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Non-collinear Magnetic States: From Density Functional Theory to Model Hamiltonians

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Recent observation of "colossal magnetoresistance" in $La_{1-x}Ca_xMnO_3$ and related compounds suggest the importance of orientational disordering of Mn magnetic moments, especially near the Curie temperature. Several interesting compounds even display non-collinear moments (NCM) in their ground states. Although self-consistent local density functional based treatments of NCM are already available (within certain simplifications), it will be instructive to have realistic tight binding methods to simulate the more complex spin configurations. In this paper the process of simplifying the *ab initio* density functional theory of NCM to tight binding form is discussed. It is suggested that in the La-based manganites, the e_g moments on the Mn ion may not be strongly coupled to the t_{2g} moments, and that these two suborbitals may become non-collinear on the same ion. A tight binding approach can model such a situation.

I. INTRODUCTION

$$H = -\sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} V_{ext}(r_i) + \frac{1}{2}\sum_{i\neq j}^{N} \frac{e^2}{\mid r_i - r_j \mid} \qquad (1)$$

is the non-relativistic Hamiltonian ($\hbar$=1, $2m_e$=1) governing a collection of N electrons with coordinates $\{r_i\}$ interacting with each other and with an external potential V_{ext}. Summation over the spin coordinates of the electrons is implicit. This is the standard Hamiltonian for the study of condensed matter systems, and for real materials (i.e. excluding jellium and other model systems) remains unsolved. Simplifications that allow progress run between two extremes: (a) to reduce to a vastly simplified model system that retains a many-body interaction which can be treated, and to hope that the model contains some of the essence of the real system, or (b) to retain much of the intrinsic complexity (structural features, multiband nature, etc.) but to simplify the treatment of interelectronic interactions, such as in an effective mean-field treatment. Spin density functional theory (SDFT) is a widely practiced, generally successful method of the second type that has strong theoretical underpinnings. [1,2]

The various ways that one can approach this problem is nowhere more evident than in the theory of high temperature superconductors during the past decade. The two extremes mentioned above can be represented by (a) simplification to a single (or three) band Hubbard model, or perhaps to a Holstein-type polaron model, or alternatively (b) use of the local spin density approximation (LSDA) to obtain a band structure, one-electron wavefunctions, and charge density. From both directions there have been promising efforts to bridge the chasm between the two approaches: extension of the Hubbard model to multi-atom, multiband, extended models [3,4] in the case of (a), and incorporation of many-body corrections using a SDFT starting point [5,6]. These approaches must be considered to be still under development, and are not the focus of this paper.

The purpose here is to discuss further complications that occur in the description of magnetism, specifically the occurrence of non-collinear magnetic (NCM) states. Such states occur in magnetic overlayers and sandwich structures that display "giant magnetoresistance" and are expected to be important in the manganite materials exhibiting "colossal magnetoresistance." Note the lack of any overt spin dependence in the Hamiltonian of Eq. (1); the implicit spin dependence arises because electrons are spin-$\frac{1}{2}$ particles, whose statistics and spin restrict the nature of the solutions. Here we discuss the relationship between the description of NCM magnetic configurations in model Hamiltonians and within SDFT.

II. SDFT FORMALISM

A familiarity with SDFT will be presumed. The widely used form of SDFT, in which one treats a majority ($\uparrow$) and minority ($\downarrow$) magnetization densities $m_\uparrow(r)$ and $m_\downarrow(r)$, is due to von Barth and Hedin. [7] (vBH) The magnetization density is equal to $g\mu_B$ times the spin density, where g$\approx$2 is the electron g factor. [In this paper m will denote the magnetization density in units of μ_B, or equivalently, twice the spin density.] In fact, before simplifying to collinear states, vBH outlined a generalized spin-matrix $[\rho_{\alpha\beta}]$ density functional theory that specifically included the vector nature of the spin density. A four-component 2×2 matrix S in spinor space,

$$S = \{\sigma_o, \sigma_x, \sigma_y, \sigma_z\} = \{\sigma_o, \vec{\sigma}\} \qquad (2)$$

where $\vec{\sigma}$ is the Pauli spin vector matrix and σ_o is the 2×2 identity matrix, spans the space with convenient

notation. The Kohn-Sham equations [2] become

$$\{[-\nabla^2 + V_{ext}(r) + \int d^3r' n(r') \frac{e^2}{\mid r - r' \mid} \tag{3}$$

$$+ v_{xc}(r; n, \vec{m})]\sigma_o + \vec{b}_{xc}(r; n, \vec{m}) \cdot \vec{\sigma}\}\Psi_i(r) \tag{4}$$

$$= \varepsilon_i \Psi_i(r). \tag{5}$$

Coupling between the spin directions arises solely through the magnetization dependence of the exchange-correlation (XC) energy. The XC potentials are the derivatives of the SDFT XC energy functional:

$$v_{xc}(r) = \frac{\delta E_{xc}[n, \vec{m}]}{\delta n(r)}, \quad \vec{b}_{xc}(r) = \frac{\delta E_{xc}[n, \vec{m}]}{\delta \vec{m}(r)} \tag{6}$$

where the designation of $\vec{b}_{xc}$ is chosen to reflect that this XC contribution couples to the spin as a magnetic field would. The densities are given by contributions from occupied states:

$$\rho(r) = \{n(r), \vec{m}(r)\} = \sum_n^{occ} \Psi_n^\dagger(r) S \Psi_n(r). \tag{7}$$

In the conventional local spin density approximation (LSDA) [7] $E_{xc}[n, m]$ depends only on $m(r) = \mid \vec{m}(r) \mid$, so one rotates into the local frame where "↑" is along $\vec{m}(r)$, the exchange potential is evaluated, and then applied to the spinor $\Psi(r)$=$\{\psi_+(r), \psi_-(r)\}$. If the spin density everywhere points in one direction, a collinear spin state is described (e.g. ferromagnetic or antiferromagnetic) and spin ↑ and spin ↓ equations decouple. Where the spin density deviates in direction, the two spin directions are coupled and the eigenspinors are no longer spin-pure.

An expression for the total energy is

$$E_{tot} = \sum_i^{occ} \varepsilon_i - \tfrac{1}{2} \int\int d^3r d^3r' n(r') \tfrac{e^2}{|r-r'|} n(r) \tag{8}$$

$$+ E_{xc}[n, \vec{m}] - \int d^3r n(r) v_{xc}(r; n, \vec{m})$$

$$- \int d^3r \vec{m}(r) \cdot \vec{b}_{xc}(r; n, \vec{m}) \tag{9}$$

i.e. the eigenvalue sum plus the XC energy, minus the "double counting" terms. Expanding E_{xc} and the term containing $\vec{b}_{xc}$ around $\vec{m} = \vec{0}$ and denoting the second functional derivative with respect to $\vec{m}(r)$ as -$\frac{1}{2} I_{xc}$ gives

$$E_{xc}[n, \vec{m}] = E_{xc}[n, \vec{0}]$$

$$- \tfrac{1}{2} \int\int d^3r d^3r' \vec{m}(r') \cdot \tfrac{1}{2} I_{xc}(r', r) \cdot \vec{m}(r)$$

$$+ O[m^3], \tag{10}$$

$$- \int d^3r \vec{m}(r) \cdot \vec{b}_{xc}(r; n, \vec{m}) =$$

$$\int\int d^3r d^3r' \vec{m}(r) \cdot \frac{1}{2} I_{xc}(r, r') \cdot \vec{m}(r')$$

$$+ O[m^3]. \tag{11}$$

The terms in both XC contributions to the energy that are linear in $\vec{m}$ vanish by symmetry at $\vec{m} = \vec{0}$. Janak [8] has shown how the second functional derivative with respect to $\vec{m}(r)$ arises in the Stoner enhancement of the magnetic susceptibility, and a similar expansion in m(r) has been used here. A point to note is that in large moment systems, expansion around $\vec{m} = \vec{0}$ may not be realistic, and expansion in $\delta\vec{m}$ around the magnetic state should be considered.

If one then imagines variations in magnetic orientations where the change in charge density is negligible, the energy is given (in schematic form) by

$$E_{tot} = E_o + E_{band}[\vec{m}] + \frac{1}{4} \vec{m} \cdot I_{xc} \cdot \vec{m}. \tag{12}$$

The variation in band energy is crucial, which highlights the importance of gaining some understanding of effects of orientation of moments on this term. We return to this point below.

III. GENERAL IMPLEMENTATION

The implementation of continuously varying non-collinear spins has only recently been accomplished, by Nordström and Singh [9] within LSDA. It requires implementing the generalization of the exchange potential given above, and then obtaining self-consistency in the four-density $\rho(r)$,i.e. $n(r)$ and $\vec{m}(r)$, rather than the two densities $n(r)$ and $m(r)$ as in conventional LSDA.

The implementation of continuous $\vec{m}(r)$ is less bothersome than it appears. [9] As introduced by vBH, one uses the LSDA functional (defined only for the magnitude $m(r)$ of $\vec{m}(r)$, by rotating at each point in space into the local frame of spin quantization, evaluating the XC potential $v_{xc}(n(r), m(r))$, and then rotating back to the global coordinate frame. In practice these rotations become trivial. As shown by Sticht *et al.* [10] from the continuity equation for the spin current,

$$\vec{m}(r) \times \vec{b}_{xc}(r) = 0, \tag{13}$$

in other words, the vector XC potential and the magnetization must be locally parallel if they are non-zero. Hence

$$\vec{b}_{xc}(r) = \frac{\delta E_{xc}[n, m]}{\delta m} \hat{m}(r), \tag{14}$$

and the evaluation of $\vec{b}_{xc}$ is no more difficult than in collinear theory.

The full SDF theory contains additional features. Vignale and Rasolt [11] prove that in general one must include an XC contribution to the vector potential to have a consistent gauge invariant theory, which then includes charge and spin current densities. This generalization has not been implemented for any real material. The full DFT theory includes effects due to the variation in the orientation of $\vec{m}$, as well as the dependence on $m(r)$ that

is included in LSDA. In the spirit of the Generalized Gradient Corrections of Perdew and others, [12] one might expect terms involving ∇m, $\nabla \times \vec{m}$, and $\nabla^2 \vec{m}$, as well as cross terms with ∇n. Note that the functional will not involve $\nabla \cdot \vec{m}$, which vanishes. [11] From the present viewpoint, this full potential NCM theory provides a detailed basis to suggest approximate schemes and to constrain them properly.

IV. ATOMIC MOMENT APPROXIMATION

One simplification, which will be called here the Atomic Moment Approximation (AMA), divides space into spherical (atomic) spheres and assigns a spin direction to each atom. This AMA, which is otherwise a self-consistent LSDA calculation, has been used to describe spin-spiral ground states and disordered local moment configurations of several systems. [13–15] The Kohn-Sham equation has the form

$$\{[-\nabla^2 + V_{sph}(r)]\sigma_o + V_{ex}(r)\hat{\zeta}_j \cdot \vec{\sigma}\}\Psi_i(r) = \varepsilon_i \Psi_i(r). \tag{15}$$

where V_{sph} and V_{ex} are the spin-diagonal and spin off-diagonal (exchange) potentials, respectively (recall that V_{sph} contains an XC contribution, while V_{ex} is purely XC), and $\hat{\zeta}_j$ is the direction of the moment at the j-th atomic site. The configuration $\{\vec{\zeta}_j\}$ can be varied to minimize the energy. This description of NCM has been used successfully during the past decade. [10,13–16]

Liechtenstein *et al.* [17] have used this method to study the energy cost of spin reorientations. They show that the change in band energy when one spin ($\vec{m}_o$) is rotated, is of the Heisenberg-like form

$$\delta E = \sum_j J_{o,j} \vec{m}_o \cdot \vec{m}_j \tag{16}$$

for small rotations. For larger relative orientations the angular dependence will vary from this simple form. For several non-collinear spins, the variation in band energy becomes more complicated and will depend on relative orientations of three, four, ... atomic moments as well as simple pairwise terms.

V. TIGHT BINDING MODELS

The AMA form of the Kohn-Sham Eq. (15) in the previous section directly suggests the type of tight binding (TB) model that has been used by You and Heine [18] to study the behavior of ferromagnetic metals near the Curie temperature. Expanding the Kohn-Sham equation in an atomic orbital basis (site j, orbital L=n, l, m), the general TB Hamiltonian matrix elements are

$$h_{jL,j'L'} = t_{jL,j'L'}\sigma_o - \frac{1}{2}\vec{\Delta}_{jL,j'L'} \cdot \vec{\sigma}. \tag{17}$$

Here $\vec{\Delta}$ is the matrix element of $V_{ex}\vec{\zeta}$ in Eq. (15) and has the obvious interpretation of the "exchange splitting" of bands (splitting between spin $\uparrow$ and spin $\downarrow$ in the local frame).

It is conventional to presume that the exchange splitting is proportional to the magnetic moment: $\Delta = Im$. In the general case interatomic coupling can be included so the Hamiltonian matrix elements become

$$h_{jL,j'L'} = t_{jL,j'L'}\sigma_o - \frac{1}{2}\vec{m}_{jL} \cdot I_{jL,j'L'} \cdot \vec{\sigma}. \tag{18}$$

Here the Stoner exchange parameter I is a 3×3 tensor in Cartesian space. The on-site and hopping amplitudes are included in t. The corresponding energy is [18,19]

$$E_{tot} = \sum_i^{occ} \varepsilon_i[\{\vec{m}_{jL}\}] + \frac{1}{4}\sum_{jL,j'L'} \vec{m}_{jL} \cdot I_{jL,j'L'} \cdot \vec{m}_{j'L'}. \tag{19}$$

The second term corrects for the double-counting of interactions in the eigenvalue sum. This form of energy expression is considerably more simplistic than the LSDA expression in Eq. (9). Note, however, that it is exactly the same form as Eq. (12), which results if charge fluctuations are negligible. (Charge fluctuations can be modelled with a Hubbard-like term if desired.)

This form of tight binding one-electron equation has spin-independent hopping, and all coupling between spins is from an "exchange" splitting. Hopping amplitudes depending on the relative spin directions of the two sites have been suggested, [18,19] but it is more difficult to implement and must be formulated so that spin-dependent hopping vanishes as the magnitude of the spin vanishes.

The specification of I presumably will be fixed by comparison with LSDA calculations. Lorenz *et al.* [16] report that, given their method of identifying I, its value is essentially constant at a value of 0.95 eV/μ_B for a variety of $3d$ and $4d$ metals showing spontaneous or induced magnetism. On the other hand, Singh's calculation [20] for the itinerant $4d$ ferromagnet $SrRuO_3$ gives the value of 0.4 eV/μ_B for that compound (where $m = 1.6\mu_B$/cell). For the ferromagnetic phase of an ordered supercell of $La_{2/3}Ca_{1/3}MnO_3$, Pickett and Singh [21] found a value of 0.70-0.75 eV/μ_B for the Mn t_{2g} states. The e_g value might differ, but within LSDA the difference should be small because non-sphericity around atoms is relatively minor. These results indicate that I is an atom-dependent, and probably material-dependent, property. In fact, both total ferromagnetic moments and band splittings are a property of the crystal as a whole, and an accurate treatment may require accounting for this fact by assigning a (perhaps small) value of I to intervening atoms such as oxygen that have been ignored up until now.

The simplicity of the tight binding language, and especially its explicit separation into orbital contributions, allows an interesting possibility: the contributions to the moment from different orbitals on the same atom may be non-collinear. Within the LSDA method, all orbitals experience a local exchange potential V_{ex} which is mildly non-spherical at most (applications to NCM so far, except Nordström and Singh [9], have assumed spherical potentials). This weak non-sphericity is felt to be one defect of the local density approximation that renders it unable to describe the antiferromagnetism of the layered cuprate insulators. [22]

Some simplifications render certain phenomena transparent. Assuming, as envisioned in the early theories of Korenman, Murray, and Prange [23] and Hubbard [24] that

(i) I is site diagonal,

(ii) I is constant within the shell being treated (e.g. same for e_g and t_{2g}), and

(iii) the moment is unchanged in magnitude as it reorients,

the change in energy due to the rotation of a moment can be obtained. The $\frac{1}{4}Im^2$ term is constant if the moment is unchanged, hence variations in energy, reflecting the intreatomic coupling of moments, come entirely from the band energy. This fact emphasizes that the variation of the band energy with spin orientation is important to understand. Kübler and coworkers [10,15] have noted in some detail the changes in the band structure that result from spiral magnetic structures.

VI. POSSIBLE RELEVANCE TO MANGANITES

The manganite perovskites seem to be a propitious system for intraatomic non-collinear moments to arise. It seems clear, on phenomenological grounds and according to calculations [21,25,26] so far, that in the $La_{1-x}Ca_xMnO_3$ system (and similar ones), the majority t_{2g} states are completely filled. This is often treated, viz. the "double exchange" picture, as a core subsystem with a full moment of 3 μ_B. If in Eq. (18) it is supposed that $\vec{m}$ represents (only) those t_{2g} spins and that they can be treated classically (and denoted by S_j), the result is the "double exchange" Hamiltonian, [27,28] with matrix elements

$$h_{jL,j'L'} = t_{jL,j'L'}\sigma_o - \frac{1}{2}I\vec{S}_j \cdot \vec{\sigma}\ \delta_{jj'}\delta_{LL'}. \qquad (20)$$

Sec. II provides a way to calculate (or at least estimate) the "Hund's rule" coupling constant $\frac{1}{2}I$.

In $CaMnO_3$ there are no other (valence) electrons, and the material is an antiferromagnetic insulator. The CMR regime is closer to the $LaMnO_3$ end, where there is one more (e_g) electron, which is a potential itinerant carrier. Electronic structure calculations [21] indicate that the structural distortion, which is mostly a Jahn-Teller effect, is instrumental in creating the semiconducting gap of $LaMnO_3$. Interestingly, the calculated moment of 3.4 μ_B is noticably lower than the Hund's rule value of 4 μ_B. This can be accounted for within LSDA by hybridization of the e_g states with the neighboring O p states, which reduces the participation of the e_g states in the occupied bands and thereby reduces the moment. However, intra-atomic non-collinearity is also a possibility: the e_g contribution to the moment might not be parallel to the t_{2g} moment. The lattice distortion of $LaMnO_3$, with its low Mn site symmetry, strongly affects the electronic and magnetic structure and provides a mechanism for breaking the cubic symmetry that otherwise would oppose intra-atomic noncollinearity. The calculation by Nordström and Singh [9] of intraatomic NCM in ferromagnetic Pu arises from a different mechanism (spin-orbit coupling).

An alternative to LSDA has been proposed [25,26] as being necessary to produce a reasonable description of the properties of $XMnO_3$ compounds. This alternative is the LSDA+U approach, [29] in which a Hubbard-like term U is added to the LSDA energy expression. The effect of this correction is to lower the eigenvalues of occupied Mn d derived states, raise the eigenvalues of unoccupied d derived states (by -$U/2$ and +$U/2$ respectively, for pure d states), and encourage integral occupation of the Mn d states. From the current viewpoint, the variant of LSDA+U introduced by Solovyev, Hamada, and Terakura [25] is suggestive. They introduce two Coulomb repulsion constants, $U_{t_{2g}} \gg U_{e_g}$, which differ (they argue) because the more localized t_{2g} electrons are screened by the less localized e_g electrons, but not *vice versa*. This distinction, if correct, indicates a large difference in the dynamical behavior of t_{2g} and e_g states, and makes intraatomic non-collinear contributions to the moment plausible.

However, there are features already within the LSDA calculations on manganites [21] that could encourage intraatomic NCM. The exchange splitting of the Mn d states leads to a strong spin-dependence of the hybridization with O p, since the majority d bands are lower in energy and overlap the O p bands. In addition, the octahedral field splits the t_{2g} and e_g states, so moment reorientations will lead to different band structure effects, and thus different energy changes originating from these two subbands. A tight-binding approach is ideal for obtaining an understanding of such tendencies.

SUMMARY

In this paper the relationship between the description of non-collinear magnetic configurations from *ab initio* SDFT to a tight binding model has been outlined. The tight binding model allows the exploration of possibilities, especially intra-atomic non-collinearites, that are more difficult to explore (or might not arise) within a local spin density treatment. It is suggested that the per-

ovskite manganites provide a promising system to look for such phenomena. Such studies are in progress.

Experience with tight binding models of NCM will also be useful for implementation the theory of spin dynamics by Antropov *et al.* [30] The description of electronic states and transport in a system of disordered spins will in any case be required to understand the new phenomenon of colossal magnetoresistance (see [21] for references).

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