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Effects of Optical Intra-gap Transitions on Superexchange Interaction in La_2CuO_4 with Nonequilibrium Photoexcited Centers

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We investigated the effects of excited many-electron states in the optical control of the magnetic state in undoped Mott-Hubbard insulator. To derive the spin Hamiltonian in material under optical pumping we have used many-electron approach based on the X-operator representation. Extending the projection operators approach on arbitrary energy spectra of the Mott-Hubbard insulator, we obtained the Hamiltonian of superexchange interaction in analytical form. The Hamiltonian includes the spin-exciton variables which are usually missing in discussion on the magnetic response to optical pumping, and is not additive over contributions from the ground and optically excited states. As a test, a microscopic background for the optical induced superexchange was analyzed in La_2CuO_4 (further La214).

Keywords: superexchange, optically excited states, Mott-Hubbard insulator.
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Introduction

An ultrafast optical manipulation of magnetic order is very actively developing area nowadays. A number of experiments with femtosecond laser pumping of magnetic insulators has revealed unusual magnetic response when the photon energy $h\nu$ is less then absorption edge E_g [1]. In the absence of the interband excitations these effects results from the intraatomic d-d excitations which form the weak and narrow absorption bands inside the optical gap of the crystal. Such optical spectra are typical for the Mott-Hubbard insulators like La214 [2] and other transition metal oxides [3, 4]. These effects are beyond the conventional single electron approach to the

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electronic structure of solids based of different implementation of the density functional theory. Nevertheless, for the materials in the ground state, the exchange interactions has been studied in the ab-initio approach (e.g. in works [5–7]), but the initial many-electron representation still looks more natural and short way to the final result when the material is in an optically excited state.

The intra-atomic optical spectra can be obtained in many-electron approach, where the quasiparticles are just the electron excitations between the many-electron states of relevant symmetry and with different numbers of particles, for La214 and it was demonstrated in the works [8, 9]. The undoped Mott-Hubbard insulators, unlike conventional materials have both a singlet and degenerate ground cell states [10].

It is essential that the optically excited states would be introduced to the superexchange theory together with the ground state on equal footing, because the intracell transitions induced by optical pumping occurs much faster than superexchange interaction ($\Delta\nu/W \ll 1$, $\Delta\nu$ is optical transition width). Therefore, in the process of superexchange the spin and interaction between them can be modified or even break down. A general theory with a fixed spin and orbital degrees of freedom (e.g. the work [11]) is a good starting microscopic point to derive anisotropy effects in the optical absorption at $\nu \sim E_g$ shows that individual contributions to superexchange are given by virtual charge transfer excitations only. Because, it is necessary to derive the microscopic Hamiltonian here, step by step, where the superexchange constant must be redefined, if possible. To achieve this, there are two acceptable approaches to study the superexchange interaction. First is the calculation with the intermediate states which arise through hopping from ligand to ligand (e.g. between the oxygens) in the perturbation theory of higher order than the fourth [12]. Another approach is the cell perturbation theory taking into account all the excited states. The latter seems more appropriate [12–15], where, however, it is necessary to work with a large number of the virtual charge transfer excitations [16]. Being based on the X-operators representation [17] the LDA+GTB approach [8, 18] includes the whole spectrum of localized many-electron states both ground and excited states with different spin and orbital moments. Nevertheless, for the materials in the ground state, the exchange interactions has been studied in the ab-initio approach It's important to understand further that the excited states in our work distinct from the virtual "excited states" occurring in a perturbation theory of superexchange [19]. These excited states may be occupied due to the optical pumping at the frequencies of specific *d*-*d* excitations only. As a result, the exchange interaction can be modified. Despite the simplicity of the idea, the magnitude and sign of the pumping effect on the exchange interaction depends on the orbital and spin symmetry of the many-electron excited states.

In this work a Hamiltonian of superexchange interaction was derived in analytical form due to the many-electron approach based on the X-operator representation [17] and technique of projection operators [20] generalized on arbitrary quasiparticle energy spectra of Mott-Hubbard insulator. The Hamiltonian can be reduced to the usual Heisenberg type only under additional assumptions. It has spin-exciton variables missing in the discussion on the optical pumping effects. The superexchange is also not additive over the states of transition element, in contrast the contributions from the virtual "excited states". The superexchange in unexcited La214 is in accordance with the phenomenological Goodenough–Kanamori rules because 180°-superexchange is antiferromagnetic (AFM), and ferromagnetic (FM) contribution from the virtual "excited states" is very small. The induced AFM contribution to the mean energy will increase $\sim 4 * 10^{-3} eV/(\%)$ at the optical induced occupation (in %) of the excited states.

1. General theory of superexchange in Mott-Hubbard materials with optically excited states

In this section, we apply the method of projection operators [20] to derive an effective spin Hamiltonian from Hamiltonian of the pd-model with any number of orbitals $\hat{H} = \hat{H}_d + \hat{H}_p + \hat{H}_{pp} + \hat{H}_{pd}$, where

$$\begin{aligned}
\hat{\mathrm{H}}_d &= \sum_{f\lambda\sigma}\Bigg[(\varepsilon_\lambda-\mu)\,d^+_{\lambda f\sigma}d_{\lambda f\sigma}+\tfrac{1}{2}U_\lambda n^\sigma_{\lambda f}n^{-\sigma}_{\lambda f}+\\
&\qquad+\sum_{\lambda'\sigma'}\left(-J_d d^+_{\lambda f\sigma}d_{\lambda f\sigma'}d^+_{\lambda' f\sigma'}d_{\lambda' f\sigma}+\sum_{f'}V_{\lambda\lambda'}n^\sigma_{\lambda f}n^{\sigma'}_{\lambda' f'}\right)\Bigg],\\
\hat{\mathrm{H}}_p &= \sum_{m\alpha\sigma}\left[(\varepsilon_\alpha-\mu)\,p^+_{\alpha m\sigma}p_{\alpha m\sigma}+\tfrac{1}{2}U_\alpha n^\sigma_{\alpha m}n^{-\sigma}_{\alpha m}+\sum_{\alpha' m'\sigma'}V_{\alpha\alpha'}n^\sigma_{\alpha m}n^{\sigma'}_{\alpha' m'}\right], \qquad (1)\\
\hat{\mathrm{H}}_{pd} &= \sum_{mf}\sum_{\alpha\lambda\sigma\sigma'}\left(t_{\lambda\alpha}p^+_{\alpha m\sigma}d_{f\lambda\sigma}+hc.+V_{\alpha\lambda}n^\sigma_{\alpha m}n^{\sigma'}_{\lambda f}\right),\\
\hat{\mathrm{H}}_{pp} &= \sum_{mm'}\sum_{\alpha\beta\sigma}\left(t_{\alpha\beta}p^+_{\alpha m\sigma}p_{\beta m'\sigma}+h.c.\right)
\end{aligned}$$

and $n^\sigma_{\lambda f} = d^+_{\lambda f\sigma}d_{\lambda f\sigma}$, $n^\sigma_{\alpha m} = p^+_{\alpha m\sigma}p_{\alpha m\sigma}$, f and m run over the positions $d_{\lambda f}$ and $p_{\alpha m}$ which are sets of localized atomic orbitals; likewise ε_λ and ε_α are energy appropriate atomic orbitals, $t_{\lambda\alpha}$ and $t_{\alpha\beta}$ are the hopping matrix elements, U_λ, U_α and J_d are the intraatomic Coulomb interactions and Hund exchange, $V_{\alpha\lambda}$ is the Coulomb repulsion between the electrons at the copper and oxygen. In this section a consideration is given to the case with one hole per cell in the undoped materials and arbitrary number of the occupied orbitals. This is relevant for the high-Tc cuprates.

In the many-electron approach it is necessary to introduce a symmetrical cell oxygen states $\hat{p}_{\theta k}$ by an unitary transformation $\hat{p}_{\theta k} = \hat{A}_k\hat{p}_{\alpha k}$, where the column vectors $\hat{p}_{\alpha k} = \begin{pmatrix} p_{xk}\\ p_{yk}\\ p_{zk}\end{pmatrix}$ and $\hat{p}_{\theta k} = \begin{pmatrix} p_{\theta_1 k}\\ p_{\theta_2 k}\\ p_{\theta_3 k}\end{pmatrix}$ at σ or π type of bonding. The transformation matrix $\hat{A}_k$ depends on the cell symmetry and index θ numbers the irreducible representations of the symmetry group of cell. The transformation matrices can be found in works for cuprates [14, 15, 21, 22], manganites (e_g — orbitals) with the orbital ordering [23–25] and cobaltites (t_{2g} — orbitals) [26, 27]. In a new symmetric cell representation the dependence of the intra-cluster and inter-cluster interactions, including Coulomb, are renormalized [14] due to strong localization of new symmetrical Wannier cell functions $\hat{p}_{\theta f}$. As a result, Coulomb interactions are taken into account in a single cell through a procedure of exact diagonalization, and the interaction between cells is calculated in the framework of cell perturbation theory (see e.g. the diagram approach [28]) The different Coulomb contributions in the cuprates investigated in the work [14, 15] in detail. In respect of other oxides the approximation is based on a sharp drop in the renormalization coefficients with increasing distance between cells [22, 23, 27]. Further, a crystal lattice is divided into unit cells, so that the Hamiltonian is represented by the sum $\hat{H}_0 + \hat{H}_1$, where the component $\hat{H}_0$ is the sum of intracell terms and component $\hat{H}_1$ takes into account the intercell hoppings and interactions.

The component H_0 is exactly diagonalized, and the exact multielectron cell states $|p\rangle$ ($|q\rangle$) and energies $\xi_{\vec{p}}$ are obtained. Then these states are used to construct the Hubbard operators of the unit cell $\vec{R}_f : X_f^{p,q} = |p\rangle\langle q|$, where the meaning of the indexes p and q is clear from Fig. 1.

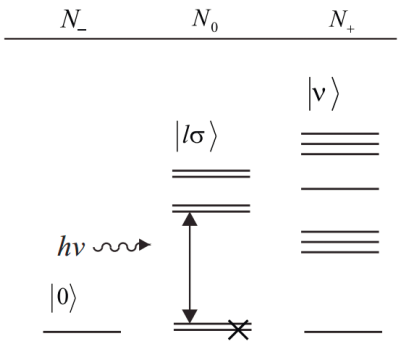

Fig. 1. A configuration space of all possible cell states involved in superexchange with one hole per cell. The sectors N_0 and N_+ correspond to states (6) and (7) respectively (N_0 is hole number per cell in undoped material, $N_- = N_0 - 1,\ N_+ = N_0 + 1$)

$$\hat{H}_0 = \sum_f \left\{ \varepsilon_0 X_f^{00} + \sum_{l\sigma} (\epsilon_l - \mu)\, X_f^{l\sigma,l\sigma} + \sum_{\nu}^{N_\nu} (E_\nu - 2\mu) X_f^{\nu,\nu} \right\} \tag{2}$$

is the sum of intracell terms. A component

$$\hat{H}_1 = \sum_{fg} \sum_{rr'} t_{fg}^{rr'} \overset{+}{X}_f^r X_g^{r'} \tag{3}$$

takes into account the intercell hoppings and interactions, where $t_{fg}^{\lambda\lambda'}$ is defined by the matrix of hopping integrals $t_{fg}^{\lambda\lambda'}$:

$$t_{fg}^{rr'} = \sum_{\lambda\lambda'} \sum_{\sigma} t_{fg}^{\lambda\lambda'} \left[\gamma_{\lambda\sigma}^*(r)\, \gamma_{\lambda'\sigma}(r') + \gamma_{\lambda'\sigma}^*(r)\, \gamma_{\lambda\sigma}(r') \right], \tag{4}$$

where the matrix element is represented by expression

$$\gamma_{\lambda\sigma}(r) = \langle (N_+, M_S)_\nu |\, c_{f\lambda\sigma}\, | (N_0, M_S)_l \rangle \times \delta\left(S_\nu, S_l \pm |\sigma|\right) \delta\left(M_\nu, M_l + \sigma\right), \tag{5}$$

where $c_{f\lambda\sigma}$ runs over all operators $p_{\theta f\sigma}$ and $d_{\lambda f\sigma}$. In the approach one assume that the quasiparticles are unit cell excitations which can be represented graphically as single-particle excitations (transitions) between different sectors $N_h = \ldots (N_- = N_0 - 1), N_0, (N_+ = N_0 + 1), \ldots$ of the configuration space of the unit cell (N_0 is hole number per cell in the undoped material, see Fig. 1) [29]. Each of these excitations forms a r-th quasiparticle band, where the vector band index $r = \{p, q\}$ in configurational space [30] numerates the initial $|p\rangle$ and final $|q\rangle$ states. The excitations with the number of electrons increasing or decreasing, form the conduction or valence bands, respectively. Note that the the possibility to derive the Hamiltonian (2) and (3) from (1) in terms of arbitrary symmetry of the material has not yet been investigated.

In the case of one hole per cell $N_0 = 1$, the cell states $|(N_0, M_S)_l\rangle$ are a superposition of different hole configurations of the same orbital symmetry:

$$|(N_0, M_S)_l\rangle = \sum_{\lambda} \beta_\lambda(h_\lambda)\, |h_\lambda, M_S\rangle. \tag{6}$$

In accordance with the spin selection rules, the non-zero matrix elements (5) are possible for the one-hole spin doublet states $C^1_{2N_\lambda} = 2N_\lambda$ in the sector N_0 and $C^2_{2N_\lambda} = N_S + 3N_T$ of the spin singlets $N_S = C^2_{N_\lambda} + N_\lambda$ (low spin partners) and $N_T = C^2_{N_\lambda}$ of spin triplets in the sector N_+:

$$|(N_+, M_S)_\nu\rangle = \sum_{\lambda\lambda'} \beta_\nu \left(h_\lambda, h_{\lambda'}\right) |h_\lambda, h_{\lambda'}, M_S\rangle \tag{7}$$

(high spin partners) in the two-hole sector N_+ and the N_λ orbital approach. The superexchange interaction appears at the second order of the cell perturbation theory with respect to hoppings [13]. That corresponds to virtual excitations from the occupied singlet and triplet bands through the insulating gap to the conduction band and back. These perturbations are described by the off-diagonal elements $t^{rr'}_{fg}$ with $r = \{0, l\sigma\}$ and $r' = \{l\sigma, \nu\}$ in expression (3). In the Hubbard model, there is only one such element, which describes the hoppings between the lower and upper Hubbard bands. To extract them, we extend the projection operator method proposed by Chao et al [20] on the arbitrary energy spectra of Mott-Hubbard material, where the total number of diagonal operators $X^{nn'}_f$ is equal to $N_\nu + N_l + 1$ and the sequence indexes l and ν ($1 \leqslant l \leqslant N_l$, $1 \leqslant \nu \leqslant N_\nu$) runs over all electron states in the configuration spaces in Fig. 1. Using a set of operators

$$p_0 = \left(X^{00}_i + \sum_{l\sigma} X^{l\sigma,l\sigma}_i\right)\left(X^{00}_j + \sum_{l\sigma} X^{l\sigma,l\sigma}_j\right), \tag{8}$$

and

$$p_\mu = X^{\mu\mu}_i + X^{\mu\mu}_j - X^{\mu\mu}_i \sum_\nu X^{\nu\nu}_j \tag{9}$$

with $\nu(\mu) = 1, 2, \ldots N_\nu$ we can identify the contribution to the superexchange from the interband transitions. As will be seen below, a approach with the operators (5) and (6) differs from the work [20] just in details. It can be checked that each of operator p_0 and p_μ is a projection operator $p_0^2 = p_0$ and $p_\mu^2 = p_\mu$. These operators also form a complete and orthogonal system, $p_0 + \sum\limits_{\mu=1}^{N_\mu} p_\mu = 1$, $p_0 p_\mu = 0$ and $p_\mu p_\nu = \delta_{\mu\nu} p_\mu$. We separate the diagonal and off-diagonal matrix elements in expression

$$\hat{H} = (\hat{H}_0 + \hat{H}_1^{in}) + \hat{H}_1^{out}. \tag{10}$$

According to the work [20], one can introduce a Hamiltonian of the exchange-coupled (ij)-th pair: $\hat{h} = (\hat{h}_0 + \hat{h}_1^{in}) + \hat{h}_1^{out} = \hat{H}_{ij}$, where $\hat{H} = \sum\limits_{ij} \hat{H}_{ij}$, and

$$\hat{h}_0 + \hat{h}_1^{in} = p_0 \hat{h} p_0 + \sum_{\mu\nu} p_\mu \hat{h} p_\nu, \tag{11}$$

and

$$\hat{h}_1^{out} = p_0 \hat{h} \left(\sum_\mu p_\mu\right) + \left(\sum_\mu p_\mu\right) \hat{h} p_0 \tag{12}$$

are intra- and inter- band contributions in $\hat{H}_1$ respectively. In the unitary transformation

$$\tilde{h} = e^G \hat{h} e^{-G} \tag{13}$$

the matrix $\hat{G}$ satisfies to equation

$$p_0 \hat{h} \left(\sum_\mu p_\mu\right) + \left(\sum_\mu p_\mu\right) \hat{h} p_0 + \left[G, \left(p_0 \hat{h} p_0 + \sum_{\mu\nu} p_\mu \hat{h} p_\nu\right)\right] = 0, \tag{14}$$

and transformed Hamiltonian are given by

$$\tilde{h} \approx \left(p_0 \hat{h} p_0 + \sum_{\mu\nu} p_\mu \hat{h} p_\nu \right) + \frac{1}{2} \left[G, \left(p_0 \hat{h} \sum_\mu p_\mu + \sum_\mu p_\mu \hat{h} p_0 \right) \right], \tag{15}$$

where the contributions from inter-band transitions involving only low-spin partners can be calculated as

$$p_0 \hat{h} \left(\sum_\mu p_\mu \right) = \sum_{ll'\sigma} \sum_\mu t_{ij}^{l0,l'\mu} \eta(\sigma) X_i^{l\sigma 0} X_j^{l'\bar{\sigma}\mu} \tag{16}$$

and

$$\left(\sum_\mu p_\mu \right) \hat{h} p_0 = \sum_\mu \sum_{ll'\sigma} t_{ij}^{\mu l'\bar{\sigma},0l\sigma} \eta(\sigma) X_i^{\mu l'\bar{\sigma}} X_j^{0l\sigma}, \tag{17}$$

where $\eta(\sigma) = \pm 1$ depending on the spin direction. Similar expressions can be obtained and for high-spin partners. The solution of Eq. (14) has the form

$$G = \sum_\mu \sum_{ll'\sigma} \frac{t_{ij}^{l0,l'\mu}}{\Delta_{ll'\mu}} \eta(\sigma) \left(X_i^{\mu l'\bar{\sigma}} X_j^{0l\sigma} - X_i^{l\sigma 0} X_j^{l'\bar{\sigma}\mu} \right), \tag{18}$$

where $\Delta_{ll'\mu} = \varepsilon_0 + \varepsilon_\mu - (\varepsilon_{l\sigma} + \varepsilon_{l'\bar{\sigma}})$, and the commutator in Eq. (15) can be represented as

$$\begin{aligned} \delta\tilde{h} = \frac{1}{2} \sum_{\mu\nu} \left\{ \left[G_\nu, \left(p_0 \hat{h} p_\mu + p_\mu \hat{h} p_0 \right) \right] \right\} = \\ = \frac{1}{2} \sum_{\mu\nu} \left\{ \left[\sum_{ll'\sigma} \frac{t_{ij}^{l0,l'\nu}}{\Delta_{ll'\nu}} \eta(\sigma) \left(X_i^{\mu l'\bar{\sigma}} X_j^{0l\sigma} - X_i^{l\sigma 0} X_j^{l'\bar{\sigma}\mu} \right), \sum_{kk's} t_{ji}^{k0,k'\mu} \eta(s) \left(X_j^{\mu k'\bar{s}} X_i^{0ks} + \right. \right. \right. \\ \left. \left. \left. + \; X_j^{ks0} X_i^{k'\bar{s}\mu} \right) \right] \right\}. \end{aligned} \tag{19}$$

Calculating commutator in the above expression (19) we obtain the effective Hamiltonian for the exchange-coupled (ij)-th pair:

$$\begin{aligned} \delta\tilde{h} = \sum_{ll'kk'} \sum_{\mu\nu} \left(\frac{t_{ij}^{l0,l'\nu} t_{ij}^{k0,k'\mu}}{\Delta_{ll'\nu}} \right) \frac{\delta_{\mu\nu}}{2} \left\{ \left(X_i^{l\uparrow,k\downarrow} X_j^{l'\downarrow,k'\uparrow} + X_i^{l\downarrow,k\uparrow} X_j^{l'\uparrow,k'\downarrow} \right) - \left(X_i^{l\uparrow,k\uparrow} X_j^{l'\downarrow,k'\downarrow} + \right. \right. \\ \left. \left. + X_i^{l\downarrow,k\downarrow} X_j^{l'\uparrow,k'\uparrow} \right) \right\} + \sum_{ll'kk'} \sum_{\mu\nu} \left(\frac{t_{ij}^{l0,l'\nu} t_{ij}^{k0,k'\mu}}{\Delta_{ll'\nu}} \right) \delta_{kl} \delta_{k'l'} \left(X_i^{00} X_j^{\mu\nu} + X_i^{\mu\nu} X_j^{00} \right) = \delta\tilde{h}_{s-ex} + \delta\tilde{h}_\rho, \end{aligned} \tag{20}$$

where only a first contribution includes the superexchange interaction $\delta\hat{H}_{s-ex} = \sum_{ij} \delta\tilde{h}_{s-ex}$. The latter can be expanded in powers of variable $X_{i(j)}^{l_0 s,ls}$, the mean value of which $\upsilon_l^+ = \bar{X}_{i,j}^{l_0 s,ls}$ is an probability of optical intracell excitation:

$$\delta\hat{H}_{s-ex} = \hat{H}_s + \hat{H}_{ex}, \tag{21}$$

where the superexchange in unexcited material and contributions from optically excited states are given by:

$$\hat{H}_s = \sum_{ij} \left\{ \sum_\mu^{N_S} \frac{2\left(t_{ij}^{l_0 0,l_0\mu}\right)^2}{\Delta_{l_0\mu}} \left(\hat{S}_{il_0} \hat{S}_{jl_0} - \frac{1}{4} \hat{n}_{il_0} \hat{n}_{jl_0} \right) - \sum_\mu^{3N_T} \frac{\left(t_{ij}^{l_0 0,l_0\mu}\right)^2}{\Delta_{l_0\mu}} \left(\hat{S}_{il_0} \hat{S}_{jl_0} + \frac{3}{4} \hat{n}_{il_0} \hat{n}_{jl_0} \right) \right\}, \tag{22}$$

$$\hat{H}_{ex} = \sum_{ij}\sum_{ll'kk'}\sum_{\mu}\frac{\left(t_{ij}^{l0,l'\mu}t_{ji}^{k0,k'\mu}\right)}{\Delta_{ll'\mu}}\Big\{\left(\delta_{l_0k}Z_{il}^{-}+\delta_{l_0l}Z_{ik}^{+}+\delta_{lk}\hat{S}_{il}\right)\left(\delta_{l_0k'}Z_{jl'}^{-}+\delta_{l_0l'}Z_{jk'}^{+}+\right.$$
$$\left.+\delta_{l'k'}\hat{S}_{jl'}\right)-\frac{1}{4}\left(\delta_{l_0k}y_{il}^{-}+\delta_{l_0l}y_{ik}^{+}+\delta_{lk}\hat{n}_{il}\right)\left(\delta_{l_0k'}y_{jl'}^{-}+\delta_{l_0l'}y_{jk'}^{+}+\delta_{l'k'}\hat{n}_{jl'}\right)\Big\}, \quad (23)$$

and $S_{il}^{+}=X_i^{l\uparrow,l\downarrow}$, $2S_{il}^{z}=\sum\limits_{\sigma}\eta\left(\sigma\right)X_i^{l\sigma,l\sigma}$, $y_{il}^{+}=\hat{n}_{il_0}X_i^{l_0l}$, $Z_{il}^{+}=\hat{S}_{il_0}X_i^{l_0l}$ are a spin, electron-exciton operators and spin-exciton at the i-th cell. The commutation relations for the latter operators have the spin character in the mean field approximation $Z_{il}^{+}\approx\hat{S}_{il_0}\upsilon_l^{+}$, and the contributions involving the spin-exciton variables result in additional effective field in Eq. (22):

$$J_{ij}^{l_0l_0}\approx 2\sum_{\mu}\sum_{ll'kk'}\frac{\left(t_{ij}^{l0,l'\mu}\right)\left(t_{ji}^{k0,k'\mu}\right)}{\Delta_{ll'\mu}}\left(\upsilon_k^{+}\delta_{l_0l}+\upsilon_l^{-}\delta_{l_0k}+\delta_{l_0l}\delta_{lk}\right)\left(\upsilon_{k'}^{+}\delta_{l_0l'}+\upsilon_{l'}^{-}\delta_{l_0k'}+\right.$$
$$\left.+\delta_{l_0l'}\delta_{l'k'}\right)=2\sum_{\mu}\frac{\left(t_{ij}^{l_00,l_0\mu}\right)^2}{\Delta_{l_0\mu}}+\mathrm{O}\left(\upsilon^{\pm}\right)+\ldots \quad (24)$$

Note that at $l=k$ and $l'=k'$ the contribution in Eq. (23) takes the form

$$\hat{H}_{ex}=\sum_{ij}\sum_{ll'}\left\{J_{A,ij}^{ll'}\left(\hat{S}_{il}\hat{S}_{jl'}-\frac{1}{4}\hat{n}_{il}\hat{n}_{jl'}\right)-J_{F,ij}^{ll'}\left(\hat{S}_{il}\hat{S}_{jl'}+\frac{3}{4}\hat{n}_{il}\hat{n}_{jl'}\right)\right\}. \quad (25)$$

It is much like to a conventional superexchange (22), but with other superexchange constants $J_{A,ij}^{ll'}=2\sum\limits_{\mu=1}^{N_s}\left(t_{ij}^{l0,l'\mu}\right)^2\Big/\Delta_{ll'\mu}$ and $J_{F,ij}^{ll'}=\sum\limits_{\mu=1}^{3N_t}\left(t_{ij}^{l0,l'\mu}\right)^2\Big/\Delta_{ll'\mu}$, which is additive over the singlet and triplet virtual μ-th "excited states" respectively.

Applicability of the expessions (24) and (25) is limited to small excitation energy $\delta_{ll_0}<E_g$, where $\delta_{ll_0}=\varepsilon_l-\varepsilon_{l_0}$ and $E_g=(\varepsilon_{\mu_0}+\varepsilon_0-2\varepsilon_{l_0})$. The usual mechanism of the superexchange (22) in the ground state is shown in Fig. 2b, while the superexchanges (25) via optically excited state is shown in Fig. 2a. At $l\neq l'$ the last represents a non-symmetrical interaction with one excited cell in the pair. The spin-exciton contribution ($\sim X_{i(j)}^{l_0l}$) in Eq. (23) beyond Heisenberg model is shown in Fig. 2c. From Eq. (24) it follows that the optical pumping effects on the superexchange are frequency selective and linear on the amplitude pumping.

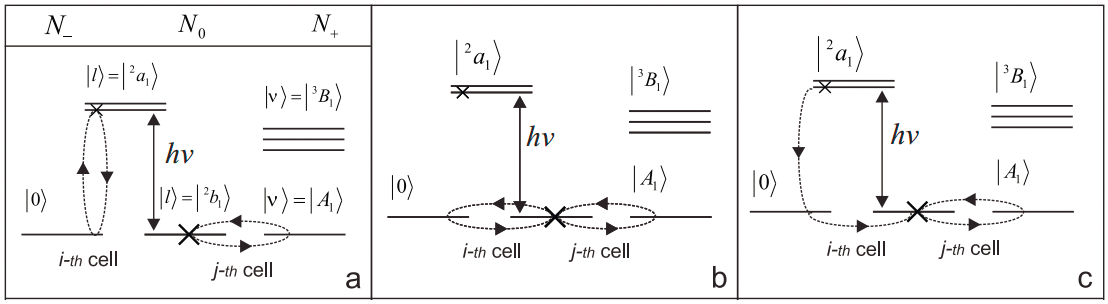

Fig. 2. Two circles (dashed line) are a sequence of intracell transitions at the light-induced superexchange J_{ij}^{ab} (a) and J_{ij}^{bb} (b) between i and j cells in Eq. (25), (c) illustrates the single circle (spin-exciton) contribution $\sim\left(t_{ij}^{a0,bA}t_{ji}^{b0,bA}\right)/\Delta_{abA}$ (for cuprates), which can be reduced to the spin Hamiltonian using additional assumptions only (see Eq. (24))

2. Optical effects on superexchange in La_2CuO_4

We test the approach to derive the superexchange in the high-T_c parent materal La214 under optical pumping. The initial Hamiltonian (1) is similar to the one of multiband *pd*-model [31]. The difference with the low energy three orbital *pd*-model [32–34] is related to an addition of the z-oriented d_{z^2} orbital and $p_z^{(ap)}$ orbital of the apical oxigen ions. In the LDA+GTB method the Hamiltonian parameters are calculated ab initio [8]. Unlike the work [34], where the method of projection operators has also been used to derive the superexchange interaction, we take into account the intracell excited states in CuO_6 cell. Some improvements are also achieved with the help of the cell representation. Indeed, a comparison of the results of the fourth-order with the calculations in higher orders of perturbation theory [12] in atomic representation and the exact diagonalization of finite clusters [12, 35–38] shows that the in-plane superexchange J depends significantly weaker on $(p_\alpha d_\lambda)$-hopping ($\sim t_{pd}$), because of the intermediate two-hole states which arise through hopping from oxygen to oxygen ($\sim t_{pp}$). These effects are partly included in the present approach even in the second-order of cell perturbation due to the exact diagonalization procedure for the intracell part of Hamiltonian (1).

Here, it is also useful to obtain the expression for the AFM contribution in Eq. (25) in the mean-field approximation:

$$\left\langle \hat{H}_{s-ex} \right\rangle \approx -\frac{1}{2}\sum_{ij}\sum_{ll'} J_{ij}^{ll'} \left\langle X_i^{l\sigma l\sigma} \right\rangle \left\langle X_j^{l'\bar{\sigma}l'\bar{\sigma}} \right\rangle \approx$$
$$\approx -\frac{zN}{2}\left[J_{\langle ij\rangle}^{l_0 l_0} p_{l_1}^2 + 2\sum_{l\neq l_0} J_{\langle ij\rangle}^{ll_0} p_l p_{l_0} + + \sum_{l,l'\neq l_0} J_{\langle ij\rangle}^{ll'} p_l p_{l'} \right], \qquad (26)$$

where $p_{l_0} = 1 - \left(\sum_{l\neq l_0} p_l \right)$ and $p_l = \left\langle X_i^{l\uparrow l\uparrow} \right\rangle = \left\langle X_i^{l\downarrow l\downarrow} \right\rangle$ is a probability to detect a cell in $|(N_0, M_S)_l\rangle$ excited state. Using the exact diagonalization procedure with LDA parameters: J_{bb} ≈0.15 eV, $\delta_{ll_0} = \delta_{ab}$=1.78 eV, E_g =2.00 eV taken from the work [8], and the band index $r = \{^2b_1, A_1\}$ associated with the first removal electron state for pair of indexes $\{l_0, \mu_0\}$ [14, 22], one can obtain the weights α_l, β_l and A_μ, B_μ at the doublet (6) and singlet, triplet (7) states:

$$\begin{aligned} \left|^2b_1\right\rangle = |(N_0, M_S)_{l_0}\rangle &= \sum_{\lambda=d_z,p_z,a} \beta_{l_0}(h_\lambda) \left| h_\lambda, \sigma_{\frac{1}{2}} \right\rangle, \\ \left|^2a_1\right\rangle = |(N_0, M_S)_l\rangle &= \sum_{\lambda=d_z,p_z,a} \alpha_l(h_a) \left| h_a, \sigma_{\frac{1}{2}} \right\rangle \end{aligned} \qquad (27)$$

and

$$\begin{aligned} |A_1\rangle = |(N_+, M'_{S'})_{\mu_0}\rangle &= \sum_{\lambda,\lambda'=b,d_x,a,p_{z,}d_z} A_{\mu_0}(h_\lambda, h_{\lambda'}) |h_\lambda, h_{\lambda'}, 0\rangle, \\ \left|^3B_1\right\rangle = |(N_+, M'_{S'})_\mu\rangle &= \sum_{\lambda=b,d_x} \sum_{\lambda'=a,p_z,d_z} B_\mu(h_\lambda, h_{\lambda'}) |h_\lambda, h_{\lambda'}, M_1\rangle, \end{aligned} \qquad (28)$$

where h_b and h_{d_x} are the holes in the b-symmetrized $p_{\theta i}$ cell states of oxygen and $d_{x^2-y^2}$ cooper states of the CuO_2 layer, respectively. Because of $\delta_{ab} < E_g$, only two contributions from the doublets $\left|^2a_1\right\rangle$ and $\left|^2b_1\right\rangle$ are available in the sum (26) over l indexes. Due to the symmetry CuO_2 layer $\gamma_\lambda(\{^2a_1, A_1\}) = 0$ at any orbital index λ, and therefore $t_{ij}^{b0,aA} = t_{ij}^{a0,aA} = 0$. Thus we evaluate the contribution from excited states like the next:

$$\langle \delta H_{s-ex} \rangle = -\frac{zN}{2} \sum_{\mu} \left\{ \frac{\left(t^{b0,b\mu}\right)^2}{\Delta_{b\mu}} p_b^2 + \ +2 \left(\frac{\left(t^{b0,a\mu}\right)^2}{\Delta_{ba\mu}} + \frac{\left(t^{a0,b\mu}\right)^2}{\Delta_{ba\mu}} \right) p_a p_b + \frac{\left(t^{a0,a\mu}\right)^2}{\Delta_{b\mu}} p_a^2 \right\} \approx$$

$$\approx -\frac{zN}{2} \left\{ 0.15(eV) \cdot p_b^2 + 2 \frac{\left(t^{a0,bA_1}\right)^2}{\Delta_{baA_1}} p_a p_b \right\}. \quad (29)$$

In unexcited material $p_b = 1$, $p_a = 0$, and Eq. (29) results in the exchange interaction $J_{bb} \sim 0.15eV$ in the ground state [16]. What are the modifications of the exchange interaction we can expect in L214 under resonance light pumping? The answer to this question depends on the ratio of the exchange interaction at the ground $\left|^2 b_1\right\rangle$ and excited $\left|^2 a_1\right\rangle$ states. Depletion of the ground state $p_b = 1 - x$ decreases J_{bb} contribution, and a new contribution J_{ba} from excited state a_1 appears (see Fig. 2a). Summing over all μ-th virtual "excited states" in the second term in Eq. (29), we finally obtain the result that the superexchange AFM contribution in La214 will increase at any small population of excited states by a factor of $\sim \ 4 \cdot 10^{-3} eV(\%)^{-1}$, i.e. the superexchange interaction is increased by 4 meV at x=0.01.

Conclusions

In summary, we have examined the response of superexchange in magnetic Mott-Hubbard materials with the arbitrary spin under optical pumping. To derive the effective spin Hamiltonian we use the initial *pd* model Hamiltonian in the Hubbard operators representation (LDA+GTB approach [8]) and method of the projection operators [20]. The effective Hamiltonian (21) contains not only spin-spin interactions involving optically excited states but more complicated interactions of non-Heisenberg type accompanied with exciton or bi-exciton. The Hamiltonian is non-additive over the ground and optically excited states, but it is additive to the virtual "excited states". To test our approach, we have calculated the superexchange interaction and D-M interaction in antiferromagnets La214 under optical pumping.

In cuprates under optical pumping with a frequency of *d-d* transitions ($\nu < E_g$) AFM superexchange enhanced by 40K on 1% of the occupation of excited state. The D-M interaction of also does not undergo radical changes since the ground and the optically excited states of cell are Kramers doublets in La214 (Fig. 2). Under irradiation with a frequency of corresponding to the charge-transfer excitations($\nu \sim E_g$), the optically induced magnetism of electron-hole pair is not appear because the electron and hole are at the many-electron spin singlet states. A spectral dependence of modified superexchange should coincide with the *d-d* absorption spectra in the transparency window $\Delta E \sim 0 \div 2eV$. Let us note here the discrepancy of our results and the general trend given in the work [39], where the excited states contribute to the FM exchange at the low "charge transfer energies" ($\Delta_{ll'\mu}$ in our notation).

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References

[1] A.Kirilyuk, A.V.Kimel, T.Rasing, Ultrafast optical manipulation of magnetic order, *Rev. Mod. Phys.*, **82**(2010), 2731–2784.

[2] C.de Graaf, R.Broer, Midinfrared spectrum of undoped cuprates: d-d transitions studied by ab initio methods, *Phys. Rev. B*, **62**(2000), 702–709.

[3] R.V.Mikhaylovskiy, E.Hendry, V.V.Kruglyak, R.V.Pisarev, T.Rasing, A.V.Kimel, Terahertz emission spectroscopy of laser-induced spin dynamics in TmFeO3 and ErFeO3 orthoferrites, *Phys. Rev. B*, **90**(2014), 184405.

[4] R.V.Mikhaylovskiy, E.Hendry, A.Secchi, J.H.Mentink, M.Eckstein, A.W.R.V.Pisarev, V.V.Kruglyak, M.I.Katsnelson, T.Rasing, A.Kimel, Ultrafast optical modification of exchange interactions in iron oxides, *Nature Communications*, **6**(2015), 1–9.

[5] M.I.Katsnelson, A.I.Lichtenstein, First-principles calculations of magnetic interactions in correlated systems, *Phys. Rev. B*, **61**(2000), 8906–8912.

[6] V.V.Mazurenko, V.I.Anisimov, Weak ferromagnetism in antiferromagnets: alfa Fe2O3 and La2CuO4, *Phys. Rev. B*, **71**(2005), 184434.

[7] D.W.Boukhvalov, A.I.Lichtenstein, V.V.Dobrovitski, M.I.Katsnelson, B.N.Harmon, V.V.Mazurenko, V.I.Anisimov, Effect of local Coulomb interactions on the electronic structure and exchange interactions in Mn12 magnetic molecules, *Phys. Rev. B*, **65**(2002), 184435.

[8] M.M.Korshunov, V.A.Gavrichkov, S.G.Ovchinnikov, I.A.Nekrasov, Z.V.Pchelkina, V.I.Anisimov, Hybrid LDA and generalized tight-binding method for electronic structure calculations of strongly correlated electron systems, *Phys. Rev. B*, **72**(2005), 165104.

[9] S.G.Ovchinnikov, V.N.Zabluda, Energy structure and optical spectra taking into account of strong electron correlations, *ZETF*, **125**(2004), 150–159.

[10] V.A.Gavrichkov, A simple metal-insulator criterion for the doped Mott-Hubbard materials, *Sol. State Comm.*, **208**(2015), 11–14.

[11] G.Khaliullin, P.Horsch, A.M.Oles, Theory of optical spectral weights in Mott insulators with orbital degrees of freedom, *Phys. Rev. B*, **70**(2004), 195103.

[12] H.Eskes, J.H.Jefferson, Superexchange in the cuprates, *Phys. Rev. B*, **48**(1993), 9788.

[13] J.H.Jefferson, H.Eskes, L.F.Feiner, Derivation of a single band model for CuO_2 planes by cell perturbation method, *Phys. Rev. B*, **45**(1992), 7959.

[14] L.F.Feiner, J.H.Jefferson, R.Raimondi, Effective single band models for high T_c cuprates. I. Coulomb interactions, *Phys. Rev. B*, **53**(1996), 8751.

[15] R.Raimondi, J.H.Jefferson, L.F.Feiner, Effective single-band models for the high-T_c cuprates. II. Role of apical oxygen, *Phys. Rev. B*, **53**(1996), 8774–8788.

[16] V.A.Gavrichkov, S.G.Ovchinnikov, Influence of Two-Particle Excited States on the Interatomic Exchange Interaction in La_2CuO_4, *Physics of the Solid State*, **50**(2008), 1081–1086.

[17] J.Hubbard, Electron Correlations in Narrow Energy Bands. IV. The Atomic Representation, *Proc. Roy. Soc.*, **A 285**(1965), 542.

[18] V.A.Gavrichkov, Z.V.Pchelkina, I.A.Nekrasov, S.G.Ovchinnikov, Pressure effect on the energy structure and superexchange interaction in undoped orthorhombic La2CuO4, *Int. J. Mod. Phys. B,* **30**(2016), 1650180.

[19] P.W.Anderson, G.Rado, (Ed.), Exchange in Insulators: Superexchange, Direct Exchange, and Double Exchange, *Elsevier Inc.*, **II**(1963), 25–81.

[20] K.A.Chao, J.Spalek, A.M.Oles, Kinetic exchange interaction in a narrow S-band, *Journal of Physics C: Solid State Physics* **10**(1977), L271.

[21] B.S.Shastry, t-J Model and Nuclear Magnetic Relaxation in High-T_c Materials, *Phys. Rev. Lett.*, **63**(1989), 1288–1291.

[22] V.A.Gavrichkov, A.A.Borisov, S.G.Ovchinnikov, Angle-resolved photoemission data and quasiparticle spectra in antiferromagnetic insulators $Sr_2CuO_2Cl_2$ and $Ca_2CuO_2Cl_2$, *Phys. Rev. B*, **64**(2001), 235124.

[23] V.A.Gavrichkov, S.G.Ovchinnikov, L.E.Yakimov, The Role of Orbital Ordering in the Formation of Electron Structure in Undoped LaMnO3 Manganites in the Regime of Strong Electron Correlations, *JETP*, **102**(2006), 972–985.

[24] V.A.Gavrichkov, S.G.Ovchinnikov, Z.V.Pchelkina, I.A.Nekrasov, Quasiparticle in CMR oxides in para- and ferromagnetic phases, *J. Phys.: Conf. Ser.*, **200**(2010), 012046.

[25] V.A.Gavrichkov, S.G.Ovchinnikov, I.A.Nekrasov, Z.V.Pchelkina, Electronic Structure of p-Type La1 – x MnO3 Manganites in the Ferromagnetic and Paramagnetic Phases in the LDA + GTB Approach, *JETP*, **112**(2001), 860–876.

[26] S.G.Ovchinnikov, Y.S.Orlov, I.A.Nekrasov, Z.V.Pchelkina, Electronic Structure, Magnetic Properties, and Mechanism of the Insulator–Metal Transition in LaCoO3 Taking into Account Strong Electron Correlations, *JETP*, **112**(2011), 140–151.

[27] Y.S.Orlov, L.A.Solovyov, V.A.Dudnikov, A.S.Fedorov, A.A.Kuzubov, N.V.Kazak, V.N.Voronov, S.N.Vereshchagin, N.N.Shishkina, N.S.Perov, K.V.Lamonova, R.Y.Babkin, Y.G.Pashkevich, A.G.Anshits, S.G.Ovchinnikov, Structural properties and high-temperature spin and electronic transitions in GdCoO3: Experiment and theory, *Phys. Rev. B*, **88**(2013), 235105.

[28] S.G.Ovchinnikov, V.V.Val'kov, Hubbard operators in the theory strongly correlated electrons, Imperial College Press, London, (2004), 241.

[29] S.G.Ovchinnikov, V.A.Gavrichkov, M.M.Korshunov, E.I.Shneyder, A.Avella, F.Mancini, (Eds.), Springer Series in Solid-State Sciences LDA+GTB method for band structure calculations in the strongly correlated materials. In the "Theoretical Methods for strongly Correlated systems", Springer, Berlin, Heidelberg, **171**(2012), 143–171.

[30] R.O.Zaitsev, Generalized diagram technique and spin waves in an anisotropic ferromagnet, *JETP*, **41**(1975), 100.

[31] Y. B.Gaididei, V.M.Loktev, On a Theory of the Electronic Spectrum and Magnetic Properties of High-T_c Superconductors, *Phys. Status Solidi B*, **147**(1988), 307.

[32] V.Varma, S.Schmitt-Rink, E.Abrahams, Charge transfer excitations and superconductivity in "ionic" metals, *Solid State Communications*, **62**(1987), 681.

[33] V.J.Emery, Theory of High-T_c Superconductivity in Oxides, *Phys. Rev. Lett.*, **58**(1987), 2794–2797.

[34] J.Zaanen, A.M.Oles, Canonical pertnrhation theory and the two-hand model for high-Tc superconductors, *Phys. Rev. B*, **37**(1988), 9423–9438.

[35] H.Eskes, G.A.Sawatzky, L.F.Feiner, Effective transfer for singlets formed by hole doping in the high-Tc superconductors, *Physica C*, **160**(1989), 424.

[36] Y.Ohta, T.Tohyama, S.Maekawa, Charge-transfer gap and superexchange interaction in insulating cuprates, *Phys. Rev. Lett.*, **66**(1991), 1228.

[37] E.B.Stechel, D.R.Jennison, Electronic structure of CuO_2 sheets and spin-driven high-T_c superconductivity, *Phys. Rev. B*, **38**(1988), 4632.

[38] J.F.Annett, R.M.Martin, A.K.McMahan, Satpathy, Electronic Hamiltonian and antiferromagnetic interactions in La_2CuO_4, *Phys. Rev. B*, **40**(1989), 2620.

[39] M.V.Eremin, Y.V.Rakitin, Kinetic exchange at low charge transfer energies, *J. Phys. C: Solid State Phys.*, **14**(1981), 247–253.

Эффекты оптических внутрищелевых переходов в суперобменном взамодействии в La_2CuO_4 с неравновесными фотовозбуждёнными центрами

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Мы исследовали эффекты возбужденных многоэлектронных состояний в оптическом способе управления магнитным состоянием недопированных Мотт-Хаббардовских материалов. Для вывода спинового гамильтониана в веществе под воздействием оптической накачки был использован многоэлектронный метод, основанный на представлении Х-операторов. С помощью обобщенного на произвольный энергетический спектр метода проекционных операторов мы получили гамильтониан суперобменного взаимодействия в аналитической форме. Гамильтониан является не аддитивными по вкладам от основных и оптически возбуждённых состояний, а также содержит спин-экситонные переменные, которые обычно отсутствуют в обсуждении магнитного отклика на оптическую накачку. В качестве конкретного приложения для теории мы рассчитали индуцированный суперобмен для оптически возбужденного купрата La_2CuO_4 (в дальнейшем La214).

Ключевые слова: суперобмен, оптически возбужденные состояния, диэлектрик Мотта-Хаббарда.