Exchange integrals of $Sr_2CuO_2Cl_2$ and $Ba_2Cu_3O_4Cl_2$ from LDA+U calculations

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The LDA+U method is used to calculate exchange integrals in strongly correlated cuprate compounds. We distinguish two approaches. The first one compares directly the total energies of different collinear spin arrangements with the corresponding ones of Heisenberg-like models. The second approach maps the energy of noncollinear spin-spiral states to the mean-field solutions of the effective spin Hamiltonian. Both approaches are applied to $Sr_2CuO_2Cl_2$ which can be described with good accuracy by a two-dimensional Heisenberg model with only nearest-neighbor exchange. It is shown that the consideration of quantum fluctuations improves the resulting exchange integrals. The variation of the results with U and the difference between the two approaches are small. Both methods have also been applied to $Ba_2Cu_3O_4Cl_2$ which has two coupled antiferromagnetic spin systems. The coupling between the two subsystems has been shown to be larger than previously estimated.

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I. INTRODUCTION

Soon after the discovery of high-T_c superconductors (HTSC's) it became clear that the understanding of the phenomena is tightly related to peculiarities of the electronic structure of the parent compounds: undoped cuprates. It is well established that the magnetic excitations in these compounds are well described by the two-dimensional (2D) Heisenberg model. For the most studied material La_2CuO_4, the exchange integral entering the model was determined experimentally by fitting data on the spin wave velocity found by inelastic neutron scattering[1] $\hbar v = 850$ meV Å to that one of quantum Monte Carlo calculations[2] $\hbar v = 1.68Ja$ ($a = 3.79$ Å) to be $J = 133$ meV. Alternatively, J was also obtained from the spin correlation length[3] ($J = 125$ meV) or by analyzing Raman scattering data ($J = 128$ meV).[4] The calculation of exchange integrals in a ''first-principle'' way, however, is a general and long standing problem. It appears not only for undoped cuprates but also for other transition metal compounds. The reason for the problem consists in the insufficiency of the local density approximation (LDA) within density functional theory (DFT). The LDA is not able to describe the magnetic state of such highly correlated systems properly.[5]

One possible way to calculate exchange integrals in cuprates uses the Emery model whose parameters can be determined by a constrained density functional calculation.[6] In a second step the Emery model is mapped onto the Heisenberg or the extended t-t'-t''-J model[7,8] which gives J values in good agreement with the experimental ones. But such a procedure involves many steps with many possible error sources. Alternative possibilities to determine exchange integrals in a ''first-principle'' way are quantum chemical methods on small clusters[9] yielding antiferromagnetic J values between 100 and 140 meV for typical 2D cuprates.

Another possibility to calculate more directly the spin excitation spectrum from band structure methods is based on the concept of adiabatic magnetic moments.[10,11] The approach consists in the mapping of constrained DFT total energy calculations of noncollinear magnetic structures on the mean-field solutions of the effective spin Hamiltonian. Originally, the approach was constructed for itinerant systems[10] for which DFT calculations can be carried out with good accuracy within the local density approximation. Later on, it was extended to rare earth metals.[11] In the case of such materials the hybridization of the localized $4f$ electrons is negligible and their behavior can be described in the atomic limit, e.g., in the Russel-Saunders scheme. But for an application to undoped cuprates the correlated electrons are also quite strongly hybridized and cannot be ignored in the cacu-lation. One of the most developed ways to cure the situation is the so-called ''LDA+U'' approach which allows one to include the most important on-site correlations in a Hartree-Fock-like scheme.[12,13] This approach was successfully applied to describe various electronic properties of cuprates (see, e.g., Ref. 14).

Here, we propose several ways to use the LDA+U approach for the calculation of exchange constants and apply it to some undoped cuprate compounds. We are going to present a critical check of the method and to outline its details whereas some results for the case of vanadates are already known (see, e.g., Refs. 15,16). Our first application

concerns $Sr_2CuO_2Cl_2$ which is a good model substance for the 2D CuO_2 plane.[17,18] We will distinguish two variants of the method. The first one compares directly the energies of different (collinear) magnetic states with the corresponding magnetic states of an appropriate Heisenberg-type Hamiltonian. The other variant is an extension of the method outlined in Refs. 10,11 to strongly correlated systems. It is based on total energy calculations of noncollinear spiral magnetic structures. We will show that both variants lead to consistent results.

In addition to the parent compounds of HTSC's, there exist many other low-dimensional cuprates[19] which are interesting by themselves due to their unconventional magnetic properties. As an example we will investigate here $Ba_2Cu_3O_4Cl_2$ which has a Cu_3O_4 plane with two antiferromagnetic subsystems and two Néel temperatures (330 and 31 K, respectively).[20–24] The coupling between the two subsystems is crucial to understand the magnetism in that compound. So, our method can be used to check the parameters derived previously from Rayleigh-Schrödinger perturbation theory[25] or the cell-perturbation method.[26] Especially, we will show that the exchange within the B-subsystem had been overestimated and the coupling between both subsystems was underestimated in the previous estimates.

II. METHOD

The most direct way to determine exchange constants compares directly the energies of different spin arrangements in the DFT calculation with the corresponding energies in a Heisenberg-type model

$$H=\frac{1}{2}\sum_{i,j} J_{ij}\vec{S}_i\vec{S}_j. \tag{1}$$

The number of necessary magnetic states is determined by the number of exchange constants in Eq. (1). In the simplest case of only nearest-neighbor exchange, as for $Sr_2CuO_2Cl_2$ (Sec. III A), one has to compare only the ferromagnetic and the antiferromagnetic solution. For a rough estimate, it is sufficient to use the classical solution of Eq. (1). However, we will show that the inclusion of quantum spin fluctuations leads to improved values of exchange constants.

The second route is based on the concept of adiabatic spin moments.[10,11] One has to calculate spin-spiral configurations corresponding to small deviations around the antiferromagnetic state. We concentrate here on compounds ($Sr_2CuO_2Cl_2$, $Ba_2Cu_3O_4Cl_2$) for which no magnetic solution can be obtained by a simple LDA-DFT calculation. Therefore, for both approaches mentioned above, it is crucial to outline first the LDA+U scheme.[13]

The main point of the LDA+U method is the construction of a new energy functional which is defined by adding a Hubbard-like term to the total energy functional in local spin density approximation (LSDA):

$$E^{\mathrm{LDA}+U}=E^{\mathrm{LSDA}}+E^{U}-E^{\mathrm{DC}}, \tag{2}$$

where E^{LSDA} is the LSDA energy functional, E^{U} takes into account on-site Coulomb and exchange interactions in the strongly correlated subshell, and E^{DC} is the so-called double counting term which subtracts the averaged Coulomb and exchange interactions already included into E^{LSDA}. In the spirit of the density functional approach the functional E^{U} is expressed in terms of the correlated part of the density matrix, and in the basis which diagonalizes this matrix it reads

$$E^{U}=\frac{1}{2}\sum_{tij\sigma} U^t n_{ti}^{\sigma} n_{tj}^{-\sigma}+\frac{1}{2}\sum_{tij\sigma}^{i\neq j}(U^t-J^t)n_{ti}^{\sigma}n_{tj}^{\sigma}. \tag{3}$$

Here, U^t and J^t, are appropriately averaged values of U_{ij}^t and J_{ij}^t, the screened Coulomb and exchange integrals between projectors onto local basis states $|t,i\rangle$ and $|t,j\rangle$ of the atom t, and n_{tj}^{σ} is the corresponding spin-projected density matrix $n_{tj}^{\sigma}=(1/\pi)\int^{E_F}dE\,\mathrm{Im}\langle t,j|G^{\sigma}(E)|t,j\rangle$, with $G^{\sigma}(E)$ and E_F being one-particle Green function and Fermi level, respectively. For the sake of simplicity we consider further on only this, so called spherically averaged LDA+U method. It is worth to note that this form can be adopted only if the spin-orbit coupling is neglected. If the local symmetry of site t is sufficiently high (i.e., all the localized functions transform according to inequivalent representations of the local subgroup of the site) the basis $|t,i\rangle$ can be constructed from the basis functions of the irreducible representation of the corresponding point group.

The following expression for the double counting term was used in our calculations:[13]

$$E^{\mathrm{DC}}=\frac{1}{2}\sum_{t}\left\{U^tN^t(N^t-1)-\frac{1}{2}J^t[N^{t\uparrow}(N^{t\uparrow}-1)+N^{t\downarrow}(N^{t\downarrow}-1)]\right\}, \tag{4}$$

where $N^{t\uparrow}$ and $N^{t\downarrow}=\Sigma_i n_{ti}^{\downarrow}$ are the number of majority and minority spin electrons in the correlated subshell of atom t, respectively, and $N^t=N^{t\uparrow}+N^{t\downarrow}$. Differentiating Eq. (2) over orbital occupancies gives the expression for the orbital dependent one-electron potential

$$V_{\sigma}^{\mathrm{LDA}+U}=V_{\sigma}^{\mathrm{LSDA}}+\sum_{it}(U^t-J^t)\left(\frac{1}{2}-n_{ti}^{\sigma}\right)|t,i\rangle\langle t,i|. \tag{5}$$

It is more convenient to rewrite this standard expression, introducing the value $U_{\mathrm{eff}}^t=U^t-J^t$, and charge and spin of each orbital $n_{ti}=n_{ti}^{\uparrow}+n_{ti}^{\downarrow}$ and $s_{ti}=(n_{ti}^{\uparrow}-n_{ti}^{\downarrow})/2$ and also to separate spin independent (V) and spin dependent (B) parts of the effective one electron potential:

$$V=\sum_t\left[V_t^{\mathrm{LSDA}}+\sum_i U_{\mathrm{eff}}^t\left(\frac{1}{2}-\frac{n_{ti}}{2}\right)|t,i\rangle\langle t,i|\right]=\sum_t \mathcal{V}_t,$$

$$B=\sum_t\left(B_t^{\mathrm{LSDA}}+\sum_i U_{\mathrm{eff}}^t s_{ti}|t,i\rangle\langle t,i|\right)=\sum_t \mathcal{B}_t. \tag{6}$$

Here we expressed the potential as a sum over atomic contributions.

Since the spin-dependent part of the effective potential enters the generalized Kohn-Sham equations similar to a

magnetic field, the noncollinear magnetic structure can be described as a corresponding rotation of this magnetic field on each site, which leads to the following expression for the effective potential:

$$V_{\sigma\sigma'}^{\mathrm{LDA}+U}=\sum_t \mathcal{V}_t I_{\sigma\sigma'}+\sum_t \mathcal{B}_t \vec{e}_t \vec{\sigma}_{\sigma\sigma'}. \tag{7}$$

Here $I_{\sigma\sigma'}$ and $\vec{\sigma}_{\sigma\sigma'}$ are the unity and Pauli matrices respectively, and $\vec{e}_t$ denotes the local spin direction defined via angles θ_t and φ_t of atom t. Explicitly, the spin-dependent part of the Hamiltonian is expressed as

$$\mathcal{B}_{\sigma\sigma'}^{\mathrm{eff}}=\sum_t \mathcal{B}_t \begin{pmatrix} \cos\theta_t & \sin\theta_t \exp(i\varphi_t) \\ \sin\theta_t \exp(-i\varphi_t) & -\cos\theta_t \end{pmatrix}. \tag{8}$$

To derive the exchange constants directly from the energy differences between different spin-arrangements it is usually sufficient to calculate only a very restricted number of collinear spin arrangements. In the case of spin spirals, they are parametrized by the following arrangements of local spins:

$$\varphi_t=\varphi_{t_0}+\vec{Q}\vec{R}; \quad \theta_t=\theta_{t_0}, \tag{9}$$

where t_0 denotes the sites in the crystal unit cell.

It can be easily seen, that in this case the matrix elements of the Hamiltonian in the basis of Bloch functions $\Psi_n^k \chi_\sigma$ have the form

$$H_{kn\sigma,k'n'\sigma'}=\begin{pmatrix} h_{k\uparrow nn'}\delta_{kk'} & b_{kk',nn'}\delta_{k,k'+q} \\ b_{kk',nn'}\delta_{k,k'-q} & h_{k\downarrow nn'}\delta_{kk'} \end{pmatrix}. \tag{10}$$

That means that only states $k,\uparrow$ and $k+q,\downarrow$ are coupled, which allows to carry out the calculations with only doubling of the matrix, i.e., the generalized Bloch theorem introduced in Ref. 27 for the plain LSDA calculations is still applicable.

Having calculated a set of spin spirals for different values of $\vec{Q}$, φ_t, and θ_t the energy of different noncollinear spin arragements can be mapped on the corresponding mean-field solutions of Eq. (1). Then the energy can be parametrized as a function of $\vec{e}_t$ in the form

$$E(\vec{e}_t)=\frac{1}{2}\sum_{tt'} J_{tt'} s_t s_{t'} \vec{e}_t \vec{e}_{t'}, \tag{11}$$

where s_t stands for the expectation value of the local spin moment. More details about the determination of exchange integrals from spin-spiral states will be discussed using the example of $Sr_2CuO_2Cl_2$.

As follows from the description above, a crucial parameter appearing in the formalism is the value of U_{eff}. This value can in principle be obtained from constrained LDA calculations. There were several attempts to estimate U_{eff} (see Refs. 6,28,29) with some uncertainty in the results since it is not *a priori* clear which constrains have to be implemented. Due to the difficulties mentioned above we will consider a large region of possible U_{eff} values and we find it very satisfactory that the resulting exchange integrals depend only moderately on U_{eff}.

Another important point is the choice of the correlated subsystem, which is defined through the set of projectors $|t,i\rangle$. In the case of cuprates we assume that only the $3d$ copper electrons are strongly correlated. The results are not sensible to the exact choice of the radial part of the projector, thus we took as a projector the radial solution of the Schrödinger equation in the copper sphere, corresponding to the Wigner-Seitz boundary conditions. All the calculations done in this work have been perfomed using the LMTO method in the atomic sphere approximation (ASA) and with the combined correction term[30] taken into account.

In order to decrease the overlap between atomic spheres additional empty spheres (ES) were used in the calculations. For $Sr_2CuO_2Cl_2$ one set of ES at the (0,0.5,0.25) position was added. The resulting atomic sphere radii were 3.614, 2.377, 2.027, 3.142, and 1.833 a.u. for Sr, Cu, O, Cl, and the empty sphere, respectively. In the case of $Ba_2Cu_3O_4Cl_2$ three sets of ES with the coordinates $E1$ (0,0,0.146), $E2$ (0.297,0,0.104), and $E3$ (0.198,0.198,0.195) were inserted with the sphere radii 2.131, 1.709, and 1.609 a.u., respectively. For the atomic spheres the following radii (in a.u.) were used $S_{\mathrm{Ba}}=3.878$, $S_{\mathrm{Cu}_A}=S_{\mathrm{Cu}_B}=2.333$, $S_{\mathrm{O}}=1.986$, and $S_{\mathrm{Cl}}=3.108$.

In order to estimate possible errors in the exchange coupling constants calculated with the LDA$+U$ method arising as a result of the use of the Hartree-Fock approximation for the E^U term of Eq. (2) we considered ferromagnetic (FM) and antiferromagnetic (AFM) solutions of a one-band Hubbard model for a square lattice with nearest-neighbor hopping in the Hartree-Fock (HF) approximation at half filling. For any nonzero value of U the self-consistent AFM solution is insulating whereas the FM solution is metallic for U smaller than the bandwidth of $8t$. As a result, the difference of the total energies of the self-consistent FM and AFM solutions E^{HF} increases as a function of U for $U<8t$. For U equal to the bandwidth E^{HF} reaches its maximum and, then, decreases approaching the well known second order expression $4t^2/U$ for $U\gg 8t$, i.e., in the strongly correlated limit. The comparison of E^{HF} to the difference E^{ED} between the energies of the highest spin state and of the ground state of the Hubbard Hamiltonian for a 3×4 cluster calculated using the exact diagonalization technique[31] shows that already for $U=8t$ the difference between $E^{\mathrm{HF}}/t=0.466$ and $E^{\mathrm{ED}}/t=0.486$ is less than 5%. The difference should decrease with the further increase of U since both energies tend to the same $4t^2/U$ value in the large U limit.

Using the same model one can check the validity of the so-called force theorem (FT) by calculating the difference of the band energies of the FM and AFM configurations using as an input value in both cases the self-consistent AFM magnetization. For $U=8t$ this approach gives the difference of the band energies $E^{\mathrm{FT}}/t=0.489$ which is within 5% of E^{HF}, thus showing that the force theorem can be safely used in this case.

These model considerations show that LDA$+U$ calculations, in which the interaction of correlated electrons is described by the Hubbard-like term E^U in the Hartree-Fock approximation, should reproduce rather accurately the variation of the energy upon the change of a magnetic structure, at

TABLE I. Exchange constants, magnetic moments μ_{AF}, μ_{FM} ($\mu = n^{\uparrow}_{Cu} - n^{\downarrow}_{Cu}$) and spin wave velocity $\hbar v$ for $Sr_2CuO_2Cl_2$. Exchange constants J and J^{QF} calculated from the energy difference between the ferromagnetic (FM) and antiferromagnetic (AFM) states are compared to J_1 obtained from the spin-spiral approach.

U_{eff} (eV)	FM-AFM		Spin-spiral approach				
	J (meV)	J^{QF} (meV)	J_1 (meV)	J_2 (meV)	μ_{AF} (μ_B)	μ_{FM} (μ_B)	$\hbar v$ (meV Å)
2	129	110					
3	164	140					
4	165	141	185	25	0.64	0.74	735
5	157	134	148	16	0.68	0.80	588
6	129	110	122	12	0.72	0.82	485

least in the cases when U is sufficiently large as compared to characteristic hopping integrals. The latter condition is usually fulfilled for cuprates and, consequently, the effective exchange coupling constants obtained by mapping the calculated energy variation onto an effective Heisenberg model should provide a quite reasonable description of magnetic interactions in the compounds under study.

III. RESULTS AND DISCUSSION

A. Exchange constants of $Sr_2CuO_2Cl_2$

At first we use the difference in total energy between the ferromagnetic E_F and antiferromagnetic spin arrangement E_A to calculate the exchange integrals of $Sr_2CuO_2Cl_2$. That energy has to be compared with the corresponding one in the spin-1/2 2D Heisenberg model (1) with only nearest neighbor exchange $J_{ij} = J$. Neglecting quantum fluctuations, the energy difference $\Delta E = (E_F - E_A)/N$ per copper ion (N: number of copper sites) gives the exchange constant $\Delta E = J$. The corresponding numbers are summarized in Table I, and they indicate a rather small variation of J by changing U_{eff} in the large region between 2 and 6 eV. That only makes the present approach reliable. The maximum number $J = 165$ meV occurs at $U_{eff} = 4$ eV and the values decrease for small and large U_{eff}. The decrease for small U_{eff} can be explained, since for $U_{eff} = 2$ or 3 eV only the antiferromagnetic solution, but not the ferromagnetic one, is insulating. For very large U_{eff} we would expect a decrease of J according to t^2/U_{eff}, but such large U_{eff} values seem to be unrealistic.[32]

We may note that the exchange constants obtained with the classical solution of Eq. (1) are systematically larger than expected. The discrepancy may be reduced by considering quantum fluctuations. The classical ferromagnetic state is also an eigenstate of the full Hamiltonian (1) such that the ferromagnetic energy is not changed by quantum fluctuations. But the classical, antiferromagnetic Néel state with an energy of $-J/2$ is not the lowest eigenstate of Eq. (1). The ground state energy of the 2D Heisenberg model is given by $-2J/3$ within a good accuracy (using $\langle \vec{S}_i \vec{S}_j \rangle = -1/3$ for the nearest-neighbor spin correlations).[33] That defines a new J^{QF} by

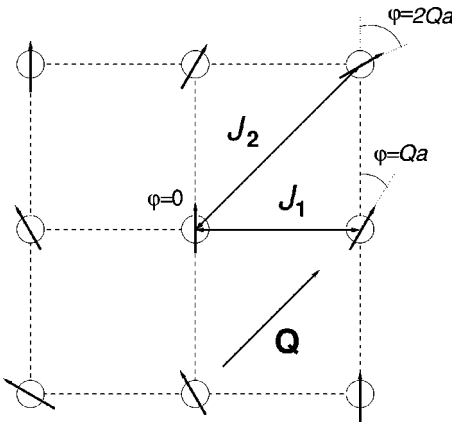

FIG. 1. Spin-spiral state in $Sr_2CuO_2Cl_2$.

$$\Delta E = \left(\frac{1}{2} + \frac{2}{3}\right) J^{QF} = \frac{7}{6} J^{QF}, \tag{12}$$

which is also listed in Table I. We see that the quantum fluctuations give rise to a considerable improvement of the derived exchange constants which are now between 110 and 140 meV.

In our second approach, we calculate the total energy for the spin-spiral shown in Fig. 1 for arbitrary values of φ in a self-consistent way. This energy (shown in Fig. 2) has to be fitted by an expression of the form (11) with the corresponding expectation value $s = s_t = \langle \hat{s} \rangle$ of the local spin operator. The naive expression $s = \mu_{AF}/2$ using only the copper magnetic moment $\mu_{AF} = n^{\uparrow}_{Cu} - n^{\downarrow}_{Cu}$ in the antiferromagnetic state underestimates the spin moment since part of the fluctuating moment sits on oxygen. That becomes evident for μ_{FM} which should be equal to unity for an insulating solution. (In the spin-spiral approach we restricted ourselves to $U = 4,5,6$ for which both magnetic solutions are insulating.) Since the

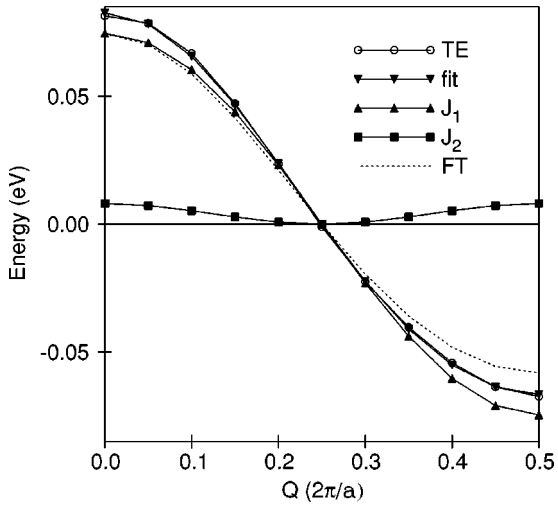

FIG. 2. Energy $E(Q)$ as function of the wave vector $Q = |\vec{Q}|$ for the spin-spiral state in $Sr_2CuO_2Cl_2$ for $U_{eff} = 5$ eV. The energy calculated using the force theorem (FT) and the total energy obtained from the self-consistent calculations (TE) are shown together with the corresponding fit to the TE curve.

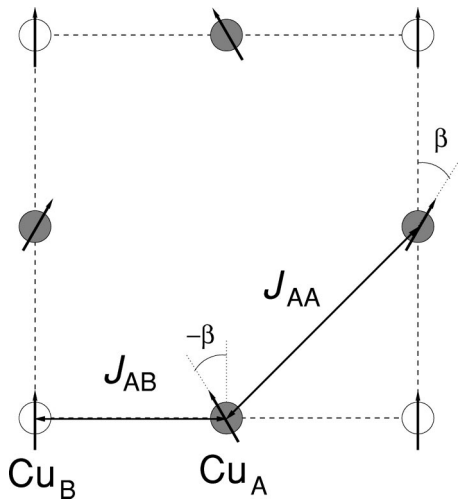

FIG. 3. Spin arrangement in $Ba_2Cu_3O_4Cl_2$ to determine exchange parameters.

oxygen part of the fluctuating moment is hard to determine, we decided to use simply the classical value $s=1/2$ in Eq. (11) which then reads for the spin spiral of Fig. 1

$$E(\varphi)=\frac{1}{2}[J_1\cos\varphi+J_2\cos(2\varphi)]. \tag{13}$$

Using $s=1/2$ corresponds to the neglect of quantum fluctuations in the previous approach. From Eq. (13) we find the exchange terms to first (J_1) and second neighbors (J_2) listed in Table I. We see that the exchange to second neighbors $J_2=25$ meV (or 12 meV) for $U=4$ eV (or 6 eV) is rather small and can be neglected. It was also checked that spin spirals corresponding to small deviations from the antiferromagnetic state [varying both angles θ and φ in Eq. (8) as it was also proposed originally in Ref. 10] lead to nearly the same exchange terms as Eq. (13) which interpolates between the antiferromagnetic and the ferromagnetic spin arrangement. The reason is that $Sr_2CuO_2Cl_2$ behaves similar to a local moment system in contrast to the ferromagnetic metals considered in Ref. 10.

Next, we can calculate the adiabatic magnon dispersion curve according to Ref. 11. The form of the spin wave dispersion has only very few deviations from that one known for the spin-1/2 2D Heisenberg model[33] and for small q is linear with the velocity, given by $\hbar v=2asJ_1=aJ_1$ and listed in Table I. First of all, we note a reasonable agreement with the experimentally found spin wave velocity $\hbar v=850$ meV Å for La_2CuO_4. It can be expected that the inclusion of quantum fluctuations leads to reduced exchange terms also in the spin-spiral approach. The neglect of quantum fluctuations is also visible in the expression for the spin wave velocity $\hbar v=2asJ_1$ that is different from the Monte Carlo result for the 2D Heisenberg model ($\hbar v=1.68aJ$).

An alternative, cheaper way with less numerical efforts is based on the force theorem (FT). It means that the self-consistent potential is calculated only once for the antiferromagnetic case ($\varphi=\pi$) and for different φ only the band energies are changed.[34] The corresponding energies together with a fit to Eq. (11) for $U_{\rm eff}=5$ eV are also shown in Fig. 2 leading only to small changes ($J_1=132$ meV, $J_2=16$ meV) in comparison to a full calculation.

TABLE II. Exchange constants of $Ba_2Cu_3O_4Cl_2$ derived using the energy difference of different spin arrangements according to Eq. (14). The values from Rayleigh-Schrödinger (RS) (Ref. 25) and cell-perturbation theory (CPT) (Ref. 26) are also given.

$U_{\rm eff}$ (eV)	J_{AA} (meV)	J_{AB} (meV)	J_{BB} (meV)
4	186	−25	8
5	152	−18	8
6	120	−18	4
RS	100	−6	12
CPT	170	−(4..5)	5

B. Exchange constants of $Ba_2Cu_3O_4Cl_2$

That compound has a Cu_3O_4 plane which can be understood as the standard CuO_2 plane (Cu_A) where each second square is occupied by an additional Cu_B in a chess-board-like pattern. We determined the exchange constants within the ''standard'' Cu_A subsystem (J_{AA}), within the Cu_B subsystem (J_{BB}) and the coupling between both (J_{AB}). For that one needs at least four different energies

$$E_{ANF}=-J_{AA}+J_{BB}/2,$$

$$E_{FAF}=J_{AA}-J_{AB}+J_{BB}/2,$$

$$E_{FFF}=J_{AA}+J_{AB}+J_{BB}/2,$$

$$E_{FNA}=J_{AA}-J_{BB}/2, \tag{14}$$

where E_{FNA} means ferromagnetic spin arrangement in the A subsystem, no coupling between A and B and antiferromagnetic B system. The notation for all the other combinations is obvious. All energies are given for a cell of 2 Cu_A and 1 Cu_B. Using Eq. (14) one obtains the exchange constants summarized in Table II. The corresponding magnetic moments $\mu_t^m=n_t^{\uparrow}-n_t^{\downarrow}$ for $t=Cu_A$ or Cu_B and for the different spin states m are given in Table III for completeness. One may note that we find J_{AA} in reasonable agreement with the above derived values for the standard CuO_2 plane. The B subsystem has an antiferromagnetic coupling which is, however, surprisingly small if we compare with previously derived parameters using the Rayleigh-Schrödinger (RS) perturbation theory.[25] The agreement with the cell-perturbation

TABLE III. Magnetic moments $\mu_t^m=n_t^{\uparrow}-n_t^{\downarrow}$ (μ_B) for $Ba_2Cu_3O_4Cl_2$, where m denotes the magnetic states and $t=Cu_A$ or Cu_B.

$U_{\rm eff}$ (eV)	$\mu_{Cu_B}^{ANA}$	$\mu_{Cu_A}^{ANA}$	$\mu_{Cu_B}^{FAF}$	$\mu_{Cu_A}^{FAF}$	$\mu_{Cu_B}^{FFF}$	$\mu_{Cu_A}^{FFF}$
4	0.75	0.71	0.76	0.82	0.73	0.81
5	0.76	0.73	0.77	0.83	0.74	0.82
6	0.77	0.75	0.78	0.85	0.76	0.83

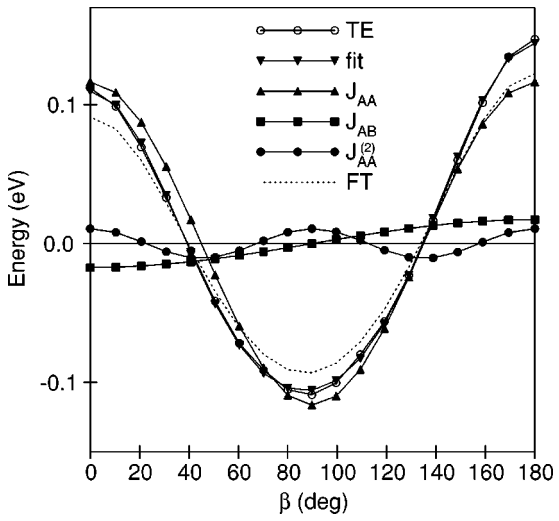

FIG. 4. Energy $E(\beta)$ as function of the spin-distortion angle β for $U_{\text{eff}}=6$ eV together with the corresponding fit in $Ba_2Cu_3O_4Cl_2$. The notation is such as in Fig. 2.

method (CPT) (Ref. 26) is better. The coupling between the A and B subsystem is ferromagnetic according to the Goodenough-Kanamori-Anderson rules[35] as it occurs via a 90° Cu-O-Cu bond. But the amount of J_{AB} of roughly -20 meV is again quite different from previous estimates. In the present situation of two coupled antiferromagnetic subsystems it is more difficult to calculate the effect of quantum fluctuations than for the simple 2D Heisenberg model and we did not try a quantitative estimate. By analogy we can expect that the numbers given in Table II may be slightly overestimated by 15 to 20 %.

To check the results we investigated also a noncollinear spin arrangement depicted in Fig. 3. As this compound possesses a more complicated crystal structure we did not perform $\vec{Q}$ dependent calculations and limit ourself only to calculations with $\vec{Q}=0$ and varying angle β (Fig. 4). In the chosen spin arrangement it is not possible to determine longer-ranged exchange terms. We may obtain J_{AA} and J_{AB} by fitting the curve

$$E(\beta)=J_{AA}\cos(2\beta)+J_{AB}\cos\beta+J_{AA}^{(2)}\cos(4\beta), \quad (15)$$

yielding the numbers of Table IV. The parameter $J_{AA}^{(2)}$, which was introduced to improve the fit, corresponds to deviations from the pure Heisenberg model, i.e., to biquadratic exchange. We see, however, that this parameter is small and decreases for large U_{eff}. Furthermore, the fit (15) has been performed for a classical value $s=1/2$ neglecting quantum fluctuations to be consistent with the alternative estimate above [see Eq. (14)].

TABLE IV. Exchange constants of $Ba_2Cu_3O_4Cl_2$ from a fit to the spin arrangement of Fig. 3. The values calculated using the force theorem are given in brackets.

U_{eff} (eV)	J_{AA} (meV)	J_{AB} (meV)	$J_{AA}^{(2)}$ (meV)
4	169 (141)	−19 (−17)	21 (20)
6	116 (99)	−17 (−15)	11 (8)

IV. SUMMARY

The two methods proposed in the present work to extract exchange constants from a LDA+U calculation give results in reasonable agreement with each other and with other approaches. The methods were tested for strongly correlated cuprates which are a good testing ground due to the great knowledge on those materials. The usage of the LDA+U method to extract exchange constants seems to be especially promising to obtain the order of magnitude, the sign and the ratio among different exchange terms for new materials. Possible candidates for further studies are especially cuprates with a spin-Peierls transition,[36] cuprate chain compounds or some low-dimensional vanadates. At present the method was only applied to spin-1/2 compounds but its extension to systems with higher spin seems to be straightforward.

In the case of $Ba_2Cu_3O_4Cl_2$ we confirmed previously performed estimates with respect to the signs and the orders of magnitude. The absolute numbers were corrected which is not so surprising taking into account the limited accuracy of Rayleigh-Schrödinger perturbation theory. That compound has two antiferromagnetic subsystems which are decoupled in a classical description. It makes a calculation of the spin wave spectrum more involved which may be a task for further studies.

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