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On the Fundamental Role of Fock Exchange in Relativistic Density Functional Theory

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Abstract

We perform a formal analysis of relativistic density functional theory for the treatment of spin-orbit coupling (SOC), non-collinear magnetization (NCM) and orbital current-density (OCD). We identify specific components of the spinors (namely, those mapped onto imaginary diagonal spin-blocks of the density matrix) that arise from the SOC operator and define the OCD. We show that these pieces of the spinors only enter in the bi-electronic part of the potential through the exact Fock exchange (FE) operator. The lack of FE therefore leads to a correspondingly incorrect physical description of SOC, NCM and OCD. This analysis is complemented with an illustrative example, where we show that, while in the absence of FE, the theory fails even at reproducing the expected right-hand relationship between the NCM and OCD, its inclusion provides results that match those from a reference SOC configuration-interaction calculation.

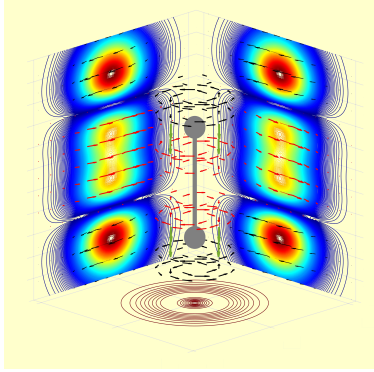


Figure 1: TOC

The density functional theory (DFT) arguably represents the most popular method for the first-principles non- or scalar-relativistic description of the electronic properties of extended systems.¹⁻⁴ Within the plethora of density functional approximations (DFAs) that have been devised in the last 50 years, hybrid ones, which include a fraction of exact non-local Fock exchange in their definition, are particularly accurate.⁵ Indeed, hybrid DFAs, first formally introduced by Becke in 1993 through the adiabatic connection theorem,⁶ partially correct for the self-interaction error present in local or semi-local formulations of the DFT.⁷⁻¹⁰ As such, hybrid functionals have proven to be particularly effective in the treatment of systems characterized by localized electronic states, like in strongly-correlated materials, defective materials, and generally for the description of insulators.¹¹⁻¹⁵

In this Letter, we provide further theoretical arguments on the benefits of hybrid DFAs, specifically in the context of relativistic DFT, when a spin-orbit coupling (SOC) operator is included in the Hamiltonian and treated self-consistently, such that the magnetization is non-collinear and there is a non-vanishing orbital current-density.

A fully relativistic description of the electronic structure of a quantum-mechanical system requires the Dirac equation to be solved (instead of the Schrödinger equation) and this leads to a four-component wavefunction (instead of a one-component wavefunction). Alternatively, the α and β small components of the wavefunction can be passed onto the Hamiltonian using appropriate decoupling transformations, resulting in the well-known two-component

relativistic theories.^{16–25}

A well-defined fully relativistic formulation exists for the DFT, based on appropriate density variables.^{26–28} In particular, it has been shown that in the two-component approach the appropriate density variables from which DFAs have to be built are the particle-number density n , the magnetization \mathbf{m} (or its curl) and the orbital current-density \mathbf{j} .^{27,29} Unfortunately, in practice, there is a lack of any relativistic DFA within the two-component approach (i.e. no exchange-correlation functionals have been devised of the type $F_{xc}[n, \mathbf{m}, \mathbf{j}]$ for the local-density approximation, LDA, of the type $F_{xc}[n, \mathbf{m}, \mathbf{j}, \text{grad}(n, \mathbf{m}, \mathbf{j})]$, for the generalized gradient approximation, GGA, and of the type $F_{xc}[n, \mathbf{m}, \mathbf{j}, \text{grad}(n, \mathbf{m}, \mathbf{j}), \text{grad}2(n, \mathbf{m}, \mathbf{j})]$ for the meta-GGA, where $\text{grad}(n, \mathbf{m}, \mathbf{j})$ and $\text{grad}2(n, \mathbf{m}, \mathbf{j})$ are the sets of first and second derivative variables associated to the three density variables, respectively).^{26,27} In the four-component approach, the appropriate density variable is the so-called four-current \mathbf{J} , but, also in this case, no explicit functionals have been devised using all of its four components.^{26–28}

Therefore, relativistic DFT calculations must be performed by modifying existing non-relativistic, one-component functionals, for which several formulations have been suggested.^{30–34} The most straightforward way of generalizing existing non-relativistic functionals to the two-component relativistic approach is known as the “collinear formulation” of the DFT, where only the particle-number density and one of the three components of the magnetization are used (namely, n and m_z).³⁴ The collinear formulation does not result in a rotationally invariant theory. Otherwise, the one-component, non-relativistic functionals are typically “hacked” in such a way to plug into them the particle-number density and the three components of the magnetization vector (namely, n and \mathbf{m}) within so-called “non-collinear formulations” of the DFT.^{30–32,35–44} In the four-component approach, the wavefunction is usually decomposed into n and m_z or n and \mathbf{m} as if it were a two-component wavefunction, using a very similar procedure.^{28,45} At variance with previous attempts, we have recently shown that the procedure from which the full n and \mathbf{m} are plugged into the functional can result in a fully rotationally invariant theory using a new non-collinear prescription.³⁰ However, the problem

remains that such non-collinear formulations of the DFT still do not make any explicit use of the orbital current-density \mathbf{j} in the definition of the exchange-correlation functional.

The orbital current-density \mathbf{j} is a current of charges induced by the magnetic field created through the SOC effect. Actually, a similar charge current can also be created in the non-relativistic theory, through application of external magnetic fields. In this respect, we note that, for over a decade, work has been done towards the inclusion of the current-density in the context of the treatment of external magnetic fields in time-dependent DFT.^{46–48} This non-relativistic current-density is however distinct from the one relevant to this Letter, being defined in terms of one-component eigenfunctions of the Kohn-Sham Hamiltonian, instead of two- or four-component spinors. The corresponding theory is therefore not applicable to the treatment of the relativistic SOC-induced current-density discussed here.

In this Letter, through a formal analysis of the relativistic DFT, we first identify specific components of the spinors (i.e. those mapped into the imaginary diagonal spin-blocks of the density matrix), which are due to the SOC, and which define the orbital current-density. Then, we show how these components (and thus the physics conveyed in the orbital current-density) do not enter into the definition of the electron-electron potential unless a Fock exchange operator is included in the Hamiltonian. Fock exchange thus allows for a proper treatment of not only local magnetic torque,²⁵ but also of the orbital-relaxation contribution to the orbital current-density, which is crucial when a SOC operator is included in the Hamiltonian for open-shell electronic configurations. We first discuss these aspects formally and then through numerical examples from relativistic DFT calculations on the I_2^+ molecule.

Our analysis is performed for the case where the wavefunction is described using complex two-component spinors Ψ_i , which are expanded in a finite set of n_f basis functions χ_μ as:

$$\Psi_i(\mathbf{r}) = \sum_{\mu=1}^{n_f} c_{\mu,i}^\alpha \begin{pmatrix} \chi_\mu(\mathbf{r}) \\ 0 \end{pmatrix} + c_{\mu,i}^\beta \begin{pmatrix} 0 \\ \chi_\mu(\mathbf{r}) \end{pmatrix}. \quad (1)$$

The fact that we formally use two- instead of four-component spinors does not take away

from the generality of the analysis. This is because, as previously stated, in practice also in the four-component case, the full four-current \mathbf{J} is not used for evaluating the xc potential term. So the four-component wavefunction needs first to be expressed in terms of quantities which originate from the two-component theory (n and \mathbf{m} in the non-collinear case, or n and m_z in the collinear case) to permit the use of existing functionals.^{26–28,45}

We start from the formal definition of the three relevant density variables (n , \mathbf{m} , and \mathbf{j}) in terms of occupied two-component spinors. The particle-number density is simply:^{26,27,49}

$$n(\mathbf{r}) \equiv \sum_i^{\text{occ}} \Psi_i^\dagger(\mathbf{r}) \Psi_i(\mathbf{r}) . \quad (2)$$

The three Cartesian components of the magnetization m_c (with $c = x, y, z$) are defined as:

$$m_c(\mathbf{r}) \equiv \sum_i^{\text{occ}} \Psi_i^\dagger(\mathbf{r}) \hat{\sigma}_c \Psi_i(\mathbf{r}) , \quad (3)$$

where the $\hat{\sigma}_c$ are the usual 2×2 complex Pauli matrices. Finally, the orbital current-density reads:^{26,27,49}

$$\mathbf{j}(\mathbf{r}) \equiv \frac{1}{2i} \sum_i^{\text{occ}} \Psi_i^\dagger(\mathbf{r}) [\nabla \Psi_i(\mathbf{r})] - [\nabla \Psi_i(\mathbf{r})]^\dagger \Psi_i(\mathbf{r}) . \quad (4)$$

In order to further analyze how different components of the occupied spinors enter into the definition of the density variables and potential, we introduce the single-particle density matrix \mathbf{D} , whose elements are:

$$[D^{\sigma\sigma'}]_{\mu\nu} \equiv \sum_i^{\text{occ}} [c_{\mu i}^\sigma]^* c_{\nu i}^{\sigma'} , \quad (5)$$

where $\sigma, \sigma' = \alpha$ or β label the different spin-blocks of the matrix. In the following, it proves useful to adopt the compact notation:

$$\mathbf{D}^{\sigma\sigma' \oplus \sigma''\sigma'''} \equiv \mathbf{D}^{\sigma\sigma'} + \mathbf{D}^{\sigma''\sigma'''} ; \quad (6)$$

$$\mathbf{D}^{\sigma\sigma' \ominus \sigma''\sigma'''} \equiv \mathbf{D}^{\sigma\sigma'} - \mathbf{D}^{\sigma''\sigma'''} . \quad (7)$$

For the particle-number density and magnetization, using the definition of the Pauli matrices, and by exploiting the Hermiticity of the density matrix, we get the following expressions:

$$n(\mathbf{r}) = \sum_{\mu\nu} \Re [D^{\alpha\alpha\oplus\beta\beta}]_{\mu\nu} \chi_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r}) ; \quad (8)$$

$$m_x(\mathbf{r}) = \sum_{\mu\nu} \Re [D^{\alpha\beta\oplus\beta\alpha}]_{\mu\nu} \chi_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r}) ; \quad (9)$$

$$m_y(\mathbf{r}) = \sum_{\mu\nu} \Im [D^{\alpha\beta\ominus\beta\alpha}]_{\mu\nu} \chi_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r}) ; \quad (10)$$

$$m_z(\mathbf{r}) = \sum_{\mu\nu} \Re [D^{\alpha\alpha\ominus\beta\beta}]_{\mu\nu} \chi_{\mu}(\mathbf{r})\chi_{\nu}(\mathbf{r}) . \quad (11)$$

It can be seen that: i) n and m_z only depend on the real part of the $\alpha\alpha$ and $\beta\beta$ diagonal spin-blocks of the density matrix; ii) m_x on the real part of the $\alpha\beta$ and $\beta\alpha$ off-diagonal spin-blocks of the density matrix; iii) m_y on the imaginary part of the $\alpha\beta$ and $\beta\alpha$ off-diagonal spin-blocks of the density matrix; iv) the imaginary part of the $\alpha\alpha$ and $\beta\beta$ diagonal spin-blocks of the density matrix does not enter into the definition of n and \mathbf{m} .

In contrast, proceeding similarly for the orbital current-density \mathbf{j} , we obtain:

$$\mathbf{j}(\mathbf{r}) = \frac{1}{2} \sum_{\mu\nu} \Im [D^{\alpha\alpha\oplus\beta\beta}]_{\mu\nu} \{ \chi_{\mu}(\mathbf{r})[\nabla\chi_{\nu}(\mathbf{r})] - [\nabla\chi_{\mu}(\mathbf{r})]\chi_{\nu}(\mathbf{r}) \} .$$

Therefore, all terms involving contributions from the $\Im\mathbf{D}^{\alpha\alpha\oplus\beta\beta}$ components of the spinors are cancelled in Eqs. (8-11), but these are the only terms that survive in the definition of the orbital current-density \mathbf{j} .

We summarize these findings in Figure 2, where a schematic representation of the spin block structure of the density matrix is given, within a two-component formulation of the relativistic DFT. Inside each spin-block, the first line reports the corresponding density variables. In the second line, we list those bi-electronic operators that make use of the corresponding spin-block of the density matrix in the definition of the electron-electron potential. It turns out that those bi-electronic operators that are included in non-hybrid

formulations of the DFT (namely, the Coulomb \mathbf{C} - also referred to as Hartree - and exchange-correlation \mathbf{V}_{xc} ones) do not make use of the imaginary $\alpha\alpha$ and $\beta\beta$ blocks of the density matrix. It can be shown that these blocks (used in the definition of the orbital current-density) are only included into the electron-electron potential through the exchange operator \mathbf{K} , whose imaginary part of the matrix elements reads:

$$\Im [K^{\sigma\sigma}]_{\mu\nu} = - \sum_{\rho,\gamma} \Im [D^{\sigma\sigma}]_{\rho\gamma} (\chi_\mu\chi_\gamma|\chi_\nu\chi_\rho), \quad (12)$$

where $(\chi_\mu\chi_\gamma|\chi_\nu\chi_\rho)$ are bi-electronic integrals, which are purely real in direct space.

So far, we have shown that the imaginary $\alpha\alpha$ and $\beta\beta$ blocks of the density matrix enter into the Kohn-Sham bi-electronic potential only if the Fock operator is included (i.e. only if hybrid functionals are considered), and that these are precisely the blocks of the density matrix which are used to build the orbital current-density.

Moreover, these imaginary components are non-zero only if a SOC operator is included in the Hamiltonian. Indeed, they arise from the presence of the corresponding purely imaginary diagonal spin-blocks of the SOC operator, which satisfy the relation $\Im \mathbf{h}_{\text{SOC}}^{\alpha\alpha} = -\Im \mathbf{h}_{\text{SOC}}^{\beta\beta}$ so that the SOC operator builds non-zero elements of $\Im \mathbf{D}^{\alpha\alpha\oplus\beta\beta}$, and correspondingly a non-vanishing orbital current-density, only in open-shell electronic configurations. Therefore, the role of exact Fock exchange is crucial for the treatment of SOC in open-shell systems.

We now discuss the effect of Fock exchange within a relativistic DFT approach on the description of the non-collinear magnetization and orbital current-density, through test calculations on a representative example: the I_2^+ open-shell molecule. All relativistic DFT calculations, with inclusion of SOC, are performed with a developmental version of the public CRYSTAL program,^{50,51} where we have recently implemented a self-consistent treatment of SOC in a two-component formalism.^{25,30} We also perform spin-orbit configuration-interaction (SO-CI) calculations with the EPCISO and CIPSI programs^{52,53} to have a reference description from a correlated wavefunction approach. Computational details on these calculations

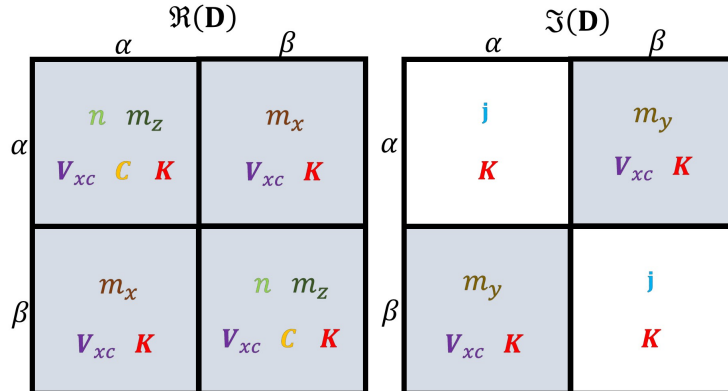


Figure 2: Schematic diagram of the spin-block structure of the complex density matrix in the framework of two-component relativistic DFT. In each block, the first line reports the density variables which make use of the corresponding spin-block in their definition. The second line indicates bi-electronic operators which make use of the corresponding spin-block in the definition of the electron-electron potential. The grey blocks are those used in non-hybrid calculations. It is clear that the diagonal spin-blocks of the imaginary part of the density matrix are only used for constructing the orbital current-density \mathbf{j} and are only included in the definition of the bi-electronic potential if the exchange operator \mathbf{K} is used in the Hamiltonian.

are provided in the ESI.

The I_2^+ linear molecule has the molecular axis along z . All calculations are performed by using the scalar-relativistic orbitals as a starting guess. Figure 3a shows the spatial distribution of the magnetization in the xz plane (the color map describes the absolute value of the magnetization $|\mathbf{m}|$, in atomic units, while black arrows describe the orientation and length of the Cartesian components of the magnetization in the selected plane). The reported values are from the reference SO-CI calculation and show a magnetization basically parallel to the molecular axis everywhere in space. Figures 3b – c show the spatial distribution of the reference SO-CI orbital current-density in the xz and xy planes, respectively, where it can be seen that: i) the orbital current-density is always perpendicular to the axis of the molecule; ii) it forms circles in the xy plane; iii) the magnetization and orbital current-density obey a right-hand rule relationship, as could be expected from Ampere’s law.

In order to investigate the effect of Fock exchange in the description of the electronic

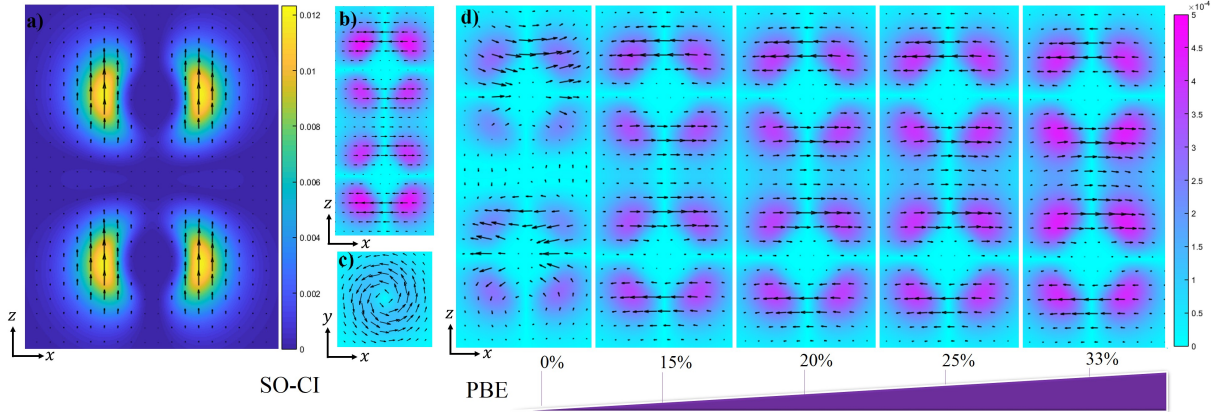


Figure 3: Spatial distribution of (a) SO-CI magnetization in the xz plane; (b) SO-CI orbital current-density in the xz plane; (c) SO-CI orbital current-density in the xy plane; (d) DFT and SO-CI orbital current-density in the xz plane (the PBE functional of the GGA is used for DFT calculations, with inclusion of different fractions of Fock exchange). All quantities are plotted in atomic units. The color map describes the absolute value of the reported quantity ($|\mathbf{m}|$ or $|\mathbf{j}|$), while black arrows describe the orientation and length of the Cartesian components of the magnetization in the selected plane.

properties of the system, we have performed relativistic DFT calculations with the PBE exchange-correlation GGA-type functional,⁵⁴ in its non-collinear “signed-canonical” formulation,³⁰ and with hybrid versions of it by inclusion of different fractions of Fock exchange (15%, 20%, 25%, and 33%). As expected from the formal analysis above, the spatial distribution of the magnetization from all DFT calculations (given in the ESI) is found to be qualitatively similar to the reference SO-CI description in all cases. This is no longer the case when it comes to the orbital current-density. Figure 3d shows the computed spatial distribution of the orbital current-density in the xz plane with the PBE functional for different fractions of Fock exchange. It is evident that the pure PBE result with no Fock exchange yields an orbital current-density distribution that is very different from the reference SO-CI result and, moreover, fails at satisfying the expected right-hand rule relationship with its magnetization. In fact, the PBE orbital current-density globally points in the opposite direction to all other calculations, while the magnetization does not, which indicates a complete failure in consistently coupling \mathbf{m} with \mathbf{j} . From the formal analysis above, this is due to the lack of the inclusion of the imaginary part of the diagonal spin-blocks of the density

matrix (i.e. those used in the definition of the orbital current-density) in the bi-electronic part of the potential. On the other hand, as soon as a fraction of Fock exchange is included in the functional, as a result of the inclusion of the $\Im\mathbf{D}^{\alpha\alpha\oplus\beta\beta}$ components of the spinors in the bi-electronic potential, the orbital current-density becomes consistent with the magnetization and with a spatial distribution qualitatively similar to the reference SO-CI result. As the fraction of Fock exchange increases, the orbital current-density becomes larger, particularly so in the bonding region. In this case, the best quantitative agreement with the reference SO-CI result is obtained with a 20% fraction of Fock exchange. In the ESI, we provide further views of the orbital current-density in the xz plane at elevated values of y (specifically $y = 1$ bohr and $y = 2$ bohr), to complement the results at $y = 0$ (center of the molecule) of Figure 3*d*. We also provide values of the integrated Cartesian components of the magnetization and orbital current-density in the plane of Figure 3*d*, where it can be seen that the inclusion of a small fraction of Fock exchange in the Hamiltonian yields values of the integrated components closer to the SO-CI result.

Further insight into the failure of non-hybrid exchange-correlation functionals in the description of the orbital current-density is also provided in the ESI where the orbital-relaxation effect on \mathbf{j} is shown along the self-consistent field (SCF) process: while the orbital current-density significantly evolves during the SCF for hybrid calculations, it almost does not change for non-hybrid functionals so that the final description turns out to depend almost entirely on the starting guess.

To summarize, in this Letter we have shown that, in the context of relativistic DFT, the bi-electronic operator makes no use of those components of the spinors that are mapped onto imaginary diagonal spin-blocks of the Kohn-Sham density matrix. This leads to a failure in properly coupling the orbital current-density with the magnetization during the SCF process and results in a poor description of the electronic structure in the presence of spin-orbit coupling. Moreover, we have shown that this problem can be rectified by the inclusion of a fraction of exact non-local Fock exchange in the Kohn-Sham Hamiltonian, as

done in hybrid functionals. Finally, we note that the limitations of non-hybrid formulations of the DFT discussed in this Letter arise from the lack of any explicit dependence on the orbital current-density of any of the existing exchange-correlation functionals.

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Supporting Information Available

Computational details, spatial distribution of the magnetization from DFT and HF calculations, discussion on the orbital-relaxation effect on the description of the orbital current-density, integrated magnetization and orbital current-density Cartesian components, elevated views of the orbital current-density.

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