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Contribution from optically excited many-electron states to the superexchange interaction in Mott-Hubbard insulators

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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 one has used a 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. The superexchange is also not additive over contributions from the ground and optical excited states, and nonzero contributions to the Dzyaloshinskii-Moriya interaction are induced in insulators with different spins at the ground and excited cell states. As a test, a microscopic background for the optical induced superexchange was analyzed in La_2CuO_4 (further La214) and $FeBO_3$ with spins $1/2$ and $5/2$, respectively.

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I. INTRODUCTION

An ultrafast optical manipulation of magnetic order is a 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 $h\nu$ (further $h = 1$) is less than absorption edge E_g [1–3]. In the absence of the interband excitations these effects result from the intra-atomic *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 $FeBO_3$ and other transition metal oxides. These effects are beyond the conventional single electron approach to the electronic structure of solids based on different implementation of the density functional theory. For example, in KKR-GF (Green's function)+DMFT (dynamical mean field theory) method leads to the complex Lippman-Schwinger integro-differential equation in a single site problem. This equation was solved for the coupling induced by nonlocal self energy Σ within only single l-channel (e.g., to $l = 2$ for transition metal), [4] and many-electron states (a configuration interaction between them) in *ab initio* approaches are not reproduced correctly. 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 $FeBO_3$ it was demonstrated in the works [8,9]. The undoped Mott-Hubbard insulators, unlike conventional materials, have both singlet and degenerate ground cell states [10]. The effects of excited states can be essentially important in these insulators, because the contribution from optical excited states can reduce or increase the Dzyaloshinskii-Moriya (DM) interaction. These changes will compete with a twist exchange from an effective three-spin interaction [11].

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 occur much faster than superexchange interaction ($\Delta\nu/W \ll 1$; $\Delta\nu$ is an 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 [12] 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. Therefore, 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 [13]. Another approach is the cell perturbation theory taking into account all the excited states. The latter seems more appropriate [13–16] where, however, it is necessary to work with a large number of the virtual charge transfer excitations [17].

Being based on the X-operators representation [18] the LDA+GTB approach [8,19] includes the whole spectrum of localized many-electron states both ground and excited with different spin and orbital moments. It's important to understand further that the excited states in our work are distinct from the virtual "excited states" occurring in a perturbation theory of superexchange [20]. 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 [18] and technique of projection operators [21] 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 $\sim 4 \times 10^{-3}$ eV/(%) at the optical induced occupation (in %) of the excited states.

In contrast cuprate, the optical induced contribution to superexchange has the FM nature in the antiferromagnet $FeBO_3$. In unexcited iron borate the FM contribution is exactly zero. Concerning the DM interaction it can be argued that the Mott-Hubbard insulators, with the observed optical d-d excitations forbidden by a spin are of particular interest. The latter is relevant to the iron borate where these transitions are observed indeed [22].

II. EXTENDED PROJECTION OPERATORS

In this section, we apply the method of projection operators [21] 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

$$\hat{\mathrm{H}}_d = \sum_{f\lambda\sigma}\left[(\varepsilon_\lambda - \mu)d^{+}_{\lambda f\sigma}d_{\lambda f\sigma} + \frac{1}{2}U_\lambda n^{\sigma}_{\lambda f}n^{-\sigma}_{\lambda f} + \sum_{\lambda'\sigma'}\left(-J_d d^{+}_{\lambda f\sigma}d_{\lambda f\sigma'}d^{+}_{\lambda' f\sigma'}d_{\lambda' f\sigma} + \sum_{f'}V_{\lambda\lambda'}n^{\sigma}_{\lambda f}n^{\sigma'}_{\lambda' f'}\right)\right],$$

$$\hat{\mathrm{H}}_p = \sum_{m\alpha\sigma}\left[(\varepsilon_\alpha - \mu)p^{+}_{\alpha m\sigma}p_{\alpha m\sigma} + \frac{1}{2}U_\alpha n^{\sigma}_{\alpha m}n^{-\sigma}_{\alpha m} + \sum_{\alpha' m'\sigma'}V_{\alpha\alpha'}n^{\sigma}_{\alpha m}n^{\sigma'}_{\alpha' m'}\right],$$

$$\hat{\mathrm{H}}_{pd} = \sum_{mf}\sum_{\alpha\lambda\sigma\sigma'}\left(t_{\lambda\alpha}p^{+}_{\alpha m\sigma}d_{f\lambda\sigma} + \mathrm{H.c.} + V_{\alpha\lambda}n^{\sigma}_{\alpha m}n^{\sigma'}_{\lambda f}\right), \quad \hat{\mathrm{H}}_{pp} = \sum_{mm'}\sum_{\alpha\beta\sigma}(t_{\alpha\beta}p^{+}_{\alpha m\sigma}p_{\beta m'\sigma} + \mathrm{H.c.}) \tag{1}$$

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 are run over the positions $d_{\lambda f}$ and $p_{\alpha m}$, 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 intra-atomic Coulomb interactions and Hund exchange, and $V_{\alpha\lambda}$ 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-T_c cuprates.

In the many-electron approach it is necessary to introduce a symmetrical cell oxygen state $\hat{p}_{\theta k}$ by a unitary transformation $\hat{p}_{\theta k} = \hat{A}_k\hat{p}_{\alpha k}$, where the column vectors $\hat{p}_{\alpha k} = \left(\begin{smallmatrix}p_{xk}\\ p_{yk}\\ p_{zk}\end{smallmatrix}\right)$ and $\hat{p}_{\theta k} = \left(\begin{smallmatrix}p_{\theta_1 k}\\ p_{\theta_2 k}\\ p_{\theta_3 k}\end{smallmatrix}\right)$ 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 [15,16,23,24], manganites(e_g orbitals) with the orbital ordering [25–27], and cobaltites (t_{2g} orbitals) [28,29]. In a new symmetric cell representation the dependence of the intracluster and intercluster interactions, including Coulomb, are renormalized [15] 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 [30]) The different Coulomb contributions in the cuprates are investigated in the works [15,16] in detail. In respect of other oxides the approximation is based on a sharp drop in the renormalization coefficients with increasing distance between cells [29,31]. 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 ξ_p are obtained. Then these states are used to construct the Hubbard operators of the unit cell $\vec{R}_f$: $X^{p,q}_f = |p\rangle\langle q|$, where the meaning of the indexes p and q is clear from Fig. 1 and

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

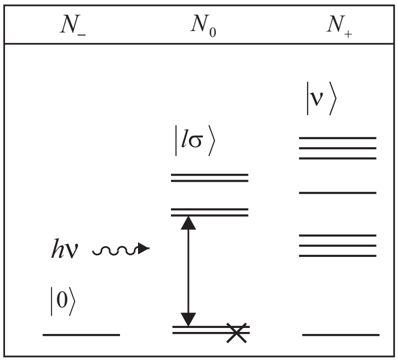

FIG. 1. Configuration space of all possible cell states involved in superexchange with one hole per cell. The sectors N_0 and N_+ correspond to states (6) and (7), respectively.

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, and $t_{fg}^{rr'}$ is the matrix of hopping integrals

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

where the matrix element is represented by the expression

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

In the approach one assumes that the quasiparticles are unit cell excitations which can be represented graphically as single-particle excitations (transitions) between different sectors $N_h = \cdots (N_- = N_0 - 1), N_0, (N_+ = N_0 + 1), \ldots$ of the configuration space of the unit cell (N_0 is hole number per cell in the undoped material; see Fig. 1) [32]. Each of these excitations forms an rth quasiparticle band, where the vector band index $r = \{p,q\}$ in configurational space [33] 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 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 nonzero 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_+:

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

(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 [14]. 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 $t_{fg}^{rr'}$ 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.* [21] on the arbitrary energy spectra of Mott-Hubbard material, where the total number of diagonal operators $X_f^{nn'}$ 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

$$p_0 = \left(X_i^{00} + \sum_{l\sigma} X_i^{l\sigma,l\sigma} \right)\left(X_j^{00} + \sum_{l\sigma} X_j^{l\sigma,l\sigma} \right) \tag{8}$$

and

$$p_\mu = X_i^{\mu\mu} + X_j^{\mu\mu} - X_i^{\mu\mu} \sum_{\nu} X_j^{\nu\nu}, \tag{9}$$

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, an approach with the operators (5) and (6) differs from the work [21] just in details. It can be checked that each of operators 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, $p_0 + \sum_{\mu=1}^{N_\mu} p_\mu = 1$, $p_0 p_\mu = 0$, and $p_\mu p_\nu = \delta_{\mu\nu} p_\mu$. We separate the diagonal and off-diagonal matrix elements in expression

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

According to the work [21], one can introduce a Hamiltonian of the exchange-coupled (ij)th pair: $\hat{h} = (\hat{h}_0 + \hat{h}_1^{\text{in}}) + \hat{h}_1^{\text{out}} = \hat{H}_{ij}$, where $\hat{H} = \sum_{ij} \hat{H}_{ij}$, and

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

with

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

are intra- and interband 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 interband 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

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

Similar expressions can be obtained and for high-spin partners. The solution of Eq. (14) has the form

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

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

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

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

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

where only a first contribution includes the superexchange interaction $\delta\hat{H}_{s-\mathrm{ex}} = \sum_{ij}\delta\tilde{h}_{s-\mathrm{ex}}$. 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 a probability of optical intracell excitation and

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

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

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

and

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

and $S_{il}^+ = X_i^{l\uparrow,l\downarrow}$, $2S_{il}^z = \sum_\sigma \eta(\sigma)X_i^{l\sigma,l\sigma}$, $y_{il}^+ = \hat{n}_{il_0}X_i^{l_0 l}$, $Z_{il}^+ = \hat{S}_{il_0}X_i^{l_0 l}$ are a spin, electron-exciton operators, and spin-exciton at the ith 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):

$$\begin{aligned}J_{ij}^{l_0l_0} &\approx 2\sum_{\mu}\sum_{ll'kk'}\frac{\big(t_{ij}^{l0,l'\mu}\big)\big(t_{ji}^{k0,k'\mu}\big)}{\Delta_{ll'\mu}}\big(\upsilon_k^+\delta_{l_0l} + \upsilon_l^-\delta_{l_0k} + \delta_{l_0l}\delta_{lk}\big)\big(\upsilon_{k'}^+\delta_{l_0l'} + \upsilon_{l'}^-\delta_{l_0k'} + \delta_{l_0l'}\delta_{l'k'}\big)\\ &= 2\sum_{\mu}\frac{\big(t_{ij}^{l_0 0,l_0\mu}\big)^2}{\Delta_{ll'\mu}} + \mathrm{O}(\upsilon^{\pm}) + \cdots .\end{aligned} \tag{24}$$

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

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

It is much like a conventional superexchange (22), but with other superexchange constants $J_{A,ij}^{ll'} = 2\sum_{\mu=1}^{N_s}\big(t_{ij}^{l0,l'\mu}\big)^2/\Delta_{ll'\mu}$ and $J_{F,ij}^{ll'} = \sum_{\mu=1}^{3N_t}\big(t_{ij}^{l0,l'\mu}\big)^2/\Delta_{ll'\mu}$, which is additive over the singlet and triplet virtual μth excited states, respectively.

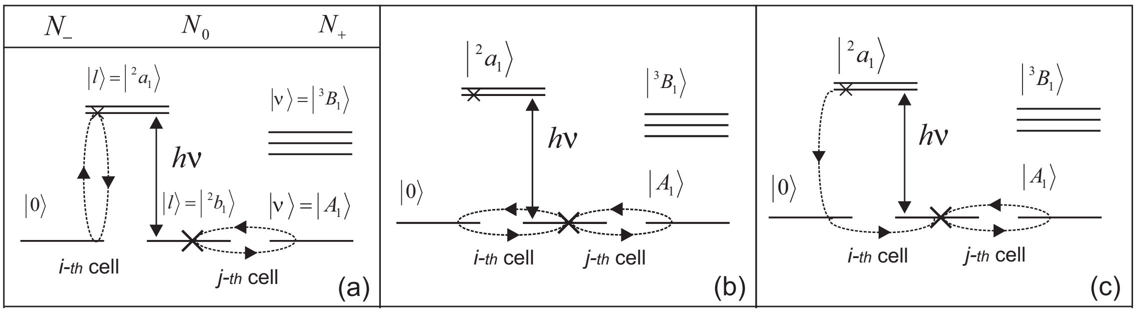

FIG. 2. Two circles (dashed line) are a sequence of intracell transitions at the light-induced superexchange J_{ij}^{ab} (a) and J_{ij}^{bb} (b) between i and j cells in Eq. (25); (c) illustrates the single circle (spin-exciton) contribution $\sim (t_{ij}^{a0,bA} t_{ji}^{b0,bA})/\Delta_{abA}$ (for cuprates),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

Applicability of the expressions (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. 2(b), while the superexchanges (25) via optical excited state is shown in Fig. 2(a). At $l \neq l'$ the last represents a nonsymmetrical interaction with one excited cell in the pair. The spin-exciton contribution ($\sim X_{i(j)}^{l_0 l}$) in Eq. (23) beyond Heisenberg model is shown in Fig. 2(c). From Eq. (24) it follows that the optical pumping effects on the superexchange are frequency selective and linear on the amplitude pumping.

III. OPTICAL EFFECTS ON SUPEREXCHANGE IN COPPER OXIDE AND IRON BORATE

A. La$_2$CuO$_4$

We test the approach to derive the superexchange in the high-T_c parent material La214 under optical pumping. The initial Hamiltonian (1) is similar to the one of the multiband *pd* model [34]. The difference with the low energy three orbital *pd* model [35–37] is related to an addition of the z-oriented d_{z^2} orbital and $p_z^{(ap)}$ orbital of the apical oxygen ions. In the LDA+GTB method the Hamiltonian parameters are calculated *ab initio* [8].

Unlike the work in [37], 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 [13] in atomic representation and the exact diagonalization of finite clusters [13,38–41] 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:

$$\begin{aligned} \langle H_{s-\mathrm{ex}} \rangle &\approx -\frac{1}{2} \sum_{ij} \sum_{ll'} J_{ij}^{ll'} \langle X_i^{l\sigma l\sigma} \rangle \langle X_i^{l'\bar{\sigma} l'\bar{\sigma}} \rangle \\ &\approx -\frac{zN}{2} \left[J_{\langle ij \rangle}^{l_0 l_0} p_{l_0}^2 + 2 \sum_{l \neq l_0} J_{\langle ij \rangle}^{l l_0} p_l p_{l_0} + \sum_{l \neq l_0} J_{\langle ij \rangle}^{ll'} p_l p_{l'} \right], \end{aligned} \tag{26}$$

where $p_{l_0} = 1 - (\sum_{l \neq l_0} p_l)$ and $p_l = \langle X_i^{l\uparrow l\uparrow} \rangle = \langle X_i^{l\downarrow l\downarrow} \rangle$ is a probability to detect a cell in $|(N_0, M_S)_l\rangle$ excited state. Using the exact diagonalization procedure with LDA parameters, $J_{bb} \approx 0.15$ eV, $\delta_{ll_0} = \delta_{ab} = 1.78$ eV, and $E_g = 2.00$ eV taken from the work [8], and the band index $r = \{^2b_1, A_1\}$ associated with the first removal electron state for a pair of indexes $\{l_0, \mu_0\}$ [15,24], one can obtain the weights α_l, β_l and A_μ, B_μ at the doublet (6) and singlet, triplet (7) states:

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

and

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

where h_b and h_{d_x} are the holes in the b-symmetrized $p_{\theta i}$ cell states of oxygen and $d_{x^2-y^2}$ copper states of the CuO$_2$ layer, respectively. Because of $\delta_{ab} < E_g$, only two contributions from the doublets $|^2a_1\rangle$ and $|^2b_1\rangle$ 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

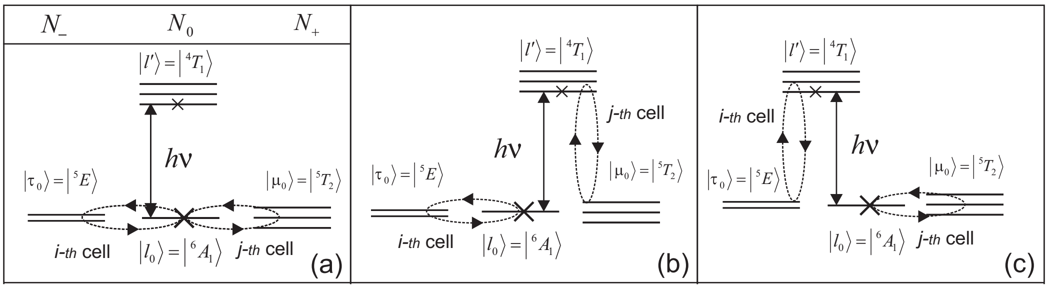

FIG. 3. Sequence of intracell transitions at the superexchange $J_{ij}^{(a)}(l_0\tau_0,l_0\mu_0)$ (a), optical induced superexchange $J_{ij}^{(b)}(l_0\tau_0,l'\mu_0)$ (b), and $J_{ij}^{(c)}(l'\tau_0,l_0\mu_0)$ (c) in FeBO$_3$.

evaluate the contribution from excited states like the next:

$$\begin{aligned}\langle\delta H_{s-\mathrm{ex}}\rangle &= -\frac{zN}{2}\sum_{\mu}\left\{\frac{(t^{b0,b\mu})^2}{\Delta_{b\mu}}p_b^2 + 2\left(\frac{(t^{b0,a\mu})^2}{\Delta_{ba\mu}} + \frac{(t^{a0,b\mu})^2}{\Delta_{ba\mu}}\right)p_a p_b + \frac{(t^{a0,a\mu})^2}{\Delta_{b\mu}}p_a^2\right\}\\ &\approx -\frac{zN}{2}\left\{0.15(\mathrm{eV})\times p_b^2 + 2\frac{(t^{a0,bA_1})^2}{\Delta_{baA_1}}p_a p_b\right\}.\end{aligned} \tag{29}$$

In unexcited material $p_b = 1$, $p_a = 0$, and Eq. (29) results in the exchange interaction $J_{bb} \sim 0.15$ eV in the ground state [17]. 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 $|{}^2b_1\rangle$ and excited $|{}^2a_1\rangle$ 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. 2(a)]. Summing over all μth 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 $\sim 4\times 10^{-3}$ eV(%)$^{-1}$, i.e., the superexchange interaction is increased by 4 meV at $x = 0.01$.

B. FeBO$_3$

Unlike La214, the high spin $S_{l_0} = 5/2$ (see Fig. 3) at the ground cell state is observed in FeBO$_3$, and even the optically excited electron-hole pair at $\nu \sim E_g$ will have magnetic properties. In addition, the first excited state $|l'\rangle$ of the cell in FeBO$_3$ differs from the ground state $|l_0\rangle$ due to the reduced spin $S_{l'} = 3/2$. To compare the superexchange in these different materials it is necessary to extend the calculations from the Kramers doublets in La214 to the arbitrary spin multiplets in FeBO$_3$. This leads to cumbersome expressions, but their physical meaning is interesting enough to obtain some qualitative conclusions on the superexchange in AFM iron borate under optical pumping.

In accordance with the transition procedure to the representation of the Hubbard operators, any one-electron operators can be represented as a superposition of the many-electron X-operators:

$$\begin{aligned}c^{+}_{\lambda f\sigma} = &\sum_{l\mu}\left[\gamma_\lambda^{(t)}(l\mu)\alpha_{f\sigma}^{(t)+}(\mu l) + \gamma_\lambda^{(s)}(l\mu)\alpha_{f\sigma}^{(s)+}(\mu l)\right]\\ &+ \sum_{\tau l}\left[\gamma_\lambda^{(t)}(\tau l)\beta_{f\sigma}^{(t)+}(l\tau) + \gamma_\lambda^{(s)}(\tau l)\beta_{f\sigma}^{(s)+}(l\tau)\right],\end{aligned} \tag{30}$$

where $c^{+}_{\lambda(\alpha)f\sigma}$ runs over all $d^{+}_{\lambda f\sigma}$ and $p^{+}_{\theta f\sigma}$ operators taken into account, and new operators $\alpha_{f\sigma}^{(s,t)+}(l\mu)$ and $\beta_{f\sigma}^{(s,t)+}(\tau l)$ are calculated in accordance with the rule of addition of angular momenta [42]:

$$\begin{aligned}\alpha_{f\sigma}^{(s)+}(l\mu) &= \eta(\sigma)\sum_{-M_\mu}^{M_\mu}\sqrt{\frac{S_l - \eta(\sigma)M_\mu + \frac{1}{2}}{2S_l + 1}}X_f^{M_\mu,M_l=M_\mu-\sigma}, & \alpha_{f\sigma}^{(t)+}(\tau l) &= \sum_{-M_\mu}^{M_\mu}\sqrt{\frac{S_l + \eta(\sigma)M_\mu + \frac{1}{2}}{2S_l + 1}}X_f^{M_\mu,M_l=M_\mu-\sigma},\\ \beta_{f\sigma}^{(s)+}(\tau l) &= \eta(\sigma)\sum_{-M_l}^{M_l}\sqrt{\frac{S_\tau - \eta(\sigma)M_l + \frac{1}{2}}{2S_\tau + 1}}X_f^{M_l,M_\tau=M_l-\sigma}, & \beta_{f\sigma}^{(t)+}(l\tau) &= \sum_{-M_l}^{M_l}\sqrt{\frac{S_\tau + \eta(\sigma)M_l + \frac{1}{2}}{2S_\tau + 1}}X_f^{M_l,M_\tau=M_l-\sigma},\end{aligned} \tag{31}$$

where the operators $\alpha_{f\sigma}^{(s,t)+}(l\mu)$ and $\beta_{f\sigma}^{(s,t)+}(\tau l)$ are defined on a set $\{N_- \leftrightarrow N_0\}$ of all possible quasiparticle states in the valence band, and $\{N_0 \leftrightarrow N_+\}$ states in the conduction band, respectively, and the matrix elements $\gamma_\lambda^{(s,t)}(l\tau)$ and $\gamma_\lambda^{(s,t)}(\mu l)$ have the same meaning as in Eq. (5). The operators (31) affect immediately all components of the spin multiplets $S_\tau = -M_\tau \div M_\tau$, $S_l = -M_l \div M_l$, and $S_\mu = -M_\mu \div M_\mu$ in sectors N_-, N_0, and N_+.

The representation (31) does not lead to any fundamental differences in previously used cell perturbation theory, since contributions from the low spin (s) and high spin (t) partners are similar to contributions (25) from the singlet and triplet states in AFM and FM superexchange for La214. Using the generalized projection operators (with replacement p_0 to $\sum_\tau p_\tau$) the commutator (19) may be written in the same form, wherein

$$\hat{h}_1^{\text{out}} = \sum_{\tau l l' \mu}\left[t_{ij}^{\mu l',\tau l}\sum_\sigma \alpha_{i\sigma}^{(s)+}(\mu l')\beta_{j\sigma}^{(t)}(\tau l) + t_{ij}^{l\tau,l'\mu}\sum_\sigma \beta_{i\sigma}^{(t)+}(l\tau)\alpha_{j\sigma}^{(s)}(l'\mu)\right] \tag{32}$$

and

$$G = \sum_{\tau l l' \mu}\left[\frac{t_{ij}^{\mu l',\tau l}}{\Delta_{\tau l l' \mu}}\sum_\sigma \alpha_{i\sigma}^{(s)+}(\mu l')\beta_{j\sigma}^{(t)}(\tau l) - \frac{t_{ij}^{l\tau,l'\mu}}{\Delta_{\tau l l' \mu}}\sum_\sigma \beta_{i\sigma}^{(t)+}(l\tau)\alpha_{j\sigma}^{(s)}(l'\mu)\right], \tag{33}$$

where $\Delta_{\tau l l'\mu} = (\varepsilon_\mu + \varepsilon_\tau) - (\varepsilon_l + \varepsilon_{l'})$. Here, for example, contributions only from $|\tau_0\rangle$, $|l_0\rangle$, and $|\mu_0\rangle$ ground states in N_-, N_0, N_+ sectors for FeBO$_3$ (Fig. 3) have AFM character:

$$\hat{H}_s = \sum_{i\neq j}\frac{J_{ij}^{(a)}(l_0\tau_0,l_0\mu_0)}{(2S_{\tau_0}+1)(2S_{l_0}+1)}\left\{\left(\hat{S}_{il_0}\hat{S}_{jl_0} - \frac{1}{4}\hat{n}_{il_0}\hat{n}_{jl_0}\right) - \left(\hat{S}_{i\tau_0}\hat{S}_{j\mu_0} - \frac{1}{2}\hat{n}_{i\tau_0}\hat{n}_{j\mu_0}\right)\right\} \tag{34}$$

with the exchange constant $J_{ij}^{(a)} = 2(t_{ij}^{l_0\tau_0,l_0\mu_0})^2/\Delta_{\tau_0 l_0\mu_0}$, where $\Delta_{\tau_0 l_0 \mu_0} = (\varepsilon_{\mu_0} + \varepsilon_{\tau_0} - 2\varepsilon_{l_0})$, and factor $(2S_{\tau_0}+1)^{-1}(2S_{l_0}+1)^{-1} = 1/30$ according to the one-electron nature of superexchange between cells with high spins and a sum over all the λ orbitals in Eq. (4).

To derive Eq. (34), we also used the relations between the operators (31) and spin, and also commutation relations between the different components of the spin:

$$\begin{aligned}\hat{n}_{l_0\sigma} &= (2S_{\tau_0}+1)\beta_\sigma^{(t)+}(l_0\tau_0)\beta_\sigma^{(t)}(\tau_0 l_0) = (2S_{l_0}+1)\alpha_{\bar\sigma}^{(s)}(l_0\mu_0)\alpha_{\bar\sigma}^{(s)+}(\mu_0 l_0),\\ S_{l_0}^+ &= (2S_{\tau_0}+1)\beta_\uparrow^{(t)+}(l_0\tau_0)\beta_\downarrow^{(t)}(\tau_0 l_0) = -(2S_{l_0}+1)\alpha_\downarrow^{(s)}(l_0\mu_0)\alpha_\uparrow^{(s)+}(\mu_0 l_0)\end{aligned} \tag{35}$$

and

$$\begin{aligned}\hat{n}_{\tau_0\sigma} + \hat{n}_{\tau_0}/(2S_{\tau_0}) &= (2S_{\tau_0}+1)\beta_\sigma^{(t)}(\tau_0 l_0)\beta_\sigma^{(t)+}(l_0\tau_0), \quad S_{\tau_0}^+ = (2S_{\tau_0}+1)\beta_\downarrow^{(t)}(\tau_0 l_0)\beta_\uparrow^{(t)+}(l_0\tau_0),\\ \hat{n}_{\mu_0\sigma} &= (2S_{l_0}+1)\alpha_{\bar\sigma}^{(s)+}(\mu_0 l_0)\alpha_{\bar\sigma}^{(s)}(l_0\mu_0), \quad S_{\mu_0}^+ = -(2S_{l_0}+1)\alpha_\uparrow^{(s)+}(\mu_0 l_0)\alpha_\downarrow^{(s)}(l_0\mu_0).\end{aligned} \tag{36}$$

Unlike La214, in the optically unexcited FeBO$_3$ the FM contribution in Eq. (22) from high spin partners to the superexchange is absent, since the ground state of the cell in the undoped material has the highest possible spin 5/2. Noteworthy in Eq. (34) is that the optical pumping with a frequency $\nu \sim E_g$ generates an exchange-coupled electron-hole pair. The superexchange in this pair is equal in magnitude and opposite in sign to superexchange in ground AFM state, i.e., the optic excited electron and hole in FeBO$_3$ will be connected by the FM superexchange [see second term in Eq. (34)]. In this case, the spin both at the hole S_{τ_0}, and the electrons S_{μ_0} in many-electron states are equal to 2 (see Fig. 3).

By adding the excited state $|l'\rangle$ to the ground states $|\tau_0\rangle$, $|\mu_0\rangle$, and $|l_0\rangle$, it is possible to investigate the effects of optical pumping at a frequency of d-d transitions. In accordance with the new sequence of quasiparticle transitions (Fig. 3), in the commutator (19) $\alpha_\sigma^{(s)+}(S_{l_0} = 5/2 \to S_{\mu_0} = 2)$ and $\beta_\sigma^{(t)+}(S_{\tau_0} = 2 \to S_{l_0} = 5/2)$ are replaced by $\alpha_\sigma^{(t)+}(S_{l'} = 3/2 \to S_{\mu_0} = 2) = \alpha_\sigma^{(t)+}(l'\mu_0)$ and $\beta_\sigma^{(s)+}(S_{\tau_0} = 2 \to S_{l'} = 3/2) = \beta_\sigma^{(s)+}(\tau_0 l')$, respectively. Thus the following relations for new operators are satisfied

$$\begin{aligned}\hat{n}_{l_0\sigma} &= (2S_{\tau_0}+1)\beta_\sigma^{(t)+}(l_0\tau_0)\beta_\sigma^{(t)}(\tau_0 l_0), \quad \hat{n}_{l'\sigma} = (2S_{l'}+1)\alpha_\sigma^{(t)}(l'\mu_0)\alpha_\sigma^{(t)+}(\mu_0 l'),\\ S_{l_0}^+ &= (2S_\tau+1)\beta_\uparrow^{(t)+}(l_0\tau)\beta_\downarrow^{(t)}(\tau l_0), \quad S_{l'}^+ = (2S_{l'}+1)\alpha_\downarrow^{(t)}(l'\mu)\alpha_\uparrow^{(t)+}(\mu l'),\\ \hat{n}_{l'\sigma} &= (2S_\tau+1)\beta_{\bar\sigma}^{(s)+}(l'\tau)\beta_{\bar\sigma}^{(s)}(\tau l'), \quad \hat{n}_{l_0\sigma} = (2S_{l_0}+1)\alpha_{\bar\sigma}^{(s)}(l_0\mu)\alpha_{\bar\sigma}^{(s)+}(\mu l_0),\\ S_{l'}^+ &= -(2S_\tau+1)\beta_\uparrow^{(s)+}(l'\tau)\beta_\downarrow^{(s)}(\tau l'), \quad S_l^+ = -(2S_{l_0}+1)\alpha_\downarrow^{(s)}(l_0\mu)\alpha_\uparrow^{(s)+}(\mu l_0).\end{aligned} \tag{37}$$

Unlike La214 superexchange in the optically excited FeBO$_3$ contains qualitatively new contributions,

$$\hat{h}_s = -\sum_{ij}\left\{\frac{J_{ij}^{(b)}(l_0\tau_0 l'\mu_0)}{(2S_{\tau_0}+1)(2S_{l'}+1)} + \frac{J_{ij}^{(c)}(l'\tau_0 l_0\mu_0)}{(2S_{\tau_0}+1)(2S_{l_0}+1)}\right\}\left(\hat{S}_{il_0}\hat{S}_{jl'} + \frac{1}{4}\hat{n}_{il_0}\hat{n}_{jl'}\right), \tag{38}$$

where

$$J_{ij}^{(b)}(l_0\tau_0,l'\mu_0) = 2\left(t_{ij}^{l_0\tau_0,l'\mu_0}\right)^2/\Delta_{\tau_0 l_0 l'\mu_0}, \quad J_{ij}^{(c)}(l'\tau_0,l_0\mu_0) = 2\left(t_{ij}^{l'\tau_0,l_0\mu_0}\right)^2/\Delta_{\tau_0 l_0 l'\mu_0}. \tag{39}$$

From this relation it follows that under the optical pumping with a frequency $\nu < E_g$ there is the contribution similar to Eq. (25), and because of the reduced spin $S_{l'} = 3/2$ at the first excited state $|l'\rangle$ (Fig. 3) it has a FM nature.

C. Effects of DM interaction

The effects of DM interaction are observed in La214 and FeBO_3 due to canting of magnetic moments in a nonexcited ground state [43–46]. Using the ideas from the Appendix in [47], where the author starts from the localized electron orbital states and considers the spin-orbit coupling as a perturbation, the ground state may be written

$$|\tilde{l}_0\rangle \approx |l_0\rangle + \frac{\langle l'|\xi_{il_0}(\hat{L}_i\hat{S}_{il_0})|l_0\rangle}{\delta_{l_0l'}}|l'\rangle, \tag{40}$$

where the spin-orbital interaction ξ_{il_0} just gives corrections to the ground state $|l_0\rangle$ of the $i(j)$th cell due to the same total moment $(L_i + S_i)$ at the $|l'\rangle = |^4T_1\rangle$ state in FeBO_3. Following Eq. (22) and Eq. (25) the DM interaction $\hat{H}_{DM} = \hat{H}_{DM}^{(0)} + \hat{H}_{DM}^{(ex)}$ with contribution $\hat{H}_{DM}^{(0)}$ in unexcited material and optical induced contribution $\hat{H}_{DM}^{(ex)}$ can be derived in the form

$$\begin{aligned}\hat{H}_{DM}^{(0)} \approx i\sum_{ij}&\left\{\frac{J_{ij}^{(b)}(l_0\tau_0,l'\mu) + J_{ij}^{(c)}(l'\tau_0,l_0\mu)}{(2S_{\tau_0}+1)(2S_{l_0}+1)}\right\}\\ &\times\frac{\{\langle l'|\xi_{il_0}\hat{L}_i|l_0\rangle - \langle l'|\xi_{jl_0}\hat{L}_j|l_0\rangle\}}{\delta_{l_0l'}}[\hat{S}_{il_0}\times\hat{S}_{jl_0}]\end{aligned} \tag{41}$$

and

$$\begin{aligned}\hat{H}_{DM}^{(ex)} \approx -2i\sum_{ij}&\left\{\frac{J_{ij}(l'\tau_0,l'\mu_0)(S_{l_0}+S_{l'}+1)}{(2S_{\tau_0}+1)(2S_{l_0}+1)(2S_{l'}+1)}\right\}\\ &\times\left\{\frac{\langle l'|\xi_{il_0}\hat{L}_i|l_0\rangle}{\delta_{l_0l'}}[\hat{S}_{il_0}\times\hat{S}_{jl'}]\right.\\ &\left.-\frac{\langle l'|\xi_{jl_0}\hat{L}_j|l_0\rangle}{\delta_{l_0l'}}[\hat{S}_{il'}\times\hat{S}_{jl_0}]\right\}.\end{aligned} \tag{42}$$

Therefore, a relative orientation of the spins and the DM vector is changed under optical pumping because of the induced FM superexchange (38) in FeBO_3. Note also that

$$\hat{H}_{DM}^{(ex)} \approx -\sum_{ij}\vec{D}_{ij}^{l'l_0}\{[\hat{S}_{il_0}\times\delta\hat{S}_{jl}] - [\delta\hat{S}_{il}\times\hat{S}_{jl_0}]\} \neq 0, \tag{43}$$

at forbidden simultaneous optical transitions in ith and jth cells in the exchange-coupled pair with an inversion center and $\delta\hat{S}_{il} = (\hat{S}_{jl} - \hat{S}_{jl_0})$, where the magnitude of the DM vector

$$D_{i,j}^{l'l_0} = 2i\,J_{ij}(l'\tau_0,l'\mu_0)\frac{\langle l'|\xi_{il_0}\hat{L}_i|l_0\rangle}{\delta_{l_0l'}}, \tag{44}$$

and $J_{ij}(l'\tau_0,l'\mu_0)$ is equal to the expression in the first braces of Eq. (42). The spin forbidden optical *d-d* excitations are authentically observed in magnetic materials (see, e.g., the works [22,48] and references therein).

IV. 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 [21]. The effective Hamiltonian (21) contains not only spin-spin interactions involving optical excited states but more complicated interactions of non-Heisenberg type accompanied with exciton or biexciton. The Hamiltonian is nonadditive over the ground and optical excited states, but it is additive to the virtual excited states. To test our approach, we have calculated the superexchange interaction and DM interaction in antiferromagnets La214 and FeBO_3 under optical pumping.

In cuprates under optical pumping with a frequency of *d-d* transitions ($\nu < E_g$) AFM superexchange enhanced by 40 K on 1% of the occupation of excited state. The DM interaction 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 optical induced magnetism of an electron-hole pair does 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 $\Delta E \sim$ 0-2 eV. Let us note here the discrepancy of our results and the general trend given in the work of [49], where the excited states contribute to the FM exchange at the low "charge transfer energies" ($\Delta_{ll'\mu}$ in our notation).

In contrast La214, the results for FeBO_3 are qualitative in nature. In iron borates under optical pumping with a frequency of *d-d* transitions, the initial AFM superexchange (34) changes its character on FM (38) due to the spin forbidden optical excitations $|^6A_1\rangle \to |^4T_1\rangle$ (Fig. 3). The initial DM interaction (41) undergoes a significant perturbation (42) since the mutual orientation of the spins and the DM vector is changed by the induced FM contribution. The magnitude of the induced DM interaction (42) depends on the nature of the forbidden optical *d-d* transitions. In particular, the nonzero DM interaction is induced at the forbidden simultaneous *d-d* transitions in the exchange-coupled (i,j)th pair with a center of inversion. The irradiation with a frequency of corresponding to charge-transfer excitations results in the induced exchange-coupled electron-hole pairs, since the electron and hole have high spins $S_{\mu_0} = S_{\tau_0} = 2$ in FeBO_3. The superexchange in the induced electron-hole pair is equal in magnitude but opposite in sign to the AFM superexchange between the cells at the ground states in unexcited iron borate.

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