d-p model and spin-orbital order in vanadium perovskites

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Using the multiband *d-p* model and unrestricted Hartree-Fock approximation we investigate the electronic structure and spin-orbital order in a three-dimensional VO_3 lattice. The main aim of this paper is testing if a simple *d-p* model with partly filled $3d$ orbitals (in vanadium ions) and $2p$ orbitals (in oxygen ions) is capable of reproducing correctly nontrivial coexisting spin-orbital order observed in the vanadium perovskites. We point out that the multiband *d-p* model has to include partly filled e_g orbitals in vanadium ions. The results suggest weak self-doping as an important correction beyond the ionic model and reproduce the possible ground states with broken spin-orbital symmetry in vanadium ions: either C-type alternating orbital order accompanied by G-type antiferromagnetic spin order or G-type alternating orbital order accompanied by C-type antiferromagnetic spin order. Both states are experimentally observed and compete with each other in YVO_3 whereas only the latter was observed in $LaVO_3$. Orbital order is induced and stabilized by particular patterns of oxygen distortions arising from the Jahn-Teller effect. In contrast to time-consuming *ab initio* calculations, the computations using the *d-p* model are very quick and should be regarded as very useful in solid-state physics, provided the parameters are selected carefully.

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I. INTRODUCTION

The spin and orbital ordering found in three-dimensional (3D) vanadium perovskites is an old but still very interesting problem with many challenges. It was discussed in numerous experimental and theoretical papers, considering undoped [1–24] and doped by charged defects [25–27] vanadium perovskites. On the theoretical side, the first insightful explanation of the alternating orbital (AO) order was given by Mizokawa *et al.* in 1999 [1]. They studied the competition between two types of spin-orbital order in vanadates within the so-called lattice model. It was claimed that Jahn-Teller (JT) distortions of the lattice [28] (see Fig. 1) are primarily responsible for the onset of this order. Sizable tilting of the apical axes of octahedra (out of an ideal cubic structure) was assumed to be the main driving factor which distinguishes between low-temperature and high-temperature orders in $LaVO_3$ or YVO_3 [1].

Easy-to-grasp presentation of the spin and orbital order in the ground state as perceived today by experimentalists was presented by Blake *et al.* [7]. The phase diagram of the vanadium perovskites RVO_3 [21] shows several spin- and/or orbital ordered phases. In the regime of compounds with low values of ionic radii r_R of rare-earth ions R as in YVO_3, two antiferromagnetic (AF) phases with complementary spin-orbital order appear: (i) G-type AF (G-AF) order accompanied by C-type alternating orbital order (C-AO) with staggered orbitals on ab planes and repeated orbitals along the c axis (below the magnetic transition at $T_{\rm N2} = 77$ K) and (ii) C-type AF (C-AF) order accompanied by G-type AO (G-AO) order for $T_{\rm N2} < T < T_{\rm N1}$, where $T_{\rm N1} = 116$ K is the high-temperature magnetic transition [21].

It is well understood now that at zero temperature, i.e., when YVO_3 is orthorhombic, the zx and yz orbitals on vanadium

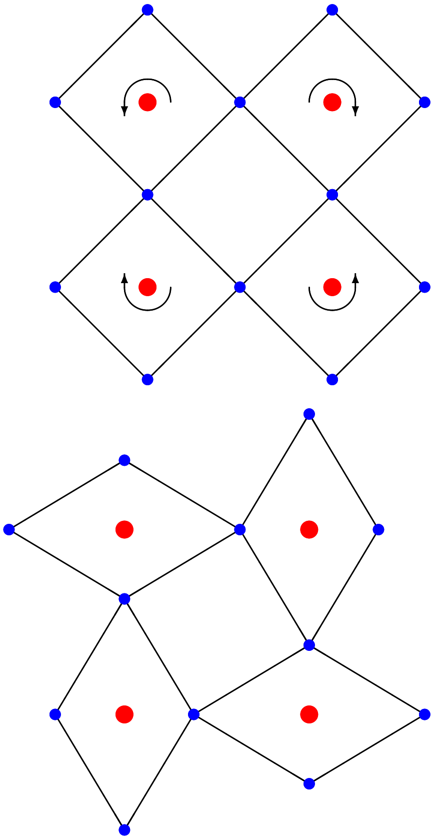

FIG. 1. Schematic of *cooperative and static* Q_4 JT distortions involving rotations of octahedra groups (upper panel) and Q_2 distortions (lower panel). For a description and classification of different JT modes see Ref. [28]. Red/blue dots denote positions of vanadium/oxygen ions on the ab plane.

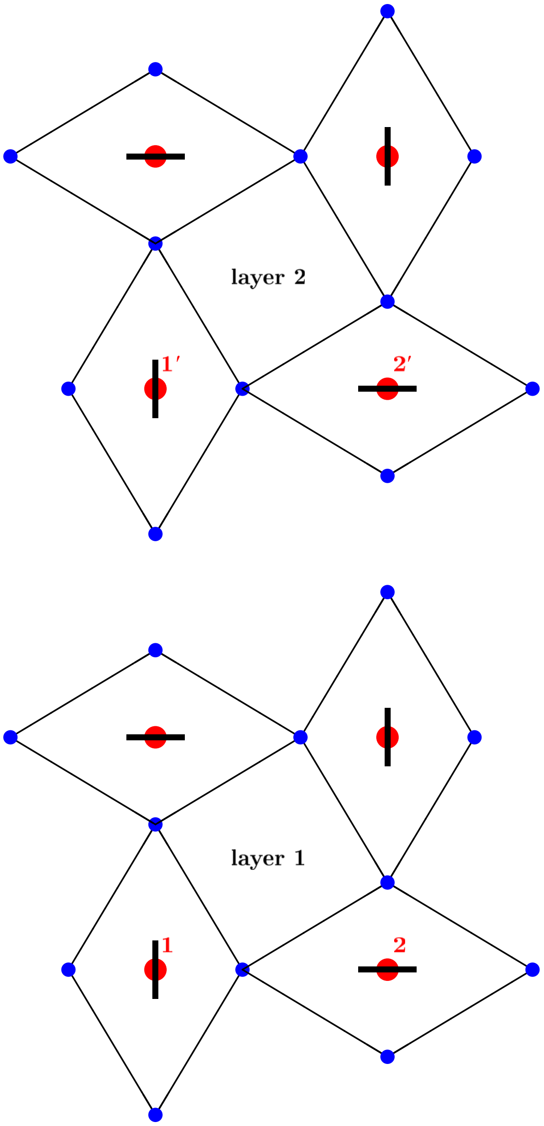

FIG. 2. Schematic of JT distortions used for Hartree-Fock computations in the low-temperature phase of YVO_3. The long bars denote preferred yz or zx orbitals—their cooperative arrangement forms C-AO order. Spins are not shown. The numbers shown close to vanadium positions identify the ions (see the corresponding entries in Table II). Horizontal and vertical directions on the figure correspond to x and y axes, respectively; note that the x, y axes are at a 45° angle to the crystallographic a, b axes, i.e., our x direction corresponds to the crystallographic (1,1,0) direction. The orbital order is repeated in consecutive layers when moving up along the z axis (this coincides with the crystallographic c axis).

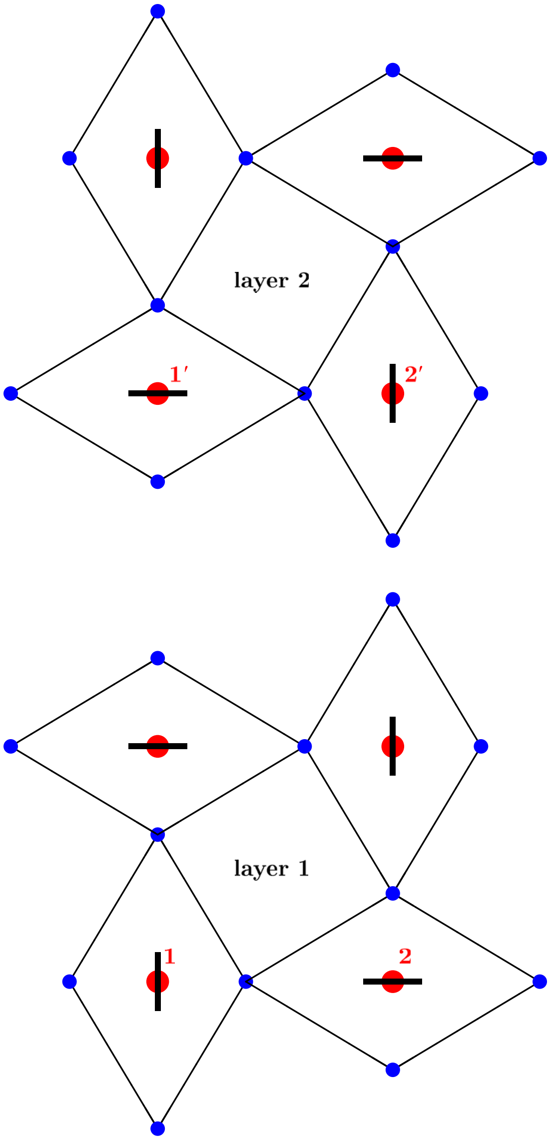

FIG. 3. Schematic of JT distortions used for Hartree-Fock computations in the zero-temperature phase of $LaVO_3$. Here, over the first layer 1, layer 2 is stacked, and the orbitals $\{yz, zx\}$ form G-AO order, i.e., alternate along the c axis. The meaning of other symbols is the same as in Fig. 2.

ions alternate between two sublattices forming orbital C-AO long-range order and this order resembles AF spin order on a single ab plane, see Fig. 2, whereas along the c axis this order is repeated, i.e., there is an analogy to ordinary spin ferromagnetic order [7]. At the same time the spins are arranged according to an ordinary 3D Néel state (G-AF spin order). At intermediate temperatures $T > 77$ K (when YVO_3 is monoclinic) this order is reversed: the G-AO order is accompanied by C-AF spin order, see Fig. 3. The magnetic transition at $T = 77$ K is triggered by the dimerization in spin-orbital chains which requires spin fluctuations at finite temperature [29]. Altogether this transition takes place between two types of spin-orbital order along the c axis which follow the complementarity predicted by the Goodenough-Kanamori rules [30].

The purpose of this paper is to investigate the spin-orbital order in vanadium perovskites within the multiband d-p model, i.e., to go beyond the usually used picture of a Mott insulator with $S = 1$ spins and t_{2g} orbital degrees of freedom or the effective degenerate Hubbard model of t_{2g} electrons. The d-p model includes nonzero on-site Coulomb interactions defined both on oxygen and on transition-metal ions and takes into account the possibility of finite self-doping, explained below and applied before to ruthenium, iridium, and titanium oxides [31–33]. The d-p model was developed in these papers into a realistic method, capable of computationally cheap and fast realistic investigation of the electronic structure of complex transition-metal oxides.

Up to now, the on-site Coulomb interactions on oxygen ions are being neglected in the majority of papers (as a simplification—to reduce the computational effort). However, when Coulomb repulsion elements on oxygens are neglected, the true d-p model parameters are replaced by effective parameters. In particular, the effective Hubbard repulsion on vanadium ions U_d is smaller by about 50% than the true U_d repulsion [33]. Also the so-called *self-doping* [31–33], see below, is neglected in traditional effective $3d$-electron models where one assumes that a cation (for example, La in $\mathrm{LaVO_3}$ or Y in $\mathrm{YVO_3}$) behaves according to the *idealized ionic model*, i.e., donates *all* valence electrons into a $\mathrm{VO_3}$ unit (for La these are as follows: two $4s$ electrons and one $3d$ valence electron). However, in reality, this charge transfer is smaller—it is not exactly 3 but $(3-x)$ instead. Strictly speaking, we mean by this statement that the occupation number of valence electrons on La as obtained say by Mulliken (or Bader) population analysis (during a parallel *ab initio* computation) will amount to some finite value of $x>0$. This redistribution of electron charge is called here *self-doping*.

In the present paper we use up-to-date estimations of crystal-field splittings, spin-orbit interaction in vanadium ions, and JT distortions. The model is used to study possible types of order and to establish the easy spin axis. We also extracted from our computations highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps which can serve as an estimation of the band gap.

The paper is organized as follows. We define the model and its parameters in Sec. II. The numerical method and its caveats are addressed in Sec. III. The results are presented and discussed in Sec. IV. In Sec. V we present the main conclusions and a short summary.

II. HAMILTONIAN

We introduce the multiband d-p Hamiltonian for the $\mathrm{VO_3}$ 3D cluster which includes five $3d$ orbitals in each vanadium ion and three $2p$ orbitals in each oxygen ion (with the parameters given in Table I),

$$\mathcal{H}=H_{\mathrm{kin}}+H_{\mathrm{so}}+H_{\mathrm{diag}}+H_{\mathrm{int}}, \tag{2.1}$$

where H_{kin} stands for the kinetic energy, H_{so} stands for spin-orbit coupling, H_{diag} stands for the diagonal part of kinetic energy (also including local crystal-field splittings), and H_{int} stands for the intra-atomic Coulomb interactions. Optionally one can add the JT part H_{JT}, and this will be discussed in Sec. III A. The cluster geometry and precise forms of different terms are standard; for the detailed formulas see Refs. [31,32].

TABLE I. Parameters of the multiband model (2.1) (all in eV) used in the calculations. For the hopping integrals we adopt the values from Refs. [36,45], i.e., $(pd\sigma)$, $(pd\pi)$, $(pp\sigma)$, $(pp\pi)=-2.2, 1.1, 0.6, -0.15$ eV which correspond to V-O distances of 2.0 Å (we use Slater notation [34]). The charge-transfer energy (defined for bare levels) is taken as $\Delta=5.0$ eV.

ζ	U_d	J_{H}^{t}	J_{H}^{e}	U_p	J_{H}^{p}
0.026	8.0	0.8	0.9	4.4	0.8

The kinetic part of the Hamiltonian is as follows:

$$H_{\mathrm{kin}}=\sum_{\{i\mu;j,\nu\},\sigma}\left(t_{i,\mu;j,\nu}c^{\dagger}_{i,\mu,\sigma}c_{j,\nu,\sigma}+\mathrm{H.c.}\right), \tag{2.2}$$

where we employ a general notation with $c^{\dagger}_{j,\nu,\sigma}$ standing for the creation of an electron at site j in an orbital ν with up- or down-spin $\sigma=\uparrow,\downarrow$. The model includes all five $3d$ orbital states $\nu\in\{xy,yz,zx,x^2-y^2,3z^2-r^2\}$ and three $2p$ oxygen orbital states $\nu\in\{p_x,p_y,p_z\}$. Alternatively, i.e., when choosing a more intuitive notation, we can write $d^{\dagger}_{j,\nu,\sigma}$ for d orbitals, whereas we can write $p^{\dagger}_{j,\nu,\sigma}$ for p orbitals. The matrix $t_{i,\mu j,\nu}$ is assumed to be nonzero only for nearest-neighbor vanadium oxygen d-p pairs and for nearest-neighbor oxygen oxygen p-p pairs. The next-nearest hopping elements are neglected. (The nonzero $t_{i,\mu;j,\nu}$ elements are listed in the Appendix of Ref. [31]; we use the Slater notation [34]). As a side remark we recall that models taking into account only three t_{2g} orbitals and neglecting the remaining two e_g orbitals are not accurate enough [35].

The spin-orbit part $H_{\mathrm{so}}=\zeta\sum_i\mathbf{L}_i\cdot\mathbf{S}_i$, is a one-particle operator (the scalar product of angular momentum and spin operators at site i), and therefore it can be represented in the form similar to the kinetic part H_{kin} [36–39],

$$H_{\mathrm{so}}=\sum_i\left\{\sum_{\mu\neq\nu;\sigma,\sigma'}t^{\mathrm{so}}_{\mu,\sigma;\nu,\sigma'}d^{\dagger}_{i,\mu,\sigma}d_{i,\nu,\sigma'}+\mathrm{H.c.}\right\}, \tag{2.3}$$

with $t^{\mathrm{so}}_{\mu,\sigma;\nu,\sigma'}$ as the elements restricted to single vanadium sites. They all depend on spin-orbit strength ζ ($\zeta=0.026$ eV; this value was adopted from Ref. [40]), which is weak, but it can have an influence on the preferred spin direction. For a detailed formula and tables listing $t_{i\ \nu,\sigma';\mu,\sigma}$ elements, see Refs. [31,37].

The diagonal part H_{diag} depends only on electron number operators. It takes into account the effects of local crystal fields and the difference in reference orbital energies (here we employ the electron notation),

$$\Delta=\varepsilon_d-\varepsilon_p, \tag{2.4}$$

between d and p orbitals (for bare orbital energies). We can fix the reference energy $\varepsilon_d=0$ for d orbitals to zero and use only $\Delta=-\varepsilon_p$ as a parameter, thus we write

$$\begin{aligned}H_{\mathrm{diag}}=&\sum_{i;\mu=x,y,z;\sigma}\varepsilon_p p^{\dagger}_{i,\mu,\sigma}p_{i,\mu,\sigma}\\&+\sum_{m;\mu=xy,yz,\ldots;\sigma}f^{\mathrm{cr}}_{\mu,\sigma}d^{\dagger}_{m,\mu,\sigma}d_{m,\mu,\sigma}.\end{aligned} \tag{2.5}$$

The first sum is restricted to oxygen sites, whereas the second one runs over vanadium sites. The crystal-field splitting strength vector $(f^{\mathrm{cr}}_{\mu,\sigma})$ describes the splitting within t_{2g} levels. For example, in $\mathrm{YVO_3}$ the xy orbital is lowered by ~0.017 eV (according to Ref. [15]). At the same time, the $\{yz,zx\}$ doublet is also split (this was discussed in some papers, most clearly in Refs. [11,19]) in accordance with local JT distortion of a particular $\mathrm{VO_6}$ octahedron. *We assume ad hoc* that either yz is lower than the zx orbital which should correspond to an O_4 square (on the *ab* plane) when distorted from an ideal square into an elongated along the y-direction rhombus or the opposite: zx is lower than the yz orbital which should correspond to O_4 distorted into an elongated along the x-direction rhombus (compare Figs. 1 and 2). This splitting value should be 0.1–0.2 eV which is an educated guess (compare with the estimation from Ref. [15]).

The distance between t_{2g} levels and e_g levels is large, 1.5–2.0 eV [20,22,41]). We do not take into account a possible splitting within e_g levels as from our previous experience with transition-metal perovskites, and we do not expect it to be an important factor.

The on-site Coulomb interactions $H_{\rm int}(d)$ for d orbitals take the form of a degenerate Hubbard model [42],

$$H_{\rm int}(d) = \sum_{m,\mu<\nu}\left(U_d - \frac{5}{2}J^d_{\mu\nu}\right) n_{m\mu}n_{m\nu} + U_d\sum_{m\mu} n_{m\mu\uparrow}n_{m\mu\downarrow} - 2\sum_{m,\mu<\nu} J^d_{\mu\nu}\vec{S}_{m\mu}\cdot\vec{S}_{m\nu} + \sum_{m,\mu\neq\nu} J^d_{\mu\nu} d^\dagger_{m\mu\uparrow}d^\dagger_{m\mu\downarrow}d_{m\nu\downarrow}d_{m\nu\uparrow}. \tag{2.6}$$

where $n_{m\mu} = \sum_\sigma n_{m\mu\sigma}$ is the electron density operator in orbital μ, $\{\mu,\nu\}$'s enumerate different d orbitals, and $J_{d,\mu\nu}$ is the nontrivial tensor of on-site interorbital exchange (Hund's) elements for d orbitals; $J_{d,\mu\nu}$ has different entries for the $\{\mu,\nu\}$ pairs corresponding to two t_{2g} orbitals ($J^t_{\rm H}$) and for a pair of two e_g orbitals ($J^e_{\rm H}$) and still different for the case of cross-symmetry terms [43,44]; all these elements are included, and we assume the Racah parameters: $B = 0.1$ eV and $C = 4B$.

The local Coulomb interactions $H_{\rm int}(p)$ at oxygen sites (for $2p$ orbitals) are analogous,

$$H_{\rm int}(p) = \sum_{i,\mu<\nu,\sigma}\left(U_p - \frac{5}{2}J^p_{\rm H}\right) n_{i\mu}n_{i\nu} + U_p\sum_{i\mu} n_{i\mu\uparrow}n_{i\mu\downarrow} - 2J^p_{\rm H}\sum_{i,\mu<\nu}\vec{S}_{i\mu}\cdot\vec{S}_{i\nu} + J^p_{\rm H}\sum_{i,\mu\neq\nu} p^\dagger_{i\mu\uparrow}p^\dagger_{i\mu\downarrow}p_{i\nu\downarrow}p_{i\nu\uparrow}, \tag{2.7}$$

where the intraatomic Coulomb repulsion is denoted as U_p and all off-diagonal elements of the tensor $J^p_{\mu\nu}$ are equal (as they connect the orbitals of the same symmetry), i.e., $J^p_{\mu\nu} \equiv J^p_{\rm H}$. (Up to now, as already mentioned above, $H_{\rm int}(p)$ was neglected in the majority of studies, i.e., for simplicity it was being assumed that $U_p = J^p_{\rm H} = 0$.)

In the following we use the parameters U_d, $J^d_{\mu\nu}$, U_p, and $J^p_{\rm H}$ similar to those used before for titanium oxides [32,33]; for the hopping integrals we follow the studies by Mizokawa and Fujimori [36,45]. The value of $U_p \sim 4.0$ eV was previously used in copper oxides [46,47], but in addition in some test computations we considered a larger value of $U_p = 6$ eV. (This choice, i.e., $U_p = 6$ eV is advocated and reasonably explained in Refs. [47,48].) Concerning the parameter Δ an educated guess is necessary as no information for the vanadium perovskites is available. However, we have found before that in titanium oxides $\Delta = 6.5$ eV is reasonable [32,33]. Here for vanadium oxides a smaller value should be more appropriate. Old-fashioned computations, such as those reported in the classical textbook of Harrison [49] and shown in tables therein suggest a value lower by 1.5 eV (i.e., $\Delta = 5.0$ eV); a still lower value of 4.0 eV was suggested by Bocquet *et al.* and Imada *et al.* [50] (note that in these papers the parameter U_p enters only indirectly). We have tried all values in the range of $4.0 < \Delta < 6.5$ eV and found that the most interesting and sensible physical results could be obtained for $\Delta = 5.0$ eV.

Our reference system is $LaVO_3$ where the total electron number in the d-p subsystem is $N_e = 17 + 3 = 20$ per one VO_3 unit provided we assume an ideal ionic model with no self-doping ($x = 0$), i.e., all three La valence electrons are transferred to the VO_3 unit. Another possibility is when the self-doping is finite: We consider $x = 0.5$ (then the cation La donates not 3 but rather on the average of 3–0.5 = 2.5 electrons and $N_e = 20 - x = 19.5$); or the extreme $N_e = 19$ when the self-doping is $x = 1.0$. Note that in the following for our computations we use only certain discrete numbers for x as the studied cluster is finite and the total electron number must be an even integer; moreover the total electron number should hit some magic number so that the ground-state wave function of the studied *small cluster* is a closed shell and not an open shell.

The problem of how to fix x is a difficult question. If one wants to be sure what is a precise value of x, then the best way would be to perform independent auxiliary *ab initio* or local density approximation with Coulomb interaction U (LDA + U) computations and extract the electronic population on the cation R (in RVO_3) analogously, such as was performed in Ref. [33]. This is however rather expensive. Without such auxiliary *ab initio* computations one is left with speculations. It seems that for the case of a La or a Y cation a safe guess is that $x \in [0.0, 0.5]$, i.e., all three, or almost all three $5d^16s^2$ valence electrons are transferred to the vanadium octahedron.

III. NUMERICAL STUDIES

A. Computational problems concerning the Jahn-Teller Hamiltonian

The important part of the electronic Hamiltonian in perovskites, namely, the influence of JT distortions on the electronic structure rarely can be treated in a satisfactory way during the computations. Let us explain what we mean by this statement. An effective Hamiltonian which describes cooperative JT lattice distortions for octahedra in the vanadium perovskites can be assumed in the complicated form which is quadratic in JT distortions and contains in addition the terms $\propto d^\dagger_{i\nu\sigma}d_{i\mu\sigma}$ coupled linearly with JT distortions, for details and an explicit (quite complicated) formula, see, for instance, Ref. [51]. JT distortions $\{Q_i\}$ ($i = 1,\ldots,6$) (used notation is the same as in Ref. [28]) can be treated as quasiclassical continuous variables. There should be appended (to all Q's) an additional (extra) subscript m to distinguish between different octahedra which could have (in principle) different, one from another, distortions. Let us recall that (see Ref. [28]) $\{Q_4, Q_5, Q_6\}$ modes cause tilting (rotations) of the VO_6 octahedron. The Q_2 mode causes a distortion of the squares formed by four oxygens (on the *ab* plane a square undergoes distortion into an elongated rhombus), whereas the Q_3 mode causes differences in apical vanadium oxygen bond lengths (tetrahedral distortion).

In the course of normal computations (when looking for a ground-state energy minimum) the search for the energy minimum due to the electronic degrees of freedom must be supplemented with an extra search for the optimal values of continuous classical degrees of freedom (Q_i modes). Then the Hamiltonian becomes intractable, even so for very small clusters, even so if the cooperative pattern of JT distortions is explicitly assumed. Let us remark that assuming a cooperative and static pattern of JT distortions (with a certain amount of symmetry) would mean that instead of $Q_{2m}, Q_{3m}, \ldots$ (a lot of separate sets of $Q_{2m}, Q_{3m}, \ldots$, one set for each individual octahedron m) one can consider a single set of $|Q_2|, |Q_3|, \ldots$ and the dependence on the octahedron number m within the lattice is realized through alternating plus/minus signs to individual Q's and changing them according to the assumed global symmetry of the static-cooperative JT distortions. Anyway, even with this great simplification there are at least five extra $\{Q_i\}$ variables which makes looking for ground-state energy minimum during HF iterations extra expensive.

To overcame this difficulty most often a semiempirical treatment of JT terms is used: namely, one assumes an explicit form and the magnitudes of the lattice distortions, usually suggested by the experiment. Thus the distorted lattice is frozen, and we take this as an experimental fact (and do not ask any more about the origin of these distortions). Then computations become more feasible. The $Q_{2m}, Q_{3m}, \ldots$ modes and the JT Hamiltonian do not enter computations anymore—their only role was to deform the lattice and to change V-O distances. Instead, one collects all V-O and O-O bond lengths (as suggested by experiment) and because of modified bond lengths one modifies the matrix of kinetic hopping parameters. In this respect quite popular is the Harrison scaling [49] when the difference in V-O bond lengths (versus some reference bond lengths, for example, those in the hypothetical undistorted crystal of ideal cubic symmetry) causes renormalization of the hopping elements. The second important consequence of changed V-O distances is the creation of local crystal fields acting upon central V ions: These will split yz/zx doublets as already discussed above for H_{diag} and $f^{\text{cr}}_{\mu,\sigma}$.

To simplify the numerical effort, we performed exactly such computations but only for the scenario shown in Fig. 2, i.e., only Q_2 distortions were included, whereas the Q_4 distortions were neglected. This choice is purely pragmatic: Nonzero Q_4's, Q_5's, and Q_6's significantly increase the computational effort by drastically lowering the symmetry and therefore increasing the complexity of the kinetic hopping matrix. We emphasize that the d-p model is definitely not an *ab initio* approach thus it can account only for a qualitative description of generic physical properties; one should not expect that all the physical details will be described properly. Therefore certain simplifications in modeling are not a capital offense. In this respect one can still ask if indeed octahedral tilting and finite Q_4 distortions are mandatory for spin-orbital order to emerge. Numerous experimental and theoretical papers addressed directly and indirectly these questions: (i) Quoting Ref. [52] where the proof was given that V-O-V angles deviating strongly from 90° are not primarily a driving force stabilizing C-type orbital order in vanadates or that (ii) orbital fluctuations (at zero temperature) are not strong but, in fact, almost suppressed [18]. For a more general discussion of these problems see Ref. [21]. We suggest that for the description of the onset of spin-and-orbital order, our simplified scenarios with local crystal fields and with geometries depicted in Figs. 2 and 3 are quite enough and that the apical axes nonzero tiltings influence only the distances between the true HF ground state and other (higher in energy) stable HF states.

To summarize, and, at the same time, to give an explicit example: In YVO_3 we studied the zero-temperature geometry as shown in Fig. 2 with repeating layer 1 (along the c axis): the V-O bond lengths were set as 2.042, 1.99, and 1.99 Å [7,8] for a long, a short, and an apical bond, respectively. The Slater integrals were scaled following Harrison's rules [49] to fit the experimental V-O bond lengths. The changes in O-O bond lengths caused by JT distortions were neglected (they are expected to be small and less important). On top of it the values of local crystal-field splitting of the yz/zx doublet were assumed to be ±0.1 eV.

B. Unrestricted Hartree-Fock computations

We use the unrestricted HF approximation (with a single determinant wave function) to investigate the model (2.1). The technical implementation is the same as that described in Refs. [26,31,32,36,45,53] featuring the averages $\langle d^{\dagger}_{m,\mu,\uparrow} d_{m,\mu,\uparrow}\rangle$ and $\langle p^{\dagger}_{i,\mu,\uparrow} p_{i,\mu,\uparrow}\rangle$ (in the HF Hamiltonian) which can be treated as order parameters. At the beginning some initial values (a guess) have to be assigned to them. During HF iterations the order parameters are recalculated self-consistently until convergence. If in the course of computations all the averages $\langle d^{\dagger}_{m,\mu,\uparrow} d_{m,\mu,\uparrow}\rangle, \ldots$ would be treated as independent, convergence (if any) would indeed be too slow. Therefore the common strategy is to employ an explicit type of symmetry of the order in the ground state (which lowers the number of order parameters) and to perform HF iterations strictly under this assumption. During the present computations the chosen scenarios for the ground-state symmetry were those with either: (i) the orbital order of G type, C type, or absent; (ii) the spin order of G-AF, C-AF, or absent; (iii) the x or z easy magnetization axis. One remark: The hypothetical ground-state symmetries which would violate Goodenough-Kanamori rules [30] were also considered (these are as follows: a ground state with C-AF spin order and C-type orbital order and a ground state with G-AF spin order and G-type orbital order; during computations we found such states to be locally stable in unrestricted HF for some parameters, but they never became true ground states).

Within each of the above scenarios the number of independent order parameters is lowered, but still it is large enough so that the HF convergence is rather poor. This was caused mainly by not imposing any restrictions on order parameters associated with oxygens (no orbital equivalence by symmetry and no assumption on oxygen magnetic properties) and not imposing any symmetry restriction on order parameters associated with vanadium e_g orbitals. We found that imposing any such restrictions is quite risky as any symmetries and orbital equivalences as could be *a priori* assumed, in fact, turn out to be too restrictive and only approximate ones. This happens at least for scenarios shown in Figs. 2 and 3. For computations and a quick scan of the phase diagram we used a 2×2×4 cluster. (A single HF run on an ordinary desktop can be performed in about 10 min; bigger 4×4×4 clusters require from several hours up to one day).

The simplified and popular remedy for poor HF convergence is the so-called dumping technique. A better remedy is the technique known in quantum chemistry and called level shifting [54]. It is based on replacing the true HF Hamiltonian by a different Hamiltonian—the one with the identical eigenvectors (one-particle eigenfunctions) as the original Hamiltonian and with identical *occupied* eigenenergies. The original eigenenergies of virtual states are however uniformly shifted upwards by a fixed constant value. Thus if we apply the shift say by 5.0 eV, then the gap between the HOMO-LUMO gap we obtain will be artificially enlarged exactly by 5.0 eV. (So, it has to be corrected by subtracting from the obtained HOMO-LUMO gap the fixed value of 5.0 eV).

When applying virtual level shifting we can obtain some additional information. Namely, when the HOMO-LUMO splitting (after correcting for the shift) is negative, then the single-determinant HF ground state we obtained is not correct (this assumes that a sufficient number of different HF starting conditions was tried). One possibility is that the true ground state is conducting, another is that a single-determinant HF wave function breaks down due to very strong electronic correlations and the multiconfiguration HF method is required.

IV. RESULTS AND DISCUSSION

A. Zero-temperature ground state in LaVO$_3$

The symmetry of LaVO$_3$ at zero temperature is monoclinic [12,55] which should correspond to G-type orbital order (which is induced, or to say it directly, is enforced by cooperative crystal-field splittings of yz/zx doublets). The bond lengths at zero temperature were difficult to find in the literature—following Ref. [4] we took 2.04 Å/1.98 Å for long/short V-O distances within the ab plane and 1.98 Å for apical V-O bonds. With this choice we assumed the following local crystal-field values: 1.8 eV as the distance between t_{2g} levels and e_g levels and an *ad hoc* choice: ±0.10 eV as splitting between yz/zx orbitals, also the xy orbital energy is lowered (due to tetragonal distortion of V-O apical bonds) by 0.1 eV.

The experimentally found spin order is C-AF with average magnetic moment $|\langle m\rangle| \in (0.6, 0.7)$ and easy magnetization axis c [55,56]. The estimations of the band gaps are in between 1.1 and 1.8 eV [20,22,23,57]; the most popular value is 1.1 eV. Below in Table II we collected the obtained results for hypothetical self-dopings $x = 0$, 0.5, 1.0 (we recall that we do not know which one of these values is closest to the true one). Some comments about the legend in Table II: the indices $m = 1$ and 2 in $\langle n_{1,xy,\uparrow}\rangle, \ldots$, etc., stand for two nonequivalent vanadium ions, see Fig. 2. $E_{\rm HF}$ is the HF energy per one VO$_3$ unit, G is the HOMO-LUMO gap, $\langle m\rangle$ is an average magnetic moment per V ion (when expressed in μ_B, it should be two times larger). In Table II the spin-order type with an easy magnetization direction is indicated, and finally x is the self-doping level which was fixed during computations.

TABLE II. Spin and orbital order and the electron occupations on vanadium ions for the zero temperature HF ground states of LaVO$_3$ and YVO$_3$. Subscripts x and z in C-AF$_x$ and C-AF$_z$ denote the axis of easy-magnetization (compare Fig. 2).

x	0.0	0.5	1.0
	LaVO$_3$ (monoclinic)		
orbital order	G-AO	G-AO	none
spin order	C-AF$_z$	C-AF$_z$	C-AF$_x$
$E_{\rm HF}$ (eV)	32.555	26.573	20.673
G (eV)	3.92	1.99	2.89
$\lvert\langle m\rangle\rvert$	0.99	0.77	0.52
	YVO$_3$ (orthorhombic)		
orbital order	C-AO	C-AO	none
spin order	G-AF$_z$	G-AF$_z$	C-AF$_x$
$E_{\rm HF}$ (eV)	32.734	26.802	20.935
G (eV)	3.99	2.02	2.86
$\lvert\langle m\rangle\rvert$	0.99	0.77	0.52
	electron occupations both for LaVO$_3$ and YVO$_3$		
$\langle n_{1,xy,\uparrow}\rangle$	1.00	0.86	0.54
$\langle n_{1,xy,\downarrow}\rangle$	0.05	0.06	0.54
$\langle n_{1,yz,\uparrow}\rangle$	1.00	0.60	0.12
$\langle n_{1,yz,\downarrow}\rangle$	0.04	0.06	0.12
$\langle n_{1,zx,\uparrow}\rangle$	0.09	0.23	0.12
$\langle n_{1,zx,\downarrow}\rangle$	0.06	0.08	0.12
$\langle n_{1,x^2-y^2,\uparrow}\rangle$	0.10	0.12	0.13
$\langle n_{1,x^2-y^2,\downarrow}\rangle$	0.08	0.10	0.13
$\langle n_{1,3z^2-r^2,\uparrow}\rangle$	0.13	0.16	0.18
$\langle n_{1,3z^2-r^2,\downarrow}\rangle$	0.10	0.13	0.18
$\langle n_{2,xy,\uparrow}\rangle$	0.05	0.06	0.54
$\langle n_{2,xy,\downarrow}\rangle$	1.00	0.86	0.54
$\langle n_{2,yz,\uparrow}\rangle$	0.06	0.08	0.12
$\langle n_{2,yz,\downarrow}\rangle$	0.09	0.23	0.12
$\langle n_{2,zx,\uparrow}\rangle$	0.04	0.06	0.12
$\langle n_{2,zx,\downarrow}\rangle$	1.00	0.60	0.12
$\langle n_{2,x^2-y^2,\uparrow}\rangle$	0.08	0.10	0.13
$\langle n_{2,x^2-y^2,\downarrow}\rangle$	0.10	0.12	0.13
$\langle n_{2,3z^2-r^2,\uparrow}\rangle$	0.10	0.13	0.18
$\langle n_{2,3z^2-r^2,\downarrow}\rangle$	0.13	0.16	0.18

Now we summarize the results obtained for different electronic filings of VO$_3$ octahedra (self-doping). We start with self-doping $x = 0$ which stands for an ideal ionic model. The best HF ground state reproduces the experimental spin-orbital order found in LaVO$_3$, see the $x = 0$ column of Table II. However, the next candidate for the HF ground state with C-AF spin order is parallel with the x axis (see Fig. 2), which corresponds to the (1,1,0) crystallographic direction and is only by 0.3 meV energetically higher (not shown). Note that when spin-orbit interaction is neglected the change is here insignificant: instead of 0.3 meV we obtained a 0.2-meV energy difference. (A general discussion of the role played by spin-orbit interaction in the vanadium perovskites was presented in Refs. [10,58,59]).

For spin order along the z axis site $m = 1$ corresponds to magnetization $m_1 \simeq 0.99$ and, site $m = 2$ corresponds to $m_2 \simeq -0.99$. We observe that when quantum fluctuations are absent as in our calculation, the magnetization is somewhat reduced due to minority-spin electron density in the occupied t_{2g} orbitals, whereas this reduction is almost fully compensated by majority-spin electron density in the empty t_{2g} and two

e_g orbitals. In this way we arrive at $|\langle m\rangle| \simeq 0.99$ which results from electron delocalization by d-p hybridization. It is remarkable that total electron density in e_g orbitals is close to 0.40 which definitely shows that e_g orbitals contribute to the electronic structure. What concerns the average occupation of $2p$ electrons: (i) On oxygens aligned along the x axis (see Fig. 2) it is 5.80 with average moments either 0.0 or ± 0.01 (changing not randomly but in a regular way); (ii) for oxygens aligned along the y axis the corresponding numbers are 5.86 for the charge and 0.0 or ± 0.01 for the moments; (iii) for oxygens aligned along the z axis (this coincides with the crystallographic c direction) the occupation is 5.80, and no moments are found. The next HF stable state is by 1.3 meV higher than the true ground state—it has G-AF spin order parallel to the z axis. Note that this state violates Goodenough-Kanamori rules [30].

The states with different spin orders are almost degenerate. Most probably a more complicated geometry featuring sizable octahedral axes tilting should account for bigger differences, such as those reported in Ref. [1]. Summarizing, spin-orbital order for $x = 0$ is *ideally reproduced* with respect to the present paradigm of spin-orbital order in vanadates [7], but the average spin and band gap we obtained do not agree too well with the experimental values.

Consider now doping $x = 0.5$: The best HF ground state we obtained here also reproduces correctly the experimental spin-orbital order found in LaVO$_3$, see the third column of Table II. The next candidate for the ground state is the one with C-AF spin order but this time aligned along the x axis (see Fig. 2). Actually, it is by 2.0 meV higher; note that the spin-orbit interaction is here more important and responsible for so large an energy difference; when this interaction is absent one finds instead the energy difference of 0.6 meV. The magnetization of $|\langle m\rangle| \simeq 0.77$ corresponds better to the experiment—one finds here definitely weaker magnetization contributions from two occupied t_{2g} orbitals but a larger magnetization in the third t_{2g} orbital. Altogether, electron density in t_{2g} orbitals is lower than that at $x = 0$, but at the same time the e_g-electron density (but not magnetization) is somewhat enhanced.

The oxygen electron occupations indicate charge delocalization by d-p hybridization in the presence of spin-orbit coupling: (i) For oxygens along the x-axis electron density is 5.73 whereas magnetic moments are ± 0.01; (ii) for oxygens along the y axis electron densities of 5.57 and 5.59 are accompanied by ± 0.01 moments (arranged with a suitable regularity, both spins, and the tiny charge modulation); (iii) for oxygens along the z axis (this coincides with the crystallographic c axis) occupations are 5.81 with zero moments or 5.76 with ± 0.02 moments—again both spins and tiny charge-density wave are arranged with a suitable regularity. Note that the average spin value of 0.77 and the HOMO-LUMO gap of 1.99 eV fit rather well to the experimental results. Thus we suggest that for LaVO$_3$ the self-doping is $x \approx 0.5$ and that the entries from the third column in Table II are a rather faithful description of the experimental situation.

At this point we would like to make a short digression and explain in a more transparent way why a weak ($x = 0.5$) self-doping effect is important in LaVO$_3$. It is true that the spin and orbital order for $x = 0$ and $x = 0.5$ are qualitatively identical. However, the average magnetization (per V ion) is ~ 1.0 for the pure ionic model $x = 0$, and this is unrealistic. At the same time for $x = 0.5$ the average computed magnetization value drops to 0.77—this is more realistic and quite close to the experimental value. We conclude that self-doping reduces the order parameter by including the covalency effect.

There is also a second argument: The band gap we computed for $x = 0.5$ is much closer to the experimental value than the band gap we computed for $x = 0$. It is well known that Hartree-Fock computations tend to overestimate band gaps. And indeed, for $x = 0.5$ we obtained $G \approx 2.0$ eV, whereas the experimental values indicate $1.1 < G < 1.8$ eV. However our overestimation of the gap (probably by $\approx 30\%$) is not that severe as in the case of $x = 0$ where we obtain $G \approx 4.0$ eV. These two facts clearly suggest that including the weak self-doping effect is important for realistic modeling of the vanadium perovskites.

For large self-doping $x = 1.0$ orbital order disappears. Only xy orbitals are occupied by approximately one electron, whereas all the densities in all other (t_{2g} and e_g) orbitals are close to 0.25 with a somewhat enhanced density of 0.36 in $3z^2 - r^2$ orbitals. Note that this large density follows from the delocalization of $2p$ electrons from oxygen ions. The ground state has solely spin C-AF order with the x easy axis of magnetization. This state contradicts experimental observations and excludes so high a self-doping level. No entry in the last column of Table II provides direct evidence that the spins align indeed along the x axis. To supplement this information we must make another digression. Thus we note that at the mth vanadium ion $\langle d^\dagger_{m,\mu,\uparrow} d_{m,\mu,\uparrow}\rangle = \langle d^\dagger_{m,\mu,\downarrow} d_{m,\mu,\downarrow}\rangle$, i.e., the average zth spin component vanishes. Then we inspect the real parts of a subclass of complex order parameters (which we get on convergence from the HF output), namely, $\langle d^\dagger_{m,\mu,\uparrow} d_{m,\mu,\downarrow}\rangle$. When the summation over μ is performed, i.e., if we calculate $\mathrm{Re}\{\sum_\mu \langle d^\dagger_{m,\mu,\uparrow} d_{m,\mu,\downarrow}\rangle\}$, we obtain the value 0.52 which is just the average spin component along the x direction. The imaginary part of the same sum (here it is zero) corresponds to the average spin component along the y-direction. This ends our digression.

B. Zero-temperature ground state in YVO$_3$

The symmetry of YVO$_3$ at zero temperature is orthorhombic [7,12]. This corresponds to C-AO order accompanied by G-AF$_z$ spin order. The bond lengths and average magnetization values were reported in Refs. [2,5,7,12,14]; the band gaps are 1.2–1.6 eV [23,57].

Our HF results on occupation numbers are virtually the same (two digits accuracy), such as those for LaVO$_3$ (shown in Table II). As about spin order just like it was shown in detail for LaVO$_3$ the z and x easy spin directions are degenerate within 1-meV accuracy (at least for our simplified geometries shown in Figs. 2 and 3). The $T = 0$ ground state for YVO$_3$ has C-AO order coexisting with G-AF$_c$ spin order and is best reproduced by HF results for self-doping $x \approx 0.5$. For $x = 1.0$ we find that the orbital order vanishes.

C. Zero-temperature ground state in BaVO$_3$

To test how accurately the d-p model works in the vanadium perovskites we decided to test one more completely different case: perovskite quasicubic BaVO$_3$ (with V-O bonds equal to approximately 2.0 Å), which is known to be a conductor [60] down to $T = 0$. This time we cannot use crystal-field splittings as the substance is indeed very close to cubic, all octahedra are undistorted, and therefore t_{2g} levels remain unsplit. The other significant difference (with respect to $LaVO_3$) is that the Ba cation donates not three but two electrons into one VO_3 unit.

With this input we run our computations only to find that for any doping (including the ideal-ionic picture with zero self-doping) and for any starting conditions the obtained HOMO-LUMO gaps (after correcting for virtual level shift) are negative. This is a clear indication that $BaVO_3$ is a conductor in nice agreement with the experimental findings. The same conclusion would be also reached for $CaVO_3$—although $CaVO_3$ is not quasicubic, and local crystal fields do split t_{2g} levels. Here the decisive factor is probably not symmetry but the number of electrons transferred from a Ca cation to a VO_3 unit which is at most 2 (ideal ionic model) or (very likely) much smaller, say within the (1.0,1.5) interval.

D. Remarks on the high-temperature ($T > 77$-K) ground state of YVO_3

First we should clearly state that for $T > 0$ K the HF computations of the ground state should not apply directly as we do not know the value of entropy and do not determine the minimum of the thermodynamic potential. However just out of curiosity we did them anyway.

The bond lengths and average magnetization values were reported in Refs. [2,5,7,12,14]; band gaps are 1.2–1.6 eV [23,57]. The symmetry of YVO_3 for $T > 77$ K is monoclinic [7,12]. Our HF occupation numbers we obtained are very close to those shown in Table II. The symmetry of the obtained ground state is G-AO order with C-AF$_z$ spin order in accordance with the experiment.

The only disagreement with the experiment is that experimentally [14] the easy axis of magnetization is neither in the c direction nor it is strictly located on the ab plane; one finds spin components of both types. Such a possibility was not investigated during our computations. However, to be on the defensive side, let us recall once more that (like it was shown in detail for $LaVO_3$) the z and x easy spin directions are degenerate within 1.0-meV accuracy (at least for our simplified geometries presented in Figs. 2 and 3).

V. SUMMARY AND CONCLUSIONS

In some examples we have shown that the d-p model is capable of reproducing spin-orbital order in the vanadium perovskites. The three basic fundamentals leading to nonzero orbital order are as follows: (i) The electronic configuration of V ions which is close to V^{3+}; (ii) nonzero local crystal fields (originating from collective JT deformations) which split yz/zx orbitals; (iii) zero or small self-doping due to cations (i.e., electron donors to the VO_3 lattice). With these ingredients orbital order is generic—it comes out correctly for any reasonable Hamiltonian parameter set.

However the question *what kind* of magnetic order accompanies orbital order is more subtle. In particular different spin easy-axis orientations are difficult to find as the states stable in HF (candidates for being the true ground state) are almost energetically degenerate. In addition to this problem the stability and the type of dominating magnetic order depend strongly on tiny effects occurring on oxygens: small (± 0.01) spin modulations and small charge modulations, i.e., $\pm(0.01 - 0.03)$. If one imposes the same additional assumptions (for example, the assumption that oxygens on ab planes are nonmagnetic—which may seem to be obvious but which is incorrect) with the hope that HF convergence will improve then the order in which the types of magnetic order appear may even come out completely wrong.

The above problem (i.e., how to include tiny magnetization modulations on oxygens) is nonexistent for *ab initio* LDA or LDA with local Coulomb interaction U (LDA + U) approaches but at a cost of a manyfold increase in computational time and effort. On the other hand, the d-p model is not *ab initio*, and HF computations performed on the d-p model cannot reach the level of physical reliability, such as the LDA + U does, but still, for extremely cheap and quick preliminary computations in new perovskite materials with orbital and spin degrees of freedom, they are indeed of invaluable help.

Summarizing, the multiband model considered here reproduces the experimentally observed coexisting G-AO and C-AF spin orders in the vanadium perovskites. We emphasize that the minimal multiband model for the vanadium perovskites has to include all five $3d$ orbitals on vanadium ions. Electron densities in e_g orbitals are typically even larger than that in the nominally empty third t_{2g} orbital. This redistribution of electron charge follows from rather strong d-p hybridization with two e_g orbitals which contribute to the total electronic charge and magnetization of vanadium ions. Our calculations suggest finite but rather low self-doping of $x = 0.5$ in the vanadium perovskites.

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