Calculations of Magnetic Exchange Interactions in Mott–Hubbard Systems

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An efficient method to compute magnetic exchange interactions in systems with strong correlations is introduced. It is based on a magnetic force theorem which evaluates linear response due to rotations of magnetic moments and uses a novel spectral density functional framework combining our exact diagonalization based dynamical mean field and local density functional theories. Applications to spin waves and magnetic transition temperatures of 3d metal mono–oxides as well as high–$T_c$ superconductors are in 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\textsuperscript{1}. By now itinerant magnets are well described by local spin density approximation (LSDA) of density functional theory (DFT)\textsuperscript{2}, where methodologies based on spin–spiral frozen–magnon technique\textsuperscript{3}, the use of magnetic force theorem\textsuperscript{4} via an evaluation of linear response due to rotations of magnetic moments as well as spin dynamics calculations\textsuperscript{5} have allowed to access a great variety of physical properties such as spin wave spectra, magnetic ordering temperatures, interatomic exchange constants, dynamical susceptibilities, etc\textsuperscript{6,7,8,9,10}.

However, there is large class of systems where calculations of exchange interactions is still a challenging theoretical problem. These are strongly correlated systems like high–$T_c$ superconductors or atomic magnets where the on–site Coulomb interaction $U$ is comparable or larger than the bandwidth. In cases where magnetic ordering and/or lattice distortions result in a non–degenerate equilibrium state, techniques such as LDA+U\textsuperscript{11} or GW\textsuperscript{12} have been applied to describe spectroscopy, magnetic moments, and even spin wave spectra of systems such as MnO\textsuperscript{13}. However, in general, excitation spectra of strongly correlated systems are not representable by single Slater determinants and show such features as atomic multiplets\textsuperscript{14}, Zhang–Rice singlets\textsuperscript{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 GW. While versions of static\textsuperscript{16} as well as dynamic\textsuperscript{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 work we develop a novel approach which is capable to deal with this problem. Our method is based on LDA+Dynamical Mean Field Theory (DMFT)\textsuperscript{18}, a recently developed electronic structure method describing correctly both itinerant and atomic limits and accessing ordered and disordered moment regimes on equal footing. This is achieved by treating correlated electrons with frequency dependent self–energies deduced from solving corresponding Anderson impurity problem (AIM) subjected to a self–consistency condition. Conveniently formulated using a spectral density functional\textsuperscript{19}, this LDA+DMFT method incorporates realistic band structure effects and has already helped to solve several long–standing problems, e.g. temperature–dependent magnetism of Fe and Ni\textsuperscript{20}, volume collapse in Ce\textsuperscript{21}, and Pu\textsuperscript{21}, as well as electronic structure of doped Mott insulators\textsuperscript{22}.

In order to deduce exchange constants for general wave vector $q$ we utilize a linear response based magnetic force theorem\textsuperscript{4,23} and demonstrate the accuracy of our method on several Mott–Hubbard insulators including late transition metal oxides as well as parent materials of high–$T_c$ superconductors. To solve the impurity problem which is the nucleus of the dynamical mean field algorithm we apply a newly implemented cluster exact diagonalization method and calculate self–consistently local Green functions, self–energies and static linear response functions. Both the deduced spin wave spectra as well as magnetic ordering temperatures evaluated using a Monte Carlo simulations of the mapped Heisenberg Hamiltonians are found in good agreement with experiment.

Our implementation is based on a most recent many–body band structure algorithm\textsuperscript{24} which allows us to avoid computationally expensive solution of the Dyson equation $[\omega – H_0(k) – \Sigma(\omega)]G(k,\omega) = 1$ for the electronic Green function $G(k,\omega)$ at a large grid of frequencies $\omega$. 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
\[
\left(\omega - H_0(k) - \Sigma(\infty) \frac{V^+}{V} P\right) G(k, \omega) = I
\]
where \( I \) is the unit matrix and an auxiliary Green function \( G_{\alpha\beta}(k, \omega) \) is a matrix in the space of poles, while the physical Green function \( G(k, \omega) \) corresponds to the first element of \( G(k, \omega) \). In Eq. (1), weights \( V_i^+, V_i \) and poles \( P_i \) can be viewed as matrices which 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
3. 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 \( \tau \) are the atoms in the basis). The local magnetic field \( B_\tau \) at every atomic site \( \tau \) 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

\[
J_{\tau R \tau' R'}^{\alpha\beta} = \sum_q \sum_{kj} f_{kj} - f_{k+qj} \langle \psi_k \mid \sigma \times B_\tau \rangle_\alpha \langle \psi_{k+q} \mid \sigma \times B_{\tau'} \rangle_\beta \epsilon_{kj} \epsilon_{k+qj}
\]

Here, \( \sigma \) is the Pauli matrix while the one–electron energy bands \( \epsilon_{kj} \) and quasiparticle wave functions \( \psi_k \) appear as the solutions of the equation \( 2 \). when using quasiparticle representation for the Green function \( G(k, \omega) \) in the form.

\[
G(k, \omega) = \sum_j \frac{\psi_{kj}^+ \psi_{kj}}{\omega - \epsilon_{kj}}
\]

While viewed non–interacting 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” \( \epsilon_{kj} \) including its \( k \) dispersion which is borrowed from the non–interacting Hamiltonian \( H_0(k) \). 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
22, the magnetic force theorem can be introduced for a Luttinger–Ward functional which would involve calculations of full frequency dependent integrals between the self–energies and the Green functions. The present method utilizes (i) the Hartree Fock values for the local magnetic fields, and (ii) rational fit, i.e. Eq. (1), to the self–energy, which allows us to perform all frequency sums analytically while retaining all major many–body multiplet features of the spectrum in the convenient linear response expression
3.

To illustrate the method we consider several transition–metal oxides MnO, FeO, CoO, NiO as well as parent high–T\(_c\) compound CaCuO\(_2\). All these materials are antiferromagnetic insulators with an energy gap of a few eV and Neel temperatures \( T_N \) of a few hundred K. Staying below \( T_N \) 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, while in many cases either degeneracy of the latter 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. On the other hand, the LDA+DMFT is a method valid both in ordered and local moment regimes. Here, we consider the \( d \) electrons of transition metal elements as strongly correlated thus requiring dynamical treatment using DMFT. The \( s \) and \( p \) electrons are assumed to be weakly correlated and well described by the LDA Hamiltonian \( H_{LDA}(k) \) including the full potential terms of the linear muffin–tin orbital (LMTO) method
25. To consider relativistic effects, the spin–orbit coupling is taken into account in all cases. To obtain the one–particle potential \( H_0(k) = H_{LDA}(k) - V_{dc} \) entering
2 we subtract the double counting term \( V_{dc} \) as pre-
scribed by Ref. [11]. We use the experimental lattice structure for all materials.

In order to solve the Anderson impurity problem we implement cluster exact diagonalization (ED) method. For transition metal mono–oxides the clusters 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 cluster exact diagonalizations provide a good description of photoemission spectra in these materials [26, 27]. For the 2D system, such as CaCuO_{2} this is reduced to a Cu d orbital surrounded by an oxygen square. This treatment allows us to capture both an effect of atomic multiplets and of the Zhang–Rice singlet [15] being the lowest lying singlet |15\rangle. 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 cluster ED method gives smaller magnetic transition temperatures which are now closer to the experiment.

It is interesting to discuss the physical reasons why T_N decreases when going from NiO to MnO. 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} mean 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 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 519K to 327K in this case. Second, since S_{Ni} = 1 while S_{Mn} = 5/2, the prefactor S(S + 1)/S^2 would account for a 40% difference so that 327×1.4/2=229K is the Neel temperature that we need to compare with our predicted T_N=172K 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. We illustrate this calculation on a case of NiO for which the magnon spectra have been measured long time ago [32]. Fig. 1 shows the results of our simulations using several levels of approximations. In accord with our pre-
TABLE I: Comparison between calculated 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 (in K) in selected Mott–Hubbard systems. Hubbard I approximations and experimental magnetic transition temperatures of several realistic Mott–Hubbard 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 the future work.

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