizing single Slater determinant of Eq. (4) is denoted by $\Phi[\rho_0, \mathbf{X}_0]$ for $\rho_0(\mathbf{r})$ and $\mathbf{X}_0(\mathbf{r})$. Similarly to Eq. (20), the scaled Slater determinant $\Phi[\rho_0, \mathbf{X}_0]^\zeta$ is defined as

$$\Phi[\rho_0, \mathbf{X}_0]^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N) := \zeta^{3N/2} \Phi[\rho_0, \mathbf{X}_0](\zeta \mathbf{r}_1, \dots, \zeta \mathbf{r}_N). \quad (33)$$

The expectation value of the electron density with respect to $\Phi[\rho_0, \mathbf{X}_0]^\zeta$ is calculated as

$$\begin{aligned} \rho_0^\zeta(\mathbf{r}) &:= \langle \Phi[\rho_0, \mathbf{X}_0]^\zeta | \hat{\rho}(\mathbf{r}) | \Phi[\rho_0, \mathbf{X}_0]^\zeta \rangle_{\Omega_\zeta} \\ &= \zeta^3 \rho_0(\zeta \mathbf{r}). \end{aligned} \quad (34)$$

As for the expectation value of $\hat{\mathbf{X}}(\mathbf{r})$ with respect to $\Phi[\rho_0, \mathbf{X}_0]^\zeta$, we assume the following form:

$$\begin{aligned} \mathbf{X}_0^\zeta(\mathbf{r}) &:= \langle \Phi[\rho_0, \mathbf{X}_0]^\zeta | \hat{\mathbf{X}}(\mathbf{r}) | \Phi[\rho_0, \mathbf{X}_0]^\zeta \rangle_{\Omega_\zeta} \\ &= \zeta^d \mathbf{X}_0(\zeta \mathbf{r}), \end{aligned} \quad (35)$$

where d is the real number.²⁵ As shown in Appendix B, the relation between $T_s[\rho_0, \mathbf{X}_0]$ and $T_s[\rho_0^\zeta, \mathbf{X}_0^\zeta]$ is

$$T_s[\rho_0^\zeta, \mathbf{X}_0^\zeta] = \zeta^2 T_s[\rho_0, \mathbf{X}_0]. \quad (36)$$

Letting $\lim_{\zeta \rightarrow 1} d/d\zeta$ act on the both sides of Eq. (36), we get

$$\begin{aligned} & - \int_{\Omega} \rho_0(\mathbf{r}) \mathbf{r} \cdot \nabla \left\{ \frac{\delta T_s[\rho, \mathbf{X}]}{\delta \rho(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} d\mathbf{r} - \int_{\Omega} \mathbf{X}_0(\mathbf{r}) \cdot \left\{ (\mathbf{r} \cdot \nabla - d + 3) \frac{\delta T_s[\rho, \mathbf{X}]}{\delta \mathbf{X}(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} d\mathbf{r} + \int_{S_\Omega} \rho_0(\mathbf{r}) \\ & \times \left\{ \frac{\delta T_s[\rho, \mathbf{X}]}{\delta \rho(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} \mathbf{r} \cdot d\mathbf{S} + \int_{S_\Omega} \mathbf{X}_0(\mathbf{r}) \cdot \left\{ \frac{\delta T_s[\rho, \mathbf{X}]}{\delta \mathbf{X}(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} \mathbf{r} \cdot d\mathbf{S} = 2T_s[\rho_0, \mathbf{X}_0], \end{aligned} \quad (37)$$

where S_Ω stands for the surface of the cube Ω . Subtracting Eq. (37) from Eq. (32), and using both Eq. (30) and the relation $E_{xc}[\rho, \mathbf{X}] = T[\rho, \mathbf{X}] + W[\rho, \mathbf{X}] - T_s[\rho, \mathbf{X}] - U[\rho]$, we finally get

$$\begin{aligned} & T[\rho_0, \mathbf{X}_0] - T_s[\rho_0, \mathbf{X}_0] + E_{xc}[\rho_0, \mathbf{X}_0] + \int_{\Omega} \rho_0(\mathbf{r}) \mathbf{r} \cdot \nabla \left\{ \frac{\delta E_{xc}[\rho, \mathbf{X}]}{\delta \rho(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} d\mathbf{r} \\ & + \int_{\Omega} \mathbf{X}_0(\mathbf{r}) \cdot \left\{ (\mathbf{r} \cdot \nabla - d + 3) \frac{\delta E_{xc}[\rho, \mathbf{X}]}{\delta \mathbf{X}(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} d\mathbf{r} + \int_{S_\Omega} \rho_0(\mathbf{r}) \left\{ \frac{\delta T_s[\rho, \mathbf{X}]}{\delta \rho(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} \mathbf{r} \cdot d\mathbf{S} \\ & + \int_{S_\Omega} \mathbf{X}_0(\mathbf{r}) \cdot \left\{ \frac{\delta T_s[\rho, \mathbf{X}]}{\delta \mathbf{X}(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} \mathbf{r} \cdot d\mathbf{S} = 0. \end{aligned} \quad (38)$$

This is the virial relation of the ECS theory, which is expressed with the use of functionals defined in the reference system. It gives the relation between $E_{xc}[\rho_0, \mathbf{X}_0]$, its kinetic part $T[\rho_0, \mathbf{X}_0] - T_s[\rho_0, \mathbf{X}_0]$ and $T_s[\rho_0, \mathbf{X}_0]$.

Equation (38) is applicable to the extended system, but we can easily reduce it to the virial relation for the isolated system. In the case of the isolated system, the wave function is

normalized to unity in the whole space instead of Ω , as mentioned in Appendix A. Then, volume integrals throughout Ω in the above derivation are entirely changed into integrals throughout the whole space. The surface integrals in Eqs. (37) and (38) vanish because they become integrals over an infinitely distant surface. Accordingly, the virial relation for the isolated system is given by

$$\begin{aligned}
& T[\rho_0, \mathbf{X}_0] - T_s[\rho_0, \mathbf{X}_0] + E_{xc}[\rho_0, \mathbf{X}_0] + \int_{\Omega} \rho_0(\mathbf{r}) \mathbf{r} \cdot \nabla \left\{ \frac{\delta E_{xc}[\rho, \mathbf{X}]}{\delta \rho(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} d\mathbf{r} \\
& + \int_{\Omega} \mathbf{X}_0(\mathbf{r}) \cdot \left\{ (\mathbf{r} \cdot \nabla - d + 3) \frac{\delta E_{xc}[\rho, \mathbf{X}]}{\delta \mathbf{X}(\mathbf{r})} \Big|_{\substack{\rho=\rho_0 \\ \mathbf{X}=\mathbf{X}_0}} \right\} d\mathbf{r} = 0.
\end{aligned} \tag{39}$$

Choosing the paramagnetic current density $\mathbf{j}_p(\mathbf{r})$ as $\mathbf{X}(\mathbf{r})$ and substituting $d=4$ into Eq. (39), we revisit the virial relation for $E_{xc}[\rho_0, \mathbf{j}_{p0}]$ of CDFT. This relation exactly coincides with the previous result that has been derived for an isolated system in the absence of the external magnetic field.²⁴

IV. CONCLUDING REMARKS

In the first half of this paper, we present the coupling-constant expression for the exchange-correlation energy functional under the assumption that basic variables are non-interacting v -representable. This expression is similar to that of the conventional DFT except that the arbitrary physical quantity $\mathbf{X}(\mathbf{r})$ is added to it as the basic variable. The expression is expected to be useful for developing the approximate form of the exchange-correlation energy functional, because various kinds of approximations have been proposed on the basis of the coupling-constant expression in the previous theories such as DFT (Ref. 7–12) and CDFT.²² Noninteracting v -representability introduced here is just an assumption, but may be reasonable even in the ECS theory. The reason is a lot of successful applications which have been done within the conventional DFT.²⁶ Furthermore, from the practical viewpoint, the noninteracting v -representability is advantageous in permitting easier calculations such that basic variables are simply constructed from N lowest eigenstates of the ECS single-particle equation.

In the latter half, we discuss the virial theorem of the ECS theory. The result has an advantage of being applicable to the extended system, as compared with the previous one which is restricted to the isolated system.^{23,24} The present virial relation is expected to be a good starting point toward the approximation of the exchange-correlation energy functional, since the density-moment expansion for the conventional exchange-correlation energy functional is based on its virial relation.^{14–18} Also, the virial relation can be regarded as a sum rule for checking the validity of the approximate form. If the exchange-correlation energy functional is expanded with respect to $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$, then the sum rule can be utilized to determine the expansion coefficients. We know that such an approach had already been used in the development of the density-gradient expansion for the exchange-correlation energy functional.^{27–29}

At the end of this section, we shall give a comment on the meaning of the above sum rule. Even though the approximate functional is satisfied with some of sum rules, it would not necessarily give the quantitatively better results than the functional which is not satisfied with sum rules. The sum

rule does not always guarantee to make a good functional. However, to say the least of it, the sum rule may fairly get rid of the difficulties which lead to the nonphysical results, from the approximate functional.

APPENDIX A: NORMALIZATION OF THE SCALED FUNCTION

Let us consider the case such that the coordinates of electrons are scaled with ζ , where ζ is the scaling factor and takes a positive value. Suppose that the scaled function of the wave function $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is given by $\Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N) := A\Psi(\zeta\mathbf{r}_1, \dots, \zeta\mathbf{r}_N)$, where A is a normalization constant. In the following, we consider two kinds of systems, i.e., extended and isolated systems.

We first consider an extended system. In this case $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is usually required to be periodic in coordinates of electrons with period L , and to be normalized in the cube of side L , i.e.,

$$\Psi(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = \Psi(\mathbf{r}_1, \dots, \mathbf{r}_j + L\mathbf{e}_\alpha, \dots, \mathbf{r}_N), \tag{A1}$$

$$\int_{\Omega} \cdots \int_{\Omega} |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N = 1, \tag{A2}$$

where \mathbf{e}_α ($\alpha=x, y, z$) stands for the unit vector of x , y , or z direction. The integral is taken throughout the cube whose volume is $\Omega=L^3$. Due to the periodic condition (A1) of $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$, the scaled function $\Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N)$ has the period $\zeta^{-1}L$:

$$\Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_j, \dots, \mathbf{r}_N) = \Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_j + \zeta^{-1}L\mathbf{e}_\alpha, \dots, \mathbf{r}_N). \tag{A3}$$

Accordingly, $\Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N)$ should reasonably be normalized to unity in the cube of side $\zeta^{-1}L$. We have

$$\int_{\Omega_\zeta} \cdots \int_{\Omega_\zeta} |\Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N = 1, \tag{A4}$$

where Ω_ζ is the volume of the scaled cube of side $\zeta^{-1}L$. Using Eq. (A4), we obtain the normalization factor A as $\zeta^{3N/2}$.

In the case of the isolated system, $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ must decay to zero at infinity because $|\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2$ is a probability

distribution function. Thus, $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ is normalized to unity in the whole space of the system:

$$\int \cdots \int |\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N = 1. \quad (\text{A5})$$

From the definition of the scaled wave function, $\Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N)$ also vanishes at infinity. Therefore, $\Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N)$ should be normalized to unity in the whole space. We have

$$\int \cdots \int |\Psi^\zeta(\mathbf{r}_1, \dots, \mathbf{r}_N)|^2 d\mathbf{r}_1 \cdots d\mathbf{r}_N = 1. \quad (\text{A6})$$

Equation (A6) leads to the normalization factor $A = \zeta^{3N/2}$.

APPENDIX B: PROOF OF EQ. (36)

In the ECS theory, the kinetic energy functional of the reference system is defined by Eq. (4). The minimizing single Slater determinant $\Phi[\rho_0, \mathbf{X}_0]$ consists of N orbitals which satisfy the following equation.¹

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m} + \lambda[\rho_0, \mathbf{X}_0](\mathbf{r}) \right\} \phi_k(\mathbf{r}) + \int_{\Omega} \boldsymbol{\mu}[\rho_0, \mathbf{X}_0](\mathbf{r}') \cdot \left(\frac{\delta \mathbf{X}_0(\mathbf{r}')}{\delta \phi_k^+(\mathbf{r})} \right) d\mathbf{r}' = \sum_{j=1}^N \varepsilon_{kj} \phi_j(\mathbf{r}), \quad (\text{B1})$$

where $\lambda[\rho_0, \mathbf{X}_0](\mathbf{r})$ and $\boldsymbol{\mu}[\rho_0, \mathbf{X}_0](\mathbf{r})$ are determined by requiring $\Phi[\rho_0, \mathbf{X}_0]$ to reproduce $\rho_0(\mathbf{r})$ and $\mathbf{X}_0(\mathbf{r})$.¹ After the changes of variables, we get the equation for $\phi_k(\mathbf{r})_{\zeta} = \zeta^3 \phi_k(\zeta \mathbf{r})$ which are constituent orbitals of the scaled single Slater determinant $\Phi[\rho_0, \mathbf{X}_0]_{\zeta}$:

$$\left\{ -\frac{\hbar^2 \nabla^2}{2m} + \zeta^2 \lambda[\rho_0, \mathbf{X}_0](\zeta \mathbf{r}) \right\} \phi_k(\mathbf{r})_{\zeta} + \int_{\Omega_{\zeta}} \zeta^{8-d} \boldsymbol{\mu}[\rho_0, \mathbf{X}_0](\zeta \mathbf{r}') \cdot \left(\frac{\delta \mathbf{X}_0^{\zeta}(\mathbf{r}')}{\delta \phi_k^+(\mathbf{r})_{\zeta}} \right) d\mathbf{r}' = \sum_{j=1}^N \varepsilon_{kj} \zeta^2 \phi_j(\mathbf{r})_{\zeta}. \quad (\text{B2})$$

Owing to Eqs. (34) and (35), solutions of Eq. (B2) yield $\rho_0^{\zeta}(\mathbf{r})$ and $\mathbf{X}_0^{\zeta}(\mathbf{r})$. This means that $\zeta^2 \lambda[\rho_0, \mathbf{X}_0](\zeta \mathbf{r})$ and $\zeta^{8-d} \boldsymbol{\mu}[\rho_0, \mathbf{X}_0](\zeta \mathbf{r})$ in Eq. (B2) can be regarded as the potentials which reproduce $\rho_0^{\zeta}(\mathbf{r})$ and $\mathbf{X}_0^{\zeta}(\mathbf{r})$. In addition to the fact that $\lambda[\rho, \mathbf{X}](\mathbf{r})$ and $\boldsymbol{\mu}[\rho, \mathbf{X}](\mathbf{r})$ are uniquely determined by $\rho(\mathbf{r})$ and $\mathbf{X}(\mathbf{r})$,¹ we obtain

$$\lambda[\rho_0^{\zeta}, \mathbf{X}_0^{\zeta}](\mathbf{r}) = \zeta^2 \lambda[\rho_0, \mathbf{X}_0](\zeta \mathbf{r}), \quad (\text{B3})$$

$$\boldsymbol{\mu}[\rho_0^{\zeta}, \mathbf{X}_0^{\zeta}](\mathbf{r}) = \zeta^{8-d} \boldsymbol{\mu}[\rho_0, \mathbf{X}_0](\zeta \mathbf{r}). \quad (\text{B4})$$

Accordingly, $\Phi[\rho_0^{\zeta}, \mathbf{X}_0^{\zeta}]$ is given by

$$\begin{aligned} \Phi[\rho_0^{\zeta}, \mathbf{X}_0^{\zeta}](\mathbf{r}_1, \dots, \mathbf{r}_N) &= \Phi[\rho_0, \mathbf{X}_0]_{\zeta}(\mathbf{r}_1, \dots, \mathbf{r}_N) \\ &= \zeta^{3N/2} \Phi[\rho_0, \mathbf{X}_0](\zeta \mathbf{r}_1, \dots, \zeta \mathbf{r}_N). \end{aligned} \quad (\text{B5})$$

Similarly to the derivation of Eq. (22), Eq. (B5) leads to Eq. (36), i.e.,

$$\begin{aligned} T_s[\rho_0^{\zeta}, \mathbf{X}_0^{\zeta}] &= \langle \Phi[\rho_0^{\zeta}, \mathbf{X}_0^{\zeta}] | \hat{T} | \Phi[\rho_0^{\zeta}, \mathbf{X}_0^{\zeta}] \rangle_{\Omega_{\zeta}} \\ &= \zeta^2 \langle \Phi[\rho_0, \mathbf{X}_0] | \hat{T} | \Phi[\rho_0, \mathbf{X}_0] \rangle_{\Omega} \\ &= \zeta^2 T_s[\rho_0, \mathbf{X}_0]. \end{aligned} \quad (\text{B6})$$

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