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# Towards a constrained local moment model for first principles spin dynamics

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ABSTRACT

We argue that, as originally formulated, the first principles spin dynamics of the finite-temperature and non-equilibrium properties of itinerant magnets recently proposed by Antropov *et al.* is not clearly defined within density functional theory. We show how constrained density functional theory can be used to provide a formal basis for describing the instantaneous non-collinear states that are being evolved according to the classical equation of motion of spin-dynamics. We propose a constrained local moment (CLM) model in which specific orientational configurations are maintained by local transverse constraining fields that are obtained self-consistently. A general algorithm for finding the constraining fields is used and the *existence* of a CLM state is demonstrated for specific model problems including a cell of 512 Fe atoms for which the orientations of the magnetic moments are random.

## §1. INTRODUCTION

Developing a microscopic understanding of the dynamics of metallic magnets has proven to be an abiding scientific challenge. This stems from the itinerant nature of the electrons that give rise to the magnetic moment, which are the electrons that also give rise to metallic cohesion (bonding). The itinerancy of these electrons precludes straightforward application of Heisenberg models and requires that bonding and magnetism be treated on equal footing. For the ground state, it is now clear that the local-spin-density approximation (LSDA) to density functional theory (DFT) (Hohenberg and Kohn 1964, Kohn and Sham 1965) provides a resilient framework in which to discuss the properties of metallic magnets even in quite inhomogeneous situations such as disordered alloys, surfaces, and magnetic overlayers and multilayers.

In a recent publication, Antropov *et al.* (1996) proposed first-principles spin dynamics (SD) as a general theory of the dynamics of individual magnetic moments in itinerant magnets. The ideas underpinning SD go back at least two decades to the

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realization (Hubbard 1979a,b, Hasegawa 1980, You and Heine 1982, Pindor *et al.* 1983) that, in 'good' moment systems, one can make a separation between the fast electronic degrees of freedom, which give rise to local moment formation, and the moment orientation degrees of freedom, which vary slowly in time. In SD non-equilibrium *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 the motion are described by LSDA. Thus, SD is the analogue, for the magnetic moment orientational degrees of freedom, of first principles molecular dynamics for the nuclear positional degrees of freedom. As such, it is a potentially powerful new tool for treating the finite-temperature and non-equilibrium properties of metallic magnets.

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, for example ferromagnetic and antiferromagnetic. An arbitrary non-collinear 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.

In this paper we propose a constrained DFT (Dederichs *et al.* 1984) that allows us to obtain well defined constrained local moment (CLM) states that form a proper basis for SD. The central feature of the method is that local cell-dependent constraining fields are introduced, the purpose of which is to force the local moments to point along specific pre-defined directions. A general algorithm is developed for finding the constraining fields. Results are presented for two test cases that demonstrate the existence of general non-collinear CLM states.

The rest of this paper is organized as follows. In § 2 we give a brief review of SD as proposed by Antropov *et al.*, and illustrate the difficulty of defining general non-collinear states within the LSDA. In § 3 we show how to define general non-collinear states within constrained DFT. In § 4 we show results for CLM states of bcc Fe. The calculations are based on the locally self-consistent multiple scattering (LSMS) method for describing the electronic structure (Wang *et al.* 1995) extended to treat non-collinear magnets (Stocks *et al.* 1996). Some concluding remarks are contained in §5.

## § 2. Spin dynamics and local-spin-density approximation for non-collinear states

First-principles SD is based on the adiabatic approximation for the transverse spin degree of freedom (Antropov *et al.* 1996, Niu and Kleinman, 1998). It relies on the notion that close to the $i$th atom it is possible to identify a volume $\Omega_i$ in which the magnetic moment points in the same direction when average over times long compared with the intersite hopping time (Györffy *et al.* 1995). Accordingly, a unit vector $\mathbf{e}_i$, which specifies the local moment orientation associated with the $i$th site, is defined through

$$\mathbf{e}_i = \frac{\int_{\Omega_i} \mathbf{M}_i(\mathbf{r})\, \mathrm{d}\mathbf{r}}{\left|\int_{\Omega_i} \mathbf{M}_i(\mathbf{r})\, \mathrm{d}\mathbf{r}\right|}. \tag{1}$$

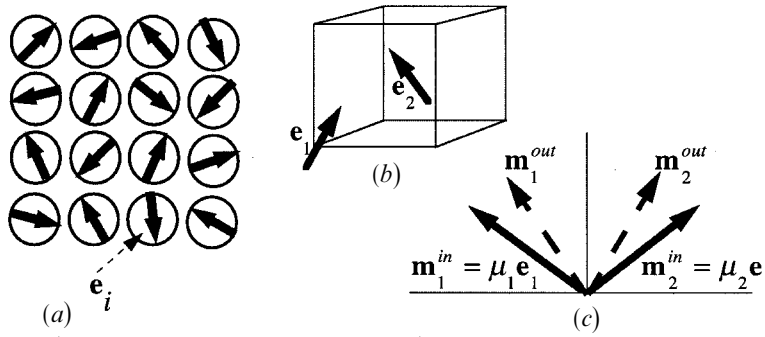



Figure 1. (*a*) A general non-collinear state. (*b*) Relative rotation corner and body centre moments in bcc Fe. (*c*) Illustration of the input and output magnetization directions during unconstrained iteration of the non-collinear Kohn–Sham equations.

In order to be definite, $\Omega_i$ can be taken as either a muffin tin or an atomic (ASA) sphere. A general non-collinear local moment state, such as that illustrated in figure 1 (*a*), is then specified by a set of local orientations $\{\mathbf{e}_i\}$. A state where the moment orientations are more or less randomly distributed may be appropriate to Fe well above the Curie temperature.

Antropov *et al.* (1996) derived an equation of motion for these orientational degrees of freedom of the form

$$\frac{\mathrm{d}\mathbf{e}_i}{\mathrm{d}t} = -2\mathbf{B}^i(\{\mathbf{e}_i\}) \times \mathbf{e}_i, \quad \forall i, \tag{2}$$

where $\mathbf{B}^i(\{\mathbf{e}_i\})$ is the effective magnetic field at the $i$th site (which depends on the total orientational configuration) and is given by

$$\mathbf{B}^i(\{\mathbf{e}_i\}) = \frac{\delta E(\{\mathbf{e}_i\})}{\delta \mathbf{M}_i}, \tag{3}$$

where $E(\{\mathbf{e}_i\})$ is the LSDA total energy corresponding to the orientational configuration $\{\mathbf{e}_i\}$ and $\mathbf{M}_i = \mu_i \mathbf{e}_i$ is the local spin moment and $\mu_i$ is its magnitude. Thus at each time step the SD algorithm consists of two parts; firstly, solution of the LSDA equations for the instantaneous orientational configuration and calculation of $B^i(\{\mathbf{e}_i\})$; secondly, integration of equation (2) to give the orientational configuration at the next time step. It is the first part of the algorithm with which the rest of this paper is concerned.

For a non-collinear systems the Kohn–Sham equations take the form

$$\left[\left(\frac{\hbar}{2m}\nabla^2 + \epsilon\right)\hat{1} - \hat{V}_{\mathrm{eff}}\right]\hat{G}(\mathbf{r},\mathbf{r}';\epsilon) = \hat{1}\delta(\mathbf{r} - \mathbf{r}'), \tag{4}$$

$$\hat{\rho}(\mathbf{r}) = -\frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\epsilon\, \hat{G}(\mathbf{r},\mathbf{r};\epsilon) f(\epsilon - \mu), \tag{5}$$

$$\hat{V}_{\mathrm{eff}} = \left(V_{\mathrm{ext}} + e^2 \int \mathrm{d}\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta E_{\mathrm{xc}}}{\delta \rho(\mathbf{r})}\right)\hat{1} + \left(\mathbf{B}_{\mathrm{ext}} + \frac{\delta E_{\mathrm{xc}}}{\delta \mathbf{M}(\mathbf{r})}\right) \cdot \hat{\boldsymbol{\sigma}}. \tag{6}$$

In equation (5), $\hat{\rho}(\mathbf{r})$ 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 $2\times 2$ spin space and Tr denotes a trace over spin. The external magnetic field $\mathbf{B}_{\text{ext}}$ remains to be specified in §4. For a recent review of LSDA techniques as applied to non-collinear magnetic states see Sandratskii (1998).

It is important to note, even in a muffin-tin model (or an atomic sphere approximation), where $\hat{\rho}(\mathbf{r})$ and $\hat{V}_{\text{eff}}$ can be decomposed into a sum of (spherically symmetric) single-site contributions ($\hat{\rho}(\mathbf{r}) = \sum_i \hat{\rho}^i(\mathbf{r})w_i(\mathbf{r})$ and $\hat{V}_{\text{eff}}(\mathbf{r}) = \sum_i \hat{v}^i(\mathbf{r})w_i(\mathbf{r})$), that the site charge densities $\hat{\rho}^i(\mathbf{r})$ and potentials $\hat{v}^i(\mathbf{r})$ are, in general, off diagonal in spin space when referenced to a single (global) frame of reference. It is, however, possible to define a local frame of reference within which they are diagonal by making use of a unitary transformation

$$\hat{U}\hat{O}_{\text{g}}\hat{U}^{\dagger} = \hat{U}\begin{bmatrix} O^i_{\text{g},11} & O^i_{\text{g},12} \\ O^i_{\text{g},21} & O^i_{\text{g},22} \end{bmatrix}\hat{U}^{\dagger} = \begin{bmatrix} O^i_{\text{l},\uparrow(\mathbf{r})} & 0 \\ 0 & O^i_{\text{l},\downarrow(\mathbf{r})} \end{bmatrix} = \hat{O}_l, \tag{7}$$

in which $\hat{O}_l$ has only *up* ($O^i_{\uparrow}$) and *down* ($O^i_{\downarrow}$) components. Here, $\hat{O}_i$ can be any site dependent quantity and the subscripts g and l refer to global and local frames of reference respectively. Clearly, a frame of reference in which $\hat{\rho}(\mathbf{r})$ is diagonal is one where the $z$ axis points along the local magnetization direction $\mathbf{M}(\mathbf{r})$. Within this frame of reference it is straightforward to calculate the *up*($\uparrow$) and *down*($\downarrow$) components of the effective potential appearing in the Schrödinger equation. It is also useful to note that, for the single-site potential, equation (7) implies that

$$\hat{v}^i = \tfrac{1}{2}(v^i_{\uparrow} + v^i_{\downarrow})\hat{I} + \tfrac{1}{2}(v^i_{\uparrow} - v^i_{\downarrow})\hat{\boldsymbol{\sigma}}\cdot\mathbf{e}_i. \tag{8}$$

The method that we use for solving the LDA equations is a generalization to non-collinear spin-polarized systems of the LSMS method (Wang *et al.* 1995). In the LSMS method the Green's function in the vicinity of site $i$ is given by

$$\hat{\mathscr{G}}_M(\{\mathbf{e}\}_i;\mathbf{r};\epsilon) = \sum_{LL'} \hat{Z}^i_L(\mathbf{r};\epsilon)\left[\hat{\underline{\tau}}_M(\{\xi\,\mathbf{e}\}_i;\epsilon)\right]^{ii}_{LL'}\hat{Z}^i_{L'}(\mathbf{r};\epsilon) - \sum_L \hat{Z}^i_L(\mathbf{r};\epsilon)\hat{J}^i_L(\mathbf{r};\epsilon), \tag{9}$$

where $M$ is the number of atoms in the local interaction zone (LIZ) (Wang *et al.* 1995) of atom $i$, $\{\xi\,\mathbf{e}\}_i$ represents a chemical and magnetic configuration of the atoms in the LIZ, and $\hat{\underline{\tau}}_M(\{\xi\,\mathbf{e}\}_i;\epsilon)$ is the corresponding scattering path matrix, which obtained from

$$\hat{\underline{\tau}} = \left[\hat{\underline{t}}^{-1} - \underline{G}_0\right]^{-1}. \tag{10}$$

Let us now illustrate the problem of defining general non-collinear magnetic states within LSDA by following the steps involved in a single self-consistent field (SCF) iteration of the Kohn–Sham equations. Suppose that we begin an SCF iteration with an *input* guess of single-site potentials $\hat{v}^i_{\text{in}}$ which are diagonal in the local frame of reference defined by the local orientation $\mathbf{e}_i$. In this frame of reference it is a simple matter to calculate the up and down components of the single site $t$-matrix and to transform to the global frame in order to set up the right-hand side of equation (10). The real-space structure constants, $G^{ij}_0(\epsilon)$ are diagonal in the global frame. Performing the inverse called for by equation (10) leads to a *output* scattering path matrix $\hat{\tau}^i_{\text{out}}$, Green's function $\hat{G}^i_{\text{out}}$ and density matrix $\hat{\rho}^i_{\text{out}}$, which are, in general, not diagonal in the original local frame. Using the output magnetization $\mathbf{M}^i_{\text{out}}$ to define an output local orientation

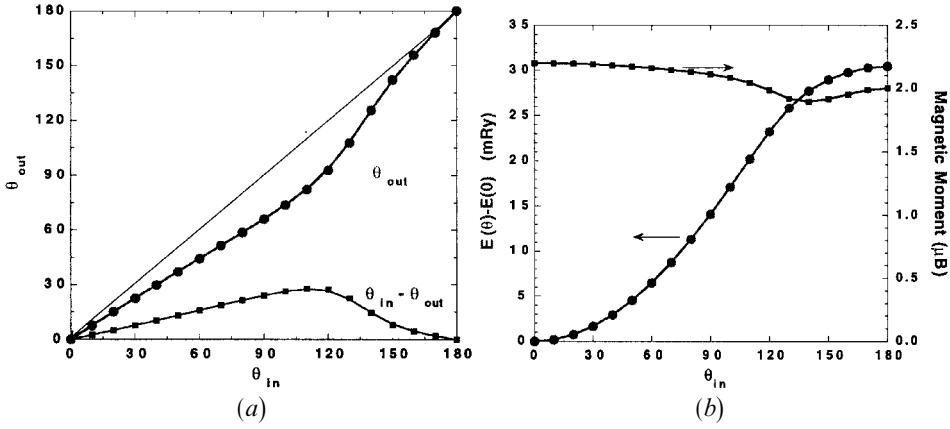



Figure 2. (*a*) Relationship between the input and output magnetization orientations during the relative rotation of the corner and body centre moments in bcc Fe using unconstrained LSDA. (*b*) Dependences of the total energy and magnetic moment on the angle between corner and body centre moments. (The lattice parameter of Fe was taken to be $a_0 = 5.27$ au.)

$\mathbf{e}_i^{\text{out}}$ according to equation (1), it is clear that $\mathbf{e}_i^{\text{out}} \neq \mathbf{e}_i$. This situation is illustrated in figures 1 (*b*) and (*c*) for the case of bcc Fe, where we specify the local orientation associated with the corner and body centre atoms to be rotated by $\pm\theta/2$ away from the collinear ferromagnetic ground state (figure 1 (*c*)) and we have shown $\mathbf{e}_i^{\text{out}}$ lagging $\mathbf{e}_i^{\text{in}}$ that is $\theta_{\text{out}}$ lagging $\theta_{\text{in}}$ (figure 1 (*a*)).

The simplest algorithm for dealing with this inconsistency is to disregard any components of the magnetization that do not point along the prescribed direction. Accordingly, we define a new *input* magnetization $\mathbf{M}_{\text{in}}^i$ by taking the projection of $\mathbf{M}_{\text{out}}^i$ along $\mathbf{e}_i$ ($\mathbf{M}_{\text{in}}^i \equiv m_{\text{in}}^i \mathbf{e}_i = \mathbf{M}_{\text{out}}^i \cdot \mathbf{e}_i$), and using this to reconstruct new single-site potentials for the next SCF iteration. For the case described above, this algorithm does have a fixed point at which the charge $\rho(\mathbf{r})$ and magnetization densities $m(\mathbf{r}) = |\mathbf{M}(\mathbf{r})|$ are, by any normal measures, self-consistent but for which $\mathbf{e}_i^{\text{out}} \neq \mathbf{e}_i$.

Figure 2 illustrates the dependence of the angle $\theta_{\text{out}}$ between the output directions (2(*a*)) and the dependencies of the magnetic moment and total energy (2(*b*)) on the relative rotation angle $\theta_{\text{in}}$, for $\theta_{\text{out}}$ in the range $0 \leqslant \theta_{\text{in}} \leqslant \pi$, that is from ferromagnetic to antiferromagnetic. Interestingly, $\mathbf{e}_i^{\text{out}}$ lags $\mathbf{e}_i^{\text{in}}$ except for $\theta = 0, \pi$ which are proper LSDA extrema corresponding to a local minimum (ferromagnetic state) and maximum (antiferromagnetic state) of the total energy. For all other values of $\theta_{\text{in}}$ this algorithm does not lead to a properly defined LSDA state in that the exchange correlation potential (which is directed along $\mathbf{e}_i$) is not collinear with the SCF magnetization (which is directed along $\mathbf{e}_i^{\text{out}}$) this is a violation of a fundamental property of DFT (Sticht *et al.* 1989). Clearly, this is not the state required by SD either. Rather, it is equivalent to that discussed by Small and Heine (1984), who also were aware of the difficulties inherent in describing general non-collinear states. It corresponds to fixing the direction of the exchange field and letting the direction of the magnetization fall where it will. In this picture (Small and Heine 1984), the non-collinearity between the exchange field and the magnetization gives rise to a *couple* which acts on the moment causing it to precess.

## §3. The constrained local moment model

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

$$\int_{\Omega_i} \mathbf{M}_i(\mathbf{r}) \times \mathbf{e}_i \, \mathrm{d}\mathbf{r} = 0, \quad \forall i, \tag{11}$$

that ensures that the local magnetization has no components normal to the directions prescribed by the orientational configuration. Such a constraint can be introduced into LSDA by the method of Lagrange multipliers (Dederichs *et al.* 1989). A full description of how we introduce the constraints and a derivation of a self-consistency algorithm for finding them will be described in a forthcoming paper. Here, we present a brief description of the resulting CLM model that highlights the important points and necessary formulae.

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

$$E_{\mathrm{con}}\left[\rho(\mathbf{r}); \mathbf{M}(\mathbf{r}); \mathbf{B}_{\mathrm{con}}(\mathbf{r})\right] = E_{\mathrm{internal}}\left[\rho(\mathbf{r}); \mathbf{M}(\mathbf{r}); \mathbf{B}_{\mathrm{con}}(\mathbf{r})\right] + \int \mathrm{d}\mathbf{r}\, \mathbf{M}(\mathbf{r}) \cdot \mathbf{B}_{\mathrm{con}}(\mathbf{r}). \tag{12}$$

Here $E_{\mathrm{internal}}$ is the internal total energy to be identified with $E(\{\mathbf{e}_i\})$ and is given by

$$\begin{aligned} E_{\mathrm{internal}}(\{\mathbf{e}_i\}) = {} & E_{\mathrm{Band}}\left[V_{\mathrm{eff}}, \mathbf{B}_{\mathrm{eff}}\right] - \int \rho(\mathbf{r})\, V_{\mathrm{eff}}(\mathbf{r})\, \mathrm{d}\mathbf{r} - \int \mathbf{M}(\mathbf{r}) \cdot \mathbf{B}_{\mathrm{eff}}(\mathbf{r})\, \mathrm{d}\mathbf{r} \\ & + E_{\mathrm{xc}}\left[\rho(\mathbf{r}), |\mathbf{M}(\mathbf{r})|\right] + E_{\mathrm{Coulomb}}\left[\rho(r)\right] + \int \mathbf{M}(\mathbf{r}) \cdot \mathbf{B}_{\mathrm{con}}(\mathbf{r})\, \mathrm{d}\mathbf{r}, \end{aligned} \tag{13}$$

where

$$\begin{aligned} V_{\mathrm{eff}} &= V_{\mathrm{Coulomb}}\left[\rho(\mathbf{r})\right] + V_{\mathrm{xc}}\left[\rho(\mathbf{r})\right], \\ \mathbf{B}^i_{\mathrm{eff}} &= \mathbf{B}^i_{\mathrm{xc}}\left[\mathbf{M}(\mathbf{r})\right] + \mathbf{B}^i_{\mathrm{con}}(\mathbf{r}) = \mathbf{e}_i B^i_{\mathrm{xc}}(\mathbf{r}) + \mathbf{B}^i_{\mathrm{con}}(\mathbf{r}), \end{aligned} \tag{14}$$

and self-consistency is enforced by

$$\begin{aligned} \rho(\mathbf{r}) &= \mathrm{Tr}\, \hat{\rho}(\mathbf{r}), \\ \mathbf{M}(\mathbf{r}) &= \mathbf{e}_i\left[\mathbf{e}_i \cdot \mathrm{Tr}\, \hbar \hat{\rho}(\mathbf{r})\right] \end{aligned} \tag{15}$$

and

$$\frac{\delta E_{\mathrm{con}}\left[\rho(\mathbf{r}); \mathbf{M}(\mathbf{r}); \mathbf{B}_{\mathrm{con}}(\mathbf{r})\right]}{\delta \mathbf{e}_i} = 0, \quad \forall i. \tag{16}$$

Note that $\mathbf{e}_i$ is determined by $\int_i \mathrm{d}\mathbf{r}\, Tr \hbar \hat{\rho}(\mathbf{r})$ and in equation (15) we have enforced the collinearity of moments within an atomic or muffin-tin sphere. This is necessary for keeping the system conservative within the local moment model. Since the constraint in equation (11) is an integrated one, we have the luxury of choosing a functional form for $\mathbf{B}_{\mathrm{con}}(\mathbf{r})$ such that

$$\mathbf{B}_{\mathrm{con}}(\mathbf{r}) = \mathbf{c} B_{\mathrm{xc}}(\mathbf{r}). \tag{17}$$

A particular advantage of this choice is that no change to the solution of the Schrödinger equation that was outlined in the last section needs to be made, with the exception that the single-site potential in equation (19) is replaced by

$$\hat{v}^i = \tfrac{1}{2}(v^i_\uparrow + v^i_\downarrow)\hat{I} + \tfrac{1}{2}\left[(1 + c^2)^{1/2}(v^i_\uparrow - v^i_\downarrow)\right]\hat{\mathbf{h}} \cdot \mathbf{e}_i. \tag{18}$$

Using equations (3) and (16), the effective field appearing in the SD equation (equation (2)) is identified as

$$\mathbf{B}^i = -\frac{\mathbf{c}^i}{\mu_i}\int_i \mathrm{d}\mathbf{r}\, m(\mathbf{r}) B_{\mathrm{xc}}(\mathbf{r}). \tag{22}$$

This equation has a simple interpretation, namely the effective field that rotates the moment is simply the opposite of the constraint field. Physically, this is exactly the requirement that the addition of the constraining field should compensate the internal driving force so as to stabilize a density functional 'ground' state.

In closing this section we make a further point that is of more programmatic significance. 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 (16) 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;

$$\mathbf{c}^i_{\mathrm{new}} = \mathbf{c}^i_{\mathrm{in}} - (\mathbf{c}^i_{\mathrm{in}} \cdot \mathbf{e}_i)\mathbf{e}_i - \left[\mathbf{e}^i_{\mathrm{out}} - (\mathbf{e}^i_{\mathrm{out}} \cdot \mathbf{e}_i)\mathbf{e}_i\right]. \tag{20}$$

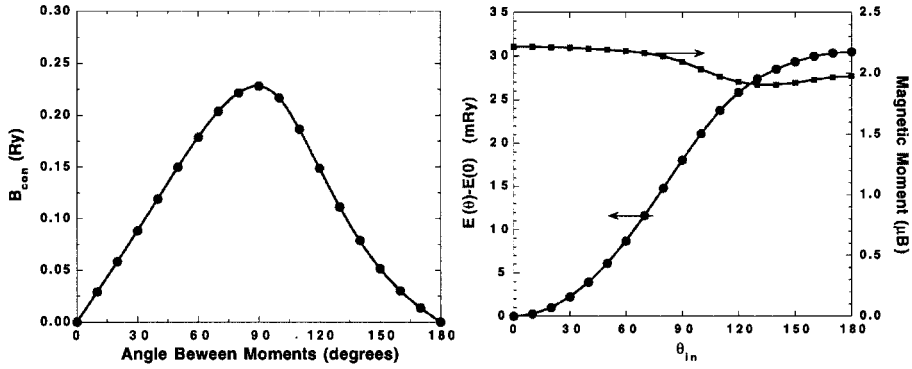
Thus, as $\mathbf{e}^i_{\mathrm{out}}$ converges to the constrained orientation $\mathbf{e}_i$, $\mathbf{c}^i_{\mathrm{in}}$ also converges to $\mathbf{c}^i$, thereby determining the constraining field (equation (17)).

## §4. Constrained local moment states of bcc Fe

In this section we investigate the existence of CLM states for two model problems that serve to illustrate the main consequences of the above discussion.

We begin by restudying the problem discussed in §2, namely the relative rotation of the moments associated with the corner and body centre sites in bcc Fe. Results are based on the LSMS method with a LIZ of three-neighbour 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 constraining field was iterated to self-consistency, together with the charge and magnetization density, using equation (20). 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 (about ten SCF iterations).

In figure 3(*a*) we show the dependence of the magnitude of the constraining field (left) and in figure 3(*b*) the dependencies of the total energy and magnetic moment on the relative angle $\theta_{\mathrm{in}}$ between the two moments. The constraining field is zero for both the ferromagnetic and the antiferromagnetic configurations; this is expected since these correspond to unconstrained extrema. Close to the ferromagnetic and antiferromagnetic states, $B_{\mathrm{con}}$ shows a linear dependence on $\theta_{\mathrm{in}}$. This is consistent with the fact that Fe is a 'good'-moment quasi-Heisenberg system close to the allowed ground states. The magnetic moment changes little as a function of $\theta_{\mathrm{in}}$ and the total energy is quadratic for substantial deviations (about 40°), again consistent with approximate Heisenberg behaviour.

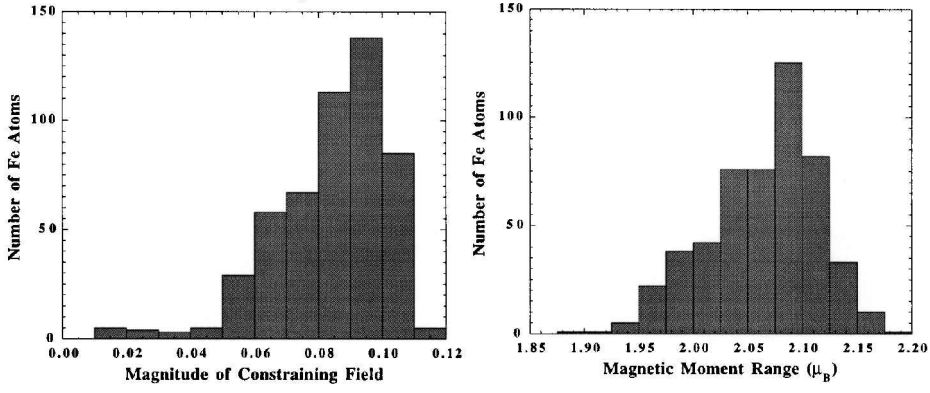



(*a*) (*b*)

Figure 3. (*a*) Dependence of SCF contraining field on the angle between corner and body centre moments $\theta_{\text{in}}$. (*b*) Dependence of the total energy and magnetic moment on $\theta_{\text{in}}$.

In figures 4(*a*) and (*b*) we show histograms of the distribution of constraining fields and magnetic moments respectively for a large-unit-cell model of a disordered local moment (DLM) state of bcc Fe. The unit cell was constructed from a $8 \times 8 \times 4$ repeat of an underlying bcc lattice. The orientational configuration $\{\mathbf{e}_i\}$ was generated by randomly distributing the orientations over the unit sphere. Such a state may be thought of as prototypical of paramagnetic Fe far above $T_{\text{C}}$. The calculations were performed on the 512-processing element Cray T3E at the National Energy Research Supercomputer Center. Again we found the constraining fields converged rapidly (a few tens of iterations). We found the convergence of the charge and magnetization densities to be slow (about 800 iterations), although it should be pointed out that we used only simple mixing with a small mixing parameter in order to keep the first search for such a complex magnetic state simple.

Both the constraining fields and the magnetic moments show a distribution of values. The centre of gravity of the constraining field ($B_{\text{con}} \approx 0.09$) corresponds to that required to give a rotation of about 30° in our two-moment study. The peak in the moment distribution is at about $2.08\mu_{\text{B}}$ which is to be compared with about $2.18\mu_{\text{B}}$ for ordered ferromagnetic Fe (see figure 3). The reduction in the average




(*a*) (*b*)

Figure 4. (*a*) Histogram of the distribution of constraining fields for a 512 atom per unit cell DLM state of bcc Fe. (*b*) Histogram of the distribution of magnetic moments.

moment and the fact that the moments are distributed in the range $1.8 \rightarrow 2.2\mu_B$ are both indicative of non-Heisenberg behaviour.

## §5. Conclusions

We have outlined a constrained DFT which provides a formal basis for defining the instantaneous states required for first principles SD. We have demonstrated the existence of CLM states for two test cases. The algorithm presented for finding the constraining fields responsible for maintaining the CLM state appears to be robust and general. To date we have not investigated the factors governing the magnitude of the constraining fields for either of our model systems, however, the data sets of results, particularly those for the 512 atom DLM state, provides a basis for such a study.

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