Ab Initio Spin Dynamics in Magnets

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A set of coupled equations of motion for the evaluation of spin dynamics in magnets is introduced. This adiabatic approach considers the orientation of the local magnetic moments to be slowly varying relative to their magnitudes. The method is implemented within the local density approximation and applied to γ-Fe, a frustrated system where we obtain new low energy magnetic configurations.

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While there has been great progress in the development of *ab initio* methods for molecular dynamics simulations, the description of spin dynamics (SD) has largely been restricted to systems described by model Hamiltonians, where the local magnetic moments (MM) are treated independently of the other electronic degrees of freedom. Here we present equations of motion (EOM) for the spin degrees of freedom starting from general principles, and show how *ab initio* SD simulations may be implemented in practice using an adiabatic approximation for the spin orientations, and the local spin density-functional approximation (LSDA) for the electronic structure.

In the description of electron-ion dynamics the time scales of the electronic and nuclear motion are dramatically different. One may solve the electronic problem assuming fixed nuclear coordinates, and treat the "slow" nuclear motion classically, with the nuclear forces arising from the instantaneous electrostatic field (the Born-Oppenheimer approximation). While such a clean decomposition is not possible for just the electronic degrees of freedom by themselves, specific adiabatic criteria may nevertheless be useful when dealing with some magnetic systems. In the majority of magnets [at least in all magnetic dielectrics and in metals with well-defined local MM) the orientation of the MM plays the role of the collective (slow) degrees of freedom, and the one-particle wave functions (which determine the magnitude of the MM) play the role of the fast degrees of freedom. The validity of such a separation of the degrees of freedom is related to the difference in energy scales for the intersite and on-site exchange parameters. Below we will utilize such a partitioning of these degrees of freedom in deriving the EOM. As a concrete illustration, we use the EOM for a 32 atom per cell simulation of γ-Fe and obtain new low energy magnetic configurations.

The Schrödinger equation for the total wave function is

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi, \tag{1}$$

where Ψ and H depend on nuclear, electronic, and spin degrees of freedom. To separate different dynamical effects we will assume that they have different effective time scales, and nuclear and spin degrees of freedom evolve slowly. Using a time analog of the WKB approximation [1] in the semiclassical limit, we can integrate out some of the degrees of freedom of Eq. (1) and partition the system into the quantum mechanical problem for the electronic degrees of freedom and semiclassical motion for the slowly evolving orientations of the MM and nuclear positions. This derivation recovers the Born-Oppenheimer approximation for the ionic motion and also leads to the following quantum-classical hybrid EOM for the spin dynamics:

$$i\hbar\frac{\partial}{\partial t}|\psi\rangle = (H_e + V_{es})|\psi\rangle, \tag{2}$$

$$\dot{\alpha} = -\frac{\partial V_{ss}}{\partial \alpha^*} - \langle\psi|\frac{\partial V_{es}}{\partial \alpha^*}|\psi\rangle,$$

$$\dot{\alpha}^* = \frac{\partial V_{ss}}{\partial \alpha} + \langle\psi|\frac{\partial V_{es}}{\partial \alpha}|\psi\rangle, \tag{3}$$

where V_{ss} and V_{es} are determined by spin-spin rotational and space-time variation of the exchange splitting interactions, respectively, ψ is the two-component wave function (depending parametrically on the spin orientations), and α and α^* are conjugate coordinates that determine the rotation of the spin density matrix (for instance, two Holstein-Primakoff variables). Equations (2) and (3) are very general. The adiabatic limit of Eq. (3) describes the quasiclassical dynamics of the local moment orientations on an adiabatic energy surface. The electronic Hamiltonian, averaged over the instantaneous electronic configuration with fixed moment directions, plays the role of the potential energy for α and α^*. This is analogous to the evaluation of Hellmann-Feynman forces from the electronic Hamiltonian averaged over instantaneous positions of the nuclei. The formal derivations of the EOM are somewhat involved and will be presented in a larger publication [2]. Our physical arguments should make plausible the first terms of Eqs. (3), while the second terms represent nonclassical interactions with the quantum system and follow from the complete formalism. Equations (2) and (3) can be considered as a first approximation for the description of the EOM of spin systems with nonadiabatic or quantum (spin tunneling) effects. We note that geometrical phase factors [3] of the total wave function can be found consistently as a natural consequence of this adiabatic expansion.

For a practical implementation of *ab initio* 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 [4], together with the "force theorem" generalized for noncollinear magnetic perturbations [5], offers a highly effective method for the calculation of $\partial V/\partial\alpha$ in Eq. (3). If we consider a "rigid" spin approximation, 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. Using the fact that the "rotational" part of the one-site scattering matrix can be presented as a vector, $\mathbf{t}^{-1} = p\mathbf{e}$, and the same for the path operator, $\mathbf{T} = T\mathbf{e}'$ (see, for instance, Ref. [5]), for a general orientation of MM the magnetic "force" (the magnetic analog of the Hellmann-Feynman forces) may be written in vector notation as

$$\frac{\partial V}{\partial \mathbf{e}} = \mathbf{I} = \frac{2}{\pi}\int^{\epsilon_f} d\epsilon \,\mathrm{Im\,Tr}\{\mathbf{p}T\}. \qquad (4)$$

The force corresponding to rotations of a single site $\mathbf{e}_i$ or 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 correspondingly both real space (short-range) and reciprocal space (long-range) magnetic orderings may be determined.

Finite temperature effects can be introduced with Eq. (3) in different ways. If we consider as usual an interaction with a thermal bath and assume that this term is proportional to the time derivative of the MM, the EOM (3) becomes

$$\frac{d}{dt}\mathbf{e} = -\frac{\gamma}{M}[\mathbf{e}\times\mathbf{I}] - \lambda[\mathbf{e}\times(\mathbf{I}\times\mathbf{e})], \qquad (5)$$

where γ is the gyromagnetic ratio and M is the absolute value of MM. In the formalism of the Nose-Hoover thermostat, the evolution of the coefficient for the friction term, λ in Eq. (5), may be expressed as

$$\frac{d}{dt}\lambda(t,T) = C\sum\{(\mathbf{I} - T\nabla_\mathbf{e})[\mathbf{e}\times(\mathbf{I}\times\mathbf{e})]\}. \qquad (6)$$

One can verify that these equations conserve not only the "length" of MM but also the total energy of the extended system (with some pseudoenergy terms), and therefore the classical canonical distribution is valid [6]. Equation (5) does not reduce to the classical (macroscopic) equation of Landau-Lifshitz. It is a microscopic, quasiclassical EOM and is the rotational analog of the Newtonian equations of motion in molecular dynamics. These equations describe the time evolution of the MM, and are valid for periods of time large in comparison to the time for the electronic degrees of freedom (responsible for the amplitude of the MM) to relax. They are suitable for the determination of equilibrium magnetic structures and the spectra of low lying excitations.

As a first illustration, we show how the EOM [Eq. (5)] 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. By choosing the local coordinate system $\mathbf{p}\|\mathbf{z}$ and $\delta p_i^+ = p_i^z\delta e_i^+$ we find

$$T_i^+ = -\sum_j T_{ij}^\uparrow p_j^+ T_{ji}^\downarrow \qquad (7)$$

and

$$\delta T_i^+ = -\sum_j T_{ij}^\uparrow \delta p_j^+ T_{ji}^\downarrow \qquad (8)$$

and then the linearized EOM [Eq. (5)] can be written as

$$\omega\cdot\delta e_i^+ = \frac{\gamma}{M}\sum_j J_{ij}(e_j^z\delta e_i^+ - e_i^z\delta e_j^+), \qquad (9)$$

with the effective exchange interactions given by

$$J_{ij} = \frac{1}{\pi}\int^{\epsilon_f} d\epsilon\,\mathrm{Im\,Tr}\{p_i T_{ij}^\uparrow p_j T_{ji}^\downarrow\}. \qquad (10)$$

This expression for J_{ij} is the same as the one obtained in Ref. [5].

Equation (9) is the same form as the EOM of the phenomenological Heisenberg model, but here it is derived from a fundamental theory. Consequently, the dispersion laws of Eq. (9) must be the same as in the Heisenberg model for any structures. For example, from the Fourier transform of Eq. (9) for a ferromagnet, we obtain

$$\omega_\mathbf{q}\,\delta e_\mathbf{q}^+ = \frac{\gamma}{M}[J(0) - J(\mathbf{q})]\delta e_\mathbf{q}^+. \qquad (11)$$

Thus the Heisenberg form for the dynamics of ferromagnons emerges in a natural way as an *analytical* solution of our *ab initio* theory. If follows directly from the linearization of the EOM [Eq. (3)] and the adiabatic, semiclassical limit.

We note in passing that it is possible to incorporate additional interactions within the same framework. For example, we may include the spin-orbit interaction and determine the direction of the orbital MM with respect to the spin. Such an interaction is needed to describe the additional energy cost associated with the coherent rotation of all spins (uniform precession). Also, by combining this approach with standard *ab initio* molecular dynamics for the description of lattice properties, we can include the phonon-magnon interaction in a consistent way.

As a concrete example, let us consider face centered cubic (fcc) iron (γ-Fe) at $T = 0$ K. This and related systems (Ni-Fe, Fe-Mn) have been studied for many years [7] as part of the "invar" problem. It also serves as a prototype model for a frustrated magnetic system. Earlier "static" calculations for fcc Fe [8,9] 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 spin-spiral (SS) and finally ferromagnetic (FM) ordering appears [9]. With our SD formalism we allow the spin system much more freedom to choose an equilibrium structure, and have found new and complex spin configurations with lower energies. We considered a unit cell consisting of 32 atoms with independent local moments. To calculate the electronic structure we used the linear-muffin-tin orbital method [10] with and without spin-orbital coupling. Initially the spins were frozen in a random orientation and the self-consistent electronic structure determined. Then the MM were allowed to relax along the direction of the forces.

Figure 1 shows the evolution of the spins for two different lattice constants, $a = 3.59$ Å and $a = 3.73$ Å. For the $a = 3.59$ Å simulation, the energy dropped smoothly and the spins ordered into the 4 atoms/cell "triple-**k**" (3**k**) structure (all spins oriented along $[\pm 1\ \pm 1\ \pm 1]$ directions), with the MM about $1.6\mu_B$ (Fig. 1). 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 approximately $2.3\mu_B$ (Fig. 1).

Subsequent static calculations for the 2**k**, 3**k**, FM, and $\uparrow\uparrow\downarrow\downarrow$ magnetic configurations, and similar configurations with an 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 3**k** structure with small MM ($0.8\mu_B$). At that volume the 3**k** is nearly degenerate with nonmagnetic Fe, being only 0.9 meV/atom more stable. The 2**k** is also very close in energy, lying only 1.2 meV above the 3**k**. 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 spin-orbit coupling increased the binding energy by approximately 5 meV/atom, but did not alter the relative energies of the various magnetic configurations.

It has been proposed [10] that the minimum energy configuration for some range of volume of fcc Fe is an incommensurate (0,0,q) SS, evolving into the FM structure for large lattice constants. Accordingly, we considered various magnetic configurations with a (0,0,q) SS superimposed (without spin-orbital coupling), and indeed the 3**k**, 2**k**, and FM structures were further stabilized by an incommensurate SS with $1/q \approx 6a$. The equilibrium configuration is a 2**k** + SS at $a = 3.44$ Å and $1/q \approx 6a$, the SS stabilizing the normal 2**k** structure by 1.8 meV; this is 1.2 meV lower than nonmagnetic Fe at its own equilibrium lattice constant (3.43 Å). The 3**k** is more weakly stabilized by a SS than the 2**k**, though the optimal q is similar; at 3.43 Å it is 0.4 meV less binding. With increasing volume the optimal $1/q$ evolves smoothly to $\approx 9a$ at $a = 3.55$ Å in both the 3**k** and 2**k** configurations. For $a > 3.45$ Å the 3**k** + SS becomes the most stable configuration, until it is overtaken by the $\uparrow\uparrow\downarrow\downarrow$ [001] structure for $a > 3.59$ Å. This latter 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 energy

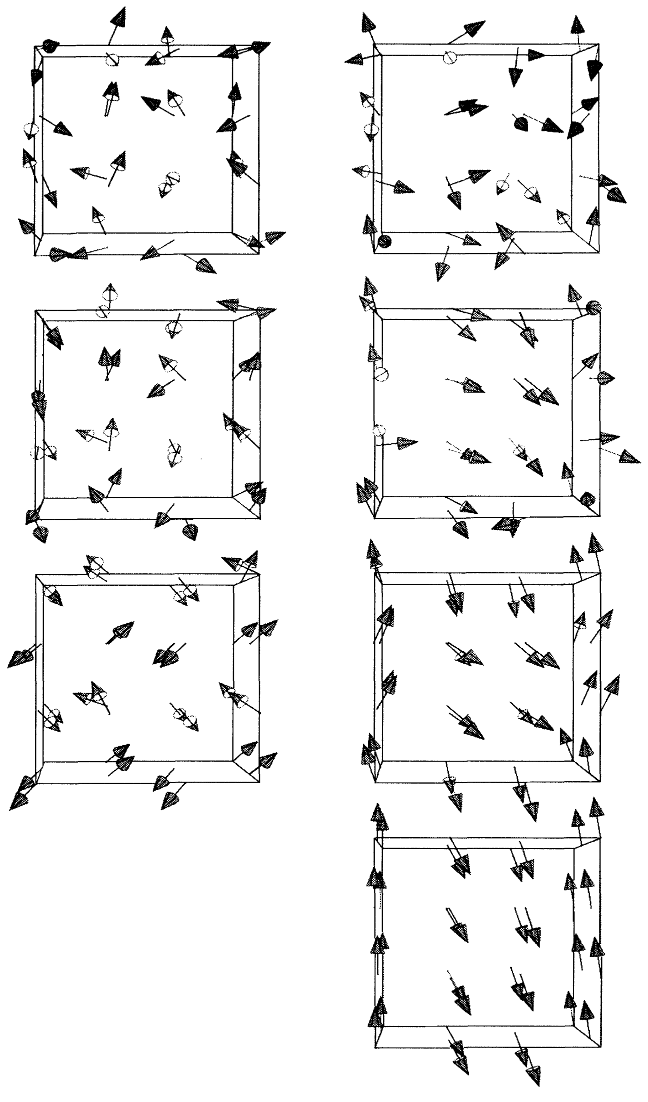

FIG. 1. The left column shows the evolution of spins in a 32-atom cell of fcc Fe with $a = 3.59$ Å. Top, the starting random configuration; middle, after 75 steps; bottom, after 200 steps. This last configuration is close to a 3**k** structure, the minimum-energy structure allowed by the simulation (no SS allowed). The right column is similar, but for $a = 3.73$ Å. Spin configurations after 0, 20, 75, and 220 steps are shown, the last being close to the $\uparrow\uparrow\downarrow\downarrow$ structure.

than the $2\mathbf{k}+$ SS and ↑↑↓↓ structures. Investigation of the effective exchange coupling parameters suggests that the variety of magnetic structures in such frustrated systems is directly related to the long-range exchange interactions for larger volumes; whereas for smaller volumes the MM are reduced, and the volume-dependent ratio of bilinear to biquadratic exchange coupling favors the stability of exotic multiple-$\mathbf{k}$ structures.

To summarize, we have described a new and general approach for studying finite temperature and dynamical effects of arbitrary spin systems. The proposed method can be naturally generalized to the case of additional spin and spin-lattice interactions, including the spin dynamics in superconducting materials, and can be applied to the study of complex solids and molecules.

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