

A New Approach to Noncollinear Spin Density Functional Theory beyond the Local Density Approximation

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ABSTRACT: The application of density functional theory to heavy elements and magnetic materials requires the generalization of existing functionals to the case of noncollinear spins. This letter describes a new idea to achieve such a generalization which, unlike previous efforts in this direction, (i) affords a nonvanishing local magnetic torque, (ii) is invariant with respect to spin-rotations, (iii) is free from numerical instabilities in regions of small magnetization, and (iv) reduces to the proper collinear limit.

Density functional theory (DFT) in the formulation of Kohn and Sham (KS) is among the preferred tools available for the calculation of the electronic structure of molecules and materials. The achievements of DFT in the description of molecules involving lighter atoms are remarkable and well-known. In the field of solid-state physics, DFT has also been very successful in explaining the basic electronic structure of materials.

A large class of phenomena of importance in both chemistry and solid-state physics involves noncollinear spins. Systems involving heavy atoms require a proper relativistic treatment of electron–nuclear and electron–electron interactions. Because of effects such as spin–orbit coupling, an accurate description of the chemistry of transition metals will necessarily involve noncollinear spins. Noncollinear spins are of importance in describing the properties of magnetic materials, even when heavy atoms are not involved. Spiral and frustrated spin structures may arise spontaneously or may be considered for specific applications. A robust and accurate extension of DFT capable of describing such phenomena is long overdue.

The extension of DFT to the case of spin polarized systems, *spin density functional theory* (SDFT), was derived¹ formally in terms of the total electron density $n(\mathbf{r})$ and the *vector magnetization density* $\mathbf{m}(\mathbf{r})$. However, all the standard approximate functionals which are accurate and useful in the calculation of the electronic structure of molecules and solids were developed under the assumption of collinear spins — $\mathbf{m}(\mathbf{r})$ pointing in the same direction at all points in space. As a result, they are functionals of $n(\mathbf{r})$ and a *scalar* spin density $s(\mathbf{r})$. The generalization of these functionals to handle noncollinear spins is nontrivial, and previous attempts to do so resulted in models which have both formal and numerical problems.

In this letter, we propose a new idea to extend the use of well-established functionals developed for collinear spins, to the general noncollinear case. Our approach applies to *generalized gradient corrected* functionals (GGAs), functionals that depend on the *kinetic energy density* τ (meta-GGAs) or the Laplacian of the density, and *hybrid* functionals. In the context of noncollinear SDFT, the exact exchange that is included in a *hybrid* functional is defined as in the two-component *generalized Hartree–Fock* (GHF) method.² On the other hand, in the case of a *local spin density approximation* (LSDA) functional, the

approach proposed in this letter is equivalent to previously published ones.³

In our approach, the xc energy depends on $\mathbf{m}(\mathbf{r})$, its Cartesian gradient $\vec{\nabla}\mathbf{m}(\mathbf{r})$, etc., through quantities that are invariant with respect to global rotations in spin space. As these invariance properties are built into the functional, important aspects of the proper physics emerge: the xc energy depends on the varying direction of the magnetization, and consequently the *exchange-correlation magnetic field* \mathbf{B}_{xc} is not necessarily parallel to \mathbf{m} .^{4,5} The xc functionals generated in this way reduce to the correct collinear limit and are free from numerical instabilities associated with regions where \mathbf{m} is small. We demonstrate our approach in a detailed characterization of the noncollinear state of a highly symmetric small chromium cluster Cr₃.

The functionals under consideration are based on an xc energy of the form

$$E_{xc} = \int d\mathbf{r} F[n_{\pm}, \gamma_a, \gamma_b, \gamma_c, \tau_{\pm}, \nabla^2 n_{\pm}] \quad (1)$$

For collinear spins, n_+ and n_- are the usual n_{\uparrow} (“up”) and n_{\downarrow} (“down”) spin densities, referred to a single arbitrary spin quantization axis. The γ quantities depend on the gradient of n_{\uparrow} and n_{\downarrow} and are defined as

$$\begin{aligned} \gamma_a &= \gamma_{\uparrow\uparrow} = \vec{\nabla}n_{\uparrow} \cdot \vec{\nabla}n_{\uparrow} \\ \gamma_b &= \gamma_{\downarrow\downarrow} = \vec{\nabla}n_{\downarrow} \cdot \vec{\nabla}n_{\downarrow} \\ \gamma_c &= \gamma_{\uparrow\downarrow} = \vec{\nabla}n_{\uparrow} \cdot \vec{\nabla}n_{\downarrow} \end{aligned} \quad (2)$$

while τ_+ and τ_- are the kinetic energy densities associated with the “up” and “down” spins, i.e., τ_{\uparrow} and τ_{\downarrow} . The xc energy is expressed in terms of the γ 's in order to ensure invariance with respect to spatial rotations. The functionals are also invariant with respect to the interchange of the spin labels, which amounts to a global rotation by 180° of the spin reference frame.

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If we want to apply the wealth of functionals of the form (eq 1) developed so far to systems of noncollinear spins, how should we proceed?

The generalization of n_+ and n_- is straightforward:

$$n_{\pm} = \frac{1}{2}n \pm \frac{1}{2}[\mathbf{m} \circ \mathbf{m}]^{1/2} \quad (3)$$

where the \circ will be used to indicate the scalar product over spin components, in contrast to \cdot which is used for the scalar product over spatial components. The second term on the right-hand side of eq 3 is the magnitude of the local magnetization vector $\mathbf{m}(\mathbf{r})$.

We propose the following generalization of the γ quantities:

$$\begin{aligned} \gamma_{a,b} &= \frac{1}{4}\vec{\nabla}n \cdot \vec{\nabla}n + \frac{1}{4}\vec{\nabla}\mathbf{m} \cdot \circ \vec{\nabla}\mathbf{m} \\ &\pm \frac{f_{\nabla}}{2}[(\vec{\nabla}n \cdot \vec{\nabla}\mathbf{m}) \circ (\vec{\nabla}n \cdot \vec{\nabla}\mathbf{m})]^{1/2} \end{aligned} \quad (4)$$

$$\gamma_c = \frac{1}{4}\vec{\nabla}n \cdot \vec{\nabla}n - \frac{1}{4}\vec{\nabla}\mathbf{m} \cdot \circ \vec{\nabla}\mathbf{m} \quad (5)$$

where

$$\vec{\nabla}\mathbf{m} \cdot \circ \vec{\nabla}\mathbf{m} \equiv \sum_{\mu=x,y,z} (\vec{\nabla}m_{\mu} \cdot \vec{\nabla}m_{\mu}) \quad (6)$$

and f_{∇} is a factor defined in terms of the standard *signum* function as follows:

$$f_{\nabla} = \text{sgn}(\vec{\nabla}n \cdot \vec{\nabla}\mathbf{m} \circ \mathbf{m}) \quad (7)$$

The generalization of the τ and Laplacian variables is similar:

$$\tau_{\pm} = \frac{1}{2}\tau \pm \frac{f_{\tau}}{2}[\mathbf{u} \circ \mathbf{u}]^{1/2} \quad f_{\tau} = \text{sgn}(\mathbf{u} \circ \mathbf{m}) \quad (8)$$

$$\begin{aligned} \nabla^2 n_{\pm} &= \frac{1}{2}\nabla^2 n \pm \frac{f_{\nabla^2}}{2}[\nabla^2 \mathbf{m} \circ \nabla^2 \mathbf{m}]^{1/2} \\ f_{\nabla^2} &= \text{sgn}(\nabla^2 \mathbf{m} \circ \mathbf{m}) \end{aligned} \quad (9)$$

where the scalar τ and spin-vector \mathbf{u} have been introduced in eqs 30–32 of ref 3. The definition of n_+ and n_- involves an arbitrary choice of sign, and therefore the connection to n_{\uparrow} and n_{\downarrow} in the collinear limit may require an interchange of the spin labels. The sign functions f_{∇} , f_{τ} , and f_{∇^2} ensure the consistency of the spin labels between the collinear limit of n_{\pm} and that of the other variables. The definitions in eqs 3–9 are our working equations and they provide the desired noncollinear extension of the functional (eq 1).

We now compare our approach with generalizations previously proposed. In some cases, the issues associated with the use of a functional beyond the LSDA for noncollinear spins are clearly acknowledged and approximations are proposed,^{3,6–9} while in other cases, the approach followed is not completely spelled out.¹⁰ In more detail:

- The definition of n_{\pm} in eq 3 is effectively identical to the one usually adopted in noncollinear LDA calculations. However, we do not resort to the notion of a local spin reference frame where the magnetization vector is aligned with a particular spin axis.¹¹ Instead, we justify the definitions in eq 3 by invoking the need for invariance with respect to spin rotations and the conservation of particle number. These definitions

involve only the magnitude of the magnetization and not its direction. As previously noted,^{4,9} the major drawback of this noncollinear extension of the LDA is the fact that the energy is not aware of changes in the direction of \mathbf{m} when its magnitude remains constant.

- The use of $\vec{\nabla}n_{\pm}$ to compute the γ 's effectively requires the choice of a particular and arbitrary spin quantization axis, namely, that given by the unit vector $\hat{\mathbf{m}}$ in the direction of \mathbf{m} . As a result, the functional derivatives contain terms such as $\hat{\mathbf{m}} \circ \vec{\nabla}\mathbf{m}$. The derivatives of \mathbf{m} are numerically unstable because small changes in small value of components of \mathbf{m} can make large changes in $\hat{\mathbf{m}}$. For example, going from $\mathbf{m} = (10^{-9}, 10^{-9}, 0)$ to $\mathbf{m} = (10^{-9}, 2 \times 10^{-9}, 0)$ produces $\Delta\hat{\mathbf{m}} = (-0.26, 0.19, 0)$. Similar considerations apply to the noncollinear generalization of τ and Laplacian as described in ref 3. This is not a detail of minor importance. Numerical problems appear to be avoided in many codes^{8–10} by neglecting unstable terms in the functional derivatives during the solution of the *self-consistent field* (SCF) equations. Such approximations make the SCF solution self-consistent but not variational, which is adequate for many applications in solid-state physics, where only first derivatives of the energy and moderate numerical accuracy are required. However, a less than strict fulfillment of the variational condition is a serious problem for the higher derivatives of the energy and the higher numerical accuracy required in applications to molecular systems.
- It can be shown that xc magnetic field \mathbf{B}_{xc} is automatically parallel to \mathbf{m} if the γ 's are computed from $\vec{\nabla}n_{\pm}$. The \mathbf{B}_{xc} associated with our noncollinear generalization of the GGAs is *not* constrained to be everywhere parallel to \mathbf{m} but can be proven to satisfy the global *zero torque theorem*.⁴ Therefore, we expect the presence of a nonvanishing local magnetic torque which is demonstrated in the example calculation described below. A nonvanishing local magnetic torque is required for a meaningful description of spin dynamics.⁵ To the best of our knowledge, there are two other methods that are able to provide a nonvanishing local magnetic torque, but they both are formally more complex and computationally more expensive. They are the EXX orbital dependent functional,⁵ which requires the solution of the optimized effective potential (OEP) equations,¹² and the two-component *generalized Hartree–Fock* (GHF),² which relies on a nonlocal description of the exchange potential.
- The term $\vec{\nabla}\mathbf{m} \cdot \circ \vec{\nabla}\mathbf{m}$ has an interesting physical basis. In fact, such a quantity arises within the standard Heisenberg exchange model from the expansion of the “non-uniformity exchange energy”. In accordance with §43 of ref 13 and §69 of ref 14, it is positive definite and independent of the absolute direction of \mathbf{m} . A similar gradient term, also invariant with respect to spin-rotations, has been considered in ref 15 as a correction beyond LSDA in the study of spin-density waves in Fe and Ni.

As a practical example, we characterized the noncollinear states of Cr₃, which are present even in the nonrelativistic case, using both LDA¹⁶ and the PBE¹⁷ GGA functional. Additionally, we include results obtained with the GHF method. We imposed D_{3h} symmetry of the cluster with an interatomic

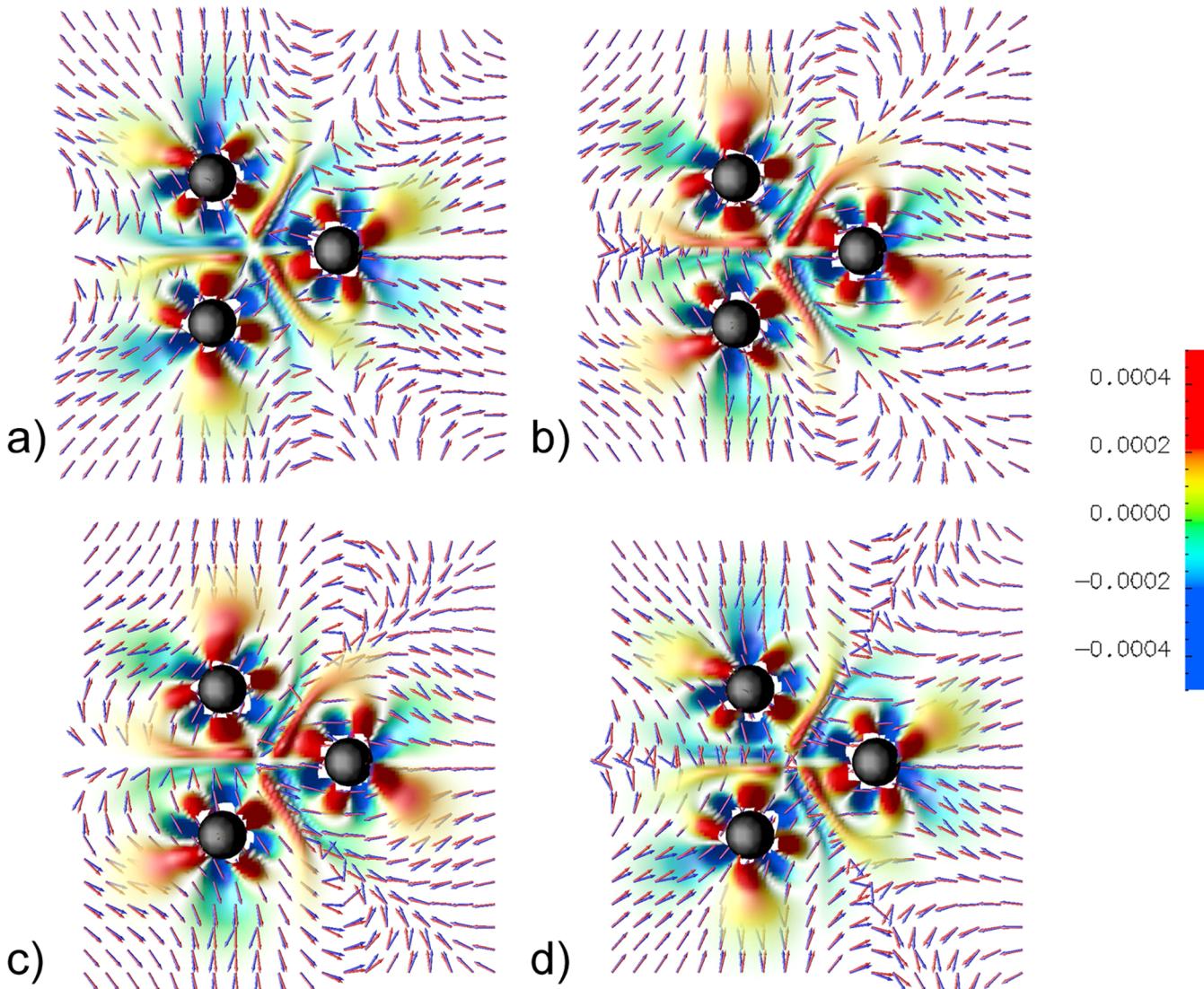


Figure 1. Four degenerate microstates corresponding to the noncollinear state of Cr_3 . In the plane of the cluster are shown the atomic centers (black balls), the normalized \mathbf{m} (red arrows), and \mathbf{B}_{xc} (blue arrows) fields. The regions where the magnitude of $\mathbf{m} \times \mathbf{B}_{\text{xc}}$ is significant are highlighted using a colormap (values in a.u.); there is no color over the atomic centers where the pseudopotentials replace the core density.

distance of 3.700 bohr, and we used the combination of a localized atomic orbital basis set and effective core potential described in ref 18. In addition to solving the variational problem in the usual way,^{3,7} which requires only functional first derivatives, we also computed \mathbf{B}_{xc} using integration by parts. This leads to an expression for \mathbf{B}_{xc} that involves first and second derivatives of both the functional and the basis functions.¹⁹ Using the calculated values of \mathbf{B}_{xc} and \mathbf{m} , we can evaluate the torque between the two fields. In Figure 1 are represented four energetically degenerate microstates corresponding to the same noncollinear state. The rich noncollinear structure of both the \mathbf{m} and the \mathbf{B}_{xc} fields is apparent, showing the largest value of their cross product closer to the atomic centers, consistently with similar EXX results.⁵ The four microstates have the same expectation value of $\langle S^2 \rangle = 3.89$, which is close to the value of 3.75 corresponding to a pure quartet state. The four microstates cannot be connected by any overall rotation of the spin frame, but rather they are connected by inverting the direction of one or more spin axis. The pairs of microstates a, d and b, c have different helicities of the \mathbf{m} field, and the

introduction of spin-orbit coupling^{7,20} breaks the degeneracy between the two pairs making b, c slightly more stable. A similar noncollinear state can be located using LDA, but the \mathbf{m} and the \mathbf{B}_{xc} fields are everywhere parallel as expected. Upon geometry optimization and numerical evaluation of the vibrational frequencies, we were able to locate a second order saddle point using LDA (2.404 bohrs), while both PBE (2.622 bohrs) and GHF (3.617 bohrs) optimize to a minimum. We believe it is significant that both GHF and our noncollinear extension of PBE characterize the stationary point as a minimum. Previously reported results,²¹ obtained with a noncollinear implementation of PBE that does not afford nonvanishing local magnetic torque,¹⁰ found the optimized structure of the same state of Cr_3 to be a second order saddle point, in agreement with LDA.

In a forthcoming paper, we will provide a more in-depth comparison with alternative approaches, additional details of the composition, and explicit computation of \mathbf{B}_{xc} , the proof that the zero torque theorem⁴ is satisfied for GGAs, and additional numerical examples.

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Notes

The authors declare no competing financial interest.

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