Defect states and spin-orbital physics in doped vanadates: Y$_{1-x}$Ca$_x$VO$_3$

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We present a model for typical charged defects in weakly doped Y$_{1-x}$Ca$_x$VO$_3$ perovskites and study how they influence the magnetic and orbital order. Starting from a multiband Hubbard model we show that the charge carriers introduced by doping are bound to the Ca defects with large binding energy of $\approx 1$ eV at small doping, and give rise to the in-gap absorption band observed in the optical spectroscopy. The central position of a generic Ca defect with eight equidistant vanadium neighbors implies a partly filled defect band and permits activated transport due to Coulomb disorder. We explore the effect of bound charge carriers on the dynamics of the $\{yz,zx\}$ orbital and spin degrees of freedom in the context of a microscopic strong-coupling model. After deriving the superexchange interactions around the doped hole we show that the transition from G-type to C-type antiferromagnetic order is triggered by the kinetic energy of doped holes via the double exchange mechanism. The defect states lead to local modification of orbital correlations within ferromagnetic chains along the $c$ axis — some of them contain hole defects while the charge-orbital coupling suppresses locally $\{yz,zx\}$ orbital fluctuations in the others. Thereby Ca defects provide a physical mechanism for spin-orbital dimerization along the ferromagnetic bonds, suggesting that in the C-AF phase of weakly doped Y$_{1-x}$Ca$_x$VO$_3$ dimerization increases with doping.

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I. EXPERIMENTAL MOTIVATION

Recent experimental and theoretical investigations of transition metal oxides have revealed the interplay between spin, charge and orbital degrees of freedom, leading to dramatic changes of magnetic and transport properties. The best known examples of this joint effect of several degrees of freedom are high-temperature superconductivity and colossal magnetoresistance (CMR). When orbital degrees of freedom contribute, as in the CMR manganites, they may strongly influence magnetic properties and also may play a key role for the charge transport. Particularly in the manganites the strong coupling between orbital states and local lattice distortions plays a prominent role, and orbital order is stabilized to a large extent by the Jahn-Teller interactions. Under these circumstances quantum orbital fluctuations are suppressed and classical orbital order determines the spin structure and dynamics. This is most clearly displayed by the large difference between the temperatures of the orbital and magnetic phase transitions in LaMnO$_3$, being $T_{OO} = 780$ K and $T_N = 140$ K.

A challenge for the theory of spin-orbital systems and a qualitatively different situation is encountered in the RVO$_3$ perovskites, where $R$ = Lu, Yb, · · · , La. In these perovskites, i.e., controlled by $t_{2g}$ valence electrons, the orbital-lattice coupling is weak while the spin-orbital coupling is the dominant interaction and thus orbital fluctuations are not suppressed. A common feature is the onset of the $G$-type alternating orbital ($G$-AO) order below the characteristic orbital ordering temperature $T_{OO}$ which is in these compounds relatively low, $T_{OO} \approx 200$ K, and comes close to the Néel temperature $100 < T_N < 140$ K for the magnetic transition to the antiferromagnetic (AF) phase with AF order in $ab$ planes accompanied by ferromagnetic (FM) order along the $c$ axis, the C-AF phase. Unlike $e_g$ orbitals in the CMR manganites, in this class of compounds the $t_{2g}$ orbitals may form orbital ordered states which are subject to strong orbital quantum fluctuations. The consequences of quantum spin-orbital interplay in the RVO$_3$ perovskites were discussed in the theory and have been observed in several experiments. The changes of spin and orbital correlations are responsible for the temperature dependence of the optical spectral weights, as well as for the dimerization of FM interactions in the C-AF phase observed in the neutron scattering in YVO$_3$ and also in LaVO$_3$. Related instability of FM chains toward dimerization occurs at finite temperature when spin and orbital degrees of freedom couple. Orbital fluctuations and their competition with orbital-lattice coupling play also a crucial role for the explanation of the nonmonotonous dependence of the orbital transition temperature on the radius $r_R$ of $R$ ions along the RVO$_3$ series.

The phase diagram of the perovskite-type RVO$_3$ compounds 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 $R$, another AF phase with complementary $G$-type AF ($G$-AF) order accompanied by $C$-type alternating orbital ($C$-AO) order (with staggered orbitals in $ab$ planes and repeated orbitals along the $c$ axis) appears below the second magnetic transition at $T_G$ for example in YVO$_3$ $T_G = 77$ K.
addition, recent Raman experiments\textsuperscript{13,14} suggest that the short-range orbital fluctuations of the $G$-type occur in this intermediate $C$-AF phase — they coexist with the $C$-AO order and make it thus quite different from the one observed in LaVO$_3$. The magnetic exchange constants which determine the magnons in the $C$-AF phase are about a factor two smaller than those found in the low-temperature $G$-AF phase.\textsuperscript{15} Therefore, it has been argued that this phase transition in YVO$_3$ follows from large entropy of spin and orbital excitations in the $C$-AF phase\textsuperscript{16,17} but the observed reduction of the energy scales of magnetic excitations remained puzzling and could not be explained by theory so far.\textsuperscript{18}

In recent years the effect of doping in several cubic vanadium oxides systems such as La$_{1-x}$Sr$_x$VO$_3$, Pr$_{1-x}$Ca$_x$VO$_3$, Nd$_{1-x}$Sr$_x$VO$_3$, and Y$_{1-x}$Ca$_x$VO$_3$ has been systematically explored by various experimental techniques.\textsuperscript{25–34} Resistivity data, specific heat and magnetic measurements have been used to set up the phase diagram as function of doping\textsuperscript{32} In contrast to the high-$T_c$ cuprates, where the metal-insulator (MI) transition is found at a few percent doping\textsuperscript{33} in the vanadates the MI transition occurs at much higher doping concentrations\textsuperscript{28,30,36–37} 18% Sr in La$_{1-x}$Sr$_x$VO$_3$ and even up to 50% Ca in Y$_{1-x}$Ca$_x$VO$_3$. The evolution of optical spectra with doping for these two systems shows that the defects lead to impurity states which appear as absorption band deep inside the Mott gap.\textsuperscript{34} This suggests that bound small polarons are the cause of the MI transition at such high doping concentrations.\textsuperscript{33} It is eventually the growth of the mid-infrared absorption with increasing doping and the gradual shift of this absorption toward zero energy which accompanies the insulator-metal transition.

When taking all these experimental features into account one arrives at a clear physical picture\textsuperscript{28} (i) most importantly, the trends of the optical conductivity show that the edge of the Mott-Hubbard gap is essentially unaffected by doping, and only fades away when the MI transition is approached; (ii) defects play a central role, not just by introducing holes, but as generators of deep impurity states which appear in the optical conductivity as midgap absorption at low doping; and finally (iii) the defects introduce two distinct energy scales. On one hand one finds the defect binding energy of about 1 eV, i.e., in the dilute doping regime, and on the other hand there is clearly an activation energy of $\sim 0.1$ eV or less in transport experiments.\textsuperscript{24,26} Our aim here is to show how generic Ca defects doped into the Mott-insulator YVO$_3$ explain these phenomena in a natural way.

We begin our investigation with a discussion of the properties of Ca defects inserted into an orbital degenerate Mott-Hubbard insulator. We adopt a multiband Hubbard model description of the $t_{2g}$ electrons\textsuperscript{5,18} and we use the unrestricted Hartree-Fock (HF) method.\textsuperscript{39,40} This approach is chosen as it allows us to introduce in a straightforward manner the lower Hubbard band (LHB) of the $t_{2g}$ orbital states as well as the upper Hubbard bands (UHBs) with the appropriate multiplet splitting. The most pronounced effect of the defect is the Coulomb potential of the Ca-impurity which gives rise to an upward shift of the vanadium $t_{2g}$ states in the neighborhood of the defect. This leads to deep impurity states in the Mott-Hubbard gap. Interestingly, on one hand a Ca defect introduces one hole, but on the other hand it generates defect states on eight equivalent vanadium neighbors.\textsuperscript{41} Thus the topmost defect states that are split off the LHB are partially filled and pin the chemical potential.

Transport inside the narrow defect band at weak doping will be affected by the Coulomb disorder of the charged defects. Consequently one expects Anderson localization as was actually already conjectured by Mott\textsuperscript{42} for the La$_{1-x}$Sr$_x$VO$_3$ system. Subsequently we proceed to our central aim, namely the investigation of the effect of defects on the spin-orbital dynamics in the dilute limit. Hence important aspects concerning defects, namely: (i) consequences of disorder, (ii) the role played by the long-range Coulomb interaction, and most importantly (iii) the interaction effects at higher doping, will not be discussed here, but will be addressed elsewhere.

One of the striking differences between the $G$-AF and $C$-AF phase is the stability of the latter phase in doped La$_{1-x}$Sr$_x$VO$_3$ and Y$_{1-x}$Ca$_x$VO$_3$ compounds. For example, in La$_{1-x}$Sr$_x$VO$_3$ the $C$-AF order survives even beyond the insulator-to-metal transition at doping $x \simeq 0.18,43$ and disappears only at $x \simeq 0.26,30,43$ The $G$-AF of YVO$_3$, however, is fragile and is destabilized in the Y$_{1-x}$Ca$_x$VO$_3$ compounds already at $x \simeq 0.02$, where the $C$-AF phase takes over.\textsuperscript{32,33} We shall argue below that in order to understand this behavior it is crucial to treat explicitly the dynamics of orbital degrees of freedom. The cubic symmetry is broken at $V^{3+}$ ions due to the orthorhombic lattice distortion which occurs below the structural transition and favor energetically the electron occupancy of $xy$ orbital.\textsuperscript{24,25} This symmetry breaking was also confirmed by the electronic structure calculations performed for LaVO$_3$ and YVO$_3$.\textsuperscript{44–46} Due to Hund’s exchange both electrons in a $d^2$ configuration at V ion form a high-spin $S = 1$ state, so the second $t_{2g}$ electron occupies either $yz$ or $xz$ orbital, resulting in a $xy^1(yz/zz)^1$ local configuration at each $V^{3+}$ site.

The orbital state is quite different in both magnetic phases of YVO$_3$, below and above $T_{N2}$. Lattice distortions are large in the low-temperature $G$-AF phase and suggest $C$-AO order. This orbital order is further stabilized by increasing pressure.\textsuperscript{42} Above $T_{N2}$ the distortions decrease and are compatible with a weak $G$-type AO ($G$-AO) order.\textsuperscript{42} It was suggested by Ishihara\textsuperscript{47} that the phase transition at $T_{N2}$ could originate from the orbital physics and would be triggered by orbiton softening induced by the reduction of the spin order parameter. While the orbital degrees of freedom certainly play a role as the orbital order indeed changes at $T_{N2}$, there is no evidence of orbiton softening so far. It could be expected that the observed transition is caused instead by local
polarization, Eq. (3.12), distorts the V ion and residing at lower energy are not shown. Orbital orbitals are shown. The range of Ca doping in Y

\[ \text{The intensity of the mid-infrared peak increases proportionally to doping } x. \] This new excitation energy which occurs in the doped system provides a measure of the binding energy of a doped hole which confines the hole to the V\(_8\) cube in the immediate neighborhood of the charge defect, see Fig. [1]. For the undoped bonds of this cube we invoke the mechanism of local polarization of orbitals near the Ca\(^{2+}\) charge defects in the Y\(^{3+}\) background. It will be shown that such defects, together with holes introduced into the \(t_{2g}\) orbitals of vanadium ions, trigger the collapse of the G-AF order.

The major part of our study is based on an effective low-energy Hamiltonian which can be denoted as a spin-orbital t-J model; the model provides a description of magnetism and hole motion in the lower Hubbard band of a doped and orbital degenerate Mott-Hubbard insulator. In the undoped case the model coincides with the spin-orbital superexchange model\(^{29,10,12,14}\) which was shown earlier to lead to a satisfactory description of spin-orbital physics, e.g., in YVO\(_3\). The spin-orbital t-J model provides moreover the description of the kinetic energy of doped holes and describes the effect of charge impurities on the holes and the spin-orbital degrees of freedom. In the concrete case of Y\(_{1-x}\)Ca\(_x\)VO\(_3\) we show that the changes introduced by the defects have severe effects on the orbital dynamics, namely: (i) are responsible for the destabilization of the coexisting G-AF and C-AO order with increasing doping \(x\), and (ii) lead to an enhanced tendency towards dimerization in the weakly doped C-AF phase.

FIG. 1: (Color online) Schematic view of the lattice of vanadium sites with occupied \(t_{2g}\) orbitals and a single hole \(h\) introduced by doping a Ca defect \(D\) (sphere in the center) in the C-type orbital structure of the low-temperature phase in weakly doped Y\(_{1-x}\)Ca\(_x\)VO\(_3\). For clarity the Y and O ions and the orbital phases are not displayed. The hole occupies preferentially one of the V sites that form a cube around the Ca impurity due to the attractive Coulomb potential of the impurity. At the undoped V sites only the topmost occupied \(t_{2g}\) orbitals are shown. The \(|c⟩ \equiv |xy⟩\) orbitals occupied at each V ion and residing at lower energy are not shown. Orbital polarization, Eq. (3.12) distorts the \(|a⟩ \equiv |yz⟩\ (|b⟩ \equiv |xz⟩\) C-type alternating orbital order in the neighborhood of the defect (dashed box) and favors occupation of one of the two \(|\{+,−\}_i⟩\) rotated orbital states that minimize the orbital-defect interaction (see Sec. III D) phenomena close to Ca impurities in Y\(_{1-x}\)Ca\(_x\)VO\(_3\) rather than by the global change of orbital excitation scale. We suggest that it is plausible that impurities could locally destabilize the C-AO order, and introduce a microscopic model to treat this effect below. An earlier theoretical analysis within the charge-transfer model has shown that both phases are indeed energetically close\(^{48}\) and one may thus expect that small changes of the thermodynamic potential around \(T_{N2}\) could trigger a first order magnetic phase transition.

The purpose of this paper is to investigate the local changes in the electronic structure caused by Ca defects in the sublattice of Y ions, and to derive the microscopic model leading to a scenario which could explain why the G-AF phase is so fragile under Ca doping in Y\(_{1-x}\)Ca\(_x\)VO\(_3\). Optical spectroscopy has shown that the absorption in the Mott-Hubbard gap grows as a function of Ca doping in Y\(_{1-x}\)Ca\(_x\)VO\(_3\).\(^{23,33}\) In the low doping range \(x \lesssim 0.05\) it has a characteristic energy close to 1.2 eV\(^{33}\) and moves to lower energies at higher doping. The intensity of the mid-infrared peak increases proportionally to doping \(x\). This new excitation energy which occurs in the doped system provides a measure of the binding energy of a doped hole which confines the hole to the V\(_8\) cube in the immediate neighborhood of the charge defect, see Fig. [1]. For the undoped bonds of this cube we invoke the mechanism of local polarization of orbitals near the Ca\(^{2+}\) charge defects in the Y\(^{3+}\) background. It will be shown that such defects, together with holes introduced into the \(t_{2g}\) orbitals of vanadium ions, trigger the collapse of the G-AF order.

The major part of our study is based on an effective low-energy Hamiltonian which can be denoted as a spin-orbital t-J model; the model provides a description of magnetism and hole motion in the lower Hubbard band of a doped and orbital degenerate Mott-Hubbard insulator. In the undoped case the model coincides with the spin-orbital superexchange model\(^{29,10,12,14}\) which was shown earlier to lead to a satisfactory description of spin-orbital physics, e.g., in YVO\(_3\). The spin-orbital t-J model provides moreover the description of the kinetic energy of doped holes and describes the effect of charge impurities on the holes and the spin-orbital degrees of freedom. In the concrete case of Y\(_{1-x}\)Ca\(_x\)VO\(_3\) we show that the changes introduced by the defects have severe effects on the orbital dynamics, namely: (i) are responsible for the destabilization of the coexisting G-AF and C-AO order with increasing doping \(x\), and (ii) lead to an enhanced tendency towards dimerization in the weakly doped C-AF phase.

The paper is organized as follows. First, in Sec. II we describe Ca\(^{2+}\) charge defects in Y\(_{1-x}\)Ca\(_x\)VO\(_3\) within the frame of a degenerate Hubbard model for \(t_{2g}\) orbitals and analyze the effect of defects on the densities of states derived within the HF approximation. In the following Sec. III the spin-orbital t-J model is outlined. The model Hamiltonian contains apart from spin-orbital superexchange interactions also pure orbital interactions induced by the lattice, see Sec. III B. The effective double-exchange mechanism is introduced in Sec. III C. Next we derive the modified superexchange in the vicinity of the hole in Sec. III E and develop the idea of orbital polarization around charge defects in Y\(_{1-x}\)Ca\(_x\)VO\(_3\) in Sec. III D. With these terms, which supplement the spin-orbital model for undoped cubic vanadates, the complete t-J model poses a rather complex many-body problem, and we derive from it two effective one-dimensional (1D) embedded orbital models for the G-AF and C-AF phase separately, see Secs. IV B and IV C. Thereby we treat spin correlations of \(S = 1\) spins in a classical approximation and focus on the orbital dynamics that plays a decisive role for the observed phase transition in Y\(_{1-x}\)Ca\(_x\)VO\(_3\). Here we show how the orbital polarization (see also Appendix A) develops around charge defects in the orbital chains for both magnetic phases. Next we consider a hole in both magnetic phases (Sec. V), and derive the 1D orbital chain models appropriate for the G-AF phase and C-AF phase in Secs. V A and V B. Interactions around the hole are described in the G-AF phase by the \(d^2 - d^1\)
superexchange (Appendix B) and the kinetic energy is controlled as in a typical double exchange mechanism by the spin orientations (discussed also in Appendix C). This implies, e.g., free hole hopping along the c axis in the C-AF phase due to the FM alignment of spins. In Sec. VI we introduce a statistical treatment of orbital correlations and energy contributions at finite doping (Sec. VI A) and come to the conclusion that defects trigger dimerization of orbital correlations and of FM spin exchange constants along the c axis in the C-AF phase (Sec. VI B). Finally, using the effective models derived for both magnetic phases we present a scenario which explains why the phase transition from the G-AF to dimerized C-AF phase takes place already at small doping, see Sec. VII C. A summary and outlook are given in Sec. VII.

II. DEFECT STATES IN RV O₃ PEROVSKITES

A. Degenerate Hubbard model for t₂ɡ electrons

We begin with analyzing the consequences of strong Coulomb interactions in the framework of a multi-orbital Hubbard model introduced here to describe the doped Y₁₋ₓCaₓVO₃ compounds. This model will later form the basis for the derivation of an effective superexchange and a related spin-orbital t–J model for the orbital degenerate case, see Sec. III A. In the ionic picture of the undoped VVO₃, V³⁺ ions are in a d⁰ electronic configuration with partly filled t₂ɡ orbitals. As we show below, the qualitative features of the optical spectra, i.e., the multiplet splitting of the Hubbard bands and the position of defect states, may be reproduced by considering a multiband Hubbard model for t₂ɡ electrons,

\[ H = H_t + H_{CF} + H_{int} + H_{imp}, \quad (2.1) \]

where the four terms stand for the kinetic energy \(H_t\), crystal-field (CF) splitting \(H_{CF}\), local Coulomb interactions \(H_{int}\), and Coulomb potential generated by a Ca impurity \(H_{imp}\). On one hand this model can also serve as a basis for the qualitative discussion of the photoemission (PES) and inverse PES in the vicinity of the Mott-Hubbard gap. On the other hand, it provides the basis for the derivation of the spin-orbital Hamiltonian which serves for a transparent description of the magnetic and orbital structure, as well as of spin and orbital excitations. Our aim here is to explore further the changes of the excitation spectra resulting from the presence of Ca²⁺ defects in the lattice of V³⁺ ions and their impact on the vanadium t₂ɡ electrons, with help of this simplified Hamiltonian.

The kinetic energy is given by:

\[ H_t = - \sum_{\gamma} \sum_{(ij)\parallel\gamma\alpha} t_{\alpha} \left( d_{i\alpha\sigma}^\dagger d_{j\alpha\sigma} + d_{i\alpha\sigma} d_{j\alpha\sigma}^\dagger \right), \quad (2.2) \]

where \(d_{i\alpha\sigma}^\dagger\) is electron creation operator for an electron at site \(i\) in orbital state \(\alpha\) with spin \(\sigma = \uparrow, \downarrow\). The summation runs over three cubic axes, \(\gamma = a, b, c\), the bonds \(\langle ij\rangle\parallel\gamma\), and the hopping \(t_{\alpha}\) conserves the t₂ɡ orbital flavor. The effective hopping \(t_{\alpha}\) originates from two subsequent \(d - p\) hopping processes via the intermediate \(2p_x\) oxygen orbital along each V–O–V bond. In principle it can be derived from the charge-transfer model with \(p - d\) hybridization \(t_{pd}\) and charge-transfer energy \(\Delta_{50}\) and one expects in the present case \(t = t_{pd}^2/\Delta \sim 0.2 \text{ eV}\). Only two t₂ɡ orbitals, labelled by \(\alpha(\gamma)\), are active along each bond \(\langle ij\rangle\parallel\gamma\) and contribute to the kinetic energy Eq. (2.2), while the third one lies in the plane perpendicular to the \(\gamma\) axis and the hopping via the intermediate oxygen \(2p_x\) oxygen is forbidden by symmetry. This motivates a convenient notation used below,

\[ |a\rangle \equiv |yz\rangle, \quad |b\rangle \equiv |xz\rangle, \quad |c\rangle \equiv |xy\rangle, \quad (2.3) \]

where the orbital inactive along a cubic direction \(\gamma\) is labelled by its index as \(\gamma\).

In agreement with a commonly accepted picture, information obtained from the electronic structure calculations and with the results obtained using the point charge model we assume that the \(xy\) \((c)\) orbitals are energetically favored and thus occupied and inactive at low temperature, while the remaining \(yz\) and \(xz\) orbitals are nearly degenerate and represent the t₂ɡ orbital doublet, with both orbitals active for the hopping (and the superexchange) along the \(c\) cubic axis.

The nonequivalence of the t₂ɡ orbital states is described by a CF splitting term which favors the \(c\) orbitals,

\[ H_{CF} \equiv - \sum_{i\alpha\sigma} \Delta_{\alpha} n_{i\alpha\sigma}, \quad (2.4) \]

where \(n_{i\alpha\sigma} \equiv \langle d_{i\alpha\sigma}^\dagger d_{i\alpha\sigma} \rangle\) is an electron density operator, and \(\Delta_{\alpha} = \delta_{\alpha,c} \Delta_c \) with \(\Delta_c > 0\). As a result, when \(\Delta_c \geq t\) as we estimated for \(c\) orbitals are filled by one electron at each site in a strongly correlated system, and the second electron occupies one of the orbitals in the \(\{a, b\}\) doublet, leading to the \(c_1^\dagger(a, b)_i\) configuration at each site \(i\). This broken symmetry situation corresponds to electron densities

\[ n_{ic} \simeq 1, \quad n_{ia} + n_{ib} \simeq 1, \quad (2.5) \]

within t₂ɡ orbitals at undoped V³⁺ ions. Note that one expects that the cubic symmetry with \(n_{ic} = 2/3\) is restored at high temperature, but this situation will not be analyzed here as it has no influence on the mechanism of the phase transition from the G-AF to C-AF phase which occurs in Y₁₋ₓCaₓVO₃ at low temperature under increasing doping.

The local Coulomb interactions between t₂ɡ electrons at V³⁺ ions are described by the degenerate Hubbard
Hamiltonian\(^{\text{21}}\) with the interacting part:

\[
H_{\text{int}} = U \sum_{i,\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + \left( U - \frac{5}{2} J_H \right) \sum_{i,\alpha<\beta} n_{i\alpha} n_{i\beta} \\
+ J_H \sum_{i,\alpha<\beta} \left( d_{i\alpha\uparrow}^\dagger d_{i\alpha\downarrow}^\dagger d_{i\beta\uparrow} d_{i\beta\downarrow} + d_{i\beta\uparrow}^\dagger d_{i\beta\downarrow}^\dagger d_{i\alpha\uparrow} d_{i\alpha\downarrow} \right) \\
- 2J_H \sum_{i,\alpha<\beta} \vec{S}_{i\alpha} \cdot \vec{S}_{i\beta} .
\] (2.6)

Here \(n_{i\sigma} = \sum_\alpha n_{i\alpha\sigma}\) is the corresponding electron density operator in orbital \(\alpha\) at site \(i\), and spin operators \(\vec{S}_{i\alpha} = \{S_{i\alpha\uparrow}, S_{i\alpha\downarrow}, S_{i\alpha}^z\}\) are related to fermion operators in the standard way, i.e.,

\[
S_{i\alpha}^+ \equiv d_{i\alpha\uparrow}^\dagger d_{i\alpha\downarrow}, \quad S_{i\alpha}^- \equiv \frac{1}{2}(n_{i\alpha\uparrow} - n_{i\alpha\downarrow}).
\] (2.7)

The first term in Eq. (2.6) describes the intraorbital Coulomb interaction \(U\) between electrons with antiparallel spins. The second term stands for the interorbital Coulomb (density) interaction, the third one is called frequently the “pair-hopping” term, and the last one is Hund’s exchange \(J_H\). The choice of coefficients in Eq. (2.6) guarantees that the interactions satisfy the rotational invariance in the orbital space\(^{\text{21}}\). This Hamiltonian is exact when it describes only one type of 3d orbitals which are partly occupied, as \(t_{2g}\) orbitals in the present case of the \(\text{RuO}_3\) perovskites, and the interactions are then given by two parameters: (i) the intraorbital Coulomb element \(U\) and (ii) the interorbital (Hund’s) exchange element \(J_H\). These elements may be expressed by the Racah parameters \(\{A, B, C\}\). For \(t_{2g}\) electrons one finds\(^{\text{21}}\)

\[
U = A + 4B + 3C, \quad J_H = 3B + C.
\] (2.8) (2.9)

Finally we introduce the Coulomb interaction between the \(t_{2g}\) electrons at a V-site \(\vec{R}_i\) and the effectively negative charged defects\(^{\text{51}}\) with charge \(Q_D = e\) at site \(\vec{R}_n\),

\[
H_{\text{imp}} = \sum_{i \in \mathcal{C}_n} W(|\vec{r}_i - \vec{R}_n|) n_i ,
\] (2.10)

where \(n_i = \sum_\alpha n_{i\alpha}\) is the total \(t_{2g}\) electron density. Here \(i \in \mathcal{C}_1\) (\(i \in \mathcal{C}_\infty\)) denotes a calculation where in the sum only nearest (all) V neighbors of a defect are considered. The Coulomb potential itself is long-ranged,

\[
W(r) = \frac{eQ_D}{\epsilon_{\text{c}} r} ,
\] (2.11)

and screened by the dielectric function \(\epsilon_\omega\) of core electrons. We identify \(\epsilon_\omega\) with the high frequency dielectric constant which, e.g., for \(\text{VVO}_3\) lies in the interval \(\epsilon(\omega) = 5.0 \pm 0.3\) in the whole frequency range \(0.8 < \omega < 3.5\) eV\(^{\text{54}}\). The most pronounced effect of this potential term is an upward shift of the vanadium states in the neighborhood of the defects. This gives rise to bound states in the Mott-Hubbard gap. It is important to realize that on one hand a Ca-defect \(D\) introduces one hole, but on the other hand it generates defect states on eight equivalent vanadium neighbors. Thus the topmost defect states that are split from the LHB are only partially filled and pin the chemical potential \(\mu\).

In general the coordinates of the defects \(\vec{R}_n\) will be statistically distributed. In fact, defects will also feel some repulsion and avoid clustering. We will not explore these aspects here, as we are concerned mainly with the dilute doping regime. Nevertheless it is clear that transport is strongly affected by disorder and results from the motion of holes in the defect band.

Furthermore, in the immediate neighborhood of a Ca defect the strength of Coulomb interaction influences the orientation of \(t_{2g}\) orbitals filled by electrons. This effect modifies the orbital state and will be described below via an extra crystal field term which acts on the orbitals of the V ions in the vicinity of a defect (see Sec. III.D). Such more subtle effects concern the low-energy behavior and are analyzed in the framework of the effective spin-orbital \(t-J\) model in Sec. III. Therefore, we do not analyze it here, similar as the intersite orbital interactions which originate from the distortions of \(\text{VVO}_3\) octahedra.

### B. Unrestricted Hartree-Fock analysis of the degenerate Hubbard model

Qualitative insight into the correlated electronic structure of partly filled \(t_{2g}\) states can be obtained from the HF approximation. When the HF approximation is used, the “pair-hopping” term does not contribute and the local spin exchange interactions \(\vec{S}_{i\alpha} \cdot \vec{S}_{i\beta}\) contribute only with the Ising term \(\propto S_{i\alpha}^z S_{i\beta}^z\) i.e., one may use an approximate expression,

\[
-2\vec{S}_{i\alpha} \cdot \vec{S}_{i\beta} \approx \frac{1}{2} \sum_\sigma \left( n_{i\alpha\sigma} n_{i\beta\bar{\sigma}} - n_{i\alpha\bar{\sigma}} n_{i\beta\sigma} \right) .
\] (2.12)

As a result, local electron interactions Eq. (2.6) are given approximately by electron density operators \(\{n_{i\alpha}\}\):

\[
H_{\text{int}} \approx U \sum_{i,\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + (U - 2J_H) \sum_{i,\alpha<\beta,\sigma} n_{i\alpha\sigma} n_{i\beta\bar{\sigma}} \\
+ (U - 3J_H) \sum_{i,\alpha<\beta,\sigma} n_{i\alpha\sigma} n_{i\beta\bar{\sigma}} .
\] (2.13)

The form given in Eq. (2.13) violates the rotational invariance of local Coulomb interactions\(^{\text{51}}\) but is sufficient for our purpose since all the terms which appear in the HF approximation arise from it\(^{\text{55}}\). One finds the following
effective one-particle problem in an effective field, 
\[
H_{\text{int}}^{\text{HF}} = U \sum_{i,\sigma} n_{i\alpha\sigma} (n_{i\alpha\bar{\sigma}}) \\
+ (U - 2J_H) \sum_{i,\alpha < \beta, \sigma} (n_{i\alpha\sigma} (n_{i\beta\bar{\sigma}}) + (n_{i\alpha\bar{\sigma}}) n_{i\beta\sigma}) \\
+ (U - 3J_H) \sum_{i,\alpha < \beta, \sigma} (n_{i\alpha\sigma} (n_{i\beta\bar{\sigma}}) + (n_{i\alpha\bar{\sigma}}) n_{i\beta\sigma}) .
\]
(2.14)

The HF potentials are determined by the average densities \{\langle n_{i\alpha\sigma} \rangle\} when \(H_{\text{int}}\) is replaced by \(H_{\text{int}}^{\text{HF}}\) in Eq. 2.13.

We emphasize that although the quantum effects such as spin fluctuations and "pair hopping" of double occupancies are neglected, the essential features of the Coulomb interaction are reproduced. This can be seen by considering charge excitations \(d^n d^n \rightarrow d^\alpha d^{\alpha - 1}\) along a given bond \((ij)\) in the lattice of transition metal ions with \(d^n\) electronic configuration. To analyze excited states we assume that the electron number \(n\) is lower than the half-filled shell, i.e., \(n < 5\) for the \(3d\) shell. Below we focus on \(n = 2\) for the present problem of \(V^{3+}\) ions in \(\text{YVO}_3\), where the \(3d^2\) shell is half-filled at \(n = 3\).

There are three types of \(d^{\alpha + 1}\) excited states: (i) high-spin (HS) states with all electrons in the same spin state (realized for a FM \((ij)\) bond); (ii) low-spin (LS) states with all orbitals being singly occupied, and (iii) LS states with one doubly occupied orbital. The energies of these excitations are:

\[
E_{\text{HS}} = U - 3J_H ,
\]
(2.15)
\[
E_{\text{LS}}^{(1)} = U - 2J_H + (n - 1)J_H ,
\]
(2.16)
\[
E_{\text{LS}}^{(2)} = U + (n - 1)J_H ,
\]
(2.17)

The HS excitation energy obtained in the HF approximation reproduces the exact value obtained by the diagonalization of the atomic ion Hamiltonian Eq. 2.6. The remaining energies are systematically lower by \(J_H\) than the exact values, as the quantum fluctuation effects (spin-flips and "pair-hopping") were neglected.

In the relevant regime of parameters for the \(\text{RVO}_3\) perovskites, the electrons in the undoped \(\text{YVO}_3\) are localized in a Mott insulator. We consider here representative parameters with \(U = 4\) eV and \(J_H = 0.6\) eV. In this parameter range one may simplify the problem of calculating the electronic structure in the HF approximation as the \(c\) orbitals are occupied at each site by one \(t_{2g}\) electron, and the magnetic state is determined by their magnetic moments. This follows from large Hund’s exchange which dictates that the spin direction of both \(t_{2g}\) electrons \((c\) electron and \((a, b)\) one) agree at each site. As a result, one obtains the high-spin \(S = 1\) state at each \(V^{3+}\) ion.

We discuss first the numerical calculations of the density of states \(N(\omega)\) for the undoped system. The results were obtained by solving the equations derived using the HF approximation, see Eq. 2.14, on a cluster with \(N_0 = L_x \times L_y \times L_z\) sites (here we use \(L_x = L_y = L_z = 10\)). We considered the \(c\) orbitals singly occupied and ordered as in the \(C-\text{AF}\) phase of the undoped \(\text{YVO}_3\). The second electron at each site occupies one of the remaining \(t_{2g}\) orbitals \{\(a, b\)\}. The partial density of states for the \{\(a, b\)\} orbital doublet with eigenenergies \(\epsilon_m\) in the cluster,

\[
N(\omega) = \sum_m \delta(\omega - \epsilon_m),
\]
(2.20)

is shown in Fig. 2. The chemical potential \(\mu\) in the undoped case is naturally chosen in the middle of the gap: \(\mu = (\epsilon_{N_0} + \epsilon_{N_0 + 1})/2\), where \(\epsilon_{N_0}\) is the highest occupied energy for \(N_0\) electrons in \{\(a, b\)\} orbitals in the system.

The spectra are characterized by four subbands: (i) the LHB centered at \(E_{\text{LHB}}\) and (ii) the UHB which itself is split into three subbands (multiplet structure) corresponding to the HS excitations at \(E_{\text{HS}} = U - 3J_H\) Eq. (2.15), and two LS transitions centered at \(E_{\text{LS}}^{(1)} = U - J_H\) Eq. (2.16) and \(E_{\text{LS}}^{(2)} = U + J_H\) Eq. (2.17), respectively. These energies are relative to \(E_{\text{LHB}}\). HF results for these excitations calculated for \(U = 4\), \(J_H = 0.6\) and \(t_0 = 0.2\) eV \((t_a = t_b = t_c = t_0)\) are listed in Table I and compared...
TABLE I: Excitation energies of YVO$_3$ inferred from optical data and calculated from the present theory. Here $\Delta_{\text{MH}}$ is the Mott-Hubbard gap, and $E_{\text{HS}}$, $E^{(1)}_{\text{LS}}$, and $E^{(2)}_{\text{LS}}$ are the energies (all in eV) of the high-spin and the two low-spin transitions measured from the center of the lower Hubbard band $E_{\text{LHB}}$. The last column gives the defect energy $E_D$ relative to $E_{\text{LHB}}$ at $x = 0.02$ Ca-doping.

| energy    | $\Delta_{\text{MH}}$ | $E_{\text{HS}}$ | $E^{(1)}_{\text{LS}}$ | $E^{(2)}_{\text{LS}}$ | $E_D$ |
|-----------|----------------------|-----------------|-----------------------|-----------------------|-------|
| Ref. 32   | 1.7                  | 2.2             | 3.0–3.7               | 4.0–4.5               | —     |
| Ref. 33   | 1.7                  | 2.2             | —                     | —                     | 1.2   |
| theory    | 1.6                  | 2.2             | 3.4                   | 4.6                   | 1.0   |

with experimental values for YVO$_3$ obtained by Fukuoka et al.$^{33,57}$ and by Küppersbusch$^{57}$ deduced from optical spectroscopy and ellipsometry, respectively. Interestingly the LS-transitions found in the ellipsometry study find a reasonable correspondence within the HF calculation. These values are also consistent with the underlying multiplet splitting of YVO$_3$ in the optical spectral weight study of Ref. 12.

Next we turn to the Mott-Hubbard gap (see Fig. 2) which may be expressed as:

$$\Delta_{\text{MH}} \simeq U - 3J_H - W_{\text{eff}},$$  \hfill (2.21)

where $W_{\text{eff}}$ is the effective bandwidth of a Hubbard subband. A significant reduction of $W_{\text{eff}}$ compared to the free bandwidth $W$ is well known from the single band Hubbard model$^{58}$ In a recent study a LHB width $W_{\text{eff}} \approx 3t_0$ was estimated for the incoherent hole motion of $t_2g$ electrons$^{59}$ Thus with the choice $t_0 \approx 0.2$ eV we obtain for the Mott-Hubbard gap $\Delta_{\text{MH}} \simeq 1.6$. We also note, that our estimate of the bandwidth of the LHB in the HF calculation is much smaller, namely $W_{\text{HF}} \approx t_0$. This is due to the neglect in the HF approximation of processes describing the incoherent motion of holes. A related interesting quantity that can be inferred from optical spectroscopy is the width of the HS-transition$^{33}$

$$\Gamma_{\text{HS}} \simeq 1.3 \pm 0.2 \text{ eV in YVO}_3.$$  

As the width of the optical transition should be determined by the convolution of the LHB and HS-band, one expects $\Gamma_{\text{HS}} \simeq 2W_{\text{eff}}$. Thus $\Delta_{\text{MH}}$ and the width $\Gamma_{\text{HS}}$ find a natural explanation in terms of the multiplet splitting and the effective Hubbard bandwidth $W_{\text{eff}}$.

The counting of states that contribute to the partial density of states $N(\omega)$ is straightforward; there is one electron per site which can occupy either $a$ or $b$ orbital and there are two spin flavors. Thus the filling is $f(\mu) = 1/4$ as the total number of states is $N_f = 4N_0$, where $N_0$ is the number of sites, and there are $N_0$ electrons that occupy the LHB. All subbands of the UHB have also the same weight of $N_0$ each. This can be seen from the integrated and normalized density of states

$$f(\omega) = \int \frac{d\omega'}{\omega'} N(\omega') / \int \frac{d\omega'}{\omega'},$$ \hfill (2.22)

which is displayed as the dashed curve in Fig. 2. While we use a broadening parameter $\gamma = 0.1$ eV to smoothen the density of states $N(\omega)$, no such broadening is used in the calculation of $f(\omega)$.

It is well known that the number of states in the UHB depends on the hole doping, and in addition to spin, there is one LHB and three UHBs, all of them with the same weight one at $x = 0$. At finite doping $x > 0$ each added hole moves an empty state above the Fermi energy in the LHB and generates also three other unoccupied states in the LHB which are taken from the subbands of the UHB, see Fig 3(c). This corresponds to four possibilities to fill up a hole (with spin and orbital flavor) and thus $4x$ empty states belong to the LHB at doping $x$. Yet it is also important to emphasize here that this does not imply that there are really $4x$ free states in the LHB that can all be simultaneously occupied. Actually there is only space for $x$ electrons, as with each electron added three states are shifted back to the UHBs.
the LHB is approximately given by the center of the HS-band is finite doping; vertical dashed line indicates the filling of the system at finite doping; $D^*$ marks defect states split from the highest LS excitation; further notations and parameters as in Fig. 2.

C. Hartree-Fock calculation for defect states

The major change in the spectra induced by doping is the occurrence of the defect states $D$ inside the Mott-Hubbard gap. Figure 4 shows the density of states at 2% Ca-doping. The spectra were obtained by a calculation using the HF approximation for well separated defects acting on $t_{2g}$ electrons with the defect potential, Eq. (2.10), which includes the interaction with the eight nearest neighbor V ions at distance $d_1 = \sqrt{3}d_{VO}$ ($d_{VO} \approx 2.0$ Å is the vanadium-oxygen distance). The estimate of the nearest neighbor defect potential $V_D$ appropriate for YVO$_3$ is straightforward, i.e., $W(d_1) = V_D \approx 1.0$ eV, where we used the dielectric constant of core electrons $\epsilon_c \approx 5.0$. The summation in Eq. (2.10) was restricted to $i \in C_1$, thus only a short-range defect potential was included, and disorder effects do not come into play. Thereby the interpretation of spectra and energy scales is simplified and more transparent for our purposes.

The calculations show that for large $V_D \approx 1.0$ eV the energy $E_D$ of the defect states $D$ relative to the center of the LHB is approximately given by $E_D \approx V_D$ (see Table I). The complementary splitting of the defect states from the center of the HS-band is $E_D' \approx 1.2$ eV, and appears also consistent with optical spectroscopy data. Depending on the value of the defect potential, the defect states $D$ appear either at the upper edge of the LHB, or develop to a separated maximum within the Mott-Hubbard gap, see Fig. 5. Figure 5(b) nicely shows that each UHB (HS, LS)$^{(1)}$ and LS$^{(2)}$ has its own defect satellite. Such states can be observed, however, only when a satellite of a given Hubbard subband is well separated from the next subband.

We emphasize that in the model with two orbital flavors each Ca$^{2+}$ defect introduces one hole into eight defect states that are split off from the LHB. The filling fraction at doping concentration $x = N_x/N_0$ is therefore,

$$f(\mu) = \frac{N_0 - N_x}{4N_0} = \frac{1}{4}(1 - x), \quad (2.23)$$

which fixes the chemical potential $\mu$. The total number of occupied electron states is now simply obtained by multiplication with $4N_0$:

$$N^{\text{occ}} = (1 - x)N_0, \quad (2.24)$$

and the number of holes is $N^h = xN_0$. The number of states in the LHB, however, is reduced to $N_{\text{LHB}} = (1 - 8x)N_0$ due to the appearance of $N_D = 8xN_0$ defect states, of which $N^{\text{occ}} = 7xN_0$ are occupied.

Although there is a similarity to defect bands in doped semiconductors, a striking difference is that the defect states here are completely derived from the LHB. Hence the defect band in Fig. 5(c) would be fully occupied if no holes were added. However each added defect generates not only the defect states but also contributes a single hole. We suggest that it is the motion of the holes in
III. SPIN-ORBITAL t-J MODEL

A. Model Hamiltonian for Y_{1-x}Ca_xVO_3

We now turn to the derivation of an effective low-energy Hamiltonian which describes the interactions of the spin and orbital degrees of freedom as well as the motion of doped holes. For the undoped case the effective microscopic spin-orbital model that describes electrons in t_{2g} orbitals of V ions has already been worked out in Refs. [9,10,12,14]. In the undoped compound one deals with the t_{2g} electronic high-spin (S = 1) state at each V^{3+} ion, and an {a, b} orbital degree of freedom.

When a correlated insulator with active orbital degrees of freedom is doped, rather complex processes occur when holes are doped. The motion of a hole may generate spin, orbital order that occur by hole doping in YVO_3 perovskites and includes the superexchange and the orbital interactions induced by the lattice. Therefore, designing a microscopic model which captures the essential physical mechanisms in such a situation and is mathematically tractable at the same time is a nontrivial and demanding task. Below we introduce such a microscopic model to describe the changes of magnetic and orbital order that occur by hole doping in Y_{1-x}Ca_xVO_3. It stems from the spin-orbital model for the undoped RVO_3 perovskites and includes the superexchange and the orbital interactions induced by the lattice [9,13]. As in Sec. II, the kinetic energy arises from the hopping t between two t_{2g} orbitals at neighboring V sites, and the orbital flavor is conserved. Electron-electron interactions are described by the degenerate Hubbard model [22] Eq. (2.6), written in this case for two t_{2g} orbitals {a, b}, with intraorbital Coulomb element U and Hund’s exchange J_H, see Eqs. (2.8) and (2.9).

As in other Mott (or charge-transfer) insulators characterized by the realistic regime of parameters with t ≪ U [22] the magnetic and orbital interactions of strongly correlated t_{2g} electrons in the RVO_3 perovskites are then described within the spin-orbital superexchange H_{J}, with the superexchange constant

\[ J = \frac{4t^2}{U}. \]  

A realistic model for the undoped RVO_3 perovskites contains also the orbital interactions H_orb which follow from the orbital-lattice coupling and are responsible both for the energetic proximity of the G-AF and C-AF phases in YVO_3 [21,10,13] and for the systematic trends observed for the orbital and magnetic phase transition of the series of RVO_3 perovskites [14]. Here we present an appropriate extension of this model adequate for weakly doped Y_{1-x}Ca_xVO_3 compounds, which includes the charge-orbital interactions around the Ca^{2+} defects. It generates an attractive potential and confines a hole to the immediate neighborhood of the charge defect.

Strong electron correlations in the Y_{1-x}Ca_xVO_3 compounds motivate the spin-orbital t-J model,

\[ H_{tJ} = \mathcal{P} \left( H_t + H_{J} + H_{Hund} + H_{orb} + H_{imp} + H_{D} + H_I \right) \mathcal{P}, \]  

where \mathcal{P} are the projection operators which remove triply (and higher) occupied V ions and guarantee that either the {a, b} orbital doublet is singly occupied (at V^{3+} ion) and spin is S = 1, or the {a, b} doublet is empty (at V^{4+} ion), i.e., it contains a hole generated by doping. The spin-orbital superexchange for \( d^2 - d^1 \) pairs of V^{4+} - V^{3+} ions (H_{J}) and the orbital-lattice interactions (H_{orb}) stand for the effective strong coupling model [2,23] that was used before to explain the temperature variation of optical spectra [12] and the phase diagram [14] of the RVO_3 perovskites. When holes are doped, several other terms are needed: (i) the hopping of {a, b} electrons in the restricted space (H_t) Eq. (2.7); (ii) Hund’s exchange H_{Hund} between s = 1/2 spins of an {a, b} electron and a c electron at site i; (iii) the impurity potential H_{imp} given by Eq. (2.10); (iv) the polarization interaction at the V sites near the charge defects (H_D); (v) the superexchange for \( d^2 - d^1 \) pairs of V^{4+} - V^{3+} ions (H_I). These terms are introduced in Secs. III-C, III-D and III-E respectively.

B. Superexchange in the undoped YVO_3

The third term in Eq. (3.2) is the spin-orbital superexchange H_J. The anisotropic electron distribution between the ab planes and the c axis, see Eqs. (2.8), is responsible for a particular form of the superexchange H_J, with broken cubic symmetry [10,13]. In fact, this symmetry breaking is responsible for strong {a, b} orbital fluctuations which stabilize the C-AF phase with FM interactions along the c axis. The superexchange interactions between two V^{3+} ions in the undoped YVO_3 with S = 1 spins at sites i and j arise from virtual excitations \( d^0_i d^0_j \rightarrow d^1_i d^1_j \) along the concerned bond (ij), promoted by the hopping t which couples pairs of identical active \( t_{2g} \) orbitals. A single hopping process generates a \( d^1 \) configuration at site i, either with three different orbitals occupied by a single electron each, or with a double occupancy in one of the two active orbitals. Therefore, the \( d^1_i \) excited state may be either a high-spin \( 4A_2 \) state with energy \( (U - 3J_H) \), see Eq. (2.15), or one of three low-spin states: \( 2E, 2T_1 \) or \( 2T_2 \) with energies \( \frac{1}{2} U \) and \( (U + 2J_H) \) — they are shown in Fig. 1 of Ref. [8] see also Eqs. (2.18) and (2.19).

This perturbative consideration leads to the spin-orbital superexchange model for S = 1 spins in cubic...
vanadates\(^2\)

\[ \mathcal{H}_J = \frac{1}{12} J \sum_{\langle ij \rangle \parallel c} n_i n_j \left\{ 4r_1(2 + \hat{S}_i \cdot \hat{S}_j) \left( \vec{\tau}_i \cdot \vec{\tau}_j - \frac{1}{4} \right) \right. \]
\[ \left. + (\hat{S}_i \cdot \hat{S}_j - 1) \left( \frac{7}{4} - \tau_i^x \tau_j^x - \tau_i^y \tau_j^y + 5 \tau_i^z \tau_j^z \right) \right. \]
\[ \left. + 3r_3(\hat{S}_i \cdot \hat{S}_j - 1) \left( \frac{1}{4} + \tau_i^x \tau_j^x + \tau_i^y \tau_j^y - \tau_i^z \tau_j^z \right) \right\} \]
\[ + \frac{1}{24} J \sum_{\langle ij \rangle \parallel ab} n_i n_j \left\{ 4r_3 \left( \hat{S}_i \cdot \hat{S}_j + 2 \right) \left( \tau_i^x \tau_j^x - \frac{1}{4} \right) \right. \]
\[ \left. + 3(1 - \hat{S}_i \cdot \hat{S}_j) \left( \frac{19}{12} + \frac{1}{2} \tau_i^x + \frac{1}{2} \tau_j^x - \frac{1}{3} \tau_i^z \tau_j^z \right) \right. \]
\[ \left. + 3r_3(1 - \hat{S}_i \cdot \hat{S}_j) \left( \frac{5}{4} + \frac{1}{2} \tau_i^x + \frac{1}{2} \tau_j^x + \tau_i^z \tau_j^z \right) \right\} \right]. \tag{3.3} \]

where \(\langle ij \rangle\) is a nearest neighbor bond and \(J\) is the superexchange constant given in Eq. (3.1). The superexchange Eq. (3.3) follows from the degenerate Hubbard model Eq. (2.1) as described in Ref. 13 for the case when \(c\) orbitals are occupied, see Eq. (2.5), and a second electron occupies the \(\{a, b\}\) doublet at each site, i.e., \(n_i = 1\) with

\[ n_i \equiv n_{ia} + n_{ib}. \tag{3.4} \]

It depends on Hund’s exchange,

\[ \eta = \frac{J_H}{U}, \tag{3.5} \]

due to the charge excitations to the states of the UHBs described above and shown in Fig. 2 via the coefficients (the coefficient \(r_2 = 1\) arises for the intermediate energy LS excitations at \(V^{+2}\) ions),

\[ r_1 = \frac{1}{1 - 3\eta}, \quad r_3 = \frac{1}{1 + 2\eta}. \tag{3.6} \]

The operators \(\vec{\tau}_i \equiv \{ \tau_i^x, \tau_i^y, \tau_i^z \}\) describe orbital \(\tau = 1/2\) pseudospins defined here (for each direction \(\gamma = a, b, c\)) by the doublet of active \(\{a, b\} \equiv \{yz, xz\}\) orbitals, and are given by the Pauli matrices, i.e.,

\[ \tau_i^x = \frac{1}{2} \sigma_i^x, \quad \tau_i^y = \frac{1}{2} \sigma_i^y, \quad \tau_i^z = \frac{1}{2} \sigma_i^z. \tag{3.7} \]

As both orbitals are active along the \(c\) axis, the orbital part is then given by a scalar product \(\vec{\tau}_i \cdot \vec{\tau}_j\).

The orbital-orbital interactions which follow from lattice distortions of both the Jahn-Teller type and GdFeO\(_3\)-type are of the form acts 10,12,13

\[ \mathcal{H}_{\text{orb}} = V_{ab} \sum_{\langle ij \rangle \parallel ab} \tau_i^x \tau_j^x - V_c \sum_{\langle ij \rangle \parallel c} \tau_i^x \tau_j^x. \tag{3.8} \]

The interactions in the \(ab\) planes \(V_{ab} > 0\) follow from the Jahn-Teller distortions, while the ones along the \(c\) axis \(V_c > 0\) favor the \(C\)-AO phase and thus help to stabilize the \(G\)-AF order in the undoped YVO\(_3\). These interactions increase along the RVO\(_3\) perovskites towards the compounds with small ionic radii, and it happens to be just for YVO\(_3\) that they tip the balance between the two types of magnetic order in favor of the \(G\)-AF phase which is more stable at low temperature.\(^{24}\)

C. Effective double exchange model

The first term \(\hat{H}_t \equiv \mathcal{P} \mathcal{H}_t \mathcal{P}\) in Eq. (3.2) is the kinetic energy which after projection describes only hopping processes within the LHB. In the LHB only an electron at nearest neighbor site of the hole can hop by interchanging its position with the hole \(^{27}\). The remaining hopping processes describe either excitations to the UHBs that are included in the superexchange \(\mathcal{H}_J\) between two \(V^{3+}\) ions, or low spin charge excitations at the hole site that contribute to the superexchange \(\mathcal{H}_t\) for \(V^{4+}-V^{5+}\) pairs of ions, see below.

Further restriction on the hopping is introduced by the breaking of cubic symmetry in doped \(Y_{1-x}Ca_xVO_3\) by the actual anisotropic electron distribution over the \(t_{2g}\) orbitals given by Eqs. (2.5). This leads to the symmetry breaking between the bonds in \(ab\) planes and along the \(c\) axis.\(^{12,13}\) As we have discussed in Sec. III hole doping occurs in the orbital doublet \(\{a, b\}\), and the \(c\) orbitals are filled also in doped systems by one electron each. Therefore, the \(c\) electrons are immobile in the strongly correlated regime and contribute only to virtual \(d_{x^2}d_{y^2} \rightarrow d_{z^2}d_{z^2}\) excitations which generate the superexchange along the considered bond \(\langle ij \rangle \parallel ab\).

In the large \(U\) regime \((U \gg t)\) the kinetic energy of the \(\{a, b\}\) electrons is finite only in a doped system when the hopping process may occur in the restricted space. Furthermore, the hopping elements depend on the electronic configuration in \(c\) orbitals. In case of empty \(c\) orbitals, as e.g. in \(Sr_2Vo_2\), the hopping elements in Eq. (2.2) would be given by the bare tight binding element \(^{24}\) i.e., \(t_a \equiv t\). On the contrary, the present situation with filled \(c\) orbitals in doped \(Y_{1-x}Ca_xVO_3\) perovskites resembles the case of doped manganites\(^{2,24,25,26}\) where the hopping elements between active \(e_g\) orbitals are strongly renormalized by the \(t_{2g}\) spins \(S = 3/2\) on both sites. In the manganites this follows from strong Hund’s exchange coupling \(J_H\) between \(e_g\) and \(t_{2g}\) electrons which stabilizes a HS \(S = 2\) state at each \(Mn^{3+}\) site.\(^{2}\) Here one has instead a spin \(S = 1/2\) of a \(c\) electron at each site which couples by Hund’s exchange to the spin \(s = 1/2\) of a second electron in the \(\{a, b\}\) doublet, and a HS state with spin \(S = 1\) arises. Therefore the constrained hopping Hamiltonian \(\mathcal{H}_t\) which follows from the symmetry of \(t_{2g}\)
orbital states,
\[ \hat{H}_t = -t \sum_{\langle ij \rangle \in c} (a_{i \sigma}^\dagger a_{j \sigma} + b_{i \sigma}^\dagger b_{j \sigma} + \text{H.c.}) \]
\[ -t \sum_{\langle ij \rangle \in a} (b_{i \sigma}^\dagger b_{j \sigma} + \text{H.c.}) - t \sum_{\langle ij \rangle \in b} (a_{i \sigma}^\dagger a_{j \sigma} + \text{H.c.}) . \]

and contains the operators which act in the projected space, with electron number per site being either \( n_i = 2 \) or \( n_i = 1 \). When two electrons are present \( (n_i = 2) \), they interact by the local exchange term \( \hat{H}_{\text{Hund}} \) in Eq. \((3.10)\), which reads:
\[ \hat{H}_{\text{Hund}} = -2J_H \sum_i (\vec{S}_i^a + \vec{S}_i^b) \cdot \vec{S}_i^c . \]

Altogether, Eqs. \((3.9)\) and \((3.10)\) define the double exchange model\(^{25} \) for strongly correlated \( \{a, b\} \) electrons interacting with localized spins \( s=1/2 \) of \( c \) electrons. In the effective model which follows from it and is described in Sec. V the effective hopping amplitude \( t_{ij} \leq t \) for the mobile \( \{a, b\} \) electron does depend on the directions of two electron spins in \( c \) orbitals along a bond \( \langle ij \rangle \). We analyze the kinetic energy obtained in both AF phases below in Sec. V.

D. Orbital-charge interaction near Ca defects

When an Y ion in \( \text{Y}_1-x\text{Ca}_x\text{VO}_3 \) is replaced by a Ca impurity, the lattice is disturbed and two interaction terms arise due to the presence of the impurity. The first of them is the Coulomb potential due to the Ca impurity, introduced before in Eq. \((2.10)\), while the second one is a crystal field term \( \hat{H}_D \) considered here as the second last term in the spin-orbital \( t-J \) Hamiltonian Eq. \((3.2)\). The former term causes that a hole in the VO\(_3\) subsystem is confined to the immediate neighborhood of the Ca\(^{2+}\) charge defect in the Y\(^{3+}\) sublattice by the electrostatic potential Eq. \((2.10)\), as we have verified by numerical calculations reported in Sec. II. The latter term originates from the quadrupolar component of electrostatic field generated by a charge defect at the V\(^{3+}\) ions. Replacing an Y\(^{3+}\) ion by a Ca\(^{2+}\) ion implies that an effective negative charge \( e \) is introduced at the Ca impurity, i.e., in the center of the cube shown in the inset of Fig. 6. It interacts with an electron in the \( \{a, b\} \) orbital doublet of the considered V\(^{3+}\) ion, and the repulsive energy between this ion and the Ca defect has to be minimized. This may be achieved by an optimal choice of the occupied \( t_{2g} \) orbital in the \( \{a, b\} \) subspace.

Thus, the repulsive Coulomb potential of the Ca defect generates an orbital polarization at surrounding it V ions with a pronounced tendency toward electron occupation of one of the two linear combinations of the active \( \{a, b\} \) orbitals at site \( i \),
\[ |\pm\rangle_i \equiv \frac{1}{2} \left( a_i^\dagger \pm b_i^\dagger \right) |0\rangle , \]

being eigenstates of \( \sigma_i^z \) Pauli matrix. A properly chosen linear combination, either \( |+\rangle_i \) or \( |-\rangle_i \), state at site \( i \), maximizes the average distance between the interacting electronic charges at the V\(^{3+}\) and at the Ca\(^{2+}\) impurity, and minimizes the electrostatic interaction energy. The orbital states which satisfy this condition and are favored at V\(^{3+}\) ions are shown in the inset of Fig. 6. The lifting of orbital degeneracy will be described by the following orbital-defect polarization term acting in the \( \{a, b\} \) sector.
\[ \hat{H}_D = D \sum_{i \in C_1} \lambda_i \tau_i^z , \]

where \( \tau_i^z \) is defined in Eqs. \((3.7)\). The summation over \( i \in C_1 \) in Eq. \((3.12)\) includes the V sites which belong to the cube \( C_1 \) around the considered Ca site, and the sign factor \( \lambda_i = \pm 1 \) (for \( D > 0 \)) selects the proper orbital state which minimizes the charge-orbital interaction at each site \( i \). This polarized orbital is labeled as \( \alpha = 2 \) in Fig. 6. It is occupied in V\(^{3+}\) ions, but an extra hole introduced by doping does remove the electron from this topmost occupied orbital at a V\(^{3+}\) ion.

As an illustrative example of the expected consequences of the orbital-defect polarization interaction \( D \), see Eq. \((3.12)\), we present the change of the orbital state for a single bond in Appendix A. One finds a first order transition from the orbital singlet with fluctuating
orbitals to a fully polarized orbital state at large $D$. We show below that although the considered bond interacts with its neighbors and orbital fluctuations are reduced from those in a single bond, the main features of this orbital transition survive also in a crystal.

E. Superexchange for $V^{4+}$-$V^{3+}$ bonds

As already discussed in Sec. II.C, doping by a hole transfers a $V^{3+}$ ion into a $V^{4+}$ ion and excitations to the UHB are then removed at the hole site, see Fig. 3. For the orbital background this implies a charge defect and one may consider the problem of hole propagation, either in the orbital model or in the spin-orbital strong-coupling model. Simultaneously, however, superexchange interactions change in a drastic way and may be treated in an analogous way as the superexchange between $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$ ions in doped manganites. Here the superexchange couples spin $S = 1$ of a $V^{3+}$ ion with spin $s = 1/2$ at the hole site, and may be derived by realizing that: (i) only charge excitations $d_i^\dagger d_i^\dagger = d_i^\dagger d_i$ along the bond contribute and they depend on the orbital degree of freedom, (ii) only charge excitations to the LS ($S = 0$) states contribute and can be treated in perturbation theory, and (iii) the excitation energies are given by Hund’s exchange $J_H$ as in the manganites. There are two $d_2$ singlet states: (i) interorbital singlets with energy $(U - J_H)$, excited in $c_i^\dagger c_j^\dagger (a/b)_{i}^\dagger = c_j^\dagger (a/b)_{i}^\dagger c_i^\dagger$ processes, and (ii) double occupancies of the $c$ orbitals, excited in $c_i^\dagger c_j^\dagger (a/b)_{i}^\dagger = c_j^\dagger (a/b)_{i}^\dagger c_i^\dagger$ processes. Due to the symmetry of the Coulomb interactions in the $t_{2g}$ subspace, the latter excitations contribute via two eigenstates with energies $(U - J_H)$ and $(U + 2J_H)$, respectively. Therefore, taking the energy difference with respect to the energy $(U - 3J_H)$ of the initial HS state at site $j$, one finds two excitation energies: $2J_H$ and $5J_H$.

Note that for the particular occupancy $c^\dagger (a/b)_{i}^\dagger$ of $t_{2g}$ orbitals realized for $V^{3+}$ ions in $\text{YVO}_3$, see Eq. (2.23), the $c_i^\dagger$ excited states are generated only in charge excitations along the bonds in the $ab$ plane, while the former interorbital $c_i^\dagger (a/b)_{i}^\dagger$ singlets may arise on the bonds along all three directions. Therefore, the superexchange between the hole site ($V^{4+}$ ion) and the neighboring undoped ($V^{3+}$) sites is anisotropic. More details concerning the derivation of the superexchange between the $s = 1/2$ spin of $V^{4+}$ ion and its $V^{3+}$ neighbors with $S = 1$ spins are presented in Appendix B.

While the superexchange in the $ab$ plane depends in principle on the orbital $\{a, b\}$ flavor at the $d^2$ site and on the bond direction, i.e., whether or not the hopping of the electron with either $a$ or $b$ orbital flavor is allowed (or not) along the considered bond $\{ij\}$, see Appendix B, we present here the superexchange after averaging over the orbital configuration at the $d^2$ site. This simplification is well justified as we consider below (in Sec. V) the effective 1D models along the $c$ axis, where the spin and orbital configurations at the neighboring sites along the bonds parallel to either $a$ or $b$ axes are averaged out. Therefore, we introduce the exchange constants:

$$I_c \equiv \frac{i^2}{4J_H}, \quad I_{ab} \equiv \left(\frac{i^2}{8J_H} + \frac{2t^2}{5J_H}\right), \quad (3.13)$$

and write the superexchange terms as follows,

$$\mathcal{H}_t = I_c \sum_{\langle i,j\rangle} \left(\vec{s}_i \cdot \vec{s}_j - \frac{1}{2}\right) (1 - n_i)n_j$$

$$+ I_{ab} \sum_{\langle ij\rangle \neq \langle ab\rangle} \left(\vec{s}_i \cdot \vec{s}_j - \frac{1}{2}\right) (1 - n_i)n_j. \quad (3.14)$$

Here the spin operators $\vec{s}_i$ refer to $s = 1/2$ spin at the hole site, while $\vec{s}_j$ stands for $s = 1$ spins of the undoped $V^{3+}$ sites neighboring with the hole site, so the superexchange energy contributes for the bonds between $V^{4+}$ and $V^{3+}$ ions, i.e., when $(1 - n_j)n_j = 1$. This result is used below (in Sec. V) to derive and investigate 1D orbital models which contain one doped hole.

IV. ONE-DIMENSIONAL ORBITAL PHYSICS

A. Motivation and calculation method

In this section we analyze the perturbation of the spin-orbital structure due to the presence of defects, both for the $G$-AF and the $C$-AF phase. The main difference between the two phases arises from the magnetic order along the $c$ axis, being either AF (FM) in the $G$-AF ($C$-AF) phase of $Y_{1-x}\text{Ca}_x\text{VO}_3$. On the contrary, in the $ab$ plane both phases share a common AF and AO structure. Thus for our estimate of the difference of the free energies the orbital correlations along the $c$ axis will be of particular importance.

The microscopic model Hamiltonian given in Eq. (4.2) is too complex to treat simultaneously spin and orbital dynamics in a controlled approximation. Previous work has shown that larger $S = 1$ spins have weaker quantum effects and could be treated classically, in contrast to the orbital $\tau = 1/2$ pseudospins, which undergo strong orbital quantum fluctuations in the $C$-AF phase along the $c$ axis, and play a crucial role to explain its anisotropic magnetic properties. The temperature dependence of the optical spectral weights and the phase diagram of the $\text{RVO}_3$ perovskites. We emphasize that the bonds in $ab$ planes are AF and thus similar in both magnetic phases. To capture the difference between the $G$-AF and $C$-AF phase we focus here on the 1D orbital models along the $c$ axis derived from the microscopic spin-orbital model Eq. (3.12). These orbital models are solved below for finite 1D clusters coupled to the mean field (MF) terms which arise from the bonds in $ab$ planes and capture the main difference between both magnetic phases, the $G$-AF and $C$-AF phase of $Y_{1-x}\text{Ca}_x\text{VO}_3$. We analyze these models below in Secs. IV and V.
allows one to include the leading quantum fluctuations in the ground state; a similar cluster calculation was used recently to investigate the phase diagram of the Kugel-Khomskii model for a bilayer.\textsuperscript{28}

The orbital chains derived from the full spin-orbital model Eq. (3.2) are solved self-consistently using the MF terms arising from the interactions with the neighboring V\textsuperscript{3+} ions along the bonds parallel to a and b axes. This simplification arises when bond orbital correlations are treated classically and replaced by their MF values. The orbital order parameter is then defined as

\begin{equation}
\langle \tau^z \rangle_X = \frac{1}{N_0} \sum_i \langle \tau^z_i \rangle e^{i \Phi x - r_i},
\end{equation}

where \( X = C, G \) and \( \Phi_C = (0, \pi, \pi), \Phi_G = (\pi, \pi, \pi) \) are vectors from the reciprocal space that correspond to the orbital alternation in the C-AO and G-AO phase, respectively. This approach is well justified here as the interactions in \( ab \) planes are Ising-like. Furthermore, it allows one to focus on the quantum fluctuations along the 1D orbital chains parallel to the c axis, where both \( \{a, b\} \) orbital flavors are active, and on the role played by the orbital polarization term Eq. (3.12).

### B. Orbital chain in the G-AF phase

We consider first the undoped G-AF phase with classical spin order,

\begin{equation}
\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle_c = -1, \quad \langle \vec{S}_i \cdot \vec{S}_j \rangle_{ab} = -1,
\end{equation}

and C-AO order, stable at low temperature in undoped YVO\textsubscript{3}. Orbital interactions in the \( ab \) planes will be included in form of MF terms which contain contributions both from the superexchange \( \propto J \) and from the Jahn-Teller-type orbital interactions \( \propto V_{ab} \). These two interactions support each other, similar to the situation encountered in LaMnO\textsubscript{3}. For the present G-AF phase with C-AO order the MF terms acting on every site of an orbital chain along the c axis are the same and have alternating sign between two neighboring chains. We consider here a representative orbital chain with the C-AO order with the orbital order parameter, \( \langle \tau^z \rangle_C > 0 \) defined in Eq. (4.1) and stabilized by an effective field,

\begin{equation}
h_C = \{2J\eta(v_1 + r_3) + 4V_{ab}\} \langle \tau^z \rangle_C.
\end{equation}

The field originates from four bonds perpendicular to the chain and belonging to an \( ab \) plane and acts on the orbital pseudospins \( \{\tau_i^z\} \) within the chain, see below. The effective 1D orbital model for the orbital chain along the c axis within the G-AF phase takes therefore the form,

\begin{equation}
\mathcal{H}_{G}^{D} = \frac{1}{6} J (2r_1 + 1 - 3r_3) \sum_{i=1}^{N} \tau_i^z \cdot \tau_{i+1}^z - 2 \sum_{i=1}^{N} \tau_i^z - h_C \sum_{i=1}^{N} \tau_i^z.
\end{equation}

The sign selected in the last term \( \propto h_C \) gives indeed a positive orbital order parameter \( \langle \tau^z \rangle_C \), see Eq. (4.1) when calculated self-consistently for the considered orbital chain. The charge-orbital interactions \( \propto D \) acts only at the bond \{12\} which belongs to a cube surrounding a Ca site, i.e., at sites \( i = 1 \) and \( i = 2 \), and favors the orbital alternation in Fig. 6. A schematic view of the orbital chain in the G-AF phase is presented in Fig. 7(a).

We emphasize that only finite orbital interaction \( V_c > 0 \) accompanied by the planar field \( \propto h_C > 0 \) stabilizes the observed C-AO order in the G-AF phase, while the superexchange term alone (at \( V_c = 0 \) and \( h_C = 0 \)) would favor instead alternation of occupied \( \{a, b\} \) orbitals for

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{(Color online) Schematic view of a section of an orbital chain parallel to the c axis. A Ca defect D in the vicinity of the chain is shown in the top part, close to the bond \{12\}, and marked by dark filled circles; more distant nonequivalent sites are labeled as \( i = 3, \cdots, 6 \). The orbital chains correspond to: (a) the G-AF phase with \( a \) electrons in \( |a\rangle \) states (dark semicircles) corresponding to C-AO order along the chain (here sites \( i = 1 \) and \( i = 2 \) are equivalent); (b) the C-AF phase with G-AO order represented by alternating \( \{a, b\} \) occupied orbital states along the chain (dark semicircles); (c) the C-AF phase with G-AO order of \( \{a, b\} \) orbitals as in (b) and a hole \( h \) at site \( i = 1 \) near the defect D. The orbitals on two top sites \( i = 1, 2 \) belong to the V\textsubscript{8} cube around Ca defect D (see Fig. 5), and are modified toward the \(|\pm\rangle \) orbital states by the increasing orbital polarization interaction D, see Eq. (3.12). The hole in (c) is confined to sites \( i = 1, 2 \) by the trapping Coulomb potential \( E_D \). Away from the defect D, orbital correlations in (a) are (almost) uniform and support AF spin coupling, while in (b) and (c) they generate instead FM interactions that alternate between strong (s) and weak (w) exchange bonds.}
\end{figure}
finite Hund’s exchange $\eta > 0$, with $\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle < 0$. For the parameters of Fig. 8 one finds that orbital fluctuations along the orbital chain are quenched in the C-AO order and the FO order is classical with $\langle \tau^z \rangle_C = 0.5$ in absence of charge-orbital interaction. This result is independent of the chain length $L_z$. We show below how the classical C-AO order is modified by finite charge-orbital interaction $D$ which we treat here as a free parameter.

When a charge defect is introduced, the FO order in the chain is locally disturbed, and the occupied orbitals on the two equivalent sites $i = 1$ and $i = 2$ of the bond (12) gradually rotate with increasing $D$ toward the linear combinations which minimize the charge-orbital interaction, see the inset of Fig. 8. One thus expects that a final state obtained for sufficiently large polarization interaction $D$ has fully polarized orbitals, as shown schematically in Fig. 7(a). The FO order along the orbital chain parallel to the $c$ axis remains undisturbed away from the Ca defect, while close to it the occupied orbitals change to $|+\rangle$ orbitals for the sign selected in Eq. (4.1).

The above scenario was confirmed by an exact diagonalization of orbital chains of size $L_z = 8$ sites which demonstrated local nature of the perturbation introduced by a Ca impurity. The orbital state near the charge defect changes gradually under increasing interaction $D$, as shown in Fig. 8. (We have verified that the length of $L_z = 8$ sites is sufficient and longer chains of $L_z = 10$ or 12 sites give practically the same numerical results.) For the present case of classical C-AO order, the bond (12) decouples easily from the chain and the occupied orbitals at sites $i = 1, 2$ are rotated, as shown by increasing expectation value of $\langle \tau^z_i \rangle$, see Fig. 8(a). This local change near the defect is accompanied by weak negative polarization at the next nearest neighbors of the defect (site $i = 3$), and has practically no effect at more distant sites $i = 4$ and $i = 5$. The orbital moments near the defect, $\langle \tau^z_i \rangle = \langle \tau^z_j \rangle$, are gradually suppressed only near the defect, while the $\langle \tau^z_i \rangle$ ones remain close to 0.5 away from it (for $i > 2$) [Fig. 8(b)]. Therefore, the AF spin interactions along the chain, supported by FO order, are only weakened between the first and second neighbor of the defect site, i.e., at the bond (23) in Fig. 7(a). Altogether, the numerical results demonstrate that the orbital state is disturbed only locally near a Ca defect and these local modifications of the orbital state do not destabilize the coexisting G-AF and C-AO order away from the defect.

### C. Orbital chain in the C-AF phase

In order to derive the form of the orbital chain for the C-AF phase we use the following spin correlations in the classical state:

$$\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle_c = 1, \quad \langle \vec{S}_i \cdot \vec{S}_j \rangle_{ab} = -1. \quad (4.5)$$

The FM spin correlation function along the $c$ axis suppresses then all low-spin contributions to the superexchange Eq. (4.3) and the orbitals participate in strong quantum fluctuations along the chain, induced by the SU(2)-symmetric interaction $\propto \vec{\tau}_i \cdot \vec{\tau}_{i+1}$ with a large prefactor $J_{R1}$. The model Hamiltonian which describes the 1D orbital chain in the C-AF phase shown in Fig. 7(b) takes a similar form to the one for the G-AF phase discussed in Sec. [IVB].

$$\mathcal{H}_{C}^{1D} = J_{R1} \sum_{i=1}^{N} \vec{\tau}_i \cdot \vec{\tau}_{i+1} - V_c \sum_{i,j+1} \tau^z_i \tau^z_{i+1}$$

$$- D \sum_{i=1}^{2} \tau^z_i - h_G \sum_{i=1}^{N} (-1)^i \tau^z_i. \quad (4.6)$$

The G-AO order is here stabilized again by the planar field due to the vanadium neighbors in the $ab$ plane:

$$h_G = \{ 2\eta (r_1 + r_3) + 4V_{ab} \} \langle \tau^z \rangle_G, \quad (4.7)$$

which is here proportional to the orbital order parameter $\langle \tau^z \rangle_G$, alternating along the chain, see Eq. (4.1). However, in contrast to the classical FO order considered in Sec. [IVB] the orbital order is here rather weak as it competes with the orbital fluctuations along the chain.122 Thus the ground state is stabilized by strong $\{a, b\}$ quantum orbital fluctuations, while the real orbital order parameter $\langle \tau^z \rangle_G$ is reduced. Moreover, the orbital interactions $\propto V_c$ along the chain favor C-AO order and are in
conflict with the G-AO order in the present case. This reduces the orbital order parameter \( \langle \tau^z \rangle \) further as the field \( h_C \) is considerably smaller than \( h_C \), see Eq. (4.3).

First, we performed a self-consistent calculation for a reference chain of \( L_z = 8 \) sites in absence of Ca defects, i.e., with no polarization term \( (D = 0) \), which gives the orbital order parameter \( \langle \tau^z \rangle \) \( \approx 0.296 \) for the present parameters, see Fig. 8. We considered the orbital chain given by Eq. (4.6) near the charge defect, with orbitals polarized near the defect \( (D > 0) \) and coupled to the neighboring sites in \( ab \) planes by the MF terms. The relevant G-AO order is shown in Fig. 7(b). Due to the strong \( \{a, b\} \) orbital fluctuations along the chain, the orbital state changes here much slower with increasing charge-orbital interaction \( D \) than in the G-AF phase, see Fig. 9. The increasing orbital moments \( \langle \tau^z \rangle = \langle \tau^z \rangle \) near the charge defect gradually disturb the fluctuations along the chain and induce also finite \( \langle \tau^z \rangle \) moments on more distant sites which alternate along the chain, see Fig. 12(a). In contrast, the \( \langle \tau^z \rangle \) moments are first undisturbed as long as the change in the orbital ground state is small, but next they are gradually suppressed at the nearest neighbor sites of the charge defect when \( D \) increases beyond \( D > J \), cf. Appendix A. Away from the defect the weak orbital order is practically undisturbed due to the MF terms, while near the charge defect, i.e., on the bond \( \langle 12 \rangle \), the orbital state is locally modified by the charge-orbital interaction for \( D > 2J \).

Further evidence that the bond \( \langle 12 \rangle \) close to the charge defect decouples from the orbital chain when the charge-orbital interaction is sufficiently large is given by the orbital correlations \( \langle \tilde{\tau} \cdot \tilde{\tau} \rangle \). For the present parameters one finds \( \langle \tilde{\tau} \cdot \tilde{\tau} \rangle \approx -0.437 \) for the reference chain of \( L_z = 8 \) sites in absence of charge defect \( (D = 0) \), see Fig. 10(a). The orbital fluctuations are only weakly reduced by the G-AO order from the value of \( \langle \tilde{\tau} \cdot \tilde{\tau} \rangle \approx -0.452 \) obtained for a free chain, see Fig. 10(b).

When charge-orbital interaction is introduced \( (D > 0) \), the orbital fluctuations near the defect \( \langle \tilde{\tau} \cdot \tilde{\tau} \rangle \) are first reduced by the perturbative positive term \( \propto D^2 \) when \( D \ll J \), but then \( (D \sim J) \) their reduction becomes close to linear in \( D \), and finally this bond decouples from the orbital chain \( (D \sim 2J) \) as the orbital fluctuations are locally suppressed by uniformly polarized orbitals, see Fig. 12(a). Therefore, the correlation function \( \langle \tilde{\tau} \cdot \tilde{\tau} \rangle \) changes sign at \( D \approx 2.15J \) and becomes positive for larger values of \( D \), approaching the limit of fully polarized orbitals, with FO correlation near the defect \( \langle \tilde{\tau} \cdot \tilde{\tau} \rangle = 0.25 \). At the same time, the remaining correlations are only weakly modified and correspond approximately to
those obtained for a shorter orbital chain with open ends under the influence of the MF terms. The largest change is found for the \(\langle \vec{r}_2 \cdot \vec{r}_1 \rangle\) correlation which approaches the classical value \(-0.25\) when \(D > 4J\) (not shown), but the remaining orbital correlations are only weakly influenced by the presence of the charge defect.

The essential feature of the evolution of orbital correlations with increasing orbital-charge interaction \(D\) is the gradual decoupling of the bond \(\langle 12 \rangle\), next to the charge defect, from the fluctuating orbital chain. This phenomenon is more pronounced for a free orbital chain, shown in Fig. 10(b). In this case one finds a somewhat surprising effect of induced dimerized correlations along the chain, as explained below. In addition to the perturbative regime of weak \(D < J\), where the orbital correlations are modified by terms \(\propto D^2\), one recognizes here two distinct regimes, separated by a critical value \(D_c \approx 2.39J\) at which the ground state changes abruptly and the bond \(\langle 12 \rangle\) polarized by the charge-orbital interaction decouples from the fluctuating chain, see Fig. 7(b). At \(D = D_c\) a quantum transition takes place from a jointly fluctuating orbital chain to broken chain with its ends neighboring with a static orbital-polarized bond near the charge defect. We remark that this transition from fluctuating to polarized orbitals near the charge defect is similar to the one which takes place for a single bond, see Appendix A. Common features are that the transition is also discontinuous here and occurs to the state with the orbitals near the charge defect being almost fully polarized, with \(\langle \vec{r}_1 \cdot \vec{r}_2 \rangle > 0.17\).

The two regimes separated by the above transition are quite distinct. For \(D < D_c\) the charge-orbital interaction disturbs orbital fluctuations along the chain as they become gradually suppressed on the bond \(\langle 12 \rangle\), and triggers dimerized orbital correlations. Orbital fluctuations are then enhanced on the bonds neighboring with the disturbed bond, represented here by the bond \(\langle 23 \rangle\), see Fig. 7(b). This perturbation generates alternation between weaker and stronger orbital correlations along the chain. In contrast, for \(D > D_c\) the orbitals freeze in the polarized state on the \(\langle 12 \rangle\) bond, and thus the orbital fluctuations become restricted by the constraint imposed by this bond at both ends of the remaining chain. Thus the role of stronger and weaker fluctuating bonds along the broken chain is now reversed, and the fluctuations on the bond \(\langle 23 \rangle\) become weak.

One finds that the above quantum transition for a free chain changes to a crossover for an embedded chain, see Fig. 10(a). Also in this latter case it leads to dimerized orbital correlations along the orbital chain but this alternation is much weaker than for a free chain. This might suggest that charge-orbital interaction could be responsible for dimerization along the orbital chains, and would imply dimerized FM interactions in the C-AF phase. When spin interactions are evaluated for the orbital correlations of Fig. 10(b), FM interactions are indeed weak on bonds \(\langle 23 \rangle\) and \(\langle 45 \rangle\) (shown by dashed lines) and strong on bonds \(\langle 34 \rangle\) and \(\langle 56 \rangle\) (shown by long-dashed lines). However, the coupling with other orbital chains along the bonds in \(ab\) planes reduces considerably these dimerized interactions, see Fig. 10(a). Nevertheless, we introduced average orbital correlation functions for strong and weak bonds, \(\langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_s^w\) and \(\langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_s^w\) as shown in Fig. 10(b), and found that they differ from each other. We shall use them below in Sec. VIB and demonstrate that the dimerization is indeed predicted by the present \(t-J\) orbital model Eq. (52), yet its mechanism is more subtle. Apart from the orbital polarization in the vicinity of a defect which we have discussed here, the orbital order is also disturbed by a hole introduced with each defect.

V. DOPED HOLE IN ORBITAL CHAINS

A. Orbital \(t-J\) model for the \(G\)-AF phase

We first analyze the local changes of spin and orbital correlations introduced by a hole in the \(G\)-AF phase. There are two distinct processes how the hole acts on the spin-orbital structure, namely via: (i) superexchange between \(s=1/2\) and \(S=1\) sites, and (ii) double exchange which involves hole motion in the LHB (with spins in the HS configuration). The double exchange hopping process, i.e., \((\frac{1}{2}, 1) \rightarrow (1, \frac{1}{2})\), is controlled by the spin orientation of the involved spins of electrons in \(xy\) orbitals. One should note that two DE processes, one forward and one backward, are indeed distinct from the superexchange process \((\frac{1}{2}, 1) \rightarrow (0, \frac{1}{2}) \rightarrow (\frac{1}{2}, 1)\) which involves an \(S = 0\) intermediate state with an excitation energy \(\propto J_H\). Interestingly this latter proportionality makes this kind of superexchange larger than the conventional superexchange \(\propto J\), i.e., between \(S = 1\) spins, which results from virtual excitations across the Mott-Hubbard gap \(\propto U\). The formal aspects of this kind of exchange were discussed in Sec. IIIE.

Due to large binding energy between the hole and the Ca impurity, the hole is confined to one of the topmost occupied orbitals of the \(V^{3+}\) cube shown in Fig. 6. As discussed in Sec. III the motion of the hole along the bond \(\langle 12 \rangle\) parallel to the \(c\) axis is of particular relevance. A schematic picture is given in Fig. 7(c), where one of the polarized orbitals in Fig. 7(a) is replaced by a hole. The AF order in the \(ab\) plane is stabilized mainly by the superexchange driven by the excitations in \(c\) orbitals which are unaffected by the doped hole. This implies that the hole motion is confined to the \(\langle 12 \rangle\) bond along the \(c\) axis, and the effective hopping element is determined here by the double exchange.

As usual in the double exchange model the AF order is disturbed and spins cant in order to find a compromise between the loss of the magnetic energy with respect to the AF spin order, and the kinetic energy, which would be minimal for FM spins. In the present model with hole confinement near the charge defect, it suffices to analyze the double exchange mechanism on the bond \(\langle 12 \rangle\) along...
the $c$ axis, see Fig. 11 supplemented by the magnetic energy contributions arising due to other bonds which start at either $i = 1$ or $i = 2$. In the initial state $|i\rangle$ shown in Fig. 11(a) the spin of an $a \equiv yz$ electron at site $i = 1$ is parallel to the one of the electron in $c$ orbital. The hopping process to the final state $|f\rangle$ with the $a$ electron moved to site $i = 2$ is possible after the spins at both sites are canted by angle $\theta$ away from their AF order in the $G$-AF phase, see Fig. 11(a). In this case the hopping amplitude is given by

$$t(\theta) \equiv t \sin \theta. \quad (5.1)$$

Consequently, the orbital chain containing a hole in the $G$-AF phase is described by the orbital Hamiltonian

$$\mathcal{H}_G^h(\theta) = -t(\theta)(a_i^\dagger a_2 + b_i^\dagger b_2 + \text{H.c.}) + J \sum_{i=1}^{N} (\vec{\tau}_i \cdot \vec{\tau}_j - V_c \sum_{i=1}^{N} \vec{\tau}_i \cdot \vec{\tau}_j) - D \sum_{i=1}^{2} \tau_i^\tau - h_C \sum_{i=1}^{N} \tau_i^z. \quad (5.2)$$

As in Eq. 3.2, the creation operators $\{a^\dagger, b^\dagger\}$ of spinless fermions act in the restricted space, and the hopping occurs along the (12) bond. The orbital chain depends on the orbital MF $h_C$, see Eq. 4.3, and on the spin canting angle $\theta$ via the hopping $t(\theta)$, as given in Eq. 5.1.

We performed exact diagonalization of the orbital chain Eq. 5.3 for representative parameters of a doped $Y_{1-x}Ca_x\text{VO}_3$ system. Thereby we investigated the total energy including the magnetic energy $\mathcal{E}_G^{\text{mag}}(\theta)$ which follows from the bonds which are influenced by the spin canting at sites $i = 1$ and $i = 2$, see Appendix C. As expected, one finds that the energy is lowered when the spin order at the hole site and in its neighborhood is locally disturbed and permits hopping with the reduced hopping element given by Eq. 5.1. The kinetic energy $\propto t(\theta)$ is gained and part of the magnetic energy Eq. 5.1 is lost when the spins cant and rotate away from their orientation in the ideal $G$-AF phase. The optimal angle is found to be given by $\sin \theta \approx 0.42$ at $D = 2J$ and $\sin \theta \approx 0.43$ at $D = 0$, see Fig. 12. Thus, the dependence of $\theta_0$ on the charge-orbital polarization term is surprisingly weak and we may consider the angle $\sin \theta_0 \approx 0.42$ obtained for $D = 2J$ as a representative value for the analysis of doped $Y_{1-x}Ca_x\text{VO}_3$, see Sec. VII B. We have found that already rather weak charge-orbital interaction $D < J$ polarizes almost entirely the occupied orbital within the (12) bond which decouples from the remaining part of
the orbital chain.

It is worth noting that the spin structure is robust and its local modification is moderate. This contradicts naive expectations based on rather small magnetic exchange constants between $S = 1$ spins, being only a fraction of $J$ and determined by neutron experiments,\cite{Johrendt} that the kinetic energy would dominate over magnetic one since $t \gg J$. Instead, we have found that the canting of the spin structure is only moderate for the realistic parameters, see Fig. 12. This surprising result follows from large AF superexchange interactions in the vicinity of the hole, $I_c \approx 1.92J$ and $I_{ab} \approx 4.1J$, which are enhanced by small charge excitation energies $\propto J_H$. Here we used $J_H = 0.64$ eV for $\eta = J_H/U = 0.13$. Indeed, these exchange constants ($I_c$ and $I_{ab}$) are larger by approximately one order of magnitude than the exchange constants $J_e$ and $J_{ab}$ between $S = 1$ spins.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure13}
\caption{(Color online) Orbital order parameter $\langle \tau_i^z \rangle$ in the C-AF phase around the charge defect neighboring with the bond (12) shown in Fig. 11(c), obtained for an embedded orbital chain with finite field $h_G$ for increasing orbital polarization interaction $D$, see Eq. (5.12). Parameters: $V_{ab} = 0.2J$, $V_c = 0.7J$ and $t = 6.25J$.}
\end{figure}

\section{B. Orbital $t$-$J$ model for the C-AF phase}

In contrast to the G-AF phase discussed before, the spin structure of the C-AF phase is already tuned to optimize the double exchange, i.e., the hole hopping term is $t$ near the charge defect, see Fig. 11(b). An intriguing question here, however, is to what extent the spin structure is affected indirectly via the perturbations of the orbital chain. After introducing a hole, an orbital chain with an even number of sites as considered in Sec. IV C becomes an open chain with an odd number of sites and an additional constraint — the orbital at one of its ends is polarized by the charge-orbital interaction $\propto D$, and this orbital may interchange its position with the hole.

The orbital Hamiltonian which describes a hole in the C-AF phase (with G-AO order) is easily derived from Eq. (4.6).

$$H_{C} = -t(a_i^\dagger a_{i+1} + b_i^\dagger b_{i+1} + \text{H.c.}) + J \sum_{i} \tau_i^z \tau_{i+1}^z - D \sum_{i} \tau_i^z - h_G \sum_{i} (1)^i \tau_i^z. \quad (5.3)$$

It depends on the MF $h_G$ defined in Eq. (4.7) which stabilizes the G-AO order and is relevant for the C-AF phase. Here we adopted the usual notation that the bond (12) belongs to the cube surrounding the charge defect, see Fig. 1(c). As the lone electron at the undoped site is delocalized over the bond (12), the corresponding orbital is practically decoupled from the orbital chain along the $c$ axis, and is easily polarized to minimize the charge-orbital interaction by a rather weak interaction, $D \ll J$. Therefore, the order parameter $\langle \tau_i^z \rangle$ vanishes at this bond, i.e., for $i = 1$ and $i = 2$, see Fig. 13. One finds as well that the orbital moments $\langle \tau_i^z \rangle$ are undisturbed and alternate in the remaining part of the chain, as expected for the G-AO order.

The most important consequence of the fragmentation of the orbital chain by the presence of a doped hole is the alternation of orbital correlations $\langle \tau_i^z \tau_{i+1}^z \rangle$ shown in Fig. 13. The hole due to the confinement by the defect potential moves predominantly on the bond (12) which leads to strong orbital fluctuations on sites 1 and 2. These strong fluctuations suppress the correlations on the neighbor bond (23) (and on the equivalent bond ($1L_z$) under periodic boundary conditions).

Therefore, bonds with enhanced and reduced orbital fluctuations $|\langle \tau_i^z \tau_{i+1}^z \rangle|$ alternate along the chain and, in analogy to Sec. IV C we introduce the average orbital correlation functions for strong and weak bonds: $\langle \tau_i^z \tau_{i+1}^z \rangle_{hs}$ and $\langle \tau_i^z \tau_{i+1}^z \rangle_{hw}$. This alternation is most pronounced in a free chain, see Fig. 14(b), but is sufficiently robust to survive the coupling of the chain to its neighboring sites in the $ab$ planes of the C-AF phase, see Fig. 14(a). Therefore, we find here dimerization of the orbital interactions around a hole which is the driving force toward dimerized FM spin interactions in a doped C-AF phase, see Sec. VI B. We also note that the alternation of orbital bond strength induced by the holes in the C-AF phase is reminiscent to the bond alternation induced by large charge-orbital interaction $D$, see Fig. 10(b).

\section{VI. SCENARIO FOR THE G-AF TO C-AF MAGNETIC TRANSITION}

\subsection{A. Statistical averaging in doped phases}

To demonstrate that a phase transition from the G-AF to C-AF phase indeed occurs with increasing doping $x$ in the $Y_{1-x}Ca_xVO_3$ system, we use here a statistical
We introduce statistical weights or probabilities,

\[ w_h \equiv \frac{1}{L^2}, \quad w_e \equiv \frac{3}{L^2}, \quad w_0 \equiv \frac{L^2 - 4}{L^2}, \quad (6.1) \]

for finding a chain doped by a hole \((w_h)\) or an undoped chain next to a defect \((w_e)\), respectively. Chains separated from a cube with a defect site occur with the complementary probability \(w_0 = 1 - w_h - w_e\). These weights will be used below to: (i) estimate to what extent dimerized interactions develop in the doped C-AF phase (in Sec. [VI.B]), (ii) obtain the energy of both AF phases which compete with each other, and (iii) investigate whether a phase transition could occur from the G-AF to the C-AF phase in the low doping regime, see Sec. [VI.C]

### B. Dimerization in orbital chains

As we have shown in Sec. [VI.B] a doped hole breaks the orbital chains, suppresses locally the orbital fluctuations and thus induces dimerized orbital correlations (see Fig. [10]). To some extent a similar dimerization occurs also in the undoped orbital chains that are direct neighbors of charge defects (see Fig. [10]). Although the dimerized orbital correlations occur in the chain that contains a hole, we assume that the magnetic order and excitations will reflect an average alternation in the doped \(Y_{1-x}Ca_xVO_3\) crystal. Therefore, we average here the orbital correlations which occur on stronger and weaker fluctuating orbital bonds over the entire sample.

The orbital correlation function for the undoped chain \(\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle^{(0)} = -0.437\) is modified when doping \(x\) increases, and the fraction of bonds with stronger and weaker fluctuations gradually increases. Using the stronger and weaker orbital correlations calculated for the C-AF phase both for an undoped chain near the charge defect, \(\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle_{e(hw)}\) (Sec. [I.V.C]), and for a chain containing a hole, \(\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle_{hs(hw)}\) (Sec. [VI.B]), the average orbital correlations for strong and weak bonds can be evaluated as follows:

\[
\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle_s = (1 - w_h - w_e)\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle^{(0)} + w_e\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle_{es(hw)} + w_h\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle_{hs(hw)}; (6.2)
\]

\[
\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle_w = (1 - w_h - w_e)\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle^{(0)} + w_e\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle_{ew(hw)} + w_h\langle \vec{\tau}_i \cdot \vec{\tau}_{i+1} \rangle_{hw}(6.3)
\]
The average orbital correlation function, shown in Fig. 15(a), increases with doping. At the same time the average orbital correlation function, 

$$\langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_a = \frac{1}{2} \left( \langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_s + \langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_w \right),$$

increases somewhat with $x$, indicating overall reduction of orbital fluctuations with increasing doping.

The FM exchange constants along the $c$ axis also alternate when the orbital state in dimerized, see Fig. 15(b). They follow from the superexchange term in the spin-orbital model Eq. (3.3) by inserting average orbital correlations on strong (weak) bond into the formula for the exchange constant, which follows from the superexchange along the $c$ axis:

$$J_{cs} = \frac{1}{2} \left\{ \epsilon \eta_1 - [r_1 - \eta(r_1 + r_3)] \right\} \times \left( \frac{1}{4} + \langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_s - \frac{2}{3} \eta_3 \langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_s \right),$$

$$J_{cw} = \frac{1}{2} \left\{ \epsilon \eta_1 - [r_1 - \eta(r_1 + r_3)] \right\} \times \left( \frac{1}{4} + \langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_w - \frac{2}{3} \eta_3 \langle \vec{r}_i \cdot \vec{r}_{i+1} \rangle_w \right).$$

Anisotropy between the exchange constants $J_{cs}$ and $J_{cw}$, shown in Fig. 15(b), is caused by the alternating orbital correlations between strong and weak bonds, and increases with increasing doping $x$. The exchange constants may be thus expressed by the average exchange $J_a$ and the anisotropy $\delta_c > 0$ as follows:

$$J_{cs} = J_a (1 + \delta_c),$$

$$J_{cw} = J_a (1 - \delta_c).$$

The average FM interaction $J_a < 0$ is gradually weakened by reduced orbital fluctuations in a doped system. One finds $J_a = -0.245J$ and $J_a = -0.229J$ for $x = 0$ and $x = 0.02$, respectively. In the present approach the anisotropy increases linearly with doping $x$ and amounts to $\delta_c = 0.117$ at $x = 0$. This anisotropy is much weaker than that found in the undoped YVO$_3$ at $T = 85$ K, where $\delta_c = 0.35$. However, one should keep in mind that the above experimental result concerns the undoped compound ($x = 0$), where the present mechanism of dimerization is absent and only thermal spin fluctuations contribute. One expects that the present anisotropy of the FM exchange constants would be enhanced by the interchain coupling and by thermal fluctuations, both effects not included in the present approach, and it would be then higher then in the undoped compound YVO$_3$.

C. Transition to dimerized C-AF phase

The energy of the doped $G$-AF and C-AF phase was analyzed in a similar way — we evaluated the energy changes with respect to the undoped phases by weighting the terms arising for the orbital chains near the charge impurity, either with or without the hole, and we used thereby the weighting factors $w_h$ and $w_0$, see Eqs. (6.1). In the undoped YVO$_3$ (at $x = 0$) one finds the G-AF phase, but the energy of the C-AF is only larger by a rather small energy $\sim 1$ meV per site, as estimated before. The magnetic excitations and optical experiments suggest that $J \sim 30$ meV. We therefore define the energy of the C-AF phase at $x = 0$ as $E_{C}(0) = 0.03J$ and use it as a parameter below.

The energies for both phases are given by:

$$E_G(x) = w_c E_{G_c} + w_h E_{G_h},$$

$$E_C(x) = w_0 E_{C(0)} + w_c E_C + w_h E_{C_h}.$$
By evaluating the energy contributions to $E_G(x)$ and $E_C(x)$ we derived the energies of both phases shown in Fig. 16. One finds that the energy of the C-AF phase decreases faster than that of the G-AF phase when doping increases. This results predominantly from the full contribution of the hopping $t$ on the bond (12) occupied by the hole in the C-AF phase, while only a fraction of the kinetic energy $t \sin \theta_0$ is released when it has to compete with robust AF order which hinders it in the G-AF phase.

**VII. DISCUSSION AND SUMMARY**

In this paper we addressed the microscopic reasons responsible for the fast disappearance of the fragile G-AF phase with doping in Y$_{1-x}$Ca$_x$VO$_3$ compounds. Our investigation of the electronic structure in the C-AF phase demonstrated that the undoped system is a multiorbital Mott-Hubbard insulator and the upper Hubbard band consists of three subbands. The multiplet splitting corresponds to excitations identified in the optical spectroscopy.12,15,37 Next we have considered doped systems and we introduced a model for generic defects in the perovskite structure. The model is consistent with the experimentally observed variation of the optical spectra which show a distinct absorption deep in the Mott-Hubbard gap.32 Our interpretation of this maximum as originating from the vanadium states localized in the immediate neighborhood of defects turned out to be consistent with independent estimates of the binding energy of a hole close the Ca ion. This was further supported by the spectra obtained by analyzing the occupied and unoccupied vanadium states within the Hartree-Fock approximation. In this way we derived large binding energy of the hole being $\sim 1$ eV, which guarantees that the hole is confined to a cube built by vanadium ions around the Ca defect.

By reconsidering the local interaction parameters defining the multiband Hubbard model for the Y$_{1-x}$Ca$_x$VO$_3$ compounds and by analyzing the spectral functions obtained in the Hartree-Fock approach, we arrived at the conclusion that electron correlations are sufficiently strong to justify the description of doped materials with the effective spin-orbital $t$-$J$ model. This model was presented and analyzed for both competing AF phases: the G-AF phase stable at low doping, and the C-AF phase which takes over above the critical doping $x_c \approx 0.02$. The crucial observation is that the kinetic energy of the hole is controlled by the spin configuration, i.e., by a double exchange mechanism similar to that responsible for the ferromagnetic phase in doped manganites.24,25 This makes the hopping processes in the two phases distinct along the $c$ axis, where one phase has FM and the other one AF spin correlations. In the $ab$ plane both phases have similar AF correlations, i.e., hole hopping is suppressed here by the spin order. Thus, the main difference arises from the hopping along the $c$ axis which is not hindered in the C-AF phase and favors this phase. However, spins in the G-AF phase may adjust by tilting due to the double exchange and allow also for substantial gain of the kinetic energy. One might expect that the spins would cant to an almost FM alignment to favor the kinetic energy as $t \gg J$, where $J/4$ is the typical AF superexchange constant between $S = 1$ spins, which also determines the spin waves in the G-AF phase of YVO$_3$.

Yet the double exchange mechanism, i.e., the canting of spins, is not controlled by $J$ but by the exchange interactions $I_c$ and $I_{ab}$ around the hole site. These interactions couple the $s = 1/2$ spin at a V$^{4+}$ ion with the neighboring $S = 1$ spins — they are much larger than the energy scale $J$ as these processes arise from exchange interactions violating Hund’s exchange $J_H$ but not creating $d^9$ configurations which cost the energy $U$, see Eqs. 78. Thus, the canting of spins is opposed by rather strong AF interactions and the kinetic energy gain in the G-AF phase turns out to be only a fraction of the one obtained from the FM bonds in the C-AF phase.29 As a result, the G-AF phase is stable in a window of low Ca doping, approximately for $0 \leq x < 0.02$. In this way we have identified the leading mechanism stabilizing the C-AF phase in doped Y$_{1-x}$Ca$_x$VO$_3$ which stems from spin-orbital physics: free hole hopping $\propto t$ on the bonds in the vicinity of the Ca defects accompanied by orbital fluctuations along the remaining FM bonds along the $c$ axis.

We have analyzed the differences in spin and orbital correlations around the defect states between the two AF phases: the G-AF and the C-AF phase. In the G-AF phase, stable at low doping, no orbital fluctuations can occur along the $c$ axis due to the static nature of the C-AO order. It is for this reason that the orbital correlations are rather easily modified in the neighborhood of the Ca defect and the occupied orbital states follow the orbital polarization interaction imposed by the de-

![FIG. 16: (Color online) Energies of two competing magnetic phases as function of doping concentration $x$: G-AF phase (dashed line) and C-AF phase (solid line) obtained from Eqs. (6.8) and (6.9), respectively. Parameters: $V_{ab} = 0.2J$, $V_c = 0.7J$, $t = 6.25J$, $E_C(0) = 0.03J.$](image)
fect. On the contrary, in the C-AF phase strong orbital fluctuations oppose the orbital polarization. Thus the orbitals are prevented to rotate toward the orientations preferred by the charge-orbital polarization interactions, as shown in Fig. 10.

As an important byproduct of the present study we have discovered that dimerization of orbital correlations along the c axis is a natural consequence of doping and may be considered as induced by hole defects in the orbital chains. In fact, a doped hole breaks the orbital chain and generates alternating orbital bond correlations. Due to the spin-orbital coupling, this alternation in the orbital subsystem induces the alternation of stronger and weaker effective FM exchange interactions along the c axis. Therefore, the performed analysis leads to a prediction that dimerization of the FM exchange interactions should be enhanced by doping. We emphasize that this mechanism of dimerization is distinct from thermal fluctuations that are necessary to stabilize dimerized spin and orbital interactions in the undoped spin-orbital chain. We expect that both mechanisms: (i) orbital-Peierls dimerization and (ii) defect induced dimerization of orbital correlations analyzed here, will support each other in doped Y$_1-x$Ca$_x$VO$_3$.

Summarizing, we have shown that a phase transition to the C-AF phase can be explained by the double exchange mechanism using the spin-orbital physics of the doped RVO$_3$ vanadates, as the kinetic energy of doped holes is much lower in the C-AF phase and this energy gain compensates the loss of the magnetic superexchange energy already at rather low doping $x \approx 0.02$. We have shown that the experimentally observed magnetic transition to the C-AF phase may be reproduced within the presented microscopic model using the parameters consistent with other experimental data.

Another challenging problem, not addressed here, is a surprising stability of the C-AF phase under doping in La$_{1-x}$Sr$_x$VO$_3$ compounds. The present calculations have shown that large binding energy confines doped holes to the immediate neighborhood of Ca ions in Y$_{1-x}$Ca$_x$VO$_3$. If a similar hole confinement takes place also in La$_{1-x}$Sr$_x$VO$_3$, it could explain the insulating state found in these compounds in a broad range of doping $0 < x < 0.18$. Although the theoretical explanation of the evolution of electronic and magnetic properties of La$_{1-x}$Sr$_x$VO$_3$ has still to be constructed, we note that large binding energy between holes and defect states is consistent with these observations. Therefore, we suggest that it is a necessary ingredient of any realistic theoretical approach to the doped vanadium perovskites.

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Appendix A: Orbital polarization transition

In order to get a qualitative insight into the mechanism of local suppression of orbital fluctuations near the impurity in the C-AF phase we consider a quantum transition to the orbital polarization on a single bond (between sites $i = 1$ and $i = 2$ in Fig. 7) from the singlet state $\tau_i^1, \tau_j^1 = -3/4$ to the fully polarized state with $\langle \tau_i^1 \rangle = 1/2$. The orbital Hamiltonian obtained from Eq. (3.2) for the present toy orbital model with a bond $\langle \tau_i^1 \rangle$ along the c axis is

$$H = J_{r1} \left( \tau_i^1 \cdot \tau_2^1 + \frac{1}{4} - D \left( \tau_i^1 + \tau_2^1 \right) \right). \quad (A1)$$

We have chosen here the polarization interaction $-D$ which favors $\langle \tau_i^1 \rangle = 1/2$, but an equivalent result is obtained for $+D$. The Hamiltonian Eq. (A1) is easily diagonalized using the basis $|n\rangle$:

$$|1\rangle = a_1^\dagger a_2^\dagger |0\rangle,$$
$$|2\rangle = \frac{1}{\sqrt{2}} \left( a_1^\dagger b_2^\dagger + b_1^\dagger a_2^\dagger \right) |0\rangle,$$
$$|3\rangle = b_1^\dagger b_2^\dagger |0\rangle,$$
$$|4\rangle = \frac{1}{\sqrt{2}} \left( a_1^\dagger b_2^\dagger - b_1^\dagger a_2^\dagger \right) |0\rangle, \quad (A2)$$

where $|0\rangle$ stands for the vacuum. One finds that the Hamiltonian matrix $H_{nm} = \langle n|H|m\rangle$ takes the following form,

$$H_{nm} = \begin{pmatrix}
\frac{1}{2}J_{r1} & -\frac{1}{\sqrt{2}}D & 0 & 0 \\
-\frac{1}{\sqrt{2}}D & \frac{1}{2}J_{r1} & -\frac{1}{\sqrt{2}}D & 0 \\
0 & -\frac{1}{2}D & \frac{1}{2}J_{r1} & 0 \\
0 & 0 & 0 & -\frac{1}{2}J_{r1}
\end{pmatrix}, \quad (A3)$$

and the triplet components $\{|1\rangle, |2\rangle, |3\rangle\}$ are coupled by the orbital polarization term $\propto D$. The eigenvalues are:

$$\lambda_1 = \frac{1}{2}J_{r1}, \quad (A4)$$
$$\lambda_{2,3} = \frac{1}{2}J_{r1} \pm D, \quad (A5)$$
$$\lambda_4 = -\frac{1}{2}J_{r1}. \quad (A6)$$

As expected, the splitting between the singlet $|4\rangle$ and the triplet $\{|1\rangle, |2\rangle, |3\rangle\}$ state is $J_{r1}$ at $D = 0$. It decreases linearly with increasing $D$ and one finds a quantum transition at the critical value of polarization interaction,

$$D_c = J_{r1}. \quad (A7)$$
This transition is first order and occurs as a level crossing between the singlet and fully polarized triplet component with energy \( \lambda_3 = \frac{1}{3} J r_1 - D \). Above the transition (for \( D > J r_1 \)), the orbital state is fully polarized by the charge-orbital interaction and \( \langle \tau^i_i \rangle = 1/2 \) for \( i = 1, 2 \). In this orbital state fluctuations present in the orbital singlet are suppressed and triplet correlations take over, \( \langle \tau^1_1 \tau^2_2 \rangle = 1/4 \).

The described orbital transition modifies also the magnetic state in the coupled spin-orbital system. While the fluctuating orbitals in the singlet state support FM spin correlations, such a polarized orbital state at \( D > D_c \) supports instead AF spin correlations along the bond in the spin-orbital model Eq. (3.3).

**Appendix B: Superexchange for the \( d^1-d^2 \) bond**

Here we present the derivation of the superexchange between the \( V^{4+} \) ion generated by a doped hole and its \( V^{3+} \) neighbors. When a hole is doped at a vanadium ion in YVO\(_3\), the resulting spin electronic configuration is \( c_1^1 \{ xy_1^1 \} \), corresponding to \( S = 1/2 \) spin. The superexchange interaction follows from an interchange of charge between two sites in the excitation process, \( (c^1_1)(c^1_2(a/b)^1)_j = (c^1_1(a/b)^1)_j(c^1_2) \), and involves only Hund’s exchange \( J_H \) due to the intermediate low-spin \( (S = 0) \) excited state \( (c^1_1(a/b)^1)_j \). Note that these excitations contribute to the AF superexchange, while the charge transitions between two ions in FM configuration do not involve any excitation energy and are treated explicitly by the hopping term Eq. (3.9), similar as in doped manganites.\(^23\)

The actual occupancy \( c_1^1 \) and \( c_1^1(a/b)^1 \) of \( V^{4+} \) and \( V^{3+} \) ions is responsible for different contributions to the AF superexchange between the bonds along the \( c \) axis and in the \( ab \) planes. Consider first a bond \( (ij) \parallel c \). The excitations occur here solely by the hopping of an \( a \) (or \( b \)) electron to the neighboring site occupied by the hole and back, as shown in Figs. 17(a) and 17(b). The excited state, either \( c_1^1a_1^1 \) or \( c_1^1b_1^1 \), has to be next projected on the low-spin \( (S = 0) \) state, with the excitation energy of \( 2J_H \). As usual, the final state has the same charge distribution as the initial one, and the spin configuration is either the same as in Fig. 17(c), or the \( z \)-th components of spins at both sites have been changed by one, see Fig. 17(d). One finds

\[
H_i^{(c)} = \frac{t^2}{4J_H} \sum_{(ij)\parallel c} \left( \vec{S}_i \cdot \vec{S}_j - \frac{1}{2} \right) \times \{ n_i(1-n_j) + n_j(1-n_i) \},
\]

where \( n_i \) is the number of electrons in the \( \{a,b\} \) orbital doublet, see Eq. (3.4).

The charge transitions which contribute to the superexchange along the bonds in \( ab \) plane, \( (ij) \in ab \), have a richer structure as both \( t_{2g} \) electrons at a given \( V^{3+} \) ion may be allowed to hop to the hole site. While the \( c \) electron hopping is allowed along each bond, the second electron is either allowed to hop or not, depending on its flavor; we show in Fig. 18 a case with both electrons contributing to the superexchange. First, the electron in the degenerate \( \{a,b\} \) orbitals may hop to the hole site, see Fig. 18(b). This process is similar to the one for the bond along the \( c \) axis, but is allowed only for half of the bonds, depending on whether the hopping for the occupied orbital flavor is allowed or not (here we consider an \( a \) electron with the hopping allowed along the \( b \) axis). It leads to two final states shown in Figs. 18(c) and 18(d). As a new feature one finds in addition the transitions by both \( c \) electrons which create a double occupancy in \( c \) orbital on the undoped site, \( c_1^2 \), and leave behind the \( a \) (or \( b \)) electron [Fig. 18(e)]. This state has been projected onto the \( t_{2g}^2 \) eigenstates with energies \( 2J_H \) and \( 5J_H \), see Fig. 1 of Ref. 18. The final states, shown in Figs. 18(f) and 18(g), have again the same \( z \)-th spin states as the initial state, or the spins are flipped. One finds thus the superexchange,

\[
H_i^{(ab)} = \frac{t^2}{4J_H} \sum_{(ij)\parallel a} \left( \vec{S}_i \cdot \vec{S}_j - \frac{1}{2} \right) \times \{ n_{ia}(1-n_j) + n_{ja}(1-n_i) \} + \frac{t^2}{4J_H} \sum_{(ij)\parallel b} \left( \vec{S}_i \cdot \vec{S}_j - \frac{1}{2} \right) \times \{ n_{ib}(1-n_j) + n_{ja}(1-n_i) \} + \frac{2t^2}{5J_H} \sum_{(ij)\parallel ab} \left( \vec{S}_i \cdot \vec{S}_j - \frac{1}{2} \right) \times \{ n_i(1-n_j) + n_j(1-n_i) \}.
\]
The first two terms contribute only when the electron in the \{a, b\} doublet is allowed to hop along the bond \(\langle ij \rangle\) in the \(ab\) plane, while the last term arises from the \(c^2\) double occupancies and has no orbital dependence.

Note that after the charge excitation the same orbital configuration has to be reached in the final state. Therefore, neither in this case (Fig. 13), nor for the bond along the \(c\) axis considered in Fig. 17 orbital fluctuations are present. The orbital dependence occurs in the interactions derived for the \(ab\) plane Eq. (12), but for the calculations for 1D orbital chains along the \(c\) axis, performed in this paper, it suffices to average over the orbital configuration on the sites around the hole. Using the constraint Eq. (2.3) one finds:

\[
\begin{align*}
H_i^{(c)} &= \frac{t^2}{4J_H} \sum_{(ij)\parallel c} \left( \vec{S}_i \cdot \vec{S}_j - \frac{1}{2} \right) (2 - n_j - n_i), \\
H_i^{(ab)} &= \frac{t^2}{8J_H} \sum_{(ij)\parallel ab} \left( \vec{S}_i \cdot \vec{S}_j - \frac{1}{2} \right) (2 - n_j - n_i) \\
&\quad + \frac{2t^2}{5J_H} \sum_{(ij)\parallel ab} \left( \vec{S}_i \cdot \vec{S}_j - \frac{1}{2} \right) (2 - n_j - n_i) \tag{B3}
\end{align*}
\]

This result is used in Sec. III to investigate 1D orbital chains which contain one doped hole.

**Appendix C: Energy evaluation in the double exchange model**

Here we present the technical details of the calculations performed in Sec. IIIA. The optimal canting angle for the \(d^3 - d^2\) bond in the G-AF phase is obtained by minimizing the orbital problem Eq. (5.2) together with the magnetic energy \(E_{G}^{mag}(\theta)\) which follows from the bonds which are influenced by the spin canting at sites \(i = 1\) and \(i = 2\). This energy consists of several contributions due to the bonds along the \(c\) axis and in the \(ab\) planes. When the considered site, either \(i = 1\) or \(i = 2\), is undoped, this energy is determined by the superexchange Eq. (3.9) between two \(S = 1\) spins, while for the hole site it follows from the superexchange Eq. (5.14) between the spin \(s = 1/2\) at the hole site and its \(S = 1\) neighbor spin. Using the MF approximation for the superexchange terms one finds:

\[
E_{G}^{mag}(\theta) = I_c \sum_{i=1,2} \{ (s_i^z S_{i-1}^z) + (s_i^z S_{i+1}^z) \} (1 - n_i) n_j \\
+ I_{ab} \sum_{i=1,2} \sum_{(ij)\parallel ab} \langle s_i^z S_j^z \rangle (1 - n_i) n_j \\
+ J_s \left\{ (1 - n_2) \langle S_1^z S_N^z \rangle + (1 - n_1) \langle S_2^z S_N^z \rangle \right\} \\
+ J_{ab}^s (1 - n_2) \sum_{(1j)\parallel ab} \langle S_1^z \rangle \langle S_j^z \rangle \\
+ J_{ab}^s (1 - n_1) \sum_{(2j)\parallel ab} \langle S_2^z \rangle \langle S_j^z \rangle \tag{C1}
\]

The hole disturbs the G-AF order locally, so the other bonds are only weakly influenced and one may evaluate the correlation functions in Eq. (C1) using the classical spin order in this phase, see Eqs. (4.2). When the hole is at site \(i = 1\), i.e., in the \(|f\rangle\) state of Fig. 11a) (the other \(|i\rangle\) configuration with a hole at site \(i = 2\) is equivalent), we have used:

\[
\begin{align*}
\langle s_1^z S_2^z \rangle + \langle s_1^z S_N^z \rangle &= - \frac{1}{2} \cos(2\theta) - \frac{1}{2} \cos \theta, \tag{C2} \\
\langle s_1^z S_1^z \rangle &= - \frac{1}{2} \cos \theta, \tag{C3} \\
\langle S_2^z S_3^z \rangle &= - \cos \theta. \tag{C4}
\end{align*}
\]

Finally, the ground state of the orbital chain containing one hole in the G-AF phase may be found by minimizing the energy obtained from the 1D orbital chain Eq. (6.2), including the correction of the magnetic energy \(E_{G}^{mag}(\theta)\) Eq. (C1),

\[
E_G(\theta) = \langle H_G^h(\theta) \rangle + E_{G}^{mag}(\theta). \tag{C5}
\]
These excitations are obtained by diagonalizing the on-site Hamiltonian $\text{Eq. (2.6)}$ in the subspace of three degenerate $t_{2g}$ orbitals.

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We note that the topmost occupied orbital $\alpha = 2$ does not change as function of the strength of the orbital polarization field $\Delta_c$.

Here $(a/b)^i$ denotes a single occupancy of the $\{a, b\}$ orbital doublet at site $i$.

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Note that the exchange bonds around the hole seem to be frustrated in the latter C-AF phase, but this spin reorientation does not generate any loss of the superexchange energy since the processes that generate it are absent on the FM bonds, see Eq. (3.14).