Calculation of Magnetic Exchange Interactions in Mott-Hubbard Systems

Xiangang Wan,[1,2] Quan Yin,[1] and Sergej Y. Savrasov[1]
[1]*Department of Physics, University of California, Davis, One Shields Avenue, Davis, California 95616, USA*
[2]*National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China*

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An efficient method of computing magnetic exchange interactions in systems with strong correlations is introduced. It is based on a magnetic force theorem that evaluates linear response due to rotations of magnetic moments and uses a generalized spectral density functional framework allowing us to explore several approximations ranging from local density functional to exact diagonalization based dynamical mean field theory. Applications to spin waves and magnetic transition temperatures of 3*d* metal monoxides as well as high-T_c superconductors are in good agreement with experiment.

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Obtaining a quantitative theory of magnetic materials spanning from itinerant to atomic limit, above and below their temperatures of magnetic ordering has been a theoretical challenge for many years [1]. By now itinerant magnets are well described by local spin density approximation (LSDA) of density functional theory (DFT) [2], where methodologies based on spin-spiral frozen-magnon technique [3], the use of magnetic force theorem [4] via an evaluation of linear response due to rotations of magnetic moments as well as spin dynamics calculations [5] have allowed access to a great variety of magnetic properties [6–10].

However, there is a large class of systems where calculations of exchange interactions is still a challenging theoretical problem. These are strongly correlated systems such as high-T_c superconductors or atomic magnets where the on-site Coulomb interaction U is comparable to or larger than the bandwidth. In cases where magnetic ordering and/or lattice distortions result in a nondegenerate equilibrium state, techniques such as LDA + U [11] or *GW* [12] have been applied to describe spectroscopy, magnetic moments, and even spin-wave spectra of systems such as MnO [13]. However, in general, excitation spectra of strongly correlated systems are not representable by single Slater determinants and show such features as atomic multiplets [14], Zhang-Rice singlets [15], Kondo resonances, etc. In Mott-Hubbard insulators the energy gap is much larger than the magnetic ordering temperature above which a local moment regime takes place, i.e., the system becomes paramagnetic but remains insulating. These properties cannot be accessed either by static mean field approaches such as LSDA or LDA + U or by perturbation theory over the Coulomb interaction such as the *GW* approximation. While versions of static [16] as well as dynamic [17] coherent potential approximations have been introduced in the past to access disordered local moment regime, developing a generalized framework having a capability to compute exchange interactions in both itinerant and atomic limits as well as in many intermediated cases would open new opportunities in computational design of new magnetic materials.

In the present Letter we explore a spectral density functional framework [18] to deal with this problem. It is based on a combination of LDA and dynamical mean field theory [18], a recently developed electronic structure method which has helped to solve several long-standing problems [19–22]. It describes correctly both itinerant and atomic limits and accesses ordered and disordered moment regimes on equal footing. This is achieved by treating correlated electrons with frequency dependent self-energies extracted from solving corresponding Anderson impurity problem (AIM) subjected to a self-consistency condition.

In order to deduce exchange constants for general wave vector $\mathbf{q}$ we use a linear response based magnetic force theorem [4,23] and explore several levels of approximations: standard LSDA, as well as approximations for solving the impurity problem: Hartree Fock solution (so-called LDA + U [11]), atomic exact diagonalization [24] known as Hubbard I and newly implemented cluster exact diagonalization (CED) which takes into account the effect of hybridization locally. These methods are used to calculate self-consistently local Green functions, self-energies, and static linear response functions of several Mott-Hubbard insulators. We find consistent improvement of the accuracy delivered by each subsequent method as compared to experiment for both the deduced spin-wave spectra as well as for magnetic ordering temperatures which are evaluated using Monte Carlo simulations of the mapped Heisenberg Hamiltonians.

Our implementation is based on a most recent many-body band structure algorithm [25] which allows us to avoid the computationally expensive solution of the Dyson equation $[\omega - H_0(\mathbf{k}) - \Sigma(\omega)]G(\mathbf{k},\omega) = 1$ for the electronic Green function $G(\mathbf{k},\omega)$ at a large grid of frequencies ω. This is achieved by assuming a pole expansion for the self-energy $\Sigma(\omega) = \Sigma(\infty) + \sum_i V_i^+(\omega - P_i)^{-1}V_i$ so that the entire problem is reduced to a matrix equation with an energy-independent Hamiltonian

$$\begin{pmatrix} \omega - H_0(\mathbf{k}) - \Sigma(\infty) & V^+ \\ V & P \end{pmatrix} \mathcal{G}(\mathbf{k}, \omega) = I, \qquad (1)$$

where I is the unit matrix and the auxiliary Green function $\mathcal{G}_{\alpha\beta}(\mathbf{k}, \omega)$ is a matrix in the space of poles, while the physical Green function $G(\mathbf{k}, \omega)$ corresponds to the first element of $\mathcal{G}(\mathbf{k}, \omega)$. Weights V_i^+, V_i and poles P_i can be viewed as matrices that provide a best fit to real $\Sigma(\omega)$.

It is remarkable that the present procedure allows us to use an expression for the interatomic exchange constants similar to a linear response formula derived within DFT [4]. Consider second-order change in the total energy related to the rotations of the magnetic moments appeared at sites $R + \tau$ and $R' + \tau'$ of the lattice (here R are the lattice translations and τ are the atoms in the basis). The local magnetic field $\mathbf{B}_\tau$ at every atomic site τ is approximately described by the values of the self-energy taken at $\omega = \infty$ [for example, $B_\tau^z = \Sigma_\tau^{\uparrow\uparrow}(\infty) - \Sigma_\tau^{\downarrow\downarrow}(\infty)$]. Thus, according to the magnetic force theorem which assumes a rigid rotation of atomic spin, a linear response theory expresses the interatomic exchange constants in the form

$$J^{\alpha\beta}_{\tau R \tau' R'} = \sum_{\mathbf{q}} \sum_{\mathbf{k} j j'} \frac{f_{\mathbf{k}j} - f_{\mathbf{k}+\mathbf{q}j'}}{\epsilon_{\mathbf{k}j} - \epsilon_{\mathbf{k}+\mathbf{q}j'}} \langle \psi_{\mathbf{k}j} | [\sigma \times \mathbf{B}_\tau]_\alpha | \psi_{\mathbf{k}+\mathbf{q}j'} \rangle \times \langle \psi_{\mathbf{k}+\mathbf{q}j'} | [\sigma \times \mathbf{B}_{\tau'}]_\beta | \psi_{\mathbf{k}j} \rangle e^{i\mathbf{q}(\mathbf{R}-\mathbf{R}')} \qquad (2)$$

Here, σ is the Pauli matrix while the one-electron energy bands $\epsilon_{\mathbf{k}j}$ and quasiparticle wave functions $\psi_{\mathbf{k}j}$ appear as the solutions of Eq. (1), when using a quasiparticle representation for the Green function $\mathcal{G}(\mathbf{k}, \omega)$. While viewed noninteracting-like, this formula indeed contains major information about many-body features in the excitation spectrum. In particular, multiplet transitions as well as delocalized parts of the electronic states are represented by separate "energy bands" $\epsilon_{\mathbf{k}j}$ including its $\mathbf{k}$ dispersion which is borrowed from the noninteracting Hamiltonian $H_0(\mathbf{k})$. Thus, genuine redistribution of spectral weight driven by the many-body interactions is correctly captured by the present method which will give an important feedback on the calculated exchange interactions.

There are two essential approximations which are made to make the theory computationally tractable. As has been discussed recently [23], the magnetic force theorem can be introduced for a Lattinger-Ward functional which would involve calculations of full frequency dependent integrals between the self-energies and the Green functions. The present method uses (i) the Hartree Fock values for the local magnetic fields, and (ii) rational fit to the self-energy, which allows us to perform all frequency summations analytically while retaining all major many-body multiplet features of the spectrum in the convenient linear response expression (2).

To illustrate the method we consider several transition-metal oxides MnO, FeO, CoO, NiO as well as parent high-T_c compound $CaCuO_2$. It is well known that LSDA significantly underestimates the band gap of MnO and NiO and fails to predict insulating character for FeO, CoO, and $CaCuO_2$. The LDA + U corrects for these failures but needs to assume a symmetry breaking for FeO and CoO. It is clear that being a Hartree Fock approximation the LDA + U would converge to a single Slater determinant ground state, whereas in many cases either degeneracy of it or proximity of low-lying excited states needs to be included in statistical averagings for the one-electron Green functions. All static mean field theories would necessarily fail to describe paramagnetic insulating behavior while the LDA + DMFT should be valid for both ordered and local moment regimes. Here, we consider the d electrons of transition-metal elements as strongly correlated thus requiring dynamical treatment. The s and p electrons are assumed to be weakly correlated and well described by the LDA Hamiltonian $H_{\mathrm{LDA}}(\mathbf{k})$ including the full potential terms of the linear muffin-tin orbital (LMTO) method [26]. To consider relativistic effects, the spin-orbit coupling is taken into account in all cases. To obtain the one-particle potential $H_0(\mathbf{k}) = H_{\mathrm{LDA}}(\mathbf{k}) - V_{\mathrm{dc}}$ entering (1) we subtract the double counting term V_{dc} as prescribed by Ref. [11]. To avoid overcounting, we also neglect local spin density terms in $H_{\mathrm{LDA}}(\mathbf{k})$ while performing calculations using the LDA + U and LDA + DMFT method. We use the experimental lattice structures for all materials.

For transition-metal mono-oxides the clusters needed for our newly implemented CED solver are chosen to include d orbitals of transition-metal ions hybridized with oxygen p orbitals in the octahedral environment. It has been known for many years that such treatment provides a good description of photoemission spectra in these materials [27,28]. For $CaCuO_2$ this is reduced to a Cu d orbital surrounded by an oxygen square. This allows us to capture both the effect of atomic multiplets and the Zhang-Rice singlet [15] being the lowest lying excitation of undoped high-T_c compunds. Remarkably that similar effect is also present in low-energy excitations of all transition-metal oxides: the coupling of an oxygen hole to a local moment of transition-metal ion would lead to an appearance of low-spin state generalizing the Zhang-Rice singlet physics. During iterations towards self-consistency, the Anderson impurity problem is exact diagonalized each time with the positions of 3d levels, the d-p hybridization matrix elements as well as the O2p levels extracted from the $H_{\mathrm{LDA}}(\mathbf{k})$. The latter being a density functional is allowed to recompute and readjust the parameters of AIM. The values of the Coulomb interaction U as well as the Hund's exchange J were obtained earlier by the constrained LDA calculation [11]. The AIM gives access to the frequency dependent self-energies of d electrons which are then rationally approximated by assuming three-pole fit for the self-energy.

Our calculated ground state properties including magnetic moments and energy gaps are found to be in good agreement with experiment both below and above magnetic ordering temperatures. Below T_N this result is in accord with the previous LDA + U studies [11] while our numerical results indeed show that dynamical correlations only marginally influence values of magnetic moments in cases such as MnO, NiO, and $\mathrm{CaCuO_2}$. On the other hand, for CoO and FeO, their t_{2g} bands are only partially occupied and the ground states become degenerate. Therefore small value of spin-orbital coupling has a large effect on an appeared orbital moments which are evaluated to be $0.36\mu_B$ and $1.02\mu_B$ in our cluster exact diagonalized LDA + DMFT calculations for FeO and CoO, respectively. The LDA + U is also capable of recovering the insulating character here but by assuming symmetry lowered orbitally ordered solution.

Based on the self-consistently obtained local Green functions and self-energies we evaluate the interatomic exchange constants as integral over the **q** space using (6,6,6) reciprocal lattice grid and use Monte Carlo simulations [7] of the correspondingly mapped Heisenberg Hamiltonians to find Néel temperature (T_N), and show the results in Table I. Because of underestimation of energy gap, LSDA significantly overestimates T_N as seen in Table I. (Because for FeO, CoO, and $\mathrm{CaCuO_2}$, LSDA converges to a completely wrong metallic state, we omit quoting those predictions.) The LDA + U method fixes the gap problem and this makes T_N smaller but still much larger than the experimental ones. This is in agreement with the previously reported results for MnO [13]. Hubbard I approximation further reduces T_N while our best results are seen to be obtained by allowing d electrons to fluctuate between the bath and impurity as prescribed by our CED calculation. This effect is missing in the Hubbard I solver and seriously affects the electronic structure of studied materials as, for example, it redistributes the d-electron spectral weight to low energies and leads to the Zhang-Rice singlet or its generalized low-spin states. In an extreme situation, where the hybridization is much larger than the local Coulomb U, the magnetization would eventually disappear due to strong fluctuation in the number of d electrons at the impurity site. So it is easy to understand why the CED method gives smaller magnetic transition temperatures that are now closer to the experiments.

TABLE I. Comparison of calculations using various approximations and experimental magnetic transition temperatures (in K) in selected Mott-Hubbard systems. Hubbard I and cluster ED denote the results of LDA + DMFT calculations using Hubbard I and cluster exact diagonalization impurity solver.

	LSDA	LDA + U	Hubbard I	Cluster ED	Experiment
MnO	423	240	180	172	122[a]
FeO	⋯	344	297	211	198[a]
CoO	⋯	407	356	300	291[a]
NiO	965	603	542	519	523[a]
$\mathrm{CaCuO_2}$	⋯	765	698	602	537[b]

[a] Reference [29]
[b] Reference [30]

It is interesting to discuss the physical reasons why T_N decreases when going from NiO to MnO. This trend is seen in all our calculations with correlations included as seen from Table I. These Mott-Hubbard insulators show almost atomic values of magnetic moments $M = 10 - n$ corresponding to d^n configurations, which would under assumption of the same antiferromagnetic exchange constant J_{AF} meaning that the ordering temperatures should increase with increasing the moments. However, J_{AF} will decrease significantly due to the change in the lattice parameter. Also, during the evaluation of T_N we need to account for the quantum averaging for atomic spins directions which gives a prefactor $S(S+1)/S^2$ deviating from 1 for small S. To sort out these effects we first performed a sample calculation for NiO with the expanded lattice constant of MnO. The T_N for NiO has dropped from 519 to 327 K in this case. Second, because $S_{\mathrm{Ni}} = 1$ while $S_{\mathrm{Mn}} = 5/2$, the prefactor $S(S+1)/S^2$ would account for a 40% difference so that $327 \times 1.4/2 = 229$ K is the Néel temperature that we need to compare with our predicted $T_N = 172$ K for MnO. The residual discrepancy can be attributed to different exchange splittings which also affects J_{AF} as pointed out earlier [31].

We now discuss our calculated spin-wave dispersions along major symmetry directions in the Brillouin Zone (BZ). We first illustrate the results of NiO in Fig. 1. In accord with our predictions for the T_N, the spin waves are seriously overestimated by the LSDA but get closer to the experiment once correlations are taken into account. The best accuracy is achieved when using the CED as the impurity solver. Second, we discuss our calculated spin-wave spectra for other transition-metal oxides. Table II shows our calculated spin-wave dispersion coefficients

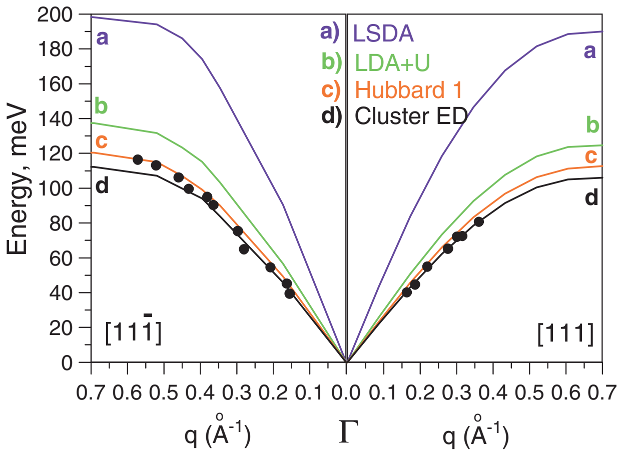

FIG. 1 (color online). Theoretical spin-wave dispersions for NiO (solid lines) calculated by LSDA, LDA + U, Hubbard I and cluster exact diagonalization (CED) diagonalization impurity solvers in comparison with the experiment (circles) [35].

TABLE II. Calculated and experimental spin-wave dispersion coefficient (in meV Å) along (100) direction.

	LSDA	LDA + U	Hubbard I	Cluster ED	Experiment
MnO	178.0	103.3	86.3	81.5	49.5[a]
FeO	···	94.9	74.5	59.1	51.0[b]
CoO	···	152.8	133.5	118.3	112.0[c]

[a] Ref. [32]
[b] Ref. [33]
[c] Ref. [34]

for FeO, CoO, and MnO, which we extracted by fitting the spin-wave energy to linear form $E(q) = aq$. This is valid for antiferromagnets as long as we do not approach very small q's where the Goldstone theorem is violated due to spin-orbit effect or unless we are near the BZ boundary. Again the trend to reduce the disagreement with experiments is seen when doing more and more accurate many-body calculations.

In summary, we presented a linear response method to calculate the exchange interaction parameters of strongly correlated systems valid as long as mapping of total energy functional to rigid spin based Heisenberg Hamiltonians makes sense. By using the rational interpolation for the self-energy, our approach is very efficient, and this has allowed us to describe quantitatively spin-wave dispersions and magnetic transition temperatures of several realistic Mott-Hubbard insulators with many atoms per unit cell. Applications to metallic systems are more challenging as they may need much larger clusters to account for such subtle effects as, e.g., the Kondo screening, and will be carried out in future work.

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