Constrained density functional theory for first principles spin dynamics

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Constrained density functional theory is used to formulate a theory of general noncollinear spin systems which makes it possible to implement first principles spin dynamics in a manner that is *firmly* grounded in density functional theory. At each time step, local constraining fields are calculated from a self-consistent algorithm. In addition to discussing the conceptual basis of the resulting constrained local moment model we illustrate the theory by explicit calculations for the relative rotation of the corner and body center moments of bcc iron. © *1999 American Institute of Physics.* [S0021-8979(99)58508-3]

I. INTRODUCTION

In a recent publication Antropov *et al.*[1] proposed first principles spin dynamics (SD) as a general theory of the dynamics of individual magnetic moments in itinerant magnets. In SD nonequilibrium *local moments* in a magnetic system (e.g., magnets above the Curie temperature T_c), evolve from one time step to the next according to a classical equation of motion. The instantaneous states, between which the classical Landau–Lifshitz equation evolves the system, and the effective field which drives their motion, are described by local spin density approximation (LSDA).[2] Thus, SD is the analog, for the magnetic moment orientational degrees of freedom, of first principles molecular dynamics for the nuclear positional degrees of freedom.

Unfortunately, there is a fundamental problem with the current formulation of SD. This results from the fact that standard LSDA is a theory of the ground state and, for spin-polarized systems, there are typically only a few magnetic configurations that are extrema of LSDA. These correspond to highly ordered moment configurations, e.g., ferromagnetic and antiferromagnetic. An arbitrary noncollinear state, such as may be encountered during a simulation of the paramagnetic state, does not generally correspond to a LSDA extremum and is therefore not well defined.

II. THE CONSTRAINED LOCAL MOMENT MODEL

First principles SD is based on the adiabatic approximation for the transverse spin degree of freedom[1,3] to define a magnetic moment on each lattice site, which points in the direction $\mathbf{e}_i$ when averaged over times long compared to the intersite hopping time.[4] A distribution of such moments defines an orientational configuration $\{\mathbf{e}_i\}$, which is the instantaneous states of spin dynamics. These then evolve from one time step to the next according to a Landau–Lifshitz equation.[2]

In general, the distribution of moments at a particular SD time step will be noncollinear. For example, a noncollinear state in which the distribution of moments is more-or-less random may be appropriate to Fe well above it's Curie temperature. As already mentioned, the problem is that these states are not extrema of LSDA.[6] However, they can be made so by using constrained density functional theory[5,6] and the introduction of local, cell dependent, constraining field the purpose of which is to force the local moments to point along the specific directions appropriate to the current time step of SD. The resulting constrained local moment (CLM) states now form a proper basis for SD. The problem at hand now is to find a sufficiently general algorithm to calculate the constraining fields.

For a noncollinear system the Kohn–Sham equations take the form

$$\left[\left(\frac{\hbar}{2m}\nabla^2+\epsilon\right)\hat{1}-\hat{V}_{\mathrm{eff}}\right]\hat{G}(\mathbf{r},\mathbf{r}';\epsilon)=\hat{1}\,\delta(\mathbf{r}-\mathbf{r}'), \tag{1}$$

$$\hat{\rho}(\mathbf{r})=-\frac{1}{\pi}\int_{-\infty}^{\infty}d\epsilon\hat{G}(\mathbf{r},\mathbf{r};\epsilon)f(\epsilon-\mu), \tag{2}$$

$$\hat{V}_{\mathrm{eff}}=\left(V_{\mathrm{ext}}+e^2\int d\mathbf{r}'\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\frac{\delta E_{\mathrm{xc}}}{\delta\rho(\mathbf{r})}\right)\hat{1}+\left(\mathbf{B}_{\mathrm{ext}}+\frac{\delta E_{\mathrm{xc}}}{\delta\mathbf{M}(\mathbf{r})}\right)\cdot\hat{\boldsymbol{\sigma}}. \tag{3}$$

In Eq. (2) $\hat{\rho}(\mathbf{r})$ is the density matrix from which the charge $\rho(\mathbf{r})=\mathrm{Tr}\,\hat{\rho}(\mathbf{r})$ and magnetization $\mathbf{M}(\mathbf{r})=\mathrm{Tr}\,\hat{\boldsymbol{\sigma}}\hat{\rho}(\mathbf{r})$ can be readily calculated. In these equations $\hat{O}$ signifies a matrix in 2×2 spin space and Tr denotes a trace over spin. For a recent review of LSDA techniques as applied to noncollinear magnetic states see Sandratskii.[7]

To properly formulate SD within density functional theory, it is necessary to solve the LSDA equations subject to an appropriate constraint

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$$\int_{\Omega_i} \mathbf{M}_i(\mathbf{r}) \times \mathbf{e}_i d\mathbf{r} = 0; \quad \forall i, \tag{4}$$

that ensures that the local magnetization has no components normal to the directions prescribed by $\{\mathbf{e}_i\}$. Such a constraint can be introduced into LSDA by the method of Lagrange multipliers.[5] A full description of how we introduce the constraints and a derivation of a self-consistent algorithm for finding them will be described in a forthcoming article. Here, we present a brief summary of the resulting CLM model that highlights the important points and necessary formulas.

In the CLM model the specific orientational configuration is maintained by local *transverse* constraining fields that are obtained self-consistently. The generalized energy functional in the presence of the constraining field takes the form

$$E_{\mathrm{con}}[\rho(\mathbf{r});\mathbf{M}(\mathbf{r});\mathbf{B}_{\mathrm{con}}(\mathbf{r})] = E_{\mathrm{int}}[\rho(\mathbf{r});\mathbf{M}(\mathbf{r});\mathbf{B}_{\mathrm{con}}(\mathbf{r})] + \int d\mathbf{r}\, \mathbf{M}(\mathbf{r}) \cdot \mathbf{B}_{\mathrm{con}}(\mathbf{r}). \tag{5}$$

Here E_{int} is the internal total energy to be identified with $E(\{\mathbf{e}_i\})$. The constraining fields are obtained from the condition

$$\frac{\delta E_{\mathrm{con}}[\rho(\mathbf{r});\mathbf{M}(\mathbf{r});\mathbf{B}_{\mathrm{con}}(\mathbf{r})]}{\delta \mathbf{e}^i} = 0, \quad \forall i. \tag{6}$$

Since the constraint in Eq. (4) is an integrated one, we have the luxury of choosing a functional form for $\mathbf{B}_{\mathrm{con}}(\mathbf{r})$ such that

$$\mathbf{B}^i_{\mathrm{con}}(\mathbf{r}) = \mathbf{c}^i B^i_{\mathrm{xc}}(\mathbf{r}), \tag{7}$$

where $\mathbf{c}^i$ is transverse to the local orientation $\mathbf{c}^i$. Equations (4)–(6) result in a practical formula for the constraining fields as follows. Let us assume we make an initial guess of the constraining field $\mathbf{c}^i_{\mathrm{in}}$. Let us also assume the size of the moment has already converged. Equation (6) then provides us with the following iterative algorithm for finding an improved (new) guess of the constraining field to be put into the next iteration:

$$\mathbf{c}^i_{\mathrm{new}} = \mathbf{c}^i_{\mathrm{in}} - (\mathbf{c}^i_{\mathrm{in}} \cdot \mathbf{e}_i)\mathbf{e}_i - [\mathbf{e}^i_{\mathrm{out}} - (\mathbf{e}^i_{\mathrm{out}} \cdot \mathbf{e}_i)\mathbf{e}_i]. \tag{8}$$

Thus, as $\mathbf{e}^i_{\mathrm{out}}$ converges to the constrained orientation $\mathbf{e}_i$, $\mathbf{c}^i_{\mathrm{in}}$ also converges to $\mathbf{c}^i$, thereby determining the constraining field, Eq. (7).

III. CONSTRAINED LOCAL MOMENT STATES OF BCC FE

In this section we investigate the nature of CLM states discussed above for a simple test case, namely, the relative rotation of the moments associated with the corner and body center sites in bcc Fe. Results are based on the locally self-consistent multiple scattering (LSMS)[8] method with an LIZ of three-neighbor shells. While this is insufficient to give results that are fully converged with respect to LIZ size it is sufficient to illustrate the CLM model. The three-neighbor shell however becomes increasingly insufficient after 90° of rotation. The constraining field was iterated to self-consistency, along with the charge and magnetization density, using Eq. (8). Converged charge and magnetization densities for ferromagnetic (collinear) Fe were used to initialize the calculations and the constraining field was initialized to zero. We found that the constraining field converged rapidly [~10 self-consistent field (SCF) iterations].

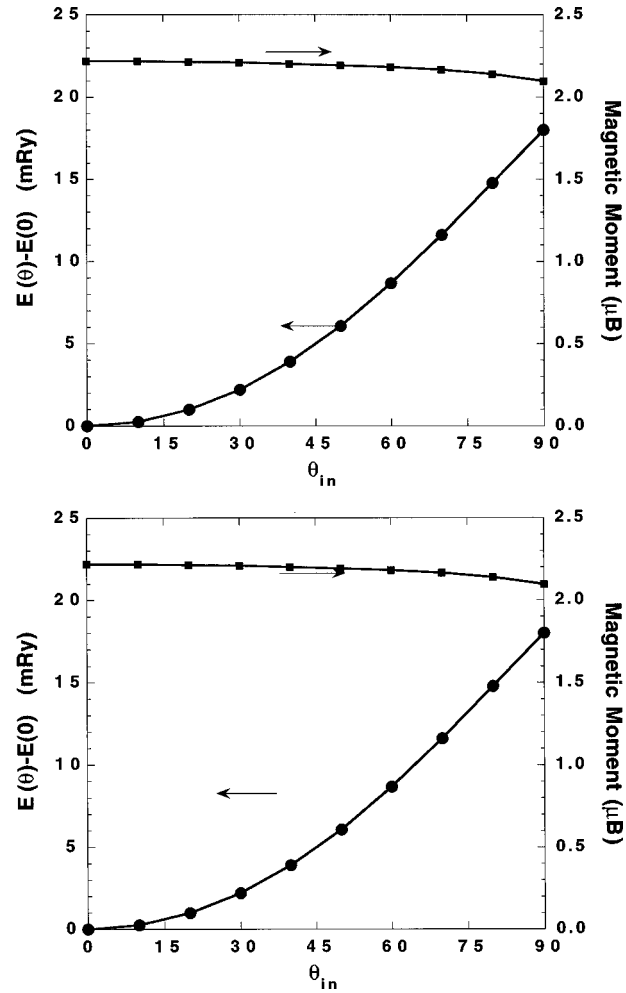

FIG. 1. (Top) Dependence of SCF constraining field on the angle between corner and body center moments (θ_{in}). (Bottom) Dependence of the total energy and magnetic moment on θ_{in}.

In Fig. 1 we show the dependence of the magnitude of the constraining field (top) and the total energy and magnetic moment (bottom) on the relative angle θ_{in} between the two moments. The constraining field is zero for the ferromagnetic configuration; this is expected since this corresponds to a unconstrained extrema. Close to the ferromagnetic state B_{con} shows a linear dependence on θ_{in}. This is consistent with Fe being a ''good'' moment, quasi-Heisenberg, system close to the allowed ground states. The magnetic moment changes little as a function of θ_{in} and the total energy is quadratic for substantial deviations (~40°), again consistent with approximate Heisenberg behavior.

Although the constraint imposed through Eqs. (4) and (7) is an integral one it is profitable to examine the extent to which the local moment rotates rigidly. Clearly, if it does not, this brings into question the efficacy of the SD approach. Rigid rotation implies that the constraint implicit in Eq. (4) applies **r** point by **r** point, which in turn implies that, in a

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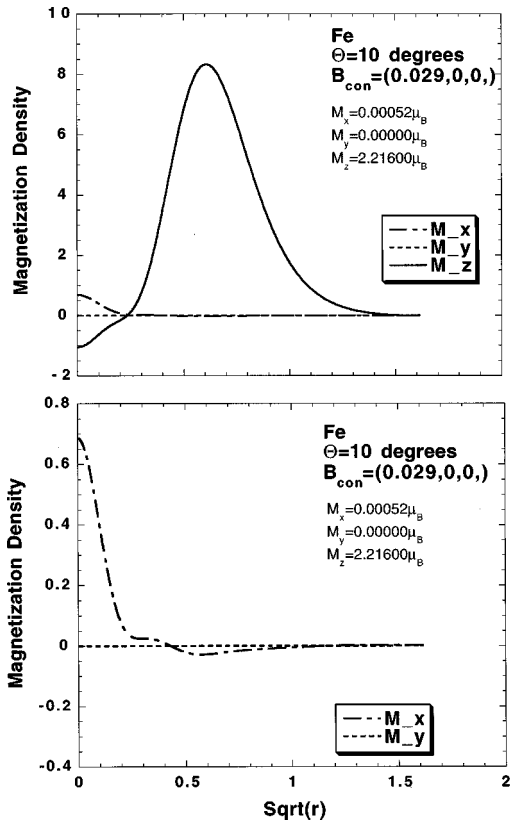

FIG. 2. Radial dependence of the x, y and z components (upper) and x and y (lower) of the magnetization appropriate to a relative rotation of 10° of the corner and body centered moments of bcc iron.

local frame of reference in which the axis of quantization is along $\mathbf{e}_i$, the x and y components of the magnetization (M_x and M_y) vanish $\mathbf{r}$ point by $\mathbf{r}$ point.

In Fig. 2 we show, for a 10° rotation, the radial dependence of M_x, M_y and M_z for a constraining field close to the self-consistent one. Clearly the transverse components of the magnetization are small for all $\mathbf{r}$. This is a further illustration of the fact that Fe is a good moment system. Close to the nucleus we observe a small negative contribution to the local magnetization M_z which we believe is (antiparallel) s,p spin polarization induced by the rotated d spin polarization.

IV. CONCLUSIONS

We have outlined a CLM model of general noncollinear spin systems which makes it possible to implement first principles spin dynamics in a manner grounded in constrained density functional theory. We have presented a general algorithm for finding the local constraining fields responsible for maintaining general noncollinear orientational configurations. We have presented results for nonequilibrium noncollinear states in bcc Fe that demonstrate that CLM states exist. Although not shown here, we have also obtained CLM states in large unit cell (up to 1024 atom) calculations of Fe having randomly oriented moments. Similar calculations for Ni and Co are ongoing.

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