In-gap excitation effect on a superexchange in La$_2$CuO$_4$ by creating nonequilibrium photoexcited centers

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We propose a multielectron approach to calculate superexchange interaction in magnetic Mott-Hubbard insulator La$_2$CuO$_4$(further La214) that allows to obtain the effect of optical pumping on the superexchange interaction. We use the cell perturbation theory with exact diagonalization of the multiband $pd$ Hamiltonian inside each CuO$_6$ unit cell and treating the intercell hopping as perturbation. To incorporate effect of optical pumping we include in this work the excited single-hole local states as well as all two-hole singlets and triplets. By projecting out the interband intercell electron hopping we have obtained the effective Heisenberg-like Hamiltonian with the local spin at site $R_i$, being a superposition of the ground and excited single-hole states. We found that antiferromagnetic contribution to the exchange energy in La214 will increase in accordance to $\sim 4 \cdot 10^{-3} eV(\%)^{-1}$ at the resonance light occupation of the excited single hole in-gap state.

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I. INTRODUCTION

Understanding the energy transfer between charge, orbital, and spin degrees of freedom is the important problem for many fields of solid state physics. Since the first experiments\textsuperscript{1,2} optical excitation of electronic spins and ultrafast magnetization dynamics have obtained much attention.\textsuperscript{3,4} A possibility to control the exchange interaction by light is important in many physics areas, from quantum computing\textsuperscript{5,6} to strongly correlated materials\textsuperscript{7,8}. In many experiments the effect of optical pumping on the exchange interaction in the Mott-Hubbard insulators like manganites\textsuperscript{9,10} ferroborates\textsuperscript{11,12} TmFeO$_3$, ErFeO$_3$\textsuperscript{13} etc. has been found. The origin of interatomic exchange interaction in all these oxides is related to the superexchange mechanism via oxygen.\textsuperscript{14} There are some simplified model calculations of the superexchange interaction under light irradiation in the three atomic model\textsuperscript{15,16} that in complete theory should be extended to the crystal lattice. The calculation of the superexchange interaction for the crystal lattice can be easily done for some simplified model like the Hubbard model.\textsuperscript{17,18} Within the LDA+DMFT approach the first-priciple calculations of the exchange interaction in correlated materials has been carried out in the work.\textsuperscript{19} An idea of generalization of this approach to nonequilibrium optically excited magnets has been also proposed in work.\textsuperscript{20} Without any practical conclusions. Nevertheless up to now the microscopic calculation of the superexchange interaction in La214 under light irradiation is absent.

It is known that in the Hubbard model the superexchange $J$ results from the projecting out the interatomic hopping $t^{ab}$ accompanying the interband excitation from the low Hubbard band (LHB=$a$) to the upper Hubbard band (UHB=$b$). Due to the large insulator gap $U >> t^{ab}$ the interband excitation requires too much energy, and only virtual interband excitations from LHB to UHB and back are possible providing the exchange coupling $J$ $\sim$ $(t_{ab})^2/U$.\textsuperscript{17} The convenient mathematical tool for projecting out the irrelevant at large $U$ UHB is given by the projection operators.\textsuperscript{17} In this paper we calculate the exchange interaction in La214 under optical pumping within the hybrid LDA+GTB (generalized tight binding) approach. Previously we have carried out similar calculation for La214 in the ground state.\textsuperscript{21} The LDA+GTB method allows to calculate the electronic structure of strongly correlated oxides like cuprates\textsuperscript{22} manganites\textsuperscript{23} boroxide\textsuperscript{24,25} and cobaltates.\textsuperscript{26} We use the cell perturbation theory with exact diagonalization of the multiband $pd$- Hamiltonian inside each CuO$_6$ unit cell with \textit{ab initio} calculated parameters and treating the intercell hopping as perturbation. We restrict ourselves here by the antiferromagnetic undoped cuprate La214, nevertheless all ideas and methods used may be applied to any Mott-Hubbard insulator. To incorporate effect of optical pumping we include in this work the excited single-hole local states as well as all excited two-hole singlets and triplets. It requires a generalization of the projection operators used here in comparison to the papers.\textsuperscript{17,21} Finally we have obtained the modification of exchange interaction induced by the light irradiation.

II. EFFECTIVE SUPEREXCHANGE HAMILTONIAN

In the GTB approach one can assume that the quasiparticles are unit cell excitations which can be represented graphically as single-particle excitations (transitions) between different sectors $N_h = \ldots(N_0 - 1), N_0, (N_0 + 1), \ldots$ of the configuration space of the unit cell ($N_0$ is hole number per cell in the undoped material, see Fig 1).\textsuperscript{17} Each of these transitions forms a $r$-th quasi-
particle band, where the vector band index \( r = \{ i, i' \} \) in configurational space numerates the initial \( i \) and final \( i' \) many-electron states in the transition. The transitions, the number of electrons increasing or decreasing, form the conduction or valence bands, respectively. For undoped La214 due to electroneutrality the proper subspace is \( d9p6 + d10p5 \) with one hole per CuO\(_2\) cluster, it has one hole, \( N_0 = 1 \). The hole addition requires \( N_+ = 2 \) states \( d9p5 + d10p4 + d8p6 \). The hole removal results in \( N_- = 0 \) states that for cuprates is given by a hole vacuum \( d10p6 \). In the LDA+GTB method the Hamiltonian parameters are calculated ab initio and the GTB cell approach is used to take into account strong electron correlations explicitly. A crystal lattice is divided into unit cells, so that the Hamiltonian is represented by the sum \( H_0 + H_1 \), where the component \( H_0 \) is the sum of intracellular terms and component \( H_1 \) takes into account the intercell hoppings and interactions. The component \( H_0 \) is exactly diagonalized. The exact multielectron cell states \( |i\rangle \) and energies \( \xi_i \) are determined. Then these states are used to construct the Hubbard operators of the unit cell \( \tilde{R}_f : X_{i,i'}^e = |i\rangle \langle i'| \), where the meaning of the indexes \( i \) and \( i' \) is clear from Fig. 1.

\[
H_0 = \sum_f \left\{ \varepsilon_0 X_{f0}^{00} + \sum_{l,\sigma} (\epsilon_l - \mu) X_{f,l}^{l,l,\sigma} + \sum_{\nu} (\nu - 2\mu) X_{f}^{\nu,\nu} \right\} 
\]

(1)

is the sum of intracellular terms and component \( H_1 \) takes into account the intercell hoppings and interactions. Here

\[
H_1 = \sum_{fg} \sum_{\lambda \lambda'} t^{\lambda \lambda'}_{fg} c_{\lambda \sigma}^+ c_{\lambda' \sigma} + h.c.
\]

(2)

where \( t^{\lambda \lambda'}_{fg} \) is the matrix of hopping integrals, and

\[
t^{\lambda \lambda'}_{fg} = \sum_{\lambda \lambda'} \sum_{\sigma} t^{\lambda \lambda'}_{fg} \times \left[ \gamma_{\lambda \sigma}^{l \lambda \lambda'} (r) \gamma_{\lambda' \sigma} (r') + \gamma_{\lambda' \sigma}^{l \lambda \lambda'} (r) \gamma_{\lambda \sigma} (r') \right],
\]

(3)

where matrix elements:

\[
\gamma_{\lambda \sigma} (r) = \langle (N_+, M'_\lambda S'_\lambda)_{\mu} | c_{\lambda \sigma} | (N_0, M_s)_{l} \rangle \times \delta (S'_\lambda, S \pm |\sigma|) \delta (M'_\lambda, M + \sigma),
\]

(4)

Consideration is restricted by the case with one hole per cell \( N_0 = 1 \) in the undoped materials and an arbitrary number \( N_\lambda \) of the occupied \( \lambda \) orbitals, i.e. number of electrons \( N_e = 2N_\lambda - 1 \). This is relevant for the high-\( T_c \) cuprates. In this case of one hole per cell, the \( |(N_0, M_s)_{l}| \) cell states are a superposition of different hole configurations of the same orbital \( l \) symmetry:

\[
|(N_0, M_s)_{l}\rangle = \sum_{\lambda} \beta_l (h_\lambda) |h_\lambda, M_s\rangle
\]

(5)

Thus, there are one-hole spin doublet states, \( C_{2N_\lambda}^{1} = 2N_\lambda \), where \( C_n^m \) is the number of combinations. Besides,
and \( \mu (1 \leq \mu \leq N_\mu) \) runs over all electron states in the configuration spaces in Fig.1. Using a set of generalized operators

\[
p_0 = \left( X_1^{00} + \sum_i X_i^{l_l} \right) \left( X_j^{00} + \sum_i X_j^{l_l} \right),
\]

and

\[
p_\mu = X_i^{\mu \mu} + X_j^{\mu \mu} - \sum_\nu X_i^{\mu \nu} X_j^{\nu \nu}
\]

with \( \nu(\nu) = 1, 2, ..., N_\mu \), we can identify the contribution to the superexchange from the interband transitions. As will be seen below, a generalized approach with the operators \( P_0 \) and \( P_\mu \) is a projection operator \( p_0 = p_0 \) and \( (p_0^2 = p_0) \). These operators also form a complete and orthogonal system, \( p_0 + \sum_{\mu=1}^{N_\mu} p_\mu = 1, p_0 p_\mu = 0 \) and \( p_\mu p_\nu = \delta_{\mu \nu} p_\mu \). We highlight the diagonal and off-diagonal matrix elements in expression:

\[
H = (H_0 + H_1^n) + H_1^{out},
\]

According to the work we introduce a Hamiltonian of the exchange-coupled \((ij)\)-th pair: \( h = (h_0 + h_1^n) + h_1^{out} = H_{ij} \), where \( H = \sum_{ij} H_{ij} \) and

\[
h_0 + h_1^n = p_0 h p_0 + \sum_{\mu \nu} p_\mu h p_\nu
\]

and

\[
h_1^{out} = p_0 h \left( \sum_\mu p_\mu \right) + \left( \sum_\mu p_\mu \right) h p_0
\]

are intra- and inter-band contributions in \( H_j \) respectively. We perform the standard unitary transformation to project out the interband hopping and to derive superexchange interaction

\[
\hat{h} = e^{G} \hat{h} e^{-G},
\]

where the matrix \( G \) satisfies the equation

\[
p_0 \hbar \left( \sum_\mu p_\mu \right) + \left( \sum_\mu p_\mu \right) h p_0 +
\]

\[
+ \frac{1}{2} \left[ G, \left( p_0 h p_0 + \sum_{\mu \nu} p_\mu h p_\nu \right) \right] = 0,
\]

and transformed Hamiltonian are given by

\[
\hat{h} \approx \left( p_0 h p_0 + \sum_{\mu \nu} p_\mu h p_\nu \right) +
\]

\[
+ \frac{1}{2} \left[ G, \left( p_0 h \sum_\mu p_\mu + \sum_{\mu \nu} p_\mu h p_\nu \right) \right] \tag{14}
\]

where the contributions from inter-band transitions can be calculated as:

\[
p_0 h \left( \sum_\mu p_\mu \right) = \sum_{l'l'} t_{ij}^{l'l' \mu \nu} X_i^{l'0} X_j^{l' \mu}
\]

\[
\left( \sum_\mu p_\mu \right) h p_0 = \sum_{l'l'} t_{ij}^{l'0 \mu \nu} X_i^{l0} X_j^{l' \mu}
\]

Note, due to the absence of additivity over \( l \)-number of the excited state in the projective operator \( p_0 \), the solution of Eq.13 has the form

\[
G = \sum_\mu \sum_{l'l'} t_{ij}^{l'l' \mu \nu} \left( X_i^{l' \mu} X_j^{l0} \right)
\]

\[
\Delta_{ll'} = \varepsilon_0 + \varepsilon_\mu - (\varepsilon_{l} + \varepsilon_{l'})
\]

and the commutator in Eq.14 can be represented as

\[
\delta h = \frac{1}{2} \sum_{\mu \nu} \{ [G_{\nu}, (p_0 h p_\mu + p_\mu h p_0)] \} =
\]

\[
= \frac{1}{2} \sum_{\mu \nu} \left\{ \left[ \sum_{l'l'} \Delta_{ll'} t_{ij}^{l'l' \mu \nu} \left( X_i^{l' \mu} X_j^{l0} - X_i^{l0} X_j^{l' \mu} \right) \right] \sum_{kk'} t_{ij}^{l0, k' \mu} \left( X_i^{0k} X_j^{k' \mu} + h.c. \right) \right\}
\]

\[
\tag{17}
\]

The right part of the expression (14) for effective Hamiltonian \( h \) can now be derived explicitly. Calculating commutator in the above expression (17) hence we obtain the effective Hamiltonian for the exchange-coupled \((ij)\)-th pair as
\[ \delta \hat{h} = \sum_{i, l' k' \sigma'} \sum_{\mu \nu} \left( \frac{\delta_{i,j}}{\Delta_{l' \mu}} \right) \delta_{\mu \nu} \left\{ X_{i}^{\dagger, k^\prime} X_{j}^{l', k^\prime} + X_{i}^{l, k} X_{j}^{l', k^\prime} - X_{i}^{l, k} X_{j}^{l', k^\prime} \right\} + \sum_{i, l' k' \sigma'} \sum_{\mu \nu} \left( \frac{\delta_{i,j}}{\Delta_{l' \mu}} \right) \delta_{k,l'} \left( X_{i}^{00} X_{j}^{\mu \nu} + X_{i}^{\mu \nu} X_{j}^{00} \right) = \delta \hat{h}_{s-ex} + \delta \hat{h}_{\rho}, \]

(18)

and only a first contribution includes superexchange interaction \( \delta H_{s-ex} = \sum_{i,j} \delta \hat{h}_{s-ex} \):

\[ \delta H_{s-ex} = \sum_{i,j} \sum_{l' k' \sigma'} \sum_{\mu} \frac{2 \left( \delta_{i,j} \right)^{2}}{\Delta_{l' \mu}} \left( S_{i} S_{j} - \frac{1}{4} n_{i} n_{j} \right), \]

(19)

where \( S_{i}^{+} = X_{i}^{l, l_{i}}, 2 S_{i}^{-} = \sum_{\sigma} \left( X_{i}^{\sigma, l_{i}} - X_{i}^{l_{i}, \sigma} \right), Z_{i}^{+} = \hat{S}_{i} X_{i}^{l_{i}} \) and \( y_{i}^{-} = n_{i} X_{i}^{l_{i}} \) are a spin-exciton and electron-exciton operators at the \( i \)-th cell. For simplicity, we assumed that \( X_{i}^{l, l_{i}} = X_{i}^{l_{i}, l} = X_{i}^{l, l'}. \) Note that the contribution in Eq. (19) at \( l = k \) and \( l' = k' \)

\[ \delta H_{s} = \sum_{i,j} \sum_{l' \mu} \sum_{\mu} \frac{2 \left( \delta_{i,j} \right)^{2}}{\Delta_{l' \mu}} \left( \hat{S}_{i} \hat{S}_{j} - \frac{1}{4} n_{i} n_{j} \right), \]

(20)

where \( \hat{S}_{i} \hat{S}_{j} = \frac{1}{2} \sum_{\sigma} \left( X_{i}^{\sigma \sigma} X_{j}^{\sigma' \sigma'} - X_{i}^{\sigma \sigma} X_{j}^{\sigma' \sigma'} \right) \), is an analogue of the conventional superexchange with exchange constant \( J_{i,j}^{ll'} = 2 \sum_{\mu} \left( \delta_{i,j} \right)^{2} / \Delta_{l' \mu}. \)

\[ \delta H_{s-ex} = -\frac{1}{2} \sum_{i,j} \sum_{l'} \left( J_{i,j}^{ll'} \right) \left( X_{i}^{l, l_{i}} \right) \left( X_{j}^{l', l_{j}} \right) \approx -\frac{zN}{2} \left( J_{i,j}^{l_{i}l_{j}} p_{l_{i}l_{j}}^{2} + 2 \sum_{l \neq l_{i}} J_{i,j}^{l_{i}l_{j}} p_{l_{i}} + \sum_{l, l' \neq l_{i}} J_{i,j}^{l_{i}l_{j}} p_{l_{i}} p_{l_{j}} \right), \]

(21)

An exciton energy can not exceed the semiconductor gap \( E_{g} = \left[ \epsilon_{0} + \epsilon_{0} - 2 \epsilon_{l_{i}} \right] \), because of the divergence of superexchange contributions \( \delta H_{s-ex} \rightarrow \infty \) at \( \delta_{l_{i}} \rightarrow E_{g}. \) At \( \delta_{l_{i}} > E_{g} \) the exciton cell state decays into an electron-hole pair state. Therefore photocarriers are generated under light pumping with a frequency \( h\nu \) higher than the absorption edge, and the superexchange on the photoexcited intracell states can be calculated in approach (19) only at the light pumping with the frequency in the transparency region of the material. It’s partly colored magnetic nondoped materials.

Let’s obtain the contribution (20) to the exchange energy of the system in the framework of mean-field approximation.

The standard mechanism of the superexchange in the ground state is shown in Fig. 2a, while the superexchange via optically excited term is shown in Fig. 2b, the formation of spin-exciton interaction that is beyond the Heisenberg model is shown in Fig. 2c.
III. RESULTS FOR COPPER OXIDE La214

We test the approach on the high-$T_c$ parent material La214. At the LDA parameters of Hamiltonian taken from $J_{bb} \approx 0.15\ eV$, $\delta_{b1} = \delta_{ab} = 1.78\ eV$, $E_g = 2.00\ eV$, and the $r = \{2b_1, A_1\}$ - band index $\{1, \mu = 1\}$ first removal electron state.

Using the exact diagonalization procedure with LDA parameters, one obtains the weights $\alpha_l, \beta_l$ and $A_\mu, B_\mu$ at the doublet and singlet, triplet states:

\[
(N_0, M_S)_{l=1} = |2b_1\rangle = \sum_{\lambda = d_x, p_x, a} \beta_{l=1}(h_\lambda) |h_\lambda, \sigma_+^{a1}_l\rangle; (N_0, M_S)_{l=2} = |2a_1\rangle = \sum_{\lambda = d_x, p_x, a} \alpha_{l=2}(h_\lambda) |h_\lambda, \sigma_+^{a1}_l\rangle, \tag{22}
\]

\[
(N_+, M_{S'})_{\mu=1} = |A_1\rangle = \sum_{\lambda, \lambda' = b, d_x, a, p_x, d_z} A_{\mu=1}(h_\lambda, h_{\lambda'}) |h_\lambda, h_{\lambda'}, 0\rangle, \\
(N_+, M_{S'})_{\mu=2} = |3B_1\rangle = \sum_{\lambda = b, d_x} \sum_{\lambda' = a, p_x, d_z} B_{\mu=2}(h_\lambda, h_{\lambda'}) |h_\lambda, h_{\lambda'}, M_1\rangle, \tag{23}
\]

where $h_b$ and $h_{d_x}$ are the holes in the $b$-symmetrized cell states of oxygen and $d_x^2-y^2$ cooper states of the CuO$_2$ layer, respectively.

Because of $\delta_{ab} < E_g$, just two contributions from the doublets $|2a_1\rangle$ and $|2b_1\rangle$ are available in the sum \[15\] over $l$. Due to the symmetry CuO$_2$ layer $\gamma_\lambda(\{2a_1, A_1\}) = 0$ at any $\lambda$ and therefore $t_{ij}^{b0,A} = t_{ij}^{a0,A} = 0$. Thus we evaluate the contribution \[22\] like the next:

\[
\langle \delta H_{\text{ex}} \rangle = -\frac{ZN}{2} \sum_{\mu} \left[ \frac{(t_{b0,b_1})^2}{\Delta_{b_1}} p_b^2 + 2\left(\frac{(t_{a0,b_1})^2}{\Delta_{a_1}} + \frac{(t_{a0,b_1})^2}{\Delta_{b_1}} \right) p_a p_b + \frac{(t_{a0,a_1})^2}{\Delta_{a_1}} p_a^2 \right] \sim \]

\[
\sim -\frac{ZN}{2} \left[ 0.15(eV) \cdot p_b^2 + 2\frac{(t_{a0,b_1})^2}{\Delta_{b_1}} p_a p_b \right] \tag{24}
\]

Without external irradiation $p_b = 1, p_a = 0$, and Eq. \[24\] results in the exchange interaction $J_{bb}$ (the first term in the right side of Eq. \[24\]) in the ground state obtained earlier in the work \[15\]. What are the modifications
of the exchange interaction that we can observe in L214 under resonance light pumping? The answer to this question depends on the ratio of the exchange interaction in the ground and excited states. Depletion of the ground state $p_b = 1 - x$ decreases $J_{bb}$, and a new contribution $J_{ba}$ via excited orbital $a_1$ appears (see Fig.2). Using LDA parameters, and summing over all $\mu$ in the second term in Eq. (24), we finally obtain the result shown in Fig.3. So most likely superexchange contribution (24) will increase at any small population of excited states in La214 by a factor of $\sim 4 \cdot 10^{-3} eV(\%)^{-1}$.

IV. CONCLUSION

In summary, we would like to emphasize that optical pumping results in the occupation of some high energy multielectron states with different overlapping of the excited wavefunctions between neighboring ions vs the ground state orbitals. It is evident that this pumping results in the modification of the exchange interaction. Nevertheless an accurate calculation of a large number of contributions from different multielectron excited states is not a trivial theoretical problem. The gain of the Hubbard operators approach is the ability to control each excited state and its contribution to the ionic spin and orbital moment. Our approach to the exchange interaction via excited states is just a straightforward generalization of the previously developed projection technique for the Hubbard model and for the ground state of La214 within the realistic multiband pd model. The obtained effective Hamiltonian contains not only spin-spin interactions via excited states but also more complicated exchange interactions accompanied with exciton or bi-exciton that are beyond standard Heisenberg model.

For undoped insulating cuprates the theory results in a prediction of the antiferromagnetic coupling strengthening proportional to the concentration of the excited states At the concentration of excited states 1% an increased exchange interaction is estimated by the magnitude $\sim 40K$. For simplicity we have assumed stationary pumping with resonance absorption. Then the spectral dependence of the modified exchange coupling should coincide with the $d - d$ absorption spectrum. Due to the short time of the local electronic excitations $\leq 1$ (fs) a dynamics of exchange interaction for the time intervals more then 10 (fs) probably can be also treated in our approach. It is evidently that the spin-exciton effects found here may be important in the dynamical regimes.

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