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This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/1800743> since 2021-09-10T12:07:23Z

Published version:

DOI:10.1103/PhysRevB.102.235118

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Adiabatic Connection in Spin-Current Density Functional Theory

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(Dated: November 21, 2020)

The spin-current density functional theory (SCDFT), when formulated in a basis of Pauli spinors, provides a proper theoretical framework for the study of materials in an arbitrarily oriented external magnetic field and/or upon inclusion of spin-dependent relativistic effects, such as spin-orbit coupling. The SCDFT is formulated in terms of the particle-number density n , the Cartesian components of the magnetization m_x, m_y, m_z , the orbital-current density \mathbf{j} and the three spin-current densities $\mathbf{J}^x, \mathbf{J}^y$ and \mathbf{J}^z , where each of these density variables depends on specific blocks of the density matrix. Exchange-correlation (xc) functionals within the SCDFT should therefore depend on all of these eight fundamental density variables: $F_{xc}[n, m_x, m_y, m_z, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z]$, which makes their parametrization a formidable task. Here, we formulate the adiabatic connection of the SCDFT for a treatment of exact Fock exchange in the theory. We show how the inclusion of a fraction of Fock exchange in standard functionals of the (spin) DFT (either in their collinear or non-collinear versions: $F_{xc}[n]$, $F_{xc}[n, m_z]$, $F_{xc}[n, m_x, m_y, m_z]$) allows for the two-electron potential to depend on all those blocks of the density matrix that correspond to the eight density variables of the SCDFT, in a sensible and yet practical way. In particular, in the local-density and generalized-gradient approximations (LDA and GGA) of the SCDFT, the treatment of the current densities solely from the Fock exchange term is formally justified by the short-range behaviour of the exchange hole. We discuss that the adiabatic coupling strength parameter modulates the two-electron coupling of the orbital- and spin-current densities with the particle-number density and magnetization. Formal considerations are complemented by numerical tests on a periodic model system in the presence of spin-orbit coupling and in the absence of an external magnetic field.

Keywords:

I. INTRODUCTION

The original density functional theory (DFT) formulation of Kohn and Sham (KS-DFT)¹ for treating a non-relativistic fermionic system in an external potential is formulated entirely from the particle-number density n . The extension of this theory to the treatment of a system in an external magnetic field or to the relativistic realm requires the inclusion of additional auxiliary density variables. The first of such extensions was the spin DFT (SDFT) of von Barth and Hedin with the additional variable being the magnetization \mathbf{m} , in which the one-electron equations are expressed as Pauli-like instead of Schrödinger-like ones.² The current DFT (CDFT) with the orbital-current \mathbf{j} and current-spin DFT (CSDFT) with both \mathbf{m} and \mathbf{j} of Vignale and Rasolt allows for treating spin-(non)polarized systems in the presence of an external magnetic field oriented along the z Cartesian axis.^{3,4} For treating instead an arbitrarily oriented magnetic field, Vignale and Rasolt introduced the spin-current DFT (SCDFT), including also the spin-current densities $\mathbf{J}^x, \mathbf{J}^y$ and \mathbf{J}^z .³ This latter formulation of the theory was then generalized to the proper description of spin-dependent relativistic effects, such as spin-orbit coupling (SOC) by Bencheikh.⁵ The SCDFT is formulated in the basis of two-component Pauli spinors, which means that it can be used in tandem with approaches that allow in principal to exactly reproduce the electronic states

(positive energy solutions) of the Dirac equation.^{6–8}

The SCDFT has however so far had very limited applications in condensed matter physics, because of the intrinsic complexity of the corresponding functionals, whose dependence on the extended set of auxiliary density variables needs to be parametrized. The SCDFT calculations which have been reported thus far, have therefore made use of a functional that need not be parametrized. This is the exact exchange functional of the optimized effective potential method EXX-OEP, which was applied by Trushin and Görling to the study of topological insulators.⁹ This seminal work highlighted the importance of including the spin-current densities into the functional for a qualitatively correct description of pressure-induced topological phase transitions in SnTe and AlBi. At the same time, the EXX-OEP approach lacks of a treatment of electron correlation.

In this article, we provide a way forward by formulating the adiabatic connection of the SCDFT for a simultaneous treatment of exact Fock exchange with electron correlation. This shows how readily-available standard functionals of the (S)DFT can be extended to include a dependence on all those blocks of the density matrix that correspond to the eight density variables of the SCDFT, thus providing a formally sound and yet practical strategy for generalizing the KS-DFT to include spin-dependent relativistic effects and/or arbitrarily-oriented external magnetic fields. The formalism is particularly

simple in the LDA or GGA, in which case the application of existing (S)DFT functionals is straightforward.

II. FORMAL CONSIDERATIONS

We use the notation that bold italic latin letters are Cartesian vectors (ex. \mathbf{a} , \mathbf{A}), while bold regular font capital latin letters (ex. \mathbf{A}) are general matrices. Pauli spinor crystalline-orbitals (COs) $\Psi_{i\mathbf{k}}$ are expressed in terms of Bloch functions $\varphi_{\mu\mathbf{k}}$ as follows:

$$\Psi_{i\mathbf{k}}(\mathbf{r}) = \sum_{\mu} [\alpha c_{\mu i\mathbf{k}}^{\alpha} + \beta c_{\mu i\mathbf{k}}^{\beta}] \varphi_{\mu\mathbf{k}}(\mathbf{r}), \quad (1)$$

where the $c_{\mu i\mathbf{k}}^{\sigma}$, with $\sigma = \alpha$ or β are the associated CO coefficients and α and β are the spin eigenfunctions. The \mathbf{k} are points in the first Brillouin zone, with volume Ω . The occupied COs can be mapped to a set of density variables that allow in turn to define the exchange-correlation (xc) fields of the SCDFEFT. The first is the usual particle-number density:

$$n(\mathbf{r}) = \sum_i \int_{\Omega'_i} d\mathbf{k} \Psi_{i\mathbf{k}}^{\dagger}(\mathbf{r}) \Psi_{i\mathbf{k}}(\mathbf{r}), \quad (2)$$

where Ω'_i is the subset of \mathbf{k} points inside Ω associated with one-electron energies $\epsilon_{i\{\mathbf{k}\}} \leq \epsilon_F$ below the Fermi level ϵ_F . In systems with broken time-reversal symmetry (TRS), the states carry a non-vanishing magnetization \mathbf{m} whose Cartesian components m_t are defined as:

$$m_t(\mathbf{r}) = \sum_i \int_{\Omega'_i} d\mathbf{k} \Psi_{i\mathbf{k}}^{\dagger}(\mathbf{r}) \sigma^t \Psi_{i\mathbf{k}}(\mathbf{r}), \quad (3)$$

in which σ^t are the Pauli spin matrices and $t = x, y, z$ is a Cartesian component. The n and \mathbf{m} are convected according to the orbital-current \mathbf{j} and spin-current \mathbf{J}^t densities, respectively:

$$\mathbf{j}(\mathbf{r}) = \frac{1}{2i} \sum_i \int_{\Omega'_i} d\mathbf{k} \Psi_{i\mathbf{k}}^{\dagger}(\mathbf{r}) [\nabla \Psi_{i\mathbf{k}}(\mathbf{r})] + h.c.; \quad (4)$$

$$\mathbf{J}^t(\mathbf{r}) = \frac{1}{2i} \sum_i \int_{\Omega'_i} d\mathbf{k} \Psi_{i\mathbf{k}}^{\dagger}(\mathbf{r}) \sigma^t [\nabla \Psi_{i\mathbf{k}}(\mathbf{r})] + h.c. \quad (5)$$

where $h.c.$ denotes the Hermitian conjugate.

In the context of a relativistic fermionic system in the absence of an external magnetic field, it is worth appreciating that while a non-vanishing \mathbf{j} and \mathbf{m} only occur in systems with broken TRS (i.e. open-shell systems), the \mathbf{J}^t are present in any system with sufficiently large SOC. This means that the basic set of density variables for treating a closed-shell system in the presence of SOC is n , \mathbf{J}^x , \mathbf{J}^y and \mathbf{J}^z , while for an open-shell system, all eight density variables (n , m_x , m_y , m_z , \mathbf{j} , \mathbf{J}^x , \mathbf{J}^y and \mathbf{J}^z) are required. On the other hand, in the more general case which also includes external magnetic fields, a more ample discussion on the minimal set of basic density variables is provided by Trushin and Görling.⁹

The need for all eight density variables (n , m_x , m_y , m_z , \mathbf{j} , \mathbf{J}^x , \mathbf{J}^y and \mathbf{J}^z) in the SCDFEFT is best viewed by expressing them in terms of the elements of the momentum-space complex single-particle density matrix:

$$P_{\mu\nu\mathbf{k}}^{\sigma\sigma'\oplus\sigma''\sigma'''} = \sum_i \left\{ \left[c_{\mu i\mathbf{k}}^{\sigma} \right]^* c_{\nu i\mathbf{k}}^{\sigma'} \pm \left[c_{\mu i\mathbf{k}}^{\sigma''} \right]^* c_{\nu i\mathbf{k}}^{\sigma'''} \right\} \theta(\epsilon_F - \epsilon_{i\{\mathbf{k}\}}),$$

in which $\sigma, \sigma', \sigma'', \sigma''' = \alpha$ or β and θ is the Heaviside function. Indeed, we can identify eight distinct spin-blocks of the density matrix (the real and imaginary parts of $\mathbf{P}_{\mathbf{k}}^{\alpha\alpha\oplus\beta\beta}$, $\mathbf{P}_{\mathbf{k}}^{\alpha\alpha\ominus\beta\beta}$, $\mathbf{P}_{\mathbf{k}}^{\beta\alpha\oplus\alpha\beta}$ and $\mathbf{P}_{\mathbf{k}}^{\beta\alpha\ominus\alpha\beta}$). The eight density variables of the SCDFEFT indeed each use one of these eight distinct spin-blocks of the density matrix in their definition. For the particle-number and magnetization densities:

$$n(\mathbf{r}) = \text{Tr} \left\{ \text{Re} \left[\mathbf{P}_{\mathbf{k}}^{\alpha\alpha\oplus\beta\beta} \right] \mathbf{X}_{\mathbf{k}}(\mathbf{r}) \right\}, \quad (6a)$$

$$m_x(\mathbf{r}) = \text{Tr} \left\{ \text{Re} \left[\mathbf{P}_{\mathbf{k}}^{\beta\alpha\oplus\alpha\beta} \right] \mathbf{X}_{\mathbf{k}}(\mathbf{r}) \right\}, \quad (6b)$$

$$m_y(\mathbf{r}) = -\text{Tr} \left\{ \text{Im} \left[\mathbf{P}_{\mathbf{k}}^{\beta\alpha\ominus\alpha\beta} \right] \mathbf{X}_{\mathbf{k}}(\mathbf{r}) \right\}, \quad (6c)$$

$$m_z(\mathbf{r}) = \text{Tr} \left\{ \text{Re} \left[\mathbf{P}_{\mathbf{k}}^{\alpha\alpha\ominus\beta\beta} \right] \mathbf{X}_{\mathbf{k}}(\mathbf{r}) \right\}, \quad (6d)$$

where Tr denotes the trace operator $\text{Tr} \{ \mathbf{P}_{\mathbf{k}} \mathbf{X}_{\mathbf{k}}(\mathbf{r}) \} = \sum_{\mu\nu} \int_{\Omega} d\mathbf{k} P_{\mu\nu\mathbf{k}} X_{\mu\nu\mathbf{k}}(\mathbf{r})$ and we have defined the shorthand notation $X_{\mu\nu\mathbf{k}}(\mathbf{r}) = \varphi_{\mu\mathbf{k}}^*(\mathbf{r}) \varphi_{\nu\mathbf{k}}(\mathbf{r})$. For the current densities:

$$\mathbf{j}(\mathbf{r}) = \frac{1}{2} \text{Tr} \left\{ \text{Im} \left[\mathbf{P}_{\mathbf{k}}^{\alpha\alpha\oplus\beta\beta} \right] \mathbf{Y}_{\mathbf{k}}(\mathbf{r}) \right\}, \quad (6e)$$

$$\mathbf{J}^x(\mathbf{r}) = \frac{1}{2} \text{Tr} \left\{ \text{Im} \left[\mathbf{P}_{\mathbf{k}}^{\beta\alpha\oplus\alpha\beta} \right] \mathbf{Y}_{\mathbf{k}}(\mathbf{r}) \right\}, \quad (6f)$$

$$\mathbf{J}^y(\mathbf{r}) = \frac{1}{2} \text{Tr} \left\{ \text{Re} \left[\mathbf{P}_{\mathbf{k}}^{\beta\alpha\ominus\alpha\beta} \right] \mathbf{Y}_{\mathbf{k}}(\mathbf{r}) \right\}, \quad (6g)$$

$$\mathbf{J}^z(\mathbf{r}) = \frac{1}{2} \text{Tr} \left\{ \text{Im} \left[\mathbf{P}_{\mathbf{k}}^{\alpha\alpha\ominus\beta\beta} \right] \mathbf{Y}_{\mathbf{k}}(\mathbf{r}) \right\}, \quad (6h)$$

in which $\text{Tr} \{ \mathbf{P}_{\mathbf{k}} \mathbf{Y}_{\mathbf{k}}(\mathbf{r}) \} = \sum_{\mu\nu} \int_{\Omega} d\mathbf{k} P_{\mu\nu\mathbf{k}} \mathbf{Y}_{\mu\nu\mathbf{k}}(\mathbf{r})$ and we have used the following compact notation:

$$\mathbf{Y}_{\mu\nu\mathbf{k}}(\mathbf{r}) = \varphi_{\mu\mathbf{k}}^*(\mathbf{r}) [\nabla \varphi_{\nu\mathbf{k}}(\mathbf{r})] - [\nabla \varphi_{\mu\mathbf{k}}^*(\mathbf{r})] \varphi_{\nu\mathbf{k}}(\mathbf{r}).$$

It follows from Eq. (6) that density-functional approximations (DFAs) which depend on all density variables include the dependence on all eight blocks of the density matrix (i.e. on all parts of the wavefunction). On the other hand, conventional DFAs of the (S)DFT depending only on the particle-number and magnetization densities include only at most half (only four blocks) of the density matrix in their definition.

Minimization of the total energy of the system w.r.t. the eight density variables, under the constraint of orthonormality and N-representability leads to the Kohn-Sham SCDFEFT single-particle equations (written in the absence of external magnetic fields):^{3,5,10}

$$\left[\frac{1}{2} \left(-i\nabla + \frac{1}{c} \mathbf{A} \right)^2 + \mathbf{V} \right] \Psi_{i\mathbf{k}}(\mathbf{r}) = \epsilon_{i\mathbf{k}} \Psi_{i\mathbf{k}}(\mathbf{r}), \quad (7)$$

in which the potentials \mathbf{A} and \mathbf{V} are defined in terms of the functional derivatives of the xc energy E_{xc} .^{3,5,10}

$$\frac{1}{c}\mathbf{A} = \frac{\delta E_{xc}}{\delta \mathbf{j}} + \sum_t \boldsymbol{\sigma}^t \frac{\delta E_{xc}}{\delta \mathbf{J}^t}, \quad (8)$$

$$\mathbf{V} = V_{\text{ext}} + V_H + \frac{\delta E_{xc}}{\delta n} + \sum_t \boldsymbol{\sigma}^t \frac{\delta E_{xc}}{\delta m_t} - \frac{1}{2c^2} \mathbf{A} \cdot \mathbf{A}, \quad (9)$$

where V_{ext} is the potential from the external field created by the presence of the nuclei (including the electron-nuclear and nuclear-nuclear terms), while V_H is the Coulomb or Hartree potential. Hence, as usual, the problem of finding the ground state energy of the system comes down to finding good DFAs F_{xc} to express E_{xc} :

$$E_{xc}[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z] = \int d\mathbf{r} F_{xc}[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z]. \quad (10)$$

In Eq. (10), we can express the xc energy $E_{xc} = E_x + E_c$ in terms of independent exchange E_x and correlation E_c contributions. Let us first concentrate on approximating the larger $E_x = E_x[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z]$ from the following adiabatic connection formula:^{11,12}

$$E_x[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z] = \int_0^1 d\lambda \varepsilon_\lambda[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z]. \quad (11)$$

where ε_λ is the exchange energy at arbitrary coupling strength λ , ε_0 is the exchange energy of the non-interacting KS reference and ε_1 is the exchange energy of the fully-interacting system of interest. Following the usual procedure, we approximate the integral over the coupling strength parameter λ using a two-point quadrature and write:

$$E_x[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z] \approx aE_F[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z] + (1-a) \int d\mathbf{r} F_x[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z], \quad (12)$$

where E_F is the energy contribution from the exact non-local Fock exchange operator and can in turn be written as a sum of terms $E_n, E_{m_t}, E_{\mathbf{j}}, E_{\mathbf{J}^t}$ each depending on one of the eight distinct spin-blocks of the density matrix that define the density variables, as follows:

$$\begin{aligned} E_F &= E_n[n] + E_{\mathbf{j}}[\mathbf{j}] + \sum_t \left(E_{m_t}[m_t] + E_{\mathbf{J}^t}[\mathbf{J}^t] \right) \\ &= -\frac{1}{8} \sum_{\text{spin}} \sum_{\mu\nu} \int_{\Omega} d\mathbf{k} P_{\mu\nu\mathbf{k}}^{\sigma\sigma'\oplus\sigma''\sigma'''} K_{\mu\nu\mathbf{k}}^{\sigma\sigma'\oplus\sigma''\sigma'''}, \end{aligned} \quad (13)$$

in which $K_{\mu\nu\mathbf{k}}^{\sigma\sigma'\oplus\sigma''\sigma'''}$ is an element of the Fock exchange operator in the Bloch function basis and the sum over spin indices runs over all eight distinct spin-blocks of the density matrix as defined in Eq. (6).

For the F_x , we consider local and semi-local approximations (LDA, GGA or meta-GGA) of the SCDFt, in

which F_x depends on the value of the eight density variables at the point \mathbf{r} in space as well as (possibly) their first and second derivatives evaluated at \mathbf{r} . Pittalis *et al.*¹⁰ have provided the first exact constraints on the form of the F_x in the SCDFt by studying the short range behaviour of the exchange hole (x hole), providing expressions for the on-top x hole (containing the variables that should enter all DFAs of the SCDFt) and the curvature of the x hole (containing the variables that should enter only into meta-GGA DFAs of the SCDFt). Their results show that the current densities \mathbf{j} and the \mathbf{J}^t only enter into the functional as their square (for example $\mathbf{j} \cdot \mathbf{j}$) at the level of the curvature of the x hole, but not in the on-top x hole. This means that only meta-GGA approximations to the F_x of the SCDFt should contain an explicit dependence on \mathbf{j} and the \mathbf{J}^t , while LDA or GGA ones should not. From Eq. (12) we can then write in the LDA or GGA of the SCDFt:

$$E_x[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z] \approx aE_F[n, \mathbf{m}, \mathbf{j}, \mathbf{J}^x, \mathbf{J}^y, \mathbf{J}^z] + (1-a) \int d\mathbf{r} F_x[n, \mathbf{m}]. \quad (14)$$

Therefore, LDA or GGA approximations to F_x can be built through a usual non-collinear scheme which includes no explicit dependence on the current densities.¹³⁻¹⁷ Crucially, while all eight density variables enter into the definition of E_F in a uniform and consistent way, this is not the case for F_x . Indeed, the four blocks of the density matrix that define the current densities \mathbf{j} and \mathbf{J}^t from Eq. (6) only enter into (semi-)local approximations to F_x in those high-order terms of the Taylor expansion that define meta-GGA functionals.

In this article, we then disregard the contribution of the current-densities to the smaller E_c , such that we write $E_c = E_c[n, \mathbf{m}]$, and thus assume (as conventionally done) that we can write both the exchange and correlation parts of the functional using a common set of density variables. This defines a practical yet formally sound strategy for the definition of DFAs of the SCDFt, which is consistent with the current state of the art. As a matter of fact, hybrid GGAs defined through the non-relativistic equivalent of Eq. (14) have historically formed some of the most successful DFAs and there is no *a priori* reason to expect differently for the SCDFt.^{12,18-25}

The consequence of Eq. (14) is that — unlike in the standard KS theory — the coupling strength parameter λ of Eq. (11) not only “turns on” the electron-electron $1/r_{ij}$ interaction, but, in doing so, also modulates the coupling of the current densities \mathbf{j} and the \mathbf{J}^t to the other density variables n and the m_t . As we show below in section IV, this allows to properly relax all density variables through the self-consistent field (SCF) process and obtain physically meaningful solutions, when applied to the study of actual materials.

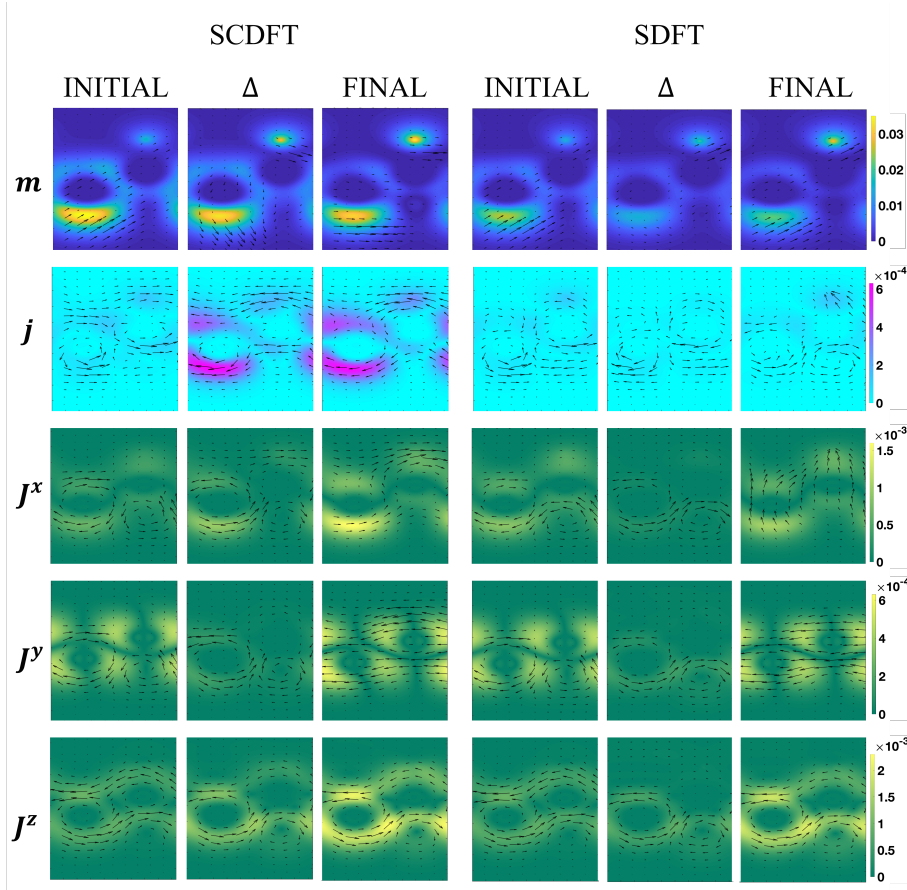


FIG. 1: Color maps of the spatial distribution of the auxiliary density variables of the SCDFT for an infinite radical chain of Ge_2H . The periodic direction is along the x axis and the plots are provided in the xy plane. The color identifies the absolute value of the density variables while the length and direction of the superimposed black arrows represent the magnitude and direction of the in-plane (x and y) Cartesian components of the density variables. The spatial distribution is reported at the start of the SCF process (“Initial”) and at the end (“Final”). The difference between the two is also reported (Δ). The left plots are from the SCDFT while the right plots are from the SDFT.

III. COMPUTATIONAL DETAILS

Relativistic two-component periodic SCDFT calculations are performed on an infinite chain of Ge_2H , with three atoms in the primitive unit cell and a lattice parameter of 2.464 \AA . The chain of Ge_2H provides us with a very simple model system with both space-inversion and time-reversal symmetries broken. Despite its simplicity, it nonetheless allows us to display all of the practical benefits of the proposed approach. All calculations are performed with our self-consistent treatment of SOC in a two-component spinor basis,^{16,26,27} as implemented in a developmental version of the CRYSTAL17 code.^{28,29} Crystalline orbitals are expressed as a linear combination of atom-centered atomic orbitals.³⁰ Details on the used basis set and pseudopotential, as well as the numerical integration on the direct-space DFT grid can be found

in Ref. 27. Convergence is achieved when the difference in energy between two successive cycles does not exceed 1×10^{-10} a.u. Calculations are performed using the SVWN5 exchange-correlation (xc) functional of the LDA in its canonical non-collinear formulation.^{13,31,32} Integration of the density matrix and diagonalization of the Fock matrix is performed in reciprocal space, with sampling on 100 points. A Fermi smearing was applied with a smearing width of 1×10^{-3} a.u. Truncation of the Coulomb and exchange infinite lattice series is controlled by five parameters, which are here set to 8 8 8 8 20 (keyword TOLINTEG, see user’s manual for more details).³³ The initial guess magnetization is obtained from a scalar relativistic (SR) atomic Hartree-Fock calculation and rotated, using an approach which we discuss elsewhere, unless otherwise specified.¹⁶ The orientation of the vector \underline{w} in Eq. (60) of Ref. 16 (which roughly corresponds

to the orientation of the guess magnetization on each atom) is along the xyz diagonal, unless explicitly stated otherwise. Calculations were performed both with and without the spin-dependent part of the pseudopotential (i.e. the spin-orbit effective core potential, SOREP) to confirm the SOC-induced origin of the orbital-current \mathbf{j} and spin-current \mathbf{J}^x , \mathbf{J}^y , \mathbf{J}^z densities.

IV. NUMERICAL CONSIDERATIONS

To show the practical benefits of the SCDFE strategy formally discussed in section II, it is insightful to look at the spatial distributions of the auxiliary density variables and how they evolve during the SCF procedure. In Fig. 1, we report color maps in the xy plane of (from top to bottom) the \mathbf{m} , \mathbf{j} , \mathbf{J}^x , \mathbf{J}^y and \mathbf{J}^z as obtained after the first diagonalization (denoted by “Initial” above the left panels), at the end of the SCF (denoted by “Final”), along with their difference (denoted by Δ). Data are reported from a hybrid functional of the SCDFE (Becke’s half-and-half, BHandH, with a fraction $a = 0.5$ of Fock exchange¹²) as well as from a reference LDA functional of the SDFT.

While in the SCDFE calculation all density variables evolve jointly and in a significant way during the SCF procedure, the SDFT one provides a minor relaxation of the density variables after the first diagonalization. With the SCDFE, the orbital relaxation is particularly strong on both the magnetization \mathbf{m} (that completely rotates from the xy direction of the initial guess to the x direction) and orbital current density \mathbf{j} (that is very small at the start and builds up during the SCF), as well as in the \mathbf{J}^x and \mathbf{J}^z spin current densities. From the formal arguments elaborated above, this is a manifestation of the fact that the standard SDFT two-electron potential only uses four of the eight blocks of the density matrix in its definition and can therefore not couple the n and \mathbf{m} with the current densities through the two-electron term. As a matter of fact, this implies that the result of an SDFT calculation largely depends on the choice of

the initial guess for the orbitals in the SCF procedure. This is investigated in further detail in Tables S1-S2 of the ESI,³⁴ (see also Refs. 35–41 therein) where we provide values of the total energies and expectation values of the magnetization from the SDFT and SCDFE calculations as obtained by using different orbitals as a starting guess for the SCF procedure. The tables, along with the associated color maps in Figure S1, show that the SDFT calculations lead to very different values for the magnetization of the final solution, precisely because of their inability to rotate \mathbf{m} during the SCF procedure (i.e. lack of local magnetic-torque) and also to relax the other auxiliary density variables. On the other hand, consistent final solutions are always obtained from SCDFE calculations, regardless of the starting guess, so long as a sufficiently large fraction of Fock exchange is used in the calculation (here found to be $a \geq 0.25$). The fact that we find consistent solutions starting from the familiar value of $a = 1/4$ is likely not to be a coincidence. Indeed, the arguments formulated by Perdew *et al.*⁴² for including such an optimal fraction of Fock exchange in the xc energy E_{xc} are completely independent of the particular set of density variables that enter into the functional, and therefore there is no reason to believe that they should not hold in the context of the SCDFE formulation.

V. CONCLUSIONS

In conclusion, in this article we have discussed the adiabatic connection for exact Fock exchange in the context of the SCDFE. We have shown both formally and through numerical calculations that such a formulation: i) allows to easily include all pieces of the wavefunction in the two-electron potential, which ensures the proper relaxation of the eight relevant density variables along the SCF process, and ii) the formalism is particularly simple within the LDA or GGA of the SCDFE, in which case SCDFE calculations are made possible starting from standard LDA or GGA functionals of the (S)DFT by inclusion of a fraction of Fock exchange.

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¹ W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

² U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

³ G. Vignale and M. Rasolt, Phys. Rev. B **37**, 10685 (1988).

⁴ G. Vignale and M. Rasolt, Phys. Rev. Lett. **59**, 2360 (1987).

⁵ K. Bencheikh, J. Phys. A **36**, 11929 (2003).

⁶ T. Saue, ChemPhysChem **12**, 3077 (2011).

⁷ M. Reiher and A. Wolf, *Relativistic quantum chemistry: the fundamental theory of molecular science* (John Wiley & Sons, 2014).

⁸ M. Reiher and A. Wolf, The Journal of chemical physics **121**, 10945 (2004).

⁹ E. Trushin and A. Görling, Phys. Rev. B **98**, 205137 (2018).

¹⁰ S. Pittalis, G. Vignale, and F. Eich, Phys. Rev. B **96**, 035141 (2017).

¹¹ J. Harris, Phys. Rev. A **29**, 1648 (1984).

¹² A. D. Becke, The J. Chem. Phys. **98**, 1372 (1993).

¹³ J. Kubler, K.-H. Hock, J. Sticht, and A. Williams, J. Phys. F **18**, 469 (1988).

¹⁴ J. E. Peralta, G. E. Scuseria, and M. J. Frisch, Phys. Rev. B **75**, 125119 (2007).

¹⁵ G. Scalmani and M. J. Frisch, J. Chem. Theo. Comput. **8**, 2193 (2012).

¹⁶ J. K. Desmarais, J.-P. Flament, and A. Erba, J. Chem. Phys. **151**, 074107 (2019).

- ¹⁷ C. R. Jacob and M. Reiher, *International Journal of Quantum Chemistry* **112**, 3661 (2012).
- ¹⁸ C. Adamo and V. Barone, *J. Chem. Phys.* **110**, 6158 (1999).
- ¹⁹ D. I. Bilc, R. Orlando, R. Shaltaf, G.-M. Rignanese, J. Íñiguez, and P. Ghosez, *Phys. Rev. B* **77**, 165107 (2008).
- ²⁰ A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- ²¹ A. D. Becke, *J. Chem. Phys.* **107**, 8554 (1997).
- ²² J. Heyd, G. E. Scuseria, and M. Ernzerhof, *J. Chem. Phys.* **118**, 8207 (2003).
- ²³ F. A. Hamprecht, A. J. Cohen, D. J. Tozer, and N. C. Handy, *J. Chem. Phys.* **109**, 6264 (1998).
- ²⁴ V. N. Staroverov, G. E. Scuseria, J. P. Perdew, E. R. Davidson, and J. Katriel, *Phys. Rev. A* **74**, 044501 (2006).
- ²⁵ A. Erba, *J. Phys.: Condens. Matter* **29**, 314001 (2017).
- ²⁶ J. K. Desmarais, J.-P. Flament, and A. Erba, *J. Phys. Chem. Lett.* **10**, 3580 (2019).
- ²⁷ J. K. Desmarais, J.-P. Flament, and A. Erba, *Physical Review B* **101**, 235142 (2020).
- ²⁸ R. Dovesi, A. Erba, R. Orlando, C. M. Zicovich-Wilson, B. Civalieri, L. Maschio, M. Rérat, S. Casassa, J. Baima, S. Salustro, et al., *WIREs Comput. Mol. Sci.* **8**, e1360 (2018).
- ²⁹ A. Erba, J. Baima, I. Bush, R. Orlando, and R. Dovesi, *J. Chem. Theory Comput.* **13**, 5019 (2017).
- ³⁰ J. Desmarais, A. Erba, and R. Dovesi, *Theor. Chem. Acc.* **137**, 28 (2018).
- ³¹ P. A. Dirac, in *Math. Proc. Camb. Philo. Soc.* (Cambridge University Press, 1930), vol. 26-3, pp. 376–385.
- ³² S. H. Vosko, L. Wilk, and M. Nusair, *Can. J. Phys.* **58**, 1200 (1980).
- ³³ R. Dovesi, V. Saunders, C. Roetti, R. Orlando, C. Zicovich-Wilson, F. Pascale, B. Civalieri, K. Doll, N. Harrison, I. Bush, et al., *CRYSTAL17 User's Manual*, Università di Torino, Torino (2017), <http://www.crystal.unito.it>.
- ³⁴ See Supplemental Material at URL for distributions of the auxiliary density variables and total energies, expectation values of the magnetization Cartesian components for different starting guesses and fractions of Fock exchange and a discussion on the effect of SDFT vs. SCDFE for the calculation of the spin-orbit splitting of the band structure.
- ³⁵ S.-M. Huang, S.-Y. Xu, I. Belopolski, C.-C. Lee, G. Chang, B. Wang, N. Alidoust, G. Bian, M. Neupane, C. Zhang, et al., *Nat. Comms.* **6**, 1 (2015).
- ³⁶ B. Lv, H. Weng, B. Fu, X. P. Wang, H. Miao, J. Ma, P. Richard, X. Huang, L. Zhao, G. Chen, et al., *Phys. Rev. X* **5**, 031013 (2015).
- ³⁷ S.-Y. Xu, I. Belopolski, N. Alidoust, M. Neupane, G. Bian, C. Zhang, R. Sankar, G. Chang, Z. Yuan, C.-C. Lee, et al., *Science* **349**, 613 (2015).
- ³⁸ J. Buckeridge, D. Jevdokimovs, C. Catlow, and A. Sokol, *Phys. Rev. B* **93**, 125205 (2016).
- ³⁹ J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- ⁴⁰ D. Figgen, K. A. Peterson, M. Dolg, and H. Stoll, *J. Chem. Phys.* **130**, 164108 (2009).
- ⁴¹ H. Stoll, B. Metz, and M. Dolg, *J. Comput. Chem.* **23**, 767 (2002).
- ⁴² J. P. Perdew, M. Ernzerhof, and K. Burke, *J. Chem. Phys.* **105**, 9982 (1996).