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

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Using the multi-band d – p model and unrestricted Hartree-Fock approximation we investigate the electronic structure and spin-orbital order in three-dimensional VO₃ lattice. The main aim of this investigation is testing if simple d – p model, with partly filled 3d orbitals (at vanadium ions) and 2p orbitals (at oxygen ions), is capable of reproducing correctly nontrivial coexisting spin-orbital order observed in the vanadium perovskites. We point out that the multi-band d – p model has to include partly filled ε₉ orbitals at 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 on 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 YVO₃ while only the latter was observed in LaVO₃. 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 d – p model are very quick and should be regarded as very useful in solid state physics, provided the parameters are selected carefully.

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, Khomskii, and Sawatzky 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 order in LaVO₃ or YVO₃ [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 RVO₃ [21] shows several spin- and/or orbital ordered phases. In the regime of compounds with low values of ionic radii rᵣ of rare earth ions R as in YVO₃, 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 in ab planes and repeated orbitals along the c axis (below the magnetic transition at Tₜ₂ = 77 K) and (ii) C-type AF (C-AF) order accompanied by G-type AO (G-AO) order for Tₜ₂ < T < Tₙ₁, where Tₙ₁ = 116 K is the high-temperature magnetic transition [21].

It is well understood now that at zero temperature, i.e., when YVO₃ is orthorhombic, the zx and yz orbitals on vanadium ions alternate between two sublattices forming...
FIG. 2. Schematic view 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 45 deg angle to the crystallographic $a$, $b$ axes, i.e., our $x$ direction corresponds to crystallographic $(1,1,0)$ direction. The orbital order is repeated in consecutive layers when moving up along the $z$ axis (this coincides with crystallographic $c$ axis).

FIG. 3. Schematic view of JT distortions used for Hartree-Fock computations in the zero-temperature phase of LaVO$_3$. Here over the first layer 1 the 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.

orbital C-AO long range order and this order resembles AF spin order in a single $ab$ plane, see Fig. 2, while along the $c$ axis this order is repeated, i.e., there is an analogy to ordinary spin ferromagnetic (FM) order \cite{7}. At the same time the spins are arranged according to 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 \cite{20}. 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 \cite{30}.

The purpose of this paper is to investigate the spin-orbital order in vanadium perovskites within the multi-band $d$-$p$ 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 effective degenerate Hubbard model of $t_{2g}$ electrons. The $d$–$p$ model includes non-zero 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 \cite{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 LaVO$_3$ or Y in YVO$_3$) behaves according to the idealized ionic model, i.e., donates all valence electrons into a VO$_3$ unit (for La these are: 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 $\sigma$-valence electrons on La as obtained say by Mulliken (or mean by this statement that the occupation number of $-\sigma$-valence electrons and one 3d valence electron).

In the present investigation we use up-to-date estimations of crystal-field splittings, spin-orbit interaction at 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 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. III. 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 multi-band $d-p$ Hamiltonian for VO$_3$ three-dimensional (3D) cluster which includes five 3d orbitals at each vanadium ion and three 2p orbitals at each oxygen ion,

$$H = H_{\text{kin}} + H_{\text{so}} + H_{\text{diag}} + H_{\text{int}}.$$  
(2.1)

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

The kinetic part of the Hamiltonian is:

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

where we employ a general notation, with $c_{\mu,\sigma}^{\dagger}$ standing for the creation of an electron at site $j$ in an orbital $\nu$ 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 $\epsilon_{\mu,\sigma}^{\dagger} d_{i,\mu,\sigma}$ for $d$ orbitals, while $p_{\mu,\sigma}$ for $p$ orbitals. The matrix $t_{i,\mu;j,\nu}$ is assumed to be non-zero 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 $^{31}$. As a side remark we recall that models taking into account only three $2g$ orbitals and neglecting remaining two $e_g$ orbitals are not accurate enough $^{35}$.

The spin-orbit part, $H_{\text{so}} = \zeta \sum_i \mathbf{L}_i \cdot \mathbf{S}_i$, is a one-particle operator (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 $H_{\text{kin}}$ $^{36,39}$.

$$H_{\text{so}} = \sum_i \left\{ \sum_{\mu\neq\nu,\sigma} t_{\mu,\nu,\sigma}^{so} d_{i,\mu,\sigma}^{\dagger} d_{i,\nu,\sigma} + H.c. \right\},$$  
(2.3)

with $t_{\mu,\nu,\sigma}^{so}$ elements restricted to single vanadium sites. They all depend on spin-orbit strength $\zeta$ ($\zeta = 0.026$ eV; this value was adopted from Ref. 40) which is weak but it can have influence on the preferred spin direction. For detailed formula and tables listing $t_{i,\nu,\sigma}^{so}$ elements, see Refs. 31, 37.

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

$$\Delta = \epsilon_d - \epsilon_p,$$  
(2.4)

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

$$H_{\text{diag}} = \sum_{i,\mu;x,y,z} \epsilon_p P_{\mu,i,\sigma}^\dagger P_{\mu,i,\sigma} + \sum_{m;\mu;x,y,z,\sigma} f_{\mu,\sigma}^\dagger d_{m,\mu,\sigma} d_{m,\mu,\sigma}. $$  
(2.5)

The first sum is restricted to oxygen sites, while the second one runs over vanadium sites. The crystal-field splitting strength vector ($f_{\mu,\sigma}$) describes the splitting within $2g$ levels. For example, in YVO$_3$ the $xy$ orbital is lowered by $\sim 0.017$ 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 particular VO$_6$ octahedron. We assume ad-hoc that either $yz$ is lower than $zx$ orbital which should correspond to O$_2$ square (in ab plane) when distorted from ideal square into elongated along y-direction rhombus, or the opposite: $zx$ is lower than $yz$ orbital which should correspond to O$_4$ distorted into elongated along x-direction rhombus (compare Figs. 1 and 2). This splitting value should be $0.1-0.2$ eV what 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 we do not expect it to be an important factor.

The on-site Coulomb interactions $H_{\text{int}}(d)$ for $d$ orbitals take the form of a degenerate Hubbard model [32],

$$H_{\text{int}}(d) = \sum_{m,\mu<\nu} \left( U_d - \frac{5}{2} J_d^{\mu\nu} \right) n_{m\mu} n_{m\nu} + U_d \sum_{m,\mu<\nu} n_{m\mu \uparrow} n_{m\mu \downarrow} - 2 \sum_{m,\mu<\nu} J_d^{\mu\nu} \vec{S}_{m\mu} \cdot \vec{S}_{m\nu} + \sum_{m,\mu\neq\nu} J_d^{\mu\nu} d_{m\mu \uparrow}^\dagger d_{m\nu \uparrow}^\dagger d_{m\nu \downarrow} d_{m\mu \downarrow}, \quad (2.6)$$

where $n_{m\mu} = \sum_{\sigma} n_{m\mu \sigma}$ is the electron density operator in orbital $\mu$, $\{\mu, \nu\}$ enumerate different $d$ orbitals, and $J_d^{\mu\nu}$ is the non-trivial 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 ($J_d^{\mu\nu}$), and for a pair of two $e_g$ orbitals ($J_d^{\mu\nu}$), and still different for the case of cross-symmetry terms [33, 43]. all these elements are included and we assume the Racah parameters: $B = 0.1$ eV and $C = 4B$.

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

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

where the intratomic 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., $J_p^{\mu\nu} = J_p^{\nu\mu}$. (Up to now, as already mentioned above, $H_{\text{int}}(p)$ was neglected in the majority of studies, i.e., for simplicity it was being assumed that $U_p = J_p^{\mu\nu} = 0$.)

In the following we use the parameters $U_d$, $J_d^{\mu\nu}$, $U_p$, and $J_p^{\mu\nu}$ similar to those used before for titanium oxides [32, 33]; for the hopping integrals we follow the studies by Mizokawa and Fujimori [36, 13]. The value $U_p \sim 4.0$ eV was previously used in copper oxides [46, 47] but in addition in some test computations we considered a larger value $U_p = 6$ eV. (This choice, i.e., $U_p = 6$ eV is advocated and reasonably explained in Refs. [17, 48].) Concerning the parameter $\Delta$ an educated guess is necessary as no information for the vanadium perovskites is available. However, we have found that before 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 $4.0 < \Delta < 6.5$ 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 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 average 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 close-shell and not an open-shell.

The problem 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 VO$_3$) analogously like it was done 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 La or Y cation a safe guess is that $x \in [0.0, 0.5]$, i.e., all three, or almost all three 5$d^3$6$s^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

| $\zeta$ | $U_d$ | $J_d^1$ | $J_d^2$ | $U_p$ | $J_p^1$ |
|-------|-------|--------|--------|-------|--------|
| 0.026 | 8.0   | 0.8    | 0.9    | 4.4   | 0.8    |

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 $\propto d_{Îµm}^I d_{Îηn}^I$ coupled linearly with JT distortions, for details and explicit (quite complicated) formula, see for instance Ref. [51]. JT distortions $\{Q_i\}$ (i = 1, ..., 6) (used notation is the same as in Ref. [28]) can be treated as quasi-classical continuous variables. There should be appended (to all $Q_i$’s) an additional (extra) subscript $m$ to distinguish between different octahedra which could have (in principle) different, one from another, distortions. Let us remind that (see Ref. [28]) $\{Q_4, Q_5, Q_6\}$ modes cause tilting (rotations) of the VO$_6$ octahedron. The $Q_2$ mode causes distortion of squares formed by four oxygens (in ab plane a square undergoes distortion into an elongated rhombus), while the $Q_3$ mode causes differences in apical vanadium-oxygen bond lengths (tetrahedral distortion).

In the course of normal computations (when looking for ground state energy minimum) the search for energy minimum due to 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 if the cooperative pattern of JT distortions is explicitly assumed. Let us remark that JT distortions are not pri-

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 $Q_{2m}, Q_{3m}$, ... 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 hypothetical undistorted crystal of ideal cubic symmetry) causes renormalization of the hopping elements. The second important consequence of changed V–O distances is creation of local crystal fields acting upon central V-ions: these will split $yz/zx$ doublets as already discussed above for $H_{\text{diag}}$ and $f^\pi_{\nu,\sigma}$.

To simplify the numerical effort, we performed exactly such computations but only for scenario shown in Fig. 2, i.e., only $Q_2$ distortions were included, while the $Q_4$ distortions were neglected. This choice is purely pragmatic: non-zero $Q_4$’s, $Q_5$’s, and $Q_6$’s significantly increase computational effort by drastically lowering the symmetry and therefore increasing the complexity of 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 than V–O–V angles deviating strongly from 90° are not pri-

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 the Harrison’s rules [49] to fit the experimental V–O bond lengths. The changes of 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 $yz/zx$ 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 [21]. The technical implementation is the same as that described in Refs. [26, 31, 32, 36, 45, 53] featuring the averages $\langle d_{Îµm,Îνn}^I \rangle$ and $\langle p^I_{Îµ,Îν} \rangle$ (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 conver-
gence. If in the course of computations all the averages \( \langle d_{n,m}^\dagger d_{m,p} \rangle, \ldots \) would be treated as independent, convergence (if any) would indeed be too slow. Therefore the common strategy is to employ 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 present computations the chosen scenarios for the ground state symmetry were those with either: (i) orbital order of G-type, or C-type, or absent; (ii) spin order G-AF, or C-AF, or absent; (iii) \( x \) or \( z \) easy magnetization axis. One remark: the hypothetical ground state symmetries which would violate Goodenough-Kanamori rules \([30]\) were also considered (these are: ground state with C-AF spin order and C-type orbital order and also 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 state).

Within each of the above scenarios the number of independent order parameters is lowered but still 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, no assumption on oxygens magnetic properties) and not imposing any symmetry restriction on order parameters associated with vanadium \( e_g \) orbitals. We found that imposing any of 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 2\( \times 2 \times 4 \) cluster. (A single HF run on an ordinary desktop can be done in about 10 minutes; bigger 4\( \times 4 \times 4 \) clusters require from several hours up to one day).

The simplified and popular remedy for poor HF convergence is the so-called dumping technique. Better remedy is the technique known in quantum chemistry and called level shifting \([53]\). 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 highest occupied molecular orbital and the lowest unoccupied molecular orbital (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 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 multi-configuration 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 \(ab\) 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 \( e_g \) levels and \( e_g \) levels, and an ad-hock choice: ±0.10 eV as splitting between \( yz/zx\) orbitals, also \( xy \) 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 \( \langle m \rangle \in (0, 0.6, 0.7) \) and easy magnetization axis \( c \) \([55,\, 56]\). The estimations of 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 remind 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 \( \langle n_{1,xy,1} \rangle, \ldots \) etc., stand for two nonequivalent vanadium ions, see Fig. 2. \( E_{HF} \) 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 \( \mu_B \) it should be twice larger). In Table II the spin-order type with an easy magnetization direction is indicated, and finally \( x \) is self-doping level which was fixed during computations.

Now we summarize the results obtained for different electronic filling 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 parallel with the \( x \) axis (see Fig. 2), which corresponds to (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 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 \( m_1 \approx 0.99 \) and site \( m = 2 \) to \( m_2 \approx -0.99 \). We observe that when quantum fluctua-
tions are somewhat absent as in our calculation, the magnetization is somewhat decreased due to minority-spin electron density in the occupied $t_{2g}$ orbitals, while 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 $|\langle m \rangle| \approx 0.99$ 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 2$p$ 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 order 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 present paradigm of spin-orbital order in vanadates [2] but 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 energy difference; when this interaction is absent one finds instead the energy difference of 0.6 meV. Magnetization of $|\langle m \rangle|$ of 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 presence of spin-orbit coupling: (i) for oxygens along the $x$ axis electron density is 5.73 while 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 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 $x≈0.5$ 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 aver-
age magnetization (per V ion) is $\sim 1.0$ 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 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, while 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 case of $x = 0$ where we obtain $G \approx 4.0$ eV. These two facts clearly suggest that including weak self-doping effect is important for realistic modelling of the vanadium perovskites.

For large self-doping $x = 1.0$ orbital order disappears. Only $xy$ orbitals are occupied by approximately one electron, while all the densities in all other ($t_{2g}$ and $e_g$) orbitals are close to 0.25, with somewhat enhanced density of 0.36 in $3z^2 - r^2$ orbitals. Note that this large density follows from the delocalization of 2$p$ electrons from oxygen ions. The ground state has solely spin $C$-AF order with $x$ easy axis of magnetization. This state contradicts experimental observations and excludes so high self-doping level. No entry in the last column of Table II provides the 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 $m$-th vanadium ion, $\langle d_{m,\mu,\uparrow}^\dagger d_{m,\mu,\downarrow}\rangle = \langle d_{m,\mu,\downarrow}^\dagger d_{m,\mu,\uparrow}\rangle$, i.e., the average $z$-th 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 $\langle d_{m,\mu,\uparrow}^\dagger d_{m,\mu,\downarrow}\rangle$. When the summation over $\mu$ is performed, i.e., if we calculate $Re\{\sum_\mu \langle d_{m,\mu,\uparrow}^\dagger d_{m,\mu,\downarrow}\rangle\}$, 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 $y$ direction. This ends our digression.

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

The symmetry of YVO$_3$ at zero temperature is orthorhombic $\overline{1}$ $12$. This corresponds to $C$-AO order accompanied by $G$-AF$_z$ spin order. The bond lengths and average magnetization values were reported in Refs. $2 \ 5 \ 7 \ 12 \ 14$; band gaps are $1.2 - 1.6$ eV $23 \ 57$. Our HF results on occupation numbers are virtually the same (two digits accuracy) like 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$_z$ 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 quasi-cubic BaVO$_3$ (with V–O bonds equal approximately 2.0 Å), which is known to be a conductor $69$ 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 Ba cation donates not 3 but 2 electrons into one VO$_3$ unit.

With this input we run our computations only to find that for any doping (including 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$_3$ — though CuVO$_3$ is not quasi-cubic 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 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 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 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 $\overline{1}$ $12$. 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 $c$ direction nor it is strictly located in the $ab$ plane; one finds spin components of both types. Such a possibility was not investigated during our computations. However, to be on defensive side, let us remind 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

On 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 non-zero orbital-order are: (i) the electronic configuration of V ions which is close to $V^{3+}$; (ii) non-zero 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 true ground state) are almost energetically degenerate. In addition to this problem the stability and the type of dominating magnetic order depends strongly on tiny effects occurring on oxygens: small ($\pm 0.01$) spin modulations and small charge modulations, i.e., $\pm (0.01 - 0.03)$. If one imposes same additional assumptions (for example the assumption that oxygens in $ab$ planes are nonmagnetic — which may seem to be obvious but which is incorrect) in 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 non-existent for ab-initio LDA or LDA with local Coulomb interaction $U$ (LDA+$U$) approaches but at a cost of many-fold increase of 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 can not 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 multi-band model considered here reproduces the experimentally observed coexisting G-AO and C-AF spin order in the vanadium perovskites. We emphasize that the minimal multi-band 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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