

## Spin dynamics in magnets: Equation of motion and finite temperature effects

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General equations of motion are introduced for the evaluation of spin dynamics in magnetic materials. The theory uses the adiabatic separation of diagonal and off-diagonal components of the spin density matrix. This adiabatic approach considers the orientation of the local magnetic moments to be slowly varying relative to their magnitudes. The angles of the magnetization density are introduced as *collective* variables in density functional theory. The equations and technique can be simultaneously combined with those of first-principles molecular dynamics for the consistent treatment of spin-lattice interactions. Stochastic and deterministic approaches for treating finite temperature effects are introduced for such dynamics. The method is implemented within the local density approximation and applied to  $\gamma$ -Fe, a frustrated system where we obtain additional low-energy magnetic configurations. [S0163-1829(96)04026-X]

### INTRODUCTION

The theoretical description of the properties of magnets has a long history fraught with complexities. The difficulty of reconciling experimental results which indicate local magnetic moments (MM's) and bandlike itinerant electrons has been recounted numerous times. There have been a number of theoretical approaches suggested and quite a number of successes.<sup>1-3</sup> For highly correlated (nearly localized) systems, the Hubbard model and its extensions have provided considerable insight, although the parameters entering the model are frequently empirical or obtained by other theoretical methods which better lend themselves to first-principles calculations. Among these methods, the local spin density approximation (LSDA) to density functional (DF) theory<sup>4</sup> has proven accurate and popular for calculating ground-state, static magnetic properties. Questions still abound concerning the high-temperature and excited-state properties, where local changes in the MM directions or magnitudes destroy the periodicity which is so convenient for accurate electronic structure calculations. Methods designed for disordered alloys have been utilized to gain insight into the average high-temperature magnetic structure,<sup>5</sup> and different tight-binding (TB) and DF methods have been proposed<sup>6-8</sup> to consider the states with deviated directions of MM's for  $T=0$ ; however, there remain many open questions which we believe a more general finite temperature *ab initio* approach to spin dynamics (SD) can address.

We recently presented a brief description of a general method for treating the motion of MM's in magnetic materials.<sup>9</sup> The basic idea is to treat the angles defining the MM directions as slow degrees of freedom [like the nuclear coordinates in the Born-Oppenheimer adiabatic approach to molecular dynamics (MD)]. The equations of motion (EOM's) can be solved using force (or torque) techniques

within first-principles self-consistent-field (SCF) theory. Also, by combining *ab initio* SD and MD, simulations involving spin-lattice interactions may be undertaken.

The physical picture underlying the SD formalism which we present is not completely new, although the general derivation of the EOM's and their implementation with first-principles techniques are of fundamental importance. In the first section the adiabatic time-dependent density functional approach for magnetic systems is presented. We begin with the time-dependent Pauli (the spinor form of the Schrödinger) equation and obtain the desired EOM's for SD. The basic assumption and physical arguments for the validity of the EOM's are also presented. Specific formulas are given for implementing the method within a standard multiple-scattering formalism. In Sec. II relativistic considerations, including spin-orbit (SO) coupling, are discussed, and in Sec. III an orbital-dependent variant of the formalism is presented, which is appropriate for adiabatic Hartree-Fock types of treatments of the electronic structure. Section IV deals with the inclusion of the temperature into the EOM's, while Sec. V outlines the generalization required to simultaneously run both MD and SD simulations. Section VI gives a brief description of the method employed for the calculation of the electronic structure. In Sec. VII we describe the results obtained from implementing the SD formalism for  $\gamma$ -Fe and Ni-Fe. Finally, we summarize the content of the paper and discuss the prospects for future applications of SD.

### I. ADIABATIC DENSITY FUNCTIONAL SPIN DYNAMICS

The theory of magnetism is fundamentally the theory of electronic structure. The most widely used and successful techniques to study the electronic structure of extended solids are based on the DF formalism.<sup>4</sup> The equations to be solved are familiar from SCF methods in which each elec-

tron moves in the average ‘‘charge’’ and ‘‘spin’’ SCF’s  $V(\mathbf{r})$  and  $\mathbf{B}(\mathbf{r})$  of the electrons and ions. Each one-electron state  $\Psi$  is a solution of the Schrödinger-Pauli equation with the effective Hamiltonian

$$H = H_L - \hat{\boldsymbol{\sigma}} \cdot \mathbf{B}, \quad (1)$$

$$H_L = -\nabla_{\mathbf{r}}^2 + \sum_{\mathbf{R}} V_{\mathbf{rR}} + 2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + V_{xc},$$

where  $V_{\mathbf{rR}}$  describes the interaction between the electrons and the nuclear charges (we use Ry units),  $V_{xc}$  and  $\mathbf{B}$  are the scalar and vector parts of the exchange-correlation potential, respectively, and the one-electron equation has the form

$$i \frac{\partial \Psi}{\partial t} = [H_L - \hat{\boldsymbol{\sigma}} \cdot \mathbf{B}(\mathbf{r}, t)] \Psi, \quad (2)$$

where

$$\Psi = \begin{pmatrix} \Psi_+ \\ \Psi_- \end{pmatrix}$$

is the electronic spinor. The field  $\mathbf{B}(\mathbf{r}, t)$ , in general, has both a time and space dependence for both magnitude and direction. Except for this time and space dependence for  $\mathbf{B}$ , Eq. (2) is fairly standard. Below we show how the time dependence can be separated into an EOM for the local magnetization (or local MM) and (with the adiabatic approximation) a standard single-particle electronic spin-polarized equation. For a derivation of the nonstationary Schrödinger equation in the framework of the DF approach, see, e.g., Ref. 10.

The full electronic dynamics of Eq. (2) can be equally well described by the dynamics of the one-particle density matrix  $\hat{\rho}(\mathbf{r}, t)$  which can be expanded as

$$\hat{\rho}(\mathbf{r}, t) = n(\mathbf{r}, t) \hat{I}/2 + \mathbf{m}(\mathbf{r}, t) \cdot \hat{\boldsymbol{\sigma}}/2, \quad (3)$$

where  $n(\mathbf{r}, t)$  is the charge density and  $\mathbf{m}(\mathbf{r}, t)$  is the magnetization density. Among these four variables, two components,  $n$  and  $m_z$ , are spin diagonal, whereas the  $m_x$  and  $m_y$  components are spin off-diagonal elements of the density matrix. Here we are considering a system with noncollinear magnetic ordering among spatial regions surrounding the atoms.

We introduce global and local coordinate axes, so that the local  $z$  axes, centered at atomic sites, are not necessarily parallel. The starting point of our adiabatic approximation is the assumption that the effective time scales for the evolution of the diagonal ( $n$  and  $m_z$ ) and off-diagonal ( $m_x$  and  $m_y$ ) density matrix components are different, with the dynamics of the diagonal elements being much faster compared to that of the off-diagonal elements. In other words, we assume that on the time scale when the charge density and the  $z$  component of the magnetization density are varied, the orientation of the magnetization can be considered as fixed. The geometric picture of this evolution can be thought as a slow rotation of the local coordinate axes in time. The physical idea of this adiabatic separation in the electronic theory of magnetism is not new and has been discussed since the 1950s. Discussions can be found in Refs. 1 and 2 and especially in Ref. 3 (dis-

ussion of the spin adiabatic approximation for one particle in an external magnetic field can be found in Refs. 11–13 and references therein).

This approximation is motivated by the following observation. The interatomic exchange parameters among MM’s (e.g., the  $J_{ij}$  parameters in a Heisenberg Hamiltonian) are small ( $< 100$  meV) compared to the characteristic electronic energies such as intraatomic exchange, bandwidth, etc. Thus the MM directions correspond to the slow degrees of freedom within the adiabatic approximation while the evolution of the magnitudes of the MM’s is determined by the change of the electronic wave functions (fast degrees of freedom). Using the analogy with the Born-Oppenheimer approximation, the moment directions correspond to the slow nuclear motion, and the forces or torques governing their rotation arise from the rapid relaxation of the electronic system to the instantaneous directions (or positions) of the moments.

The starting point for this spin variant of the adiabatic technique relies on the possibility of instantaneously diagonalizing a time-dependent Hamiltonian (1) whose time evolution is slow enough so that no level transition is induced by the dynamics. Using the canonical transformation  $\Psi = U\chi$ ,<sup>3,12,13</sup> where

$$U(\xi) = (1 + |\xi|^2)^{-1/2} \begin{pmatrix} 1 & \xi \\ -\xi^* & 1 \end{pmatrix} \quad (4)$$

and  $\xi = -\exp(-i\varphi)\tan\theta/2$ , the new diagonal (adiabatic) Hamiltonian can be rewritten as

$$H_{\text{diag}} = -\hat{\sigma}_z B_z - iU^\dagger(\xi) \frac{d}{dt} U(\xi), \quad (5)$$

where the diagonal for the second term is

$$U^\dagger(\xi) \frac{d}{dt} U(\xi) = \frac{\xi \dot{\xi}^* - \xi^* \dot{\xi}}{1 + |\xi|^2} \hat{\sigma}_z = i(1 - \cos\theta) \dot{\varphi} \hat{\sigma}_z. \quad (6)$$

This transformation depends on the atomic site and we introduce a site index to emphasize the different local (or atomic) coordinate axes. We write all equations in the local coordinate systems (which are slowly precessing in time). Now the time-dependent electronic equations may be written as

$$i \frac{d}{dt} \chi(\mathbf{r}, t) = \left( H_L - \sum_i \hat{\sigma}_{z_i} (B - B_g)_{z_i} \right) \chi(\mathbf{r}, t). \quad (7)$$

In arriving at this equation we neglected all spin-flip elements (proportional to  $\hat{\sigma}_+$  or  $\hat{\sigma}_-$ ), and all ‘‘magnetic’’ gradients involving  $\nabla\theta(\mathbf{r})$  or  $\nabla\varphi(\mathbf{r})$  (see the discussion of the rigid-spin approximation below). The term  $B_g(\mathbf{r}) = [1 - \cos\theta(\mathbf{r})]\dot{\varphi}(\mathbf{r})$  (Refs. 3 and 11) can be dropped due to the presence of  $\dot{\varphi}(\mathbf{r})$ . Finally, our equation for  $\chi_+$  and  $\chi_-$  can be written as

$$i \frac{d}{dt} \begin{pmatrix} \chi_+(r, t) \\ \chi_-(r, t) \end{pmatrix} = \left( H_L - \sum_i \hat{\sigma}_{z_i} B_{z_i}(\mathbf{r}, t) \right) \begin{pmatrix} \chi_+(\mathbf{r}, t) \\ \chi_-(\mathbf{r}, t) \end{pmatrix}. \quad (8)$$

Now in the adiabatic limit one can define a set of instantaneous eigenstates associated with the Hamiltonian evaluated at time  $t$  by solving the time-independent equation

$$\left( H_L - \sum_i \hat{\sigma}_{z_i} B_{z_i} \right) \begin{pmatrix} \chi_+(\mathbf{r}) \\ \chi_-(\mathbf{r}) \end{pmatrix} = \varepsilon \begin{pmatrix} \chi_+(\mathbf{r}) \\ \chi_-(\mathbf{r}) \end{pmatrix}. \quad (9)$$

Equation (9) is the standard problem of any spin-polarized DF method<sup>8</sup> allowing for noncollinear local moment directions in the stationary case. The dynamics of  $\chi_+$  and  $\chi_-$  determines the dynamics of the diagonal (in local axes) components of  $\hat{\rho}$  in the adiabatic limit for  $T=0$ .

We next obtain the EOM for the other components of  $\hat{\rho}$ . It can be obtained by multiplication of Eq. (2) by  $\Psi^* \hat{\sigma}$  from the left and adding the corresponding conjugate equation. We obtain

$$\dot{\mathbf{m}}(\mathbf{r}, t) = \gamma \mathbf{m} \times \mathbf{B} + \frac{i}{2} \nabla (\Psi^* \hat{\sigma} \cdot \nabla \Psi - \text{c.c.}), \quad (10)$$

where c.c. is the complex conjugate and  $\gamma$  is the gyromagnetic ratio. A modified Hamilton form of this equation was presented in Ref. 9 [there the term with  $V_{ss}$  is the precession term in Eq. (10) while the term with  $V_{es}$  is responsible for orbital- and coordinate-dependent interactions]. The structure of the second term in Eq. (10) is complicated and contains spatial derivatives of wave functions. Depending on the choice of the wave function, different forms of these gradient terms can be obtained.<sup>14</sup> Among the quantum effects arising from these terms are longitudinal spin fluctuations (i.e., the change of amplitude of the local MM's due to the appearance of electron-hole pairs). Consideration of such processes is obviated by the reduction of the exact, nonstationary Eq. (2) to the SD equations, where Eq. (8) allows for changes in the moment magnitude. We would like to stress that both the moment directions and moment amplitudes (along with the charge density) are time dependent in our approach, and, as we will see later, can be treated as functions of temperature. This is an important difference compared to previous models of classical SD. We now proceed with a detailed description of the quasiclassical spin approximation, which is also a more suitable starting point for the inclusion of temperature effects.

In considering local magnetic properties it is common to assume that the magnetization density in the immediate vicinity of an atom has a uniform orientation. With this ansatz we gain an important reduction of Eq. (10). Specifically, we assume that space is divided into spheres or polyhedra, and that within each such region  $\Omega_i$  we associate a unit vector  $\mathbf{e}_i$  with the instantaneous magnetization direction. We call this the ‘‘rigid’’-spin approximation (RSA).<sup>15</sup> If such a region is associated with one particular atom then the moment  $\mathbf{M}_i = \mu \mathbf{e}_i$  of this region is the average or ‘‘rigid’’ atomic magnetic moment. By the term ‘‘rigid’’ we mean that in the time evolution of the orientation there is a simultaneous (or rigid) rotation of the magnetization density at each point inside the atomic sphere (or polyhedra) by the same angle, whereas the amplitude of the magnetization density [the  $m_z(\mathbf{r})$  component] changes its value according to Eq. (8). This approximation of a uniform direction of the magnetization density surrounding an atom is a standard assumption in experimental analysis of magnetic structures and has so far been used in band structure calculations for ordered<sup>8</sup> and disordered<sup>6,7,5</sup> magnets. We also refer to this as the quasiclassical approximation when the spin direction is rotated and the magnitude

is governed by quantum equations. Our approach thus makes use of the standard LSDA, but in addition introduces the angles of the magnetization density as *collective* variables.

We will assume that the last term in Eq. (10) can be omitted within the RSA, and for the spatially averaged magnetization inside an atomic sphere one may write

$$\frac{d\mathbf{e}}{dt} = -\frac{2}{\mu} \mathbf{e} \times \mathbf{I}, \quad (11)$$

where  $\mathbf{I} = -\mu \mathbf{B}$  and  $\mathbf{M} = \mu \mathbf{e}$ . Equation (11) describes the precession of the  $\mathbf{M}_i$  of the  $i$ th sphere under the action of internal and external (due to intersite interactions) fields. The quantity  $\mathbf{I}$  can be considered as an effective time-dependent spin splitting, and has units of energy (see also Ref. 7). As the moment direction changes, self-consistency will generally require  $\mathbf{I}$  and the potentials to change as well. Equations (11) and (9) are the basis of our quantum classical variant of *ab initio* SD. These equations are useful under the following approximations.

(i) It is possible to identify well-defined regions having more or less uniform distribution of spin direction, with the spin density outside equal to zero. This implies the existence of well-defined local MM's (we assume here also a case of several on-site rigid MM's with different directions). This approximation seems justified in metals of the Fe group, in strong-itinerant-electron magnets such as Heusler alloys, and in rare-earth magnets, etc. The opposite limiting case is the weak itinerant magnets like  $\text{ZrZn}_2$ ,  $\text{Sc}_3\text{In}$ , or some magnetic impurities in metals of the Fe group. Here the magnetization arises because of specific narrow peaks in the electronic density of states (DOS) at the Fermi level, fulfilling the Stoner criteria. Under such circumstances the concept of the moments rotating nearly rigidly probably breaks down and the excitations can be more from electron-hole pairs than from moment rotations or magnons.

(ii) The adiabatic approximation is valid, which seems quite reasonable for all magnets with local MM's, because the ratio between intersite exchange parameters and relevant electronic energies is small in this case. The concrete conditions for the validity of the adiabatic approximation are different for different magnetic systems. For magnetic dielectrics or for rare-earth materials the criterion is simple,  $J \ll U$  (where  $U$  is the on-site Hubbard parameter), and it holds without any real restrictions. In  $3d$  magnets the situation is rather more complicated, since the magnetism may be determined by a rather small group of  $d$  electronic states near the Fermi level (see paragraph above), and the ‘‘adiabatic’’ condition  $J \ll W$  ( $W$  is an effective bandwidth) is not necessarily satisfied, since  $W$  may correspond to the width of a DOS peak rather than the total bandwidth (see Ref. 16). However, according to experiments in Fe, Co, and Ni,<sup>17</sup> the local MM's are well defined (in the paramagnetic region also). This circumstance leads us to believe that the adiabatic approximation is qualitatively valid for most magnetic systems.

From the formal point of view, under ‘‘adiabatic approximation’’ we understand something analogous to the ‘‘static approximation’’ in the functional integral approach to the Hubbard model,<sup>2</sup> where the initial many-electron system is

mimicked by the system of classical MM's, when the directions and amplitudes are determined self-consistently from the requirement of minimizing the free energy.

For a practical implementation of SD, we must resort to a specific means for calculating the electronic structure to obtain the ‘‘forces,’’ i.e., the first variation of the total energy for a differential rotation of a local moment. The formalism of multiple-scattering theory<sup>18</sup> together with the ‘‘force theorem’’ generalized for noncollinear magnetic perturbations<sup>19</sup> offers a highly effective method for the implementation of the RSA and the calculation of  $\mathbf{I} = \delta E / \delta \mathbf{e} = \partial E / \partial \mathbf{e}$  in Eq. (11). We can define the orientation of the local moment by defining at each site a local axis  $\mathbf{e}_i$  for the spin density matrix. In this case the ‘‘rotational’’ part of the inverse one-site scattering matrix  $P$  can be represented as a vector (using the decomposition of the  $P$  matrix into scalar and vector parts in spin space):

$$P(\varepsilon) = p_0 \cdot \hat{I} + \mathbf{p} \cdot \hat{\sigma} = p_0 \cdot \hat{\mathbf{I}} + p \mathbf{e} \cdot \hat{\sigma}, \quad (12)$$

where  $p_0 = \text{Tr}_\sigma P / 2$  and  $\mathbf{p} = \text{Tr}_\sigma (P \cdot \hat{\sigma}) / 2$ . Here  $\hat{\sigma}$  is a vector of Pauli matrices. And for the path operator  $T$  matrix the same spin-space decomposition is required:

$$\tau(\varepsilon) = T_0 \cdot \hat{I} + \mathbf{T} \cdot \hat{\sigma} = T_0 \cdot \hat{\mathbf{I}} + T \mathbf{e} \cdot \hat{\sigma}, \quad (13)$$

$T_0 = \text{Tr}_\sigma \tau / 2$ , and  $\mathbf{T} = \text{Tr}_\sigma (\tau \cdot \hat{\sigma}) / 2$  (in general  $\mathbf{p}$  and  $\mathbf{T}$  are not parallel). On the level of time-dependent multiple-scattering formalism one can say that  $T_0$  and  $T^z$  are ‘‘fast’’ variables, whereas  $T^y$  and  $T^x$  are ‘‘slow’’ variables. Then the variation of the single-site scattering matrix is given by

$$\delta P(\varepsilon) = \delta \mathbf{p} \cdot \hat{\sigma} = p(\varepsilon) \delta \mathbf{e} \cdot \hat{\sigma} = p(\varepsilon) (\delta \boldsymbol{\varphi} \times \mathbf{e}) \cdot \hat{\sigma}, \quad (14)$$

where  $\delta \boldsymbol{\varphi}$  is the rotation angle of the unit vector  $\mathbf{e}$  (see Ref. 19). For a general orientation of MM's the effective spin splitting may be written in vector notation as

$$\mathbf{I}_i = \frac{2}{\pi} \int_{\varepsilon_f}^{\varepsilon_f} d\varepsilon \text{Im Tr}\{T_{ii} \mathbf{p}_i\}, \quad (15)$$

where  $\varepsilon_f$  is the Fermi energy and  $\mathbf{T}(\varepsilon)$  has the same spin direction for any energy. The parameter  $\mathbf{I}_i$  corresponding to rotations at a single site  $\mathbf{e}_i$  or to a collective mode such as a spin wave  $\mathbf{e}_{\mathbf{Q}} = \mathbf{e}_i \exp\{i\mathbf{Q} \cdot \mathbf{R}_i\}$  may be calculated, and consequently both real-space (short-range) and reciprocal-space (long-range) spin splittings may be determined.

Within this multiple-scattering implementation an expression for updating the amplitude of the magnetic moments can also be found. If we use the relation

$$\mathbf{M}_i = \mu_i \mathbf{e}_i = -\frac{1}{\pi} \int_{\varepsilon_f}^{\varepsilon_f} d\varepsilon \text{Im Tr}(\tau_{ii} \hat{\sigma}) \quad (16)$$

and the sum rule for the collinear state<sup>9,19,20</sup>

$$\delta \tau_{ii} = -\sum_j T_{ij}^\dagger \delta p_j T_{ji}^\dagger, \quad (17)$$

the expression for the change of amplitude of the MM's can be written

$$\dot{\mu}_i = \frac{2}{\pi} \int_{\varepsilon_f}^{\varepsilon_f} d\varepsilon \text{Im Tr} \left\{ \sum_j T_{ij}^\dagger p_j T_{ji}^\dagger \mathbf{e}_i \cdot \dot{\mathbf{e}}_j \right\}. \quad (18)$$

This expression is the time-dependent analog of the linear-response technique used to accelerate self-consistency in standard electronic structure methods.

As an illustration, we show how the EOM, Eq. (11), may be solved in the case of small deviations from the ordered ground state ( $\mathbf{e}' = \mathbf{e} + \delta \mathbf{e}$ ), which corresponds to linear spin-wave excitations. In this case

$$\frac{d \delta \mathbf{e}}{dt} = -\frac{2}{\mu} ([\delta \mathbf{e} \times \mathbf{I}] + [\mathbf{e} \times \delta \mathbf{I}]). \quad (19)$$

By choosing the local coordinate system  $\mathbf{p} \parallel \mathbf{z}$  and  $\delta p_i^+ = p_i^z \delta e_i^+$  we find

$$T_{ii}^+ = -\sum_j T_{ij}^\dagger p_j^+ T_{ji}^\dagger \quad (20)$$

from Eq. (17) and

$$T_{ii}^z = -\sum_j T_{ij}^\dagger p_j^z T_{ji}^\dagger \quad (21)$$

which allows the linearized EOM Eq. (11) to then be rewritten for the collinear state as

$$\omega \cdot \delta e_i^+ = \frac{2}{\mu_i} \sum_j J_{ij} (e_j^z \delta e_i^+ - e_i^z \delta e_j^+) \quad (22)$$

with the effective exchange interactions given by

$$J_{ij} = \frac{1}{\pi} \int_{\varepsilon_f}^{\varepsilon_f} d\varepsilon \text{Im Tr}\{p_i T_{ij}^\dagger p_j T_{ji}^\dagger\}. \quad (23)$$

This expression for  $J_{ij}$  is the same as the one obtained in Ref. 19.

Equation (22) is the same form as the EOM of the phenomenological Heisenberg model. Consequently, the dispersion laws of Eq. (22) are the same as for the Heisenberg model. For example, from the Fourier transform of Eq. (22) for a ferromagnet we obtain

$$\omega_{\mathbf{q}} \cdot \delta e_{\mathbf{q}}^+ = \frac{2}{\mu} [J(0) - J(\mathbf{q})] \delta e_{\mathbf{q}}^+. \quad (24)$$

Thus the Heisenberg form for the dynamics of ferromagnons emerges in a natural way as an *analytical* solution of our *ab initio* theory. It follows directly from the linearization of the EOM, Eq. (11), and the adiabatic, quasiclassical limit.

While on the topic of magnons we would like to conclude this section by mentioning that, strictly speaking, the off-diagonal components of the density matrix are not isolated and this leads to the decay of spin waves even for  $T=0$  (see Ref. 1). It is possible to develop expressions for slow and fast relaxation terms within our formalism; however, in the usual nonrelativistic spin DF formalism<sup>4</sup> many such effects are prohibited, and we leave a treatment of relaxation effects to a second paper.<sup>20</sup> For those wishing to optimize magnetic ground-state structures (perhaps starting from a disordered array of moments), we note that the convergence to a final state may be aided in the nonrelativistic DF formalism by postulating a ‘‘friction’’ force in the EOM's and using these equations to evolve the system to a minimum total energy configuration (see Secs. VI and VII).

## II. RELATIVISTIC EFFECTS

For the modeling of some spin systems the inclusion of magnetic anisotropy effects is necessary. Here we will consider the influence of relativistic effects on precessional motion only and describe SD within the framework of the second order of perturbation theory (order  $1/c^2$ ). The four-component Dirac equation for the non-spin-polarized case can be transformed in the usual fashion<sup>21</sup> to

$$H = -\Delta + V - \frac{1}{c^2} \Delta^2 - \frac{i}{c^2} \boldsymbol{\sigma} \cdot (\nabla V \times \nabla) + \frac{1}{2c^2} \Delta V, \quad (25)$$

where the three last terms in Eq. (25) represent the mass-velocity corrections, SO coupling, and Darwin term. The averaged value of the SO operator can be treated as an additional field and we can substitute

$$\mathbf{B} \rightarrow \mathbf{B} - \overline{(\boldsymbol{s}\mathbf{L})} \quad (26)$$

where

$$\overline{(\boldsymbol{s}\mathbf{L})} = \frac{1}{c^2} \int d\mathbf{r} \frac{1}{r} \frac{dV}{dr} \Psi_+^* (-i\mathbf{r} \times \nabla) \Psi_+ \quad (27)$$

is the average value of the product of the orbital atomic moment  $\mathbf{L}$  and  $\boldsymbol{s}$ , the SO interaction coupling parameter.

Then instead of Eq. (11) we may write

$$\frac{d}{dt} \mathbf{e} = \frac{\gamma}{\mu} [(\mathbf{I} + \mathbf{I}_{\text{SO}}) \times \mathbf{e}] \quad (28)$$

where  $\mathbf{I}_{\text{SO}} = -M(\boldsymbol{s}\mathbf{L})$  at each particular site.

Equation (28) corresponds to keeping terms to order  $1/c^2$  in the relativistic EOM for the spin of a particle with no anomalous magnetic moment.<sup>21</sup> One can ask how the expressions for the exchange parameters presented above will transform for the magnetic relativistic case. For collinear structures the expressions for the exchange parameters have been described in Refs. 22 and 23, and for the generalization to the relativistic noncollinear case, techniques are described in Ref. 20.

There are other terms to order  $1/c^2$  which arise in a many-electron system such as ‘‘own spin–other orbit’’ and magnetic dipole interactions (see the discussion of Breit’s equation in Ref. 21). The additional SO effects may be incorporated into  $\mathbf{I}_{\text{SO}}$  while the dipole interactions require the addition of  $\mathbf{I}_{\text{dd}}$  to Eq. (28), where

$$\mathbf{I}_{\text{dd}} = -\frac{2}{c^2} \sum_{j < i} \mu_i \mu_j \left[ \frac{\mathbf{e}_j}{r_{ij}^3} - \frac{3\mathbf{r}_{ij}(\mathbf{e}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right]. \quad (29)$$

In this equation  $\mathbf{r}_{ij}$  is a vector connecting the MM at atom  $i$  with the one at atom  $j$ . The dipolar term is long range and known to be important on the scale of magnetic domains.

We caution that the RSA for the spin magnetization is inconsistent with SO coupling since the orbital moment may have a different orientation from the spin moment and induce off-diagonal components in the spin magnetization density.

Within the approach presented above we have not introduced a separate EOM for the orbital moment. In many 3d systems it may be sufficient to follow the spin magnetization with the orbital moment arising from solving the relativistic

equations with the instantaneous moment directions. The implementation of SO coupling using this approach for non-collinear magnets in the LSDA was presented in Ref. 9. In other cases (see Sec. III below) it may be necessary to let the on-site magnetic moment directions  $\mathbf{e}_{iL}$  evolve with a separate EOM and a separate force  $\mathbf{I}_{iL}$  for each orbital state  $L = (l, m)$ . In the LSDA such separate intra-atomic motion cannot be described because the potential does not depend on the orbital. These issues will certainly have to be faced when dealing with strongly correlated materials (oxides of  $d$  metals,  $f$  systems, and so on), where the magnetism is frequently carried by localized electrons not well described in the LSDA. For this reason we consider Hartree-Fock approaches in the next section.

## III. ORBITAL SPIN DYNAMICS IN THE ADIABATIC TIME-DEPENDENT HARTREE-FOCK APPROXIMATION

While the LSDA methods have been very successful in describing the magnetic properties for a wide variety of materials, there are some notable failures. For Mott insulators, for most materials containing partially occupied  $f$  orbitals, and for other strongly correlated systems it is often advantageous to start from a Hartree-Fock type of description. Several hybrid or intermediate techniques have been proposed to simultaneously treat systems which contain both localized and itinerant electron orbitals. Techniques like the self-interaction correction<sup>24</sup> (SIC) and the LDA+ $U$  methods<sup>25</sup> are related to the spin-unrestricted Hartree-Fock approximation (HFA),<sup>26</sup> which we consider in this section.

First of all, we write the equation for the nonstationary HFA:

$$i \frac{\partial \psi_{\nu\sigma}(\mathbf{r})}{\partial t} = \left( -\Delta + V^{\text{ext}} + 2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \right) \psi_{\nu\sigma}(\mathbf{r}) - \sum_{\mu\sigma} K_{\mu\nu}^{\sigma}(\mathbf{r}) \psi_{\mu}(\mathbf{r}) \quad (30)$$

where  $V^{\text{ext}}$  is an external potential,  $\mu$  and  $\nu$  are orbital quantum numbers,  $\sigma = \pm$  are spin indices,  $n(\mathbf{r}) = \sum_{\nu\sigma} |\psi_{\nu\sigma}(\mathbf{r})|^2$ , and

$$K_{\mu\nu}^{\sigma} = 2 \int d\mathbf{r}' \frac{\psi_{\mu\sigma}^*(\mathbf{r}') \psi_{\nu\sigma}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \psi_{\nu\sigma}^*(\mathbf{r}). \quad (31)$$

Let us introduce the explicit spin notation

$$V_{\mu\nu} = -\frac{1}{2}(K_{\mu\nu}^+ + K_{\mu\nu}^-) \quad (32)$$

and

$$B_{\mu\nu} = \frac{1}{2}(K_{\mu\nu}^+ - K_{\mu\nu}^-); \quad (33)$$

then, by going to an arbitrary coordinate system with an arbitrary direction of the quantized spin axis, Eq. (30) will take the form

$$i \frac{\partial \psi_{\nu\sigma}(\mathbf{r})}{\partial t} = \left( -\Delta + V^{\text{ext}} + 2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \right) \psi_{\nu\sigma}(\mathbf{r}) - \sum_{\mu} V_{\mu\nu}(\mathbf{r}) \psi_{\mu}(\mathbf{r}) - \sum_{\mu} [\hat{\boldsymbol{\sigma}} \cdot \mathbf{B}_{\mu\nu}(\mathbf{r})] \psi_{\mu}(\mathbf{r}). \quad (34)$$

$\mathbf{B}_{\mu\nu}$  is a vector of amplitude  $|\mathbf{B}_{\mu\nu}|$  with the direction determined by spin orientations. To proceed to a derivation of the orbital-dependent EOM we choose an alternative derivation from that of Sec. I. By defining variables  $\xi_{\nu} = -\psi_{\nu-}/\psi_{\nu+}$ ,<sup>27,12</sup> we obtain the set of equations

$$i \frac{\partial \xi_{\nu}}{\partial t} = -\frac{1}{\psi_{\nu+}^2} \nabla \cdot (\psi_{\nu+}^2 \nabla \xi_{\nu}) + \sum_{\mu} \psi_{\nu+} \psi_{\mu+} (V_{\mu\nu} - V_{\nu\mu}) + \frac{1}{2} \sum_{\mu} \left( \frac{\psi_{\mu+}}{\psi_{\nu+}} \right) \{ B_{\mu\nu}^{+} - B_{\mu\nu}^{-} \xi_{\nu} \xi_{\mu} - B_{\mu\nu}^z (\xi_{\mu} + \xi_{\nu}) \}, \quad (35)$$

where  $B^{\pm} = B^x \pm iB^y$ .

The condition of neglecting the first term in the right-hand side of Eq. (35) is the same as the one which has been discussed in Sec. I (RSA). However, the matrix structure of the other terms does not allow reduction to a coupled set of equations for the  $\xi_{\nu}$  due to the presence of the  $\psi_{\mu+}/\psi_{\nu+}$  term. Because of this, the separation of the slow spin dynamics from the electronic variables is possible only in simplified versions of the HFA, where only diagonal ( $\mu=\nu$ ) terms in Eq. (85) are present, namely, the SIC (Ref. 24) and LDA+ $U$  (Ref. 25) methods. Then, instead of Eq. (11) for the vector

$$\mathbf{e} = \left( -\frac{\xi + \xi^*}{1 + |\xi|^2}, i \frac{\xi - \xi^*}{1 + |\xi|^2}, \frac{1 - |\xi|^2}{1 + |\xi|^2} \right)$$

we immediately obtain

$$\dot{\mathbf{e}}_{\nu} = -\frac{2}{\mu_{\nu}} [\mathbf{e}_{\nu} \times \mathbf{I}_{\nu}], \quad (36)$$

with  $\mathbf{I}_{\nu} = \delta E / \delta \mathbf{e}_{\nu}$ , and where  $\mu_{\nu}$  is the value of the magnetic moment for the given orbital state. In calculating  $\mathbf{I}_{\nu}$  it is convenient to use the local force theorem, which is valid not only in DFT,<sup>19</sup> but in the HFA as well (see the Appendix). The  $\mathbf{I}_{\nu}$  contains contributions not only from the spin interactions between different sites, but also from the interaction of the different orbital states (for instance,  $d$  and  $f$ ) at one site. We also note that the approach using the variable  $\xi_{\nu}$  has been used as one of the possible ways to calculate nonadiabatic corrections for the case of a single spin in an external magnetic field.<sup>12</sup>

The independent treatment of the SD for different orbital states at one site we believe is important. This is particularly true for materials containing rare-earth elements, where the  $4f$  moments can thermally disorder with increasing temperature faster than the  $5d$  moments (e.g., in rare-earth-Fe<sub>2</sub> compounds). We have discussed this phenomenon and its importance for magneto-optic application in Ref. 28. The extent to which such independent orbital polarizations are significant in the thermal properties of pure  $3d$  magnetic materials is unknown; however, one can well imagine that at high tem-

peratures the extended  $s$  and  $p$  electrons will “sample” many local  $d$  moments pointing in various directions, and that the  $s$  and  $p$  net moments could change with a different temperature dependence than the local  $d$  moments.

It is possible to consider intra-atomic noncollinear magnetic ordering even among the orbitals with the same  $l$  but different  $m_l$ . This can happen, for example, in systems where there is a large difference in bonding between  $e_g$  and  $t_{2g}$  orbitals, a topic discussed some time ago by Goodenough<sup>29</sup> (see Ref. 16 for a discussion of how the LDA+ $U$  method with an  $m_l$ -dependent Hubbard  $U$  might be implemented to study such effects). From what we have discussed above it is clear that the assumptions for SD (the criteria for the RSA and adiabatic approximation) may be orbital dependent, in which case the formulation of a consistent set of EOM's for SD will be more complicated than Eqs. (8) and (11).

## IV. FINITE TEMPERATURE DESCRIPTION

### A. Stochastic method

While the description of finite temperature effects in DF theory has been developed,<sup>30</sup> here we have in mind a somewhat different program whereby the MM's and their interactions, as determined by electronic structure methods, can be coupled to a thermobath for the evaluation of equilibrium thermal properties. We use the same assumptions as made in Sec. I for the deterministic EOM, but now there are additional terms associated with the thermobath. Several approaches are available for introducing this bath, and the choice of bath will depend on which method drives the MM system to thermal equilibrium most efficiently. We first describe a stochastic method based on Langevin-type dynamics similar to the approach used in MD. We spend more time and give more details for the second method, involving the deterministic approach, since at the present time we feel this method has advantages for applications. First, we describe the approach based on using the stochastic differential equations of Langevin type.<sup>31</sup> In this approach the interaction of the dynamical system with the thermobath is described by the addition to the EOM of a frictional force, and second, some random forces, describing the fluctuations. If we assume that the latter are the result of a large number of very weak random events, then due to the central limit theorem the fluctuations must be describable as a random Gaussian process. If in addition we assume that the durations of the random events and the intervals between them are much less than the time scale of the movements of our chosen MM, then the random processes are uncorrelated on this longer time scale and constitute white noise. For spin systems the Langevin dynamics procedure has been described in Ref. 32. We write the corresponding EOM in a more general form,

$$\frac{d}{dt} \mathbf{e}_i = -\frac{2}{\mu_i} [\mathbf{e}_i \times \mathbf{I}_i] + \mathbf{R}_i + \mathbf{g}_i, \quad (37)$$

where  $\mathbf{R}_i$  is a relaxation term and  $\mathbf{g}_i$  is a random force. In the case of magnetic noise the appearance of a random force implies an additional term in the Hamiltonian of the form  $\mathbf{e} \cdot \mathbf{I}_f$ , where  $\mathbf{I}_f$  is a random, rapidly fluctuating spin splitting arising from the bath. The conditions of conservation of the

amplitude of the MM and the fluctuation-dissipation theorem set up additional limitations on the choice of relaxation and random forces. In general, the relaxation term also contains a random part. If we would like to take into account the conservation of the amplitude explicitly for each term, we obtain the stochastic EOM in the form<sup>32</sup>

$$\frac{d}{dt} \mathbf{e}_i = - \left[ \mathbf{e}_i \times \left( \frac{2}{\mu_i} \mathbf{I}_i + \mathbf{g}_i \right) \right] - \lambda [\mathbf{e}_i \times (\mathbf{I}_i \times \mathbf{e}_i)], \quad (38)$$

where  $\lambda$  is the friction coefficient, and  $\mathbf{g}$  is a random force of Gaussian white noise type having the precondition

$$\langle \mathbf{g}_i \rangle = 0, \quad \langle g_{i\alpha}(t) g_{j\beta}(t') \rangle = 2d \cdot \delta_{ij} \delta_{\alpha\beta} \delta(t-t'), \quad (39)$$

where  $\alpha$  and  $\beta$  are Cartesian indices, and  $d$  is the intensity of the noise. It can be shown<sup>32</sup> that Eq. (38) satisfies for any  $\lambda$  the relaxation to the Gibbs distribution if  $d = \lambda T$ , which is the analog of the Einstein formula for rotational Brownian motion.

The stochastic Eq. (38) is equivalent to the Fokker-Planck equation for the distribution function  $P(\{\mathbf{e}_i\}, t)$  as a function of angles and time, which under condition (39) leads to the equilibrium Gibbs distribution:

$$P_{\text{eq}}(\{\mathbf{e}_i\}) = C \exp[-E(\{\mathbf{e}_i\})/T] \prod_j \sin \theta_j \quad (40)$$

with the integrating element  $d\theta d\varphi$ . It is generally accepted that with an appropriate choice of the friction coefficient such an approach describes not only the equilibrium state itself, but also quasiequilibrium states (the kinetic stage of the evolution of the nonequilibrium system).<sup>31</sup>

To reach proper equilibrium, the classical equations for the MM orientations must be accompanied by a stochastic electronic quantum equation [the analog of the deterministic Eq. (8)]. Here we present the following quantum stochastic equation to describe also the relaxation and noise associated with the amplitude of the MM (or the  $m_z$  component in our local coordinate systems):

$$i \frac{d}{dt} \chi(\mathbf{r}, t) = \left( H_L - \sum_i \hat{\sigma}_{z_i} B_{z_i} \right) \chi(\mathbf{r}, t) - i [\hat{R} + c(t) \hat{g}] \chi(\mathbf{r}, t), \quad (41)$$

where  $\hat{R}$  is a friction operator and  $\hat{g}$  is an operator of quantum noise. For the choice of the random function  $c(t)$ , we may require the same condition as in Eq. (39), but for different temperature ranges it should be done with some caution because the quantum noise is not white.<sup>31</sup> The choice of  $\hat{R}$  and  $\hat{g}$  operators must satisfy the condition of norm conservation of the wave function  $\chi(\mathbf{r}, t)$ . Equation (41) for  $T \neq 0$  can be understood as a formal equation with fast relaxing terms, leading to the corresponding proper EOM for the adiabatic (diagonal) density matrix at finite temperatures with conservation of the total magnetic moment of system.

We propose the choice of the relaxation operator (without the noise term) in a form very close to its classical analog,

$$\hat{R} = \lambda \sum_i (a_i \mu_{z_i} - \hat{\sigma}_{z_i} B_{z_i}), \quad (42)$$

where  $a_i$  is some function such that this term will drive the evolution of the amplitude of the magnetization density to its equilibrium value. One can think about the system of coupled Eqs. (41) and (39) as an analog of the Bloch equations used in magnetic resonance,<sup>33</sup> where the evolution of  $M_x$ ,  $M_y$ , and  $M_z$  components of the total magnetization is described with essentially different time scales ( $T_1$  and  $T_2$  relaxation rates).

## B. Deterministic method

It is possible to describe the thermal properties of magnetic systems in terms of a generalized MD which evolves at constant temperature, rather than microcanonically at constant energy. It was proven by Nosé that one can relate the canonical ensemble of a desired Hamiltonian to the microcanonical ensemble of a new Hamiltonian in a phase space with one additional degree of freedom.<sup>34</sup> This additional degree of freedom can be interpreted as a dynamical realization of a heat bath. Using a specific construction of the new Hamiltonian with heat bath, one can evolve the microcanonical equations in this larger phase space. If the equations evolve ergodically, then averages of observables along the trajectory will converge to the microcanonical average. As a consequence, the canonical ensemble is then obtained in the subspace consisting of the original degrees of freedom. One of the main limitations is that Nosé's construction requires a very specific coupling of the desired Hamiltonian to the heat bath, which is not always ergodic. Shortly after, Hoover developed a more transparent and generalizable interpretation, called the Nosé-Hoover approach.<sup>35</sup> The Nosé-Hoover equations can be obtained from Nosé's microcanonical dynamics through a coordinate transformation. This method has proved extremely powerful and simple to implement, but has several notable limitations. An important aspect of the Nosé-Hoover equations is the need for them to be strongly chaotic in the full phase space, which is not always the case. For example, they fail to describe the proper diffusion of a Brownian particle, as well as the thermal properties of harmonic and near-harmonic potentials. This is especially problematic for path integral approaches to quantum mechanics, or to classical systems at low temperature. To resolve these shortcomings, a canonical dynamics was proposed which is, from the outset, non-Hamiltonian.<sup>36</sup> The generality of this approach has allowed its extension to general dynamical systems, Brownian motion, and the Schrödinger equation, both in equilibrium and far from equilibrium.<sup>37</sup> Below we outline the application to the classical-quantum hybrid scheme suggested above.

The method, termed *global demons*,<sup>37,38</sup> is a prescription to add dynamical fluctuations from any desired ensemble to a classical or quantum system, resulting in a time-reversal-invariant dynamics. The approach allows for simulation of many physical types of boundary conditions, including constant temperature, constant pressure, and so forth. For the simulation of a heat bath, one uses a small number of new dynamical degrees of freedom, which can be coupled to the physical degrees of freedom in ways which simulate anything from equilibrium or nonequilibrium steady states to irreversible situations such as indentation and fracture.<sup>35</sup> In the simulation of systems near phase transitions, the problem of critical slowing down, which hampers stochastic-based approaches, is greatly reduced with global demons.<sup>38</sup> An-

other feature is that one does not need to know the equilibrium measure or nonequilibrium properties in order to simulate it (compare to Metropolis sampling which requires the use of a measure). This is important in the study of staggered fermions, where the measure is not known, only its gradients.<sup>37</sup>

Classical MD is based on the Hamiltonian  $H(x)$ , with  $x$  representing all degrees of freedom; for example,  $x=(\mathbf{R},\mathbf{P})$  or  $x=(\mathbf{S})$ . The microcanonical dynamics of this system is then defined by a Poisson tensor  $J_{ij}(x)$ , and the brackets  $\{x_i, x_j\}=J_{ij}(x)$ . The only formal difference between the conjugate variables  $(\mathbf{R},\mathbf{P})$  and the spin degrees of freedom  $\mathbf{S}$  is that the former are canonical, while the latter are noncanonical. When one formulates either the microcanonical or the canonical dynamics for  $H(x)$  through the Poisson tensor  $J_{ij}(x)$ , this distinction is unimportant. Hence we can treat all degrees of freedom  $x$  on equal footing. The constant energy (microcanonical) dynamics for the magnetic system have the general form

$$\dot{x}_i = J_{ij}(x) \frac{\partial H(x)}{\partial x_j}. \quad (43)$$

When the dynamics is ergodic, the classical trajectory  $x(t)$  reproduces the constant-energy ensemble  $\delta(E-H)$ , where  $E$  is determined from the initial conditions. Using global demons, the constant-temperature (canonical) dynamics, which are non-Hamiltonian, are of the form<sup>37</sup>

$$\begin{aligned} \dot{x}_i &= J_{ij}(x) \left[ \frac{\partial H(x)}{\partial x_j} - \frac{\kappa}{nT} g(w) A_j(x) \right], \\ \dot{w} &= \frac{\kappa}{nT} J_{ij}(x) \left[ \frac{\partial H(x)}{\partial x_i} A_j(x) - \frac{\partial A_j}{\partial x_i} \right]. \end{aligned} \quad (44)$$

Here the heat bath is described by the global demon  $w$ , so denoted since it is inherently nonlocal, coupling globally to all degrees of freedom,  $n$  is the number of degrees of freedom, the coupling strength  $\kappa$  is typically  $\sim \sqrt{n}$ , and  $A_j(x)$  and  $g(w)$  are (arbitrary) functions which couple the heat bath ( $w$ ) to the physical coordinates  $x$ . In practice, a minimum of two global demons is needed. When the above equations are evolved, averages along a single trajectory will reproduce the canonical ensemble given by  $\rho = \exp[-H(x)/T] \exp[-G(w)/T]$ , with  $g(w) = dG/dw$ . The distinction between this method and the original approach by Nosé is that this dynamics is canonical in the full space.

For a Hamiltonian written in terms of canonical variables,  $x=(\mathbf{R},\mathbf{P})$ ,

$$H(\mathbf{R},\mathbf{P}) = \sum_{i=1}^n \frac{\mathbf{P}_i^2}{2m_i} + V(\{\mathbf{R}_i\}), \quad (45)$$

one particular realization of the canonical dynamics is<sup>36</sup>

$$\dot{\mathbf{R}}_i = \mathbf{P}_i/m_i - \frac{\kappa_1}{nT} w_1 \mathbf{R}_i^3, \quad (46)$$

$$\dot{\mathbf{P}}_i = -\frac{\partial V}{\partial \mathbf{R}_i} - \frac{\kappa_2}{nT} w_2^3 \mathbf{P}_i,$$

$$\dot{w}_1 = \frac{\kappa_1}{nT} \sum_i \left[ \frac{\partial V}{\partial \mathbf{R}_i} \mathbf{R}_i - 3T \mathbf{R}_i^2 \right],$$

$$\dot{w}_2 = \frac{\kappa_2}{nT} \left[ \sum_i \frac{\mathbf{P}_i^2}{m_i} - nT \right].$$

These dynamics will reproduce the ensemble  $\rho(\mathbf{R},\mathbf{P},w_1,w_2) = \exp[-H(\mathbf{R},\mathbf{P})/T] \exp(-w_1^2/2T - w_2^4/4T)$ .

The same formulation works for the noncanonical spin coordinates  $\mathbf{x}=\mathbf{S}$ . In this case the Poisson tensor is  $J_{ij}(S) = \varepsilon_{ijk} S_k$ , so that we have for a general  $H(\mathbf{S})$

$$\begin{aligned} \dot{S}_i &= J_{ij} \left[ \frac{\partial H}{\partial S_j} - \frac{\kappa}{nT} g(w) A_j(S) \right], \\ \dot{w} &= \frac{\kappa}{nT} J_{ij} \left[ A_j \frac{\partial H}{\partial S_i} - T \frac{\partial A_j}{\partial S_i} \right]. \end{aligned} \quad (47)$$

These dynamics will reproduce the ensemble  $\rho(S,w) = \delta(S-S_0) \exp[-H(S)/T] \exp(-w^2/2T)$ , which includes the constraint over the magnitude of the spin  $S_0$ . The magnitude of  $S$  is set by the initial conditions.

It is possible to recast this deterministic SD in a form similar to the stochastic dynamics presented previously. If we use one global demon (usually at least two are needed for simple systems), take  $\mathbf{A}=\mathbf{S} \times (\delta E/\delta \mathbf{S})$ ,  $g(w)=w$ ,  $\mathbf{S}=(\mu/2)\mathbf{e}$ , and define the ‘‘friction’’  $\lambda = \kappa g(w)/nT$ , then

$$\frac{d}{dt} \mathbf{e} = -\frac{2}{\mu} [\mathbf{e} \times \mathbf{I}] - \lambda [\mathbf{e} \times (\mathbf{I} \times \mathbf{e})], \quad (48)$$

where

$$\frac{d}{dt} \lambda = \left( \frac{\kappa}{nT} \right)^2 \sum (\mathbf{I} - T \nabla_{\mathbf{e}}) [\mathbf{e} \times (\mathbf{I} \times \mathbf{e})], \quad (49)$$

which conserves the ‘‘length’’ of the MM. As we mentioned above, it is no longer necessary to adjust the kinetic energy for temperature control. Although  $\lambda$  has the appearance of a friction, it is not dissipative, but adds and removes energy from the spin in order to simulate the canonical distribution. We note that Eq. (48) does not reduce to the classical (macroscopic) equation of Landau and Lifshitz, but is rather a microscopic, quasiclassical EOM and is the rotational analog of the Newtonian EOM in MD.

For simultaneous MD and SD (discussed in the next section), the equations are unchanged, except that the Hamiltonian now depends explicitly on all degrees of freedom:  $H(\mathbf{R},\mathbf{P},\mathbf{S})$ . Because one can couple select spins to a heat bath and allow thermalization to occur through the interactions, one can simulate many different situations, including thermal gradients. Such approaches have been used to extract transport coefficients.<sup>35,39</sup> It follows that one can also thermalize different subsystems at different temperatures. It is important to thermalize the electrons separately at a low temperature to keep their wave functions in the ground state so that the DF approach can be applied.<sup>40</sup> As a result of the use of different temperatures, the coupling between slow and fast degrees of freedom will generate heat flow from hot to cold reservoirs and a net entropy production. If the coupling is strong, the system will be driven to a nonequilibrium steady state, which is no longer characterized by the equilibrium canonical dis-



tribution. If the coupling is weak, the averages of observables will be close to the canonical averages at appropriate temperatures.

We are presently testing these various schemes for including temperature with SD and will report on optimized strategies in a future paper.

## V. SIMULTANEOUS MOLECULAR AND SPIN DYNAMICS

In this section we use the path integral formalism<sup>42</sup> to separate out the slow (adiabatic) degrees of freedom for both MD and SD. The simultaneous treatment of both those dynamics is necessary for a consistent analysis of spin-lattice interactions, particularly at finite temperatures. We will begin with a general quantum-mechanical formulation of the problem and then discuss the transition to the classical equations. A quite different derivation of these equations has been presented in Ref. 41 where a more physically transparent time-dependent WKB approach was used.

We choose the Hamiltonian in the form

$$H = H_{\mathbf{R}} + H_{\mathbf{r}}\{\mathbf{R}, \xi\} \quad (50)$$

where  $H_{\mathbf{R}}$  is the Hamiltonian of the nuclear subsystem [see Eq. (47)], and  $H_{\mathbf{r}}$ , the electronic Hamiltonian, depends on the nuclear coordinates and the unit vectors of magnetization  $\mathbf{e}_i = \mathbf{e}_i(\xi_i)$  (see Sec. III). We assume that the RSA is valid and that both variables  $\mathbf{e}$  and  $\mathbf{R}$  are slow variables (i.e., the adiabatic approximation is valid for these variables).

Let us introduce the basis states  $|\mathbf{R}_i(t)\rangle$  for the nuclear motion and spin coherent states  $|\xi_i(t)\rangle$  (see Ref. 43). At the initial time  $t=0$  the nuclear and spin coordinates are  $\mathbf{R}'_i$  and  $\xi'_i$ , respectively, and the final coordinates are  $\mathbf{R}''_i$  and  $\xi''_i$ . Then the evolution operator of slow variables will take the form

$$\langle \mathbf{R}''_i, \xi''_i | \hat{U}(t) | \mathbf{R}'_i, \xi'_i \rangle = \text{Tr} \langle \mathbf{R}''_i, \xi''_i | \exp(-i\hat{H}t) | \mathbf{R}'_i, \xi'_i \rangle, \quad (51)$$

where Tr means the trace over the fast electronic coordinates. The electronic propagator within the adiabatic approximation can be expressed through the spectrum and eigenfunctions of stationary levels depending on the  $\mathbf{R}_i$  and  $\xi_i$  as parameters:

$$\begin{aligned} & \int_{\mathbf{r}_i(t)=\mathbf{r}''_i}^{\mathbf{r}_i(0)=\mathbf{r}'_i} D\mathbf{r}(t) \exp\left\{ i \int_0^t d\tau L(\dot{\mathbf{r}}, \mathbf{r}, \mathbf{R}, \xi) \right\} \\ &= \sum_n \psi_n(\mathbf{r}'_i) \psi_n^*(\mathbf{r}''_i) \exp[-iE_n(\{\mathbf{R}, \xi\}, t)], \quad (52) \end{aligned}$$

where  $L$  is the electronic Lagrangian corresponding to the Hamiltonian  $H_{\mathbf{r}}(\{\mathbf{R}, \xi\})$ , and  $\psi_n(\mathbf{r})$  is a solution of the equation

$$H_{\mathbf{r}}(\{\mathbf{R}, \xi\}) \psi_n(\mathbf{r}, \{\mathbf{R}, \xi\}) = E_n(\{\mathbf{R}, \xi\}) \psi_n(\mathbf{r}, \{\mathbf{R}, \xi\}). \quad (53)$$

Choosing the ground state  $n=0$  and performing calculations according to Ref. 42 in the adiabatic approximation we have

$$\begin{aligned} & \langle \mathbf{R}''_i, \xi''_i | \hat{U}(t) | \mathbf{R}'_i, \xi'_i \rangle \\ &= \int_{\substack{\mathbf{R}_i(0)=\mathbf{R}'_i, \xi(0)=\xi'_i \\ \mathbf{R}_i(t)=\mathbf{R}''_i, \xi(t)=\xi''_i}} D\mathbf{R}(t) D\xi(t) \exp\left\{ i \int_0^t d\tau L \right\} \end{aligned} \quad (54)$$

where the Lagrangian can be written as

$$\begin{aligned} L = & \sum_i \frac{m_i \dot{\mathbf{R}}_i^2}{2} + \sum_i \mathbf{A}_i \cdot \dot{\mathbf{R}}_i + \frac{s}{2} \sum_i \frac{\xi_i^* \dot{\xi}_i - \xi_i \dot{\xi}_i^*}{1 + |\xi_i|^2} \\ & + U(\mathbf{R}, \xi_i, \xi_i^*), \end{aligned} \quad (55)$$

where  $U(\mathbf{R}, \xi_i, \xi_i^*) \equiv E_0(\mathbf{R}, \xi_i, \xi_i^*)$  is the energy of the ground state  $\chi_0$  of the electronic subsystem which depends on slow variables as parameters. In Eq. (55),

$$\mathbf{A} = i \langle \chi_0 | \nabla_{\mathbf{R}} | \chi_0 \rangle, \quad (56)$$

so that  $s=1/2$ , and we assume for simplicity that on each atom there is one electron. If on each atom there is an integer number  $n$  of magnetic electrons with the same direction of spin, then after summation over all electrons we can substitute  $s=n/2$  for  $s=1/2$  in Eq. (55).

The first term in Eq. (55) is the normal kinetic energy of the nuclei, whereas the second one arises from the geometric phase<sup>44</sup> for the adiabatic variables  $\mathbf{R}_i$ ,<sup>42</sup> and the third term corresponds to the geometric phase for the spin variables and is the analog of the kinetic energy for the spin variables. Equation (55) contains all quantum effects for the  $(\mathbf{R}, \xi)$  subsystem.

For the case of magnetic dielectrics the above quantity  $U$  can be presented similarly to the Heisenberg model representation:

$$U(\mathbf{R}_i, \xi_i, \xi_i^*) = U_0(\mathbf{R}_i) - 2 \sum J_{ij}(\{\mathbf{R}\}) \mathbf{e}_i \cdot \mathbf{e}_j, \quad (57)$$

where  $J_{ij}$  are exchange parameters depending only on nuclear coordinates. Then the path integral (54) corresponds to the Schrödinger equation

$$\hat{H}_{\text{eff}} \chi = \varepsilon \chi, \quad (58)$$

with

$$\begin{aligned} H_{\text{eff}} = & \sum_i \frac{1}{2m_i} [\hat{\mathbf{P}}_i - \mathbf{A}_i(\mathbf{R}_i)]^2 + U_0(\{\mathbf{R}_i\}) \\ & - \frac{2}{s^2} \sum_i J_{ij}(\{\mathbf{R}_i\}) \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_j \end{aligned} \quad (59)$$

where  $\mathbf{P}_i = -i\nabla_i$  and  $s$  is the spin operator with  $\hat{\mathbf{s}}^2 = s(s+1)$ ,  $s=n/2$ . Thus we have an exact quantum description of the lattice (phonon) and the spin (magnon) degrees of freedom.

For metals, however, a corresponding quantum description of the spin subsystem in the adiabatic approximation is not possible. First of all,  $n$  is not an integer, and second, the spin part of the Hamiltonian does not have a simple form as in Eq. (59); and also there is no simple way to treat the unit vectors  $\mathbf{e}_i$  as operators. We can, nevertheless, utilize a quasiclassical set of equations for the MD and SD. These equa-

tions can be obtained by using the saddle point approximation for the path integral in Eq. (54). We obtain

$$m\ddot{\mathbf{R}} = -\nabla_{\mathbf{R}}U + \dot{\mathbf{R}} \times \boldsymbol{\beta}, \quad (60)$$

$$\dot{\mathbf{e}} = -2 \left[ \mathbf{e} \times \frac{\delta U}{\delta \mathbf{e}} \right], \quad (61)$$

where

$$\boldsymbol{\beta} = \nabla_{\mathbf{R}} \times \mathbf{A}. \quad (62)$$

It is worthwhile to note that the term  $\dot{\mathbf{R}} \times \boldsymbol{\beta}$  is determined by the geometric phase.<sup>11</sup> It can be important near degeneracy points in electronic spectra.<sup>44</sup> Equations (60)–(62) are the basis for the simultaneous description of spin and nuclear (molecular) dynamics.

The interactions at finite temperatures can be described through using either the Langevin equation, or the global demon thermobath. To be precise, we write in explicit form the Langevin type of dynamics (the global demon equations can be easily written following the discussion in Sec. IV)

$$m\ddot{\mathbf{R}} = -\nabla_{\mathbf{R}}U + \dot{\mathbf{R}} \times \boldsymbol{\beta} - \gamma \dot{\mathbf{R}} \times \mathbf{f}, \quad (63)$$

$$\dot{\mathbf{e}} = -2 \left[ \mathbf{e} \times \left( 2 \frac{\delta U}{\delta \mathbf{e}} + \mathbf{g} \right) \right] - \lambda \left[ \mathbf{e} \times \left( \frac{\delta U}{\delta \mathbf{e}} \mathbf{e} \right) \right], \quad (64)$$

where  $\gamma$  and  $\lambda$  are the friction coefficients for the nuclear motions and spin rotations, and  $\mathbf{g}$  and  $\mathbf{f}$  are the corresponding random forces with the conditions

$$\langle \mathbf{f}_i \rangle = 0, \quad \langle f_{i\alpha}(t) f_{j\beta}(t') \rangle = 2\gamma T_l \cdot \delta_{ij} \delta_{\alpha\beta} \delta(t-t'), \quad (65)$$

$$\langle \mathbf{g}_i \rangle = 0, \quad \langle g_{i\alpha}(t) g_{j\beta}(t') \rangle = 2\lambda T_s \cdot \delta_{ij} \delta_{\alpha\beta} \delta(t-t'), \quad (66)$$

$$\langle f_{i\alpha}(t) g_{j\beta}(t') \rangle = 0. \quad (67)$$

Equations (63)–(67) can be used in the case when the ‘‘spin’’ temperature  $T_s$  is not equal to the lattice temperature  $T_l$ . The concept of spin and lattice temperature has been extensively discussed in the magnetic resonance and physical kinetics literature (see, for instance, Ref. 45).

Equations (63)–(67) (or their analog using global demons) provide a basis for the description of problems associated with the interaction of the spin and lattice degrees of freedom (e.g., the Invar problem<sup>50</sup>). The equations can be used not only for magnetically ordered systems, but also for paramagnetic systems with local MM’s above the ordering temperature. Another example one can consider is the problem of the description of ESR spectra in liquids or polymer molecules in external magnetic fields. Here the characteristic frequencies for the motion of atoms (the bending motion of polymer molecules, diffusion in liquids, etc.) are comparable with the spin frequencies, so the simultaneous description of spin and lattice degrees of freedom is necessary.

## VI. METHOD OF CALCULATION

We employ a tight-binding version of the linear muffin-tin orbital method (LMTO) method, using the atomic sphere approximation (ASA) and the ‘‘combined correction’’ term.<sup>46</sup> In the collinear case, the ASA Hamiltonian with a single

orbit per  $L$  channel has the schematic form

$$H = (\backslash)_0 + (\backslash)_1 S + \text{c.c.} + S(\backslash)_2 S + V_{\text{MTZ}} \dot{S}. \quad (68)$$

Here the quantities  $(\backslash)$  are matrices diagonal in the site-momentum representation and constructed from the potential parameters.<sup>46</sup> The structure constants  $S$  connecting neighboring sites are diagonal in the spin index  $\sigma$ ;  $\dot{S}$  is the energy derivative of  $S$ . The overlap matrix has the same structure, except that  $V_{\text{MTZ}} \rightarrow 1$ .

The LMTO basis is constructed starting from atom-centered Hankel functions (usually of energy 0), which are then replaced (‘‘augmented’’) by numerical solutions of the wave equation inside the augmentation spheres. The  $V_{\text{MTZ}} \dot{S}$  term is the integral of the original Hankel functions through all space in a constant potential  $V_{\text{MTZ}}$ . The remaining terms arise from replacing integrals of products of two Hankel functions with the numerical functions in the various spheres. The  $(\backslash)_0$  term arises from two orbitals centered on the same site, and one is augmenting the orbitals in the sphere where they are centered. The  $(\backslash)_1 S$  terms arise when only one orbital is centered at the augmentation site; the three-center  $S(\backslash)_2 S$  terms arise when neither is centered at the augmentation site.

To formulate the noncollinear problem, we assume that the axis of spin quantization is fixed within each augmentation sphere, and that the spin is negligible outside each sphere. Thus we use a single potential in the interstitial region for both spin components. This approximation is adequate for  $d$  and  $f$  shell magnetism, since the local moments are well localized within the augmentation spheres. It is clearly not adequate when the magnetization is not well localized, as is the case in some molecules. Now the axis of spin quantization may rotate at each site. The  $S$  are rotated by  $U_{RL}$ , diagonal in the site-momentum representation and unitary in  $\sigma$ , and the Hamiltonian may be written schematically as

$$H = \begin{pmatrix} + & \\ & - \end{pmatrix}_0 + \begin{pmatrix} + & \\ & - \end{pmatrix}_1 U^\dagger S U + \text{c.c.} \\ + U^\dagger S U \begin{pmatrix} + & \\ & - \end{pmatrix}_2 U^\dagger S U + V_{\text{MTZ}} U^\dagger \dot{S} U. \quad (69)$$

The potential parameter arrays are shown explicitly with their spin-up, spin-down components. For a SS of wave vector  $q$ ,  $U_{RL}$  is 1, but  $S$  is<sup>47</sup>

$$S(\mathbf{k}, \mathbf{q}, \theta) = S(\mathbf{k} - \mathbf{q}/2) \begin{bmatrix} \cos^2(\theta/2) & -(\sin\theta)/2 \\ -(\sin\theta)/2 & \sin^2(\theta/2) \end{bmatrix} \\ + S(\mathbf{k} + \mathbf{q}/2) \begin{bmatrix} \sin^2(\theta/2) & (\sin\theta)/2 \\ (\sin\theta)/2 & \cos^2(\theta/2) \end{bmatrix}. \quad (70)$$

Here  $\theta$  is a rotation of the spins from the  $z$  axis before rotation of each unit cell by  $q$  relative to its neighbors. A superposition of general noncollinear rotations and the SS has the same form as Eq. (69), but with  $S(\mathbf{k})$  replaced with  $S(\mathbf{k}, \mathbf{q}, \theta)$ . The order of rotation is, then, first a rotation of all spins from the  $z$  axis by  $\theta$ , then a rotation of each unit cell by  $q$  relative to its neighbor, and finally a rotation of each site within the cell by  $U_{RL}$ .

Some quite general spin configurations are possible. For example, consider a two-atom cell of length 2, with the atoms stacked along the  $z$  axis. A SS along  $z$  with  $q=1/2$ ,  $\theta=0$ , and with site rotations  $U_1$  and  $U_2$  defined by the Euler angles  $(0, \pi/2, 0)$  and  $(\pi/2, \pi/2, 0)$ , respectively, leads to a periodic arrangement of spins rotated just as in a simple  $q=1/2$  SS:  $(\uparrow \rightarrow \downarrow \leftarrow)$ . When instead  $\theta=\pi/2$  and  $U_1$  and  $U_2$  are defined by Euler angles  $(0, 0, 0)$  and  $(\pi/2, 0, 0)$ , the arrangement of spins becomes  $(\uparrow \leftarrow \downarrow \leftarrow)$ .

In the nonmagnetic case, the energy moments of the output density accumulated inside sphere  $R$  from eigenvector  $z$  have the form

$$Q_{RL}^j = (\rho_{RL}^{1\dagger} \rho_{RL}^1 + \rho_{RL}^{2\dagger} \rho_{RL}^2) (\varepsilon - E_{RL})^j, \quad (71)$$

where

$$\rho_{RL}^1 = \sum_{R'L'} (1 + o \sqrt{\Delta} S_{RL,R'L'} \sqrt{\Delta}) z_{R'L'}, \quad (72)$$

$$\rho_{RL}^2 = \sum_{R'L'} \sqrt{p^\gamma} \sqrt{\Delta} S_{RL,R'L'} \sqrt{\Delta} z_{R'L'},$$

and  $E_{RL}$ ,  $o_{RL}$ ,  $\sqrt{\Delta_{RL}}$ , and  $p_{RL}^\gamma$  are the potential parameters defined in the usual way.<sup>46</sup>

The collinear magnetic case is identical to the nonmagnetic case, except that there are two spin channels uncoupled from one another. The noncollinear case is also identical, except that now the two spin channels are coupled and  $S$  is rotated into  $U^\dagger S U$  with separate spin quantization axes for each site. The moments  $Q_{\sigma\sigma'RL}^j$  are no longer diagonal in  $\sigma$ : suppressing the  $RL$  index, the  $Q$  take the form

$$Q_{\sigma\sigma'}^j = \sum_{\varepsilon, occ} (\rho_\sigma^{1\dagger} \rho_{\sigma'}^1 + \rho_\sigma^{2\dagger} \rho_{\sigma'}^2) (\varepsilon - E_{RL})^j. \quad (73)$$

The  $Q_{\sigma=\sigma'}$  correspond to the charge density in the usual way; the  $Q_{\sigma \neq \sigma'}$  are used in the generation of the magnetic forces [for the torque expression through the noncollinear (in general) moments of the DOS, see Refs. 20 and 48]. It is well known that the above formulas only approximate the interstitial contribution to the Hamiltonian. Because the method only has a provision for representing the charge density inside augmentation spheres, there is no way to represent the interstitial density. Accordingly, the moments are renormalized by requiring that the total charge inside all spheres accumulated from each eigenvector is unity. For close-packed systems, the renormalization is small (typically 0.98). Similarly, the forces calculated from the moments in this way use only the ASA part of the Hamiltonian. Extensive testing on Fe and other close-packed  $d$ -bonded systems shows that the force formula is accurate, whether or not the combined correction is used.

In the ASA where only the spherical parts of the charge density and potential are taken, the first three DOS moments  $Q_{\sigma=\sigma'RL}^0$ ,  $Q_{\sigma=\sigma'RL}^1$ , and  $Q_{\sigma=\sigma'RL}^2$  are sufficient to completely specify the potential inside sphere  $R$ . This is because the method has only two kinds of orbitals per  $RL$  channel, and thus only three possible kinds of wave-function products. Consequently, there is only one potential consistent with these moments. Thus the method proceeds by starting

with some spin splittings  $\mathbf{I}_i$  (with local  $z$  components defined by DOS moments<sup>48</sup>), generating a potential consistent with the input energy moments and the corresponding potential parameters, making the output moments from eigenstates of  $H$ , Eq. (71), mixing the input and output energy moments, and repeating the procedure until self-consistency is reached. When the total energy is minimized with respect to the local magnetic moment angles, the ground state is found when the angular forces vanish simultaneously with self-consistency in the charge. The postulated (in nonrelativistic theory) magnetic ‘‘friction’’ force as we relax the system to a minimum energy structure was chosen to be proportional to the difference  $\mathbf{I} - \mathbf{I}^*$ , where the quasiequilibrium spin splitting  $\mathbf{I}^*$  is proportional to  $\mathbf{e}$  [ $\mathbf{e}$  is the direction of the atomic MM’s obtained from Eq. (9)]. In this case the total magnetic moment of the system is not conserved. When SD simulations are evolved, and also in the determination of minimum energy structures, it is necessary to move the angles slowly enough that deviations from self-consistency are small. In dynamical simulations, we found that time steps of order 1–5 a.u. were small enough to keep the electron density near self-consistency.

It is known that the local density approximation underestimates the lattice constants of the transition metals, especially for the  $3d$  series. The gradient corrections dramatically reduce the error (though they tend to overestimate the MM’s by about 10%). Since gradient-corrected calculations are probably better predictors of the ground state, we show results of simulations using a local DF, and corresponding simulations for the gradient-corrected functional of Perdew and Wang.<sup>49</sup>

For the sake of computational efficiency, these simulations were performed with an *spd* basis. As we shall show, the magnetic ground state is extremely sensitive to the lattice constant; the neglect of  $f$  orbitals leads to a small error, but one that is nevertheless significant for fcc Fe. Additional errors arising from the ASA approximation to the LDA functional are also considered.

## VII. NUMERICAL RESULTS

As a concrete example, let us consider face-centered cubic (fcc) iron ( $\gamma$ -Fe) at  $T=0$  K. This and related systems (Ni-Fe, Fe-Mn) have been studied for many years<sup>50</sup> as part of the ‘‘Invar’’ problem. It also serves as a prototype model for a frustrated magnetic system. Earlier ‘‘static’’ calculations<sup>47</sup> for fcc Fe have shown a dependence of the magnetic ordering on volume. Near the equilibrium volume fcc Fe was found to be nonmagnetic, but with increasing volume the antiferromagnetic (AFM) state first becomes stable, and then a spin-spiral (SS) state, and finally ferromagnetic (FM) ordering appears.<sup>47</sup> With our SD formalism we allow the spin system much more freedom to choose an equilibrium structure and we considered a unit cell consisting of 32 atoms.

The evolution of the spins for two different lattice constants,  $a=3.59$  and  $3.73$  Å, has been calculated within the local density approximation using the functional of von Barth and Hedin.<sup>4</sup> For the  $a=3.59$  Å simulation, the energy dropped smoothly and the spins ordered into the four atoms per cell ‘‘triple- $\mathbf{k}$ ’’ ( $3\mathbf{k}$ ) structure (all spins oriented along  $[\pm 1 \pm 1 \pm 1]$  directions), with the MM about  $1.6\mu_B$ .

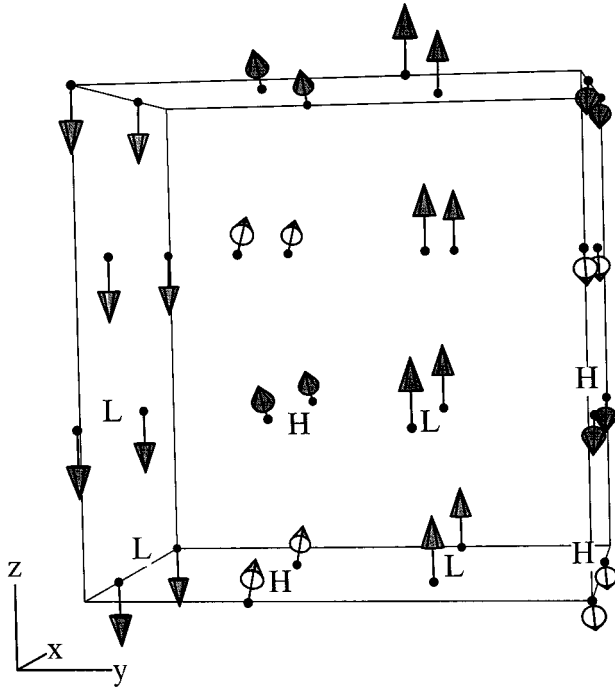


FIG. 1. Magnetic moment arrangement of eight-atom cell found by the simulation. *H* marks the high-spin moments; *L* marks the low-spin moments. All moments are oriented in the *x-z* plane. For small *a*, *H* lie along the *x* axis. For increasing  $a > 3.50$  Å, the *H* spins rotate smoothly in the *x-z* plane, increasing to an orientation where all NN angles are approximately 0, 60°, or 120°.

For  $a = 3.73$  Å, the evolution of the spins was more complex, relaxing into a nearly stable structure of 16 atoms/cell, and then finding a slightly more stable configuration with spins ordered in a  $\uparrow\uparrow\downarrow\downarrow$  pattern along [001] and a moment of about  $2.3\mu_B$  (see Fig. 1 in Ref. 9).

Subsequent static calculations for the 2k, 3k, FM, and  $\uparrow\uparrow\downarrow\downarrow$  magnetic configurations, and similar configurations with a SS superimposed, showed that the energetically most favorable configuration exhibited a complex volume dependence. Considering first only cases with no SS (as no SS was accessible to the simulation), we find the system to be magnetically ordered at the theoretical equilibrium volume ( $a = 3.44$  Å), in a 3k structure with small MM ( $0.8\mu_B$ ). At that volume the 3k is nearly degenerate with nonmagnetic Fe, being only 0.9 meV/atom more stable. The 2k is also very close in energy, lying only 1.2 meV above the 3k. With increasing lattice constant the lowest-energy structure is overtaken by the mixed FM/AFM  $\uparrow\uparrow\downarrow\downarrow$  [001] structure for  $a > 3.59$  Å, and is in turn overtaken by FM ordering for  $a > 3.73$  Å. Including SO coupling increased the binding energy by approximately 5 meV/atom, but did not alter the relative energies of the various magnetic configurations.

We considered various magnetic configurations with a (0,0,*q*) SS superimposed (without SO coupling), and the 3k, 2k, and FM structures were further stabilized by an incommensurate SS with  $1/q \approx (5-6)a$ . The equilibrium configuration is a 3k+SS at  $a = 3.44$  Å and  $1/q \approx 6a$ , the SS stabilizing the normal 3k structure by 1.8 meV; this is 2.0 meV lower than nonmagnetic Fe at its own equilibrium lattice constant (3.43 Å). With increasing volume the optimal

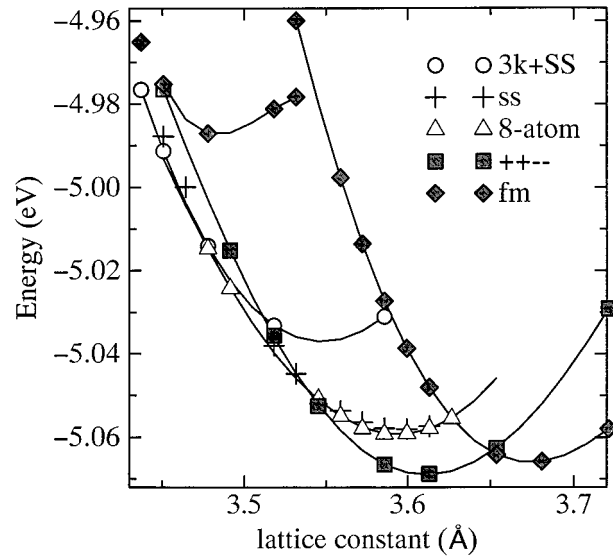


FIG. 2. Total energies as a function of *a* for several configurations. The global minimum energy structure is the  $\uparrow\uparrow\downarrow\downarrow$  configuration. For small *a*, the eight-atom configuration is lowest in energy; for large *a*, the FM configuration is lowest, as discussed in the text. Note the two distinct energy-volume curves for the FM configuration, corresponding to a low-spin and a high-spin state.

$1/q$  evolves slowly from  $\approx 6a$  at  $a = 3.44$  Å to  $\approx 5a$  at  $a = 3.55$  Å in both the 3k and 2k configurations. At  $a = 3.55$  Å the 2k+SS overtakes the 3k+SS. For  $a > 3.61$  Å,  $\uparrow\uparrow\downarrow\downarrow$  [001] is the most stable structure; it is in turn overtaken by FM ordering for  $a > 3.73$  Å. Remarkably, the simple (0,0,*q*) SS is never the most stable structure, though at  $a = 3.59$  Å it is only 1 meV higher in energy than the 2k+SS and  $\uparrow\uparrow\downarrow\downarrow$  structures.

When the local functional of Vosko was used in place of the von Barth–Hedin functional, essentially similar results were obtained. Corresponding calculations with the gradient correction of Perdew and Wang shared some features in common with local density results, namely, a very strong dependence of magnetic moment on lattice constant and the favoring of complex noncollinear orderings at small lattice constants, the  $\uparrow\uparrow\downarrow\downarrow$  ordering at intermediate lattice constants, and FM ordering at large lattice constants. Apart from these general tendencies, gradient corrections dramatically change the results. Simulations with gradient corrections were performed at  $a = 3.57, 3.61,$  and  $3.65$  Å. The latter two evolved to the  $\uparrow\uparrow\downarrow\downarrow$  configuration, although the evolution to  $\uparrow\uparrow\downarrow\downarrow$  for  $a = 3.65$  Å was rather tortuous, owing to the existence of other nearly degenerate orderings. The  $a = 3.57$  Å simulation evolved to the noncollinear eight-atom configuration shown in Fig. 1. This AFM configuration has two inequivalent atoms (a low-spin state marked *L* and a high-spin state marked *H*), and may be viewed as a four-atom structure with a commensurate (0,1/2,0) SS superimposed. For  $a < 3.48$  Å, the angle  $\phi$  between NN in Fig. 1 is  $\pi/2$ , so that all spins are aligned at (0, 90°, or 180°). For increasing  $a > 3.48$  Å,  $\phi$  smoothly decreases to a value where every angle is approximately (60° or 120°). This configuration is the most stable we found for  $a < 3.54$  Å (Fig. 2). For  $3.54 < a < 3.65$  Å, which includes the global minimum energy at  $a = 3.61$  Å, the  $\uparrow\uparrow\downarrow\downarrow$  is the most stable. For  $a > 3.65$  Å, fcc Fe ordered ferromag-

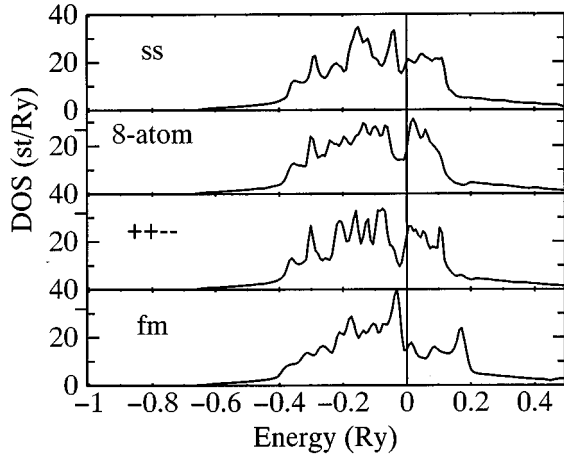


FIG. 3. Calculated DOS's per atom at  $a=3.58$  Å. A pronounced minimum in the DOS near the Fermi level is present in the eight-atom and  $\uparrow\uparrow\downarrow$  structures, suggesting that the low-energy structures are stabilized by the formation of a pseudogap.

netically. Once again, the SS was never the stable structure, though it is nearly degenerate with the eight-atom configuration (Fig. 2). The corresponding DOS's and MM's as function of structure are shown on Figs. 3 and 4.

The low-energy magnetic configurations are generally different stacking sequences along [001] planes, with all spins lying perpendicular to the stacking. Moreover, with the exception of the eight-atom structures, the remaining structures had all spins within a plane ferromagnetically aligned. To investigate the effective exchange coupling parameters, we consider an effective planar Hamiltonian coupling neighboring planes along the [001] direction, with spins in each plane

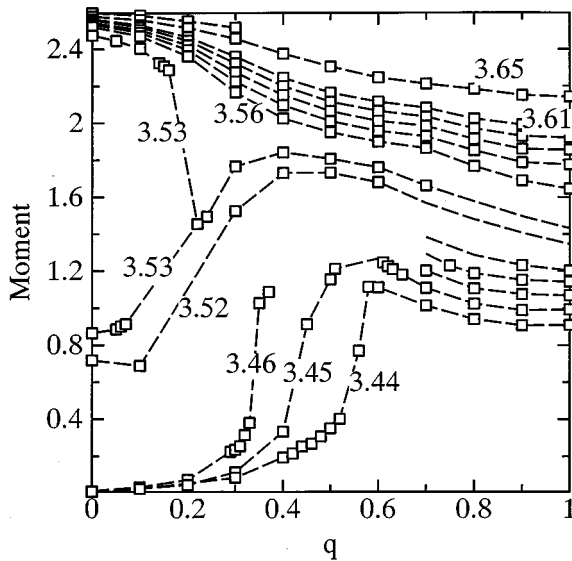


FIG. 4. Magnetic moment as a function of  $q$  and  $a$  for the SS state. A split between a high-spin and a low-spin configuration can be seen for  $a=3.53$  Å. At  $q=0$ , the high-spin configuration is very weakly dependent on  $a$ , while the low-spin state is extremely sensitive to  $a$ . The transition from low spin to high spin is much milder for  $q=1$ .

TABLE I. Pair exchange parameters (in mRy) according to the model Hamiltonian Eq. (74).

$a$ (a.u.)	Bilinear		Biquadratic		Bicubic	
	$J^1$	$J^2$	$J^1$	$J^2$	$J^1$	$J^2$
3.59	-0.22	1.89	0.39	-0.49	-0.15	-0.17
3.65	-2.65	1.42	0.22	-0.58	-0.12	-0.04
3.72	-4.34	1.16	0.14	-0.60	-0.17	0.01

aligned ferromagnetically in the plane. The coupling may be decomposed as a Fourier series of the rotation angle  $\phi_i - \phi_j$  between planes  $i$  and  $j$ . To determine the coupling parameters, we consider a cell of four independent planes. By considering a continual rotation starting from a FM ( $++++$ ) configuration to the AFM ( $+-+-$ ), and another from the FM to the  $+-+-$  configuration, the total energy may be decomposed into a Fourier series for either rotation. Thus for each Fourier component, there are two independent quantities and sufficient information to extract two parameters, namely, the first- and second-neighbor couplings  $J^1$  and  $J^2$  (more-distant-neighbor coupling is neglected). We assume an effective exchange Hamiltonian

$$H_{\text{eff}} = \sum_{k=1,2,3} (J_k^1 \cos 2\pi k \varphi_1 + J_k^2 \cos 2\pi k \varphi_2). \quad (74)$$

While the model  $H_{\text{eff}}$  does not reproduce all magnetic configurations exactly, it does by construction fit the FM-AFM and FM- $(+-+-)$  energy differences exactly, and does reasonably well for other configurations such as the SS, and is thus sufficient for the qualitative description we seek. The  $J$  values for the bilinear, biquadratic, and bicubic terms are listed in Table I. It is seen that the nearest-neighbor (NN) bilinear coupling rapidly evolves from nearly zero at  $a=3.59$  Å to a large negative value. Near the point where it becomes comparable to the 2NN bilinear term, there is a transition from the AFM ( $+-+-$ ) configuration to the FM. The rather large (and more slowly varying) 2NN bilinear term accounts for configurations favoring AFM second neighbors. When the first NN bilinear term is very small, higher-order terms such as the biquadratic become relatively important, explaining why noncollinear ordering is found there.

We next turn to an investigation of errors associated with the ASA and also the neglect of  $f$  orbitals in the basis. We investigated both of these errors by comparing to full-potential spin-polarized calculations. Our implementation of a full-potential program is essentially similar to that discussed in Ref. 51, but using the local functional of von Barth and Hedin (BH), with a gradient correction of Langreth and Mehl (LM). The BH+LM and Vosko+Perdew-Wang (PW) functionals produce similar results—a detailed comparison of the two functionals for spin-polarized systems will be presented elsewhere—but for our present purpose, we only seek to establish the validity of the ASA for fcc Fe.

Figure 5 compares several ASA calculations of FM fcc Fe and a full-potential calculation, and thus offers a basis for comparing the relative importance of the various approximations. All the data show a low-spin and high-spin magnetic configuration, with similar moments and a transition from

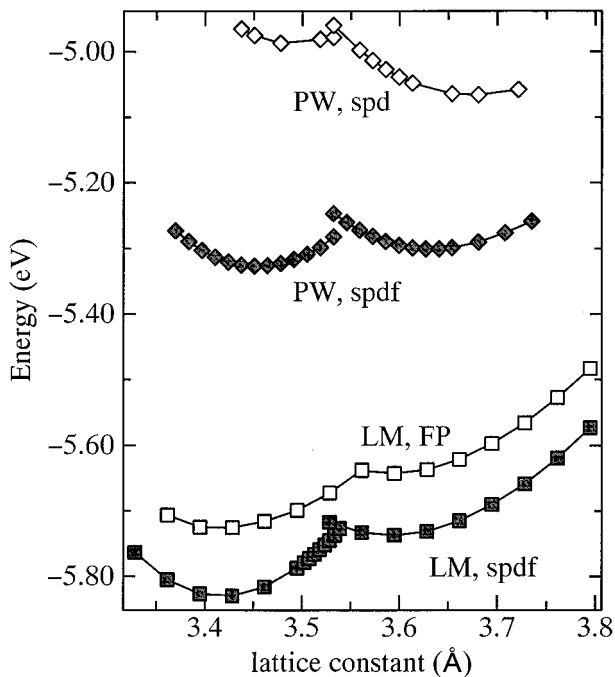


FIG. 5. Total energy for FM fcc Fe calculated in various approximations. ‘‘PW’’ signifies the Vosko+PW functional, ‘‘LM’’ signifies the BH+LM functional, ‘‘FP’’ signifies a full-potential calculation, spdf an ASA calculation with  $f$  orbitals included, and spd and ASA calculation without  $f$  orbitals.

the low-spin to the high-spin configuration at  $a \approx 3.55$  Å. The dark squares show ASA results with  $f$  orbitals included, using the BH+LM functional. Apart from a small, approximately constant shift of 100 meV, they compare very closely to corresponding full-potential results using the same functional (open squares). This shift may be attributed within the ASA approximation to the electrostatic double-counting terms: for example, the muffin-tin correction to the ASA electrostatic energy is about 200 meV. This error is almost completely independent of magnetic configuration, so we may safely conclude that the ASA functional introduces a negligible error to the relative magnetic orderings for fcc Fe.

The dark diamonds in the figure show ASA results for the Vosko+PW functional, again with  $f$  orbitals included. The two functions produce rather similar results (apart from an approximately constant shift of 400 meV), the Vosko+PW functional favoring a slightly larger lattice constant. The open diamonds are results for the Vosko+PW functional with  $f$  orbitals neglected. Here one sees that the neglect of  $f$  orbitals introduces a small, approximately linear term in the total energy and thus leads to a slight overestimate of the lattice constant.

Addition of  $f$  orbitals affected all the noncollinear magnetic configurations in approximately the same way, largely preserving the MM’s and relative energies of differing configurations for a given lattice constant, but adding a small linear shift that reduced the position of the minimum energy for each configuration. Figure 6 shows the same magnetic configurations as in Fig. 2, but now with  $f$  orbitals included. Because the minima occur at a smaller lattice constant, the  $3\mathbf{k}+\text{SS}$  structure is the most stable, with a minimum energy at 3.49 Å. It is nearly degenerate, however, with the eight-

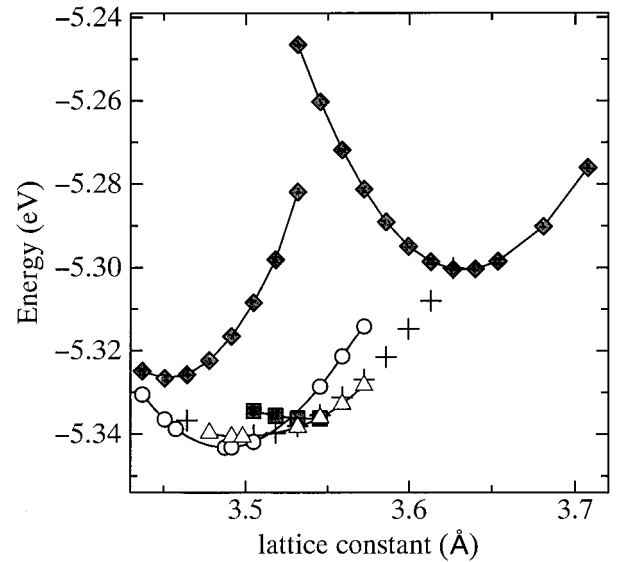


FIG. 6. Energies as in Fig. 3, but with  $f$  orbitals included.

atom configuration and the SS, which both have minima near  $a = 3.49$  Å (Fig. 6). It is remarkable that such different magnetic orderings are so close in energy. The SS and the  $3\mathbf{k}+\text{SS}$  each have a MM of approximately  $1.1\mu_B$  at the minimum lattice constant while the eight-atom configuration has two inequivalent atoms, with MM’s of  $0.8\mu_B$  and  $1.6\mu_B$ , respectively.

It is difficult to compare our results directly with experimental data. Some spin-density-wave-like states have been observed.<sup>50</sup> We do find spin-density-wave-like magnetic configurations, such as the  $3\mathbf{k}+\text{SS}$ , but it is clear that the relative orderings of these energies will be affected by lattice distortions which we have not taken into account. Nevertheless, it is interesting that the addition of gradient corrections significantly affects the magnetic ordering in fcc Fe and therefore suggests the importance of searching for a more adequate exchange-correlation potential.

We have conducted a preliminary investigation of alloying fcc Fe with Ni. Dynamical simulations were performed with the 32-atom cell as mentioned above, but with two of the Ni atoms substituted (6% Ni) and also with eight atoms substituted in an  $L1_0$  arrangement (25% Ni). The 25% case exhibited a strong tendency to order ferromagnetically. Simulations for the 6% case were made at  $a = 3.57$ , 3.61, and  $a = 3.65$  Å. The magnetic configurations ordered very much along the lines of bulk fcc Fe. For small lattice constants, the most stable configuration resembled the eight-atom configuration shown in Fig. 7 and for intermediate lattice constants it resembled the  $\uparrow\uparrow\downarrow\downarrow$  structure; see Fig. 7. In this structure the magnetization of the Ni was almost completely suppressed, although in the lower-symmetry structure [Fig. 7(a)], the Ni moment was approximately  $0.4\mu_B$ . Again, the global minimum appeared to be the  $\uparrow\uparrow\downarrow\downarrow$ -like structure. We defer a more detailed study of the Ni-Fe alloy to future work.

## VIII. CONCLUSIONS

We have presented an approach for treating spin dynamics in magnetic materials. Our approach goes beyond the standard Heisenberg model Hamiltonians with fixed spins in

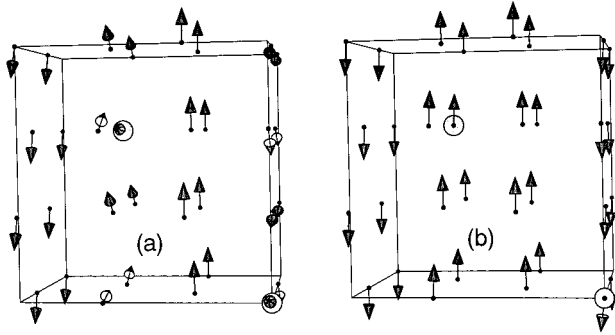


FIG. 7. Orderings found in fcc Fe doped with 6% Ni. Shaded circles indicate Ni atoms. (a) A configuration resembling the eight-atom structure, favored at small lattice constants; (b) a configuration essentially identical to the  $\uparrow\uparrow\downarrow\downarrow$  structure, favored for intermediate  $a$ .

that the moments and their interactions are obtained from the electronic structure using band theory. The moments are free to change their directions and magnitudes during a simulation in response to temperature, changes in the local spin environment, or lattice motion.

In order to arrive at a set of equations of motion for spin dynamics we have had to make use of ideas appropriate for the adiabatic evolution of the electronic system. In principle, one would prefer a more direct quantum-mechanical approach such as modern quantum Monte Carlo techniques provide; however, even with foreseeable increases in computing power over the next ten years, it seems likely that such direct methods will be limited to modest-size systems (certainly much smaller than the thousands of moments we would like to consider). Nevertheless, accurate many-body simulations on even modest-size systems will be valuable for testing the physical picture and accuracy of the SD equations we propose. Another more basic approach than the SD equations is to solve the time-dependent nonadiabatic spin DF equations directly. There would be no need to separate the SD (moment) equations from the electronic ones. Such an approach could certainly be implemented for larger systems than would be feasible with the quantum Monte Carlo approach, but there would still be trouble treating finite temperature, defects, alloys, and the nonuniform systems we seek to study.

While the aforementioned more fundamental and precise theoretical methods for treating electron dynamics will eventually be used to study SD, the utility of the approach to SD which we propose will first be assessed by comparison to experiment. The ability to realistically calculate  $S(\mathbf{q}, \omega)$  as a function of temperature (even above  $T_c$ ) offers a means of directly comparing theory with neutron and magnetic x-ray scattering results. These comparisons will be the initial tests of *ab initio* SD. There are many materials where our formalism should be applicable; and even in those systems with strong correlations, some hybrid scheme such as the LDA+ $U$  approach may be suitable. The extension of these ideas to the simultaneous treatment of MD and SD offers an even greater range of problems and physical systems for exploration. Such simulations will be very demanding on computer resources; however, with the advent of massively parallel computers and the concomitant development of order- $N$

methods, the task is manageable now for modest system sizes. For example, recent implementation of the basic SD equations on the Intel Paragon at Oak Ridge<sup>52</sup> has been completed for a system containing 512 independent atoms. We expect that the introduction of an empirical TB approach for SD will greatly facilitate the expansion of feasible system sizes to thousands of atoms, and combined with TBMD it will be a cost-effective means of exploring the full dynamics of many large systems. An example of great current interest where lattice relaxation and thermal spin excitations play a role is in the determination of the temperature-dependent electrical conductivity in materials exhibiting giant or colossal magnetoresistance.

Finally, we would also like to mention that the quasiclassical approximation used in the derivation of the SD EOM's forms a natural basis for studying aspects of quantum tunneling in magnetic systems. The imaginary-time formalism (a method for following quasiclassical periodic trajectories) provides a method which permits the system to explore classically forbidden regions and tunneling matrix elements for the ground state<sup>53</sup> as well as excited states in the imaginary-time-dependent DF formalism<sup>41</sup> in the cases of magnetic and nonmagnetic systems.

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#### APPENDIX

Here we present a simple proof of the local force theorem in the HFA. Taking into account the expression for the total energy in the HFA,<sup>26</sup>

$$\begin{aligned}
 E = & \sum_i \int d\mathbf{r} \psi_i^*(\mathbf{r})(-\Delta + V^{\text{ext}})\psi_i(\mathbf{r}) \\
 & + \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \\
 & - \sum_{ij} \delta_{\sigma_i, \sigma_j} \int \int d\mathbf{r} d\mathbf{r}' \frac{\psi_i^*(\mathbf{r})\psi_i^*(\mathbf{r}')\psi_j(\mathbf{r}')\psi_j(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|},
 \end{aligned} \tag{A1}$$

where  $i = (\nu_i, \sigma_i)$  are the orbital and spin quantum numbers, the HF equation is

$$\begin{aligned}
 H_{\text{HF}}\psi_i(\mathbf{r}) = & (-\Delta + V^{\text{ext}})\psi_i(\mathbf{r}) + 2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \psi_i(\mathbf{r}) \\
 & - \sum_j \delta_{\sigma_i, \sigma_j} \int d\mathbf{r}' \frac{\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}')\psi_j^*(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \\
 = & \varepsilon_i \psi_i(\mathbf{r}).
 \end{aligned} \tag{A2}$$

The total energy can be rewritten as

$$E = \sum_j \varepsilon_j - E_{\text{DC}}, \quad (\text{A3})$$

where the energy of double-counting terms is given by

$$E_{\text{DC}} = \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}')n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} - \sum_{\mu\nu} \delta_{\sigma_i\sigma_j} \int d\mathbf{r} d\mathbf{r}' \frac{\psi_{\mu}^*(\mathbf{r})\psi_{\mu}^*(\mathbf{r}')\psi_{\nu}(\mathbf{r}')\psi_{\nu}(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}. \quad (\text{A4})$$

Let us assume that under rotations of the local coordinate systems or other slow (quasistatic) perturbations of the system the wave functions  $\{\psi_i\}$  are changed by  $\delta\psi_i$ . Then, calculating the variation of  $E_{\text{DC}}$  under such a perturbation, one can show that

$$\delta E_{\text{DC}} = \sum_i \int d\mathbf{r}' \psi_i^*(\mathbf{r}) \delta_1 \hat{H}_{\text{HF}} \psi_i(\mathbf{r}) = \sum_i \delta_1 \varepsilon_i, \quad (\text{A5})$$

where  $\delta_1 \hat{H}_{\text{HF}}$  is the variation of the HF Hamiltonian in (A1),

$$\delta_1 \hat{H}_{\text{HF}} = 2 \int \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}')\psi_i(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \sum_j \delta_{\sigma_i\sigma_j} \int \int d\mathbf{r} d\mathbf{r}' \times \frac{[\delta\psi_j^*(\mathbf{r}')\psi_i(\mathbf{r}') + \psi_j^*(\mathbf{r}')\delta\psi_i(\mathbf{r}')] }{|\mathbf{r}-\mathbf{r}'|} \psi_j(\mathbf{r}). \quad (\text{A6})$$

The term (A6) is exactly the variation of the sum of HF energies due to variation of the potential under self-consistency. Consequently, taking into account (A5) and (A6) we have

$$\delta E = \sum_j (\delta\varepsilon_j - \delta_1\varepsilon_j) = \sum_j \delta^* \varepsilon_j, \quad (\text{A7})$$

where  $\delta^*$  is the variation for the potential being kept fixed. Equation (A7) is the local force theorem in the HFA.

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<sup>1</sup>*Magnetism*, edited by H. Suhl (Academic, London, 1973), Vol. IV; S. V. Vonsovskii, M. I. Katsnelson, and A. V. Trefilov, Phys. Met. Metall. **76**, 247 (1993).

<sup>2</sup>T. Moriya and H. Hasegawa, J. Phys. Soc. Jpn. **48**, 1490 (1980); *Electron Correlation and Magnetism in Narrow-Band Systems*, edited by T. Moriya (Springer-Verlag, Berlin, 1981); T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).

<sup>3</sup>V. Korenman, J. L. Murray, and R. E. Prange, Phys. Rev. B **16**, 4032 (1977); **16**, 4058 (1977).

<sup>4</sup>U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972); O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976); R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. **61**, 689 (1989).

<sup>5</sup>T. Oguchi, K. Terakura, and N. Hamada, J. Phys. F **13**, 145 (1983); A. J. Pindor, J. Staunton, G. M. Stocks, and H. Winter, *ibid.* **13**, 979 (1983).

<sup>6</sup>M. V. You and V. Heine, J. Phys. F **12**, 177 (1982); D. M. Edwards, J. Magn. Magn. Mater. **45**, 151 (1984).

<sup>7</sup>L. M. Small and V. Heine, J. Phys. F **14**, 3041 (1984).

<sup>8</sup>L. M. Sandratskii and P. G. Guletskii, J. Phys. F **16**, L43 (1986); J. Sticht, K. H. Höck and J. Kübler, J. Phys. Condens. Matter **1**, 8155 (1989).

<sup>9</sup>V. P. Antropov, M. I. Katsnelson, M. van Schilfgaarde, and B. N. Harmon, Phys. Rev. Lett. **75**, 729 (1995).

<sup>10</sup>E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984); E. K. U. Gross and W. Kohn, *ibid.* **66**, 2850 (1985).

<sup>11</sup>*Geometric Phases in Physics*, edited by A. Shapere and F. Wilczek (World Scientific, Singapore, 1989).

<sup>12</sup>N. Papanicolaou, J. Phys. (Paris) **49**, 1493 (1988).

<sup>13</sup>W. Dittrich and M. Reuter, *Classical and Quantum Dynamics* (Springer-Verlag, Berlin, 1994).

<sup>14</sup>D. Bohm, R. Schiller, and J. Tiomno, Nuovo Cimento Suppl. **1**, 48 (1955); T. Takabayasi, Prog. Theor. Phys. **14**, 283 (1955). Whereas we utilized a quasichlassical adiabatic approximation and separated the time evolution of diagonal and off-diagonal

components of the spin density matrix to obtain a set of coupled EOM's, in these papers the authors did not describe the adiabatic or quasichlassical assumption and used a different choice of dynamical variables in a hydrodynamic approach. We believe that their dynamics does not follow directly from the Pauli equation due to their specific choice of the current operator. But the addition of the temperature effects we describe in the present paper can be made in their formalism as well.

<sup>15</sup>S. H. Liu, Phys. Rev. B **13**, 3962 (1976); **15**, 4281 (1977).

<sup>16</sup>V. Yu. Irkhin, M. I. Katsnelson, and A. V. Trefilov, J. Phys. Condens. Matter **5**, 8763 (1993).

<sup>17</sup>P. Genoval, A. A. Manuel, E. Walker, and M. Petar, J. Phys. Condens. Matter **3**, 4201 (1991); C. M. Schneider, P. Schuster, M. S. Hammord, and J. Kirschner, Europhys. Lett. **16**, 689 (1991).

<sup>18</sup>P. Lloyd and P. V. Smith, Adv. Phys. **21**, 69 (1972); J. Koringa, Phys. Rep. **238**, 341 (1994).

<sup>19</sup>A. I. Liechtenstein, M. I. Katsnelson, and V. A. Gubanov, J. Phys. F **14**, L125 (1984); A. I. Liechtenstein, M. I. Katsnelson, V. P. Antropov, and V. A. Gubanov, J. Magn. Magn. Mater. **67**, 65 (1987).

<sup>20</sup>V. P. Antropov, M. I. Katsnelson, M. van Schilfgaarde, and B. N. Harmon (unpublished).

<sup>21</sup>V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Relativistic Quantum Theory*, Course of Theoretical Physics Vol. 4 (Pergamon, Oxford, 1971).

<sup>22</sup>V. A. Gubanov, A. I. Liechtenstein, and A. V. Postnikov, *Magnetism and the Electronic Structure in Crystals* (Springer-Verlag, Berlin, 1992).

<sup>23</sup>V. P. Antropov and A. I. Liechtenstein, in *Application of Multiple Scattering Theory to Materials Science*, edited by W. H. Butler, P. H. Dederichs, A. Gonis, and R. Weaver, MRS Symposia Proceedings No. 253 (Materials Research Society, Pittsburgh, 1992), p. 325.

<sup>24</sup>A. Svane and O. Gunnarsson, Phys. Rev. B **37**, 9919 (1988).

<sup>25</sup>V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).



- <sup>26</sup>S. Massida, M. Pasternak, and A. Baldereschi, *Phys. Rev. B* **46**, 11 705 (1992); J. B. Grant, and A. K. McMahan, *ibid.* **46**, 8440 (1992); T. Mizokawa and A. Fujimori, *ibid.* **51**, 12 880 (1995).
- <sup>27</sup>G. V. Skrotskii, *Sov. Phys. Usp.* **144**, 681 (1984).
- <sup>28</sup>B. N. Harmon, V. P. Antropov, and M. I. Katsnelson, in *Condensed Matter Theories*, edited by E. V. Ludena (Nova Science, New York, in press).
- <sup>29</sup>J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963).
- <sup>30</sup>U. Gupta and A. K. Rajagopal, *Phys. Rep.* **87**, 259 (1982).
- <sup>31</sup>M. Kac, *Probabilities and Related Topics in the Physical Sciences* (Interscience, New York, 1959); R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II* (Springer-Verlag, Berlin, 1991); C. W. Gardiner, *Quantum Noise* (Springer-Verlag, Berlin, 1991).
- <sup>32</sup>R. Kubo and N. Hashitsume, *Prog. Theor. Phys. Suppl.* **46**, 210 (1970); H. Hasegawa and H. Ezawa, *ibid.* **69**, 41 (1980); S. I. Denisov, *Phys. Solid State*, **36**, 1745 (1994).
- <sup>33</sup>R. Lenk, *Fluctuations, Diffusion and Spin Relaxation* (Elsevier, Amsterdam, 1986).
- <sup>34</sup>S. Nosé, *Prog. Theor. Phys. Suppl.* **103**, 1 (1991).
- <sup>35</sup>W. G. Hoover, *Computational Statistical Mechanics* (Elsevier, Amsterdam, 1991).
- <sup>36</sup>A. Bulgac and D. Kusnezov, *Phys. Rev. A* **42**, 5045 (1990); D. Kusnezov, A. Bulgac, and W. Bauer, *Ann. Phys. (N.Y.)* **204**, 155 (1990).
- <sup>37</sup>D. Kusnezov, *Phys. Rev. Lett.* **74**, 246 (1995); *Phys. Lett. A* **184**, 50 (1993); *Phys. Lett. B* **289**, 395 (1992).
- <sup>38</sup>D. Kusnezov and J. Sloan, *Nucl. Phys. B* **409**, 635 (1993).
- <sup>39</sup>N. I. Chernov, G. L. Eyink, J. L. Lebowitz, and Ya. G. Sinai, *Phys. Rev. Lett.* **70**, 2209 (1993).
- <sup>40</sup>P. Blöchl and M. Parrinello, *Phys. Rev. B* **45**, 9413 (1992).
- <sup>41</sup>V. P. Antropov and B. N. Harmon, *J. Appl. Phys.* **79**, 5409 (1996).
- <sup>42</sup>A. Inomata, H. Kuratsuji, and C. C. Jerry, *Path Integrals and Coherent States of SU(2) and SU(1,1)* (World Scientific, Singapore, 1992).
- <sup>43</sup>J. R. Klauder and B.-S. Skagerstam, *Coherent States: Applications in Physics and Mathematical Physics* (World Scientific, Singapore, 1985).
- <sup>44</sup>C. A. Mead, *Rev. Mod. Phys.* **64**, 51 (1992).
- <sup>45</sup>D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics* (Plenum, New York, 1974); M. Goldman, *Spin Temperature and Nuclear Magnetic Resonance in Solids* (Oxford University Press, Oxford, 1970).
- <sup>46</sup>O. K. Andersen, M. Pawłowska, and O. Jepsen, *Phys. Rev. B* **34**, 5253 (1986).
- <sup>47</sup>O. Mriyasov, A. I. Liechtenstein, L. Sandratskii, and V. A. Gubanov, *J. Phys. Condens. Matter* **3**, 7683 (1991); M. Uhl, L. Sandratskii, and J. Kübler, *Phys. Rev. B* **50**, 291 (1994).
- <sup>48</sup>V. P. Antropov, M. van Schilfgaarde, and B. N. Harmon, *J. Magn. Magn. Mater.* **140–144**, 1355 (1995).
- <sup>49</sup>J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**, 6671 (1992).
- <sup>50</sup>E. F. Wasserman, *Phys. Scr.* **T25**, 209 (1989); Y. Tsunoda, *J. Phys. Condens. Matter* **1**, 10 427 (1989); T. Jo, *ibid.* **1**, 7971 (1989); Y. Tsunoda, *Prog. Theor. Phys. Suppl.* **101**, 133 (1990).
- <sup>51</sup>V. Ozoliņš and M. Körling, *Phys. Rev. B* **48**, 18 304 (1993).
- <sup>52</sup>V. P. Antropov, B. N. Harmon, Yang Wang, G. M. Stocks, W. A. Shelton, and D. M. C. Nicholson, *J. Appl. Phys.* (to be published).
- <sup>53</sup>M. I. Katsnelson, V. P. Antropov, M. van Schilfgaarde, and B. N. Harmon, *JETP Lett.* **62**, 439 (1995); M. I. Katsnelson, M. van Schilfgaarde, V. P. Antropov, and B. N. Harmon (unpublished).