



Calculation of exchange integrals in transition metals oxides using the LDA + U approach

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Abstract

We propose a method of the calculation of effective exchange coupling constants between the magnetic ions in transition metal oxides based on the mapping of the energy of noncollinear spin-spiral states calculated with the LDA + U method to the mean-field solutions of the effective spin Hamiltonian. The approach is applied to $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, which can be described with good accuracy by a 2D Heisenberg model with only nearest-neighbor exchange. The same method is also used to determine the exchange constants in the charge ordered low-temperature phase of NaV_2O_5 . © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Exchange integrals; Cuprates; Vanadates

Theoretical determination of effective exchange coupling constants between the magnetic ions in transition metal oxides is a general and long standing problem. In principle, the exchange coupling constants can be calculated on the base of the density functional theory (DFT) from comparison of the total energies of different collinear magnetic states with the corresponding magnetic states of an appropriate Heisenberg-type Hamiltonian. Another possibility to calculate directly the spin excitation spectrum from band structure methods and to determine exchange constants is based on the concept of adiabatic magnetic moments [1]. The approach consists in the mapping of constrained DFT total energy calculations for noncollinear magnetic structures on the mean-field solutions of the effective spin Hamiltonian. However, the local spin density approximation (LSDA) or more involved generalized gradient approximation, which are commonly used in band structure calculations, are not able to describe properly the magnetic state of such highly correlated systems as

cuprates or vanadates [2]. One of the most developed ways to cure the situation is the so-called “LDA + U ” approach which allows to include the most important on-site correlations in a Hartree–Fock-like scheme [3].

The main point of the LDA + U method is to add a Hubbard-like term to the LSDA total energy functional. The resulting orbital-dependent one-electron potential can be written as a sum of spin-independent V and spin-dependent B parts

$$V_t = V_t^{\text{LSDA}} + \sum_i U_{\text{eff}}^t \left(\frac{1}{2} - \frac{n_{ii}}{2} \right) |t, i\rangle \langle t, i|,$$

$$B_t = B_t^{\text{LSDA}} + \sum_i U_{\text{eff}}^t s_{ii} |t, i\rangle \langle t, i|. \quad (1)$$

where $|t, i\rangle$ is a projector onto a localized orbital of the atom t and $n_{ii} = n_{ii}^\uparrow + n_{ii}^\downarrow$ and $s_{ii} = (n_{ii}^\uparrow - n_{ii}^\downarrow)/2$ are charge and spin of the orbital, respectively. Here we neglect for simplicity nonspherical contributions to the screened Coulomb U^t and exchange J^t integrals and define $U_{\text{eff}}^t = U^t - J^t$.

The spin-dependent part of the effective potential enters the generalised Kohn–Sham equations like an effective magnetic field and a noncollinear magnetic structure can be defined via rotations of this effective

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magnetic field on each site, which leads to the following expression for the effective potential:

$$V_{\sigma\sigma'}^{\text{LDA}+U} = \sum_t V_t I_{\sigma\sigma'} + \sum_t B_t \mathbf{e}_t \sigma_{\sigma\sigma'} \quad (2)$$

Here $I_{\sigma\sigma'}$ and $\sigma_{\sigma\sigma'}$ are the unity and Pauli matrices, respectively, and \mathbf{e}_t denotes the local spin direction at a site t defined via angles θ_t and φ_t . In the case of a spin spiral $\theta_t = \theta_0$ is a constant and $\varphi_t = \theta_0 + \mathbf{Q}\mathbf{r}$, with \mathbf{Q} being the wave vector of the spiral. In order to determine the effective exchange coupling constants, the energies calculated for different spin spirals can be mapped on the corresponding mean-field solution of a Heisenberg-type Hamiltonian.

In the case of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, we calculated the total energy of the spin-spiral shown in Fig. 1 for different values of \mathbf{Q} . This energy has to be fitted by an expression $(s^2/2)(J_1 \cos \varphi + J_2 \cos 2\varphi)$, where s is the expectation value of the local spin operator. The evaluation of s as $\mu_{\text{Cu}}/2$ using the Cu magnetic moment only underestimates the spin moment since a part of it sits on oxygen. As the oxygen part of the moment is hard to determine, we decided to use the value $s = \frac{1}{2}$. We found the exchange coupling constants to first neighbors $J_1 = 148$ and 122 meV for $U_{\text{eff}} = 5$ and 6 eV, respectively. The exchange to second neighbors $J_2 = 16$ meV (12 meV) is found to be rather weak. The total energy for $U_{\text{eff}} = 5$ eV and the results of the fit are shown in Fig. 2. The calculated value of J_1 compares well with the exchange constant of 133 meV determined for La_2CuO_4 by fitting data on the spin wave velocity found by inelastic neutron scattering [4] $\hbar v = 850$ meV \AA to that one of quantum Monte Carlo calculations [5]. An alternative way with less numerical efforts is based on the force theorem [6] (FT) and leads to only small changes ($J_1 = 132$ meV, $J_2 = 16$ meV) in comparison to the full calculation.

The same approach was used to calculate the exchange constants in $\alpha'\text{-NaV}_2\text{O}_5$. The recently deter-

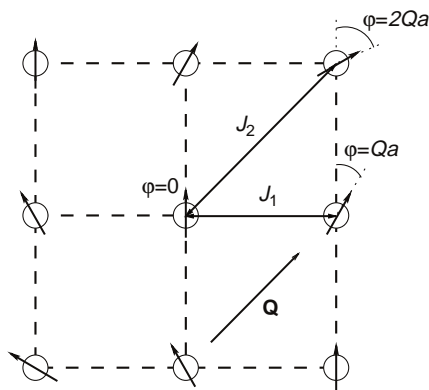


Fig. 1. Spin-spiral state in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.

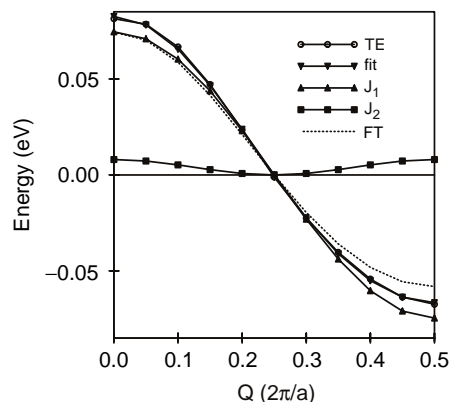


Fig. 2. The energy of the spin-spiral state in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ as a function of $Q = |\mathbf{Q}|$ calculated for $U_{\text{eff}} = 5$ eV. The total energy (TE) and the energy calculated using the force theorem (FT) are shown together with the fits to the TE curve.

mined low-temperature structure of this compound suggests that two families of ladders formed by V ions exist below the transition temperature. An analysis of the shifts of V and O ions from their averaged high-temperature positions allows to assume that a charge disproportionation into V^{4+} and V^{5+} ions occurs only in one of the ladders whereas another one consists of $V^{4.5+}$ ions. However, the consecutive rungs of the second “disordered” ladder are structurally inequivalent which can lead to a dimerisation of the corresponding exchange constants. We performed calculations for a number of spin spirals, their parameters being fixed by the requirement to make possible an independent determination of the exchange integral J_1 along the ordered ladder and two different integrals J_2 and J_3 along the disordered one. It should be noted that even for the ordered ladder the V magnetic moment is not localized completely on V^{4+} ion but spreads over a rung. Taking this into account, the introduced exchange constants describe the effective interaction not between magnetic V ions but rather between the rungs. The FT based calculations performed with $U_{\text{eff}} = 3$ eV gave the values of 38 , 57 , and 73 meV for J_1 , J_2 , and J_3 , respectively. This result confirms that there is a strong dimerisation of the exchange interaction along the “disordered” ladder. The large difference between J_1 , calculated for the charge ordered ladder, and J_2 and J_3 supports the conclusion of Ref. [7] that the charge ordering leads to weaker intra ladder exchange interaction.

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