General superexchange Hamiltonians for magnetic and orbital physics in e_g and t_{2g} systems

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Material-specific super-exchange Hamiltonians are the key to studying spin and orbital physics in strongly correlated materials. Recently, via an irreducible-tensor operator representation, we derived the orbital superexchange Hamiltonian for t_{2g}^1 perovskites and successfully used it, in combination with many-body approaches, to explain orbital physics in these systems. Here, we generalize our method to e_g^n and t_{2g}^n systems at arbitrary integer filling n, including both spin and orbital interactions. The approach is suitable for numerical implementations based on *ab initio* hopping parameters and realistic screened Coulomb interactions and allows for a systematic exploration of superexchange energy surfaces in a realistic context.

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I. INTRODUCTION

In strongly correlated transition-metal oxides, spin- and orbital-ordering or spin- and orbital-liquid phenomena are often studied with low-energy superexchange Hamiltonians, derived from multiband Hubbard models in highly symmetric cases and in a basis of pseudospin operators [1–4]. This captures the essence of the Kugel-Khomskii [1] superexchange mechanism but misses the important material dependencies. An alternative approach starts from material-specific Hubbard models constructed from *ab initio* calculations, solving them using many-body techniques, e.g., via the dynamical mean-field theory (DMFT) [5,6]. This method is very powerful and has allowed us to study superexchange-driven phase transitions [7–10] for the actual materials, identify their mechanisms, and calculate the associated energy gains [11] and response functions [12]. For exploring entire energy surfaces, identifying possible unusual symmetry-breaking ordering, or calculating spin- and orbital-wave spectra, the systematic solution of realistic multiorbital Hubbard models is, however, computationally very costly.

Recently, we have shown that integrating the two approaches can lead both to further insights and efficiency increases, providing guidance for limiting heavy many-body calculations only to targeted cases. This made it possible to clarify the origin of orbital ordering in the t_{2g}^1 perovskites [13]. In this paper, we generalize the approach to e_g^n and t_{2g}^n systems with arbitrary n, including the spin-dependent terms of the superexchange Hamiltonian. In addition to giving analytical expressions, our method enables lightweight numerical implementations for realistic Coulomb interactions in combination with *ab initio* Wannier functions and is thus the ideal tool for the study of strongly correlated materials of any symmetry in a realistic setting.

This paper is organized as follows. In Sec. II, we introduce the general formalism by applying it to a well-known case, the single-band Hubbard model. In Sec. III, we derive the general analytic formulas of superexchange couplings for e_g^n systems. In Sec. IV, we do the same for t_{2g}^n systems. Comprehensive tables summarizing the main results are provided in each case. In Sec. V, we discuss energy surfaces. Finally, in Sec. VI, we present our conclusions.

II. FORMALISM

The superexchange Hamiltonian has the form:

$$\hat{H}_{\rm SE} = \frac{1}{2}\sum_{ij}\hat{H}_{\rm SE}^{ij}, \tag{1}$$

where i and j are neighboring sites coupled via hopping integrals. This Hamiltonian acts in the subspace of states with $|n_i, n_j\rangle$, where n_i and n_j are the site occupations with the constraint $n_i+n_j = N = 2n$, where n is the number of electrons per site. From strong-coupling second-order perturbation theory, Eq. (1) can be written as

$$\hat{H}_{\rm SE} = -\hat{H}_{\rm T}(\hat{H}_U - E_0)^{-1}\hat{H}_{\rm T},$$

so that

$$\hat{H}_{\rm SE}^{ij} = -\hat{H}_{\rm T}(\hat{P}_{ij} + \hat{P}_{ji})\hat{H}_{\rm T}.$$

Here, $\hat{P}_{ij}$ is an operator which projects, with an energy denominator, to atomic excited states of type $|n_i+1, n_j-1\rangle$, and $\hat{H}_{\rm T}$ is the hopping part of the Hubbard Hamiltonian from which the superexchange interaction is derived, while $\hat{H}_U$ is the electron-electron repulsion.

Let us start from the well-known case of magnetic exchange for the single-band Hubbard model:

$$\hat{H} = \underbrace{-\sum_{\sigma}\sum_{i,j} t^{i,j} c_{i\sigma}^{\dagger} c_{j\sigma}}_{\hat{H}_{\rm T}} + \underbrace{U\sum_{i}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}}_{\hat{H}_U}, \tag{2}$$

where $\hat{n}_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$, $t^{i,j}$ is the hopping integral and U the screened Coulomb parameter. Since the atomic limit of the half-filled Hubbard Hamiltonian has only spin degrees of freedom, one can write the associated exchange Hamiltonian in an

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irreducible tensor basis as

$$\hat{H}_{\mathrm{SE}}^{ij} = \sum_{qq'} \sum_{\nu\nu'} \hat{s}_i^{q,\nu} D_{q\nu,q'\nu'}^{ij} \hat{s}_j^{q',\nu'}, \tag{3}$$

where $q = 0, 1$ is the rank of the operators and ν the associated components. For $q = 0$, the only component is $\nu = s$, while for $q = 1$, we have instead $\nu = x, y, z$ in the real harmonics representation. For convenience, we normalize the tensors such that

$$\sum_\sigma \langle 0|c_{i\sigma} \left(\hat{s}_i^{q,\nu}\right)^2 c_{i\sigma}^\dagger |0\rangle = 1. \tag{4}$$

With this convention, the irreducible tensors are

$$\hat{s}_i^{0,s} = \frac{1}{\sqrt{2}} \sum_\sigma c_{i\sigma}^\dagger c_{i\sigma}, \tag{5}$$

$$\hat{s}_i^{1,\nu} = \frac{1}{\sqrt{2}} \sum_{\sigma\sigma'} c_{i\sigma}^\dagger \langle\sigma|\hat{\sigma}^\nu|\sigma'\rangle c_{i\sigma'}, \tag{6}$$

where $\hat{\sigma}_\nu$ is the $\nu = x, y, z$ Pauli matrix. At half-filling ($n_i = n_j = 1$), we define the projectors as

$$\hat{P}_{ij} = \sum_{\alpha_+\alpha_-} \frac{|\alpha_+\rangle_i |\alpha_-\rangle_j\, {}_j\langle\alpha_-|\, {}_i\langle\alpha_+|}{E_{\alpha_+} + E_{\alpha_-} - 2E_0}, \tag{7}$$

where $|\alpha_\pm\rangle_i$ are atomic (site i) multiplets with $n_i \pm 1$ electrons, quantum number $\alpha_\pm$ and energy $E_{\alpha_\pm}$. In the case of the single-band Hubbard model, $|\alpha_+\rangle_i$ and $|\alpha_-\rangle_i$ are, respectively, the doubly occupied and the vacuum state; in general, however, α_+ and α_- will label several excited states with different energies. Here, E_0 is the energy of the ground state with $N = n_i + n_j = 2$ electrons in the atomic limit, here, $E_0 = 0$. The tensor elements in Eq. (3) are obtained using the orthogonality properties of irreducible tensors. To this end, we multiply by a pair of irreducible operators, one for site i and one for site j, and trace over all states in the atomic ground multiplet. This yields

$$\begin{aligned} D_{0s,0s}^{ij} &= -\frac{\mathrm{Tr}\left[\hat{s}_i^{0,s}\hat{s}_j^{0,s}\hat{H}_{\mathrm{T}}(\hat{P}_{ij}+\hat{P}_{ji})\hat{H}_{\mathrm{T}}\right]}{\mathrm{Tr}\left[\left(\hat{s}_i^{0,s}\right)^2\left(\hat{s}_j^{0,s}\right)^2\right]} \\ &= -2\frac{|t^{i,j}|^2}{U}, \end{aligned}$$

and

$$\begin{aligned} D_{1\nu,1\nu'}^{ij} &= -\frac{\mathrm{Tr}\left[\hat{s}_i^{1,\nu}\hat{s}_j^{1,\nu'}\hat{H}_{\mathrm{T}}(\hat{P}_{ij}+\hat{P}_{ji})\hat{H}_{\mathrm{T}}\right]}{\mathrm{Tr}\left[\left(\hat{s}_i^{1,\nu}\right)^2\left(\hat{s}_j^{1,\nu'}\right)^2\right]} \\ &= 2\frac{|t^{i,j}|^2}{U}\delta_{\nu,\nu'}. \end{aligned}$$

All crossed terms involving a tensor with $q = 0$ and one with $q = 1$ vanish due to the spin-rotational invariance of the Hubbard model. This gives the expected result:

$$\begin{aligned} \hat{H}_{\mathrm{SE}}^{ij} &= 2\frac{|t^{i,j}|^2}{U}\left(\sum_\nu \hat{s}_i^{1,\nu}\hat{s}_j^{1,\nu} - \hat{s}_i^{0,s}\hat{s}_j^{0,s}\right) \\ &= 4\frac{|t^{i,j}|^2}{U}\left(\mathbf{S}_i\cdot\mathbf{S}_j - \frac{n_i n_j}{4}\right), \end{aligned} \tag{8}$$

where $\mathbf{S}_i$ is the usual spin operator.

III. TWO-BAND HUBBARD MODEL

We now generalize to the case of the two-band e_g Hubbard model:

$$\hat{H} = \underbrace{-\sum_\sigma \sum_{ij} t_{m,m'}^{i,j} c_{i,m\sigma}^\dagger c_{j,m'\sigma}}_{\hat{H}_{\mathrm{T}}} + \hat{H}_U, \tag{9}$$

where $m = x^2{-}y^2$ and $3z^2{-}r^2$. The $t_{m,m'}^{i,j}$ are effective hopping integrals, obtained by downfolding the high-energy degrees of freedom. In transition-metal systems, these include, for example, p bands of oxygen or fluorine ions which build the bridge between two d transition metal atoms. We adopt the Kanamori form of the Coulomb interaction:

$$\begin{aligned} \hat{H}_U &= U\sum_i\sum_m \hat{n}_{i,m\uparrow}\hat{n}_{i,m\downarrow} \\ &\quad + \frac{1}{2}\sum_i\sum_{m\neq m'}\sum_{\sigma\sigma'}(U-2J-J\delta_{\sigma,\sigma'})\hat{n}_{i,m\sigma}\hat{n}_{i,m'\sigma'} \\ &\quad - J\sum_i\sum_{m\neq m'} c_{i,m\uparrow}^\dagger c_{i,m\downarrow}^\dagger c_{i,m'\uparrow}c_{i,m'\downarrow} \\ &\quad - J\sum_i\sum_{m\neq m'} c_{i,m\uparrow}^\dagger c_{i,m\downarrow} c_{i,m'\downarrow}^\dagger c_{i,m'\uparrow}, \end{aligned} \tag{10}$$

where the last two terms are the pair-hopping and spin-flip interaction. For e_g electrons, the Kanamori interaction is the exact atomic limit Coulomb tensor. A detailed derivation can be found in Ref. [14].

As observed already above, terms with different spin ranks are decoupled due to the spin rotational invariance of the Hamiltonian, so that we can perform the calculation in two steps. Like in the single-band Hubbard model, the half-filled case has no orbital degeneracy since the Hund's rule ground multiplet is the state with $S = 1$ and therefore is not relevant in the context of orbital physics. Thus, here, we focus on $n = 1$ and 3. First, we consider the pure orbital superexchange, describing the paramagnetic phase (spin rank $q = 0$ terms). In the magnetic phase, additional superexchange couplings (spin rank $q = 1$ terms) are present, which influence both the magnetic and orbital states.

A. Paramagnetic case, $n = 1$

The superexchange terms with spin rank $q = 0$ can be expressed as

$$\hat{H}_{\mathrm{SE}}^{ij} = \sum_{rr'}\sum_{\mu\mu'} \hat{\tau}_i^{r,\mu} D_{r\mu,r'\mu'}^{ij} \hat{\tau}_j^{r',\mu'}, \tag{11}$$

where operator $\hat{\tau}_i^{r,\mu}$ is the μ component of the tensor with orbital rank r. In the e_g^1 configuration, it is convenient to define the orbital pseudospin states as

$$|\nearrow\rangle = |3z^2{-}r^2\rangle, \quad |\searrow\rangle = |x^2{-}y^2\rangle. \tag{12}$$

An atomic state with a single electron ($n = 1$) is then given by $|m,\sigma\rangle = c_{m,\sigma}^\dagger|0\rangle$, where $m = |\nearrow\rangle, |\searrow\rangle$ is the orbital and σ the spin component. We normalize the tensors such that

$$\sum_{m\sigma} \langle 0|c_{i,m\sigma} \left(\hat{\tau}_i^{r,\mu}\right)^2 c_{i,m\sigma}^\dagger|0\rangle = 1. \tag{13}$$

This leads to the expressions:

$$\hat{\tau}_i^{0,s} = \frac{1}{2}\sum_{m\sigma}\hat{n}_{i,m\sigma}, \tag{14}$$

$$\hat{\tau}_i^{1,\mu} = \frac{1}{2}\sum_{mm'\sigma} c^\dagger_{i,m\sigma}\hat{\sigma}^\mu_{m,m'}c^\dagger_{i,m'\sigma}, \tag{15}$$

where $\hat{\sigma}^\mu_{m,m'}$ are the elements of the Pauli matrices. We now split the tensor elements appearing in Eq. (11) in contributions from excited multiplets with doubly ($B^{ij}_{r\mu,r'\mu'}$) and singly ($C^{ij}_{r\mu,r'\mu'}$) occupied orbitals:

$$D^{ij}_{r\mu,r'\mu'} = B^{ij}_{r\mu,r'\mu'} + C^{ij}_{r\mu,r'\mu'}. \tag{16}$$

The doubly-occupied-orbital multiplets for site i are

$$|0,0\rangle_a = \frac{c^\dagger_{i,3z^2-r^2\uparrow}c^\dagger_{i,3z^2-r^2\downarrow} + c^\dagger_{i,x^2-y^2\uparrow}c^\dagger_{i,x^2-y^2\downarrow}}{\sqrt{2}}|0\rangle, \tag{17}$$

$$|0,0\rangle_b = \frac{c^\dagger_{i,3z^2-r^2\uparrow}c^\dagger_{i,3z^2-r^2\downarrow} - c^\dagger_{i,x^2-y^2\uparrow}c^\dagger_{i,x^2-y^2\downarrow}}{\sqrt{2}}|0\rangle, \tag{18}$$

and have Coulomb energies equal, respectively, $U+J$ and $U-J$. Summing up all terms of this kind, we find

$$B^{ij}_{r\mu,r'\mu'} = -2\sum_{a_1b_1c_1d_1}\tau^{ir\mu}_{a_1c_1}\tau^{jr'\mu'}_{b_1d_1}\frac{t^{i,j}_{c_1,d_1}\overline{t^{i,j}_{a_1,b_1}}}{U}\xi^B_\mu + (ir\mu)\leftrightarrow(jr'\mu'). \tag{19}$$

The labels a_1, b_1, c_1, d_1 indicate orbital quantum numbers, and

$$\tau^{ir\mu}_{ac} = \frac{\langle a,\sigma|\hat{\tau}_i^{r,\mu}|c,\sigma\rangle}{\sum_{m\sigma}\langle 0|c_{i,m\sigma}\left(\hat{\tau}_i^{r,\mu}\right)^2c^\dagger_{i,m\sigma}|0\rangle}, \tag{20}$$

where $\sigma=\sigma_a=\sigma_c$. Since the operator $\hat{\tau}_i^{r,\mu}$ traces over spin, the matrix element in Eq. (20) is spin independent. Finally, the energy denominators are collected in

$$\xi^B_\mu = v_1\delta_{\mu,0} + v_0(1-\delta_{\mu,0}), \tag{21}$$

with

$$v_0 = \tfrac{1}{2}(f_1 - f_{-1}), \quad v_1 = \tfrac{1}{2}(f_1 + f_{-1}), \tag{22}$$

and

$$f_\alpha = \frac{1}{1+\alpha J/U}. \tag{23}$$

Using the definition in Eq. (20) to treat the operators as matrices, we can rewrite the result in a compact form:

$$B^{ij}_{r\mu,r'\mu'} = -\frac{2}{U}\mathrm{tr}(t^{j,i}\tau^{ir\mu}t^{i,j}\overline{\tau^{jr'\mu'}})\xi^B_\mu + (ir\mu)\leftrightarrow(jr'\mu'), \tag{24}$$

where the (lowercase) trace is over orbital indices only. The second term in Eq. (16) arises from the remaining four excited multiplets:

$$|1,\sigma\rangle = c^\dagger_{i,3z^2-r^2\sigma}c^\dagger_{i,x^2-y^2\sigma}|0\rangle, \tag{25}$$

$$|1,0\rangle = \frac{c^\dagger_{i,3z^2-r^2\uparrow}c^\dagger_{i,x^2-y^2\downarrow} + c^\dagger_{i,3z^2-r^2\downarrow}c^\dagger_{ix^2-y^2\uparrow}}{\sqrt{2}}|0\rangle, \tag{26}$$

$$|0,0\rangle = \frac{c^\dagger_{i,3z^2-r^2\uparrow}c^\dagger_{i,x^2-y^2\downarrow} - c^\dagger_{i,3z^2-r^2\downarrow}c^\dagger_{i,x^2-y^2\uparrow}}{\sqrt{2}}|0\rangle. \tag{27}$$

They correspond to the triplet and singlet states, which have Coulomb energies equal to $U-3J$ and $U-J$. In matrix form, it is given by

$$C^{ij}_{r\mu,r'\mu'} = -\frac{4}{U}[\mathrm{tr}(\tau^{ir\mu}t^{i,j}\sigma^x\overline{\tau^{jr'\mu'}}\sigma^x t^{j,i})]\xi^C_{\mu'} + (ir\mu)\leftrightarrow(jr'\mu'), \tag{28}$$

where σ^x is a Pauli matrix, and

$$\xi^C_\mu = v_2\delta_{\mu,0} - \frac{v_3}{2}(1-\delta_{\mu,0}), \tag{29}$$

with the energy denominators:

$$v_2 = \tfrac{1}{4}(3f_{-3} + f_{-1}), \quad v_3 = \tfrac{1}{2}(3f_{-3} - f_{-1}). \tag{30}$$

The irreducible elements of the orbital superexchange tensor $\hat{D}^{ij}$ are collected in Table I.

In the simple limit of a cubic perovskite, along the quantization axis $\hat{z}$, the only relevant effective hopping integral is the $dd\sigma$ hopping integral t between two $3z^2-r^2$ orbitals. This approximation is often used for describing the low-energy bands of $LaMnO_3$ or $KCuF_3$. Simplifying further by setting $J=0$ yields

$$B^{ij}_{r\mu,r\mu'} = -\frac{4t^2}{U}\sum_{a_1}\tau^{ir\mu}_{a_1a_1}\tau^{jr'\mu'}_{a_1a_1}\delta_{a_1,3z^2-r^2}\,\delta_{\mu,0}\delta_{\mu',0}, \tag{31}$$

$$C^{ij}_{r\mu,r\mu'} = -\frac{4t^2}{U}\sum_{a_1a_2}\tau^{ir\mu}_{a_1a_1}\sigma^x_{a_1,a_2}\tau^{jr'\mu'}_{a_2a_2}\delta_{\mu,0}\delta_{\mu',0}. \tag{32}$$

It follows that the only nonzero terms are

$$D^{ij}_{1z,1z} = \frac{\Gamma}{4}, \qquad D^{ij}_{0s,0s} = -\frac{3\Gamma}{4}, \qquad D^{ij}_{0s,1z} = -\frac{\Gamma}{4},$$

where $\Gamma = 4t^2/U$. This gives, of course, the usual Kugel-Khomskii [1,15] Hamiltonian:

$$\hat{H}^{i,j}_{\mathrm{SE}} = \frac{\Gamma}{4}\left(\hat{O}^i_z\hat{O}^j_z - 3\frac{\hat{n}^i\hat{n}^j}{4n_in_j} - \frac{\hat{n}^i}{2n_i}\hat{O}^j_z - \hat{O}^i_z\frac{\hat{n}^j}{2n_i}\right), \tag{33}$$

where $\hat{O}^i_z = \frac{1}{2}\hat{\sigma}_z$ is the $\hat{z}$ component of the conventional orbital pseudospin operator, and $n_i=1$. The expression along the other directions is obtained by rotating the quantization axes.

B. Magnetic terms, $n = 1$

Spin rank $q=1$ tensor elements can be obtained in an analogous way. The irreducible tensors here are

$$\hat{\tau}_i^{0,s;1,\nu} = \frac{1}{2}\sum_{m\sigma}c^\dagger_{i,m\sigma}\hat{\sigma}^\nu_{\sigma,\sigma'}c_{i,m\sigma'}, \tag{34}$$

$$\hat{\tau}_i^{1,\mu;1,\nu} = \frac{1}{2}\sum_{mm'}\sum_{\sigma\sigma'}c^\dagger_{i,m\sigma}\hat{\sigma}^\mu_{m,m'}\hat{\sigma}^\nu_{\sigma,\sigma'}c_{i,m'\sigma'}, \tag{35}$$

and are normalized as rank $q=0$ operators. The results obtained are given in Table I. One may notice that the only change with respect to $q=0$ is the (U,J)-dependent denominators in the table, which yield the transformation $\mathcal{V}\longrightarrow\tilde{\mathcal{V}}$.

TABLE I. Key tensor elements for the e_g^1 and e_g^3 configuration and spin ranks $q = 0$ and 1. The elements for the e_g^3 configuration are obtained setting a minus in front of all linear terms, i.e., those for which $r = 0$, $r' \neq 0$, or $r' = 0$, $r \neq 0$. The elements for imaginary tensors must be multiplied by i (linear terms, involving a single operator) or $i \times i$ (for products of two operators). The prefactors are obtained from the weights: $v_0 = \frac{1}{2}(f_1 - f_{-1})$, $v_1 = \frac{1}{2}(f_1 + f_{-1})$, $v_2 = \frac{1}{4}(3f_{-3} + f_{-1})$, and $v_3 = \frac{1}{2}(3f_{-3} - f_{-1})$. The rest of the matrix elements are given by symmetry: $D^{ij}_{r'\mu',r\mu} = s_\mu s_{\mu'} \overline{D^{ji}_{r\mu,r'\mu'}}$, where $s_\mu = 1$ is for real operators and $s_\mu = -1$ for imaginary ones. Since the model is rotationally invariant for spins, $q = 1$, $\nu = x, y, z$ elements are identical. They can be obtained from the table for $q = 0$, replacing $\mathcal{V}_0 \longrightarrow \tilde{\mathcal{V}}_0$, $\mathcal{V}_1 \longrightarrow \tilde{\mathcal{V}}_1$, $\mathcal{V}_2 \longrightarrow \tilde{\mathcal{V}}_2$, and $\mathcal{V}_3 \longrightarrow \tilde{\mathcal{V}}_3$. All hopping integrals are defined as $t^{i,j}_{m,m'}$ and are assumed to be real, as typically is the case in the absence of spin-orbit interaction.

r μ	r' μ'	e_g^1	e_g^3	$D^{ij}_{r\mu,r'\mu'} \times U/2$
0 s	0 s	$-\mathcal{V}_0$	$-\mathcal{V}_0$	$\left(t^2_{3z^2-r^2,3z^2-r^2} + t^2_{x^2-y^2,x^2-y^2} + t^2_{3z^2-r^2,x^2-y^2} + t^2_{x^2-y^2,3z^2-r^2}\right)$
0 s	1 z	$-\mathcal{V}_1$	$+\mathcal{V}_1$	$\left(t^2_{3z^2-r^2,3z^2-r^2} - t^2_{x^2-y^2,x^2-y^2} + t^2_{x^2-y^2,3z^2-r^2} - t^2_{3z^2-r^2,x^2-y^2}\right)$
0 s	1 x	$-\mathcal{V}_1$	$+\mathcal{V}_1$	$2(t_{3z^2-r^2,3z^2-r^2}t_{3z^2-r^2,x^2-y^2} + t_{x^2-y^2,x^2-y^2}t_{x^2-y^2,3z^2-r^2})$
1 z	1 z	$+\mathcal{V}_2$	$+\mathcal{V}_2$	$\left(t^2_{3z^2-r^2,3z^2-r^2} + t^2_{x^2-y^2,x^2-y^2} - t^2_{3z^2-r^2,x^2-y^2} - t^2_{x^2-y^2,3z^2-r^2}\right)$
1 x	1 x	$+\mathcal{V}_2$	$+\mathcal{V}_2$	$2(t_{3z^2-r^2,3z^2-r^2}t_{x^2-y^2,x^2-y^2} + t_{3z^2-r^2,x^2-y^2}t_{x^2-y^2,3z^2-r^2})$
1 z	1 x	$+\mathcal{V}_2$	$+\mathcal{V}_2$	$2(t_{3z^2-r^2,3z^2-r^2}t_{3z^2-r^2,x^2-y^2} - t_{x^2-y^2,x^2-y^2}t_{x^2-y^2,3z^2-r^2})$
1 y	1 y	$+\mathcal{V}_3$	$+\mathcal{V}_3$	$2(t_{3z^2-r^2,3z^2-r^2}t_{x^2-y^2,x^2-y^2} - t_{3z^2-r^2,x^2-y^2}t_{x^2-y^2,3z^2-r^2})$
q = 0		$\mathcal{V}_0 = \frac{v_1+2v_2}{2} = \frac{f_1+2f_{-1}+3f_{-3}}{4}$, $\mathcal{V}_1 = \frac{v_1}{2} = \frac{f_1+f_{-1}}{4}$,		
		$\mathcal{V}_2 = \frac{2v_2-v_1}{2} = \frac{3f_{-3}-f_1}{4}$, $\mathcal{V}_3 = \frac{v_0+v_3}{2} = \frac{3f_{-3}-2f_{-1}+f_1}{4}$		
q = 1		$\tilde{\mathcal{V}}_0 = -\frac{f_1+2f_{-1}-f_{-3}}{4}$, $\tilde{\mathcal{V}}_1 = -\mathcal{V}_1$, $\tilde{\mathcal{V}}_2 = \frac{f_1+f_{-3}}{4}$, $\tilde{\mathcal{V}}_3 = \frac{f_{-3}+2f_{-1}-f_1}{4}$		

C. The $n = 3$ case

The superexchange Hamiltonian for the e_g^3 configuration can be obtained from the $n = 1$ case by using the electron-hole transformation of the atomic-limit Hamiltonian. The pseudospin states are, in this case, defined as

$$|\nearrow\rangle = c^\dagger_{i,x^2-y^2\sigma} c^\dagger_{i,3z^2-r^2\uparrow} c^\dagger_{i,3z^2-r^2\downarrow}|0\rangle, \tag{36}$$

$$|\searrow\rangle = c^\dagger_{i,3z^2-r^2\sigma} c^\dagger_{i,x^2-y^2\uparrow} c^\dagger_{i,x^2-y^2\downarrow}|0\rangle, \tag{37}$$

and can be viewed as hole orbitals. Going to the hole representation, the final change in the tensor elements amounts to an extra minus in front of terms with either $r = 0$, $r' \neq 0$ or $r' = 0$, $r \neq 0$, as explained in Table I.

IV. THREE-BAND t_{2g} MODEL

The family of t^n_{2g} materials includes, for example, titanates, vandates, ruthenates, and iridates, compounds in the $n = 1, 2, 4$, and 5 electronic configuration, respectively. Also, in the t_{2g} case, half-filled systems ($n = 3$) have no orbital degrees of freedom since the Hund's rule ground multiplet is the $S = \frac{3}{2}$ state and therefore are orbitally trivial. For $n = 2$ and 4, the ground multiplet is usually the high-spin state $S = 1$ with orbital degeneracy three. The orbital degeneracy is three also for the $n = 1$ and 5 atomic ground states. In all cases, the maximum orbital rank is thus $r = 2$. The starting Hubbard model is the t_{2g} three-band Hubbard Hamiltonian. The latter has the same form given in Eqs. (9) and (10) except that the orbital index m now takes the values xz, xy, yz, and the screened Coulomb integrals U and J in Eq. (10) differ in value from those for the e_g orbitals. This is discussed in detail in Ref. [14], where the integrals in each case are derived starting from atomic functions. The effective hopping integrals in this case are typically the $dd\pi$ terms between Wannier functions into which oxygen p states or other high-energy states have been downfolded. As in the e_g case, we calculate first the paramagnetic ($q = 0$) and then the magnetic ($q = 1$) terms of the superexchange Hamiltonian.

A. Paramagnetic terms, $n = 1, 2$

We define the $q = 0$ tensorial operators as follows:

$$\hat{\tau}^{r,\mu}_i = \alpha^r_\mu \sum_{mm'} \sum_\sigma c^\dagger_{i,m\sigma} \langle m|\hat{o}^r_\mu|m'\rangle c_{i,m'\sigma}.$$

The matrix elements $\langle m|\hat{o}^r_\mu|m'\rangle$ and prefactors α^r_μ are listed in Table II. In analogy with the e_g case, we normalize the tensors such that

$$\sum_{m\sigma} \langle 0|c_{i,m\sigma} \left(\hat{\tau}^{r,\mu}_i\right)^2 c^\dagger_{i,m\sigma}|0\rangle = 1. \tag{38}$$

For $n = 1$, the formula for $q = 0$ can already be found in Ref. [13]; the tensor elements are reported in Tables III and IV with the notation adopted in this paper.

Here, we thus present the derivation for the more complicated $n = 2$ case, with total spin $S = 1$. We define the orbital pseudospin states as $|m_3\rangle = |m_1 m_2\rangle$, where m_1 and m_2 are the occupied orbitals, and m_3 is the empty one. The $n = 2$ triplet states can then be written as $|m_3, \sigma_3\rangle$, with

$$|-1, \sigma_3\rangle = c^\dagger_{i,xy\sigma} c^\dagger_{i,yz\sigma}|0\rangle \delta_{\sigma_3,2\sigma} + \frac{1}{\sqrt{2}}(c^\dagger_{i,xy\uparrow} c^\dagger_{i,yz\downarrow} + c^\dagger_{i,xy\downarrow} c^\dagger_{i,yz\uparrow})|0\rangle \delta_{\sigma_3,0}, \tag{39}$$

$$|0, \sigma_3\rangle = c^\dagger_{i,yz\sigma} c^\dagger_{i,xz\sigma}|0\rangle \delta_{\sigma_3,2\sigma} + \frac{1}{\sqrt{2}}(c^\dagger_{i,yz\uparrow} c^\dagger_{i,xz\downarrow} + c^\dagger_{i,yz\downarrow} c^\dagger_{i,xz\uparrow})|0\rangle \delta_{\sigma_3,0}, \tag{40}$$

TABLE II. Prefactors for the irreducible tensors with $q=0$, t_{2g}^n case. The small r denotes the orbital quantum number. The rank for second-order classical tensors is R; it splits the original reducible tensor of dimension 9 into a scalar, a five-component symmetric and traceless tensor, and a three-component asymmetric tensor.

R	$r\,\mu$	α^r_μ	$\langle m\vert\hat{o}^r_\mu\vert m'\rangle$
0	$0\ s$	$\frac{1}{n_i\sqrt{6}}$	$\delta_{m,m'}$
2	$1\ z$	$\frac{1}{2}$	$\delta_{m,m'}(\delta_{m,xz}-\delta_{m,yz})$
2	$1\ x$	$\frac{1}{2\sqrt{2}}$	$[(\delta_{m,xz}+\delta_{m,yz})\delta_{m',xy}$ $+(\delta_{m',xz}+\delta_{m',yz})\delta_{m,xy}]$
2	$2\ 3z^2{-}r^2$	$\frac{1}{2\sqrt{3}}$	$\delta_{m,m'}(\delta_{m,xz}+\delta_{m,yz}-2\delta_{m,xy})$
2	$2\ x^2{-}y^2$	$\frac{1}{2}$	$(\delta_{m,xz}\delta_{m',yz}+\delta_{m,yz}\delta_{m',xz})$
2	$2\ xz$	$\frac{1}{2\sqrt{2}}$	$[(\delta_{m,xz}-\delta_{m,yz})\delta_{m',xy}$ $+(\delta_{m',xz}-\delta_{m',yz})\delta_{m,xy}]$
1	$1\ y$	$\frac{i}{2\sqrt{2}}$	$[(\delta_{m,xz}\delta_{m',xy}-\delta_{m,yz}\delta_{m',xy})$ $-(\delta_{m',xz}\delta_{m,xy}-\delta_{m',yz}\delta_{m,xy})]$
1	$2\ yz$	$\frac{i}{2\sqrt{2}}$	$[(\delta_{m,xz}\delta_{m',xy}+\delta_{m,yz}\delta_{m',xy})$ $-(\delta_{m',xz}\delta_{m,xy}+\delta_{m',yz}\delta_{m,xy})]$
1	$2\ xy$	$\frac{i}{2}$	$(\delta_{m,xz}\delta_{m',yz}-\delta_{m,yz}\delta_{m',xz})$

$$|{+1},\sigma_3\rangle = c^\dagger_{i\,xz\sigma}c^\dagger_{i\,xy\sigma}|0\rangle\delta_{\sigma_3,2\sigma} + \frac{1}{\sqrt{2}}(c^\dagger_{i\,xz\uparrow}c^\dagger_{xy\downarrow}+c^\dagger_{i\,xz\downarrow}c^\dagger_{i\,xy\uparrow})|0\rangle\delta_{\sigma_3,0}, \tag{41}$$

where σ_3 is the spin component of orbital state $|m_3\rangle$. In this basis, the norm of the irreducible tensor operators is

$$\sum_{m_3,\sigma_3}\langle m_3,\sigma_3|\left(\hat{\tau}_i^{r,\mu}\right)^2|m_3,\sigma_3\rangle = \frac{2S{+}1}{2}. \tag{42}$$

We now proceed to calculate the first term in Eq. (16), the one arising from three-electron states with a doubly occupied orbital. These can be split into the six $S=\frac{1}{2}$ states:

$$\left|\frac{1}{2},\frac{\sigma}{2},m\right\rangle_a = \frac{1}{\sqrt{2}}(c^\dagger_{i,m'\uparrow}c^\dagger_{i,m'\downarrow}{+}c^\dagger_{i,m''\uparrow}c^\dagger_{i,m''\downarrow})c^\dagger_{i,m\sigma}|0\rangle, \tag{43}$$

with Coulomb energy $3U-4J$ and the additional six $S=\frac{1}{2}$ states:

$$\left|\frac{1}{2},\frac{\sigma}{2},m\right\rangle_b = \frac{1}{\sqrt{2}}(c^\dagger_{i,m'\uparrow}c^\dagger_{i,m'\downarrow}{-}c^\dagger_{i,m''\uparrow}c^\dagger_{i,m''\downarrow})c^\dagger_{i,m\sigma}|0\rangle, \tag{44}$$

with Coulomb energy $3U-6J$. It is convenient to introduce the shortcuts:

$$\tau^{ir\mu}_{a_3c_3} = \frac{\langle a_3,\sigma_3|\hat{\tau}_i^{r\mu}|c_3,\sigma_3\rangle}{\mathrm{Tr}\left(\hat{\tau}_i^{r\mu}\right)^2}\frac{2S+1}{2}, \tag{45}$$

and

$$v_0 = \tfrac{1}{2}(f_2{-}f_0), \quad v_1 = \tfrac{1}{2}(f_2{+}f_0). \tag{46}$$

The matrix element $\tau^{ir\mu}_{a_3c_3}$ does not depend on the spin since the operator traces over the spins; it is also the same for each site, but we leave the site index i for clarity. We thus obtain

$$\begin{aligned}B^{ij}_{r\mu,r'\mu'} = &-\frac{2}{U}\big[\mathrm{tr}(t^{j,i}\tau^{ir\mu}t^{i,j}\overline{\tau^{jr'\mu'}}) \\ &+\mathrm{tr}(t^{i,j}t^{j,i})\mathrm{tr}(\tau^{ir\mu})\mathrm{tr}(\tau^{jr'\mu'}) \\ &-\mathrm{tr}(t^{j,i}\tau^{ir\mu}t^{i,j})\mathrm{tr}(\tau^{jr'\mu'})-\mathrm{tr}(\tau^{ir\mu}) \\ &\times\mathrm{tr}(t^{i,j}\overline{\tau^{jr'\mu'}}t^{j,i})\big]\xi^B_\mu + (ir\mu)\leftrightarrow(jr'\mu'),\end{aligned} \tag{47}$$

where $\xi^B_\mu = v_1\delta_{\mu,0}+v_0(1-\delta_{\mu,0})$. The second term in Eq. (16) arises from three-electron states with one electron per orbital. These are the $S=\frac{3}{2}$ quartet:

$$\left|\frac{3}{2},\frac{3\sigma}{2}\right\rangle = c^\dagger_{i,xz\sigma}c^\dagger_{i,yz\sigma}c^\dagger_{i,xy\sigma}|0\rangle, \tag{48}$$

$$\left|\frac{3}{2},\frac{\sigma}{2}\right\rangle = \frac{1}{\sqrt{3}}(c^\dagger_{i,xz\sigma}c^\dagger_{i,yz\bar{\sigma}}c^\dagger_{i,xy\sigma}|0\rangle + c^\dagger_{i,xz\bar{\sigma}}c^\dagger_{i,yz\sigma}c^\dagger_{i,xy\sigma}|0\rangle + c^\dagger_{i,xz\sigma}c^\dagger_{i,yz\sigma}c^\dagger_{i,xy\bar{\sigma}}|0\rangle), \tag{49}$$

with energy $3U-9J$ and the two doublets:

$$\left|\frac{1}{2},\frac{\sigma}{2}\right\rangle_a = \frac{1}{\sqrt{6}}(c^\dagger_{i,xz\sigma}c^\dagger_{i,yz\bar{\sigma}}c^\dagger_{i,xy\sigma}|0\rangle + c^\dagger_{i,xz\bar{\sigma}}c^\dagger_{i,yz\sigma}c^\dagger_{i,xy\sigma}|0\rangle - 2c^\dagger_{i,xz\sigma}c^\dagger_{i,yz\sigma}c^\dagger_{i,xy\bar{\sigma}}|0\rangle), \tag{50}$$

$$\left|\frac{1}{2},\frac{\sigma}{2}\right\rangle_b = \frac{1}{\sqrt{2}}(c^\dagger_{i,xz\sigma}c^\dagger_{i,yz\bar{\sigma}} - c^\dagger_{i,xz\bar{\sigma}}c^\dagger_{i,yz\sigma})c^\dagger_{i,xy\sigma}|0\rangle, \tag{51}$$

with energy $3U-6J$; here, $\bar{\sigma}=-\sigma$. Collecting all contributions, we arrive at the final result:

$$C^{ij}_{r\mu,r'\mu'} = -\frac{4}{U}(\mathrm{tr}\{[\mathrm{tr}(\tau^{ir\mu})-\tau^{ir\mu}](\overline{t^{i,j}}\tau^{jr'\mu'}\overline{t^{j,i}})\})\gamma_{\mu'} + (ir\mu)\leftrightarrow(jr'\mu'), \tag{52}$$

where $\gamma_\mu = v_2\delta_{\mu,0}+\frac{v_3}{2}(1-\delta_{\mu,0})$ with

$$v_2 = \tfrac{1}{3}(2f_{-3}+f_0), \quad v_3 = \tfrac{1}{3}(4f_{-3}-f_0). \tag{53}$$

The elements of the total superexchange tensor are listed in Tables III and IV.

Let us now consider the simple limit of cubic perovskites and the approximation in which the only effective hopping integrals along a crystal axis direction are the $dd\pi$ intraorbital ones. This approximation is often adopted for the description of t_{2g} perovskites in simple models. If we define $\hat{z}$ as the quantization axis, these are $t_{xz,xz}=t_{yz,yz}=t$. Setting in addition $J=0$, we obtain the Hamiltonian:

$$\begin{aligned}\frac{H^{i,j}_{\mathrm{SE}}}{\Gamma} = &-\frac{8\delta_{n,2}+5\delta_{n,1}}{3}\hat{\tau}_i^{0,s}\hat{\tau}_j^{0,s} + \frac{1}{6}\hat{\tau}_i^{2,3z^2-r^2}\hat{\tau}_j^{2,3z^2-r^2} \\ &+\frac{1}{2}\hat{\tau}_i^{1,z}\hat{\tau}_j^{1,z}+\frac{1}{2}\hat{\tau}_i^{2,x^2-y^2}\hat{\tau}_j^{2,x^2-y^2}+\frac{1}{2}\hat{\tau}_i^{xy}\hat{\tau}_j^{xy} \\ &-\frac{\delta_{n,2}+2\delta_{n,1}}{3\sqrt{2}}\left(\hat{\tau}_i^{2,3z^2-r^2}\hat{\tau}_j^{0s}+\hat{\tau}_i^{0s}\hat{\tau}_j^{2,3z^2-r^2}\right),\end{aligned} \tag{54}$$

The first term, proportional to the product of two $r=0$ operators, does not contribute to determining the ground state; it just gives an energy shift. With the constraint $n_{xy}=n-n_{xz}-n_{yz}$, for a bond along $\hat{z}$, the Hamiltonian reduces to the expected

TABLE III. Nonzero tensor elements (spin rank $q=0$) for diagonal hopping integrals, t_{2g}^2 and t_{2g}^1 configuration. The matrix elements for imaginary tensors must be multiplied by i (linear terms, involving a single operator) or $i\times i$ (for products of two operators). For the t_{2g}^2 configuration, $v_0=\frac{1}{2}(f_2-f_0)$, $v_1=\frac{1}{2}(f_2+f_0)$, $v_2=\frac{1}{3}(2f_{-3}+f_0)$, and $v_3=\frac{1}{3}(4f_{-3}-f_0)$. For the t_{2g}^1 configuration, $w_0=\frac{1}{3}(f_2-f_{-1})$, $w_1=\frac{1}{3}(f_2+2f_{-1})$, $w_2=\frac{1}{4}(3f_{-3}+f_{-1})$, and $w_3=\frac{1}{2}(3f_{-3}-f_{-1})$. The rest of the matrix can be obtained by symmetry: $D^{ij}_{r'\mu',r\mu}=s_\mu s_{\mu'}\overline{D^{ji}_{r\mu,r'\mu'}}$, where $s_\mu=1$ is for real operators and $s_\mu=-1$ for imaginary ones. The tensors for spin rank $q=1$ can be obtained by replacing $\mathcal{W}_i\longrightarrow\tilde{\mathcal{W}}_i$ and $\mathcal{V}_i\longrightarrow\tilde{\mathcal{V}}_i$. The couplings $\mathcal{W}_i$ or $\mathcal{V}_i$ are identical for tensors with the same R value. All hopping integrals in the table are defined as $t^{i,j}_{m,m'}$ and are real.

$r\ \mu$	$r'\ \mu'$	t_{2g}^1	t_{2g}^2		$D^{ij}_{r\mu,r'\mu'}\times U/2$
$0\ s$	$0\ s$	$-\mathcal{W}_0$	$-\mathcal{V}_0$		$\left(t^2_{xz,xz}+t^2_{yz,yz}+t^2_{xy,xy}\right)$
$0\ s$	$1\ z$	$-\mathcal{W}_1$	$-\mathcal{V}_1$	$\frac{\sqrt{2}}{\sqrt{3}}$	$\left(t^2_{xz,xz}-t^2_{yz,yz}\right)$
$0\ s$	$2\ z^2$	$-\mathcal{W}_1$	$-\mathcal{V}_1$	$\frac{\sqrt{2}}{3}$	$\left(t^2_{xz,xz}+t^2_{yz,yz}-2t^2_{xy,xy}\right)$
$1\ z$	$1\ z$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$\left(t^2_{xz,xz}+t^2_{yz,yz}\right)$
$1\ z$	$2\ z^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\frac{1}{\sqrt{3}}$	$\left(t^2_{xz,xz}-t^2_{yz,yz}\right)$
$2\ z^2$	$2\ z^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\frac{1}{3}$	$\left(t^2_{xz,xz}+t^2_{yz,yz}+4t^2_{xy,xy}\right)$
$1\ x$	$1\ x$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$(t_{xz,xz}+t_{yz,yz})t_{xy,xy}$
$2\ xz$	$2\ xz$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$(t_{xz,xz}+t_{yz,yz})t_{xy,xy}$
$1\ x$	$2\ xz$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$(t_{xz,xz}-t_{yz,yz})t_{xy,xy}$
$2\ x^2{-}y^2$	$2\ x^2{-}y^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$2t_{xz,xz}t_{yz,yz}$
$1\ y$	$1\ y$	$+\mathcal{W}_3$	$+\mathcal{V}_3$		$(t_{xz,xz}+t_{yz,yz})t_{xy,xy}$
$2\ yz$	$2\ yz$	$+\mathcal{W}_3$	$+\mathcal{V}_3$		$(t_{xz,xz}+t_{yz,yz})t_{xy,xy}$
$2\ xy$	$2\ xy$	$+\mathcal{W}_3$	$+\mathcal{V}_3$		$2t_{xz,xz}t_{yz,yz}$
$1\ y$	$2\ yz$	$+\mathcal{W}_3$	$+\mathcal{V}_3$		$(t_{xz,xz}-t_{yz,yz})t_{xy,xy}$
$\mathcal{W}_0=f_{-3}+\frac{5}{9}f_{-1}+\frac{1}{9}f_2=\frac{w_1+4w_2}{3}$,				$\mathcal{V}_0=\frac{8}{9}f_{-3}+\frac{10}{9}f_0+\frac{2}{3}f_2=\frac{4(v_1+v_2)}{3}$	
$\mathcal{W}_1=\frac{3}{8}f_{-3}+\frac{11}{24}f_{-1}+\frac{1}{6}f_2=\frac{w_1+w_2}{2}$,				$\mathcal{V}_1=-\frac{1}{3}f_{-3}+\frac{1}{3}f_0+\frac{1}{2}f_2=\frac{2v_1-v_2}{2}$	
$\mathcal{W}_2=\frac{3}{4}f_{-3}-\frac{1}{12}f_{-1}-\frac{1}{6}f_2=\frac{2w_2-w_1}{2}$,				$\mathcal{V}_2=\frac{2}{3}f_{-3}+\frac{1}{12}f_0-\frac{1}{4}f_2=\frac{2v_2-v_1}{2}$	
$\mathcal{W}_3=\frac{3}{4}f_{-3}-\frac{5}{12}f_{-1}+\frac{1}{6}f_2=\frac{w_0+w_3}{2}$,				$\mathcal{V}_3=\frac{2}{3}f_{-3}-\frac{5}{12}f_0+\frac{1}{4}f_2=\frac{v_0+v_3}{2}$	
$\tilde{\mathcal{W}}_0=\frac{1}{3}f_{-3}-\frac{5}{9}f_{-1}-\frac{1}{9}f_2$,				$\tilde{\mathcal{V}}_0=\frac{4}{9}f_{-3}-\frac{10}{9}f_0-\frac{2}{3}f_2$	
$\tilde{\mathcal{W}}_1=\frac{1}{8}f_{-3}-\frac{11}{24}f_{-1}-\frac{1}{6}f_2$,				$\tilde{\mathcal{V}}_1=-\frac{1}{6}f_{-3}-\frac{1}{3}f_0-\frac{1}{2}f_2$	
$\tilde{\mathcal{W}}_2=\frac{1}{4}f_{-3}+\frac{1}{12}f_{-1}+\frac{1}{6}f_2$,				$\tilde{\mathcal{V}}_2=\frac{1}{3}f_{-3}-\frac{1}{12}f_0+\frac{1}{4}f_2$	
$\tilde{\mathcal{W}}_3=\frac{1}{4}f_{-3}+\frac{5}{12}f_{-1}-\frac{1}{6}f_2$,				$\tilde{\mathcal{V}}_3=\frac{1}{3}f_{-3}+\frac{5}{12}f_0-\frac{1}{4}f_2$	

[2,3] limit:

$$\frac{H_{\rm SE}^{i,j=i+\hat{z}}}{\Gamma}=-\frac{1}{4}\left(\hat{n}^i_{xz}+\hat{n}^i_{yz}+\hat{n}^j_{xz}+\hat{n}^j_{yz}\right)+\frac{1}{4}\left(\hat{n}^i_{xz}\hat{n}^j_{xz}+\hat{n}^i_{yz}\hat{n}^j_{yz}\right)+\frac{1}{4}(c^\dagger_{i,xz}c_{i,yz}c^\dagger_{j,yz}c_{j,xz}+c^\dagger_{i,yz}c_{i,xz}c^\dagger_{j,xz}c_{j,yz}). \quad (55)$$

This Hamiltonian is often adopted for studying spin-orbital physics in titanates and vanadates. In this simplified case, only two orbitals play a role for a given bond, while in the full superexchange Hamiltonian, all three orbitals are active.

B. Magnetic case, $n=1,2$.

The operators of spin rank $q=1$ are defined as

$$\hat{\tau}_i^{r,\mu;1\nu}=\alpha^r_\mu\sum_{mm'}\sum_{\sigma\sigma'}c^\dagger_{i,m\sigma}\langle m|\hat{o}^r_\mu|m'\rangle\hat{\sigma}^\nu_{\sigma,\sigma'}c_{i,m'\sigma'},$$

with the same α^r_μ introduced for rank $q=0$, so that

$$\sum_{m\sigma}\langle 0|c_{i,m\sigma}\left(\hat{\tau}_i^{r,\mu;1,\nu}\right)^2c^\dagger_{i,m\sigma}|0\rangle=1, \quad (56)$$

and in addition,

$$\sum_{m_3\sigma_3}\langle m_3,\sigma_3|\left(\hat{\tau}_i^{r,\mu;1,\nu}\right)^2|m_3,\sigma_3\rangle=1. \quad (57)$$

In calculating the norm above, since we restricted the lower-energy space to the $S=1$ multiplet, $S=0$ intermediate states are discarded. The resulting tensor elements can be found in Tables III and IV for the t_{2g}^1 and t_{2g}^2 cases. As in the e_g case, the Coulomb denominators are modified when the spin rank changes from zero to one, leading to the transformation $\mathcal{V}\longrightarrow\tilde{\mathcal{V}}$ for $n=2$ and $\mathcal{W}\longrightarrow\tilde{\mathcal{W}}$ for $n=1$, as explained in Table III.

TABLE IV. Additional relevant quadratic ($r \neq 0$, $r' \neq 0$) and linear terms ($r = 0$, $r' \neq 0$) for t_{2g}^1 and t_{2g}^2 configurations, spin rank $q = 0$. The tensors for spin rank $q = 1$ can be obtained by replacing $\mathcal{W}_i \longrightarrow \tilde{\mathcal{W}}_i$ and $\mathcal{V}_i \longrightarrow \tilde{\mathcal{V}}_i$. Prefactors and hopping integrals are defined in the caption of Table III.

$r\ \mu$	$r'\ \mu'$	t_{2g}^1	t_{2g}^2		$D^{ij}_{r\mu,r'\mu'} \times U/2$
$0\ s$	$0\ s$	$-\mathcal{W}_0$	$-\mathcal{V}_0$		$\left(t^2_{xz,xy} + t^2_{xz,yz} + t^2_{xy,xz} + t^2_{xy,yz} + t^2_{yz,xz} + t^2_{yz,xy}\right)$
$0\ s$	$1\ x$	$-\mathcal{W}_1$	$-\mathcal{V}_1$	$\frac{2}{\sqrt{3}}$	$[(t_{xz,xz} + t_{xz,yz})t_{xz,xy} + (t_{yz,xz} + t_{yz,yz})t_{yz,xy} + (t_{xy,xz} + t_{xy,yz})t_{xy,xy}]$
$0\ s$	$1\ z$	$-\mathcal{W}_1$	$-\mathcal{V}_1$	$\frac{\sqrt{2}}{\sqrt{3}}$	$\left(t^2_{yz,xz} + t^2_{xy,xz} - t^2_{xz,yz} - t^2_{xy,yz}\right)$
$0\ s$	$2\ xz$	$-\mathcal{W}_1$	$-\mathcal{V}_1$	$\frac{2}{\sqrt{3}}$	$[(t_{xz,xz} - t_{xz,yz})t_{xz,xy} + (t_{yz,xz} - t_{yz,yz})t_{yz,xy} + (t_{xy,xz} - t_{xy,yz})t_{xy,xy}]$
$0\ s$	$2\ x^2{-}y^2$	$-\mathcal{W}_1$	$-\mathcal{V}_1$	$\frac{2\sqrt{2}}{\sqrt{3}}$	$(t_{xz,xz}t_{xz,yz} + t_{yz,xz}t_{yz,yz} + t_{xy,xz}t_{xy,yz})$
$0\ s$	$2\ z^2$	$-\mathcal{W}_1$	$-\mathcal{V}_1$	$\frac{\sqrt{2}}{3}$	$\left(t^2_{yz,xz} + t^2_{xy,xz} + t^2_{xz,yz} + t^2_{xy,yz} - 2t^2_{xz,xy} - 2t^2_{yz,xy}\right)$
$1\ z$	$1\ z$	$-\mathcal{W}_2$	$-\mathcal{V}_2$		$\left(t^2_{xz,yz} + t^2_{yz,xz}\right)$
$1\ z$	$2\ z^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\frac{1}{\sqrt{3}}$	$\left[t^2_{xz,yz} - t^2_{yz,xz} - 2\left(t^2_{xz,xy} - t^2_{yz,xy}\right)\right]$
$2\ z^2$	$2\ z^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\frac{1}{3}$	$\left[t^2_{xz,yz} + t^2_{yz,xz} - 2\left(t^2_{xz,xy} + t^2_{xy,xz} + t^2_{yz,xy} + t^2_{xy,yz}\right)\right]$
$1\ z$	$1\ x$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\sqrt{2}$	$[(t_{xz,xz} + t_{xz,yz})t_{xz,xy} - (t_{yz,xz} + t_{yz,yz})t_{yz,xy}]$
$1\ z$	$2\ xz$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\sqrt{2}$	$[(t_{xz,xz} - t_{xz,yz})t_{xz,xy} - (t_{yz,xz} - t_{yz,yz})t_{yz,xy}]$
$1\ z$	$2\ x^2{-}y^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$2(t_{xz,xz}t_{xz,yz} - t_{yz,xz}t_{yz,yz})$
$2\ z^2$	$1\ x$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\frac{\sqrt{2}}{\sqrt{3}}$	$[(t_{xz,xz} + t_{xz,yz})t_{xz,xy} + (t_{yz,xz} + t_{yz,yz})t_{yz,xy} - 2(t_{xy,xz} + t_{xy,yz})t_{xy,xy}]$
$2\ z^2$	$2\ xz$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\frac{\sqrt{2}}{\sqrt{3}}$	$[(t_{xz,xz} - t_{xz,yz})t_{xz,xy} + (t_{yz,xz} - t_{yz,yz})t_{yz,xy} - 2(t_{xy,xz} - t_{xy,yz})t_{xy,xy}]$
$2\ z^2$	$2\ x^2{-}y^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\frac{2}{\sqrt{3}}$	$(t_{xz,xz}t_{xz,yz} + t_{yz,xz}t_{yz,yz} - 2t_{xy,xz}t_{xy,yz})$
$1\ x$	$1\ x$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$[(t_{xz,yz} + t_{yz,xz})t_{xy,xy} + (t_{xz,xy} + t_{yz,xy})(t_{xy,xz} + t_{xy,yz})]$
$1\ x$	$2\ xz$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$[(-t_{xz,yz} + t_{yz,xz})t_{xy,xy} + (t_{xz,xy} + t_{yz,xy})(t_{xy,xz} - t_{xy,yz})]$
$2\ xz$	$2\ xz$	$-\mathcal{W}_2$	$-\mathcal{V}_2$		$[(t_{xz,yz} + t_{yz,xz})t_{xy,xy} - (t_{xz,xy} - t_{yz,xy})(t_{xy,xz} - t_{xy,yz})]$
$2\ x^2 - y^2$	$2\ x^2{-}y^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$		$2t_{xz,yz}t_{yz,xz}$
$1\ x$	$2\ x^2{-}y^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\sqrt{2}$	$[(t_{xz,xz} + t_{yz,xz})t_{xy,yz} + (t_{xz,yz} + t_{yz,yz})t_{xy,xz}]$
$2\ xz$	$2\ x^2{-}y^2$	$+\mathcal{W}_2$	$+\mathcal{V}_2$	$\sqrt{2}$	$[(t_{xz,xz} - t_{yz,xz})t_{xy,yz} + (t_{xz,yz} - t_{yz,yz})t_{xy,xz}]$

C. The $n = 4$ and 5 case

For $n = 5$ and 4, electron-hole transformation of the atomic states yields the corresponding changes. To obtain the same prefactors (aside from a sign) for spin operators with rank zero, one must then also replace $n_i \longrightarrow 6 - n_i$, yielding the number of holes, in the definition. As in the e_g case, in the hole representation, the only modification with respect to the analogous electron case is the change of sign in the terms which mix operators with orbital rank zero and higher.

V. ENERGY SURFACES

It is now easy to use the superexchange Hamiltonians to calculate energy surfaces in the static mean-field approximation. We use as an example the case of t_{2g}^1 perovskites in the $GdFeO_3$-type structure, for which we performed extensive many-body calculations based on DMFT [13]. For the calculations, we use hopping integrals for t_{2g} Wannier functions, obtained *ab initio* via the linearized augmented plane-wave method, as implemented in the WIEN2K code [16]. We define the most occupied orbital at a Ti site as

$$|\theta, \phi\rangle = -\,|\pi - \theta, \phi \pm \pi\rangle$$
$$= \sin\theta\cos\phi|xz\rangle + \cos\theta|xy\rangle + \sin\theta\sin\phi|yz\rangle. \quad (58)$$

The orbitals for equivalent Ti sites in the unit cell are related via space-group symmetries; in the $GdFeO_3$-type structure, with four atoms per unit cell, if at site Ti_1 the most occupied orbital is $|\theta, \phi\rangle_1$, the corresponding states at sites 2, 3, and 4, where site 3 is on top of site 1 and site 4 on top of 2, are given by, respectively, $|\theta, \phi\rangle_2 = |\theta, \frac{\pi}{2} - \phi\rangle_1$, $|\theta, \phi\rangle_3 = |-\theta, \phi\rangle_1$, and $|\theta, \phi\rangle_4 = |-\theta, \frac{\pi}{2} - \phi\rangle_1$. Thus, the superexchange energy gain for orbital ordering in the paramagnetic phase is

$$\Delta E(\theta, \phi) = \sum_{r\mu, r'\mu'}^{>} \left(8\overline{D}^{ab}_{r\mu,r'\mu'}\tau_2^{r'\mu'}\tau_1^{r\mu} + 4\overline{D}^{c}_{r\mu,r'\mu'}\tau_3^{r'\mu'}\tau_1^{r\mu}\right),$$

where $\tau_i^{r\mu} = {}_i\langle\theta, \phi|\hat{\tau}^{r,\mu}|\theta, \phi\rangle_i$, and the sum is for $r + r' > 0$. Furthermore,

$$\overline{D}^{ab}_{r\mu,r'\mu'} = \frac{1}{8}\sum_{i=j,j+\hat{z}}\left(D^{ii+\hat{x}}_{r\mu,r'\mu'} + D^{ii-\hat{x}}_{r\mu,r'\mu'} + D^{ii+\hat{y}}_{r\mu,r'\mu'} + D^{ii-\hat{y}}_{r\mu,r'\mu'}\right),$$

$$\overline{D}^{c}_{r\mu,r'\mu'} = \frac{1}{4}\sum_{i=j,j+\hat{x}}\left(D^{ii+\hat{z}}_{r\mu,r'\mu'} + D^{ii-\hat{z}}_{r\mu,r'\mu'}\right).$$

Analogous expressions can be written for the ferromagnetic and antiferromagnetic phases. In Fig. 1, we show the resulting energy surfaces as a function of θ and ϕ, in the paramagnetic, antiferromagnetic, and ferromagnetic cases, using the

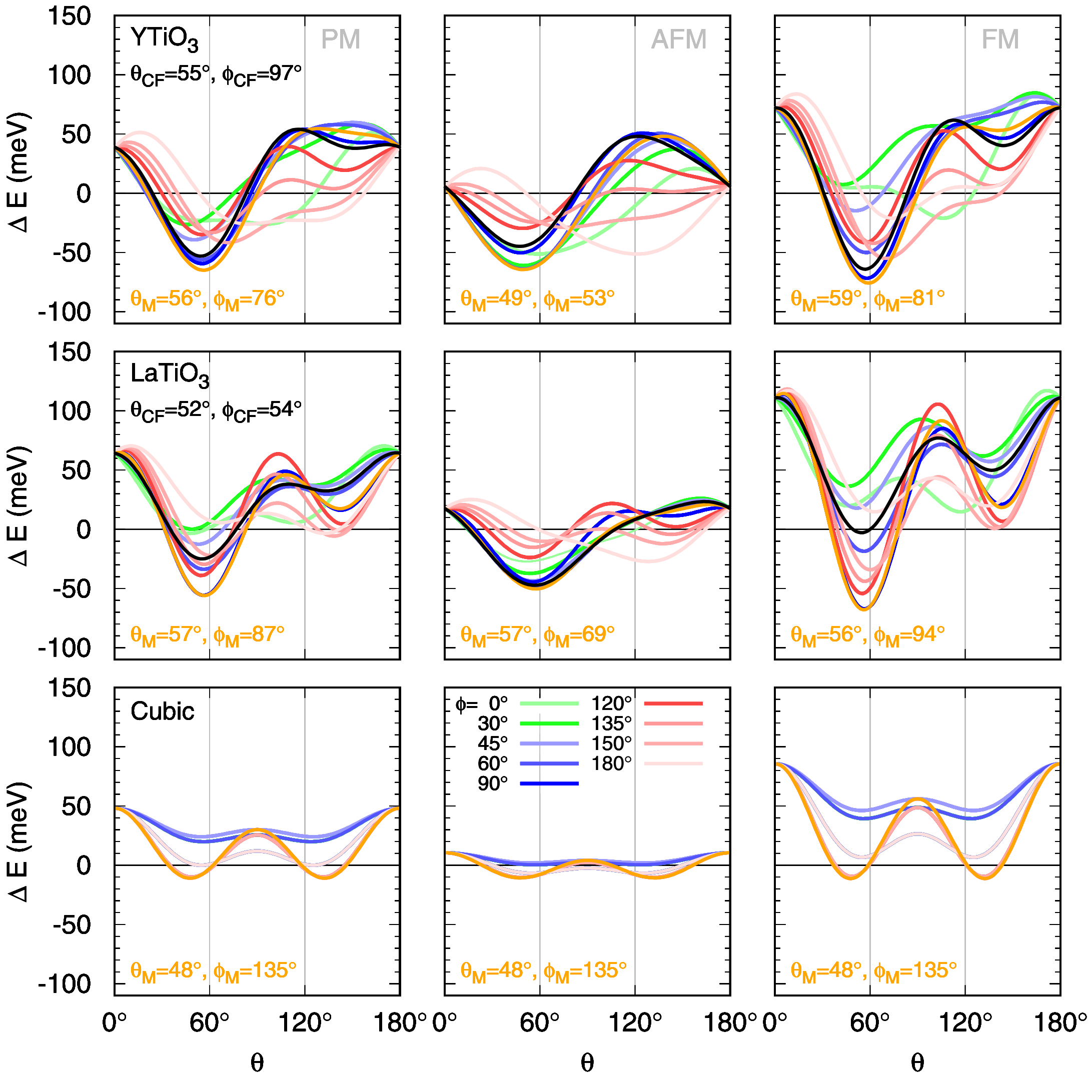

FIG. 1. Total superexchange energy gain for $YTiO_3$ (top panel), $LaTiO_3$ (middle panel), and a hypothetical cubic perovskite with only $dd\pi$ hopping integrals (bottom panel). The different lines, as shown in the inset, correspond to ϕ values between 0 and π. The orange line is the ϕ yielding the absolute minimum, which is identified by the angles θ_M, ϕ_M, given at the bottom of each panel. Equivalent solutions can be obtained by symmetry via the transformation $\theta_M, \phi_M \longrightarrow \pi - \theta_M, \phi_M + \pi$. The hopping integrals for $YTiO_3$ and $LaTiO_3$ have been obtained *ab initio*, downfolding oxygen and other high-energy states. The angles defining the lowest energy crystal-field state $\theta_{\rm CF}, \phi_{\rm CF}$ are also given; the black lines are the $\phi = \phi_{\rm CF}$ curves. PM: paramagnetic. AFM: antiferromagnetic (G-type). FM: ferromagnetic. Coulomb parameters: $U = 5$ eV, $J = 0.64$ eV.

same hopping parameters entering the DMFT calculations of Ref. [13]. Paramagnetic DMFT results show that orbital ordering occurs at angles determined by the crystal-field splitting [13]. For $LaTiO_3$, these angles are $\theta_{\rm CF} \sim 52^\circ$ and $\phi_{\rm CF} \sim 54^\circ$, while for $YTiO_3$, we found $\theta_{\rm CF} \sim 55^\circ$ and $\phi_{\rm CF} \sim 97^\circ$. They differ from those that minimize the energy curves in Fig. 1, as can be seen from the left panels, because in the figure only superexchange interactions are considered. The curves corresponding to $\phi_{\rm CF}$ are shown in black for comparison. Figure 1 explains, however, why the ground state of $YTiO_3$ is ferromagnetic and that of $LaTiO_3$ antiferromagnetic. In the case of $YTiO_3$, the angles $\theta_{\rm CF}, \phi_{\rm CF}$ are close to those yielding the superexchange minimum for ferromagnetism (right top panel, orange line, angles $\theta_{\rm M}, \phi_{\rm M}$). For the orbital $|\theta_{\rm CF}, \phi_{\rm CF}\rangle$, the energy gain for ferromagnetism is thus larger than the energy gain for antiferromagnetism. For $LaTiO_3$, instead, at the angles $\theta_{\rm CF}, \phi_{\rm CF}$, ferromagnetism is strongly suppressed since the associated energy gain is basically zero, while the energy gain for antiferromagnetism remains sizable. This is in line with our previous conclusions based on extensive DMFT studies and the associated calculation of magnetic superexchange couplings for the orbitally ordered phase [10,17,18]. This behavior is hard to understand in terms of a simple cubic model (bottom row of the figure), for which paramagnetic, ferromagnetic, and antiferromagnetic structures have minima at the same angles.

VI. CONCLUSIONS

We have shown how general superexchange Hamiltonians for correlated materials can be obtained, exploiting the properties of irreducible tensors. We give the analytical formulas for the e_g^n and t_{2g}^n cases and provide ready-to-use tables with the final results. The representation of the superexchange interaction presented can be obtained numerically for materials in a straightforward way. Exact diagonalization provides the atomic states for realistic Coulomb tensors. This allows us to calculate the superexchange Hamiltonian by projection, calculating simple traces for hopping integrals from *ab initio* Wannier functions and without approximations on the Coulomb tensor. Using these Hamiltonians, it is possible to calculate, in mean-field theory, energy surfaces comparing different types of orbital ordering and determine the energy gain resulting from such ordering, i.e., the stability of the ordered phase.

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