

Wannier functions and exchange integrals: The example of LiCu_2O_2

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Starting from a single band Hubbard model in the Wannier function basis, we revisit the problem of the ligand contribution to exchange and derive explicit formulas for the exchange integrals in metal oxide compounds in terms of atomic parameters that can be calculated with constrained LDA and LDA+U. The analysis is applied to the investigation of the isotropic exchange interactions of LiCu_2O_2 , a compound where the Cu-O-Cu angle of the dominant exchange path is close to 90° . Our results show that the magnetic moments are localized in Wannier orbitals which have strong contribution from oxygen atomic orbitals, leading to exchange integrals that considerably differ from the estimates based on kinetic exchange only. Using LSDA+U approach, we also perform a direct *ab initio* determination of the exchange integrals LiCu_2O_2 . The results agree well with those obtained from the Wannier function approach, a clear indication that this modelization captures the essential physics of exchange. A comparison with experimental results is also included, with the conclusion that a very precise determination of the Wannier function is crucial to reach quantitative estimates.

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I. INTRODUCTION

In order to explain the homeopolar chemical bond in the hydrogen molecule, Heitler and London¹ have derived the direct and exchange Coulomb integrals which can be written in the following form:

$$U = \int \frac{\phi_i^*(x)\phi_i(x)\phi_i^*(x')\phi_i(x')}{|x-x'|} dx dx' \quad (1)$$

and

$$J_{ij}^{Coulomb} = \int \frac{\phi_i^*(x)\phi_j(x)\phi_j^*(x')\phi_i(x')}{|x-x'|} dx dx', \quad (2)$$

where i and j are site indices, and $\phi_i(x)$ is a wave function centered at the lattice site i . Taking into account the exchange Coulomb integral allows one to obtain bonding ($E=U-J_{ij}^{Coulomb}$), as well as antibonding ($E'=U+J_{ij}^{Coulomb}$) states of H_2 . Heitler and London have shown that the properties of the hydrogen molecule can be described correctly using these combinations of wave functions.

Then, in 1928, Heisenberg² has used the exchange Coulomb integral $J_{ij}^{Coulomb}$ to explain ferromagnetism. Heisenberg has supposed that this exchange Coulomb integral corresponds to the exchange coupling in a spin model defined by the Hamiltonian:

$$H = \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (3)$$

and that it is the main source of ferromagnetism in $3d$ metal compounds. However, if $\phi_i(x)$ in Eq. (1) is the atomic wave function centered on the i th atom, then the overlap between wave functions on neighboring atoms is negligibly small. Therefore, the exchange interaction derived through Eq. (2) can be neglected.

In 1959, Anderson³ has suggested an alternative type of exchange interaction process based on hopping (kinetic exchange interaction). In the context of the Hubbard model,⁴

$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{U}{2} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma}, \quad (4)$$

this exchange interaction can be expressed as $J_{ij}^{kin} = \frac{2t_{ij}^2}{U}$. This estimation of exchange interaction through hopping integrals is convenient and now widely used in the literature. However, if J_{ij}^{kin} is small enough, other sources of exchange coupling become important. Indeed, the proper way to discuss exchange is to consider the basis of Wannier functions W_i (where i is the composite index of band and site) proposed by Wannier⁵ in 1937 and defined as the Fourier transforms of a certain linear combination of Bloch functions ψ_{nk} (n is the band index and k is the wave vector in reciprocal space). In contrast to atomic wave functions $\phi_i(x)$, which are localized on one atom, the Wannier functions $W_i(x)$ are more extended in space and can be expressed through linear combination of atomic wave functions, $W_i(x) = \sum_{jT} \alpha_j^i \phi_j(x-T)$ [where α_j^i is the contribution of the j th atomic orbital to Wannier function $W_i(x)$ and T is a translation vector]. The Wannier functions are the most localized ones within the subspace of low-energy excitations, which facilitates a direct physical interpretation consistent with interacting localized spins. Therefore, to use Wannier states instead of atomic sets is physically motivated. In particular, as we shall see, $J_{ij}^{Coulomb}$ defined in the Wannier basis plays a crucial role in the description of exchange interactions between magnetic moments in the case of nearly 90° metal-oxygen-metal bonds.

These questions have already been discussed in several contexts in the literature. For instance, the authors of Ref. 6 have discussed two alternative ways, natural or orthogonalized magnetic orbitals, to describe the exchange interactions. They have concluded that the orthogonalized magnetic or-

bit approach clearly leads to simpler calculations and thus may be more appropriate for quantitative computations.

The competition between kinetic (J_{ij}^{kin}) and potential ($J_{ij}^{Coulomb}$) contributions to the total exchange interaction has been considered before in many works. In Ref. 7, the authors have performed model calculations of a $\text{Cu}_2\text{O}_6\text{Li}_4$ cluster for different Cu-O-Cu angles. Their computational experiments have shown that the nearest-neighbor interaction reaches a maximum around 97° and remains ferromagnetic up to angles as large as 104° . They have also concluded that the simple superexchange relation cannot be applied to Li_2CuO_2 . In Ref. 8, it was shown that unusual insulating ferromagnetism in $\text{La}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$ can be explained by intersite ferromagnetic “direct exchange” (in our notation $J_{ij}^{Coulomb}$). The authors have concluded that the latter process occurs mainly at La and O sites and overwhelms the antiferromagnetic (AFM) superexchange J_{ij}^{kin} . The value of $J_{ij}^{Coulomb}$ was calculated through a direct integration over the wave functions.

In the present paper, we revisit this issue in the context of constrained LDA and LSDA+U *ab initio* approaches. The problem we want to address can be formulated as follows. In favorable situations, the exchange integrals calculated using LSDA+U agree quite well with the standard superexchange expression $J_{ij}^{kin} = \frac{2t_{ij}^2}{U}$ if the parameters t_{ij} and U are themselves determined from constrained LDA and LSDA+U. Such an interpretation of the LSDA+U results is a well accepted criterion to test the reliability of the result. However, the standard superexchange expression $J_{ij}^{kin} = \frac{2t_{ij}^2}{U}$ often fails quantitatively, and even sometimes qualitatively, to reproduce the LSDA+U results. The main goal of this paper is to provide for such cases a generalization of the superexchange expression which is entirely expressed in terms of parameters that can be determined by constrained LDA and LSDA+U, and which can be used as an interpretation and an independent check of the LSDA+U results.

To this end, we start from the standard Hamiltonian in Wannier function basis for nearly 90° metal-oxygen-metal bond. We show how the different Coulomb interaction terms of this Hamiltonian are related to parameters defined in the atomic basis set, with emphasis on the intra-atomic exchange interaction of oxygen J_p^H to which $J_{ij}^{Coulomb}$ is proportional when neighboring Wannier orbitals overlap on the oxygen atoms. We then present a simple expression for the exchange interactions between magnetic moments in the system. The parameters that enter this expression can themselves be estimated through LDA and LSDA+U calculations. This formalism is applied to the investigation of the magnetic properties of LiCu_2O_2 , and the results are compared to those of first-principles LSDA+U approach.

The paper is organized as follows. In Sec. II, we discuss the Hubbard model in Wannier function basis. In Sec. III A, we shortly describe the crystal structure of LiCu_2O_2 and present the results of LDA calculation. In Sec. III B, we present the results of LSDA+U calculations and discuss the exchange interactions obtained between different pairs of magnetic moments in LiCu_2O_2 . In Sec. IV, we briefly summarize our results.

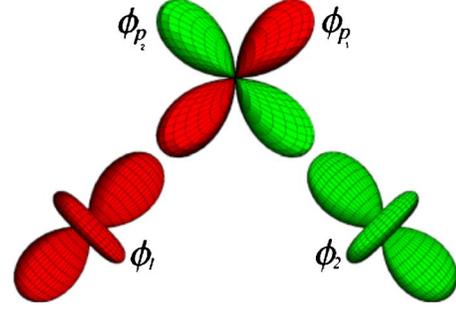


FIG. 1. (Color online) Schematic representation of a nearly 90° bond between $3d$ atoms through oxygen.

II. HUBBARD MODEL IN WANNIER FUNCTION BASIS

The general Hamiltonian in Wannier function basis $W_i(x)$ can be written in the following form:⁴

$$H = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + \frac{1}{2} \sum_{ijkl,\sigma\sigma'} (ij|U|kl) a_{i\sigma}^+ a_{j\sigma'}^+ a_{l\sigma'} a_{k\sigma}, \quad (5)$$

where

$$t_{ij} = \int W_i^*(x) \nabla^2 W_j(x) dx$$

and

$$(ij|U|kl) = \int \frac{W_i^*(x) W_k(x) W_j^*(x') W_l(x')}{|x-x'|} dx dx'.$$

We analyze the complex Hamiltonian of Eq. (5) in the context of a three-site model (see Fig. 1) with nearly 90° bonds and define two Wannier orbitals $W_1 = \alpha\phi_1 + \beta\phi_{p_1}$ and $W_2 = \alpha\phi_2 + \beta\phi_{p_2}$, which are constructed from the atomic wave functions: ϕ_1 , ϕ_2 , ϕ_{p_1} , and ϕ_{p_2} (see Fig. 1). The oxygen orbitals ϕ_{p_1} and ϕ_{p_2} can be expressed through the angle of metal-oxygen-metal bond θ in the following form:

$$\phi_{p_1} = \cos\left(\frac{\theta - 90^\circ}{2}\right) \phi_{p_y} + \sin\left(\frac{\theta - 90^\circ}{2}\right) \phi_{p_x} \quad (6)$$

and

$$\phi_{p_2} = \cos\left(\frac{\theta - 90^\circ}{2}\right) \phi_{p_x} + \sin\left(\frac{\theta - 90^\circ}{2}\right) \phi_{p_y}. \quad (7)$$

Let us first analyze the hopping term in Eq. (5). It is easy to show that

$$t_{12} = \int W_1^*(x) \nabla^2 W_2(x) dx = \beta^2 \int \phi_{p_1}^*(x) \nabla^2 \phi_{p_2}(x) dx. \quad (8)$$

If ϕ_{p_1} and ϕ_{p_2} are eigenfunctions of the Hamiltonian of Eq. (5), then using the orthogonality condition, one can obtain the following expression for the hopping term:

$$t_{12} \sim \beta^2 \cos \theta. \quad (9)$$

Clearly, if $\theta=90^\circ$, the hopping integral vanishes.

In the analysis of the Coulomb term of Eq. (5) that follows, we consider only density-density terms and on-site ex-

change integrals. On-site Coulomb interaction, intersite Coulomb interaction, and intersite exchange interaction in Wannier function basis are expressed through the corresponding parameters in the atomic basis set:

$$(ii|U|ii) = \alpha^4 U_d + 2\alpha^2 \beta^2 V_{pd} + \beta^4 U_p, \quad (10)$$

$$(ij|U|ij) = \alpha^4 V_{dd} + 2\alpha^2 \beta^2 V_{pd} + \beta^4 U_p, \quad (11)$$

$$(ij|U|ji) = \beta^4 J_p^H, \quad (12)$$

where

$$U_d = \int \frac{\phi_1^*(x) \phi_1(x) \phi_1^*(x') \phi_1(x')}{|x-x'|} dx dx' \quad (13)$$

is the on-site Coulomb interaction of 3d atom,

$$U_p = \int \frac{\phi_{p_1}^*(x) \phi_{p_1}(x) \phi_{p_2}^*(x') \phi_{p_2}(x')}{|x-x'|} dx dx' \quad (14)$$

is the on-site Coulomb interaction of oxygen atom,

$$V_{pd} = \int \frac{\phi_1^*(x) \phi_1(x) \phi_{p_1}^*(x') \phi_{p_1}(x')}{|x-x'|} dx dx' \quad (15)$$

is the Coulomb interaction between 3d atom and oxygen,

$$V_{dd} = \int \frac{\phi_1^*(x) \phi_1(x) \phi_2^*(x') \phi_2(x')}{|x-x'|} dx dx' \quad (16)$$

is the Coulomb interaction between 3d atoms, and

$$J_p^H = \int \frac{\phi_{p_1}^*(x) \phi_{p_2}(x) \phi_{p_2}^*(x') \phi_{p_1}(x')}{|x-x'|} dx dx' \quad (17)$$

is the intra-atomic exchange interaction of oxygen atom.

It was shown in Ref. 9 that the following term:

$$(ii|U|ij) = \alpha^2 \beta^2 \int \frac{\phi_1^*(x) \phi_1(x) \phi_{p_1}^*(x') \phi_{p_2}(x')}{|x-x'|} dx dx' + \beta^4 \int \frac{\phi_{p_1}^*(x) \phi_{p_1}(x) \phi_{p_1}^*(x') \phi_{p_2}(x')}{|x-x'|} dx dx', \quad (18)$$

which is the so-called correlated hybridization, could significantly change the parameters in the effective single band model for transition metal oxides. However, we do not consider it here and leave that point for further investigation.

Finally, one can write the following Hamiltonian in Wannier function basis:

$$H = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + \frac{(\alpha^4 U_d + 2\alpha^2 \beta^2 V_{pd} + \beta^4 U_p)}{2} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + \frac{(\alpha^4 V_{dd} + 2\alpha^2 \beta^2 V_{pd} + \beta^4 U_p)}{2} \sum_{ij\sigma\sigma'} n_{i\sigma} n_{j\sigma'} - \frac{\beta^4 J_p^H}{2} \sum_{ij\sigma} (n_{i\sigma} n_{j\sigma} + 2S_i^x S_j^x + 2S_i^y S_j^y), \quad (19)$$

where $n_{i\sigma} = a_{i\sigma}^+ a_{i\sigma}$ is the particle number operator, while $S_i^x = \frac{1}{2}(a_{i\uparrow}^+ a_{i\downarrow} + a_{i\downarrow}^+ a_{i\uparrow})$ and $S_i^y = \frac{1}{2i}(a_{i\uparrow}^+ a_{i\downarrow} - a_{i\downarrow}^+ a_{i\uparrow})$ are components of the spin operator. One can reduce Eq. (19) to the following form:

$$H = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + \frac{U_{eff}}{2} \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + \frac{V_{eff}}{2} \sum_{ij\sigma\sigma'} n_{i\sigma} n_{j\sigma'} - \beta^4 J_p^H \sum_{ij} \vec{S}_i \cdot \vec{S}_j, \quad (20)$$

where the effective on-site Coulomb interaction is given by $U_{eff} = \alpha^4 U_d + 2\alpha^2 \beta^2 V_{pd} + \beta^4 U_p$ and the effective intersite Coulomb interaction by $V_{eff} = \alpha^4 V_{dd} + 2\alpha^2 \beta^2 V_{pd} + \beta^4 U_p - \frac{\beta^4 J_p^H}{2}$. It is easy to show that the Heisenberg model which corresponds to this electronic Hamiltonian has the following form:

$$H = \sum_{ij} (J_{ij}^{kin} + J_{ij}^{Coulomb}) \vec{S}_i \cdot \vec{S}_j = \sum_{ij} \left(\frac{2t_{ij}^2}{U_{eff} - V_{eff}} - \beta^4 J_p^H \right) \vec{S}_i \cdot \vec{S}_j, \quad (21)$$

where $U_{eff} - V_{eff} = \alpha^4 (U_d - V_{dd}) + \frac{\beta^4 J_p^H}{2}$. In the case of a nearly 90° metal-oxygen-metal bond (Fig. 1), there is an additional ferromagnetic contribution to the total exchange interaction. The origin of this term is Hund's rule exchange interaction on the oxygen atom. As we show below, the value of $J_{ij}^{Coulomb}$ is not negligible: it can fully compensate the kinetic contribution, so that the total exchange interaction becomes ferromagnetic.

If $\beta=0$, then the Hamiltonian of Eq. (20) is the simple Hubbard model. The Coulomb parameters of the general Hamiltonian of Eq. (20) can be calculated through constrained LDA calculations or direct integration over the wave functions. In this paper, we use the constrained LDA calculation approach,¹⁰ which has given reasonable results for a number of compounds. We apply the analysis of this section to the investigation of exchange interactions in LiCu₂O₂.

III. RESULTS

A. LiCu₂O₂: LDA calculation

LiCu₂O₂ (Fig. 2) is a good example to demonstrate the competition between Coulomb $J_{ij}^{Coulomb}$ and kinetic J_{ij}^{kin} exchange interactions. Indeed, the angle of Cu–O–Cu bond in this compound is equal to 94°. This value of the angle corresponds to the middle of the ferromagnetic range,⁷ and the nearest-neighbor hopping is considerably suppressed [see Eq. (9)].

Zatsepin *et al.*¹¹ have studied the electronic structure of LiCu₂O₂ using x-ray emission and photoelectron spectroscopy as well as the first *ab initio* calculations in terms of LSDA and LSDA+U approximations. They have concluded that the results of LSDA calculations cannot reproduce the electric and magnetic properties of LiCu₂O₂. The latter are much better described by LSDA+U calculations.

Gippius *et al.*¹² have performed magnetic resonance measurements of LiCu₂O₂ in the paramagnetic and magnetically

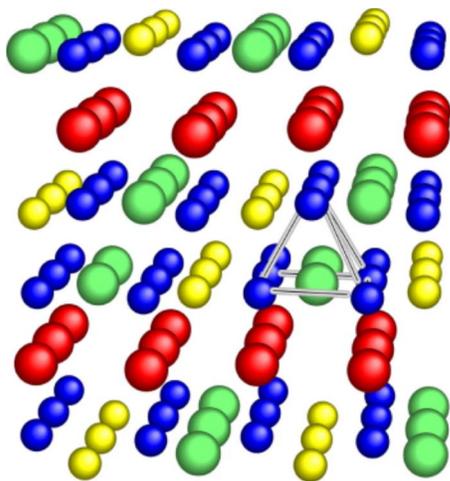


FIG. 2. (Color online) Crystal structure of LiCu₂O₂. Green (gray), red (dark gray), blue (black), and yellow (light gray) spheres are Cu²⁺, Cu⁺, O, and Li ions, respectively.

ordered states. They have also performed full potential LDA calculations. The band structure near Fermi level has been fitted by an extended tight-binding model. Using the resulting hopping parameters, the authors have estimated the values of the exchange interactions J_{ij} within a single band Hubbard model.

Experimental investigations of the magnetic ordering of LiCu₂O₂ by neutron scattering have been performed by Masuda *et al.*^{13,14} The authors have proposed different sets of exchange constants obtained by fitting the calculated spin wave dispersion relation to the experimental curves. None of the sets of parameters is in good agreement with the results of Refs. 12. One can conclude that, at present, there is no consistent theoretical and experimental description of the magnetic properties of LiCu₂O₂.

In the present paper, the electronic structure calculation of LiCu₂O₂ was performed using the tight-binding linear-muffin-tin-orbital atomic sphere approximation method in terms of the conventional local-density approximation¹⁵ and crystal structure data from Ref. 16. The band structure of LiCu₂O₂ obtained from LDA calculations is presented in Fig. 3. There are four bands near the Fermi level which are well separated from others. These bands are in good agreement with those presented in Ref. 12.

The partial density of states of LiCu₂O₂ obtained from LDA calculations is presented in Fig. 4. Copper 3*d* states of x^2-y^2 symmetry are strongly hybridized with oxygen 2*p* states. Therefore, it is more natural to use the Wannier function basis rather than atomic orbitals to describe the hybridization processes in LiCu₂O₂. We have used the projection procedure¹⁷ which is more accurate than the fitting procedure used in Ref. 12 because the Wannier states in the former method are constructed from all electron density functional theory orbitals. The resulting Wannier orbitals of LiCu₂O₂, each centered at one Cu site, are shown in Fig. 5. One can see that the Wannier orbitals strongly overlap at oxygen and Cu⁺ atoms.

As we mentioned above, one of the possible microscopic mechanisms of exchange interaction is Hubbard-like AFM

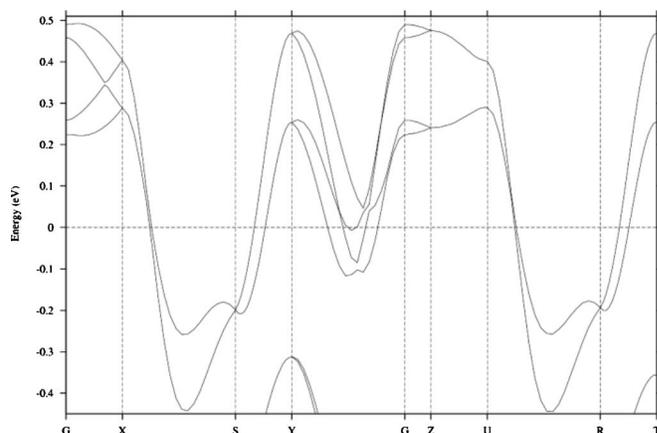


FIG. 3. Band structure of LiCu₂O₂ near the Fermi level (0 eV).

superexchange. This interaction comes from hopping processes. We have calculated the hopping integrals between orbitals of x^2-y^2 symmetry in the Wannier function basis (Table I). The corresponding interaction paths are presented in Fig. 6. One can see that for the largest hopping parameters, we have good agreement with previous band fitting results.¹² However, there are also interaction paths which were not considered before.

For nearest neighbors along the *y* axis, there is another contribution to the total exchange interaction, namely, a ferromagnetic (FM) “direct Coulomb exchange” between Wannier functions. The simplest physical representation of this situation is presented in Fig. 7. In the case of the AFM configuration, the magnetic moment of the oxygen atom located between the two copper atoms vanishes. By contrast, the magnetic moment of the oxygen atom in the FM case is not zero, and the energy gain is $J_p^H \times \beta^4$, where β is the contribution of the oxygen atomic orbital to the Wannier orbital (see previous section). In order to calculate the couplings

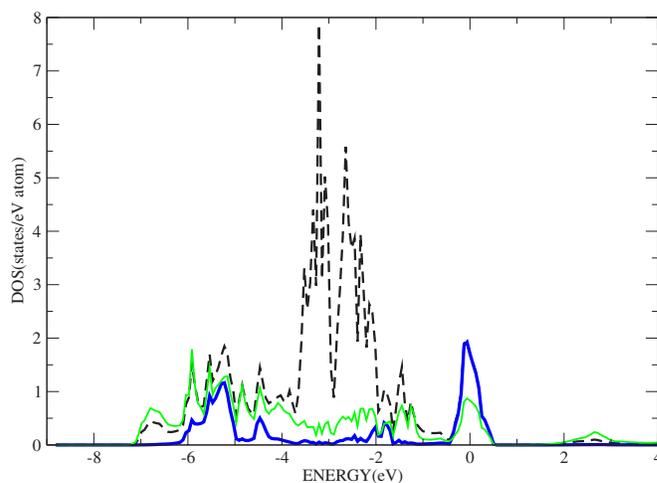


FIG. 4. (Color online) Partial density of states obtained from LDA calculations. The blue (black) solid and the dashed lines are the density of copper 3*d* states of x^2-y^2 symmetry and the total density of 3*d* states, respectively. The green (gray) solid line is the density of oxygen 2*p* states.

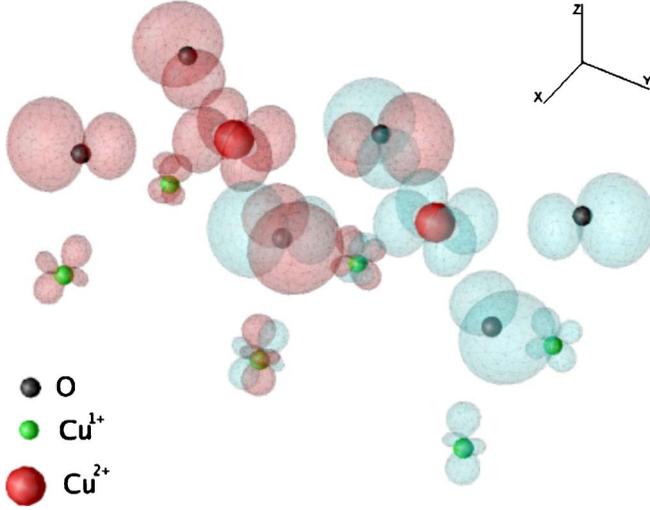


FIG. 5. (Color online) Wannier orbitals centered on neighboring copper atoms along the y axis.

between magnetic moments, we use the following expression, which comes directly from the previous section:

$$J_{ij} = \frac{2t_{ij}^2}{\alpha^4(U_d - V_{dd}) + \frac{\beta^4 J_p^H N_{ox}}{2}} - \beta^4 J_p^H N_{ox}, \quad (22)$$

where N_{ox} is the number of oxygen atoms on which the Wannier orbitals overlap. For simplicity, we neglect the intersite Coulomb interactions. The on-site Coulomb and intra-atomic exchange interaction parameters of copper atom are determined from first-principles constrained LDA calculations: $\tilde{U}_d = 10$ eV and $\tilde{J}_d^H = 1$ eV. Therefore, the effective Coulomb interaction in Eq. (22) is $U_d = \tilde{U}_d - \tilde{J}_d^H = 9$ eV. The value of the intra-atomic exchange interaction of oxygen atom J_p^H was estimated in LSDA+U calculations through the shift of oxygen $2p$ band centers for spin-up C_\uparrow and spin-down C_\downarrow : $J_p^H = (C_\uparrow - C_\downarrow)/M(O)$, where $M(O)$ is the oxygen magnetization. The obtained value of 1.6 eV is in good agreement with previous estimations.¹⁸ The value of α^2 is related to the magnetization of copper atoms. Our LSDA+U results (see Table II) show that $\alpha^2 = 0.58$. Since the magnetic moment of the oxygen atom is the result of the magnetization of two copper atoms (see Fig. 7), $\beta^2 = M(O)/2 = 0.09$. Using Eq. (22) with the parameters defined above, one can calculate the exchange couplings between magnetic moments in LiCu_2O_2 . These results are presented in Table I. One can see that the coupling

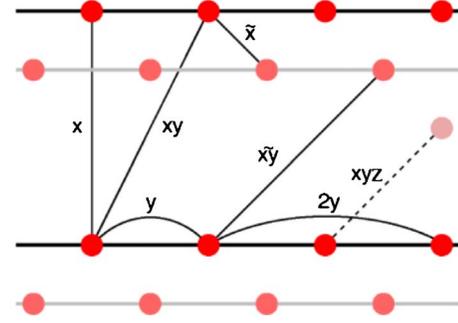


FIG. 6. (Color online) The schematic representation of interaction paths between copper atoms in LiCu_2O_2 .

between nearest neighbors along the y axis is strongly ferromagnetic. These model considerations provide a microscopic explanation of the first-principles LSDA+U results presented in the next section.

B. LiCu_2O_2 : LSDA+U calculation

The analysis of the previous section shows that one should take into account Coulomb on-site correlations and spin polarization of the oxygen atoms. This has been achieved using LSDA+U. The electronic structure of LiCu_2O_2 within LSDA+U is similar to that reported in Ref. 11. LiCu_2O_2 is an insulator with an energy gap of 0.7 eV. The values of the calculated magnetic moments (all values in units of μ_B) are 0.58 for Cu^{2+} and 0.18 for O.

The next step of the investigation is a first-principles calculation of the isotropic exchange integrals for the Heisenberg model. In order to calculate the couplings between nearest neighbors along the y axis, one should use a method which takes into account the change of magnetization of the oxygen atoms. The most appropriate one is the method¹⁹ in which the magnetic interaction J_{ij} is estimated through the total energy difference between the ferromagnetic and antiferromagnetic first-principles solutions (obtained, for instance, using the LSDA+U approach). The Heisenberg Hamiltonian describing the interaction between spins in the unit cell (Fig. 8) is given by

$$H = 2zJ\vec{S}_1 \cdot \vec{S}_2, \quad (23)$$

where z is number of nearest neighbors. The corresponding total energies of the ferromagnetic and antiferromagnetic configurations of two spins are given by

TABLE I. Calculated values of hopping parameters t_{ij} between x^2-y^2 orbitals of copper atoms for the one-orbital model and estimated exchange interaction parameters using Eq. (22) (in meV).

	y	$2y$	x	\tilde{x}	xy	$\tilde{x}\tilde{y}$	xyz
$ t_{ij} $	54	99	67	5.3	33	28	32
$ t_{ij} ^a$	64	109	73	18	25		
$J_{ij}^{x^2-y^2}$	-24	6.5	3.0	0	0.7	0.5	0.7

^aReference 12.

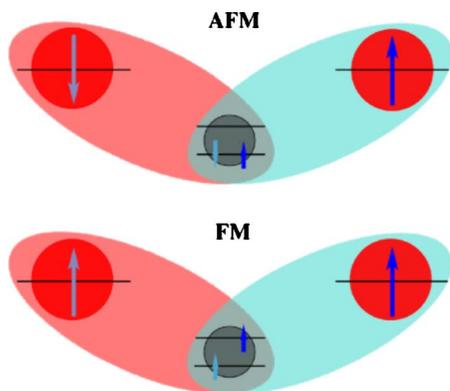


FIG. 7. (Color online) Schematic representation of AFM and FM configurations of magnetic moments at Wannier orbitals.

$$E_{\text{FM}} = 2zJS^2 \quad (24)$$

and

$$E_{\text{AFM}} = -2zJS^2. \quad (25)$$

Therefore, the exchange interaction J is expressed in the following form:

$$J = \frac{E_{\text{FM}} - E_{\text{AFM}}}{4zS^2}. \quad (26)$$

We have performed calculations for the $(1 \times 2 \times 1)$ supercell in ferromagnetic and antiferromagnetic configurations. The results are presented in Table II. One can see that in the case of the $(1 \times 2 \times 1)$ supercell, the magnetization on oxygen atoms for the antiferromagnetic configuration is zero, whereas the compensation of magnetization on oxygen atoms in the ferromagnetic configuration does not take place. Therefore, first-principles LSDA+U calculations support the model considerations presented in the previous section. The ferromagnetic configuration has a lower energy than the antiferromagnetic one. Using Eq. (26) with $z=2$ and $S=\frac{1}{2}$, we get $J_{ij}^y = -19.1$ meV.

In order to calculate the other magnetic interactions, we have implemented the Green's function method.²⁰ According to this method, we determine the exchange interaction parameter between copper atoms via the second variation of the total energy with respect to small deviations of the magnetic moments from the collinear magnetic configuration. The exchange interaction parameters J_{ij} for the Heisenberg model [Eq. (3)] with $S=\frac{1}{2}$ can be written in the following form:^{20,21}

TABLE II. Results of LSDA+U calculations for the supercell $1 \times 2 \times 1$. $M(\text{Cu}^{2+})$ and $M(\text{O})$ are magnetic moments of copper and oxygen atoms, respectively. E_{tot} is the relative total energy (in meV) normalized to 4 (number of copper pairs in unit cell).

	$M(\text{Cu}^{2+})$	$M(\text{O})$	E_{total}
FM	0.58	0.18	0
AFM	0.58	0	38

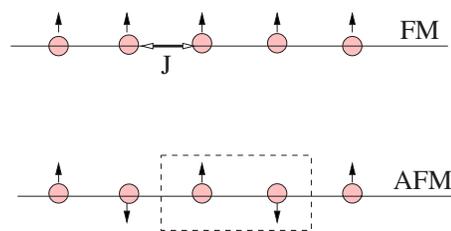


FIG. 8. (Color online) Ferromagnetic and antiferromagnetic configurations in an infinite chain with identical nearest-neighbor exchange interaction J . The dashed line rectangle denotes the unit cell used for the mapping between the Heisenberg model and the first-principles LSDA+U approach.

$$J_{ij} = \frac{1}{\pi} \int_{-\infty}^{E_F} d\epsilon \text{Im} \sum_{\substack{m, m' \\ m'', m'''}} (\Delta_i^{mm'} G_{ij\downarrow}^{m'm''} \Delta_j^{m''m'''} G_{ji\uparrow}^{m'''m}),$$

where $m(m', m'', m''')$ is the magnetic quantum number, the on-site potential $\Delta_i^{mm'} = H_{ii\uparrow}^{mm'} - H_{ii\downarrow}^{mm'}$, and the Green's function is calculated in the following way:

$$G_{ij\sigma}^{mm'}(\epsilon) = \sum_{k,n} \frac{c_{i\sigma}^{mn}(k) c_{j\sigma}^{m'n^*}(k)}{\epsilon - E_{\sigma}^n}. \quad (27)$$

Here, $c_{i\sigma}^{mn}$ is a component of the n th eigenstate, and E_{σ}^n is the corresponding eigenvalue.

Our results are summarized in Table III. One can see that LSDA+U results are in good agreement with those obtained in our model analysis (see previous section) and disagree with previous theoretical estimates.¹² This agreement between the model analysis and LSDA+U results is very encouraging, but clearly the ultimate test is to compare them with experiments.

In that respect as well, the present results are a clear improvement with respect to previous estimates. Indeed, in contrast to the results of paper of Ref. 12, the ratio between the strongest couplings $J_{ij}^{2y}/J_{ij}^y = -0.5$ is in good agreement with the results of the neutron scattering experiments of Ref. 14. This ratio is very important since it controls the pitch vector \vec{q} of the helimagnetic state of LiCu_2O_2 . The agreement is not perfect; however, our estimates are about twice larger than the integrals deduced from experiments. Interest-

TABLE III. Values of exchange interactions J_{ij} between magnetic moments of LiCu_2O_2 compound (in meV).

	y	$2y$	x	\tilde{x}	xy	\tilde{xy}	xyz
J_{ij}^a	-19.1	9.8	3.8	0	1.0	1.0	0.4
J_{ij}^b	-4	7.2	2.8	0.2	0.4		
J_{ij}^c	-5.95	3.7	0.9	3.2			
J_{ij}^d	-7.0	3.75	3.4	0			

^aThis work.

^bReference 12.

^cReference 14, Model 1.

^dReference 14, Model 3.

ingly enough, it is possible, using the simple microscopic model, Eq. (22), to identify the source of discrepancy between LSDA+U and experimental results. Indeed, the second term of Eq. (22) is very sensitive to the choice of β^2 . For example, $\beta^2=0.08$ leads to $J_{ij}^y=-18.5$ meV, which is in excellent agreement with LSDA+U results. For $\alpha^2=0.65$ and $\beta^2=0.06$, we obtain the following set of model exchange interactions: $J_{ij}^y=-10$ meV, $J_{ij}^{2y}=5$ meV, $J_{ij}^x=2.3$ meV, $J_{ij}^{xy}=0.6$ meV, $J_{ij}^{xz}=0.4$ meV, and $J_{ij}^{yz}=0.5$ meV. These model magnetic couplings are in good agreement with the experimental results.

This proves the sensitivity of the results to the precise form of the Wannier functions. Now, it is well known that several sets of localized functions can be used to describe a given band,²² and the question of which Wannier functions should be used in the case of the determination of magnetic exchange, a point already raised by Anderson a long time ago,³ has not been settled yet. The present results call for further investigation of that issue.

Another possible way to improve the agreement between theory and experiment could be the following. From the experimental point of view, LiCu₂O₂ has spiral magnetic order in the ground state. Our study was performed for collinear magnetic configurations. Therefore, it would be more natural to calculate the exchange couplings using the magnetic structure observed experimentally. This goes beyond the scope of the present paper, however.

IV. DISCUSSION

In conclusion, we have presented an analysis of the Hubbard model in the case of nearly 90° metal-oxygen-metal

bonds dealing explicitly with Wannier orbitals. This has allowed us to derive an explicit expression of exchange integrals entirely in terms of parameters that can be obtained from constrained LDA and LSDA+U. This expression can serve to interpret LSDA+U *ab initio* estimates of the exchange integrals and to establish their reliability. The analysis has been applied to the investigation of the magnetic couplings of LiCu₂O₂, allowing us to reach qualitative agreement with experiments, and to gain insight into the nature of exchange in that system. Because of the formation of a strongly hybridized, and energetically isolated combination of $3d_{x^2-y^2}$ and $2p$ orbitals, a large moment is transferred to the O ions, and the magnetization of oxygen atoms has been proven to be the main source of ferromagnetism in LiCu₂O₂.

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