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Optimized effective potential method in current-spin-density-functional theory

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Current-spin-density-functional theory (CSDFT) provides a framework to describe interacting many-electron systems in a magnetic field which couples to both spin and orbital degrees of freedom. Unlike in the usual (spin-)density-functional theory, approximations to the exchange-correlation energy based on the model of the uniform electron gas face problems in practical applications. In this work, explicitly orbital-dependent functionals are used and a generalization of the optimized effective potential method to the CSDFT framework is presented. A simplifying approximation to the resulting integral equations for the exchange-correlation potentials is suggested. A detailed analysis of these equations is carried out for the case of open-shell atoms and numerical results are given using the exact-exchange energy functional. For zero external magnetic field, a small systematic lowering of the total energy for current-carrying states is observed due to the inclusion of the current in the Kohn-Sham scheme. For states without current, CSDFT results coincide with those of spin-density-functional theory.

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I. INTRODUCTION

Density-functional theory (DFT) [1,2] is the standard tool to calculate the electronic structure of interacting many-electron systems. The original theorems of DFT have been successively extended to cover a wide range of different physical situations. One of the most important extensions is the spin-DFT (SDFT) formalism [3] which allows one to describe systems with magnetic ground states in arbitrary external magnetic fields. In SDFT, however, the magnetic field couples only to the electronic spin while the coupling to the orbital degrees of freedom is not taken into account. To include also the coupling to the orbital currents, one has to resort to the current-spin-density-functional theory (CSDFT) of Vignale and Rasolt [4,5].

Conceptually, DFT, SDFT, and CSDFT are very similar: they all map the system of interacting electrons onto a system of noninteracting particles in some effective fields. In the case of DFT, this auxiliary system yields the same electron density as the interacting one while in SDFT the magnetization densities of the two systems coincide as well. In CSDFT, also the paramagnetic current density of the auxiliary system is equal to the paramagnetic current density of the true, interacting system. In all three formalisms the energy of the interacting system is written as a functional of the corresponding densities and the value for the ground-state energy is obtained by minimizing this functional with respect to the densities.

While all three flavors of DFT are exact in principle, in practice they all require an approximation for the exchange-correlation (XC) energy (which is a piece of the total energy) as a functional of the respective densities. In both DFT and SDFT, approximations based on the uniform electron gas such as the local (spin-)density approximation [L(S)DA] are surprisingly successful and they also form a good starting point for the construction of more sophisticated functionals such as generalized-gradient approximations.

In CSDFT, however, the situation is different. While it is possible to construct LDA-type approximations along similar ideas as in (S)DFT, these functionals are awkward to use in practical calculations [6] for a clear physical reason: when a uniform electron gas is exposed to an external magnetic field, Landau levels form and, for given magnetic field, the XC energy density exhibits derivative discontinuities as a function of the density whenever a new Landau level starts to be filled. If this XC energy density is then used as the main ingredient in the construction of a LDA, these discontinuities show up in the corresponding XC potentials at those points in space where the local densities coincide with the densities of the uniform gas for which these discontinuities occur. This makes practical calculations extremely difficult. One solution to this problem is to smoothly interpolate the XC energy density between the limits of weak and strong magnetic fields [7,8] but this interpolation then misses the physics in the exchange-correlation energy arising from the Landau levels.

The problem described above is entirely due to the construction of the LDA in CSDFT. Since the appearance of Landau levels is intrinsically an orbital effect, the use of explicitly orbital-dependent approximations to the XC energy functional offers a promising alternative which we explore in the present work. In (S)DFT, orbital functionals have attracted increasing interest in recent years [9] since these approximations offer a cure for notorious problems like, e.g., the self-interaction error of local and semilocal functionals. The calculation of the XC potential corresponding to an orbital-dependent XC energy functional is technically somewhat more involved than for explicitly density-dependent approximations and can be achieved with the so-called optimized effective potential (OEP) method [10]. Here we present the extension of the OEP method to the CSDFT formalism [11] and derive a set of coupled OEP integral equations for the corresponding exchange-correlation potentials. We then introduce a simplifying approximation in the spirit of Krieger, Li, and Iafrate (KLI) [12,13] which transforms the integral equations into a set of algebraic equations that can be solved more easily in practical calculations. We present the resulting equations for fully noncollinear effective magnetic fields. This generalizes earlier work on a non-

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collinear implementation of orbital functionals in SDFT [14]. It is also similar in spirit to a recent work [15] which, however, uses a much larger set of densities.

In a previous paper [11] we have solved the OEP equations of CSDFT for two-dimensional quantum dots in external magnetic fields. In the present work we study the case of atoms at zero external magnetic field using the exact-exchange energy functional. In particular, we are interested in studying open-shell atoms which generally have degenerate ground states. It is well known [16,17] that in (S)DFT common approximations for the exchange-correlation energy do not lead to the same total energy for the different ground-state configurations. Here we investigate this problem in the framework of CSDFT because some of these ground states actually carry a nonzero current and one might hope that CSDFT is better suited to describe the degeneracies. The motivation to study simple atomic systems also aims at a better understanding of the differences between SDFT and CSDFT. The same orbital functional may perform quite differently in the three different schemes.

The present paper is organized as follows. In Sec. II we give the fundamental equations of CSDFT before we present the derivation of the noncollinear OEP and KLI equations in Sec. III. This is followed in Sec. IV by an analysis of the properties of the KLI potentials for open-shell atoms at zero external magnetic field. Numerical results are presented in Sec. V before we draw our conclusions.

II. CURRENT-SPIN-DENSITY-FUNCTIONAL THEORY

In this section we briefly describe the formalism of current-spin-density-functional theory as originally suggested by Vignale and Rasolt [4,5]. With this extension of the original DFT [1,2] formulation it becomes possible to study interacting many-electron systems in external magnetic fields. The CSDFT approach also goes beyond the widely used spin-DFT formalism [3] in the sense that, while in SDFT the magnetic field couples only to the spin degrees of freedom, in CSDFT it also couples to the orbital degrees of freedom through the vector potential.

The Hamiltonian of interacting electrons in an external electrostatic potential $v_0(\mathbf{r})$ and an external magnetic field $\mathbf{B}_0(\mathbf{r})=\nabla\times\mathbf{A}_0(\mathbf{r})$ is given by (atomic units are used throughout)

$$\hat{H}=\hat{T}+\hat{W}+\int d^3r\,\hat{n}(\mathbf{r})v_0(\mathbf{r})-\int d^3r\,\hat{\mathbf{m}}(\mathbf{r})\mathbf{B}_0(\mathbf{r})+\frac{1}{c}\int d^3r\,\hat{\mathbf{j}}_p(\mathbf{r})\mathbf{A}_0(\mathbf{r})+\frac{1}{2c^2}\int d^3r\,\hat{n}(\mathbf{r})\mathbf{A}_0^2(\mathbf{r}), \quad (1)$$

where $\hat{T}$ and $\hat{W}$ are the operators of the kinetic energy and the electron-electron interaction, respectively. The operators for the density, the magnetization density, and the paramagnetic current density are given by

$$\hat{n}(\mathbf{r})=\hat{\Psi}^\dagger(\mathbf{r})\hat{\Psi}(\mathbf{r}), \quad (2)$$

$$\hat{\mathbf{m}}(\mathbf{r})=-\mu_B\hat{\Psi}^\dagger(\mathbf{r})\boldsymbol{\sigma}\hat{\Psi}(\mathbf{r}), \quad (3)$$

and

$$\hat{\mathbf{j}}_p(\mathbf{r})=\frac{1}{2i}\{\hat{\Psi}^\dagger(\mathbf{r})\,\nabla\,\hat{\Psi}(\mathbf{r})-[\nabla\hat{\Psi}^\dagger(\mathbf{r})]\hat{\Psi}(\mathbf{r})\}, \quad (4)$$

respectively. Here we have defined field operators $\hat{\Psi}^\dagger(\mathbf{r})=(\hat{\psi}_\uparrow^\dagger(\mathbf{r}),\hat{\psi}_\downarrow^\dagger(\mathbf{r}))$ for two-component spinors, i.e., the formulation is not restricted to collinear magnetism with all the spins aligned in a single direction. $\boldsymbol{\sigma}$ is the vector of Pauli matrices and $\mu_B=1/(2c)$ is the Bohr magneton.

Following Vignale and Rasolt [4,5], the ground-state energy can be written as a functional of the three densities as

$$E[n,\mathbf{m},\mathbf{j}_p]=F[n,\mathbf{m},\mathbf{j}_p]+\int d^3r\,v_0(\mathbf{r})n(\mathbf{r})-\int d^3r\,\mathbf{m}(\mathbf{r})\mathbf{B}_0(\mathbf{r})+\frac{1}{c}\int d^3r\,\mathbf{j}_p(\mathbf{r})\mathbf{A}_0(\mathbf{r})+\frac{1}{2c^2}\int d^3r\,n(\mathbf{r})\mathbf{A}_0^2(\mathbf{r}), \quad (5)$$

where $F[n,\mathbf{m},\mathbf{j}_p]$ is a universal functional of the densities n, $\mathbf{m}$, and $\mathbf{j}_p$ in the sense that it is independent of the external fields v_0, $\mathbf{B}_0$, and $\mathbf{A}_0$. It may be decomposed in the usual way as

$$F[n,\mathbf{m},\mathbf{j}_p]=T_s[n,\mathbf{m},\mathbf{j}_p]+U[n]+E_{\mathrm{XC}}[n,\mathbf{m},\mathbf{j}_p], \quad (6)$$

where $T_s[n,\mathbf{m},\mathbf{j}_p]$ is the kinetic energy functional for noninteracting electrons,

$$U[n]=\frac{1}{2}\int d^3r\int d^3r'\frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad (7)$$

is the classical electrostatic energy, and $E_{\mathrm{XC}}[n,\mathbf{m},\mathbf{j}_p]$ is the exchange-correlation energy.

Using Eq. (6) and minimizing the total energy (5) leads to the effective single-particle Kohn-Sham equations of CSDFT, which read

$$\left[\frac{1}{2}\left(-i\,\nabla+\frac{1}{c}\mathbf{A}_s(\mathbf{r})\right)^2+v_s(\mathbf{r})+\mu_B\boldsymbol{\sigma}\mathbf{B}_s(\mathbf{r})\right]\Phi_i(\mathbf{r})=\epsilon_i\Phi_i(\mathbf{r}), \quad (8)$$

where $\Phi_i(\mathbf{r})$ are two-component, single-particle Pauli spinors. The effective potentials are given by

$$v_s(\mathbf{r})=v_0(\mathbf{r})+v_H(\mathbf{r})+v_{\mathrm{XC}}(\mathbf{r})+\frac{1}{2c^2}[\mathbf{A}_0^2(\mathbf{r})-\mathbf{A}_s^2(\mathbf{r})], \quad (9)$$

$$\mathbf{B}_s(\mathbf{r})=\mathbf{B}_0(\mathbf{r})+\mathbf{B}_{\mathrm{XC}}(\mathbf{r}), \quad (10)$$

and

$$\mathbf{A}_s(\mathbf{r})=\mathbf{A}_0(\mathbf{r})+\mathbf{A}_{\mathrm{XC}}(\mathbf{r}), \quad (11)$$

where the Hartree potential is given by

$$v_H(\mathbf{r})=\int d^3r'\frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (12)$$

The exchange-correlation potentials are functional derivatives of the exchange-correlation energy E_{XC} with respect to the corresponding conjugate densities,

$$v_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}[n,\mathbf{m},\mathbf{j}_p]}{\delta n(\mathbf{r})}, \tag{13}$$

$$\mathbf{B}_{\mathrm{XC}}(\mathbf{r}) = -\frac{\delta E_{\mathrm{XC}}[n,\mathbf{m},\mathbf{j}_p]}{\delta \mathbf{m}(\mathbf{r})}, \tag{14}$$

$$\mathbf{A}_{\mathrm{XC}}(\mathbf{r}) = c\frac{\delta E_{\mathrm{XC}}[n,\mathbf{m},\mathbf{j}_p]}{\delta \mathbf{j}_p(\mathbf{r})}. \tag{15}$$

The effective potentials are such that the ground-state densities of the Kohn-Sham system reproduce those of the interacting system. The particle density can then be computed by

$$n(\mathbf{r}) = \sum_{i=1}^{N} \Phi_i^\dagger(\mathbf{r})\Phi_i(\mathbf{r}), \tag{16}$$

the magnetization density by

$$\mathbf{m}(\mathbf{r}) = -\mu_B\sum_{i=1}^{N} \Phi_i^\dagger(\mathbf{r})\boldsymbol{\sigma}\Phi_i(\mathbf{r}), \tag{17}$$

and the paramagnetic current density by

$$\mathbf{j}_p(\mathbf{r}) = \frac{1}{2i}\sum_{i=1}^{N} \{\Phi_i^\dagger(\mathbf{r})\nabla\Phi_i(\mathbf{r}) - [\nabla\Phi_i^\dagger(\mathbf{r})]\Phi_i(\mathbf{r})\}, \tag{18}$$

where the sums in Eqs. (16)–(18) run over the occupied Kohn-Sham spinor orbitals.

As usual in DFT, the exact form of the exchange-correlation energy functional $E_{\mathrm{XC}}[n,\mathbf{m},\mathbf{j}_p]$ is unknown and needs to be approximated in practice. In the present work, we focus on a class of approximate functionals which also has attracted increasing interest in SDFT in recent years. This is the class of functionals that explicitly depend on the Kohn-Sham orbitals and are therefore only implicit functionals of the densities. In our context these functionals are appealing for two reasons: first, they are constructed without any reference to the uniform electron gas and second, they are ideally suited to describe the appearance of Landau levels which in itself may be viewed as an orbital effect.

III. OPTIMIZED EFFECTIVE POTENTIAL METHOD IN CSDFT

The calculation of the exchange-correlation potential for orbital-dependent functionals in ordinary (S)DFT is done in the framework of the optimized effective potential method [9,10,18]. This method derives its name from the fact that it yields that local potential whose orbitals minimize the total energy functional of the interacting system. This optimized potential is obtained as a solution of the so-called OEP integral equation.

Recently, the OEP equations have been derived for the noncollinear formulation of SDFT [14]. Here we derive the OEP integral equations for the exchange-correlation potentials in CSDFT [11] by calculating the functional derivatives of E_{XC} with respect to the three effective potentials v_s, $\mathbf{B}_s$, and $\mathbf{A}_s$. Making use of the correspondence both between Kohn-Sham spinors and ground-state densities as well as between Kohn-Sham spinors and effective potentials, these functional derivatives can be computed in two different ways by using the chain rule, i.e.,

$$\begin{aligned}\frac{\delta E_{\mathrm{XC}}}{\delta v_s(\mathbf{r})} &= \int d^3r'\left(v_{\mathrm{XC}}(\mathbf{r}')\frac{\delta n(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \frac{1}{c}\mathbf{A}_{\mathrm{XC}}(\mathbf{r}')\frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta v_s(\mathbf{r})}\right.\\ &\quad\left. - \mathbf{B}_{\mathrm{XC}}(\mathbf{r}')\frac{\delta \mathbf{m}(\mathbf{r}')}{\delta v_s(\mathbf{r})}\right)\\ &= \sum_{i=1}^{N}\int d^3r'\left(\frac{\delta E_{\mathrm{XC}}}{\delta \Phi_i(\mathbf{r}')}\frac{\delta \Phi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \mathrm{H.c.}\right),\end{aligned} \tag{19}$$

$$\begin{aligned}\frac{\delta E_{\mathrm{XC}}}{\delta \mathbf{B}_s(\mathbf{r})} &= \int d^3r'\left(v_{\mathrm{XC}}(\mathbf{r}')\frac{\delta n(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + \frac{1}{c}\mathbf{A}_{\mathrm{XC}}(\mathbf{r}')\frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})}\right.\\ &\quad\left. - \mathbf{B}_{\mathrm{XC}}(\mathbf{r}')\frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})}\right)\\ &= \sum_{i=1}^{N}\int d^3r'\left(\frac{\delta E_{\mathrm{XC}}}{\delta \Phi_i(\mathbf{r}')}\frac{\delta \Phi_i(\mathbf{r}')}{\delta \mathbf{B}_s(\mathbf{r})} + \mathrm{H.c.}\right),\end{aligned} \tag{20}$$

$$\begin{aligned}\frac{\delta E_{\mathrm{XC}}}{\delta \mathbf{A}_s(\mathbf{r})} &= \int d^3r'\left(v_{\mathrm{XC}}(\mathbf{r}')\frac{\delta n(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} + \frac{1}{c}\mathbf{A}_{\mathrm{XC}}(\mathbf{r}')\frac{\delta \mathbf{j}_p(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})}\right.\\ &\quad\left. - \mathbf{B}_{\mathrm{XC}}(\mathbf{r}')\frac{\delta \mathbf{m}(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})}\right)\\ &= \sum_{i=1}^{N}\int d^3r'\left(\frac{\delta E_{\mathrm{XC}}}{\delta \Phi_i(\mathbf{r}')}\frac{\delta \Phi_i(\mathbf{r}')}{\delta \mathbf{A}_s(\mathbf{r})} + \mathrm{H.c.}\right)\end{aligned} \tag{21}$$

where H.c. is the Hermitian conjugate. Equations (19)–(21) constitute a system of coupled integral equations for the unknown exchange-correlation potentials. For simplicity, we have assumed that the approximation for E_{XC} to be used depends only on the occupied spinor orbitals such as, e.g., the exact-exchange functional

$$E_x^{\mathrm{EXX}}[\{\Phi_i\}] = -\frac{1}{2}\sum_{i,j}^{\mathrm{occ}}\int d^3r\int d^3r'\,\frac{\Phi_i^\dagger(\mathbf{r})\Phi_j(\mathbf{r})\Phi_j^\dagger(\mathbf{r}')\Phi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \tag{22}$$

which we use in our numerical implementation.

For any approximation of E_{XC} given explicitly in terms of the spinor orbitals, the functional derivatives of E_{XC} with respect to these spinors can be evaluated easily. The other functional derivatives in Eqs. (19)–(21) may be computed exactly from first-order perturbation theory by considering variations of the Kohn-Sham spinors due to a perturbation $\delta\hat{H}_s(\mathbf{r}')$ of the Kohn-Sham Hamiltonian. To first order in the perturbation these variations are

$$\delta\Phi_i(\mathbf{r}) = \sum_{\substack{j=1\\ j\neq i}}^{\infty}\frac{\Phi_j(\mathbf{r})}{\epsilon_i-\epsilon_j}\int d^3r'\,\Phi_j^\dagger(\mathbf{r}')\delta\hat{H}_s(\mathbf{r}')\Phi_i(\mathbf{r}'), \tag{23}$$

where for simplicity we have assumed a nondegenerate spectrum. For arbitrary variations $\delta v_s(\mathbf{r})$, $\delta\mathbf{B}_s(\mathbf{r})$, and $\delta\mathbf{A}_s(\mathbf{r})$ in the three effective potentials, the perturbation $\delta\hat{H}_s(\mathbf{r})$ is given by

$$\delta\hat{H}_s(\mathbf{r}) = \delta v_s(\mathbf{r}) + \frac{1}{2ic}\nabla\,\delta\mathbf{A}_s(\mathbf{r}) + \frac{1}{ic}\delta\mathbf{A}_s(\mathbf{r})\,\nabla + \frac{1}{c^2}\mathbf{A}_s(\mathbf{r})\delta\mathbf{A}_s(\mathbf{r}) + \mu_B\boldsymbol{\sigma}\delta\mathbf{B}_s(\mathbf{r}). \tag{24}$$

Insertion into Eq. (23) allows us to identify the functional derivatives of the spinors with respect to the effective potentials as

$$\frac{\delta\Phi_i(\mathbf{r})}{\delta v_s(\mathbf{r}')} = \sum_{\substack{j=1\\ j\neq i}}^{\infty}\frac{\Phi_j(\mathbf{r})}{\epsilon_i-\epsilon_j}[\Phi_j^\dagger(\mathbf{r}')\Phi_i(\mathbf{r}')], \tag{25}$$

$$\frac{\delta\Phi_i(\mathbf{r})}{\delta\mathbf{B}_s(\mathbf{r}')} = \mu_B\sum_{\substack{j=1\\ j\neq i}}^{\infty}\frac{\Phi_j(\mathbf{r})}{\epsilon_i-\epsilon_j}[\Phi_j^\dagger(\mathbf{r}')\boldsymbol{\sigma}\Phi_i(\mathbf{r}')], \tag{26}$$

and

$$\frac{\delta\Phi_i(\mathbf{r})}{\delta\mathbf{A}_s(\mathbf{r}')} = \sum_{\substack{j=1\\ j\neq i}}^{\infty}\frac{\Phi_j(\mathbf{r})}{\epsilon_i-\epsilon_j}\Bigg(\frac{1}{2ic}\{\Phi_j^\dagger(\mathbf{r}')\nabla'\Phi_i(\mathbf{r}') - [\nabla'\Phi_j^\dagger(\mathbf{r}')]\Phi_i(\mathbf{r}')\} + \frac{1}{c^2}\mathbf{A}_s(\mathbf{r})\Phi_j^\dagger(\mathbf{r}')\Phi_i(\mathbf{r}')\Bigg). \tag{27}$$

From Eqs. (25)–(27) one can compute the static response functions, i.e., the functional derivatives of the densities with respect to the effective potentials. Inserting everything into Eqs. (19)–(21) one can then write the OEP integral equations in a very compact form as

$$\sum_{i=1}^{N}\Phi_i^\dagger(\mathbf{r})\Psi_i(\mathbf{r}) + \text{H.c.} = 0, \tag{28}$$

$$-\mu_B\sum_{i=1}^{N}\Phi_i^\dagger(\mathbf{r})\boldsymbol{\sigma}\Psi_i(\mathbf{r}) + \text{H.c.} = 0, \tag{29}$$

and

$$\frac{1}{2i}\sum_{i=1}^{N}\{\Phi_i^\dagger(\mathbf{r})\,\nabla\,\Psi_i(\mathbf{r}) - [\nabla\Phi_i^\dagger(\mathbf{r})]\Psi_i(\mathbf{r})\} + \text{H.c.} = 0, \tag{30}$$

where we have defined the so-called orbital shifts [9,19]

$$\Psi_i(\mathbf{r}) = \sum_{\substack{j=1\\ j\neq i}}^{\infty}\frac{\Phi_j(\mathbf{r})D_{ij}}{\epsilon_i-\epsilon_j}, \tag{31}$$

with

$$D_{ij} = \int d^3r'\Bigg(v_{\text{XC}}(\mathbf{r}')\Phi_j^\dagger(\mathbf{r}')\Phi_i(\mathbf{r}') + \frac{1}{2ic}\mathbf{A}_{\text{XC}}(\mathbf{r})\times\{\Phi_j^\dagger(\mathbf{r}')\nabla'\Phi_i(\mathbf{r}') - [\nabla'\Phi_j^\dagger(\mathbf{r}')]\Phi_i(\mathbf{r}')\} + \mu_B\mathbf{B}_{\text{XC}}(\mathbf{r}')\Phi_j^\dagger(\mathbf{r}')\boldsymbol{\sigma}\Phi_i(\mathbf{r}') - \Phi_j^\dagger(\mathbf{r}')\frac{\delta E_{\text{XC}}}{\delta\Phi_i^\dagger(\mathbf{r}')}\Bigg). \tag{32}$$

The name "orbital shifts" (31) derives from their structure as a first-order shift from the unperturbed Kohn-Sham orbital Φ_i under a perturbation whose matrix elements are given by D_{ij}. The OEP equations (28)–(30) have a very simple interpretation: they merely say that the densities do not change under this perturbation. Keeping in mind that the Kohn-Sham system already yields the exact densities, this statement is actually quite obvious.

As already mentioned, the OEP equations are a set of coupled integral equations for the exchange-correlation potentials. In this work we do not attempt a full solution of these equations but rather suggest a simplifying approximation [18] in the spirit of Krieger, Li, and Iafrate [12,13], who introduced the same approximation in the usual OEP method of SDFT. In this KLI approximation the orbital shifts are approximated by replacing the energy denominator by some constant, i.e.,

$$\Psi_i(\mathbf{r}) \approx \frac{1}{\Delta\epsilon}\Bigg(\sum_{j=1}^{\infty}\Phi_j(\mathbf{r})D_{ij} - \Phi_i(\mathbf{r})D_{ii}\Bigg). \tag{33}$$

Inserting this approximation into the OEP equations and applying the completeness relation for the Kohn-Sham spinors one obtains after some algebra a set of algebraic equations for the exchange-correlation potentials which can conveniently be written as

$$\mathcal{D}(\mathbf{r})\mathcal{V}_{\text{XC}}(\mathbf{r}) = \mathcal{R}(\mathbf{r}). \tag{34}$$

Here, we have defined the seven-component vector $\mathcal{V}_{\text{XC}}(\mathbf{r})$ as

$$\mathcal{V}_{\text{XC}}^T(\mathbf{r}) = \Big(v_{\text{XC}}(\mathbf{r}),\mathbf{B}_{\text{XC}}^T(\mathbf{r}),\frac{1}{c}\mathbf{A}_{\text{XC}}^T(\mathbf{r})\Big) \tag{35}$$

and the 7×7 matrix $\mathcal{D}(\mathbf{r})$ has the structure

$$\mathcal{D}(\mathbf{r}) = \begin{pmatrix} n(\mathbf{r}) & -\mathbf{m}^T(\mathbf{r}) & \mathbf{j}_p^T(\mathbf{r}) \\ -\mathbf{m}(\mathbf{r}) & \mu_B^2 n(\mathbf{r})\mathbb{1} & \mathcal{J}(\mathbf{r}) \\ \mathbf{j}_p(\mathbf{r}) & \mathcal{J}^T(\mathbf{r}) & \mathcal{N}(\mathbf{r}) \end{pmatrix},$$

where $\mathbb{1}$ is the 3×3 unit matrix. The matrix elements of the 3×3 matrices $\mathcal{J}$ and $\mathcal{N}$ are defined by

$$\mathcal{J}_{\alpha\beta}(\mathbf{r}) = -\frac{\mu_B}{2i}\sum_{i=1}^{N}\Bigg(\Phi_i^\dagger(\mathbf{r})\sigma_\alpha\frac{\partial\Phi_i(\mathbf{r})}{\partial r_\beta} - \frac{\partial\Phi_i^\dagger(\mathbf{r})}{\partial r_\beta}\sigma_\alpha\Phi_i(\mathbf{r})\Bigg) \tag{36}$$

and

$$\mathcal{N}_{\alpha\beta}(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N}\left(\frac{\partial\Phi_i^\dagger(\mathbf{r})}{\partial r_\alpha}\frac{\partial\Phi_i(\mathbf{r})}{\partial r_\beta} + \frac{\partial\Phi_i^\dagger(\mathbf{r})}{\partial r_\beta}\frac{\partial\Phi_i(\mathbf{r})}{\partial r_\alpha}\right) - \frac{1}{4n(\mathbf{r})}\frac{\partial n(\mathbf{r})}{\partial r_\alpha}\frac{\partial n(\mathbf{r})}{\partial r_\beta}, \tag{37}$$

where $\alpha=1$, 2, and 3 correspond to the Cartesian coordinates x, y, and z, respectively. The seven components of the vector $\mathcal{R}(\mathbf{r})$ on the right-hand side of Eq. (34) are given by

$$\mathcal{R}_1(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N}\left(\Phi_i^\dagger(\mathbf{r})\frac{\delta E_{\mathrm{XC}}}{\delta\Phi_i^\dagger(\mathbf{r})} + n_i(\mathbf{r})D_{ii} + \mathrm{H.c.}\right), \tag{38}$$

$$\mathcal{R}_{1+\alpha}(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N}\left(-\mu_B\Phi_i^\dagger(\mathbf{r})\sigma_\alpha\frac{\delta E_{\mathrm{XC}}}{\delta\Phi_i^\dagger(\mathbf{r})} + m_{i,\alpha}(\mathbf{r})D_{ii} + \mathrm{H.c.}\right),$$

$$\mathcal{R}_{4+\alpha}(\mathbf{r}) = \frac{1}{2}\sum_{k=1}^{N}\left(\frac{1}{2i}\Phi_k^\dagger(\mathbf{r})\frac{\partial}{\partial r_\alpha}\frac{\delta E_{\mathrm{XC}}}{\delta\Phi_k^\dagger(\mathbf{r})} - \frac{1}{2i}\frac{\partial\Phi_k^\dagger(\mathbf{r})}{\partial r_\alpha}\frac{\delta E_{\mathrm{XC}}}{\delta\Phi_k^\dagger(\mathbf{r})} + j_{p,k,\alpha}(\mathbf{r})D_{kk} + \mathrm{H.c.}\right), \tag{39}$$

with the density $n_i(\mathbf{r})$, magnetization density $\mathbf{m}_i(\mathbf{r})$, and paramagnetic current density $\mathbf{j}_{p,i}(\mathbf{r})$ of the single orbital $\Phi_i(\mathbf{r})$. It is worth mentioning that in order to arrive at this result we used the identity [5]

$$\boldsymbol{\nabla}(n(\mathbf{r})\mathbf{A}_{\mathrm{XC}}(\mathbf{r})) = 0, \tag{40}$$

which follows directly from gauge invariance of the exchange-correlation energy.

The KLI equations (34) can be solved by iteration: start with an intial guess for the potentials to compute the orbitals and the right-hand side of Eq. (34), then solve this equation for the new potentials and iterate until self-consistency is achieved.

In a different work [11] we have solved the KLI equations for a two-dimensional quantum dot in an external magnetic field. In the present work we use our CSDFT OEP formalism to study open-shell atoms in zero external magnetic field. In the next section we discuss some further assumptions we employed in our implementation and deduce some analytic results for the KLI potentials.

IV. OPEN-SHELL ATOMS AT ZERO MAGNETIC FIELD

We want to employ our CSDFT OEP formalism to study open-shell atoms. From the point of view of CSDFT this is interesting since some states out of the multiplet of degenerate ground states have a nonvanishing current density while others do not carry a current.

In the limit of zero external magnetic field, the Kohn-Sham equation (8) takes the form

$$\left(-\frac{\nabla^2}{2} + v_0(\mathbf{r}) + v_H(\mathbf{r}) + v_{\mathrm{XC}}(\mathbf{r}) + \frac{1}{2ic}[\boldsymbol{\nabla}\mathbf{A}_{\mathrm{XC}}(\mathbf{r})] + \frac{1}{ic}\mathbf{A}_{\mathrm{XC}}\boldsymbol{\nabla} + \mu_B\boldsymbol{\sigma}\mathbf{B}_{\mathrm{XC}}(\mathbf{r})\right)\Phi_i(\mathbf{r}) = \epsilon_i\Phi_i(\mathbf{r}). \tag{41}$$

It should be noted that the effective scalar potential of Eq. (9) contains a term quadratic in $\mathbf{A}_{\mathrm{XC}}$. This term is exactly canceled by another quadratic term which follows from evaluating the square of the canonical momentum in Eq. (8) and therefore only terms linear in $\mathbf{A}_{\mathrm{XC}}$ appear in Eq. (41).

In the following we employ the collinear approximation assuming that the Kohn-Sham spinors decompose into spin-up ($\sigma=+1$) and spin-down ($\sigma=-1$) orbitals, i.e., $\Phi_i(\mathbf{r})=(\varphi_{i,\sigma=+1}(\mathbf{r}),0)$ or $\Phi(\mathbf{r})=(0,\varphi(\mathbf{r})_{i,\sigma=-1})$. As a result the magnetization density is parallel to the z direction, $\mathbf{m}(\mathbf{r})=(0,0,m(\mathbf{r}))$. In addition, we assume cylindrical symmetry for both the densities and the corresponding conjugate potentials (that is, they do not depend on the azimuthal angle ϕ). As a consequence the magnetic quantum number is a good quantum number for the single-particle orbitals which then take the form

$$\varphi_{im\sigma}(\mathbf{r}) = g_{j\sigma}(r,\theta)\exp(im\phi)\chi(\sigma), \tag{42}$$

where we used radial coordinates and m is the magnetic quantum number [not to be confused with $m(\mathbf{r})$, the z component of the magnetization density]. σ is the spin index and $\chi(\sigma)$ is the eigenfunction of the z component of the spin operator. In the collinear approximation, $\mathbf{B}_{\mathrm{XC}}(\mathbf{r})=(0,0,B_{\mathrm{XC}}(\mathbf{r}))$ is parallel to the z axis while $\mathbf{A}_{\mathrm{XC}}(\mathbf{r})=A_{\mathrm{XC}}(\mathbf{r})\mathbf{e}_\phi$ where $\mathbf{e}_\phi$ is the unit vector in the ϕ direction. As an additional consequence of the cylindrical symmetry of our problem we have $\boldsymbol{\nabla}\mathbf{A}_{\mathrm{XC}}(\mathbf{r})=\mathbf{0}$.

We restrict ourselves to ground states whose densities can be reproduced by a single Slater determinant. For example, for the boron atom one configuration has all three up electrons and the two down electrons in states with magnetic quantum number $m=0$ while in another configuration one of the up electrons occupies an $m=1$ state with the other occupations unchanged. In this way current-carrying and zero-current states can be considered. The resulting current only has a component in the ϕ direction, $\mathbf{j}_p(\mathbf{r})=j_p(\mathbf{r})\mathbf{e}_\phi$. We may then rewrite Eq. (41) as

$$\left(-\frac{\nabla^2}{2} + v_0(\mathbf{r}) + v_H(\mathbf{r}) + v_{\mathrm{XC}}(\mathbf{r}) + \frac{1}{c}\frac{m}{r\sin\theta}A_{\mathrm{XC}}(\mathbf{r}) + \mu_B\sigma B_{\mathrm{XC}}(\mathbf{r})\right)\varphi_{im\sigma}(\mathbf{r}) = \epsilon_{im\sigma}\varphi_{im\sigma}(\mathbf{r}). \tag{43}$$

In the following we discuss a number of typical cases. For atomic closed-shell configurations, where the density is spherical and both the magnetization density and the paramagnetic current density vanish identically, both A_{XC} and B_{XC} vanish identically. Obviously, in this situation CSDFT reduces to the original density-only DFT.

For ground-state configurations where only orbitals with $m=0$ are occupied, the correct value for $j_p(\mathbf{r})$—which is zero at any point in space—is trivially obtained already within the

SDFT scheme. Therefore, we expect that $v_{\mathrm{XC}}(\mathbf{r})=v_{\mathrm{XC}}^{\mathrm{SDFT}}(\mathbf{r})$, $B_{\mathrm{XC}}(\mathbf{r})=B_{\mathrm{XC}}^{\mathrm{SDFT}}(\mathbf{r})$, and $A_{\mathrm{XC}}(\mathbf{r})=0$. Actually, any other choice of $A_{\mathrm{XC}}(\mathbf{r})$ would not make any difference for the ground-state densities. In a way this may be regarded as a simple manifestation of the nonuniqueness of the CSDFT potentials pointed out in Ref. [20].

As a third case we consider ground-state configurations with a half-filled shell as in, e.g., the nitrogen atom. Again, SDFT already gives the correct values of the total densities. Therefore, we again expect that $v_{\mathrm{XC}}(\mathbf{r})=v_{\mathrm{XC}}^{\mathrm{SDFT}}(\mathbf{r})$, $B_{\mathrm{XC}}(\mathbf{r})=B_{\mathrm{XC}}^{\mathrm{SDFT}}(\mathbf{r})$, and $A_{\mathrm{XC}}(\mathbf{r})=\mathbf{0}$.

Ground-state configurations carrying a nonvanishing paramagnetic current are the most interesting ones in our context. At zero external magnetic field, this situation arises only for open-shell atoms away from half filling. Indeed, it is for these states that we expect $A_{\mathrm{XC}}(\mathbf{r})\neq 0$ as well as $v_{\mathrm{XC}}(\mathbf{r})\neq v_{\mathrm{XC}}^{\mathrm{SDFT}}(\mathbf{r})$, $B_{\mathrm{XC}}(\mathbf{r})\neq B_{\mathrm{XC}}^{\mathrm{SDFT}}(\mathbf{r})$.

In the following we analyze the KLI equations for the above cases in order to confirm these expectations. We remind the reader that in our derivation of the OEP equations we assumed that E_{XC} depends only on the occupied orbitals. Moreover, we also assume that

$$\frac{\delta E_{\mathrm{XC}}}{\delta\varphi_{im\sigma}(\mathbf{r})}\sim\exp(-im\phi) \tag{44}$$

holds. Both of these assumptions are correct for the exact-exchange functional which we consider in our numerical implementation.

Under these assumptions, the first two KLI equations (for $\sigma=\pm1$) are

$$v_{\mathrm{XC},\sigma}(\mathbf{r})+\frac{1}{c}\frac{j_{p,\sigma}(\mathbf{r})}{n_\sigma(\mathbf{r})}A_{\mathrm{XC}}(\mathbf{r})=w_{\mathrm{XC},\sigma}^{(1)}(\mathbf{r})+w_{\mathrm{XC},\sigma}^{(2)}(\mathbf{r}), \tag{45}$$

where we have defined the spin-dependent scalar potential

$$v_{\mathrm{XC},\sigma}(\mathbf{r})=v_{\mathrm{XC}}(\mathbf{r})+\mu_B\sigma B_{\mathrm{XC}}(\mathbf{r}). \tag{46}$$

The terms on the right-hand side of Eq. (45) are given by

$$w_{\mathrm{XC},\sigma}^{(1)}(\mathbf{r})=\frac{1}{n_\sigma(\mathbf{r})}\sum_{i,m}^{\mathrm{occ}}n_{im\sigma}(\mathbf{r})u_{\mathrm{XC},im\sigma}(\mathbf{r}) \tag{47}$$

and

$$w_{\mathrm{XC},\sigma}^{(2)}(\mathbf{r})=\frac{1}{n_\sigma(\mathbf{r})}\sum_{i,m}^{\mathrm{occ}}n_{im\sigma}(\mathbf{r})d_{\mathrm{XC},im\sigma}, \tag{48}$$

with

$$u_{\mathrm{XC},im\sigma}(\mathbf{r})=\frac{1}{\varphi_{im\sigma}^{*}(\mathbf{r})}\frac{\delta E_{\mathrm{XC}}}{\delta\varphi_{im\sigma}(\mathbf{r})} \tag{49}$$

and

$$d_{\mathrm{XC},im\sigma}=\int d^3r\,n_{im\sigma}(\mathbf{r})[v_{\mathrm{XC},\sigma}(\mathbf{r})-u_{\mathrm{XC},im\sigma}(\mathbf{r})]+\frac{1}{c}\int d^3r\,j_{p,im\sigma}(\mathbf{r})A_{\mathrm{XC}}(\mathbf{r}). \tag{50}$$

Here $n_{im\sigma}(\mathbf{r})$ and $j_{p,im\sigma}(\mathbf{r})$ are the density and the paramagnetic current density of the single-orbital $\varphi_{im\sigma}(\mathbf{r})$ which, for our symmetry, are related by

$$j_{p,im\sigma}(\mathbf{r})=m\frac{n_{im\sigma}(\mathbf{r})}{r\sin\theta}. \tag{51}$$

The third KLI equation reads

$$\left(\sum_\sigma j_{p,\sigma}(\mathbf{r})v_{\mathrm{XC},\sigma}(\mathbf{r})\right)+\frac{1}{c}N(\mathbf{r})A_{\mathrm{XC}}(\mathbf{r})=\sum_\sigma[\tilde{w}_{\mathrm{XC},\sigma}^{(1)}(\mathbf{r})+\tilde{w}_{\mathrm{XC},\sigma}^{(2)}(\mathbf{r})] \tag{52}$$

with

$$N(\mathbf{r})=\sum_\sigma\sum_{i,m}^{\mathrm{occ}}\frac{j_{p,im\sigma}^2(\mathbf{r})}{n_{im\sigma}(\mathbf{r})}, \tag{53}$$

$$\tilde{w}_{\mathrm{XC},\sigma}^{(1)}(\mathbf{r})=\sum_{i,m}^{\mathrm{occ}}j_{p,im\sigma}(\mathbf{r})u_{\mathrm{XC},im\sigma}(\mathbf{r}), \tag{54}$$

and

$$\tilde{w}_{\mathrm{XC},\sigma}^{(2)}(\mathbf{r})=\sum_{i,m}^{\mathrm{occ}}j_{p,im\sigma}(\mathbf{r})d_{\mathrm{XC},im\sigma}. \tag{55}$$

It is interesting to note that $v_{\mathrm{XC},\sigma}(\mathbf{r})$ and $A_{\mathrm{XC}}(\mathbf{r})$ couple to each other only if at least one of the $j_{p,\sigma}(\mathbf{r})$ is nonvanishing.

At this point, we again consider open-shell configurations for which all occupied orbitals have $m=0$. Then $N(\mathbf{r})$ vanishes and the KLI equation (45) reduces to the KLI equation of SDFT while Eq. (52) becomes a trivial identity. As a consequence, $v_{\mathrm{XC},\sigma}(\mathbf{r})=v_{\mathrm{XC},\sigma}^{\mathrm{SDFT}}(\mathbf{r})$ and $A_{\mathrm{XC}}(\mathbf{r})$ is undetermined. As discussed above, $A_{\mathrm{XC}}(\mathbf{r})$ does not affect any of the ground-state densities and we fix it as $A_{\mathrm{XC}}(\mathbf{r})=0$.

Next we consider configurations with a half-filled shell. We assume that we have already solved the SDFT KLI equations and use the resulting orbitals and potentials plus the initial guess $A_{\mathrm{XC}}(\mathbf{r})=0$ as a start for the iterative solution of the CSDFT KLI equations. We substitute this initial guess into Eqs. (45) and (52) to compute the new potentials. The occupied orbitals of SDFT either have $m=0$ or they come in pairs with m and $-m$. This leads to the same contributions to $u_{\mathrm{XC},\sigma,i}(\mathbf{r})$ for orbitals in the same shell while for the paramagnetic current they contribute with equal magnitude but opposite sign. Hence, the KLI equations become

$$v_{\mathrm{XC},\sigma}^{\mathrm{new}}(\mathbf{r})=w_{\mathrm{XC},\sigma}^{(1)}(\mathbf{r})+w_{\mathrm{XC},\sigma}^{(2)}(\mathbf{r})=v_{\mathrm{XC},\sigma}^{\mathrm{SDFT}}(\mathbf{r}) \tag{56}$$

and

$$\frac{1}{c}N(\mathbf{r})A_{\mathrm{XC}}^{\mathrm{new}}(\mathbf{r})=0\Rightarrow A_{\mathrm{XC}}^{\mathrm{new}}(\mathbf{r})=0. \tag{57}$$

This shows that the SDFT solution along with $A_{\mathrm{XC}}(\mathbf{r})=0$ is also a CSDFT solution. We also tested numerically that the solution $A_{\mathrm{XC}}(\mathbf{r})=0$ is stable against (not necessarily small) perturbations of the initial guess.

Finally, we consider the most interesting case of ground-state configurations with a paramagnetic current different from zero. For these configurations we expect $A_{\mathrm{XC}}(\mathbf{r}) \neq 0$. Solution of the third KLI equation (52) with respect to $A_{\mathrm{XC}}(\mathbf{r})$ yields

$$A_{\mathrm{XC}}(\mathbf{r}) = c\frac{\sum_{\sigma}[\widetilde{w}^{(1)}_{\mathrm{XC},\sigma}(\mathbf{r}) + \widetilde{w}^{(2)}_{\mathrm{XC},\sigma}(\mathbf{r}) - j_{p,\sigma}(\mathbf{r})v_{\mathrm{XC},\sigma}(\mathbf{r})]}{N(\mathbf{r})}. \tag{58}$$

In this equation, the denominator increases for increasing number of electrons. The numerator also typically increases when more orbitals are occupied but, due to large cancellations for contributions arising from orbitals with opposite values of m, it increases with a slower rate than the denominator. As a consequence, we expect larger exchange-correlation vector potentials $A_{\mathrm{XC}}(\mathbf{r})$ for atoms in the first row than for atoms in the second row (but the same column) of the periodic table.

In the remainder of this section we discuss the asymptotic behavior of the exchange-correlation potentials and the vector potential.

We start by *assuming* that, for finite systems, the exchange-correlation potentials in the asymptotic region far away from the system behave as

$$v_{\mathrm{XC},\sigma}(\mathbf{r}) \overset{r\to\infty}{\sim} -\frac{1}{r} \tag{59}$$

and

$$\lim_{r\to\infty} A_{\mathrm{XC}}(\mathbf{r}) = 0. \tag{60}$$

Equation (59) certainly is a reasonable assumption: it is the well-known asymptotic behavior for $v_{\mathrm{XC},\sigma}$ of SDFT which we assume to be unchanged in CSDFT. Equation (60) then ensures that the term proportional to $A_{\mathrm{XC}}(\mathbf{r})/r$ in the Kohn-Sham equation (43) decays faster than $v_{\mathrm{XC},\sigma}(\mathbf{r})$ asymptotically. At this stage, Eq. (60) may be viewed as a working assumption in order to be able to proceed further. Below we show that it is consistent with the solution of the KLI equation.

Under this assumption we can deduce [9,21] the asymptotic behavior of the atomic orbitals from the Kohn-Sham equation (43) as

$$\lim_{r\to\infty} \varphi_{im\sigma}(\mathbf{r}) = r^{-1+1/\beta_{im\sigma}} \exp(-\beta_{im\sigma} r), \tag{61}$$

where $\beta_{im\sigma} = \sqrt{-2\epsilon_{im\sigma}}$. This implies that the spin density is dominated asymptotically by the highest occupied orbital of that spin. The same is true for the current density if the magnetic quantum number of this orbital is different from zero (as typically is the case for current-carrying states of open-shell atoms).

In order to proceed further with our analysis we restrict ourselves to the exact-exchange functional of Eq. (22). Then the KLI equation (45) allows us to establish the following relation between $v_{\mathrm{XC},\sigma}$ and A_{XC} in the asymptotic region:

$$v_{\mathrm{XC},\sigma}(\mathbf{r}) + \frac{1}{c}\frac{M_{\sigma}}{r\sin\theta}A_{\mathrm{XC}}(\mathbf{r}) \overset{r\to\infty}{\sim} -\frac{1}{r} + d_{\mathrm{XC},N_{\sigma}M_{\sigma}\sigma}, \tag{62}$$

where we tacitly assumed that we are taking the limit away from a nodal plane of the highest occupied orbital of spin σ [9,22]. Here N_{σ} is the orbital index of that orbital and M_{σ} is its magnetic quantum number. Since we are working in the collinear approximation, the Kohn-Sham equations for the two spin channels are completely decoupled and we can choose a constant shift in $v_{\mathrm{XC},\sigma}$ such that

$$d_{\mathrm{XC},N_{\sigma}M_{\sigma}\sigma} = 0. \tag{63}$$

Equation (62) together with Eq. (59) then implies

$$\frac{M_{\sigma}}{r\sin\theta}A_{\mathrm{XC}}(\mathbf{r}) \overset{r\to\infty}{\sim} 0, \tag{64}$$

which is consistent with the assumption of Eq. (60).

However, a closer inspection of the KLI equations (45) and (52) shows that they become linearly dependent in the asymptotic region and therefore do not have a unique solution. This again may be viewed as a manifestation of the nonuniqueness problem in CSDFT [20,23]. In our numerical procedure to be described in the next section we take a pragmatic approach to the problem of linearly dependent KLI equations and choose a solution with $A_{\mathrm{XC}}(\mathbf{r}) \to 0$ and a $v_{\mathrm{XC},\sigma}(\mathbf{r})$ satisfying Eq. (59).

Before concluding this section, we discuss some symmetry properties of the exchange-correlation vector potential and exchange-correlation magnetic field. By inspection of the two KLI equations (45) and (52) it is clear that under the exchange of spin-up and spin-down electrons $B_{\mathrm{XC}}(\mathbf{r})$ changes sign. Similarly, moving an electron from an orbital with magnetic quantum number m to a previously unoccupied one with $-m$ leads to $A_{\mathrm{XC}}(\mathbf{r})$ changing sign. These transformations can be performed independently leading to the same total energy.

V. NUMERICAL RESULTS FOR OPEN-SHELL ATOMS AT ZERO EXTERNAL MAGNETIC FIELD

In this section we describe the numerical results for open-shell atoms obtained within the KLI approximation of CSDFT using the exact-exchange functional of Eq. (22). In particular, we are interested in calculating total energies of current-carrying and zero-current states in various ground-state configurations. In principle, the states of the ground-state multiplet should be degenerate but in SDFT zero-current states are always lower in energy than current-carrying states. Since the current appears to be the quantity leading to these spurious energy splittings, it is interesting to see if CSDFT (where the current is one of the fundamental variables) can alleviate the problem. Since the main difference between SDFT and CSDFT is the appearance of an exchange-correlation vector potential in the Kohn-Sham equation, we also present some results for the XC potentials in the different approaches.

We have developed an atomic code for CSDFT and SDFT calculations in a basis set representation, assuming cylindrical symmetry of the Kohn-Sham potentials and densities. As basis functions we use Slater-type functions for the radial part multiplied by spherical harmonics for the angular part. For the Slater functions we employ the quadruple-ζ basis sets (QZ4P) of Ref. [24]. We have tested our code by computing the total energies of spherically symmetric atoms of the first and second rows of the periodic table in exchange-only KLI approximation and compared with results from accurate, fully numerical codes available in the literature [9,12,25]. Our code reproduces these total energies to within an average deviation of 0.1 kcal/mol for the atoms in the first row and to within an average deviation of 0.5 kcal/mol for atoms in the second row of the periodic table.

We performed self-consistent exchange-only calculations in the KLI approximation of CSDFT for open-shell atoms in current-carrying and zero-current configurations. The configurations are selected by specifying the number of occupied states for each value of the magnetic quantum number m. Once a choice has been made, the occupations remain unchanged during the self-consistency cycle. In all the cases we studied we were able to obtain self-consistent solutions for both zero-current and current-carrying states.

As expected, for zero-current states we always obtain a self-consistent CSDFT solution with vanishing exchange vector potential, $A_X(\mathbf{r}) \equiv 0$. In fact, this solution, which is equivalent to the corresponding SDFT solution, always gives the lowest total energy.

For current-carrying states we always find a nonvanishing A_X. However, as a consequence of the linear dependence of the KLI equations (45) and (52) discussed in the previous section, the exchange potential and vector potential are not uniquely determined. In fact, without additional numerical measures we obtain unphysical potentials which diverge asymptotically. This may lead to a wrong ordering of the occupied and unoccupied orbitals or even to convergence problems. A numerically convenient scheme to use the KLI equations (45) and (52) during the self-consistency cycle is to first calculate $v_{\mathrm{XC},\sigma}(\mathbf{r})$ from Eq. (45) with the $A_{\mathrm{XC}}(\mathbf{r})$ obtained in the previous iteration. In this step we impose the asymptotic behavior of $v_{\mathrm{XC},\sigma}(\mathbf{r}) \overset{r\to\infty}{\sim} -1/r$. Then, with this updated $v_{\mathrm{XC},\sigma}(\mathbf{r})$ we use Eq. (52) to obtain a new $A_{\mathrm{XC}}(\mathbf{r})$. In order to enforce the asymptotic limit $A_{\mathrm{XC}}(\mathbf{r}) \overset{r\to\infty}{\sim} 0$ we add a small quantity δ to $N(\mathbf{r})$ in Eq. (58). Total energies and current densities are very insensitive to the choice of δ: for the fixed value of $\delta = 10^{-4}$ a.u. which we use for all our calculations, total energies vary by an order of 10^{-2} kcal/mol or less if δ is varied by an order of magnitude around its chosen value.

In Fig. 1 we show the $L=0$ (i.e., spherical) component of an expansion of the exchange vector potentials in terms of Legendre polynomials, i.e., $A_X(\mathbf{r}) = \Sigma_{L=0}^{\infty} A_X^L(r) P_L(\cos\theta)$, for the oxygen and sulfur atoms in the current-carrying state. As we argued in the previous section, the exchange vector potential of sulfur is smaller than the one for oxygen which also implies that the difference between SDFT and CSDFT total energies is smaller for the heavier atom.

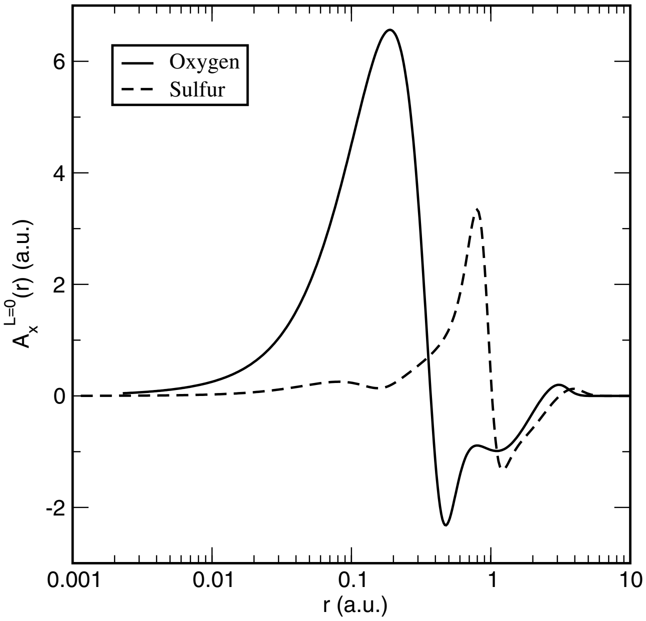

FIG. 1. Spherical component of the exchange vector potentials for current-carrying states of the oxygen and sulfur atoms.

In previous work [26–28] it has been assumed that CSDFT and SDFT calculations lead to very similar results because the term associated with the vector potential is expected to be small. In order to verify this assumption, we compare the self-consistent exchange potentials and magnetic fields for the current-carrying state of the oxygen atom for a SDFT and a CSDFT calculation. The spherical components of the exchange potentials in the two approaches are shown in Fig. 2. The potentials are hardly distinguishable on the scale of the plot which confirms the initial assumption. If one looks at the corresponding exchange magnetic fields (Fig. 3) one sees that the overall structure of the SDFT and the CSDFT results are quite similar. However, there are significant differences in magnitude close to the nucleus which can be expected to have a visible effect on the resulting chemical shifts [29]. This is also reflected by a substantial difference in the relative magnetization density $\zeta(0) = [n_\uparrow(0) - n_\downarrow(0)]/[n_\uparrow(0) + n_\downarrow(0)]$ at the nuclear position.

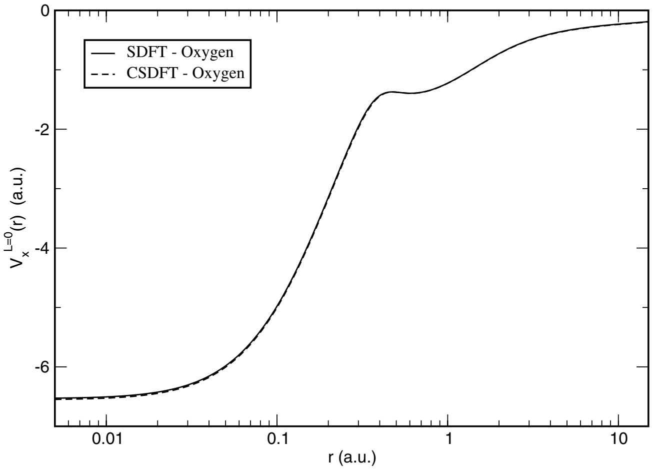

FIG. 2. Spherical component of the exchange scalar potentials for the current-carrying state of the oxygen atom computed in SDFT and CSDFT.

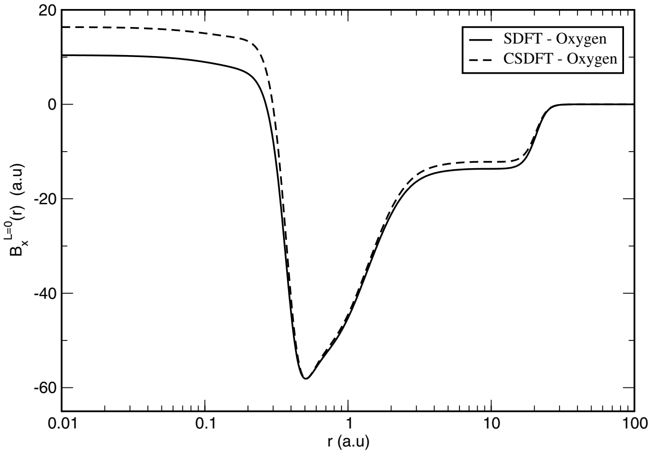

FIG. 3. Spherical component of the exchange magnetic field for the current-carrying state of the oxygen atom computed in SDFT and CSDFT.

TABLE I. Spurious energy splittings $\Delta = E(M=\pm 1) - E(M=0)$ (in kcal/mol) between current-carrying and zero-current states computed in SDFT and CSDFT.

Atom	Δ^{SDFT}	Δ^{CSDFT}	Atom	Δ^{SDFT}	Δ^{CSDFT}
B	1.66	1.38	Al	1.68	1.58
C	1.58	1.34	Si	1.76	1.63
O	2.36	2.29	S	3.04	3.01
F	2.32	2.27	Cl	3.15	3.10

For the current-carrying state of oxygen we obtain the value $\zeta(0) = -1.03 \times 10^{-3}$ in SDFT and $\zeta(0) = -1.16 \times 10^{-3}$ in CSDFT which amounts to a difference of approximately 13%. While we are confident that the difference of SDFT and CSDFT values for $\zeta(0)$ is not a numerical artifact, the absolute numbers should be read with some caution. In order to estimate the accuracy of these numerically sensitive results we have also calculated the same quantity for the nitrogen atom and obtain $\zeta(0) = -1.77 \times 10^{-3}$. This value differs by approximately 9% from the value $\zeta(0) = -1.62 \times 10^{-3}$ given in Table 10 of Ref. [9] which was obtained with a fully numerical code for spherically symmetric effective potentials.

Finally, we have calculated the spurious energy splittings between different configurations of open-shell atoms of the first two rows of the periodic table in SDFT and CSDFT. The results are collected in Table I. As mentioned before, in all cases the splittings are positive, i.e., the zero-current states are always lowest in energy. The splittings themselves are systematically lower in CSDFT than in SDFT due to the additional variational degree of freedom in the former approach. The effect of including the vector potential is more significant for the lighter atoms while for the second row the CSDFT splittings are only less than 0.1 kcal/mol smaller than the ones obtained from SDFT. Although a CSDFT approach to the degeneracy problem appeared promising our results show only a small and insufficient improvement. This finding is somewhat at odds with recent suggestions to reduce the splittings by inclusion of the current density as a variable in the construction of approximate exchange-correlation functionals [30–32]. These works, however, suggested orbital functionals in the framework of SDFT where the orbital dependence entered through the current density. No attempt was made to implement these functionals in a CSDFT framework. Finally, we point out that in a recent work [33] we showed that a pure DFT approach using the exact-exchange functional surprisingly leads to energy splittings which are almost an order of magnitude smaller than the ones obtained in SDFT.

VI. CONCLUSIONS

In this work, we have shown how one can use orbital-dependent functionals in the framework of current-spin-density functional theory. We have derived the OEP integral equations which have to be solved to obtain the corresponding exchange-correlation potentials. We have simplified these integral equations in the spirit of the well-known KLI approximation.

We have analyzed the KLI equations and the resulting potentials for open-shell atoms at zero external magnetic field and have also presented numerical results for these systems using the exact-exchange functional. We have shown that CSDFT and SDFT are equivalent for the states with zero paramagnetic current. This equivalence breaks down for current-carrying states where total energies in CSDFT are lower than those of SDFT.

We also verified that the CSDFT Kohn-Sham scheme leads to a reduction (compared to SDFT) of the spurious splittings between current-carrying and zero-current states although it is too small to recover the degeneracy between these states.

The most important result of our study, however, is the fact that the problems of LDA-type current-density functionals derived from the uniform electron gas (such as unphysical discontinuities of the corresponding exchange-correlation potentials) never appear when using orbital-dependent functionals.

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