Exact-Exchange Spin-Current Density-Functional Theory

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A spin-current density-functional theory (SCDFT) is introduced, which takes into account the currents of the spin density and thus currents of the magnetization in addition to the electron density, the noncollinear spin density, and the density current, which are considered in standard current-spin-density-functional theory. An exact-exchange Kohn-Sham formalism based on SCDFT is presented, which represents a general framework for the treatment of magnetic and spin properties. As an illustration, an oxygen atom in a magnetic field is treated with the new approach.

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Density-functional methods [1], in particular, Kohn-Sham (KS) methods, have developed into the most widely used approach to investigate electronic structures of molecules, clusters, surfaces, or solids. However, magnetic properties and generally properties and quantities related to currents cannot be described with the available KS methods relying on standard spin-density-functional theory, which is based on the spin density alone. In order to treat magnetic effects due to both spin and currents within a density-functional theory (DFT) framework, Vignale and Rasolt introduced a current-spin-density-functional formalism almost 20 years ago [2,3]. Despite the fact that magnetic effects are ubiquitous and of paramount importance, current-spin-density-functional theory (CSDFT) did not play a significant role in practice so far. The reason is that sufficiently accurate approximations for the required but not exactly known current-spin-density functionals for exchange and correlation are not available.

In recent years exact-exchange (EXX) KS methods have been developed, which treat exchange energy and potential exactly and therefore do not require any approximate exchange functionals [4]. These EXX KS methods yield band structures for semiconductors and generally one-particle spectra of electronic systems, which are strongly improved compared to methods based on the local density approximation (LDA) or generalized gradient approximations [4,5]. A development of EXX current-density-functional methods therefore seems highly promising [6].

CSDFT depends on seven variables: the electron density, the x, y, z components of the spin density, and the x, y, z components of the paramagnetic density current [2,3]. However, as demonstrated below, in general, also currents of the spin density, i.e., currents of the magnetization, may occur in the presence of magnetic fields. For a complete description of magnetic effects it therefore seems desirable to go beyond CSDFT and to include also the x, y, z components of the currents of the x, y, z components of the spin density, i.e., to include 9 more variables leading to a total of 16 variables. The resulting formalism shall be called spin-current density-functional theory (SCDFT) as opposed to current-spin-density-functional theory in order to emphasize that it depends on spin-current densities. (The term spin-current density from now on shall include, besides actual spin-current densities, also standard current densities as well as noncollinear spin densities including the standard electron density.) In this Letter we first introduce the basic SCDFT, then present an exact-exchange KS formalism based on SCDFT, and finally consider as an illustrative example an oxygen atom in a magnetic field.

The Hamiltonian operator of an electronic system in a magnetic field is given by

$$\begin{aligned}\hat{H} &= \hat{T} + \hat{V}_{\mathrm{ee}} + \sum_{i=1}^{N}\bigg[v_{\mathrm{ext}}(\mathbf{r}_i) + \frac{1}{2}\mathbf{p}_i\cdot\mathbf{A}(\mathbf{r}_i) + \frac{1}{2}\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{p}_i \\ &\quad + \frac{1}{2}\mathbf{A}(\mathbf{r}_i)\cdot\mathbf{A}(\mathbf{r}_i) + \frac{1}{2}\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r}_i)\bigg] \\ &= \hat{T} + \hat{V}_{ee} + \int d\mathbf{r}\,\boldsymbol{\Sigma}^{T}\mathbf{V}(\mathbf{r})\hat{\mathbf{J}}(\mathbf{r}). \end{aligned} \tag{1}$$

In Eq. (1), $\hat{T}$ and $\hat{V}_{\mathrm{ee}}$ are the operators of the kinetic energy and the electron-electron repulsion, v_{ext} is the external electrostatic potential, usually the potential of the nuclei, $\mathbf{B}$ designates a magnetic field with accompanying vector potential $\mathbf{A}$. By $\mathbf{r}_i$ the position of the ith electron is denoted, by $\mathbf{p}_i$ the corresponding canonical momentum operator with components $p_{x,i}$, $p_{y,i}$, and $p_{z,i}$. The vector $\boldsymbol{\sigma}$ contains the Pauli spin matrices. The sum in the first line of Eq. (1) runs over all N electrons. The vector $\boldsymbol{\Sigma}$ has four components, Σ_0 being a 2×2 unit matrix and Σ_1, Σ_2, and Σ_3 being the Pauli spin matrices $\boldsymbol{\sigma}_x$, $\boldsymbol{\sigma}_y$, and $\boldsymbol{\sigma}_z$. The four components of the vector $\hat{\mathbf{J}}(\mathbf{r})$ are the density operator $\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i) = \hat{J}_0(\mathbf{r})$ and the x, y, z components of the current operator $(\frac{1}{2})\sum_{i=1}^{N} p_{x,i}\delta(\mathbf{r}-\mathbf{r}_i) + \delta(\mathbf{r}-\mathbf{r}_i)p_{x,i} = \hat{J}_1(\mathbf{r})$, etc. The 4×4 matrix $\mathbf{V}(\mathbf{r})$ is composed of matrix elements $V_{\mu\nu}(\mathbf{r})$ with $\mu, \nu = 0, 1, 2, 3$:

$$\mathbf{V}(\mathbf{r}) = \begin{pmatrix} v_{\mathrm{ext}}(\mathbf{r}) + \frac{\mathbf{A}^2(\mathbf{r})}{2} & A_x(\mathbf{r}) & A_y(\mathbf{r}) & A_z(\mathbf{r}) \\ \frac{B_x(\mathbf{r})}{2} & 0 & 0 & 0 \\ \frac{B_y(\mathbf{r})}{2} & 0 & 0 & 0 \\ \frac{B_z(\mathbf{r})}{2} & 0 & 0 & 0 \end{pmatrix}. \tag{2}$$

The total energy E of the system is given by

$$\begin{aligned} E &= T + V_{\rm ee} + \sum_{\mu\nu} \int d\mathbf{r} V_{\mu\nu}(\mathbf{r}) \rho_{0,\mu\nu}(\mathbf{r}) \\ &= T + V_{\rm ee} + \int d\mathbf{r} \mathbf{V}^T(\mathbf{r}) \boldsymbol{\rho}_0(\mathbf{r}). \end{aligned} \quad (3)$$

In Eq. (3), T and V_{ee} denote the kinetic and the electron-electron repulsion energy, respectively, and $\boldsymbol{\rho}_0$ is the ground state spin-current density consisting of 16 components $\rho_{0,\mu\nu}$ with μ, $\nu = 0, 1, 2, 3$. The component $\rho_{0,00}$ is the regular ground state electron density, $\rho_{0,\mu 0}$ with $\mu = 1$, 2, 3 represent the x, y, z components of the spin density, $\rho_{0,0\nu}$ with $\nu = 1, 2, 3$ represent the x, y, z components of the paramagnetic current of the electron density, while $\rho_{0,\mu\nu}$ with μ, $\nu = 1, 2, 3$ represent the components of the paramagnetic currents of the spin density, i.e., currents of the magnetization. The corresponding physical currents consisting of the contributions $\rho_{0,\mu\nu}(\mathbf{r}) + \rho_{0,\mu 0}(\mathbf{r}) A_\nu(\mathbf{r})$ describe, via the continuity equation, changes of the magnetization in time and thus are meaningful physical quantities. The spin-current density $\boldsymbol{\rho}_0$ can be considered as a 4×4 matrix or, like in the second line of Eq. (3), as a 16-component vector with superindex $\mu\nu$. Similarly, $\mathbf{V}(\mathbf{r})$ can be treated as a 4×4 matrix, like in the second line of Eq. (1), or as a 16-component vector, like in the second line of Eq. (3).

The reason to introduce the matrix $\mathbf{V}(\mathbf{r})$ and to rewrite the Hamiltonian operator according to the second line of Eq. (1) is that this leads to the expression (3) for the total energy E. Starting from this expression for E it is straightforward to generalize the definitions and derivations of standard DFT. A Hohenberg-Kohn functional $F[\boldsymbol{\rho}]$ can be defined via a generalized constrained-search [7,8] by

$$F[\boldsymbol{\rho}] = \min_{\Psi \to \boldsymbol{\rho}(\mathbf{r})} \langle \Psi | \hat{T} + \hat{V}_{\rm ee} | \Psi \rangle. \quad (4)$$

The minimization (4) runs over all wave functions yielding the spin-current density $\boldsymbol{\rho}$; i.e., the wave functions are constrained to not only yield a given reference electron density, like in standard DFT, but to yield the 16 components $\rho_{\mu\nu}$ of the spin-current density. The minimizing wave function $\Psi[\boldsymbol{\rho}]$ of (4) is a functional of the spin-current density $\boldsymbol{\rho}$. The minimizing wave function $\Psi[\boldsymbol{\rho}_0]$ for the ground state spin-current density $\boldsymbol{\rho}_0$ is the ground state wave function Ψ_0 of the system, $\Psi_0 = \Psi[\boldsymbol{\rho}_0]$; i.e., in the case of the presence of magnetic fields, the ground state current-spin density determines Ψ_0 and thus all ground state properties of the system. The latter statement represents a Hohenberg-Kohn theorem for SCDFT.

A Kohn-Sham wave function $\Phi[\boldsymbol{\rho}]$ corresponding to a wave function $\Psi[\boldsymbol{\rho}]$ is defined as the minimizing wave function in the constrained-search minimization

$$T_s[\boldsymbol{\rho}] = \min_{\Phi \to \boldsymbol{\rho}(\mathbf{r})} \langle \Phi | \hat{T} | \Phi \rangle \quad (5)$$

yielding the functional $T_s[\boldsymbol{\rho}]$ of the noninteracting kinetic energy. As usual, exchange and correlation energy are defined as $E_x[\boldsymbol{\rho}] = \langle \Phi[\boldsymbol{\rho}] | \hat{V}_{\rm ee} | \Phi[\boldsymbol{\rho}] \rangle - U[\rho_{00}]$ and $E_c[\boldsymbol{\rho}] = \langle \Psi[\boldsymbol{\rho}] | \hat{T} + \hat{V}_{\rm ee} | \Psi[\boldsymbol{\rho}] \rangle - \langle \Phi[\boldsymbol{\rho}] | \hat{T} + \hat{V}_{\rm ee} | \Phi[\boldsymbol{\rho}] \rangle$ with the Coulomb energy $U[\rho_{00}]$ given by the standard expression $\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho_{00}(\mathbf{r}) \rho_{00}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$ depending only on ρ_{00}.

The many-electron KS equation corresponding to a Schrödinger equation for real electrons with Hamiltonian operator (1) is determined by the KS Hamiltonian operator

$$\hat{H}_s = \hat{T} + \int d\mathbf{r} \boldsymbol{\Sigma}^T \mathbf{V}_s(\mathbf{r}) \hat{\mathbf{J}}(\mathbf{r}) \quad (6)$$

with the 4×4 matrix $\mathbf{V}_s$ representing the KS potential, given by $\mathbf{V}_s(\mathbf{r}) = \mathbf{V}(\mathbf{r}) + \mathbf{U}(\mathbf{r}) + \mathbf{V}_{\rm xc}(\mathbf{r})$. The Coulomb potential $\mathbf{U}$ and the exchange-correlation potential $\mathbf{V}_{\rm xc}$ can be represented by 4×4 matrices; within the matrix $\mathbf{U}$ only the component $U_{00}(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho_{00}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$ is different from zero and is the standard Coulomb potential. By straightforward generalization of the arguments of the standard KS formalism [1], i.e., by invoking the variational principle for the KS system and the real electron system and by comparing the resulting Euler equations [7,8], it can be deduced that the components $\mathbf{V}_{{\rm xc},\mu\nu}$ of the exchange-correlation potential $\mathbf{V}_{\rm xc}$ are given by

$$V_{{\rm xc},\mu\nu}(\mathbf{r}) = \frac{\delta E_{\rm xc}}{\delta \rho_{\mu\nu}(\mathbf{r})}. \quad (7)$$

In the functional derivatives (7) all 16 components of $\rho_{\mu\nu}$ are treated as independent. As a result, all 16 components $V_{{\rm xc},\mu\nu}$ and subsequently $V_{s,\mu\nu}$, including components (or combinations thereof) corresponding to gauge transformations, are determined within the presented formalism. The gauge of all quantities is determined by the gauge of the external vector potential $\mathbf{A}$. [A modified version of the formalism chooses the Coulomb gauge throughout and treats only the transversal components of the spin currents [9].] While the KS wave function $\Phi[\boldsymbol{\rho}_0]$, corresponding to the ground state $\Psi_0 = \Psi[\boldsymbol{\rho}_0]$ of a real system, is uniquely defined by the constrained search (5), the functional derivatives (7) uniquely define the exchange-correlation potential $\mathbf{V}_{\rm xc}$ and subsequently yield the effective KS potential $\mathbf{V}_s$ if they are evaluated at $\boldsymbol{\rho}_0$. Like in the standard KS formalism, it is assumed that the functional derivatives (7) exist and that the spin-current density $\boldsymbol{\rho}_0$ is noninteracting v representable.

The components $V_{{\rm xc},\mu\nu}$ and subsequently $V_{s,\mu\nu}$ with μ, $\nu = 1, 2, 3$, i.e., the components coupling to actual spin currents, in general, differ from zero despite the fact that the corresponding components in the external potential $\mathbf{V}$ of Eq. (2) are zero. A similar situation occurs in the standard spin-density formalism [1]. If the spin-density of the system is spin-polarized then the KS exchange-correlation potential and the effective KS potential are spin-polarized although the external potential is not spin-polarized. Because the external potential does not contain a contribution coupling to the spin polarization it is, in principle, possible to treat spin-polarized systems within the basic non-spin-polarized KS formalism. However, for approximate exchange-correlation functionals and thus in all practical applications, a spin-polarized treatment is more preferable for spin-polarized systems. Similarly, it is possible, in principle, to treat within the original current-spin-density formalism systems that are subject to magnetic fields, because the external potential does not couple to spin currents, i.e., because $V_{\mu\nu} = 0$ for μ, $\nu = 1, 2, 3$. However, in the presence of magnetic fields, in general, spin currents occur (see below) and therefore a treatment within the spin-current density formalism presented here seems to be preferable.

If spin-orbit interactions are considered then the components $V_{\mu\nu}$ for μ, $\nu = 1, 2, 3$ of the external potential no longer are zero and the original current-spin-density formalism is no longer applicable and it is required to switch to the spin-current density formalism presented here. Indeed a generalization of the presented formalism that enables the treatment of spin-orbit interactions is possible and will be published elsewhere [10].

In order to apply the presented SCDFT, suitable exchange-correlation functionals are required. To that end, we concentrate on the exchange functionals and treat those exactly. Like in the standard KS formalism, the evaluation of the exchange energy is well known from Hartree-Fock methods and straightforward. By generalizing the treatment of the standard exact-exchange KS approach [4] also the exact-exchange potential $\mathbf{V}_x$ of SCDFT becomes accessible. The chain rule of functional differentiation yields

$$v_{x,\mu\nu}(\mathbf{r}) = \sum_{\kappa\lambda} \int d\mathbf{r}' \left[\sum_{a}^{\text{occ.}} \int d\mathbf{r}'' \frac{\delta E_x}{\delta \phi_a(\mathbf{r}'')} \frac{\delta \phi_a(\mathbf{r}'')}{\delta V_{s,\kappa\lambda}(\mathbf{r}')} + \text{c.c.} \right] \times \frac{\delta V_{s,\kappa\lambda}(\mathbf{r}')}{\delta \rho_{\mu\nu}(\mathbf{r})}. \tag{8}$$

In Eq. (8), ϕ_a stands for the KS orbitals, complex-valued two-dimensional spinors, building the KS determinant. The right-hand side of Eq. (8) due to the sum over $\kappa\lambda$ contains 16 terms. Furthermore, for each of the 16 components of $\mathbf{V}_x$ an equation (8) arises. These can be combined in the 16×16 matrix equation $\mathbf{V}_x(\mathbf{r}) = \int d\mathbf{r}' \mathbf{X}_s^{-1}(\mathbf{r}, \mathbf{r}')\mathbf{t}(\mathbf{r}')$, which is turned into

$$\int d\mathbf{r}' \mathbf{X}_s(\mathbf{r}, \mathbf{r}')\mathbf{V}_x(\mathbf{r}') = \mathbf{t}(\mathbf{r}). \tag{9}$$

Here, $\mathbf{X}_s$ is the spin-current response function of the KS system, a 16×16 matrix with matrix elements

$$X_{s,\mu\nu,\kappa\lambda}(\mathbf{r}, \mathbf{r}') = \sum_{a}^{\text{occ.}} \sum_{s}^{\text{unocc.}} \frac{\langle \phi_a | \sigma_\mu \hat{J}_\nu(\mathbf{r}) | \phi_s \rangle \langle \phi_s | \sigma_\kappa \hat{J}_\lambda(\mathbf{r}') | \phi_a \rangle}{\varepsilon_a - \varepsilon_s} + \text{c.c.} \tag{10}$$

The components $t_{\mu\nu}$ of the 16-dimensional vector $\mathbf{t}$ are given by the terms in the square brackets in the right-hand side of Eq. (8). The functional derivative $\frac{\delta E_x}{\delta \phi_a(\mathbf{r}'')}$ contained in the $t_{\mu\nu}$ can be evaluated straightforwardly because the exchange energy is known in terms of the KS orbitals, see, e.g., Ref. [4]. Equation (9) represents the EXX equation of SCDFT; it is an integral equation, which needs to be solved in each iteration of the SCDFT KS self-consistency process in order to obtain the exchange potential $\mathbf{V}_x$.

We implemented the presented EXX-SCDFT approach within a plane-wave solid state code. The quantities $X_{s,\mu\nu,\kappa\lambda}$, $v_{x,\mu\nu}$, and $t_{\mu\nu}$ are expanded in an auxiliary plane-wave basis set. The $X_{s,\mu\nu,\kappa\lambda}$ then turn into matrices of the dimension of the auxiliary basis set, while the $v_{x,\mu\nu}$ and $t_{\mu\nu}$ turn into vectors of the same dimension. The complete response function then turns into a matrix consisting of 16×16 submatrices $X_{s,\mu\nu,\kappa\lambda}$ and the complete exchange potential and right-hand side of Eq. (9) become vectors consisting of 16 subvectors $v_{x,\mu\nu}$ and $t_{\mu\nu}$. The integral equation (9) turns into a matrix equation and can easily be solved.

As an illustration we consider an oxygen atom subject to a constant magnetic field directed along the z axis. To that end, we put the oxygen atom in the centers of simple cubic supercells of 9, 10, and 11 a.u. length. Plane-wave cutoffs of 14, 20, and 24 Rydberg for the orbitals and of 4, 6, and 7.2 Rydberg for the response function, the exchange potential, and the right-hand side of Eq. (9) are chosen. All results shown below are converged with respect to supercell size and plane-wave cutoffs and are invariant with respect to gauge transformations of the external vector potential $\mathbf{A}$, within the numerical accuracy determined by the plane-wave cutoffs. The oxygen $1s$ electrons are taken into account via separable EXX pseudopotentials [11].

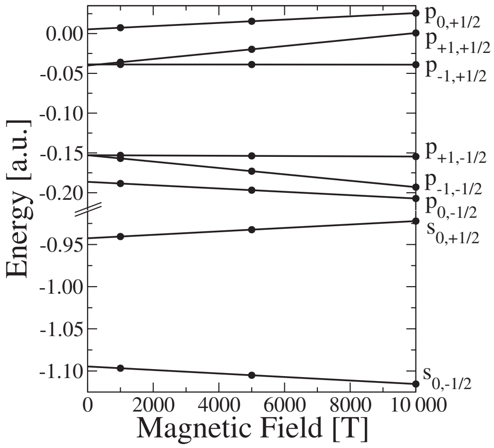

FIG. 1. Eigenvalues of oxygen KS orbitals s_{m_ℓ,m_s} and p_{m_ℓ,m_s} as functions of magnetic field strength.

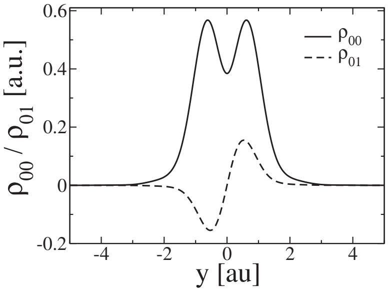

FIG. 2. Electron density ρ_{00} of oxygen and its current ρ_{01} in x direction displayed along the y axis for a magnetic field strength of 10 000 T.

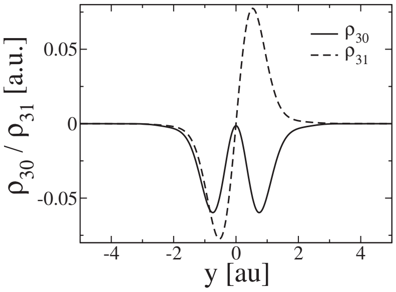

FIG. 3. Spin density ρ_{30} of oxygen and its current ρ_{31} in x direction displayed along the y axis for a magnetic field strength of 10 000 T.

In the absence of magnetic fields and spin-orbit interactions the electronic ground state of oxygen is a ninefold degenerate ^3P state of valence configuration $(2s^2, 2p^4)$. The spin and spatial angular momenta can be coupled to give $^3P_0$, $^3P_1$, and $^3P_2$ LS-coupled states. In the presence of a constant magnetic field in z direction, the $^3P_2$ state with total magnetic quantum number $M_J = -2$ is the ground state. This state is a one-determinantal state with occupied p orbitals $p_{-1,-1/2}$, $p_{0,-1/2}$, $p_{+1,-1/2}$, and $p_{-1,+1/2}$. (First and second subscripts, m_ℓ and m_s, denote magnetic quantum numbers for spatial and spin angular momentum, respectively.) A KS treatment of this state even in the limit of zero magnetic field leads to a symmetry breaking KS wave function and a lifting of the degeneracy of the p orbitals because of the partially filled p shell accompanied by a nonspherical but cylindrical electron density [4,12]. Correspondingly, the symmetry of the KS Hamiltonian operator is reduced from spherical to cylindrical symmetry around the z axis. In the presence of the magnetic field the latter is the actual symmetry of the system.

In the absence of spin-orbit interactions the change ΔE of orbital energies (and, below, of the total energy) due to the direct coupling to the magnetic field of strength B is described according to the Paschen-Back formula $\Delta E = \beta B(m_\ell + 2m_s)$ not according to the Zeeman formula. Here β stands for the Bohr magneton. The values of $\Delta E/(\beta B)$ for the curves in Fig. 1 equal $(m_\ell + 2m_s)$. For the special case of the $^3P_2$ state with $M_J = -2$ the Paschen-Back and the Zeeman formula $\Delta E = \beta g_J B M_J$ yield the same energy splitting with respect to the magnetic field strength. It is thus possible to obtain from our calculation the Landé factor g_J of oxygen despite the neglect of spin-orbit interactions. The resulting value of 1.5 agrees with the experimental one. This demonstrates that the presented SCDFT approach works correctly in practice in the sense that it correctly generates spin and angular momenta and aligns them correctly with the magnetic field. (Note that in our plane-wave supercell method spin and angular momenta as well as their coupling and alignment are not enforced by the basis set and by occupation numbers but are an outcome of the SCDFT treatment.)

In Fig. 2 the electron density ρ_{00} and its current ρ_{01} in x direction are displayed along the y axis. As usual in pseudopotential calculations ρ_{00} exhibits a minimum at the nucleus. The displayed ρ_{01} corresponds to a current around the z axis. The currents ρ_{02} and ρ_{03} are zero. Thus the magnetic field correctly aligns the spatial angular momentum along the z axis. In Fig. 3 the spin density ρ_{30}, i.e., the magnetization along the z direction, and its current ρ_{31} in x direction are displayed along the y axis. The spin densities ρ_{10} and ρ_{20} are zero; thus also the magnetization is correctly aligned along the z axis by the magnetic field. Most important, Fig. 3 clearly shows that the spin current ρ_{31} differs from zero. This demonstrates that spin currents, which can be correctly described by the presented SCDFT, are far from negligible in real systems.

In summary, we believe that the presented formalism and method provide a general and sound basis for the treatment of all sorts of magnetic and (noncollinear) spin effects in a density-functional framework. Furthermore, as mentioned above, also spin-orbit interactions can be included in a natural way in the formalism [10].

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