

# CORRELATION ENERGIES IN DISTORTED $3d-t_{2g}$ PEROVSKITE OXIDES

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Using an effective low-energy Hamiltonian derived from the first-principle electronic structure calculations for the narrow  $t_{2g}$  bands of  $\text{YTiO}_3$ ,  $\text{LaTiO}_3$ ,  $\text{YVO}_3$ , and  $\text{LaVO}_3$ , we evaluate the contributions of the correlation energy  $E_c$  to the stability of different magnetic structures that can be realized in these distorted perovskite oxides. We consider two approximations for  $E_c$  that are based on the regular perturbation theory expansion around a nondegenerate Hartree–Fock ground state. One is the second order of the perturbation theory, which allows comparing the effects of local and nonlocal correlations. The other is the local  $t$ -matrix approach, which allows treating some higher-order contributions to  $E_c$ . The correlation effects systematically improve the agreement with the experimental data and additionally stabilize the experimentally observed  $G$ - and  $C$ -type antiferromagnetic (AFM) structures in  $\text{YVO}_3$  and  $\text{LaVO}_3$ , although the absolute magnitude of the stabilization energy is sensitive to the level of approximations and is somewhat smaller in the  $t$ -matrix method. The nonlocal correlations additionally stabilize the ferromagnetic ground state in  $\text{YTiO}_3$  and the  $C$ -type AFM ground state in  $\text{LaVO}_3$ . Among two inequivalent transition-metal sites in the monoclinic structure, the local correlations are stronger at the sites with the least distorted environment. Limitations of the regular perturbation-theory expansion for  $\text{LaTiO}_3$  are also discussed.

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## 1. INTRODUCTION

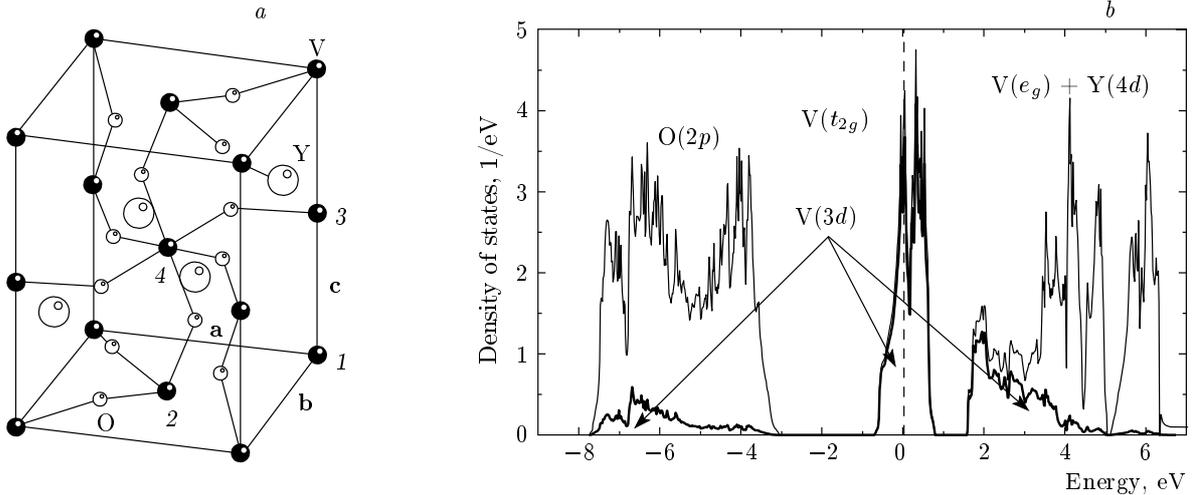
An interest in the transition-metal perovskite oxides  $\text{YTiO}_3$ ,  $\text{LaTiO}_3$ ,  $\text{YVO}_3$ , and  $\text{LaVO}_3$  is mainly related to the variety of magnetic structures that can be realized in these seemingly alike compounds. For example,  $\text{YTiO}_3$  has the ferromagnetic structure [1].  $\text{LaTiO}_3$  is a three-dimensional ( $G$ -type) antiferromagnet [2]. At the low temperature,  $\text{YVO}_3$  forms the  $G$ -type antiferromagnetic (AFM) structure, which can be transformed to a chainlike ( $C$ -type) antiferromagnetic structure at around 77 K [3]. On the contrary,  $\text{LaVO}_3$  is a  $C$ -type antiferromagnet in the entire temperature range below the magnetic transition temperature [4]. Surprisingly, the difference exists not only between titanates ( $\text{YTiO}_3$  and  $\text{LaTiO}_3$ ) and vanadates ( $\text{YVO}_3$  and  $\text{LaVO}_3$ ), which have a different number of valent electrons, but also within each group of formally isoelectronic materials. The differences are apparently related to tiny changes

in the distorted perovskite structure, which are amplified by Coulomb interactions in the narrow  $t_{2g}$  band. The details of the crystal structure can be found in Refs. [1–4]. Briefly, both titanates have an orthorhombic structure, although the details of this structure are rather different for  $\text{YTiO}_3$  and  $\text{LaTiO}_3$ .  $\text{LaVO}_3$  is crystallized in a monoclinic structure. The low-temperature phase of  $\text{YVO}_3$  is orthorhombic (shown in the Figure), which becomes monoclinic at around 77 K. The structural orthorhombic-monoclinic transition coincides with the  $G$ – $C$  AFM transition. Generally, Y-based compounds are more distorted (due to the smaller size of the  $\text{Y}^{3+}$  ions).

There are a large number of theoretical articles devoted to the origin of the magnetic ground states in the distorted  $t_{2g}$  perovskite oxides. The problem has been considered on the basis of the first-principle electronic structure calculations (see, e.g., Refs. [5]) and the model approaches for strongly correlated systems (see, e.g., Refs. [6–8]). The model theories typically

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A characteristic example of the crystal structure (a) and the electronic structure in the local-density approximation (b) of the orthorhombically distorted  $\text{YVO}_3$ . *a* — the symbols *a*, *b*, and *c* stand for orthorhombic translations, and the symbols 1–4 denote the transition-metal sites, which form the unit cell of the distorted perovskite oxides. *b* — the contributions of the atomic  $\text{V}(3d)$  states are shown. Other symbols show the positions of the main bands. The Fermi level is at zero energy

vary on the assessment of the role played by the lattice distortions [6] and the Coulomb correlations [7, 8].

We believe that any realistic theoretical description of these compounds is practically impossible without the impact from the first-principle electronic structure calculations: simply, the lattice distortion is too complex, and, had we tried to postulate a model Hamiltonian for these  $t_{2g}$  perovskite oxides, we would have inevitably faced the problem of choosing the values for a large number of model parameters, which cannot be fixed in an unbiased way. However, the conventional electronic structure calculations are also far from being perfect. Typically, they are supplemented with some additional approximations, which have serious limitations for treating the Coulomb correlations in the case of strongly correlated materials. A typical example is the local-density approximation. From this standpoint, a promising direction is to make a bridge between the first-principle electronic structure calculations and models for strongly correlated systems, and construct an appropriate model Hamiltonian entirely “from the first principles”. Fortunately, in the case of transition-metal oxides, we are typically dealing with only a small group of states located near the Fermi level and well separated from the remaining part of the spectrum (for instance,  $t_{2g}$  bands in the Figure). These states are mainly responsible for the electronic and magnetic properties of oxide materials.

Therefore, in many cases, it suffices to consider a

minimal model, consisting of only the  $t_{2g}$  bands, and include the effect of the other bands into the renormalization of interaction parameters in the  $t_{2g}$  band. Such a strategy was pursued in Refs. [9–11]. It consists of three major steps: first-principle electronic structure calculations → construction of the model Hamiltonian → solution of this model Hamiltonian.

The first applications to the distorted  $t_{2g}$  perovskite oxides were considered in Refs. [11, 12]. The present paper deals with the last part of the problem. We solve the model Hamiltonian derived in Ref. [11], and mainly focus on the role played by the correlation effects, beyond the mean-field Hartree–Fock (HF) approximation. In particular, we consider two perturbative approaches. One is the regular second-order perturbation theory for the correlation energy [13], and the other is the  $t$ -matrix approach [14–16]. In both approaches, the HF approximation is used as the starting point. This implies that the degeneracy of the HF ground state is already lifted by the crystal distortion such that the regular perturbation theory is justified. We also discuss some limitations of this treatment for  $\text{LaTiO}_3$ .

## 2. CONSTRUCTION OF THE MODEL HAMILTONIAN

Our first goal is the construction of the effective multi-orbital Hubbard model for the isolated  $t_{2g}$  bands:

$$\hat{\mathcal{H}} = \sum_{\mathbf{R}, \mathbf{R}'} \sum_{\alpha, \beta} h_{\mathbf{R}\mathbf{R}'}^{\alpha\beta} \hat{c}_{\mathbf{R}\alpha}^\dagger \hat{c}_{\mathbf{R}'\beta} + \frac{1}{2} \sum_{\mathbf{R}} \sum_{\alpha, \beta, \gamma, \delta} U_{\alpha\beta\gamma\delta} \hat{c}_{\mathbf{R}\alpha}^\dagger \hat{c}_{\mathbf{R}\gamma}^\dagger \hat{c}_{\mathbf{R}\beta} \hat{c}_{\mathbf{R}\delta}, \quad (1)$$

where  $\hat{c}_{\mathbf{R}\alpha}^\dagger$  ( $\hat{c}_{\mathbf{R}\alpha}$ ) creates (annihilates) an electron in the Wannier orbital  $\tilde{W}_{\mathbf{R}}^\alpha$  of the transition-metal site  $\mathbf{R}$ , and  $\alpha$  is a collective index, incorporating all the remaining (spin and orbital) degrees of freedom. The matrix

$$\hat{h}_{\mathbf{R}\mathbf{R}'} \equiv \|h_{\mathbf{R}\mathbf{R}'}^{\alpha\beta}\|$$

parameterizes the kinetic energy of electrons, where the site-diagonal part ( $\mathbf{R} = \mathbf{R}'$ ) describes the local level-splitting caused by the crystal field, and the off-diagonal part ( $\mathbf{R} \neq \mathbf{R}'$ ) stands for the transfer integrals,

$$U_{\alpha\beta\gamma\delta} = \int d\mathbf{r} \int d\mathbf{r}' \tilde{W}_{\mathbf{R}}^{\alpha\dagger}(\mathbf{r}) \tilde{W}_{\mathbf{R}}^{\beta}(\mathbf{r}) v_{scr}(\mathbf{r} - \mathbf{r}') \times \tilde{W}_{\mathbf{R}}^{\gamma\dagger}(\mathbf{r}') \tilde{W}_{\mathbf{R}}^{\delta}(\mathbf{r}') \equiv \langle \alpha\gamma | v_{scr} | \beta\delta \rangle$$

are matrix elements of screened Coulomb interaction  $v_{scr}(\mathbf{r} - \mathbf{r}')$ , which are supposed to be diagonal with respect to site indices. In principle,  $U_{\alpha\beta\gamma\delta}$  can also depend on the site index  $\mathbf{R}$ . Nevertheless, for simplicity of notation, here and hereafter, we drop the index  $\mathbf{R}$  in the notation for the Coulomb matrix elements (however, we do consider this dependence in all our calculations).

The procedure of mapping the first-principle electronic structure calculations onto the model Hamiltonian in (1) for distorted perovskite oxides has been discussed in detail in Refs. [10, 11]. Here, we only outline the main idea. The kinetic-energy part  $\hat{h}_{\mathbf{R}\mathbf{R}'}$  can be obtained using the downfolding method, which is exact and equivalent to the projector-operator method [17]. The Wannier functions can be formally derived from  $\hat{h}_{\mathbf{R}\mathbf{R}'}$  using the ideas of the linear-muffin-tin-orbital method [10, 18]. The matrix of screened Coulomb interactions in the  $t_{2g}$  band can be calculated using a hybrid approach, which combines the constraint density-functional theory with the random-phase approximation for the hybridization effects between transition-metal  $d$  and other atomic states [10]. The values of the model parameters obtained in such a way can be found in Ref. [11].

### 3. SOLUTION OF MODEL HAMILTONIAN

#### 3.1. Hartree – Fock approximation

The HF method provides the simplest approximation for the solution of the many-electron problem

with Hamiltonian (1). In this case, the trial many-electron wave function is searched in the form of a single Slater determinant  $|S\{\varphi_k\}\rangle$ , constructed from the one-electron orbitals  $\{\varphi_k\}$ . In this notation,  $k$  is a collective index that contains the information about the momentum  $\mathbf{k}$  in the first Brillouin zone, the band number  $n$ , and the spin ( $\sigma = \uparrow$  or  $\downarrow$ ) of the particle. The one-electron orbitals  $\{\varphi_k\}$  are subjected to the variational principle and requested to minimize the total energy

$$E_{HF} = \min_{\{\varphi_k\}} \langle S\{\varphi_k\} | \hat{\mathcal{H}} | S\{\varphi_k\} \rangle$$

for a given number of particles  $\mathcal{N}$ . This yields the following equations for  $\{\varphi_k\}$ :

$$(\hat{h}_{\mathbf{k}} + \hat{V}) |\varphi_k\rangle = \varepsilon_k |\varphi_k\rangle, \quad (2)$$

where

$$\hat{h}_{\mathbf{k}} \equiv \|h_{\mathbf{k}}^{\alpha\beta}\|$$

is the kinetic part of model Hamiltonian (1) in the reciprocal space:

$$h_{\mathbf{k}}^{\alpha\beta} = \frac{1}{N} \sum_{\mathbf{R}'} h_{\mathbf{R}\mathbf{R}'}^{\alpha\beta} \exp(-i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}'))$$

( $N$  being the number of sites) and

$$\hat{V} \equiv \|V_{\alpha\beta}\|$$

is the HF potential:

$$V_{\alpha\beta} = \sum_{\gamma\delta} (U_{\alpha\beta\gamma\delta} - U_{\alpha\delta\gamma\beta}) n_{\gamma\delta}. \quad (3)$$

In what follows, we also use the notation  $\hat{h}_{HF}$ , which stands for the total Hamiltonian of the HF method,  $\hat{h} + \hat{V}$ . Equation (2) is solved self-consistently together with the equation

$$\hat{n} = \sum_k^{occ} |\varphi_k\rangle \langle \varphi_k|$$

for the density matrix

$$\hat{n} \equiv \|n_{\alpha\beta}\|$$

in the basis of Wannier orbitals. Finally, the total energy in the HF method can be obtained as

$$E_{HF} = \sum_k^{occ} \varepsilon_k - \frac{1}{2} \sum_{\alpha\beta} V_{\beta\alpha} n_{\alpha\beta}.$$

### 3.2. Second-order perturbation theory for correlation energy

The simplest way to go beyond the HF approximation is to include the correlation interactions in the second order of the perturbation theory for the total energy [13]. The correlation interaction (or a fluctuation) is defined as the difference between true many-body Hamiltonian (1) and its one-electron counterpart, obtained at the level of HF approximation:

$$\hat{\mathcal{H}}_c = \sum_{\mathbf{R}} \left( \frac{1}{2} \sum_{\alpha\beta\gamma\delta} U_{\alpha\beta\gamma\delta} \hat{c}_{\mathbf{R}\alpha}^\dagger \hat{c}_{\mathbf{R}\gamma}^\dagger \hat{c}_{\mathbf{R}\beta} \hat{c}_{\mathbf{R}\delta} - \sum_{\alpha\beta} V_{\alpha\beta} \hat{c}_{\mathbf{R}\alpha}^\dagger \hat{c}_{\mathbf{R}\beta} \right). \quad (4)$$

By treating  $\hat{\mathcal{H}}_c$  as a perturbation, the correlation energy can be easily estimated as [13]

$$E_c^{(2)} = - \sum_S \frac{\langle G | \hat{\mathcal{H}}_c | S \rangle \langle S | \hat{\mathcal{H}}_c | G \rangle}{E_{HF}(S) - E_{HF}(G)}, \quad (5)$$

where  $|G\rangle$  and  $|S\rangle$  are the Slater determinants, respectively, corresponding to the low-energy ground state in the HF approximation and the excited state. Due to the variational properties of the HF method, the only processes that may contribute to  $E_c^{(2)}$  are the two-particle excitations, for which each  $|S\rangle$  is obtained from  $|G\rangle$  by replacing two one-electron orbitals, e.g.,  $\varphi_{k_1}$  and  $\varphi_{k_2}$ , from the occupied part of the spectrum by two unoccupied orbitals, e.g.,  $\varphi_{k_3}$  and  $\varphi_{k_4}$ . Hence, using the notation of Sec. 2, the matrix elements take the form

$$\langle S | \hat{\mathcal{H}}_c | G \rangle = \langle k_3 k_4 | v_{scr} | k_1 k_2 \rangle - \langle k_3 k_4 | v_{scr} | k_2 k_1 \rangle. \quad (6)$$

Then, we employ a common approximation of noninteracting quasiparticles and replace the denominator in Eq. (5) with the linear combination of HF eigenvalues:

$$E_{HF}(S) - E_{HF}(G) \approx \varepsilon_{k_3} + \varepsilon_{k_4} - \varepsilon_{k_1} - \varepsilon_{k_2}$$

see [13]. Matrix elements (6) satisfy the condition

$$\langle S | \hat{\mathcal{H}}_c | G \rangle \sim \frac{1}{N} \sum_{\mathbf{R}} \exp(i(\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{R})$$

if the screened Coulomb interactions are diagonal with respect to the site indices.

A good point of the second-order of the perturbation theory is that it allows estimating both on-site ( $\mathbf{R} = 0$ ) and intersite ( $\mathbf{R} \neq 0$ ) elements of this expansion relatively easily. In what follows, we use this

method in order to study the relative role played by these effects in the stability of different magnetic structures of the distorted perovskite oxides. The  $\mathbf{R} = 0$  term corresponds to the commonly used single-site approximation for the correlation interactions, which becomes exact in the limit of infinite spatial dimensions [19].

### 3.3. The $t$ -matrix approach

The basic idea of the  $t$ -matrix approach is to look at the true many-electron system as a superposition of independent two-electron subsystems, and to rigorously solve the Schrödinger equations for each of these subsystems [14, 15, 16]. Hence, we consider the two-electron Hamiltonian

$$\hat{H}(1, 2) = \hat{h}_{HF}(1) + \hat{h}_{HF}(2) + \Delta\hat{v}(1, 2),$$

where

$$\Delta\hat{v}(1, 2) = \hat{v}_{scr}(1, 2) - \hat{V}(1) - \hat{V}(2),$$

$\hat{v}_{scr}(1, 2)$  is the screened (by other bands) Coulomb interactions between electrons «1» and «2» in the  $t_{2g}$  band, and  $\hat{h}_{HF}$  ( $\hat{V}$ ) is the one-electron Hamiltonian (potential) in the HF approximation. For a periodic system, the Schrödinger equation can be written as

$$\hat{H}|\Psi_{k_1 k_2}\rangle = E_{k_1 k_2}|\Psi_{k_1 k_2}\rangle. \quad (7)$$

Any two-electron wave function  $|\Psi_{k_1 k_2}\rangle$  can be expanded in the basis of (also two-electron) Slater determinants:

$$|k_1 k_2\rangle = \frac{1}{\sqrt{2}} \{ \varphi_{k_1}(1) \varphi_{k_2}(2) - \varphi_{k_2}(1) \varphi_{k_1}(2) \},$$

etc. Apart from a normalization factor, this expansion has the form [16]

$$|\Psi_{k_1 k_2}\rangle = |k_1 k_2\rangle + \sum_{|k_3 k_4\rangle} \Gamma_{k_1 k_2}^{k_3 k_4} |k_3 k_4\rangle. \quad (8)$$

We note that the summation ranges only nonequivalent Slater determinant  $|k_3 k_4\rangle$  constructed from the one-electron orbitals  $k_3$  and  $k_4$ . For example, because

$$|k_4 k_3\rangle = -|k_3 k_4\rangle,$$

the determinant  $|k_4 k_3\rangle$  must be excluded from the sum in (8), etc. Substituting Eq. (8) in Eq. (7) and introducing the new notation

$$\Delta E_{k_1 k_2} = E_{k_1 k_2} - \varepsilon_{k_1} - \varepsilon_{k_2}$$

such that

$$\left[ \hat{h}_{HF}(1) + \hat{h}_{HF}(2) - \varepsilon_{k_1} - \varepsilon_{k_2} \right] |k_1 k_2\rangle = 0$$

(i.e.,  $\varepsilon_{k_1}$  and  $\varepsilon_{k_2}$  are the eigenvalues of the HF Hamiltonian), we obtain the following equation for  $\Delta E_{k_1 k_2}$  and  $\Gamma_{k_1 k_2}^{k_3 k_4}$ :

$$\begin{aligned} & (\Delta \hat{v} - \Delta E_{k_1 k_2}) |k_1 k_2\rangle + \\ & + \sum_{|k_3 k_4\rangle} (\varepsilon_{k_3} + \varepsilon_{k_4} - \varepsilon_{k_1} - \varepsilon_{k_2} + \\ & + \Delta \hat{v} - \Delta E_{k_1 k_2}) \Gamma_{k_1 k_2}^{k_3 k_4} |k_3 k_4\rangle = 0. \end{aligned}$$

By considering the matrix element of this equation with  $\langle k_1 k_2|$ , we can find that

$$\begin{aligned} \Delta E_{k_1 k_2} &= \langle k_1 k_2 | \Delta \hat{v} | k_1 k_2 \rangle + \\ & + \sum_{|k_3 k_4\rangle} \Gamma_{k_1 k_2}^{k_3 k_4} \langle k_1 k_2 | \Delta \hat{v} | k_3 k_4 \rangle, \quad (9) \end{aligned}$$

where the first term is the energy of the Coulomb and exchange interactions in the HF approximation (minus the potential energy), while the second term is the correlation energy. By considering the matrix elements with  $\langle k_5 k_6 | \neq \langle k_1 k_2 |$ , we can find another set of equations for  $\Gamma_{k_1 k_2}^{k_3 k_4}$ :

$$\begin{aligned} & \langle k_5 k_6 | \Delta \hat{v} | k_1 k_2 \rangle + \\ & + (\varepsilon_{k_5} + \varepsilon_{k_6} - \varepsilon_{k_1} - \varepsilon_{k_2} - \Delta E_{k_1 k_2}) \Gamma_{k_1 k_2}^{k_5 k_6} + \\ & + \sum_{|k_3 k_4\rangle} \Gamma_{k_1 k_2}^{k_3 k_4} \langle k_5 k_6 | \Delta \hat{v} | k_3 k_4 \rangle = 0. \end{aligned}$$

They are solved iteratively with respect to  $\Delta \hat{v}$ . For this, it is convenient to introduce the two-particle Green's function

$$\hat{G}_{k_1 k_2} = \sum_{|k_3 k_4\rangle} \frac{|k_3 k_4\rangle \langle k_3 k_4|}{\varepsilon_{k_3} + \varepsilon_{k_4} - \varepsilon_{k_1} - \varepsilon_{k_2} - \Delta E_{k_1 k_2}}$$

and derive a matrix equation for  $\{\Gamma_{k_1 k_2}^{k_3 k_4}\}$  to be substituted in Eq. (9). It is then rather straightforward to derive the following expression for  $\Delta E_{k_1 k_2}$ :

$$\Delta E_{k_1 k_2} = \langle k_1 k_2 | \hat{T}_{k_1 k_2} | k_1 k_2 \rangle, \quad (10)$$

where  $\hat{T}_{k_1 k_2}$  is the so-called  $t$ -matrix:

$$\hat{T}_{k_1 k_2} = \Delta \hat{v} \left[ \hat{1} + \hat{G}_{k_1 k_2} \Delta \hat{v} \right]^{-1}. \quad (11)$$

The correlation energy of the  $t$ -matrix method is obtained after subtracting the energies of Coulomb and exchange interactions in the HF approximation from

Eq. (10) and summing over all Slater determinants constructed from the occupied one-electron orbitals of the HF method:

$$E_c^{(t)} = \sum_{|k_1 k_2\rangle}^{occ} \langle k_1 k_2 | \hat{T}_{k_1 k_2} - \Delta \hat{v} | k_1 k_2 \rangle. \quad (12)$$

In practice, each HF orbital has been expanded over the basis of Wannier functions, and then all calculations of  $\hat{T}_{k_1 k_2}$  and  $E_c^{(t)}$  have been performed in this basis.

By expanding  $\hat{T}_{k_1 k_2}$  up to the second order in  $\Delta \hat{v}$ , we regain Eq. (5), obtained in the second order of the perturbation theory. Therefore, the good point of the  $t$ -matrix approach is that it allows going beyond the second order of the perturbation theory and evaluating the higher-order effects in  $\Delta \hat{v}$  on the correlation energy. Nevertheless, it was supplemented with some additional approximations.

1. When we compute the matrix elements of the form  $\langle k_3 k_4 | \Delta \hat{v} | k_1 k_2 \rangle$ , being proportional to

$$\frac{1}{N} \sum_{\mathbf{R}} \exp(i(\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{R}),$$

we consider only the  $\mathbf{R} = 0$  part of this sum and neglect all other contributions. This corresponds to the single-site approximation for the  $t$ -matrix.

2. In all matrix elements  $\langle k_3 k_4 | \Delta \hat{v} | k_1 k_2 \rangle$ , we replace  $\Delta \hat{v}$  with  $\hat{v}_{scr}$  and drop the one-electron potentials of the HF method. Strictly speaking, this procedure is justified only when both one-electron states  $k_1$  and  $k_2$  are different from  $k_3$  and  $k_4$ , for example, when they belong, correspondingly, to the occupied and unoccupied part of the spectrum, as in the second-order of perturbation theory. However, this is no longer true for the higher-order terms in  $\Delta \hat{v}$ . Nevertheless, we believe that the difference is small.

All correlation energies have been computed in the mesh of 75 points in the first Brillouin zone, corresponding to the 4 : 4 : 2 division of the reciprocal translation vectors for the distorted perovskite structure. The actual integration over the Brillouin zone has been replaced by the summation over this mesh of points.

#### 4. RESULTS AND DISCUSSIONS

First applications of the proposed method to  $\text{YTiO}_3$ ,  $\text{LaTiO}_3$ ,  $\text{YVO}_3$ , and  $\text{LaVO}_3$  have been considered in Ref. [11], where we have summarized results of HF calculations for model (1) and the behavior of

**Table 1.** The Hartree–Fock energy  $E_{HF}$  and correlation energies obtained in the second order of perturbation theory,  $E_c^{(2)}$ , and in the  $t$ -matrix approach,  $E_c^{(t)}$ , for the orthorhombic phase of  $\text{YTiO}_3$ . The Hartree–Fock energies are measured from the most stable magnetic state in meV per one formula unit. The correlation energies are measured in meV per one transition-metal site or a pair of sites, correspondingly for the on-site and intersite contributions. The  $t$ -matrix was computed in the single-site approximation. Therefore, only the site-diagonal part of  $E_c^{(t)}$  is shown. The positions of the transition-metal sites are shown in the Figure

Phase	$E_{HF}$	$E_c^{(2)}$			$E_c^{(t)}$
		Ti <sub>1</sub>	Ti <sub>1</sub> –Ti <sub>2</sub>	Ti <sub>1</sub> –Ti <sub>3</sub>	
<i>F</i>	0	–5.13	–0.38	–0.01	–4.58
<i>A</i>	2.05	–6.19	–0.37	0	–4.80
<i>C</i>	14.40	–8.32	–0.17	–0.01	–5.28
<i>G</i>	16.25	–8.48	–0.18	–0.01	–5.31

**Table 2.** The Hartree–Fock energy  $E_{HF}$  and correlation energies obtained in the second order of perturbation theory,  $E_c^{(2)}$ , and in the  $t$ -matrix approach,  $E_c^{(t)}$ , for the low-temperature orthorhombic phase of  $\text{YVO}_3$  ( $T < 77$  K). All energies are measured in meV. See the Figure for the details of the notation

Phase	$E_{HF}$	$E_c^{(2)}$			$E_c^{(t)}$
		V <sub>1</sub>	V <sub>1</sub> –V <sub>2</sub>	V <sub>1</sub> –V <sub>3</sub>	
<i>F</i>	21.66	–2.19	–0.12	–0.02	–2.16
<i>A</i>	14.59	–4.67	–0.12	–0.01	–3.31
<i>C</i>	10.14	–5.61	–0.07	0	–3.14
<i>G</i>	0	–7.07	–0.07	–0.01	–4.06

correlation energies in the second order of the perturbation theory, supplemented with the single-site approximation. In the present work, we further elaborate the problem by focusing on the following questions:

1. the role of higher-order contributions to the correlation energy;
2. the role of nonlocal (or intersite) contributions to the correlation energy.

We also consider the effects of monoclinic distortion and analyze the contributions to the correlation energy of inequivalent transition-metal sites. The results of these calculations are presented in Tables 1–5 for all

the considered compounds. First, we summarize the main results in Ref. [11].

1. The HF approximation yields the correct magnetic ground state for  $\text{YTiO}_3$ ,  $\text{LaVO}_3$ , and both phases of  $\text{YVO}_3$ . This conclusion is fully consistent with the results of accurate all-electron band-structure calculations [5], and it is quite remarkable that all these results can be reproduced in our minimal model derived for the  $t_{2g}$  bands.

2. The correlation effects favor the AFM spin alignment and additionally stabilize the experimentally observed *G*- and *C*-type AFM states in  $\text{YVO}_3$  and  $\text{LaVO}_3$ .

3. None of the considered approaches reproduces the experimental *G*-type AFM ground state of  $\text{LaTiO}_3$  (instead, the theoretical calculations steadily converge to the *A*-type AFM ground state [11, 12]).

Then, what is to happen if we go beyond the second-order perturbation theory and apply the  $t$ -matrix approach? Generally, the  $t$ -matrix approach reduces the absolute value of the correlation energy. But the magnitude of this reduction strongly depends on the magnetic state. For example, if the ferromagnetic state is only weakly affected by the higher-order correlation effects (the typical changes of  $E_c$  vary from 1% in  $\text{YVO}_3$  to 13% in  $\text{LaTiO}_3$ ),  $E_c$  in the *G*-type AFM phase can drop by nearly 50%. From this standpoint, if the second order of the perturbation theory does not solve the problem of the *G*-type AFM ground state of  $\text{LaTiO}_3$ , it seems to be unlikely that the higher-order effects can reverse the situation. Apparently,  $\text{LaTiO}_3$  is different from other perovskite oxides, and the regular perturbation-theory expansion, although justifiable for the majority of considered compounds, does not work for  $\text{LaTiO}_3$ . This seems to be reasonable because  $\text{LaTiO}_3$  has the largest correlation energies, which are comparable to the splitting of the  $t_{2g}$  levels caused by the crystal distortion ( $\approx 37$  meV [11]). Therefore, it is quite possible that the correlation effects in  $\text{LaTiO}_3$  should be considered at the first place, and the simple HF theory for the spin and orbital ordering with the subsequent inclusion of the correlation effects as a perturbation to the HF ground state may not be appropriate here [7, 8]. We note that in other materials, the situation is different: the typical values of the  $t_{2g}$ -levels splitting in  $\text{YTiO}_3$ ,  $\text{YVO}_3$ , and  $\text{LaVO}_3$  are about 100 meV [11], which exceeds the correlation energy by at least one order of magnitude. Therefore, it seems that the degeneracy of the HF ground state is already lifted by the crystal distortion, and the correlation effects are well described by means of the regular perturbation theory expansion. This is partly supported by

**Table 3.** The Hartree–Fock energy  $E_{HF}$  and correlation energies obtained in the second order of perturbation theory,  $E_c^{(2)}$ , and in the  $t$ -matrix approach,  $E_c^{(t)}$ , for the high-temperature monoclinic phase of  $YVO_3$  ( $77\text{ K} < T < 116\text{ K}$ ). All energies are measured in meV. See Table 1 for the details of the notation. In the monoclinic phase, the planes 1–2 and 3–4 are inequivalent (see the Figure). Therefore, there are two different types of on-site (denoted as  $V_1$  and  $V_4$ ) and intersite (denoted as  $V_1$ – $V_2$  and  $V_4$ – $V_3$ ) contributions to the correlation energy. The contributions  $V_1$ – $V_3$  and  $V_4$ – $V_2$  are equivalent and are both shown only for the sake of completeness

Phase	$E_{HF}$	$E_c^{(2)}$						$E_c^{(t)}$	
		$V_1$	$V_1$ – $V_2$	$V_1$ – $V_3$	$V_4$	$V_4$ – $V_3$	$V_4$ – $V_2$	$V_1$	$V_4$
<i>F</i>	11.71	–2.81	–0.02	–0.03	–1.74	–0.01	–0.03	–2.76	–1.71
<i>A</i>	13.97	–5.87	–0.03	–0.01	–3.63	–0.01	–0.01	–4.14	–2.55
<i>C</i>	0	–8.08	–0.02	–0.05	–6.98	–0.03	–0.05	–4.85	–4.33
<i>G</i>	6.63	–7.56	–0.02	–0.01	–6.49	–0.03	–0.01	–4.38	–3.76

**Table 4.** The Hartree–Fock energy  $E_{HF}$  and correlation energies obtained in the second order of perturbation theory,  $E_c^{(2)}$ , and in the  $t$ -matrix approach,  $E_c^{(t)}$ , for the monoclinic phase of  $LaVO_3$ . All energies are measured in meV. See Tables 1 and 3 for the details of the notation. In the monoclinic phase, the planes 1–2 and 3–4 (see the Figure) are inequivalent, which results in two types of V sites as well as the in-plane interactions

Phase	$E_{HF}$	$E_c^{(2)}$						$E_c^{(t)}$	
		$V_1$	$V_1$ – $V_2$	$V_1$ – $V_3$	$V_4$	$V_4$ – $V_3$	$V_4$ – $V_2$	$V_1$	$V_4$
<i>F</i>	20.98	– 3.82	–0.02	–0.15	– 4.13	–0.02	–0.15	–3.74	–4.02
<i>A</i>	20.63	–11.77	–0.22	–0.03	– 8.80	–0.02	–0.03	–8.34	–5.84
<i>C</i>	0	–13.37	–0.04	–0.26	–12.54	–0.02	–0.26	–8.86	–8.39
<i>G</i>	7.65	–10.52	–0.04	–0.02	– 9.02	–0.03	–0.02	–6.17	–5.41

recent total-energy calculations for the orthorhombic phase of  $YVO_3$  using the path-integral renormalization-group method, which is free of any perturbation-theory expansions for the correlation energy [20]. The method was applied to the same model, and the main conclusions concerning the magnetic phase diagram were similar to our present finding.

The correlations additionally stabilize the experimentally observed *G*- and *C*-type AFM states in  $YVO_3$  and  $LaVO_3$ . Moreover, in the orthorhombic phase of  $YVO_3$ , the correlation effects tend to stabilize the *G*-type AFM state; while in the monoclinic phase, they stabilize the *C*-type AFM state, being in total agreement with the experimental data. This trend is clearly seen both in the second order of the perturbation theory and in the  $t$ -matrix approach, although the latter yields somewhat smaller values for the stabilization energy associated with the correlation effects.

The higher-order correlations play an important role in  $YTiO_3$  and additionally stabilize the ferromagnetic phase. The latter emerges as the ground state

**Table 5.** The Hartree–Fock energy  $E_{HF}$  and correlation energies obtained in the second order of perturbation theory,  $E_c^{(2)}$ , and in the  $t$ -matrix approach,  $E_c^{(t)}$ , for the orthorhombic phase of  $LaTiO_3$ . All energies are measured in meV. See Table 1 for the details of the notation

Phase	$E_{HF}$	$E_c^{(2)}$			$E_c^{(t)}$
		$Ti_1$	$Ti_1$ – $Ti_2$	$Ti_1$ – $Ti_3$	$Ti_1$
<i>F</i>	4.95	–11.08	–0.52	–0.08	– 9.66
<i>A</i>	0	–22.53	–0.54	–0.07	–15.17
<i>C</i>	19.57	–17.19	–0.23	–0.11	–11.04
<i>G</i>	11.51	–23.02	–0.22	–0.09	–13.99

already in the HF approach, where the total energy difference between ferromagnetic and the next *A*-type AFM state is about 2.05 meV per one Ti site (Table 1). However, if we take the correlation effects in the sec-

second order of the perturbation theory into account (and consider the single-site approximation), this difference is reduced to only 0.99 meV. Therefore, the situation is very fragile. Nevertheless, the  $t$ -matrix approach, which affects the  $A$ -type AFM state more strongly, recovers some of these energy gains and is to make the total energy difference between ferromagnetic and  $A$ -type AFM states about 1.83 meV per one Ti site.

The intersite correlation energies estimated in the second order of the perturbation theory, can be large in some ferromagnetically coupled bonds. This is especially true for  $\text{YTiO}_3$  and  $\text{LaVO}_3$ . For example, the energy of interaction between nearest-neighbor sites «1» and «2» (see the Figure), located in the  $\mathbf{ab}$ -plane of the ferromagnetic phase of  $\text{YTiO}_3$  is about  $-0.38$  meV (Table 1). Because each transition-metal atom interacts with four nearest neighbors in the  $\mathbf{ab}$ -plane, this value corresponds to the additional energy gain

$$-0.38 \times 4 = -1.52 \text{ meV}$$

per one Ti site. Similar estimates yield

$$-0.37 \times 4 = -1.48 \text{ meV}, \quad -0.17 \times 4 = -0.68 \text{ meV},$$

and

$$-0.18 \times 4 = -0.72 \text{ meV},$$

correspondingly for the  $A$ -,  $C$ -, and  $G$ -type AFM states. Therefore, the in-plane intersite correlations tend to additionally stabilize the ferromagnetic phase relative to the AFM states  $C$  and  $G$ . In the  $A$ -type AFM phase, the sites «1» and «2» are also ferromagnetically coupled, as in the totally ferromagnetic phase. Therefore, these two phases have practically the same intersite correlation energies in the  $\mathbf{ab}$ -plane. The inter-plane correlations appear to be small in all magnetic phases of  $\text{YTiO}_3$ .

In  $\text{LaVO}_3$ , the situation is somewhat different, and this is a good example of a system where the inter-plane correlations already play a more important role. Indeed, the energies of intersite correlations are the largest in the ferromagnetic chains of  $C$ -type AFM phase, which is also the magnetic ground state of this compound. These energies are associated with the bonds «1–3» and «2–4», which are shown in the Figure, and the results are summarized in Table 4. Thus, in the case of  $\text{LaVO}_3$ , the inter-plane correlations additionally stabilize the  $C$ -type AFM ground state. But because each transition-metal atom interacts with only two nearest neighbors along the  $\mathbf{c}$  axis, the stabilization energy is not particularly large, about

$$-0.26 \times 2 = -0.52 \text{ meV}$$

per one V atom.

The intersite correlation energies are also large in the case of  $\text{LaTiO}_3$  (Table 5). However, they tend to stabilize either ferromagnetic or  $A$ -type AFM states, and do not explain the appearance of the experimental  $G$ -type AFM ground state. Again, we believe that the problem is related to the use of the regular perturbation theory expansion, which may not be justified in the case of  $\text{LaTiO}_3$ .

The monoclinic distortion realized in  $\text{LaVO}_3$  and in the high-temperature phase of  $\text{YVO}_3$  produces two inequivalent pairs of transition-metal sites, which are shown correspondingly as (1,2) and (3,4) in the Figure. Therefore, it is interesting to consider the interplay between correlation energies and the lattice distortions around different transition-metal sites. In our notations, the crystal structure around the sites «3» and «4» is more distorted than the one around the sites «1» and «2». Such a distortion directly correlates with the magnitude of the crystal-field splitting in different sublattices [11]. Then, the on-site correlations are generally stronger at the sites with the least distorted environment (site «1» in the Tables 3 and 4). This rule holds both for  $\text{YVO}_3$  and  $\text{LaVO}_3$  (although with some exception for the ferromagnetic phase of  $\text{LaVO}_3$ ). In the  $C$ -type AFM phase, which is always realized as the magnetic ground state in the monoclinic structure, the difference of on-site correlation energies associated with sites «1» and «4» is about 1 meV per one V site, as obtained in the second order of the perturbation theory. This value is further reduced to 0.5 meV per one V site by higher-order correlations in the  $t$ -matrix theory.

## 5. SUMMARY AND CONCLUSIONS

This paper is a continuation of the previous works (Refs. [10–12]) devoted to the construction and solution of an effective low-energy models for the series of distorted  $t_{2g}$  perovskite oxides on the basis of the first-principle electronic structure calculations. It deals with the analysis of correlation interactions and their contributions to stability of different magnetic structures that can be realized in these compounds. The correlation energies have been calculated on the basis of a regular perturbation theory expansion starting from the ground state of the HF method. Thus, our strategy implies that the degeneracy of the HF ground state is already lifted by the crystal distortion and the regular perturbation theory is justified. This seems to be a good approximation for the most distorted  $\text{YTiO}_3$ ,  $\text{YVO}_3$ , and even  $\text{LaVO}_3$ , where

1. the correct magnetic ground state can be formally obtained at the level of the HF approximation;
2. the correlation effects included as a perturbation into the HF ground state, systematically improve the agreement with the experimental data.

However, in  $\text{LaTiO}_3$ , the situation is completely different:

1. the HF method yields an incorrect magnetic ground state ( $A$ -type AFM instead of  $G$ -type AFM);
2. the correlation interactions, treated as a perturbation to this incorrect HF ground state, do not change the overall picture, and the  $G$ -type AFM state remains unstable relative to the  $A$ -state.

Thus, the origin of the  $G$ -type AFM ground state in  $\text{LaTiO}_3$  seems to be different from other perovskite oxides and remains a challenging problem for future theories. Apparently, one of our basic assumptions about the nondegeneracy of the HF ground state breaks down in the case of  $\text{LaTiO}_3$ , and the true ground state cannot be approached through a series of continuous corrections applied to the single-Slater-determinant HF theory. Therefore, the next important step for  $\text{LaTiO}_3$  would be to abandon this “nondegeneracy assumption” and expand the class of the possible ground states, which would include some aspects of the orbital liquid theory [7].

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