



Real-space pseudopotential method for noncollinear magnetism within density functional theory

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ABSTRACT

We present a real-space pseudopotential method for first principles calculations of noncollinear magnetic phenomena within density functional theory. We demonstrate the validity of the method using the test cases of the Cr_3 cluster and the $\text{Cr}(\sqrt{3} \times \sqrt{3})R30^\circ$ monolayer. The approach retains all the typical benefits of the real-space approach, notably massive parallelization. It can be employed with arbitrary boundary conditions and can be combined with the computation of pseudopotential-based spin-orbit coupling effects.

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Noncollinear magnetism, i.e., the absence of a spin quantization axis common to the whole system, is manifested in a wide variety of substances. Often, they arise as consequence of competing magnetic interactions in the same system (see, e.g., Refs. [1, 2] for an overview). One simple yet notable example is that of noncollinear magnetism arising from geometrically frustrated antiferromagnetic interaction. Such frustration is perhaps most easily visualized on two-dimensional triangular lattices (see, e.g., Refs. [3,4]), but can also be found in bulk structures [1,2] and has recently received much attention in the context of small transition metal clusters (e.g., refs. [5–16]).

There is obvious merit in describing noncollinear magnetic phenomena from first principles [2,17,18]. Specifically, it is interesting to employ density functional theory (DFT) [19], which has become the “work horse” of first principles calculations, towards studies of noncollinear magnetic phenomena. In principle, the generalization of the Hohenberg-Kohn theorem and the Kohn–Sham equation to spin-polarized systems, given by von Barth and Hedin [20], is not restricted to collinear magnetism. However, this aspect was not explored in practice until the work of Kübler et al. [21]. Early applications of this formalism all relied on the “atomic sphere approximation”, where the spin-quantization axis at each point within a sphere around each atom was forced to be the same, but different spheres were allowed to

possess different axes [17,21]. Nordström and Singh have shown that this additional approximation is not necessary and have performed calculations where the magnetization density was a vector quantity that could vary continuously in direction as well as magnitude over all space [22].

The above ideas have been incorporated in different approaches to solving the Kohn–Sham equation. These include planewave-related methods, e.g., the linearized augmented planewave (LAPW) approach [22–24], the pseudopotential-planewaves approach [5, 25], and the projector augmented wave method, [6,26] as well as methods including both numerical [9,27] and gaussian [15] atomic basis sets.

A different effective method for solving the Kohn–Sham equation is to sample both wave functions and potentials on a real-space grid. In particular, the finite difference approach, where the kinetic energy is expressed as a high-order finite difference expansion [28], is a simple and powerful tool when used in conjunction with pseudopotentials. Among other advantages, it can be applied to non-periodic, partially periodic (e.g., surfaces), and fully periodic structures on equal footing, as it does not depend on a particular boundary condition [31]. In addition, it is readily amenable to massive parallelization, making it an attractive tool for studies of systems with a large number of atoms [30,32]. It is therefore desirable to account for noncollinear magnetism in real-space calculations, a task which we undertake here.

Insertion of the noncollinear spin density in the Kohn–Sham equations is made possible by a two-component spinor representation of the Kohn–Sham orbitals, $\phi_i(\vec{r})$. The Kohn–Sham equation

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in terms of two components is [17]

$$\left(\left\{ -\frac{1}{2}\nabla^2 + V_{ion}(\vec{r}) + V_H(\vec{r}) + V_{xc}[n, \vec{m}](\vec{r}) \right\} \sigma_0 + \vec{b}_{xc}[n, \vec{m}](\vec{r}) \cdot \vec{\sigma} \right) \phi_i(\vec{r}) = \epsilon_i \phi_i(\vec{r}). \quad (1)$$

Here, $V_H(\vec{r})$ is the Hartree potential, $\vec{\sigma}$ is a vector of Pauli matrices, σ_0 is the 2×2 unit matrix, the charge and spin densities are given by

$$\vec{m}(\vec{r}) = \sum_{i=1}^{occ} \phi_i^\dagger(\vec{r}) \vec{\sigma} \phi_i(\vec{r}) \quad (2)$$

$$n(\vec{r}) = \sum_{i=1}^{occ} \phi_i^\dagger(\vec{r}) \phi_i(\vec{r}), \quad (3)$$

and the exchange correlation potential and magnetic exchange-correlation vector field are defined as

$$V_{xc}[n, \vec{m}](\vec{r}) = \frac{\delta E_{xc}[n, \vec{m}]}{\delta n}, \quad (4)$$

and

$$\vec{b}_{xc}[n, \vec{m}](\vec{r}) = \frac{\delta E_{xc}[n, \vec{m}]}{\delta \vec{m}}, \quad (5)$$

respectively. The general density in a noncollinear system has the form [7]

$$\tilde{n} = \frac{1}{2}(n\sigma_0 + \vec{m} \cdot \vec{\sigma}) = \frac{1}{2} \begin{pmatrix} n + m_z & m_x - im_y \\ m_x + im_y & n - m_z \end{pmatrix}, \quad (6)$$

where the explicit \vec{r} -dependence has been omitted for clarity. By diagonalizing this density at each point in space we obtain a local analogue of a collinear density

$$n_{\pm} = \frac{1}{2}(n \pm \|\vec{m}\|). \quad (7)$$

In the local spin density approximation (LSDA) [20], the spin density is parallel with the exchange-correlation magnetic vector field ($\vec{m} \parallel \vec{b}_{xc}$) [21]. The spin-dependent exchange-correlation potential and magnetic vector field can then be easily found from the functional derivatives in the locally collinear system:

$$\begin{aligned} \vec{b}_{xc} &= \frac{1}{2}(V_{xc+} - V_{xc-})\hat{m} \\ V_{xc} &= \frac{1}{2}(V_{xc+} + V_{xc-}). \end{aligned} \quad (8)$$

This procedure is strictly valid only within the LSDA. It can also be employed with generalized gradient approximation (GGA) functionals that depend explicitly only on n_{\pm} and ∇n_{\pm} [15], although it may be invalid for more general GGAs [29] and is not generally valid for an arbitrary functional form [24].

In the real-space approach to DFT, the wave-functions and potentials are sampled on a grid. The Hamiltonian matrix is neither calculated nor stored, but only operates on the trial wave-function in the process of diagonalization [30]. For evaluating the kinetic energy term, the Laplacian is expanded by finite differences. For an orthogonal grid, it is [28]

$$\begin{aligned} \nabla^2 \psi_n &= \sum_{m=-N}^N \frac{c_m}{h^2} [\psi_n(x_i + mh, y_j, z_k) \\ &+ \psi_n(x_i, y_j + mh, z_k) + \psi_n(x_i, y_j, z_k + mh)], \end{aligned} \quad (9)$$

where h is the grid spacing and c_n are the N th order finite difference coefficients for the second derivative expansion.

In the pseudopotential approximation, core electrons are suppressed by replacing the true ionic potential with a pseudopotential that accounts for their effect. This facilitates grid-based calculations as it results in slowly varying potentials and wave functions. We employ nonlocal norm conserving pseudopotentials cast in the separable Kleinman–Bylander form [28,33]. In this form, the pseudopotential due to a single atom, \hat{V}_{ion}^a , is expressed as the sum of a local term and a nonlocal term, such that

$$\hat{V}_{ion}^a \psi_n(\vec{r}) = V_{loc}(|\vec{r}_a|) \psi_n(\vec{r}) + \sum_{l,m} G_{n,l,m}^a u_{l,m}(\vec{r}_a) \Delta V_l(|\vec{r}_a|), \quad (10)$$

where $\vec{r}_a = \vec{r} - \vec{R}_a$, $V_{loc}(|\vec{r}_a|)$ is the local component of the pseudopotential, $\Delta V_l(|\vec{r}_a|) = V_l(|\vec{r}_a|) - V_{loc}(|\vec{r}_a|)$, where $V_l(|\vec{r}_a|)$ is the pseudopotential corresponding to angular momentum l , $u_{l,m}(\vec{r}_a)$ is the pseudo-wave-function corresponding to angular momentum lm , and the projection coefficients are $G_{n,l,m}^a = \frac{1}{\langle \Delta V_{l,m}^a \rangle} \int u_{lm}(\vec{r}_a) \Delta V_l(|\vec{r}_a|) \psi_n(\vec{r}) d^3r$, where $\langle \Delta V_{l,m}^a \rangle = \int u_{lm}(\vec{r}_a) \Delta V_l(|\vec{r}_a|) u_{lm}(\vec{r}_a) d^3r$. The Kleinman–Bylander form is advantageous in real space because outside the pseudopotential core cutoff radius, r_c , $V_{loc}^a(\vec{r}_a) = -Z_{ps}/|\vec{r}_a|$, where Z_{ps} is the atomic number of the pseudoion, and $\Delta V_l(\vec{r}_a) = 0$. This limited nonlocality means that the real-space matrix is sparse.

Because of the exchange-correlation magnetic vector field, the dimensions of the Hamiltonian matrix must be doubled with respect to those used in a collinear spin calculation. Fortunately, the doubled Hamiltonian remains highly sparse because additional off-diagonal elements are introduced only on the diagonals of the off-diagonal blocks, namely:

$$\hat{H} = \begin{pmatrix} -\frac{1}{2}\nabla^2 + \hat{V}_{eff} + b_{xcz} & b_{xcx} - ib_{xcy} \\ b_{xcx} + ib_{xcy} & -\frac{1}{2}\nabla^2 + \hat{V}_{eff} - b_{xcz} \end{pmatrix}, \quad (11)$$

where $\hat{V}_{eff} = \hat{V}_{ion} + V_H + V_{xc}$. Note that for the collinear magnetic case $b_{xcx} = b_{xcy} = 0$, the elements on the off-diagonal blocks vanish, and one can diagonalize each diagonal block independently, as customary.

Importantly, the above Hamiltonian can be used with any type of boundary condition, be it non-periodic, fully periodic, or partially periodic [31]. Even if the lattice periodicity requires a non-Cartesian grid, the same formalism can be used with a generalized high-order finite-difference expression that avoids the numerical evaluation of mixed derivative terms [31].

The above concepts were implemented in the PARSEC software suite [30]. To test our approach, we chose to apply it to a Cr_3 cluster and to a free standing monolayer of chromium in a triangular lattice, both of which are known cases of noncollinear frustrated antiferromagnets [1–3,6,7,15,23,24,26]. We further chose to compare our results with those previously obtained with the Vienna ab initio software package (VASP) by Hobbs et al. [6, 26]. This is a stringent comparison because the description of non-collinear magnetism in VASP is different than in the present work. It is plane-wave-based and uses projector-augmented waves rather than pseudopotentials to describe the core electrons.

Our real-space pseudopotential calculations presented below were performed using the local spin density approximation (LSDA) for the exchange correlation functional [20]. Because chromium core states are not strongly bound, a multi-reference norm-conserving pseudopotential [34], as implemented in the atomic pseudopotentials engine (APE) software suite [35], was used. A reference configuration of $3s^2 3p^6 3d^5 4s^1 4p^0$ and cutoff radii (in a.u.) of 1.75/1.85/1.20/2.80/3.75, respectively, were chosen, with the s component being the local one.

A map of the magnetic density vector, \vec{m} , of a Cr_3 cluster, in the cluster plane, is shown in Fig. 1. To facilitate comparison with

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