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Explicit inclusion of paramagnetic current density in the exchange-correlation functionals of current-density functional theory

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Current-density functional theory has been formulated in terms of the paramagnetic (or canonical) current densities $\mathbf{j}_{p\sigma}(\mathbf{r})$, where $\sigma=\uparrow,\downarrow$. Vignale and Rasolt argued that $\mathbf{j}_{p\sigma}$ enter the exchange-correlation (xc) functional $E_{\mathrm{xc}}[n_\uparrow,n_\downarrow,\mathbf{j}_{p\uparrow},\mathbf{j}_{p\downarrow}]$ (abbreviated as $E_{\mathrm{xc}}[n_\sigma,\mathbf{j}_{p\sigma}]$) only through the vorticities $\boldsymbol{\nu}_\sigma(\mathbf{r})=\nabla\times[\mathbf{j}_{p\sigma}(\mathbf{r})/n_\sigma(\mathbf{r})]$, i.e., $E_{\mathrm{xc}}[n_\sigma,\mathbf{j}_{p\sigma}]=E_{\mathrm{xc}}[n_\sigma,\boldsymbol{\nu}_\sigma]$, where $n_\sigma(\mathbf{r})$ are the spin electron densities. This has been generally accepted. Alternatively this theory was also formulated in terms of the (gauge-invariant) physical or full current densities $\mathbf{j}_\sigma(\mathbf{r})$. We show that in both formulations the paramagnetic current densities $\mathbf{j}_{p\sigma}$ can enter the exchange-correlation functional explicitly. While this discovery favors the Vignale-Rasolt formulation of current-density functional theory, it admits of the explicit $\mathbf{j}_{p\sigma}$ dependence, leading to a family of metageneralized gradient current-density functionals and their hybrid versions.

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I. INTRODUCTION

The Kohn-Sham spin density functional theory[1] is the most popular method for electronic structure calculations in condensed matter physics and quantum chemistry. In principle this theory is an exact many-body theory, but in practice the exchange-correlation (xc) energy which includes all quantum many-body effects must be approximated as a functional of the electron densities $n_\sigma(\mathbf{r})$, where $\sigma=\uparrow,\downarrow$. Development of density functional approximations with improved accuracy and broader applicabilities for this quantity has been the central task of the theory.[2]

Motivated by its successful application to real systems,[3–5] the theory has been usefully extented to treat systems in time-dependent states[6] and/or in a magnetic field[7–10] which induces the orbital current of electrons. The latter extension, current-density functional theory, has been applied to different systems (e.g., atoms,[11] molecules,[12] and solids[13]), since the pioneering work of Vignale and Rasolt (VR).[7,8] In the VR formulation of this theory, in addition to the electron densities $n_\sigma(\mathbf{r})$, the (gauge-dependent) paramagnetic or canonical current densities $\mathbf{j}_{p\sigma}(\mathbf{r})$ are chosen as only additional basic variables which are admitted into the exchange-correlation functional E_{xc} only through the vorticities defined by

$$\boldsymbol{\nu}_\sigma(\mathbf{r}) = \nabla \times [\mathbf{j}_{p\sigma}(\mathbf{r})/n_\sigma(\mathbf{r})], \tag{1}$$

for the satisfaction of the gauge-invariance principle. Gauge invariance is a basic principle that an observable must obey. By examining the gauge transformation of the usual local ingredients of the conventional density functionals, we find that while the constraint on the admissible form of the paramagnetic current densities imposed on E_{xc} for the satisfaction of the gauge-invariance requirement is sufficient when an approximate density functional only depends upon gauge-invariant quantities such as the electron densities n_σ [as in the local spin density (LSD) approximation] and their gradients ∇n_σ [as in the generalized gradient approximation[14] (GGA)] explicitly, it is not when we expand the local ingredients beyond those of GGA to include the Kohn-Sham kinetic energy densities $\tau_\sigma(\mathbf{r})$ which are not gauge invariant, as in a meta-GGA[15] and its hybrid version.[3] (The GGA current-density functional proposed in Ref. 16 is not gauge invariant, because it depends upon $\mathbf{j}_{p\sigma}$ instead of $\boldsymbol{\nu}_\sigma$ explicitly.)

Current-density functional theory may be naturally formulated[9] in light of the gauge-invariant physical or full current densities $\mathbf{j}_\sigma(\mathbf{r})$. In this formulation, there is no similar restriction on the admissible form of the physical current densities imposed on current-density functionals, since the physical current densities themselves are gauge invariant. A disadvange in using the physical current densities is that in a uniform electron gas in the presence of a uniform magnetic field, the physical current vanishes so that a LSD type approximation in terms of the physical current densities does not exist. This restricts the methods for the construction of current-density functionals. Furthermore, if we construct current-density functionals from the conventional meta-GGAs (which are generally more accurate and more universal than GGAs) by introducing the gauge-invariant physical current densities, these current-density functionals will not be gauge invariant, because the conventional meta-GGA functionals[15,17,18] employ the gauge-dependent Kohn-Sham kinetic energy densities as their local ingredients. For the satisfaction of the gauge-invariance requirement, we have to explicitly include the paramagnetic current densities (or the vector potential as additional independent variables) as well.

Current-density functionals are needed in many situations. For example, atomization, ionization, and bond breaking often involve the treatment of open-shell systems such as open-shell atoms or molecules. In most chemical reactions, open-shell free radicals are produced as short-life intermediates. Because the electrons in a free atom or free radical in open-shell states can occupy degenerate orbitals in different ways and because different occupations of degenerate orbitals usually yield different densities, calculations of these open-shell systems with the conventional density functionals are problematic. While many useful conventional density functionals have been constructed and widely used in condensed matter physics and quantum chemistry, tractable current-density functional approximations are limited in the literature.[7,8,16,19,20]

The aim of this work is to present a general method for constructing formally correct current-density functionals from the conventional density functionals by releasing the "vorticity-only" restriction, within the framework of the VR current-density functional theory. The approach allows the paramagnetic current densities to enter into $E_{\rm xc}$ explicitly and is complementary to the method suggested originally in the VR papers.[7,8] More importantly, current-density functionals constructed from conventional density functionals such as the meta-GGAs and their hybrids using the present approach are guaranteed to satisfy the gauge-invariance principle, while those constructed from conventional density functionals with the original VR procedure are not ensured to be gauge invariant, because conventional density functionals may depend on gauge. Using this method, a family of current-density meta-GGA (C-MGGA) functionals and their hybrid versions may be constructed from conventional ones. The external scalar (or Coulomb) and vector potentials for self-consistent calculations are given in a general form.

II. CONSTRUCTION OF GAUGE-INVARIANT CURRENT-DENSITY FUNCTIONALS

Consider a system of N electrons with electric charge q ($q=-e$) in the presence of an external magnetic field $\mathbf{B}$ which induces the orbital current. The Hamiltonian of the system is written as

$$\hat{H} = \sum_{k=1}^{N} \left\{ \frac{1}{2m}\left[\frac{\hbar}{i}\boldsymbol{\nabla}_k - \frac{q}{c}\mathbf{A}_\sigma(\mathbf{r}_k)\right]^2 + v_\sigma(\mathbf{r}_k)\right\} + \hat{V}_{ee}, \qquad (2)$$

where $\mathbf{A}_\sigma$ are the external vector potentials defined by $\mathbf{B} = \boldsymbol{\nabla}\times\mathbf{A}_\sigma$, v_σ are the external scalar potentials, and $\hat{V}_{ee} = \Sigma_{k<l} q^2/|\mathbf{r}_l - \mathbf{r}_k|$ is the interaction energy. The paramagnetic current densities are found from the antisymmetric wave function $\Psi(\mathbf{r}\sigma, \mathbf{r}_2\sigma_2, \cdots, \mathbf{r}_N\sigma_N)$ by

$$\mathbf{j}_{p\sigma}(\mathbf{r}) = \frac{N}{m}\,\mathrm{Re}\sum_{\sigma_2,\cdots,\sigma_N}\int d^3r_2\cdots d^3r_N \Psi^* \frac{\hbar}{i}\boldsymbol{\nabla}\Psi. \qquad (3)$$

For a given vector potential $\mathbf{A}_\sigma(\mathbf{r})$, the physical current densities $\mathbf{j}_\sigma(\mathbf{r})$ are found by

$$\mathbf{j}_\sigma = \mathbf{j}_{p\sigma} - (qn_\sigma/mc)\mathbf{A}_\sigma \qquad (4)$$

and satisfy the static continuity equation for stationary states $\boldsymbol{\nabla}\cdot\mathbf{j}_\sigma = 0$, which may be expressed as

$$\boldsymbol{\nabla}\cdot\mathbf{j}_{p\sigma} = \frac{q}{mc}\boldsymbol{\nabla}\cdot(n_\sigma\mathbf{A}_\sigma). \qquad (5)$$

Using Eq. (3) the ground-state energy can be written (in the Coulomb gauge where $\boldsymbol{\nabla}\cdot\mathbf{A}_\sigma = 0$) as

$$\begin{aligned} E_{v_\sigma,\mathbf{A}_\sigma}[n_\sigma,\mathbf{j}_{p\sigma}] &= \langle\Psi|\hat{H}|\Psi\rangle \\ &= F[n_\sigma,\mathbf{j}_{p\sigma}] + \sum_\sigma \int d^3r\, n_\sigma v_\sigma \\ &\quad - \frac{q}{c}\sum_\sigma \int d^3r\, \mathbf{j}_{p\sigma}\cdot\mathbf{A}_\sigma + \frac{q^2}{2mc^2}\sum_\sigma\int d^3r\, n_\sigma A_\sigma^2, \end{aligned} \qquad (6)$$

where

$$F[n_\sigma,\mathbf{j}_{p\sigma}] = \min_{\Psi\to\{n_\sigma,\mathbf{j}_{p\sigma}\}} \langle\Psi|\hat{T}+\hat{V}_{ee}|\Psi\rangle \qquad (7)$$

with $\hat{T} = -(\hbar^2/2m)\Sigma_{k=1}^{N}\nabla_k^2$ is the minimum expectation value of the uniform-gas energy operator $\hat{T}+\hat{V}_{ee}$ after the Levy constraint search[21] over all trial wave functions yielding n_σ and $\mathbf{j}_{p\sigma}$ for given external potentials v_σ and $\mathbf{A}_\sigma$. Since $F[n_\sigma,\mathbf{j}_{p\sigma}]$ does not contain any external potential, it is a universal functional of n_σ and $\mathbf{j}_{p\sigma}$.

To turn the variational problem into the one for solving a set of self-consistent Kohn-Sham-type one-electron equations, we decompose F into

$$F[n_\sigma,\mathbf{j}_{p\sigma}] = T_s[n_\sigma,\mathbf{j}_{p\sigma}] + U[n] + E_{\rm xc}[n_\sigma,\mathbf{j}_{p\sigma}], \qquad (8)$$

where T_s is the Kohn-Sham kinetic energy defined as

$$T_s[n_\sigma,\mathbf{j}_{p\sigma}] = \min_{\Psi^0\to\{n_\sigma,\mathbf{j}_{p\sigma}\}} \langle\Psi^0|\hat{T}|\Psi^0\rangle \qquad (9)$$

the functional F of the Kohn-Sham system of N noninteracting electrons, $U[n]$ is the Hartree potential energy given by $U[n] = (1/2)\int d^3r d^3r' n(\mathbf{r})n(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ with $n = n_\uparrow + n_\downarrow$, and $E_{\rm xc}$ the exchange-correlation energy. Since the Kohn-Sham noninteracting wave function Ψ^0 of Eq. (9) is a single (or a combination of a few) Slater determinant that delivers the minimum of $\langle\hat{T}\rangle$, we may write

$$n_\sigma(\mathbf{r}) = \sum_{k=1}^{\rm occup} |\psi_{k\sigma}|^2, \qquad (10)$$

$$T_s = \sum_\sigma \sum_{k=1}^{\rm occup} \langle\psi_{k\sigma}| - \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2|\psi_{k\sigma}\rangle, \qquad (11)$$

$$\mathbf{j}_{p\sigma}(\mathbf{r}) = \frac{\hbar}{2mi}\sum_{k=1}^{\rm occup}[\psi_{k\sigma}^*\boldsymbol{\nabla}\psi_{k\sigma} - \psi_{k\sigma}\boldsymbol{\nabla}\psi_{k\sigma}^*], \qquad (12)$$

where $\psi_{k\sigma}$ are the occupied Kohn-Sham orbitals that are the implicit functionals of n_σ and $\mathbf{j}_{p\sigma}$.

The Kohn-Sham self-consistent one-electron equation[7,8] may be derived by varying $E_{v_\sigma,\mathbf{A}_\sigma}$ of Eq. (6) with respect to $\psi_{k\sigma}$ subject to $\langle\psi_{k\sigma}|\psi_{l\sigma}\rangle = \delta_{kl}$

$$\delta\left[E_{v_\sigma,\mathbf{A}_\sigma} - \sum_{k=1}^{\rm occup}\epsilon_{k\sigma}\langle\psi_{k\sigma}|\psi_{k\sigma}\rangle\right] = 0. \qquad (13)$$

The result[8] is

$$\left\{\frac{1}{2m}\left[\frac{\hbar}{i}\boldsymbol{\nabla}-\frac{q}{c}\mathbf{A}_{\mathrm{eff}\ \sigma}(\mathbf{r})\right]^2+\frac{q^2}{2mc^2}[A_\sigma^2(\mathbf{r})-\mathbf{A}_{\mathrm{eff}\ \sigma}(\mathbf{r})^2]+v_{\mathrm{eff}\ \sigma}(\mathbf{r})\right\}\psi_{k\sigma}(\mathbf{r})=\epsilon_{k\sigma}\psi_{k\sigma}(\mathbf{r}), \tag{14}$$

where $\mathbf{A}_{\mathrm{eff}\ \sigma}$ and $v_{\mathrm{eff}\ \sigma}$ are the effective vector and scalar potentials, respectively, given by $\mathbf{A}_{\mathrm{eff}\ \sigma}=\mathbf{A}_\sigma+\mathbf{A}_{\mathrm{xc}\ \sigma}$ with

$$-\frac{q}{c}\mathbf{A}_{\mathrm{xc}\ \sigma}(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}[n_\sigma,\mathbf{j}_{p\sigma}]}{\delta\mathbf{j}_{p\sigma}(\mathbf{r})} \tag{15}$$

and $v_{\mathrm{eff}\ \sigma}=v_\sigma+u_H+v_{\mathrm{xc}\ \sigma}$ with $u_H(\mathbf{r})=\delta U[n]/\delta n(\mathbf{r})$ being the Hartree potential and

$$v_{\mathrm{xc}\ \sigma}(\mathbf{r})=\frac{\delta E_{\mathrm{xc}}[n_\sigma,\mathbf{j}_{p\sigma}]}{\delta n_\sigma(\mathbf{r})} \tag{16}$$

being the exchange-correlation scalar potentials. The ground-state energy is found by

$$E=T_s[n_\sigma,\mathbf{j}_{p\sigma}]+U[n]+\sum_\sigma\int d^3r n_\sigma v_\sigma+E_{\mathrm{xc}}[n_\sigma,\mathbf{j}_{p\sigma}]-\frac{q}{c}\sum_\sigma\int d^3r\mathbf{j}_{p\sigma}\cdot\mathbf{A}_\sigma+\frac{q^2}{2mc^2}\sum_\sigma\int d^3r n_\sigma A_\sigma^2. \tag{17}$$

Note that $\mathbf{A}_\uparrow=\mathbf{A}_\downarrow=\mathbf{A}$. This is because the external magnetic field **B** does not depend upon the spin of electrons, the external potential **A** does not either.

Consider now the gauge transformation

$$\mathbf{A}_\sigma\rightarrow\mathbf{A}'_\sigma=\mathbf{A}_\sigma-\boldsymbol{\nabla}\chi_\sigma(\mathbf{r}), \tag{18}$$

where $\chi_\sigma(\mathbf{r})$ is the arbitrary function satisfying the Laplace equation $\boldsymbol{\nabla}^2\chi_\sigma(\mathbf{r})=0$. Because $\mathbf{A}_\sigma=\mathbf{A}$, $\chi_\sigma=\chi$. Guage invariance requires that the solutions of the Kohn-Sham equation describe the same physical states if we apply to the vector potential the gauge transformation of Eq. (18). Because of the gauge-invariance requirement, the solutions $\psi_{k\sigma}$ and $\psi'_{k\sigma}$ of the Kohn-Sham equation corresponding to $\mathbf{A}_\sigma$ and $\mathbf{A}'_\sigma$ differ only by a phase factor

$$\psi_{k\sigma}\rightarrow\psi'_{k\sigma}=\psi_{k\sigma}\exp[-(iq/\hbar c)\chi_\sigma(\mathbf{r})], \tag{19}$$

since the one-electron Hamiltonian in Eq. (14) is gauge invariant.

VR discovered that under the gauge transformation

$$\mathbf{j}_{p\sigma}\rightarrow\mathbf{j}'_{p\sigma}(\mathbf{r})=\mathbf{j}_{p\sigma}(\mathbf{r})-(q/mc)n_\sigma(\mathbf{r})\boldsymbol{\nabla}\chi_\sigma(\mathbf{r}), \tag{20}$$

leading to

$$E_{\mathrm{xc}}[n_\sigma,\mathbf{j}_{p\sigma}-(q/mc)n_\sigma\boldsymbol{\nabla}\chi_\sigma]=E_{\mathrm{xc}}[n_\sigma,\mathbf{j}_{p\sigma}]. \tag{21}$$

Based on this property, they have concluded that E_{xc} depends upon the paramagnetic current densities $\mathbf{j}_{p\sigma}$ only through the vorticities $\boldsymbol{\nu}_\sigma$ of Eq. (1). A similar procedure has been used by Capelle and Gross[22] to relate the Kohn-Sham spin density functional theory to current-density functional theory. This would constrain the admissible form of $\mathbf{j}_{p\sigma}$ in the construction of current-density functionals. However, by examining the gauge transformation of the local ingredients of the conventional density functional approximations, we find that while this vorticity-only constraint is sufficient when the local ingredients of a conventional density functional only include the gauge-invariant quantities such as the electron densities n_σ and their gradients $\boldsymbol{\nabla}n_\sigma$, it is not when we construct current-density functionals from the conventional meta-GGA functionals which employ the Kohn-Sham kinetic energy densities

$$\tau_\sigma(\mathbf{r})=\sum_{k=1}^{\mathrm{occup}}\frac{\hbar^2}{2m}|\boldsymbol{\nabla}\psi_{k\sigma}(\mathbf{r})|^2 \tag{22}$$

as their additional local ingredients, because the Kohn-Sham kinetic energy densities are not gauge invariant under the gauge transfromation of Eq. (18)

$$\tau_\sigma\rightarrow\tau'_\sigma(\mathbf{r})=\tau_\sigma(\mathbf{r})+2\left\{-\frac{q}{c}\mathbf{j}_{p\sigma}(\mathbf{r})\cdot\boldsymbol{\nabla}\chi_\sigma(\mathbf{r})+\frac{q^2}{2mc^2}n_\sigma(\mathbf{r})[\boldsymbol{\nabla}\chi_\sigma(\mathbf{r})]^2\right\}. \tag{23}$$

The same conclusion also holds for the Capelle-Gross contraint on the admissible form of other currents in current-density functionals. Since the proper introduction of τ_σ in meta-GGA[15] will generally improve GGA functionals due to the satisfaction of additional exact constraints,[4,23] and due to the capability of simulating the nonlocality of exact exchange,[17,24] τ-dependent meta-GGA functionals have received the most attention in the recent development of the density functional theory. Furthermore, the Kohn-Sham kinetic energy densities have been widely used[25,26] to construct self-interaction-free correlation functionals.

The gauge-variance problem with meta-GGA functionals may be solved by admitting the explicit $\mathbf{j}_{p\sigma}$ dependence of E_{xc}. A natural way is to replace the gauge-dependent Kohn-Sham kinetic energy densities of Eq. (22) by the gauge-invariant genuine kinetic energy densities

$$\tau_\sigma\rightarrow\tau_\sigma^{gk}=\tau_\sigma-(q/c)\mathbf{j}_{p\sigma}\cdot\mathbf{A}_\sigma+(q^2/2mc^2)n_\sigma A_\sigma^2 \tag{24}$$

which may be obtained[27] by replacing the canonical momentum operator $(\hbar/i)\boldsymbol{\nabla}$ by the genuine momentum operator $(\hbar/i)\boldsymbol{\nabla}-(q/c)\mathbf{A}_\sigma$ in Eq. (2) and then performing integration by parts. A problem with this approach is that the vector potential $\mathbf{A}_\sigma$ [or both the paramagnetic and physical current densities via Eq. (4)] must enter E_{xc} as an additional independent basic variable, contradicting the assumption that we construct current-density functionals by introducing the paramagnetic current densities as only additional basic variables. Furthermore, current-density functionals constructed with this simple replacement [Eq. (24)] are not universal, since they depend upon the external vector potential $\mathbf{A}_\sigma(\mathbf{r})$.

A better way is to replace τ_σ by the modified kinetic energy densities

$$\tau_\sigma\rightarrow\tilde{\tau}_\sigma=\tau_\sigma-m|\mathbf{j}_{p\sigma}|^2/(2n_\sigma) \tag{25}$$

which are gauge invariant. This replacement is motivated by (1) the Taylor expansion[20,28] of the spherically averaged gauge-invariant exchange holes $\langle \rho_{x\sigma}(\mathbf{r},u)\rangle$ around $u=0$

$$\langle \rho_{\mathrm{x}\sigma}(\mathbf{r},u)\rangle = -\left\langle \left| \sum_{k=1}^{\mathrm{occup}} \psi^{*}_{k\sigma}(\mathbf{r})\psi_{k\sigma}(\mathbf{r}+\mathbf{u}) \right|^{2} \right\rangle / n_\sigma(\mathbf{r}) = -n_\sigma - \frac{2u^2}{3}\left[\frac{1}{4}\nabla^2 - \tilde{\tau}_\sigma + \frac{1}{8}\frac{|\nabla n_\sigma|^2}{n_\sigma}\right] + \cdots$$

where $\langle \rho_{x\sigma}(\mathbf{r},u)\rangle = (1/4\pi)\int_{\Omega_{\mathbf{u}}} d\Omega_{\mathbf{u}} \rho_{x\sigma}(\mathbf{r},\mathbf{u})$, (Note that the exchange hole proposed in Ref. 16 does not satisfy the gauge-invariance requirement.) (2) The second-order gradient expansion of the kinetic energy densities for slowly varying densities and slowly varying current densities

$$\tilde{\tau}_\sigma = \frac{\hbar^2}{m}\left[\frac{3}{10}(6\pi^2)^{2/3} n_\sigma^{5/3} + \frac{|\nabla n_\sigma|^2}{8n_\sigma} + \frac{1}{6}\nabla^2 n_\sigma + \cdots\right],$$

and (3) for one-electron densities

$$\tilde{\tau}_\sigma = \tilde{\tau}_\sigma^{W} = \frac{\hbar^2}{m}\frac{|\nabla n_\sigma|^2}{8n_\sigma}.$$

Note that in the gradient expansion of the kinetic energy densities, we have neglected a term containing ν_σ^2. This second-order term, like other density gradient terms, will vanish for a uniform density and current $\mathbf{j}_{p\sigma}$. Furthermore, its effect on the current density functionals constructed below is very small, as discussed later.

VR derived[8] from the second-order energy shift of the electron gas with slowly varying densities and slowly varying current densities in the presence of a uniform magnetic field

$$E_{\mathrm{xc}}[n_\sigma, \mathbf{j}_{p\sigma}] = E_{\mathrm{xc}}[n_\sigma, 0] + E_{\mathrm{xc}}^{\mathrm{VR}}[n_\sigma, \mathbf{j}_{p\sigma}], \tag{26}$$

where

$$E_{\mathrm{xc}}^{\mathrm{VR}} = \sum_\sigma \int d^3r \frac{mk_{F\sigma}(\mathbf{r})}{48\pi^2}\left[\frac{\chi_{L\sigma}(\mathbf{r})}{\chi_{L\sigma}^0(\mathbf{r})} - 1\right]\nu_\sigma(\mathbf{r})^2, \tag{27}$$

$E_{\mathrm{xc}}[n_\sigma, 0]$ is the conventional exchange-correlation functional, $k_{F\sigma} = (6\pi^2 n_\sigma)^{1/3}$ is the Fermi wave vector, $\chi_{L\sigma}^0 = -(q^2/24\pi^2 mc^2)k_{F\sigma}$ is the diamagnetic susceptibility for the noninteracting electron gas, and $\chi_{L\sigma}$ is for the interacting electron gas which was calculated for spin-unpolarized uniform densities within the random-phase approximation (RPA) by Vignale, Rasolt, and Geldart.[29] While the evaluation of $\chi_{L\sigma}$ for a spin-polarized electron gas is not available yet, it might be constructed from the spin-unpolarized version.

The VR linear-response current-density correction of Eq. (27) may be added to the current-density functionals constructed with the present approach from conventional density functionals. Although these (conventional) current-density functionals may have similar second-order contributions (like the VR correction) due to the local ingredient $\tilde{\tau}_\sigma$, they are very small,[30] compared with the VR correction. Therefore, this combination will essentially reduce to the ordinary LSD plus VR correction which is exact, for a uniform density in the presence of the uniform magnetic field. Thus our C-MGGA functionals and their hybrid versions may be constructed as

$$E_{\mathrm{xc}}[n_\uparrow, n_\downarrow, \mathbf{j}_{p\uparrow}, \mathbf{j}_{p\downarrow}] = E_{\mathrm{xc}}[n_\sigma, \tilde{\tau}_\sigma] + E_{\mathrm{xc}}^{\mathrm{VR}} = \int d^3r n \epsilon_{\mathrm{xc}}(n_\sigma, \nabla n_\sigma, \tilde{\tau}_\sigma, \epsilon_{\mathrm{x}\sigma}^{\mathrm{exact}}, \boldsymbol{\nu}_\sigma) \tag{28}$$

where ϵ_{xc} is the exchange-correlation energy per electron, $\epsilon_{\mathrm{x}\sigma}^{\mathrm{exact}}$ are the exact Kohn-Sham exchange energy densities which have been used to construct commonly used hybrid density functionals, and $(n_\sigma, \nabla n_\sigma, \tilde{\tau}_\sigma, \epsilon_{\mathrm{x}\sigma}^{\mathrm{exact}}, \boldsymbol{\nu}_\sigma) = (n_\uparrow, n_\downarrow, \nabla n_\uparrow, \nabla n_\downarrow, \tilde{\tau}_\uparrow, \tilde{\tau}_\downarrow, \epsilon_{\mathrm{x}\uparrow}^{\mathrm{exact}}, \epsilon_{\mathrm{x}\downarrow}^{\mathrm{exact}}, \boldsymbol{\nu}_\uparrow, \boldsymbol{\nu}_\downarrow)$. In the uniform-gas limit where the densities and currents are constant everywhere, because the vorticities of Eq. (1) vanish and the modified Kohn-Sham kinetic energy densities $\tilde{\tau}_\sigma$ of Eq. (25) reduce to the ordinary kinetic energy densities, our current-density functionals correctly reduce to the ordinary LSD, as expected.

The exchange-correlation contribution to the effective vector potential is given as

$$-\frac{q}{c}\mathbf{A}_{\mathrm{xc}\ \sigma}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[n_\uparrow, n_\downarrow, \mathbf{j}_{p\uparrow}, \mathbf{j}_{p\downarrow}]}{\delta \mathbf{j}_{p\sigma}(\mathbf{r})} = \frac{\partial(n\epsilon_{\mathrm{xc}})}{\partial\tilde{\tau}_\sigma}\frac{\delta\tilde{\tau}_\sigma}{\delta\mathbf{j}_{p\sigma}} + \frac{1}{n_\sigma}\boldsymbol{\nabla}\times\left[\frac{\partial(n\epsilon_{\mathrm{xc}})}{\partial\boldsymbol{\nu}_\sigma}\right] \tag{29}$$

and to the effective scalar potential is

$$v_{\mathrm{xc}\ \sigma} = \left[\frac{\partial(n\epsilon_{\mathrm{xc}})}{\partial n_\sigma} - \boldsymbol{\nabla}\cdot\frac{\partial(n\epsilon_{\mathrm{xc}})}{\partial\boldsymbol{\nabla} n_\sigma} + \cdots\right] + \frac{\partial(n\epsilon_{\mathrm{xc}})}{\partial\tilde{\tau}_\sigma}\frac{\delta\tilde{\tau}_\sigma}{\delta n_\sigma} + \frac{\mathbf{j}_{p\sigma}}{n_\sigma}\cdot\left[\frac{q}{c}\mathbf{A}_{\mathrm{xc}\ \sigma} + \frac{\partial(n\epsilon_{\mathrm{xc}})}{\partial\tilde{\tau}_\sigma}\frac{\delta\tilde{\tau}_\sigma}{\delta n_\sigma}\right] + \frac{\delta\epsilon_{\mathrm{x}\sigma}^{\mathrm{exact}}}{\delta n_\sigma} \tag{30}$$

where $\delta\tilde{\tau}_\sigma/\delta\mathbf{j}_{p\sigma} = (\delta\tau_\sigma/\delta|\mathbf{j}_{p\sigma}| - |\mathbf{j}_{p\sigma}|/n_\sigma)\hat{\mathbf{j}}_{p\sigma}$ with $\hat{\mathbf{j}}_{p\sigma} = \mathbf{j}_{p\sigma}/|\mathbf{j}_{p\sigma}|$ and $\delta\tilde{\tau}_\sigma/\delta n_\sigma = \delta\tau_\sigma/\delta n_\sigma + |\mathbf{j}_{p\sigma}|/2n_\sigma^2$. These current-dependent potentials may be used in self-consistent calculations with the current-dependent Kohn-Sham equation of Eq. (14), although a fully self-consistent solution of the current-dependent Kohn-Sham equation is quite demanding. Alternatively, nonself-consistent solutions to Eq. (14) may be obtained perturbatively. First, one can self-consistently solve the conventional one-electron Kohn-Sham equation which may be obtained by dropping the vector potential terms in Eq. (14), and then treat these vector potential terms as a perturbation.[31]

III. CONCLUSION

In conclusion, we show that current-density functional theory can be formulated in terms of the paramagnetic current density. This formulation allows us to construct gauge-invariant current-density functionals from the conventional density functionals such as the meta-GGAs and their hybrids by replacing the Kohn-Sham kinetic energy density with the modified kinetic energy density of Eq. (25). Our current-density functionals exactly recovers the uniform-gas limit. We also show that current-density functionals may depend upon the current density *explicitly*.

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[1] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[2] J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. E. Scuseria, and G. I. Csonka, J. Chem. Phys. (to be published).
[3] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, J. Chem. Phys. **119**, 12129 (2003); **121**, 11507 (2004) (E).
[4] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, Phys. Rev. B **69**, 075102 (2004).
[5] J. Tao and J. P. Perdew, J. Chem. Phys. **122**, 114102 (2005).
[6] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).
[7] G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987).
[8] G. Vignale and M. Rasolt, Phys. Rev. B **37**, 10685 (1988).
[9] G. Diener, J. Phys.: Condens. Matter **3**, 9417 (1991).
[10] G. Vignale and W. Kohn, Phys. Rev. Lett. **77**, 2037 (1996).
[11] E. Orestes, T. Marcasso, and K. Capelle, Phys. Rev. A **68**, 022105 (2003).
[12] A. M. Lee, N. C. Handy, and S. M. Colwell, J. Chem. Phys. **103**, 10095 (1995).
[13] G. Vignale, P. Skudlarski, and M. Rasolt, Phys. Rev. B **45**, 8494 (1992).
[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[15] J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. **91**, 146401 (2003).
[16] S. N. Maximoff, M. Ernzerhof, and G. E. Scuseria, J. Chem. Phys. **120**, 2105 (2003).
[17] T. Van Voorhis and G. E. Scuseria, J. Chem. Phys. **109**, 400 (1998).
[18] A. D. Boese and N. C. Handy, J. Chem. Phys. **116**, 9559 (2002).
[19] P. Skudlarski and G. Vignale, Phys. Rev. B **48**, 8547 (1993).
[20] A. D. Becke, J. Chem. Phys. **117**, 6935 (2002).
[21] M. Levy, Proc. Natl. Acad. Sci. U.S.A. **76**, 6062 (1979).
[22] K. Capelle and E. K. U. Gross, Phys. Rev. Lett. **78**, 1872 (1997).
[23] M. Levy, in *Density Functional Theory*, edited by E. K. U. Gross and R. M. Dreizler (Plenum, New York, 1995).
[24] A. D. Becke, J. Chem. Phys. **112**, 4020 (2000).
[25] A. D. Becke, J. Chem. Phys. **109**, 2092 (1998).
[26] J. P. Perdew, J. Tao, V. N. Staroverov, and G. E. Scuseria, J. Chem. Phys. **120**, 6898 (2004).
[27] S. N. Maximoff and G. E. Scuseria, Chem. Phys. Lett. **390**, 408 (2004).
[28] J. F. Dobson, J. Phys.: Condens. Matter **4**, 7877 (1992).
[29] G. Vignale, M. Rasolt, and D. J. W. Geldart, Phys. Rev. B **37**, 2502 (1988).
[30] J. Tao (unpublished).
[31] K. Capelle, Phys. Rev. A **60**, R733 (1999).