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Variational study of the antiferromagnetic insulating phase of V_2O_3 based on *N*th order muffin-tin-orbitals

N. B. Perkins,[1] S. Di Matteo,[2] and C. R. Natoli[3]
[1]*University of Wisconsin–Madison, 1150 University Avenue, Madison, Wisconsin 53706-1390, USA*
[2]*Equipe de Physique des Surfaces et Interfaces, Institut de Physique de Rennes, UMR CNRS-UR1 6251, Université de Rennes 1, F-35042 Rennes, France*
[3]*Laboratori Nazionali di Frascati, INFN, Casella Postale 13, I-00044 Frascati, Italy*

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Motivated by recent results of *N*th order muffin-tin-orbital (NMTO) implementation of density-functional theory, we re-examine low-temperature ground-state properties of the antiferromagnetic insulating phase of vanadium sesquioxide V_2O_3. In fact, the hopping matrix elements within the nearest-neighbor vanadium pair, obtained by the NMTO-downfolding procedure, are strongly reduced compared to those previously obtained using the downfolding procedure of Castellani *et al.* [Phys. Rev. B **18**, 4945 (1978); **18**, 4967 (1978); **18**, 5001 (1978)]. This could imply a breakdown of the molecular picture. We use the NMTO hopping matrix elements as input and perform a variational study of the ground state. We find that the formation of stable molecules throughout the crystal is not favorable in this case, though the experimentally observed magnetic structure can still be obtained in the atomic variational regime. However, the resulting ground state (two t_{2g} electrons occupying the degenerate e_g doublet) is in contrast with many well-established experimental observations. We discuss the implications of this finding in the light of the importance of nonlocal electronic correlations in V_2O_3.

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I. INTRODUCTION

Vanadium sesquioxide V_2O_3 holds a very distinct place among the variety of physical systems exhibiting a metal-insulator transition (MIT). This compound is considered as a prototype of a Mott-Hubbard system: it displays a MIT from a paramagnetic metallic (PM) phase to an antiferromagnetic insulating (AFI) phase at low temperatures (≈ 150 K), and a transition from a PM phase to a paramagnetic insulating (PI) phase at a higher temperature (≈ 500 K).[1–4] In order to understand several of its properties, the knowledge of its crystal structure plays a fundamental role: in the paramagnetic phase V_2O_3 can be characterized by a corundum cell in which V ions are arranged in V-V pairs along the *c*-hexagonal axis and form a honeycomb lattice in the basal *ab* plane. All vanadium ions are equivalent: each V^{3+} ion has $3d^2$ configuration and is surrounded by a nearly perfect oxygen octahedron. However, a slight displacement in vanadium ions away from the centers of their octahedra is at the origin of a small trigonal distortion, which removes the threefold degeneracy of the t_{2g} manifold. The energy splitting between nondegenerate a_{1g} orbital and doubly degenerate e_g orbitals is Δ_t. A first-order structural transition takes place upon cooling, and the system becomes monoclinic. Simultaneously, a peculiar antiferromagnetic (AFM) spin order emerges with ferromagnetically ordered planes, antiferromagnetically stacked perpendicularly to the monoclinic b_m axis.

In late seventies, Castellani, Natoli, and Ranninger[5] (CNR) developed a unique realistic description of V_2O_3. They realized that the peculiar structure observed in the AFI phase could not be explained in terms of a single-band Hubbard model, and that the introduction of the orbital degrees of freedom into the model was a necessary ingredient in order to explain the experimental findings. The CNR model has been considered a reliable model of V_2O_3 until the end of the nineties, when several experiments, for e.g., x-ray absorption spectroscopy (XAS) by Park *et al.*[6] and nonresonant magnetic x-ray scattering by Paolasini *et al.*[7] demonstrated that this model was in need of corrections. The failure of the CNR model came from the underestimation of the value of Hund's coupling ($J \sim 0.2–0.3$ eV), entailing a spin state $S = 1/2$ on the V^{3+} ions. Instead, the experiments mentioned above independently showed that each vanadium ion has a spin $S=1$, an observation that called for a deep revision of the theoretical description of V_2O_3. For this reason, many theoretical works followed.[8–12]

In primis, the LDA+U calculation of Ezhov *et al.*[8] suggested that the $S=1$ state with no orbital degeneracy and a purely e_g occupancy is a possible candidate for the low-temperature antiferromagnetic phase. More elaborate studies on the nature of the MIT in V_2O_3 have been proposed recently by means of LDA+DMFT approaches.[11,12] In particular, Poteryaev *et al.*[12] showed that crystal field, Coulomb correlations, and orbital degrees of freedom are strongly interrelated: in their solution the trigonal distortion, strongly enhanced by correlations, acts as an external field in the orbital Hilbert space, thereby producing drastic modifications in the orbital hybridization across the transition. This corrects the drawbacks of a purely $|e_g e_g\rangle$ atomic occupancy, as it is at least qualitatively in keeping with the result of x-ray absorption spectroscopy by Park *et al.*,[6] where an evidence of a variable occupation of a_{1g} orbitals in the three phases was found (25% in the PM phase, 20% in the PI phase, and 17% in the AFI phase).

A completely different approach was proposed by Mila *et al.*,[13] who adapted an old idea by Allen[14] that magnetic and optical properties of all phases of V_2O_3 show a loss of V^{3+} ion identity, and suggested that a good candidate for the ground state is a state in which vanadium $S=1$ ions form vertical bonds (molecules) with total spin $S_{\mathrm{tot}}=2$ and orbital (correlated) occupancy of the kind $(|e_g e_g; e_g a_{1g}\rangle + |e_g a_{1g}; e_g e_g\rangle)/\sqrt{2}$. Here the notation refers to the four electrons occupying the vertical molecule: two electrons on one of the two atoms of the molecule and the other two on the other atom. In our previous study[9] we showed that such a correlated molecular state is stabilized throughout the crystal if the *nonlocal* correlation energy due to delocalization of the electrons within the molecule is big compared to the in-plane interaction energy. The estimate for this correlation energy is $\simeq 90$ meV/atom,[15] if computed with V t_{2g} Wannier functions obtained by tight-binding (TB) fit to local-density approximation (LDA) linearized augmented plane wave (LAPW) calculation of Mattheiss[16] by downfolding procedure devised by CNR.[5] Later, Tanaka[10] further improved the molecular wave function by proposing that single-ion relativistic spin-orbit (SO) interaction plays an important role in determining both the ground state and the low-energy excitation spectrum of V_2O_3. In such a case the orbital angular momentum is unquenched and the molecular wave function is expressed in terms of complex orbitals.

Such a complex orbital molecular state is in agreement with most of the experimental results, whereas this is not the case for the atom-based correlated models.[8,11,12] Namely, the molecular state can account for the large contribution from the orbital magnetic moment, $\langle L\rangle \sim -0.5\ \mu_B$, observed in the nonresonant magnetic scattering experiments by Paolasini *et al.*[7] On the contrary, a real atomic $|e_g^1 e_g^2\rangle$ ground state contradicts the observation of unquenched angular momentum, since it gives $\langle L\rangle=0$. Even introducing the SO coupling, the situation does not improve. In fact, in terms of the complex orbital $e_g^{\pm}=\frac{1}{\sqrt{2}}(\mp e_g^1 - i e_g^2)$, the new ground state $|e_g^+ e_g^-\rangle$ still gives a zero expectation value for the orbital moment, due to its invariance under complex conjugation (modulo an overall sign).

As a consequence, another experimental fact cannot be explained using the $|e_g^1 e_g^2\rangle$ ground-state solution, namely, the observation of resonant $(1,1,1)_m$ monoclinic reflection by Paolasini *et al.*[7] It is now well established in Refs. 10 and 17 that this reflection is of magnetic origin. Specifically, it is due to a mixture of contributions of magnetic octupole and magnetic quadrupole moments of V atom. The octupole moment results from a quadrupole-quadrupole (E_2E_2) x-ray transition of even parity, corresponding to the operator $[(\mathbf{L}\otimes\hat{\mathbf{r}})\otimes\hat{\mathbf{r}}]_q^3$, whereas the quadrupole moment results from a dipole-quadrupole (E_1E_2) x-ray transition of odd parity, related to the spherical tensor $[\mathbf{L}\otimes\hat{\mathbf{r}}]_q^2$. Since the resonant scattering amplitude is related to the average values of both these operators in the ground state, it vanishes if computed in the $|e_g^+ e_g^-\rangle$ state, while, when evaluated in the complex orbital molecular state of Ref. 10, it describes well both energy and azimuthal experimental scans.

A further independent argument pointing toward the molecular state of V_2O_3 comes from the particular direction of the magnetic moment,[15] which lies in the plane orthogonal to the twofold symmetry axis of the $I2/a$ space group of the monoclinic cell. Why the magnetic moment is pointing along this direction cannot be understood from the symmetry consideration of the atomic state. As the local symmetry at the atomic site (C_1) is the lowest possible one, (i.e., no symmetry at all), the atomic magnetic moment could point anywhere in space. Indeed atom-based calculations[17] found also a component parallel to the twofold symmetry axis, confirming that in this case its direction is unconstrained. On the other hand, for a molecular state this twofold axis multiplied by the time-reversal operator is an exact symmetry of the system, thus constraining the moment to be orthogonal to it.

TABLE I. Transfer integrals (in eV) between vanadium t_{2g} Wannier functions derived by downfolding using the CNR procedure (first two columns) (Refs. 5 and 16) and the NMTO procedure (Ref. 18). Notations are explained in Table II in Ref. 9.

	Castellani *et al.* (Ref. 5)	Mattheiss (Ref. 16)	NMTO (Ref. 18)
μ	0.2	0.2	0.06
ρ	−0.72	−0.82	−0.51
$-\alpha$	−0.13	−0.14	0.08
β	−0.04	−0.05	−0.21
σ	0.05	0.05	−0.03
$-\tau$	−0.23	−0.27	−0.26

The molecular framework has been also confirmed by theoretical variational study based on the t_{2g} transfer integrals obtained by CNR-downfolding procedure[5] from O 2*s*, 2*p* and V 3*d* tight-binding parameters of Mattheiss,[16] in which the stability of the molecular state for reasonable values of Coulomb and exchange parameters was obtained.[9] These V t_{2g} transfer integrals are given in Table I together with those derived originally by CNR (Ref. 5) by downfolding from as TB fit by Ashkenazi and Cuchem[19] and also using oxygen NMR data. Yet recently, a new set of t_{2g} Wannier-function parameters has been proposed for V_2O_3,[18] on the basis of the state-of-the-art Nth order muffin-tin-orbital (NMTO) method by Andersen and Saha-Dasgupta.[20,21] The NMTO method provides a way to derive an effective band Hamiltonian with only few energy-selected Wannier-type orbitals by integrating out all others less important degrees of freedom. The main improvement provided by the NMTO technique in modeling Wannier-type functions comes from the fact that the functions obtained by this technique are more localized on a single site than those obtained by the fitting procedure of the LAPW bands, as real Wannier functions should be. In the case of the TB modeling of V_2O_3, this approach shows that the oxygen contribution to hopping matrix elements and renormalization effects due to hopping paths via the e_g tails, in addition to direct V-V t_{2g}-hopping interaction, are equally important and significantly modify the values of the TB parameters. These contributions were only partially taken into account in Refs. 5 and 16. Consequently, the t_{2g} transfer integrals obtained by the NMTO-downfolding technique differ significantly from those obtained by CNR downfolding (Table I). In particular, both vertical hopping integrals ρ and μ (defined in Ref. 9) are reduced in the NMTO set.

Our aim is to check whether the experimentally correct complex molecular wave function[10] is still stabilized by the new set of parameters. However, as the molecular correlation energy was found to be proportional to the product of ρ and

μ, one might suspect that the molecular stability will be lost with the new set of parameters.

The structure of the paper is as follows. In Sec. II we present a brief outline of the results of our previous work, Ref. 9, and set the notations. We then minimize the effective Hamiltonian with the NMTO parameters in Sec. III and perform a variational calculation with two kinds of variational functions: molecular and atomic. Finally, in Sec. IV, we discuss the result in the light of the experimental facts and try to draw some conclusions for the physics of V_2O_3.

II. MODEL, FORMALISM, AND NOTATIONS

We assume that the low-temperature AFI phase of V_2O_3 can be described by a superexchange spin-orbital Hamiltonian, H_{SE}, that can be derived perturbatively from a threefold degenerate t_{2g} Hubbard Hamiltonian, H_H, as done in Ref. 9, to which we refer for further detail. We can write the Hubbard Hamiltonian as

$$H_H = H_t + H_U, \tag{1}$$

where the kinetic term $H_t=\Sigma_{jj'}\Sigma_{mm'\sigma}t_{jj'}^{mm'}c_{jm\sigma}^{+}c_{j'm'\sigma}$ includes a summation over nearest-neighbor sites, over orbital $(m,m'=1,2,3)$, and spin $(\sigma=\uparrow,\downarrow)$ indexes. H_U describes the on-site Coulomb interactions U_1 (for electrons in the same orbital) and U_2 (for electrons in different orbitals) and Hund's coupling J. The hopping integrals $t_{jj'}^{mm'}$ $(m,m'=1,2,3)$ can be expressed via a reduced set of parameters: μ and ρ for out-of-plane hopping (i.e., within the molecule), α, β, σ, and τ for in-plane hopping. In Table I we present the numerical values of hopping matrix elements obtained by CNR,[5] by Mattheiss[16] through a fitting procedure of the LAPW calculations, (both obtained by using the CNR procedure for downfolding), and by Poteryaev *et al.*[12] through the NMTO-downfolding technique. We shall later use these parameters in the variational analysis, where we compare various ground-state energies. For the Coulomb repulsion U_2 and Hund's coupling J Ezhov *et al.*[8] and Mila *et al.*[13] suggested $J\sim1.0$ eV, $U_2\sim2.5$ eV. Recent optical studies of Qazilbash *et al.*,[22] however, yielded a smaller value for the Hund's coupling $J=0.5$ eV. We have described already[9] how the range of these two parameters is subjected to large fluctuations in the literature. In what follows, we shall fix $U_2\sim2.5$ eV and consider a range of $J\simeq0.4-1.0$ eV.

We further assume, as found experimentally, that at each site two t_{2g} electrons are bound into a $S=1$ state. We, therefore, derive from H_H an effective Hamiltonian, $H_{\text{eff}}=H_{SE}+H_{\text{trig}}$ to describe the insulating phase of V_2O_3, where H_{SE} and H_{trig} are given by

$$\begin{aligned} H_{SE} = &-\frac{1}{3}\frac{1}{U_2-J}\sum_{ij}[2+\vec{S}_i\cdot\vec{S}_j]O_{ij}^{(1)} \\ &-\frac{1}{4}\frac{1}{U_2+4J}\sum_{ij}[1-\vec{S}_i\cdot\vec{S}_j]O_{ij}^{(2)} \\ &-\frac{1}{12}\frac{1}{U_2+2J}\sum_{ij}[1-\vec{S}_i\cdot\vec{S}_j]O_{ij}^{(3)}, \end{aligned} \tag{2}$$

$$H_{\text{trig}} = +\sum\nolimits_{jm\sigma}\Delta_m n_{jm\sigma}. \tag{3}$$

Here $S_j=1$ is the spin at site j and $n_{jm\sigma}$ describes the occupation of the m orbital on site j by an electron with spin σ, whereas the $O_{ij}^{(k)}$ are orbital exchange operators presented in Appendix C of Ref. 9. Multiplied by the corresponding prefactors $-\frac{1}{3}\frac{1}{U_2-J}$, $-\frac{1}{4}\frac{1}{U_2+4J}$, or $-\frac{1}{12}\frac{1}{U_2+2J}$, they define the effective value of the exchange that depends on the orbital occupation of the two sites i and j along the bond direction $\langle ij\rangle$. The spin terms can be simply considered as projectors on the FM and AFM state. The term H_{trig} describes the trigonal distortion that splits the three degenerate two-electron states: $|e_g^1e_g^2\rangle\equiv|0\rangle$, $|a_{1g}e_g^1\rangle\equiv|-1\rangle$, and $|a_{1g}e_g^2\rangle\equiv|1\rangle$. The splitting energies due to this distortion are defined as $\Delta_1=\Delta_2=0$ and $\Delta_3=\Delta_t>0$ for orbitals $m=1$, 2, and 3, respectively. Δ_t is comparable in magnitude to the hopping integrals, which allows us to treat the term H_{trig} on the same level as H_{SE}.

III. RESULTS

In this section, we compare orbital and magnetic ground-state configurations of the effective Hamiltonian H_{eff} as obtained by a variational analysis with CNR and NMTO downfoldings to t_{2g} Wannier functions.

The trial wave function can be most generally written as

$$|\Psi\rangle = \Pi_n|\Psi_n\rangle = \Pi_n|\psi_n^o\rangle|\phi_n^s\rangle, \tag{4}$$

where $|\psi_n^o\rangle$ describes the orbital part and $|\phi_n^s\rangle$ refers to the spin part of the wave function on a site n.

In the following, we shall use as a variational wave function $|\Psi_n\rangle$ either an atomic state or a molecular state, with n labeling an atomic or a molecular site, respectively. In both cases, the average value of the H_{eff} over the corresponding state takes the form

$$\begin{aligned} \langle\Psi_n|\langle\Psi_m|H_{\text{eff}}|\Psi_m\rangle|\Psi_n\rangle = &\langle\psi_n^o|\langle\psi_m^o|H_{\text{eff}}^o|\psi_m^o\rangle|\psi_n^o\rangle\langle\phi_n^s| \\ &\times\langle\phi_m^s|H_{\text{eff}}^s|\phi_m^s\rangle|\phi_n^s\rangle. \end{aligned} \tag{5}$$

This factorization is possible only in the mean-field approximation, in which single-site wave functions, $|\Psi_n\rangle$, otherwise entangled, factor into orbital $|\psi_n^o\rangle$ and spin $|\phi_n^s\rangle$ parts. By this we explicitly neglect any coupled spin-orbit fluctuations. The spin averaging is straightforward: for a ferromagnetic (FM) bond $\langle\vec{S}_n\cdot\vec{S}_m+2\rangle_{\text{HF}}=3$ and $\langle\vec{S}_n\cdot\vec{S}_m-1\rangle_{\text{HF}}=0$, while for an antiferromagnetic bond, $\langle\vec{S}_n\cdot\vec{S}_m+2\rangle_{\text{HF}}=1$ and $\langle\vec{S}_n\cdot\vec{S}_m-1\rangle_{\text{HF}}=-2$. Orbital averaging in Eq. (5), however, requires some algebra and is discussed in Ref. 9 for both atomic and molecular states. In the following, we will first average overall possible ordered magnetic structures, and then for each type of magnetic ordering find an orbital configuration that minimizes the total energy by means of a variational procedure. Note, that we limit the number of magnetically ordered structures only to those that can be realized on the corundum unit cell.

As a preliminary step, before the full minimization of the variational energy [Eq. (5)], we can compare the correlation energy of the ferromagnetic state of the vertical pair, $2\rho\mu/(U_2-J)$, with the superexchange energy in the basal plane, in order to have an idea about the relative order of magnitude of atomic and molecular energies. We remind that the correlation energy is defined as the difference between the exact ground-state energy, $E_V=-(\rho-\mu)^2/(U_2-J)$, and the ground-state energy in the Hartree-Fock approximation, $E_V^{\mathrm{HF}}-(\rho^2+\mu^2)/(U_2-J)$. The superexchange energy in the basal plane was approximated by $(\alpha^2+\tau^2)/(U_2-J)$ in Ref. 9, where we assumed that the contributions from β and σ hopping matrix elements were negligible, and should rather be written as $(\beta^2+\tau^2)/(U_2-J)$ with the NMTO values of Table I, that shows that β is no more negligible, whereas α is.

There are two qualitatively different regimes of solutions. If the correlation energy is larger, the most appropriate variational wave function for the whole H_{eff} must be constructed in terms of molecular units with $S_z^M=2$ and orbital part $|\psi_n^\rho\rangle$ given by

$$|\psi_\pm^\rho\rangle_{ab}=\frac{1}{\sqrt{2}}(|\pm 1\rangle_a|0\rangle_b+|\pm 1\rangle_b|0\rangle_a), \qquad (6)$$

where a and b define two sites of the vertical molecule, and ± 1 and 0 denote the value of z component of the pseudospin operator defining the orbital state.

If, instead, the values of the exchange energy in the basal plane are larger than the correlation energy, the appropriate variational wave function is atomiclike and should be written as

$$|\psi_i^\rho\rangle=\cos\,\theta_i|0\rangle_i+\sin\,\theta_i(\cos\,\psi_i|1\rangle_i+\sin\,\psi_i|-1\rangle_i). \qquad (7)$$

Contrary to the molecular case, this wave function allows all three states $|0\rangle_i$, $|1\rangle_i$, and $|-1\rangle_i$ to be present without any *a priori* restriction on their relative weight. The relative weight of these three states is then determined through the minimization procedure with respect to the variational parameters θ_i and ψ_i.

As quantitatively shown in Ref. 9, Eqs. (6.19) and (6.20), in order to determine the nature (atomic or molecularlike) of the ground state, we need to compare the absolute value of the ratio of the molecular correlation energy (per atom) and the in-plane exchange energy, computed with Mattheiss's parameters and new NMTO set of parameters. We obtain $\rho\mu/(\alpha^2+\tau^2)=1.7$ and 0.26 for Mattheiss and NMTO set, respectively. The strong reduction in this ratio for NMTO set suggests that NMTO parameters do not favor the formation of the molecular state.

There are a few possible reasons for such large difference in the results of the two approaches. The discrepancy may be the consequence of the fact that NMTO method more accurately treats the effect of trigonal distortion on hopping matrix elements. In the approach of Mattheiss the influence of the trigonal distortion on matrix elements was assumed to be small and was neglected, while in the NMTO approach, the $a_{1g}-a_{1g}$ hopping along the vertical bond, ρ, decreases significantly with the increase in the trigonal distortion.

After this preliminary analysis we can now perform the minimization of the effective Hamiltonian with NMTO set of parameters and compare the results with the equivalent minimization procedure performed in Ref. 9 with Mattheiss's parameters. As in Ref. 9, we examine the following four magnetic phases: (1) AFM phase—all three in-plane bonds are antiferromagnetic; (2) RS phase—one in-plane bond is ferromagnetic and the other two are antiferromagnetic; (this is the spin structure experimentally observed in V_2O_3); (3) ARS phase—one in-plane bond is antiferromagnetic and the other two are ferromagnetic; (4) FM phase—all three in-plane bonds are ferromagnetic.

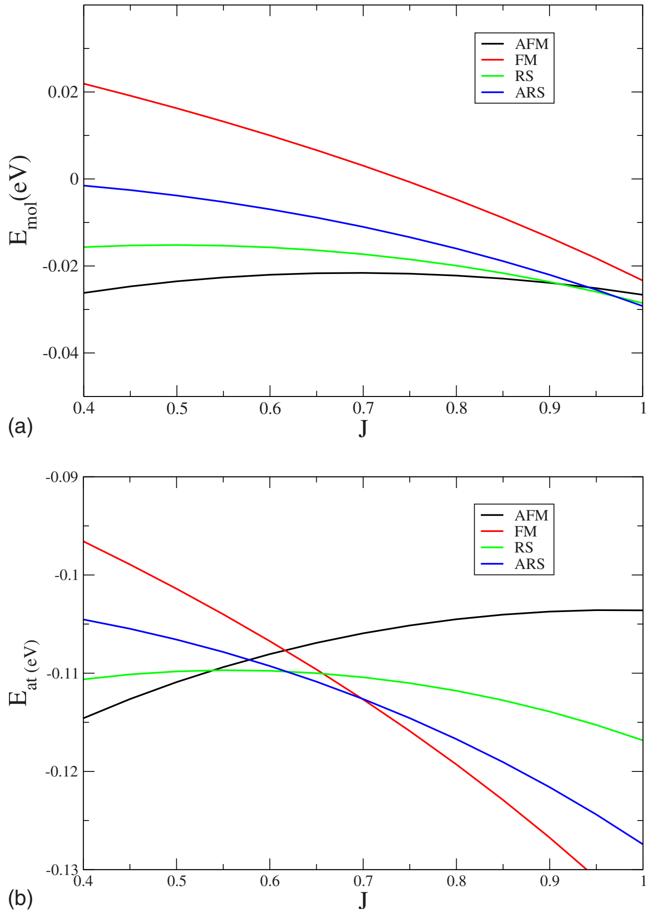

FIG. 1. (Color online) The energy per V atom as a function of J for different spin configurations (AFM, RS, ARS, and FM type). The hopping parameters are defined by NMTO method (Ref. 18) trigonal splitting $\Delta_t=0.27$ eV. In panel (a) the minimization is performed with molecular trial wave function [Eq. (6)], while in panel (b) the minimization is performed with atomic trial wave function [Eq. (7)].

Figure 1 shows the plot of energy per V ion, E_V, obtained with (a) molecular and (b) atomic variational functions using the NMTO set of parameters as a function of Hund's coupling J and for $U_2=2.5$ eV. A direct comparison between Fig. 1(a) and Fig. 1(b) shows that for all values of J the energy of the atomic state is lower than the energy of the molecular state. This confirms what we had more qualitatively suggested above—that the molecular state is not supported by the NMTO calculations.

The region of stability of experimentally observed RS magnetic structure is again rather small, as we have obtained previously with Mattheiss's parameters for the molecular state. In this case, this region also shifts toward a lower value of Hund's coupling, $J\simeq 0.54-0.62$ eV. This value is close to

$J=0.5$ eV, extracted from optical studies of Qazilbash *et al.*,[22] as well as to the old value $J=0.59$ eV given by Tanabe and Sugano[23] by fitting optical spectra and at odds with the much bigger values ($J\sim 1$ eV) recently used in the literature.[8]

For the orbital structure, the minimization gives the values of the orbital-mixing angles $\theta_i \simeq 0$ and $\psi_i \simeq \pi/2$ at all sites for the RS configurations, i.e., an orbital wave function $|\psi_i^\rho\rangle = |0\rangle_i \equiv |e_g^1 e_g^2\rangle$. This is the solution without orbital degeneracy as found by Ezhov *et al.*[8] The absence of a_{1g} electrons in the solution can be understood as follows: the small gain in the kinetic energy due to the significant reduction in the hopping matrix elements in the NMTO calculations cannot compensate the effect of the trigonal splitting, which pushes a_{1g} orbital to higher energies and favors the occupancy of the $|0\rangle$ states on all the atoms. As a result, the ground state is a nondegenerate e_g doublet and the orbital degeneracy is completely lifted, contrary to the ground states found in Refs. 9 and 13, where the important a_{1g} contribution to the kinetic energy in the molecule due to the $a_{1g}-a_{1g}$ hopping term ρ allowed a finite occupancy of a_{1g} orbitals. It is worth mentioning that even with Mattheiss set of parameters it was possible to find a ground state $|e_g e_g\rangle$, however, only for larger values of the trigonal splitting $\Delta_t > 0.4$ eV.

One more remark: due to the competing presence of the AFM, ARS, and FM phases, the stabilization energy of the RS atomic solution is rather small, the first excited state is located about 2 meV above the ground state. Despite all differences between the ground-state solutions obtained with NMTO and Mattheiss's parameters, this is a common feature which is apparent from Fig. 1 and from Figs. 5 and 8 of Ref. 9: both the stability region and the stabilization energy for the ground state with RS magnetic structure are much reduced in contrast with the spin $S=1/2$ case considered by CNR (Ref. 5). Finally, as one can see from Fig. 1(b), the RS spin structure can also be realized in the molecular state with $J \simeq 0.92-0.96$ eV, which, however, is higher than commonly accepted range of Hund's coupling values.

To illustrate more completely the properties of the effective spin-orbital model, Eq. (5), in Fig. 2 we present its ground-state phase diagram in the parameter space specified by α/τ and J/U_2. All other parameters are taken from the NMTO set and we consider the trigonal splitting $\Delta_t = 0.27$ eV. From Fig. 2 it can be seen that the ground state is successively changed from AFM to FM phase as the Hund's coupling increased. In order to gain maximum energy from orbital-dependent exchange terms, more complicated magnetic structures are realized at the intermediate values of J, and that RS structure is stabilized in a strip between AFM and ARS phases.

The examination of orbital structure for various ground states, presented on the phase diagram (Fig. 2), has shown that orbital configurations in RS and ARS states are basically the same: the orbital degeneracy is lifted and all states are occupied by only e_g electrons. For the AFM and FM phases we find a continuum of orbital degeneracies with any mixing angles θ_i and ψ_i, depending on value of the ratio J/U_2 and α/τ.

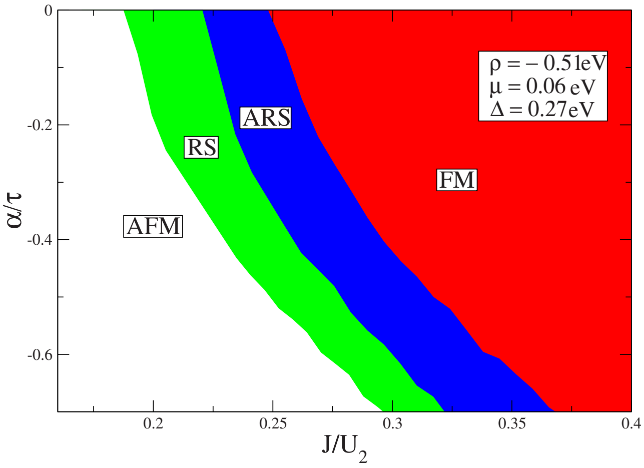

FIG. 2. (Color online) Phase diagram in the (α/τ, J/U_2) parameter plane. Other hopping parameters are taken from NMTO set from Table I. Here AFM, FM, RS, and ARS denote the corresponding types of magnetic orders. Solid lines indicate the phase boundaries.

This phase diagram is very different from other phase diagrams, which have been proposed for AFI of V_2O_3, i.e., from that of CNR model,[5] from the molecular model of Mila *et al.*,[13] and from that proposed by us in Ref. 9. The phase space occupied by RS phase is larger, and it happens at the realistic intermediate values of J/U_2.

IV. DISCUSSION

In this paper we have studied the ground state of the effective spin-orbital Hamiltonian ((2)) and compared the results obtained by CNR and NMTO downfoldings to t_{2g} Wannier functions. We computed the mean-field phase diagram and showed that the RS structure is realized at realistic intermediate values of the Hund's coupling. The phase space of the RS phase is significantly enlarged compared to our previous study,[9] although the gain in energy compared to competing phases is again small, on the order of ~ 2 meV. However, we have shown that the formation of stable molecules throughout the crystal is not favorable in this case. For all values of the Hund's coupling the minimization procedure with an atomic wave function gives a lower energy than in the minimization with a molecular wave function. Moreover, the analysis of the orbital structure of the ground state shows that the two t_{2g} electrons occupy the degenerate e_g doublet. This latter finding is not only in disagreement with the experiment of Park *et al.*,[6] as detailed in Sec. I but also with the finding that there is no detectable anisotropy of the Knight shift and no observable quadrupole splitting of the NMR spectrum,[24] which would require an almost equal weight of the three t_{2g} electrons, as obtained in the old molecular solution. Therefore, the characteristics of the ground-state configuration found starting from the NMTO set of hopping parameters (nonmolecular, purely e_g orbital filling) are rather disappointing, being in contrast with some well-established experimental facts.

We might wonder what is the origin of such a discrepancy, noticing, in particular, that the correct solution was found with the previous CNR-type t_{2g} transfer integrals. There are two possible alternative reasons.

(a) The Hubbard model does not represent a minimal model for V_2O_3: undoubtedly, the one-body parameters derived from NMTO orbitals seem to be more consistent with the spirit of the Hubbard model than those obtained by fitting the tight band parameters onto the real bands. Indeed, originally the Hubbard model was obtained by working in a Wannier-function representation for the field operators in the second quantized Hamiltonian, neglecting in the quadrilinear interaction, all terms in the creation and destruction operators not falling on the same site. Clearly, this approximation has a meaning only if one starts from the very localized Wannier basis functions, which is the case of NMTO orbitals, provided they reproduce the "correct" band structure relevant to the problem at hand. On the contrary, fitting this latter with tight-binding parameters may lead to hopping coefficients which are not derived from truly localized Wannier orbitals (in this case the corresponding Wannier wave functions have usually a finite amplitude over several distant neighbors).[25]

From this perspective, the fact that we get the wrong solution with the "good" parameters and the good solution with the "wrong" parameters, appears to be an indication that some fundamental interaction for the ground state of V_2O_3 was not taken into account in the Hubbard model. This interaction, however, was, probably, restored by the choice of the "wrong" Mattheiss's parameters. Since Mattheiss's wave functions, compared to NMTO wave functions, are more delocalized, with non-negligible amplitudes over distant neighbors, we might guess that the interaction is a correlated distant neighbor interaction, and in a sense, the simple Hubbard Hamiltonian with Mattheiss's parameters represents accidentally the good effective model for V_2O_3.

(b) The downfolding to a t_{2g} set should have been performed on a many body, rather than a single-particle basis; it is not sufficient that NMTO downfolding provides a localized Hubbard-type basis. If one agrees that the molecular ground state of V_2O_3 is stabilized because of nonlocal interactions (e.g., correlated hopping along the vertical bond), the physics of which cannot be captured within a method based on local interactions, then the NMTO downfolding, belonging to the same class of LDA-density-functional theory *ab initio* methods, must necessarily share all shortcomings of local correlated approaches. Stated differently, nonlocal correlations would lead to nonlocal one-particle effective potentials that might substantially modify the shape and the range of Wannier-type functions and, therefore, the corresponding t_{2g} transfer integrals in the case of V_2O_3.

One step in this direction has been provided by a new generation of correlated nonlocal quantum chemical *ab initio* calculations. In this approach a combined exact diagonalization *ab initio* method (EDABI) by Spalek *et al.*[26] is used as a promising method to estimate correlated hopping. This latter is based on a definite procedure of construction of the many-particle trial wave function expressed in terms of an adjustable one-particle basis, followed by the solution of a self-adjusted nonlocal and nonlinear wave equation obeyed by the basis functions. We believe that the EDABI method is particularly well suited for treating situations in which the interparticle correlations are not weak and lead to nonlocal interactions.

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