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Evaluation of the kinetic energy contribution to the exchange-correlation energy functional in the extended constrained-search theory: Application to the current density functional theory

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Abstract. We investigate the kinetic energy contribution to the exchange-correlation (xc) energy functional of the extended constrained-search (ECS) theory. First, we derive the difference between expectation values of an arbitrary quantity with respect to the ground-state wave function and that with respect to the Kohn-Sham determinant of the ECS theory. This is regarded as the generalization of Bauer’s relation that has been derived in the conventional density functional theory. Using this relation, we obtain the kinetic energy contribution to the xc energy functional of the ECS theory. As an example, these results are applied to the current density functional theory (CDFT), which leads to useful exact relations in developing and/or evaluating the approximate form of the xc energy functional of the CDFT.

1. Introduction
We have recently proposed the extended constrained-search (ECS) theory[1-3], in which arbitrary physical quantities can be chosen as basic variables in addition to the electron density. In order to perform electronic structure calculations by means of the ECS theory, we have to develop the approximate form of the exchange-correlation (xc) energy functional. In the previous theories such as the density functional theory and the current density functional theory (CDFT), exact relations that are fulfilled by the xc energy functional are utilized as constraints in developing its approximate form[4-9].

With reference to these works, some exact relations of the xc energy functional have already been presented in the ECS theory[3,10,11].

In this paper, the kinetic energy contribution to the xc energy functional is derived in the frame work of the ECS theory by generalizing Bauer’s relation[12]. By applying this general form to the CDFT that is an effective ab initio theory for the magnetic materials, we shall derive the set of exact relations that will be useful in developing and/or evaluating the approximate form of the xc energy functional of the CDFT.
2. Kinetic energy contribution to the xc energy functional of the ECS theory

Let us start with the Hamiltonian that is augmented by an arbitrary operator $\hat{O}$ via a scalar field $\lambda$;

$$\hat{H} = \hat{T} + g\hat{W} + \int v_{\text{ext}}(r)\hat{\rho}(r)dr + \lambda\hat{O},$$

(1)

where $\hat{T}$, $\hat{W}$ and $\hat{\rho}(r)$ are operators of the kinetic energy, electron-electron interaction and electron density, respectively, and where $g$ denotes the coupling constant for the electron-electron interaction.

It should be mentioned that if $\lambda$ and $g$ are equal to 0 and 1, respectively, then Eq. (1) becomes the actual Hamiltonian of a many-electron system in an external potential $v_{\text{ext}}(r)$.

If the basic variable chosen is denoted by $X(r)$, the universal functional of the ECS theory is given by [1-3]

$$F[\rho, X](\lambda, g) = \min_{\Psi \rightarrow (\rho, X)} \langle \hat{T} + g\hat{W} + \lambda\hat{O} | \Psi \rangle = \langle \hat{T} + g\hat{W} + \lambda\hat{O} | \Psi[\rho, X]_{\lambda, g} \rangle,$$

(2)

where $\Psi \rightarrow (\rho, X)$ indicates that the minimization is performed among all antisymmetric wave functions which yield the prescribed $\rho(r)$ and $X(r)$, and where $\Psi[\rho, X]_{\lambda, g}$ denotes the minimizing wave function. Note that Eq. (2) becomes the usual universal functional $F[\rho, X]$ in the case of $(\lambda, g) = (0, 1)$, i.e., $F[\rho, X](0, 1) = F[\rho, X]$. In addition, if we assume that $\rho(r)$ and $X(r)$ are noninteracting $\nu$-representable, then $F[\rho, X](0, 0)$ is equal to the kinetic energy functional of the noninteracting reference system, that is defined by $T[\rho, X] = \min_{\Phi \rightarrow (\rho, X)} \langle \Phi | \hat{T} | \Phi \rangle$ [3], where $\Phi$ denotes a single Slater determinant. Namely, if we denote the minimizing Slater determinant as $\Phi[\rho, X]$, then we get $\Psi[\rho, X]_{00} = \Phi[\rho, X]$ under the assumption. By utilizing Eq. (2) and the Hellmann-Feynman theorem, we finally obtain

$$(\Psi[\rho, X]|\hat{O} |\Psi[\rho, X]) - \langle \Phi[\rho, X] | \hat{O} | \Phi[\rho, X] \rangle = \left[ \frac{\partial E_{\nu}[\rho, X](\lambda)}{\partial \lambda} \right]_{\lambda = 0},$$

(3)

$$E_{\nu}[\rho, X](\lambda) = F[\rho, X](\lambda, 1) - F[\rho, X](\lambda, 0) - U[\rho],$$

(4)

where $U[\rho]$ stands for the Hartree term. This is the generalization of Bauer’s relation [12]. Bauer’s relation has been successfully used for the derivation of the kinetic energy contribution to the xc energy functional of the conventional DFT. It should be noted that since $F[\rho, X](0, 1)$ and $F[\rho, X](0, 0)$ are equal to $F[\rho, X]$ and $T[\rho, X]$, respectively, $E_{\nu}[\rho, X](0)$ becomes the xc energy functional $E_{\nu}[\rho, X]$ of the ECS theory.

Next, we shall derive the kinetic energy contribution to the xc energy functional of the ECS theory by means of Eqs. (3) and (4). Substitution of $\hat{O} = \hat{T}$ into Eq. (3) leads to

$$T[\rho, X] - T_{\nu}[\rho, X] = \left[ \frac{\partial E_{\nu}[\rho, X](\lambda)}{\partial \lambda} \right]_{\lambda = 0},$$

(5)

where $T[\rho, X]$ is defined by $\langle \Psi[\rho, X] | \hat{T} | \Psi[\rho, X] \rangle$. $T[\rho, X] - T_{\nu}[\rho, X]$ is called the kinetic energy contribution to the exchange-correlation energy functional. In order to get the $\lambda$-dependence of
$E_{w}[\rho, X](\lambda)$, it is necessary to know that of $\Psi[\rho, X]_{\mathrm{gs}}$ because $E_{w}[\rho, X](\lambda)$ can be rewritten as
\[
\int_{\Gamma} \langle \Psi[\rho, X]_{\mathrm{gs}} | \hat{W} | \Psi[\rho, X]_{\mathrm{gs}} \rangle \, \mathrm{d} \gamma - U[\rho].
\] Since $\Psi[\rho, X]_{\mathrm{gs}}$ is defined as the minimizing wave function in $\min_{\psi \in \langle \Psi[\rho, X] \rangle} \langle \Psi[\rho, X]_{\mathrm{gs}} | (1 + \lambda) \hat{\rho}^{\prime} + g \hat{W} | \Psi[\rho, X]_{\mathrm{gs}} \rangle$, we have
\[
\min_{\psi \in \langle \Psi[\rho, X] \rangle} \langle \Psi[\rho, X]_{\mathrm{gs}} | (1 + \lambda) \hat{\rho}^{\prime} + g \hat{W} | \Psi[\rho, X]_{\mathrm{gs}} \rangle = \langle \Psi[\rho, X]_{\mathrm{gs}} | (1 + \lambda) a_{g} \hat{\rho}^{\prime} + g \hat{W} | \Psi[\rho, X]_{\mathrm{gs}} \rangle,
\]
where $\hat{\rho}^{\prime}$ and $\hat{W}$ are defined by $(m/\hbar^{2}) \hat{\rho}^{\prime}$ and $(1/\epsilon^{2}) \hat{W}$, respectively, and $a_{g}$ denotes the Bohr radius. We assume that $\hat{X}(r)$ is normalized by a factor $f(\epsilon^{2}, m, \hbar^{2})$ so that it is independent of $\epsilon^{2}$, $m$ and $\hbar^{2}$, i.e., $\hat{X}(r)$ is given by $\hat{x}(r)/f(\epsilon^{2}, m, \hbar^{2})$ if $\hat{x}(r)$ is the usual physical operator. For example, instead of the paramagnetic current density $\hat{j}_{p}(r)$, the normalized quantity $(m/\hbar) \hat{j}_{p}(r)$ is supposed to be chosen as $\hat{X}(r)$. Under this assumption, $\Psi[\rho, X]_{\mathrm{gs}}$ depends on $\lambda$, $\epsilon^{2}$, $m$ and $\hbar^{2}$ only through the factor $(1 + \lambda) \hbar^{2}/ me^{2}$. This is because the operator in the left-hand side of Eq. (6) depends on $(1 + \lambda) \hbar^{2}/ me^{2}$ and because the search region is independent of $\lambda$, $\epsilon^{2}$, $m$ and $\hbar^{2}$. By using this fact and Eq. (4), we can say that $E_{w}[\rho, X](\lambda)$ is a function of $(1 + \lambda) \hbar^{2}/ me^{2}$ and $\epsilon^{2}$. Therefore, the right-hand side of Eq. (5) can be rewritten as three kinds of derivatives of $E_{w}[\rho, X]$ with respect to $\epsilon^{2}$, $m$ and $\hbar^{2}$. Thus, we have
\[
T[\rho, X] - T[\rho, X] = E_{w}[\rho, X] - \epsilon^{2} \left\{ \frac{\partial E_{w}[\rho, X]}{\partial (\epsilon^{2})} \right\}_{\hbar^{2}, m, a_{g}}
\]
\[
= -m \left\{ \frac{\partial E_{w}[\rho, X]}{\partial m} \right\}_{\hbar^{2}, \epsilon^{2}}
\]
\[
= \hbar^{2} \left\{ \frac{\partial E_{w}[\rho, X]}{\partial (\hbar^{2})} \right\}_{\epsilon^{2}, m, a_{g}}.
\]
Equations (7) show the exact relations between $E_{w}[\rho, X]$ and $T[\rho, X] - T[\rho, X]$. If we get one of the two functionals, then each of Eqs. (7) can be utilized as a constraint to another functional. Also, focusing only on the right-hand sides of Eqs. (7), these equalities can be utilized as constraints in developing the approximate form of $E_{w}[\rho, X]$. It should be noted that the kinetic energy contribution to $E_{w}[\rho]$ of the conventional DFT is given in terms of the derivative with respect to $\epsilon^{2}$, $m$ or $\hbar^{2}$ but $a_{g}$ alone[13]. The above relations that include $E_{w}[\rho, X]$ alone can be obtained only by expressing the kinetic energy contribution in terms of multiple kinds of derivatives.

3. Applications to the current density functional theory
In this section, we shall apply the results of the previous section to the CDFT that is regarded as the special case of the ECS theory. Since $\hat{j}_{p}(r)$ depends on $m$ and $\hbar^{2}$, we shall consider the case where the normalized quantity $\hat{j}_{p}(r) = (m/\hbar) \hat{j}_{p}(r)$ is chosen as the basic variable instead of $\hat{j}_{p}(r)$.

Substitution of $\hat{X}(r) = \hat{j}_{p}(r)$ into Eqs. (7) immediately leads to exact relations between $E_{w}[\rho, \mathbf{J}_{p}]$ and $T[\rho, \mathbf{J}_{p}] - T[\rho, \mathbf{J}_{p}]$. In order to utilize exact relations as constraints in devising the approximate form of $E_{w}[\rho, \mathbf{J}_{p}]$, it is generally preferable to eliminate $T[\rho, \mathbf{J}_{p}] - T[\rho, \mathbf{J}_{p}]$ in the exact relations. For this
end, we employ the virial relation that also gives the relation between \( E_{\text{xc}}[\rho, J_p] \) and \( T[\rho, J_p] - T[\rho, J_p][3,14] \). Thus, we have

\[
-E_{\text{xc}}[\rho_0, J_{p0}] - \int \rho_0(r) r \cdot \nabla \left( \frac{\delta E_{\text{xc}}[\rho, J_p]}{\delta \rho(r)} \right)_{\rho_0, J_{p0}} dr = - \int J_{p0} \cdot \left( r \cdot \nabla - 1 \right) \frac{\delta E_{\text{xc}}[\rho, J_p]}{\delta X(r)}_{\rho_0, J_{p0}} dr
\]

\[
= E_{\text{xc}}[\rho_0, J_{p0}] - e^2 \left( \frac{\delta E_{\text{xc}}[\rho_0, J_{p0}]}{\delta e^2} \right)_{\rho_0, J_{p0}} = -m \left( \frac{\delta E_{\text{xc}}[\rho_0, J_{p0}]}{\delta m} \right)_{\rho_0, J_{p0}} = \hbar^2 \left( \frac{\delta E_{\text{xc}}[\rho_0, J_{p0}]}{\delta (\hbar^2)} \right)_{\rho_0, J_{p0}},
\]

where \( \rho_0(r) \) and \( J_{p0}(r) \) denote ground-state values of basic variables.

Finally, we shall mention how to use Eqs. (8) in devising the approximate form of the xc energy functional of the CDFT. By means of the relation \( J_p(r) = (m/\hbar)j_p(r) \), the functional of \( \rho(r) \) and \( J_p(r) \) is formally transformed into that of \( \rho(r) \) and \( j_p(r) \). Namely, if the approximate form of \( E_{\text{xc}}[\rho, J_p] \) is developed by using Eqs. (8), then we can formally obtain the functional \( e_{\text{xc}}[\rho, j_p] = E_{\text{xc}}[\rho, (m/\hbar)j_p] \). On the other hand, it is confirmed that the functional \( e_{\text{xc}}[\rho, j_p] \) is identical with the xc energy functional of the CDFT. Thus, we can obtain the approximate form of the xc energy functional of the CDFT from that of \( E_{\text{xc}}[\rho, J_p] \).

4. Concluding remarks
The exact relations obtained here are useful in developing and/or evaluating the approximate form of the xc energy functional of the ECS theory. The results are applied to the CDFT that is one of effective ab initio theories for the magnetic materials. With the aid of the virial relation, we derive useful relations that include not the kinetic energy contribution but only the xc energy functional of the CDFT.

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