Electronic structure of $V_2O_3$: Wannier orbitals from LDA-NMTO calculations

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Using muffin-tin orbital (MTO) based NMTO-downfolding procedure within the framework of local density approximation, we construct the Wannier orbitals for the $t_{2g}$ manifold of bands in $V_2O_3$ in the paramagnetic phase. The real space representation of the one-electron Hamiltonian in the constructed Wannier function basis shows that, contrary to the popular belief, the in-plane hopping interactions are as important as the vertical pair hopping. Following the language of Di Matteo et al. [Phys. Rev. B 65 054413 (2002)], this implies, the problem of $V_2O_3$ falls in the atomic regime rather than in the molecular regime. We have also repeated our construction procedure in the low temperature monoclinic phase, for which the changes in hopping interactions are found not to be dramatic.

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I. INTRODUCTION

$V_2O_3$ has been in focus of attention since 1969 when its unusual phase diagram was discovered.1 At low temperature, pure $V_2O_3$ is an antiferromagnetic insulator (AFI) with a monoclinic, slightly distorted corundum structure, a complicated magnetic order, a moment of 1.2 $\mu_B$, and a gap of 0.66 eV.2 At $T_N$=154 K it transforms to a corundum-structured, paramagnetic metal. Upon substituting V by Ti or by application of pressure, the Neél temperature decreases and the antiferromagnetic phase vanishes above 5% Ti. Substitution of V by Cr, on the other hand, causes the Neél temperature to increase and reach 180 K for 1.8% Cr. For higher concentrations, $T_N$ stays constant and the transition is to a paramagnetic insulator. For Cr concentrations between 0.5 and 1.8% there is a second phase transition, which upon increasing temperature, or Cr concentration, is from a paramagnetic metal (PM) to a paramagnetic insulator (PI). This transition is isostructural, ends at a critical point, $(T_c, y_c) = (400 K, 0.5 \% Cr)$, and has been considered the classic example of a Mott-Hubbard transition.

In the high-temperature corundum structure (FIG. 1), all vanadium ions are equivalent and surrounded by nearly perfect oxygen octahedra. Since the covalent O-V $pd\sigma$ interaction is stronger than the $pd\pi$ interaction, the more antibonding $V d$-like $e_g$ level lies above the less antibonding $V d$-like $t_{2g}$ level and, as a consequence, the electronic configuration of $V_2O_3$ is $V^{2+}$. Now, the three-fold degenerate $t_{2g}$ level is split into an upper $a_{1g}$ and a lower, doubly degenerate $e_g$ level by a trigonal distortion, which mainly consists of a slight displacement of the vanadium ions along the vertical three-fold axis, away from the centers of their octahedra, so that the distance between a vertical vanadium pair (V 4-1 or 2-5 in FIG. 1) is slightly longer than the distance between the centers of the two octahedra.

There have been many attempts to explain these metal-insulator transitions and the spin structure of the antiferromagnetic insulating phase. The careful analysis presented in 1978 by Castellani, Natoli, and Ranninger (CNR)3 resulted in a model which remained undisputed for over twenty years: Since the $a_{1g}$ orbitals have $d_{3z^2-r^2}$ character and point towards each other, yielding a strong $dd\sigma$-like hopping integral, these orbitals on each vertical pair form bonding and antibonding levels which are split by more than twice the $a_{1g}$ crystal-field splitting and by more than the on-site Coulomb interaction. As a consequence, one electron per vanadium is used to form a spin-singlet, chemical bond between a vertical pair. The other electron enters the doubly degenerate, localized $e_g$ orbitals. Since the integrals for hopping from- and between $e_g$ orbitals are relatively small, the on-site Coulomb repulsion leads to an $S=1/2$ state and may order the occupied $e_g$ orbitals in a way consistent with the observed spin structure of the low-temperature antiferromagnetic insulator. In this structure, the spins on vanadium pairs in the $z$ and $x$ directions are aligned ferromagnetically, and those on pairs in the other two directions are aligned antiferromagnetically. This requires an orbital order in which an integral for hopping in the $x$ and $z$ directions between occupied $e_g$ orbitals is considerably smaller than between occupied and unoccupied $e_g$ orbitals. This was reviewed and discussed by Rice15 using Kugel-Khomskii’s general description of the coupling between orbital and spin degrees of freedom. The CNR model also led to a half-filled, one-band (the lowest $e_g$-band) Hubbard Hamiltonian to serve as the simplest possible electronic model for $V_2O_3$. This model was solved by Rozenberg et. al16 using the dynamical mean-field approximation (DMFT)17 and found to describe the metal-insulator transition. However, the polarized x-ray absorption experiment of Park et. al18, corroborated with multiplet calculations showed that $V 3d^2$ ions are in the
high spin ($S = 1$) state rather than in $S = 1/2$ state and the orbital occupation, which is different in different phases, is an admixture of $e_g^2\pi^2$ states with $e_g^3a_{1g}$ configurations. From that, they concluded that neither $V_2O_3$ problem can be mapped onto a single-band Hubbard model, nor the projecting out of $a_{1g}$ orbitals by means of molecular orbital formation as was done by CNR is justified. Ezkioa et. al.’s calculations within the local density approximation (LDA)+U scheme showed the importance of Hund’s rule exchange giving rise to $S = 1$ model but with only $e_g^3$ occupancy implying no orbital ordering. However, they succeeded in correctly predicting the low-temperature magnetic structure which was attributed to be stabilized by the monoclinic distortion. Nevertheless, the issue associated with the orbital ordering remained which apparently showed up its presence in several different experimental observations. To reconcile the $S = 1$ and the orbital ordering aspect, Mila et. al and Di Matteo et. al subsequently proposed two different correlated model of $c-axis$ pair states incorporating dynamical mixing of $e_g^2\pi^2$ and $e_g^3a_{1g}$ states with $S = 1$ spin configuration on each of the sites. In recent years, combined with the LDA, DMFT calculations have been carried out.

While, it is now generally accepted, a realistic theory of $V_2O_3$ must take into account the complicated electronic structure of the system, there has been no serious attempt to realistic modeling of the electronic structure of $V_2O_3$ since the early work of CNR which was crude in its various approximations and was partly semiempirical. The starting point of several of the many-body model-based calculations seem to be the vertical V-V pair model which is considered to be the predominant building blocks — the validity of such assumptions need to be re-examined in the context of accurate tight-binding (TB) modeling of $V_2O_3$.

In recent years MTO based $N-th$ order MTO method, namely NMTO method has been introduced and implemented. The method goes beyond the scope of the standard linear MTO (LMTO) method, in defining an energetically accurate basis set with a consistent description throughout the space of MT spheres and the interstitial. An important feature of the NMTO method is the so-called downfolding technique which provides an useful way to derive few-orbital Hamiltonians starting from complicated full LDA Hamiltonian by integrating out degrees of freedom not-of-interest. This procedure naturally takes into account the renormalization effect due of the integrated-out orbitals by defining energy-selective, effective orbitals which serve as the Wannier or Wannier-like orbitals for the few-orbital Hamiltonian in downfolded representation. The method provides a first-principles way of deriving the single-particle model Hamiltonian and direct generation of Wannier functions without any fitting procedure giving rise to an unique scheme that has the determinisitic nature of first-principles calculations added to the simplicity of model Hamiltonian approaches. The method has proved to be extremely successful in deriving model Hamiltonians for systems such as high-Tc cuprates, double perovskites, low-dimensional spin systems. This approach of direct generation of Wannier functions may be contrasted to that of construction of Wannier functions out of the calculated Bloch functions. Recently Anisimov et al. implemented a similar method for use in LDA+DMFT and Solovyev proposed a general LMTO-based procedure for constructing effective lattice fermion models. With other local-orbital basis sets, somewhat similar techniques can be used, but in case not all basis functions are well localized, e.g. for the set of bare LMTOs, the Wannier functions obtained for the correlated bands may not be sufficiently localized for the corresponding on-site-$U$-Hamiltonian to be realistic. For those cases, more complicated procedures for obtaining for instance those Wannier functions which minimize the spread $\langle |r - \langle r\rangle|^2 \rangle$, or those which maximize the Coulomb self-energy, has been used.

In this paper, we aim to provide an accurate tight-binding description of $V_2O_3$ by constructing the Wannier-like functions for the $t_{2g}$ Hamiltonian employing the NMTO methodology. In this context, this methodology has recently been applied for tight-binding modeling of $a_{1g}$ bands of ferromagnetic LDA+$U$ calculations to investigate the role of vertical pair from band-structure point of view. In those specific calculations, primary interest was to estimate the $c-axis$ intra-pair hopping matrix element compared to inter-pair hopping matrix elements for $a_{1g}$ bands and therefore, LDA+$U$ rather than LDA was chosen as the basis of calculations, which provides nice separation of $a_{1g}$ and $e_g^3$ bands. However, from point of view of input to realistic many-body calculations it is more suitable and preferable to start with LDA-derived Hamiltonians and the full $t_{2g}$ Hamiltonian since the $a_{1g}$ and $e_g^3$ states are both equally important as seen in experiment and the hybridization effect between $a_{1g}$ and $e_g^3$ should be taken in account. In the present work, we have therefore chosen LDA as the basis of our calculations. The present paper in that respect, should be considered as a more detail paper for the tight-binding modeling of $V_2O_3$ system. The tight-binding parameters derived in this paper in a rigorous, first-principles manner will be useful as an input to many-body variational calculation like that of Di Matteo et. al as will be discussed in section III D. The parameters can also be used for the many-body LDA+DMFT calculations. The LDA+DMFT calculations report in Ref. has been carried out using the NMTO Wannier function implementation of LDA, presented in this paper. These calculations showed the importance of correlation assisted dehybridization of $a_{1g}$ and $e_g^3$ in the description of the correlated electronic structure of $V_2O_3$ and its metal-insulator transition. Calculations within such LDA+DMFT framework has been also used to explore the comparison of doping, temperature and pressure route to metal-insulator transition in $V_2O_3$ and
to study multi-orbital effects in optical properties of V$_2$O$_3$.$^{30,31}$

In the following, in section II we discuss the crystal structure and orbital symmetry aspects in V$_2$O$_3$. Section III involves description of the results and discussion. This section is divided into several sub-sections. In the sub-section A we present the high-energy part of the LDA band-structure of rhombohedral, undoped V$_2$O$_3$ in ambient pressure. In the sub-section B we explain how downfolding within the NMTO method can be used to construct truly minimal basis sets which pick out selectively O-$p$, V-$t_{2g}$, V$e_g$ or V-$s$ bands. We also present the NMTOs - the members of such truly minimal sets of V-$t_{2g}$ and V$e_g$. With this tool at hand, in sub-section C we zoom in on the LDA $t_{2g}$ bands, where due to lowering of symmetry induced by trigonal distortion we switch on from the $t_{2g}$ representation to more appropriate $a_1g - e^g_1$ representation. We present the minimal set constructed out of $a_1g$ and $e^g_1$'s, their Wannier functions, the hopping integrals and the comparison with existing results. In sub-section D, we discuss the validity of vertical pair model and the molecular orbital based approaches in light of NMTO derived hopping integrals. We restricted our study to high temperature paramagnetic phase of pure V$_2$O$_3$ in rhombohedral, corundum structure until the sub-section E, where for the sake of completeness of our study, we also discuss the hopping integrals in the Cr-doped V$_2$O$_3$ (sub-section E) and in the low-temperature monoclinic structure (sub-section F). Finally, we conclude in section IV with summary and outlook. The essential details about the NMTO method, which will be used for construction of localized Wannier orbitals and truly minimal, downfolded basis sets can be found in the Appendix A.

II. CRYSTAL STRUCTURE AND SYMMETRY:

As mentioned in the introduction, the high temperature paramagnetic phase of V$_2$O$_3$ has the corundum structure. This structure consists of hexagonal packing of the oxygen atoms, and the vanadium atoms occupying 2/3 of the octahedral cation sites. The basic features of the corundum structure is shown in FIG. 1. The immediate surrounding of the V atoms provided by oxygen atoms has approximate octahedral symmetry. The VO$_6$ octahedra face share along the vertical direction forming V-V vertical bonds, while they edge share forming layers of honeycomb lattice, giving rise to three-dimensional network with overall rhombohedral symmetry. In the resulting corundum structure, which has R3c space group symmetry, each primitive rhombohedral unit cell contains two V$_2$O$_3$ formula units while the non-primitive hexagonal unit cell contains six V$_2$O$_3$ formula units. The experimentally determined structure of ambient pressure, pure V$_2$O$_3$, in the hexagonal setting, with lattice constants $a_H=4.952$ Å and $c_H=14.003$ Å, and V and O atoms occupying the Wyckoff positions (12c) and (18c) with internal parameters $2\gamma = 0.34630$ and $2\delta = 0.31164$, yield V-O bond lengths in the range $1.971$ Å- $2.049$ Å. The nearest-neighbor V-V distances within the hexagonal layers are $2.882$ Å while that along the vertical direction is about 6 % shorter ($2.697$ Å). As is evident from the structural figure as well as from the internal parameter value, the V atoms are displaced from their ideal positions where V atoms in the hexagonal layers would have been co-planer. This displacement causes V atoms to move away from the center of the octahedra, giving rise to three long and three short V-O bonds. The arrangement of V atoms along the hexagonal z-axis can be derived from an ideal chain structure by introducing vacancies at every third site.

The results reported in the following, for the high-temperature structure, are all carried out with rhombohedral unit cell defined by the primitive lattice translations in a Cartesian system with z-axis pointing along the vertical V-V bond and the x-axis chosen as the projection of V1-V2 onto the $xy$ plane:

$$\begin{bmatrix}
T_1 \\
T_2 \\
T_3
\end{bmatrix} = a \begin{bmatrix}
1 & 0 & \frac{\sqrt{3}}{2} \\
\frac{1}{2} & \frac{\sqrt{3}}{2} & \frac{\alpha}{2} \\
\frac{1}{2} & -\frac{\sqrt{3}}{2} & \frac{\alpha}{2}
\end{bmatrix}.$$  

where $c/a = 1.633$ and $a = 2.859$ Å. The 3-fold axis pointing along the $z-$direction are given by $T_1 + T_2 + T_3$.
FIG. 1: (Color online) The crystal structure of V\(_2\)O\(_3\) in the high-temperature paramagnetic phase. The larger (green) circles indicate the V atoms. The smaller (violet) circles surrounding the V atoms are oxygens, showing the octahedral co-ordination. The VO\(_6\) octahedra face-share along the vertical direction while they edge-share within the hexagonal layers. The unprimed and primed co-ordinate systems represent the rhombohedral co-ordinate system (z-axis pointing along the vertical V-V bond and x-axis chosen as the projection of V1-V2 in the xy plane) and the oxygen-based octahedral co-ordinate system (z’-axis pointing along O6-O5, x’-axis pointing along O3-O1) respectively.

The high-symmetry points on the Brillouin zone (BZ) as shown in FIG. 2 are given by,

2 points on the 3-fold axis and at the center of regular hexagonal faces of the BZ:

\[ Z = \pm \frac{1}{2} (G_1+G_2+G_3) = \pm \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ \frac{\alpha}{2} \end{bmatrix}, \]

6 points at the center of hexagonal faces of BZ with 2 short and 4 long edges:

\[ L = \pm \frac{1}{2} G_1 = \pm \frac{2\pi}{a} \begin{bmatrix} \frac{1}{2} \\ 0 \\ \frac{\alpha}{2} \end{bmatrix}, \quad \pm \frac{1}{2} G_2 = \pm \frac{2\pi}{a} \begin{bmatrix} -\frac{1}{2} \\ \frac{\sqrt{3}}{2} \\ \frac{\alpha}{2} \end{bmatrix}, \]

and 6 points at the center of rectangular faces:

\[ F = \pm \frac{1}{2} (G_2+G_3) = \pm \frac{2\pi}{a} \begin{bmatrix} -1 \\ 0 \\ \frac{\alpha}{2} \end{bmatrix}, \quad \pm \frac{1}{2} (G_1+G_2) \]

\[ = \pm \frac{2\pi}{a} \begin{bmatrix} \frac{1}{2} \\ \frac{\sqrt{3}}{2} \\ \frac{\alpha}{2} \end{bmatrix}, \quad \pm \frac{1}{2} (G_1+G_3) = \pm \frac{2\pi}{a} \begin{bmatrix} 1 \\ \frac{\sqrt{3}}{2} \\ \frac{\alpha}{2} \end{bmatrix} \]

The perfect octahedral crystal field surrounding of the V ions split the 3d energy levels into two-fold degenerate \( e_g \) levels, \( d_{3z^2-r^2} \) and \( d_{x^2-y^2} \) and three-fold degenerate \( t_{2g} \) levels, \( d_{x'z'} \), \( d_{y'z'} \), \( d_{x'y'} \), where the primed co-ordinate
III. RESULTS AND DISCUSSIONS

A. Corundum V₂O₅ : LDA band-structure

FIG. 4 shows the LDA one-electron band-structure of corundum V₂O₅ in PM phase, over an energy range of about 16 eV around the Fermi level (set as zero in the figure). The bands are plotted along the various symmetry directions of the rhombohedral BZ, shown in FIG. 2. The results are obtained with self-consistent potentials gener-
FIG. 3: (Color online) The crystal structure of V$_2$O$_3$ in the low-temperature monoclinic phase. For comparison, the high-temperature corundum structure is also shown in the same figure. The structures have been chosen to match at the central point of the vertical V1-V4 bond. As in FIG. the larger (red for corundum and green for monoclinic) circles indicate the V atoms. The smaller (blue for corundum and violet for monoclinic) circles surrounding the V atoms are oxygens.

ated out of the tight-binding LMTO calculation within the atomic sphere approximation (ASA). The details of the computation may be found in Appendix B. von Barth and Hedin parametrization has been used for the LDA exchange-correlation potential. The band-structure results presented in the FIG. are obtained with standard set of nearly-orthonormal LMTO’s, whose accuracy is good enough for describing the high-energy features of the band-structure. The bands are in good agreement with the linear-augmented-plane-wave (LAPW) result of Mattheiss.

Plotted bands are the orbital-projected bands or the so-called *fat-band* in the sense that the fatness of the bands in each panel is the weight of the indicated orbital in the wave-function. The co-ordinate system is chosen as that of the oxygen-based octahedral co-ordinate system with the $z'$-axis pointing along the O6-O5 direction and $x'$-axis pointing along the O3-O1 direction. As is seen, the low-lying bands below -3 eV is predominantly of oxygen character. With the choice of octahedral co-ordinate system, the V 3$d$ splits into $t_{2g}$ and $e_g$ manifolds. 12 $t_{2g}$-like bands (since there are 4 V atoms in the unit cell of the primitive rhombohedral unit cell with 3 $t_{2g}$ orbitals on each V ion) lying lower in energy compared to $e_g$-like bands cross the Fermi level, spanning an energy window from about -1.5 eV to 1.5 eV. The crystal field split $e_g$-like bands lie high up in energy from about 1.7 eV to 4 eV separated from the $t_{2g}$ manifold by a small energy gap of about 0.2 eV. V-$s$ dominated states lie further high up in energy starting from about 4.5 eV.

In the oxygen-projected band-structure, we notice, in addition to predominant fatness associated with oxygen-dominated bands lying below -3 eV, the fatness associated also with V-$d$ dominated bands. Similarly in V-$d$ projected band-structure we notice the presence of character in O-$p$ bands, which is born in by the V-$d$ – O-$p$ hybridization. It is this V-$d$ – O-$p$ hybridization, that moves the V-$d$ and O-$p$ dominated states far apart from each other with oxygen bands fully occupied and V-$d$ bands mostly empty. Due to the different orientation, $e_g$ orbitals hybridize more strongly with O-$p$ forming directed $pd\sigma$ bonds while the $t_{2g}$ orbitals bond less strongly giving rise to $pd\pi$ bonds. This is evident from the *fat-band* plots which shows that the upper part of the V-$d$ bands - the energy region dominated by the V-$e_g$ and the lower part of the O-$p$ bands has the most mixing in. We also notice the significant hybridization between V-$s$ and O-$p$ degrees of freedom.
B. Corundum $V_2O_3$: downfolded few-orbital band-structure and Wannier-functions

In the following, we demonstrate the application of NMTO-downfolding technique to produce truly minimal basis sets which may be chosen to span selected bands with as few basis orbitals as there are bands. This is illustrated by constructing truly minimal basis sets for O-p, V-t$_{2g}$, V-e$_g$ and V-s.

In the first three panels of FIG. 5, we show the bands obtained by using truly minimal sets, either O-p or V-t$_{2g}$ or V-e$_g$ in solid lines as compared to full LDA band-structure in dotted lines. The basis sets for the band-structure calculations shown in solid lines, which we call as downfolded bands, contain as many orbitals as the number of bands - hence is the name truly minimal basis set. The NMTO-downfolding procedure enables one to construct a set of O-p or V-t$_{2g}$ or V-e$_g$ muffin-tin orbitals of order $N$, NMTO, which span the O-p-like or V-t$_{2g}$-like or V-e$_g$-like bands - and no other bands - with arbitrary accuracy as $N$ increases. Such a set is exact for the energies, $\epsilon_0$,.....,$\epsilon_N$, chosen for its construction. As is seen in FIG. 5 three energy points were used for the construction of O-p, V-t$_{2g}$ and V-e$_g$ minimal sets, so the MTOs are of order $N = 2$, i.e. they are quadratic MTOs or QMTOs. Since the 18 O-p-like, 12 t$_{2g}$-like and 8 e$_g$-like bands are isolated from the above and below-lying bands, the NMTO set obtained by making the energy mesh, $\epsilon_0$,.....,$\epsilon_N$, finer and finer will converge to the Hilbert space spanned by any set of Wannier functions. In other words, the symmetrically orthogonalized set of converged NMTOs is a set of Wannier functions. As is seen, already with choice of three energy points, the downfolded bands are indistinguishable from the full LDA bands in the region of interest spanned by O-p, V-t$_{2g}$ and V-e$_g$ respectively - so, they are converged in the above-mentioned sense. The corresponding NMTOs are localized by construction as explained in the Appendix, but they are not quite orthogonal. These truly minimal NMTO sets, therefore must be symmetrically orthogonalized in order to become a set of localized Wannier functions. In FIG. 5 we show one of the three congruent orbitals of such a t$_{2g}$ NMTO set, namely $d_{x'y'}$, $d_{x^2-y^2}$ or $d_{y^2-z^2-1}$ character. In order to describe the hybridization with the O-p and the hybridization between V-t$_{2g}$ and
FIG. 5: LDA band structure of corundum-structured V$_2$O$_3$ in various energy ranges. The solid lines in different panels show the bands obtained with the truly minimal (downfolded) O-2p, V-t$_{2g}$, V-e$_g$ and V-4s NMTO basis in comparison to those obtained with full NMTO basis (shown in dotted lines). Apart from the high-energy range in the last panel, where only V-4s NMTO’s are used to form the truly minimal set, the downfolded bands in various panels are indistinguishable from the bands in the full NMTO basis, within the respective energy range of interest. The NMTO energy points, $\epsilon_{n-s}$, spanning the region of interest are shown on the right-hand side in each panel.

V-e$_g$ within the V-d manifold, the O-p character and, V-e$_g$ character for the case of d$_{x'y'}$ and V-t$_{2g}$ character for the case of d$_{x'^2−y'^2}$ or d$_{3z'^2−1}$, are folded into the tails. In fact, all the partial wave characters other than the respective active characters, d$_{x'y'}$ in the left panel, d$_{x'^2−y'^2}$ in the middle panel or d$_{3z'^2−1}$ in the last panel, are folded down in the tails. We see the strong pd$\sigma$ anti-bonds in the plots of e$_g$ NMTOs and relatively weak pd$\pi$ anti-bonds in the plot of t$_{2g}$ NMTO.

The last panel in FIG. 5 deals with the more difficult case, where the chosen bands, namely the V-s bands overlap with the other high-lying bands, e.g. V-p, O-d bands. As is seen in the figure, even for such a difficult case of bands of interest overlapping with other bands, it is possible to pick out the selected bands - in the present case four V-s bands arising from four V atoms in the unit cell. With chosen two energy points, the downfolded bands (shown in solid lines) differ from the full LDA band-structure (shown in dotted lines). Nevertheless, we see that the bottom part of the V-s derived bands has been reproduced quite well over an energy range of about 2 eV with merely two energy points. As expected, increasing the number of energy points improves the agreement. The Wannier functions of such a complex of bands which is overlapping with other band complexes are ill-defined - the corresponding set of orthogonalized NMTOs, is therefore, the set of Wannier-like functions.

As an illustrative purpose for the LMTO practitioners and to appreciate the improvements within the NMTO procedure, in FIG. 7 we also show the downfolded O-p, V-t$_{2g}$, V-e$_g$ and V-s computed within the framework of LMTO, using the standard TB-LMTO code where the nearly orthogonal LMTO’s are used for producing the truly minimal basis sets. As shown in the figure, the method works to a certain level of accuracy, provided all the l- and R-dependent $\epsilon_{\nu}$’s are put in the energy region of interest and not at the center of gravity of the respective occupied manifold as is done during the self-consistent loops of LMTO. However, within the LMTO scheme, the accuracy of the downfolded bands compared to the full basis band structure is not up to the level of satisfaction and importantly the generated minimal basis does not have the desired Wannier-like description.

C. Corundum V$_2$O$_3$: Tight-Binding Hamiltonian corresponding to t$_{2g}$ bands

A reasonable approach in the tackling the V$_2$O$_3$ problem is the t$_{2g}$ manifold that gets partially filled with two V elec-
in the plot of tight-binding Hamiltonian parameters in terms of three orbitals. In this sub-section, we therefore zoom in on to the $t_{2g}$ bands and discuss the tight-binding hopping integrals constructed out of the symmetrically orthonormalized NMTOs for the truly minimal basis set of $t_{2g}$ orbitals.

Although it would have been possible to compute the tight-binding Hamiltonian parameters in terms of three congruent orbitals $d_{x'y'}$, $d_{x'z'}$, $d_{y'z'}$, for the sake of comparison with previous results, we preferred to work with the orbitals of eigen representation of symmetry lowered $D_{4d}$ group, namely the $a_{1g}$ and the two $e_g$ orbitals which transform according to $a_{1g}$ and $e_g$ irreducible representations. As mentioned in section II, the unitary transformation relating $a_{1g}$ and $e_g$ with $d_{x'y'}$, $d_{x'z'}$, $d_{y'z'}$ is given by,

$$
\begin{pmatrix}
U_{a_{1g}} & e_g^\pi, 1 & e_g^\sigma, 2 \\
d_{x'z'} & 1/\sqrt{3} & 0 & \sqrt{2}/3 \\
d_{y'z'} & 1/\sqrt{3} & 1/\sqrt{2} & -1/\sqrt{6} \\
d_{y'z'} & 1/\sqrt{3} & -1/\sqrt{2} & -1/\sqrt{6}
\end{pmatrix}
$$

FIG.6 shows the LDA band-structure of rhombohedral V$_2$O$_3$ plotted over an energy range of -1.5 eV below the Fermi level to 4 eV above the Fermi level, now projected on to $a_{1g}$ and $e_g$ degrees of freedom. $e_g$ ($e_g^\pi$) derived bands are also seen within the energy scale of the plot. We notice significant mixing between $a_{1g}$ and $e_g$ characters in the bands of interest spanning the energy range -1.0 to 1.7 eV, arising due to $a_{1g}$-$e_g^\pi$ hopping processes between neighboring V sites. We also notice due to symmetry reason $e_g^\pi$ orbitals acquire non-significant $e_g$ ($e_g^\sigma$) character too.

In the top left panel of FIG.6 we show the downfolded band-structure obtained with truly minimal set consisting of $a_{1g}$ and $e_g$. The bands, as they should be, are identical with the downfolded bands, shown in the second panel of FIG.6 obtained using $d_{x'y'}$, $d_{x'z'}$, $d_{y'z'}$ minimal basis set. The bottom left of the figure shows the $a_{1g}$ and $e_g$ bands switching off the $a_{1g}$-$e_g^\pi$ hybridization. It is important to note that the width of the projected $a_{1g}$ band in FIG.6 is much more than that where the hybridization between $a_{1g}$ and $e_g$ is neglected. Much of the $a_{1g}$ band width therefore comes from the hybridization with $e_g^\pi$. This implies the crucial role of the $a_{1g}$ and $e_g^\pi$ hybridization in proper description of the band-structure.

The members of the truly minimal set are shown in FIG.6 the $a_{1g}$ orbital which is oriented vertically and two more planar $e_g$ orbitals. Following the mixing between $e_g$ ($e_g^\pi$) and $e_g^\sigma$ as seen in the fatband plot of FIG.6 we notice the significant presence of $e_g$ tails in the plots of $e_g^\pi$ orbitals, in addition to usual anti-bonding covalent character of the oxygen tails. The $e_g$ tails combine with the oxygen tails to produce sausage-like structures e.g. that at V sites located at 4 and 5 in the plot of $e_g^\pi$, 2.

Once we have defined the basis, in the following we compute the tight-binding hopping matrix elements between the orthonormalized, truly minimal $a_{1g}$ and $e_g$ NMTOs. As indicated in the Appendix, this is done by constructing $H^{LDA}(k)$ in the Bloch $k$-representation, in the basis of symmetrically orthonormalized NMTOs, $\{|\chi^{(N)}\rangle\}$, defined for $a_{1g}$ and $e_g^\sigma$ truly minimal set, for all $k$-points in the BZ and by subsequent Fourier transformation $H(k) \rightarrow H(r)$, for a given cluster with real-space range, $r$. Following CNR paper, for our real-space calculation, we considered a cluster of fourteen V sites - the V sites belonging to such a cluster are marked in FIG.6.
The convention adopted for numbering the V atoms is same as that of CNR. All the V atoms which have at least one shared oxygen in the VO$_6$ octahedra with that of the central V atom (marked as 1 in FIG. 1) are considered in this process. Distance-wise the short vertical V1-V4 bond forms the nearest-neighbor (NN), while the three more or less planar bonds along the directions 2, 3, and 3' form the 2nd neighbor shell with distances 6% larger than the V1-V4 bond-length of 2.697 Å. The next shell of neighbors i.e. the 3rd neighbor shell is formed by the V atoms, V$_5$, V$_6$, V$_6'$, V$_5'$, V$_6''$, V$_5''$, whose distances from the central V1 atoms differs by another 6% from that of V$_4$, V$_5$ and V$_6$. The farthest shell of neighbors, 4-th neighbor shell with distances 8% larger than the V$_1$-V$_4$ bond-length of 2.697 Å. The next shell of neighbors i.e. the 3rd neighbor shell is formed by the V atoms, V$_5$, V$_6$, V$_6'$, V$_5'$, V$_6''$, V$_5''$, whose distances from the central V1 atoms differs by another 6% from that of V$_4$, V$_5$ and V$_6$.

Before we actually attempt on numerically computing the matrix elements of the tight-binding Hamiltonian between the orthonormalized, downfolded $a_{1g}$ and $e_g$ NMTOs, a rough guess of the relative strength of various hopping matrix elements may be obtained by examining the overlap of NMTOs placed at different V sites. In FIGs. 11 and 12 we consider two such representative cases where the truly minimal NMTOs are placed along the vertical bond, 4, at sites V1 and V4 (FIG. 11) and that along the horizontal bond, 2, at sites V1 and V2 (FIG. 12). The important feature to notice is the hopping paths via the oxygen and the $e_g$ tails in addition to the V-$d$ – V-$d$ hopping paths. While the approach taken by CNR, did considered the renormalization effect coming from oxygen degrees of freedom in some form, the effect due to the renormalization coming from $e_g$'s was completed ignored, which has important consequences for hopping integrals e.g. connecting V1 and V2 sites in FIG. 12. These additional hopping paths via the $e_g$ tails increase the importance of the hopping processes in the basal plane. Focusing on to the $a_{1g} - a_{1g}$ vertical pair overlap, the biggest of all the hopping processes, we see the large, direct $a_{1g} - a_{1g}$ hopping which is bonding (negative) in nature - the red lob at V1 site overlaps with the red lob at V4 site. To understand the additional hopping contributions via the oxygen tails let us consider the renormalized $a_{1g}$ orbitals at V1 and V4 which considering only the oxygen contributions can be written, from a simplistic point of view as:

$$|Ψ_1⟩ = |d_1⟩ + λ|p_1⟩ \quad (2)$$

$$|Ψ_4⟩ = |d_4⟩ + λ|p_4⟩$$

where $λ$ is the covalency mixing parameter between V-$a_{1g}$ and O-$p$, $|p_1⟩$ and $|p_4⟩$ are the wave-function of the shared O's between the V1O$_6$ and V4O$_6$ octahedra having the same $a_{1g}$ symmetry,$|d_1⟩$ and $|d_4⟩$ are the bare $a_{1g}$ orbitals at the V1 and V4 sites. From this, we see that the overlap between the renormalized $a_{1g}$ orbitals at sites V1 and V4 is given as,

$$⟨Ψ_1,Ψ_4⟩ = ⟨d_1, d_4⟩ + λ(⟨d_1, p_1⟩ + ⟨d_1, p_4⟩) + λ^2⟨p_1, p_4⟩$$

While both the $d - d$ and $p - p$ overlaps, $⟨d_1, d_4⟩$ and $⟨p_1, p_4⟩$ are of bonding nature (the contribution $⟨p_1, p_4⟩$ is small due to the presence of prefactor $λ^2$), the sign of the correction terms, $⟨p_1, d_4⟩$ and $⟨d_1, p_4⟩$ depend on
the V1-O-V4 angle, which for the real crystal turn out to be 82.3°. Careful investigation of FIG. 11 show these overlaps to be anti-bonding (positive). These antibonding hopping paths, therefore, oppose the bonding, direct $a_{1g} - a_{1g}$ hopping, and thereby reduces the magnitude of the effective $a_{1g} - a_{1g}$ hopping from the bare $a_{1g} - a_{1g}$ hopping. We will return to this point again while discussing the crucial sensitivity of this important hopping parameter on the intricate details of the geometrical structure. We further see that the direct vertical hopping processes between $e_g^o$'s are rather weak, which get weaker by the oxygen renormalization effect.

Moving to FIG. 12 for overlap along the horizontal bond direction, 2, we see a weak overlap between the $a_{1g}$ truly minimal NMTOS while the $e_g$ like tails make the hopping between $e_g^π, 2$ and $e_g^π, 2$ nearly as strong as that between $a_{1g}$ and $e_g^π, 2$. The overlap $e_g^π, 1 - e_g^π, 1$ is anti-bonding (positive) while $e_g^π, 2 - e_g^π, 2$ and $a_{1g} - e_g^π, 2$ overlaps are bonding (negative).

In the first row of blocks in Table II we show all the hopping integrals between the central V atom (1) and the neighboring V atoms (for numbering see FIG. 1) up to 4-th neighbor obtained by Fourier transform of the downfolded $t_{2g}$ Hamiltonian in $a_{1g} - e_g^π$ basis in symmetrically orthogonalized representation. The on-site energies are shown in Table I. We see that the hoppings beyond the four predominant directions, 4, 2, 3, 3 also have non-negligible contributions. The tight-binding $t_{2g}$ bands considering interactions till 2NN, 3NN and 4NN hoppings are shown in FIG. 13. The $k$-space band-structure considering the infinite summation in the real-space Fourier series is also shown for comparison. As we see, hoppings till 4NN are essential to reproduce at least the gross features of the band-structure.

The symmetry properties of the corundum structure allows one to recast the important hopping integrals in the directions 4, 2, 3, 3 in terms of reduced parameters like $\mu, \lambda, \alpha, \beta, \sigma$ and $\tau$. The relationship of the various hopping integrals and the reduced parameters are shown in Table III.

In CNR’s original paper as well as in the later paper by Di Matteo et. al, the hopping integrals have been quoted in terms of these parameters. Di Matteo et. al
Like in FIG. 6, but for the $a_{1g}$ and two $e_{g\pi}$ NMTOs, corresponding to downfolded bands in FIG. 9. The $a_{1g}$ orbital is oriented vertically while the $e_{g\pi}$ orbitals are of more planar geometry. Due to symmetry reason, the $e_{g\pi}$ orbitals bind strongly with $e_g$ degrees of freedom at other V sites while this binding is practically negligible for $a_{1g}$.

Quoted the estimate obtained by CNR as well as the estimates obtained by TB fitting performed on LAPW band calculation of Mattheiss. These two estimates were found to be numerically not very different, although it was not clear whether the tight-binding fitting procedure included the correction due to the renormalization effect from the oxygen degrees of freedom or not. The estimate for the vertical pair hopping quoted by Di Matteo et. al. appeared to be virtually same as the estimate of $dd\sigma$ obtained by Mattheiss, although one expects some difference due to integrated out oxygen degrees of freedom. For the sake of direct comparison and for the sake of future analysis, we have extracted these reduced parameters from the estimate of our hopping integrals.

In Table IV we show the reduced parameters obtained by NMTO-downfolding technique in comparison to that of CNR and Di Matteo et. al. for the directions 4, 2, 3 and 3.
FIG. 12: Same as FIG. 11 but the NMTOs are placed one at the central V1 site and another at the neighboring V2 site along the $x$-axis. The light (dark) shaded orbitals correspond to V1 (V2). Note the importance of $e_g$ tails in providing the hopping channels, in addition to oxygen mediated and direct V-V hopping channels.
TABLE I: On-site matrix elements in the high-temperature paramagnetic metallic phase (undoped, ambient pressure V$_2$O$_3$), paramagnetic insulating ((V$_{0.962}$Cr$_{0.038}$)$_2$O$_3$) and in the low-temperature antiferromagnetic insulating (monoclinic) phase, between the $m$-orbital and the $m'$-orbital. Except for the orthonormalization, the orbitals are as defined in FIG. 10.

| | $a_{1g}$ | $e_{g,1}$ | $e_{g,2}$ | $e_{g,1}$ | $e_{g,2}$ | $a_{1g}$ | $e_{g,1}$ | $e_{g,2}$ | $a_{1g}$ |
|---|---|---|---|---|---|---|---|---|---|
| PM | | | | | | | | | |
| PI | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ |
| AFI | $a_{1g}$ | $e_{g,1}$ | $e_{g,2}$ | $e_{g,1}$ | $e_{g,2}$ | $a_{1g}$ | $a_{1g}$ | $e_{g,2}$ |
| 1 | 0.27 | 0.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| ↓ | 0.30 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| 1 | 0.28 | 0.00 | 0.01 | 0.01 | −0.04 | −0.04 | 0.00 | 0.00 |

FIG. 13: The tight-binding bands of corundum-structured V$_2$O$_3$ with various range of hopping interactions. In the first panel, hopping interactions include only the near neighbor interactions, interaction along the short vertical bond direction 4 and that along three basal bond directions, 2, 3 and 3'. In the second panel interactions until third nearest neighbors (directions 4, 2, 3, 3', 4, 8 and 8') and in the third panel interactions until forth nearest neighbors (directions 4, 2, 3, 3', 4, 8, 8', 5, 6, 6', 5, 6 and 6') are included. The last panel shows the fully converged tight-binding band-structure involving all the hopping interactions ranging from nearest-neighbor to infinity.

On examining the NMTO derived $\mu$, $\lambda$, $\alpha$, $\beta$, $\sigma$ and $\tau$ parameters in comparison to that of CNR and Di Matteo et. al. we find that the parameters are quite different from their estimates. In particular we notice the significant reduction of the vertical pair $a_{1g} - a_{1g}$ hopping, given by the parameter $\rho$ and the increased importance of the hoppings in the basal plane. In order to investigate the probable reasons for such discrepancy, one of the prime candidate on first glance appears to be the sophisticated treatment of NMTO-downfolding over that of CNR, where the effective orbitals were constructed following Anderson’s super-exchange idea, the covalency V-$d$–O-$p$ mixing parameter, $\lambda$ and the charge transfer gap $E_{3d} - E_{2p}$ were extracted from nuclear magnetic resonance and photo-emission experimental measurements which were known only to certain accuracy, and finally the matrix elements were computed in terms of second order perturbation theory in $\lambda$. Nevertheless, in spite of all the above mentioned approximations - some of which are crude- it turns out that the structural information plays a even more crucial role.

We consider in the following the specific case of verti-
TABLE III: Hopping parameters along the directions 4, 2, 3 and 3' in terms of corundum-symmetry-adopted reduced parameters \( \mu, \rho, \alpha, \beta, \sigma \) and \( \tau \).

| Direction | 4 | 2 | 3 | 3' |
|-----------|---|---|---|----|
| \( e_{g1}^{n}, e_{g2}^{n} \) | \(-\mu - \alpha \) | \(-1/4 \alpha + 3/4 \beta \) | \(-1/4 \alpha + 3/4 \beta \) | \(-1/4 \alpha + 3/4 \beta \) |
| \( e_{g2}^{n}, e_{g2}^{n} \) | \( \mu \beta \) | \(-3/4 \alpha + 1/4 \beta \) | \(-3/4 \alpha + 1/4 \beta \) | \(-3/4 \alpha + 1/4 \beta \) |
| \( e_{g1}^{n}, a_{1g} \) | \( \rho \sigma \) | \( \sigma \sigma \) | \( \sigma \sigma \) | \( \sigma \sigma \) |
| \( e_{g2}^{n}, a_{1g} \) | \( 0 \) | \(-\sqrt{3}/2 \tau \) | \(-\sqrt{3}/2 \tau \) | \(-\sqrt{3}/2 \tau \) |

TABLE IV: Comparison of TB parameters of corundum-structured V_2O_3 (in terms reduced parameters \( \mu, \rho, \alpha, \beta, \sigma \) and \( \tau \)) obtained by different procedures for V-V hopping along the four near directions, 4, 2, 3' and 3.

Calculated \( a_{1g} - a_{1g} \) hopping which doesn’t have the additional complexity of hopping via the \( e_{g2} \) tails, another crucial ingredient not taken into account in CNR’s study. In CNR paper, the direct \( d - d \) hoppings were obtained from a linear combination of atomic orbital (LCAO) kind of approach by Ashkenazi et. a.20 which assumes the correct geometry, while the trigonal distortion was assumed to be negligible (set to zero). Such an approximation is found to have a deeper implication in terms of the quantitative estimates of the effective \( V - V \) hopping. In order to have an understanding of the delicate effect of the geometry, we carried out calculations on crystal structures with varying trigonal distortions. Crystal structures with varying amount of trigonal distortions are generated by linear interpolation of the internal parameters associated with V and O atoms between that of the real crystal and that of the ideal hexagonal arrangement:

\[
z_{V} = 0.3333(1 - c) + 0.34630c
\]
\[
x_{O} = 0.3333(1 - c) + 0.31164c
\]

Putting \( c = 0(1) \) gives the ideal(real) structure. Increasing \( c \) increases the trigonal distortion which is the difference between two sets of V-O distances in VO_6 octahedra, with three short and three long V-O bond-lengths. Changing the parameter \( c \), however also changes the V1-
FIG. 14: The influence of the trigonal distortion and V1-V4 distance on the vertical $a_{1g} - a_{1g}$ pair hopping magnitude. Structures with varying amount of distortions are generated by linear interpolation of the internal parameters associated with V and O positions, $z_v = 0.3333(1-c) + 0.34630c$; $z_O = 0.3333(1-c) + 0.31146c$. This leads to simultaneous variation of the V1-V4 distance and the trigonal distortion. The dotted and the solid lines give the estimate of the direct $a_{1g} - a_{1g}$ hopping and that of the effective $a_{1g} - a_{1g}$ hopping in truly minimal $a_{1g} - e_g^\pi$ NMTO basis. The open and solid circles are the estimates of direct and effective $a_{1g} - a_{1g}$ hopping respectively, as obtained by CNR. The V1-V4 distance in CNR’s calculation were considered to be same as that in real structure while the amount of trigonal distortion was set to zero.

V4 distance which effects the bare or direct $a_{1g} - a_{1g}$ hopping. We have carried out calculations for $c=0, 1/3, 2/3$ an 1. The calculations for the hopping matrix elements are carried out for the truly minimal set of $a_{1g}$ and $e_g^\pi$ NMTOs as well as for the set where the O-p’s are kept active in addition to V-d’s. This has been done to bring out the renormalization effect coming from oxygen degrees of freedom. The results are shown in FIG. 14. We see that the $pd$ contribution given by the difference of direct $a_{1g} - a_{1g}$ and the renormalized $a_{1g} - a_{1g}$ hopping, almost vanishes for the ideal structure and increases monotonically as the trigonal distortion increases towards to the value obtained in the real structure. The $pd$ contribution, apart from the case of ideal structure, is anti-bonding whereas the direct (bare) $dd$ contribution is bonding. On top of this, comes the even stronger trend that the bonding $dd$ interaction decreases with the V1-V4 bond distance, $d$, as $\propto d^{-3.3}$. As a result, $a_{1g} - a_{1g}$ hopping integral depends strongly on the distortion. As already mentioned, in CNR’s calculation, though the bare $dd$ hopping was obtained following LCAO type of approach on a correct V-V geometry with correct V1-V4 bond distance, the trigonal distortion of the VO6 octahedra was assumed to be negligible with all V-O bond lengths to be equal. This resulted into a direct $dd$ hopping of -0.66 eV in good agreement with our corresponding estimate of -0.72 eV, while the $pd$ contribution gave rise to a small renormalization of -0.06 eV. We note that the $pd$ contribution is small and of bonding (negative) type as we obtained in our calculation with ideal structure. This in turn proves the extreme sensitivity of the hopping parameters on the correct geometry of the system. In FIG. 15 we show the comparison between overlap of V1-$a_{1g}$ and V4-$a_{1g}$ NMTOs for the real and ideal structures. Studying the figure, we notice that due to the about 14 % reduction of V1-V4 distance in case of ideal structure, the direct, bonding type $a_{1g} - a_{1g}$ overlap is much stronger than compared to that in real structure which gives rise to the strong slope observed in FIG. 14. Focusing on the $pd$ contribution, for the ideal structure, the $p-$ type tail from V4 NMTO at O5 site (referred as $p_4$ in Eqn.2) passes almost through the node of the $a_{1g}$ orbital at V1 site, as shown with solid line, and gives rise to a negligible overlap between $d_1$ and $p_4$ (c.f. Eqn. 3). For real structure, on the other hand, the change of V1-O5-V4 angle causes the $p_4$ tail having finite overlap with $a_{1g}$ orbital at V1 site which turn out to be positive (antibonding) in sign.
D. Vertical pair model and validity of molecular orbital states

In this sub-section, we discuss the consequences of the new set of NMTO derived parameter values in the context of validity of vertical pair model and the molecular orbital formation.

Di Matteo et al.\(^\text{13}\) analyzed in detail the parameter space of the \(V_2O_3\) problem in context of all possible orbital and magnetic ground states configuration of the effective many-body Hamiltonian by using variational procedure. The orbital wave-functions of the ferromagnetic state of the vertical pair of \(V\) atoms at sites \(a\) and \(b\) were postulated to be given by:

\[
|\psi_{\pm}\rangle_{ab} = \frac{1}{\sqrt{2}}(|\pm 1\rangle_a|0\rangle_b + |\pm 1\rangle_b|0\rangle_a) \tag{3}
\]

where \(|0\rangle = |e_g^\pi, 1e_g^\sigma, 2\rangle\), \(|-1\rangle = |a_{1g} e_g^\sigma, 1\rangle\) and \(|1\rangle = |a_{1g} e_g^\sigma, 2\rangle\) are three two-electron states constructed out of three one-electron states, \(e_g^\pi, 1, e_g^\pi, 2\) and \(a_{1g}\).

The correlation energy of such a state was defined as the difference between the ground state energy and its Hartree-Fock approximation. Taking into account the hopping integrals in terms of reduced parameters, the ground state energy of such a pair is given by \(-\frac{(\mu - \rho)^2}{U - J_c}\), which involves back and forth virtual hoppings out of \(e_g^\pi\) state \([-\frac{\tau}{\sqrt{2}}\] \(e_g^\pi\)], that out of \(a_{1g}\) state \([-\frac{\tau}{\sqrt{2}}\] \(e_g^\pi\)] and the correlated hopping between \(V\) atoms at \(a\) and \(b\) sites, where they exchange electrons in \(a_{1g}\) and \(e_g^\pi\) states simultaneously. \(U\) and \(J\) are Coulomb and exchange integrals respectively. The latter mechanism which arises due to entangled nature of the form of the wave-function in (3) is absent in its Hartree-Fock approximation and gives what Di Matteo et al. termed as molecular correlation energy. Two different regimes of solutions were defined depending on the relative magnitudes of the correlation energy of the ferromagnetic state of the vertical pair, namely, the molecular correlation energy and the in-plane exchange energy (governed by the hopping processes in the basal plane):

(a) If the molecular correlation energy is larger than the in-plane exchange energy then the whole crystal consists of some molecular units and the variational wave-function should be constructed in terms of molecular states given by (3).

(b) If the in-plane exchange energy is larger than the molecular correlation energy, which tend to break the stability of the correlated molecular states, one needs to construct the variational wave-function in terms of single site atomic states.

Di Matteo et al.\(^\text{13}\) approximated the in-plane exchange energy by \(\approx \frac{(\alpha^2 + \tau^2)}{U - J_c}\) [considering the hoppings along three 2NN bonds in the direction of 2, 3 and 3′ and neglecting the hoppings involving reduced parameters \(\beta\) and \(\sigma\)].

Considering the numerical values of \(\mu, \rho, \alpha\) and \(\tau\), as given by CNR and Di Matteo et al. one gets:

\[
2\mu\rho/(\alpha^2 + \tau^2) \approx 4 - 3.5
\]

while using the parameters obtained by NMTO-downfolding one gets:

\[
2\mu\rho/(\alpha^2 + \tau^2) \approx 0.83
\]

This ratio gets even smaller taking into account the hoppings related to \(\beta\) parameter which is almost as large as \(\tau\).

Therefore, while the TB parameters given by CNR and Di Matteo et al. favor the formation of stable molecular orbital states, the parameters provided by NMTO-downfolding procedure clearly do not favor it. We therefore believe that it is very much needed to repeat the calculations using the new set of hopping parameters to shed light on the long standing puzzles in \(V_2O_3\). This issue has been recently taken up in Ref.\(^\text{22}\).

E. Cr-doped \(V_2O_3\) (\((V_{0.962}Cr_{0.038})_2O_3\)): the low-energy, tight-binding Hamiltonian

The right, top panel of FIG. 9 shows the LDA band structure of 3.8% Cr doped \(V_2O_3\) in the paramagnetic insulating phase. Upon comparison with the band structure of the undoped \(V_2O_3\) in the paramagnetic metallic phase, as presented in the left, top panel of FIG. 9, one finds that the \(t_{2g}\) bandwidth is reduced in the doped compound to about 2.25 eV from about 2.5 eV in case of undoped compound. The right, bottom panel of FIG. 9 shows the \(a_{1g}\) and \(e_g^\pi\) bands switching off the \(a_{1g}-e_g^\pi\) hybridization. The lattice expansion upon Cr doping, causes bottom of the \(a_{1g}\) band to move up and the top of \(e_g^\pi\) band to move down, giving rise to \(\min\{\epsilon_{a_{1g}}\} \approx 1.69\) eV, in comparison to \(\max\{\epsilon_{e_g^\pi}\} \approx 2.02\) eV in case of undoped compound.

The middle rows of Table I and II, lists the onsite energies and hopping matrix elements corresponding to Cr doped \(V_2O_3\). The crystal field splitting is found to increase by 0.03 eV compared to undoped case. The magnitude of the dominant \(V1-V4\) hopping is found to decrease from 0.51 eV in the undoped case to 0.43 eV in the doped case. These changes in the one-electron parameters were found to be significant to drive the metal-insulator transition as explained in Ref.\(^\text{22}\).

F. Monoclinic \(V_2O_3\): the low-energy, tight-binding Hamiltonian

Finally, we thought it will be worthwhile to study the influence of the monoclinic distortion in the low-temperature crystal structure on the hopping integrals. It is of interest to know how much the crystal structure change effects the hopping matrix elements. We applied the same NMTO-downfolding machinery, described
in great detail in previous sections for V$_2$O$_3$ in corundum structure. The LDA self-consistent potentials are generated by TB-LMTO-ASA calculation with potential sphere overlap less than 18 % and empty sphere overlap less than 22 %. The truly minimal $a_1g$ and $e^*_g$ basis sets are defined within the framework of the NMTO-downfolding technique for the monoclinic structure. For the sake of comparison, we retained the corundum-symmetry-adopted $a_1g$ and $e^*_g$ basis also in the monoclinic structure. However, the further lowering of the symmetry in the monoclinic phase introduces mixing between $a_1g$ and $e^*_g$ orbitals at the same site, which is reflected as crystal field terms in the on-site block of the real-space Hamiltonian. The monoclinic distortion makes the various near neighbor distances unequal compared to that in corundum phase. While the vertical V1-V4 bond expands by 1.8 %, the horizontal V1-V2 bond expands by about 4 % making the three, basal neighbor bond distances along 2, 3 and 3′ unequal. It also makes the bond distance along 4 different from those along 5 and 5′, the bond distances along 5 and 5′ different from that of 6 and 6′ and, 6 and 6′. The tight-binding hopping integrals and hopping elements computed as elements of the orthonormalized $a_1g$ and $e^*_g$ NMTO Hamiltonian are quoted in Table I and II. Focusing on the $a_1g - a_1g$ vertical pair hopping, we find that the value is further decreased to -.44 eV compared to the value of -.51 eV in the corundum structure. This reduction is primarily driven by the 1.8 % increase in the V1-V4 bond length and slight tilting of the V1-V4 bond which decreases the magnitude of the bare $d_d$ hopping from -.72 eV in the corundum structure to -.64 eV in the monoclinic structure. The $p_d$ contribution due to integrated out oxygen tails turned out to be +0.20 eV which can be compared with the value +.21 eV, that in corundum structure. The V1-O-V4 angle remains essentially unaltered between the corundum and monoclinic structure.

Comparing the hoppings in other directions, the reduction is maximum for the horizontal V1-V2 bond which expands by 4% over the value in corundum structure. The other two near neighbor bonds in the basal plane, 3 and 3′ on the other hand contracts (the bond 3 by 0.7 % and 3′ by .2 %) which is reflected in the changes in hopping integrals. Similar distance dependent increase or decrease can be observed for farther ranged hoppings.

In brief, though the low-temperature structural change induces changes in the hopping parameters, these changes are not drastic. Till date, a direct, experimental evidence of orbital ordering is lacking and issue of orbital ordering, its existence and type in V$_2$O$_3$ still remains highly controversial. Nevertheless, the role of orbital degrees of freedom in stabilizing the magnetic structure with broken trigonal symmetry of the corundum lattice remains to be plausible idea. In that case, the monoclinic distortion may possibly be the reflection of the peculiar spin and orbital ordering rather than the cause for it.

IV. SUMMARY AND OUTLOOK

To summarize, employing the NMTO-downfolding technique and Wannier function representation of the Hamiltonian, we have derived in a first-principles manner, the effective V-V hopping interactions corresponding to the low-energy, $t_{2g}$ bands of V$_2$O$_3$. Our results show, contrary to popular believe, for modeling of V$_2$O$_3$, inter-pair V-V hoppings are equally important as V-V intra-pair hoppings. The significant changes in hopping parameters compared to CNR parameters occur primarily due to the neglect of trigonal distortion in the previous study and due to the hopping processes via the integrated out $e^*_g$ tails in addition to that via oxygen like tails, a fact not considered before. This calls the need for revisiting the many-body calculations, which start with the assumption of vertical pairs as the building blocks.

The Wannier functions corresponding to the low-energy, $t_{2g}$ bands derived in this paper will serve as the basis to define low-energy, multi-orbital Hubbard Hamiltonian for the LDA+DMFT calculations for V$_2$O$_3$, which rely on the choice of flexible, atom-centered, localized basis sets. Such calculations have been already carried out. For details please see Ref. Considering the rather delocalized nature of the real-space Hamiltonian of V$_2$O$_3$, it is quite natural to expect improvements on going beyond the single-site approximation of DMFT and taking into account the cluster effect. For such study, it is crucial to decide on a minimal cluster which has the dominating effect and the vertical pair has been often discussed as a natural choice. However, in view of NMTO-downfolding derived parameters and the breakdown of correlated molecular orbital like states, the most tempting choice of the vertical pair as the cluster seems to be hardly satisfactory. The cluster LDA+DMFT calculations with V1-V4 pair show no qualitative difference with single site DMFT results for corundum PI phase. The minimal cluster should include in addition to vertical pairs V1 and V4, the near-neighbor V atoms in the basal plane, V2, V3 and V3′, which though is a computer expensive DMFT job to carry out.
APPENDIX A: NMTO METHOD

In the following, we describe the NMTO method which provides a tool for direct generation of localized Wannier functions. The downfolding procedure is also implemented in this framework to construct truly minimal basis sets which pick out selected bands.

In the NMTO method, a basis set of localized orbitals is constructed from the exact scattering solutions for a superpositions, $\sum_R v_R(r_R)$, of short-ranged, spherically-symmetric potential wells – a so-called MT approximation to the potential. This is done by first numerically solving the radial Schrödinger’s equations, to find $\varphi_{R \ell n}(r)$, the partial waves, for all angular momenta, $l$, with non-vanishing phase-shifts, for all potential wells, $R$, and for a chosen set of energies spanning the region of interest, $\epsilon_n = \epsilon_0, \ldots, \epsilon_N$:

$$-[r \varphi_{R \ell n}(\epsilon, r)]'' = \left[\epsilon - v_R(r) - l(l+1)/r^2\right] r \varphi_{R \ell n}(\epsilon, r)$$

The partial-wave channels, $R \ell m$ are partitioned into active and passive channels. The active channels are those for which one chooses to have orbitals in the basis set, i.e. they are the chosen one-electron degrees of freedom. The passive channels are said to be downfolded.

For each active channel, $R \ell m$, a so-called kinked partial wave (KPW), $\psi_{R \ell m}(\epsilon_n, r)$, is constructed. A kinked partial wave is basically a partial wave with a tail joined continuously to it with a kink at a central, so-called hard sphere of radius $a_R$. The tail of the kinked partial wave is a screened spherical wave, $\psi_{R \ell m}(\epsilon, r)$, which is essentially the solution with energy $\epsilon$ of the wave equation in the interstitial between the hard spheres,

$$-\Delta \psi(\epsilon, r) = \epsilon \psi(\epsilon, r)$$

with the boundary condition that, independent of the energy, $\psi_{R \ell m}(\epsilon, r)$ go to $Y_{\ell m}(r_R)$ at the central hard sphere, and to zero (with a kink) at all other hard spheres at the neighboring sites. It is this latter confinement, which makes the screened spherical waves and the KPWs localized when the energy is not too high. The default value of the hard-sphere radii, $a_R$, is 90% of the appropriate covalent, atomic, or ionic radius. The above-mentioned boundary condition only applies to the active components of the spherical-harmonics expansions of the screened spherical wave on the hard spheres. For the remaining downfolded or passive components the screened spherical wave equals the corresponding partial-wave solution of Schrödinger’s equation throughout the MT-sphere, i.e. it has the proper phase shift.

If one can now form a linear combination of such kinked partial waves with the property that all kinks cancel, one finds a solution of Schrödinger’s equation with energy $\epsilon_n$. In fact, this kink-cancellation condition leads to the classical method of Korringa, Kohn and Rostoker (KKR), but in a general so-called screened representation and valid for overlapping MT potentials to leading order in the potential overlap. The screened KKR equations are a set of energy-dependent, homogeneous linear equations, with a matrix, $K_{R \ell m, R' \ell m}(\epsilon)$, whose rows and columns are labeled by the active channels. In the NMTO method, we don’t solve this set of secular equations, but proceed via construction of energy-independent MT basis sets which span the solutions $\Psi_i(r)$ with energies $\epsilon_i$ of Schrödinger’s equation to within errors proportional to $(\epsilon_i - \epsilon_0)(\epsilon_i - \epsilon_1) \ldots (\epsilon_i - \epsilon_N)$, where $\epsilon_0, \epsilon_1, \ldots, \epsilon_N$ is the chosen energy mesh with N+1 points defined already. Such an energy-independent set of Nth-order MTOs is called an NMTO set.

The members of the NMTO basis set for the energy mesh $\epsilon_0, \ldots, \epsilon_N$ are superpositions,

$$\chi^{(N)}_{R \ell m}(r) = \sum_{n=0}^N \phi(\epsilon_n, r) L^{(N)}_{n R \ell m, R' \ell m} \phi_{R' \ell m}(\epsilon_n, r)$$

(A1)

of the kinked partial waves, $\phi_{R \ell m}(\epsilon, r)$, at the N + 1 points (labeled by $n$) of the energy mesh. Expression (1) is the energy-quantized form of Lagrange interpolation,

$$\chi^{(N)}(\epsilon) = \sum_{n=0}^N \phi(\epsilon_n) l^{(N)}_{n, \epsilon} = \prod_{m=0, n \neq N}^\infty \frac{\epsilon - \epsilon_n}{\epsilon_n - \epsilon_m},$$

of a function of energy, $\phi(\epsilon)$, by an Nth-degree polynomial, $\chi^{(N)}(\epsilon)$: The Nth-degree polynomial, $l^{(N)}_{n, \epsilon}$, is substituted by a matrix with elements, $L^{(N)}_{n R \ell m, R' \ell m}$, the function of energy, $\phi(\epsilon)$, by a Hilbert space with axes, $\phi_{R \ell m}(\epsilon, r)$, and the interpolating polynomial, $\chi^{(N)}(\epsilon)$, by a Hilbert space with axes, $\chi^{(N)}_{R \ell m}(r)$.

Note that the size of the NMTO basis is given by the number of active channels and is independent of the number, N + 1, of energy points. The energy-selective and localized nature of NMTO basis makes the NMTO set flexible and may be chosen as truly minimal, that is, to span selected bands with as many (few) basis functions as there are bands. If those bands are isolated, the NMTO set spans the Hilbert space of the Wannier functions and the onthornormalized NMTOs are the Wannier functions. But even if the bands of interest overlap other bands, it may be possible to pick out those few bands and their corresponding Wannier-like functions with the NMTO method. The NMTO method can thus be used for direct generation of Wannier or Wannier-like functions.

The Lagrange coefficients, $L^{(N)}_{n, \epsilon}$, as well as the Hamiltonian and overlap matrices in the NMTO basis are expressed solely in terms of the KKR resolvent, $K(\epsilon)^{-1}$, and its first energy derivative, $\dot{K}(\epsilon)^{-1}$, evaluated at the energy mesh, $\epsilon = \epsilon_0, \ldots, \epsilon_N$. Variational estimates of the one-electron energies, $\epsilon_i$, may be obtained from the generalized eigenvalue problem,

$$\left(\left\langle \chi^{(N)} | \mathcal{H} | \chi^{(N)} \right\rangle - \epsilon_i \left\langle \chi^{(N)} | \chi^{(N)} \right\rangle \right) \mathbf{v}_i = \mathbf{0},$$

with

$$\mathcal{H} = -\Delta + \sum_R v_R(|r - R|)$$
or as the eigenvalues of the one-electron Hamiltonian matrix,

\[ H^{LDA} = \langle \chi^{(N)\perp} | \mathcal{H} | \chi^{(N)\perp} \rangle \]

in the basis of \textit{symmetrically orthonormalized} NMTOs:

\[ |\chi^{(N)\perp}\rangle \equiv |\chi^{(N)}\rangle \left( \chi^{(N)} \right)^{\top} \]

In the present paper, the orbitals shown are NMTOs \textit{after} orthonormalization because they are (slightly) more localized than the orthonormalized ones. The hopping integrals and on-site elements given in the tables are of course matrix elements of the \textit{orthonormalized} Hamiltonian.

For crystals, all calculations except the generation of the screened structure matrix are performed in the Bloch representation

\[ \chi^{(N)}_{\vec{R} \vec{m}}(\vec{k}, \vec{r}) = \frac{1}{\sqrt{L}} \sum_{\vec{T}} \chi^{(N)}_{\vec{R} \vec{m}}(\vec{r} - \vec{T}) \exp\left\{ 2\pi i \vec{k} \cdot (\vec{R} + \vec{T}) \right\} \]

where \( T \) labels the \( L(\to \infty) \) lattice translations and \( \vec{R} \) the active sites in the primitive cell. In order to obtain the orbitals and the Hamiltonian in configuration space, Fourier-transformation over the Brillouin zone is performed.

It is worth-mentioning here that this construction of a minimal NMTO basis set is different from standard Löwdin downfolding. The latter partitions a \textit{given}, large (say orthonormal) basis into active (\( A \)) and passive (\( P \)) subsets, then finds the downfolded Hamiltonian matrix as:

\[ \langle A | \varepsilon | A \rangle = \langle A | \mathcal{H} | A \rangle - \langle A | \mathcal{H} | P \rangle \langle P | \mathcal{H} - \varepsilon | P \rangle^{-1} \langle P | \mathcal{H} | A \rangle \]

and finally removes the \( \varepsilon \)-dependence of the downfolded basis by \textit{linearizing} \( \langle P | \mathcal{H} - \varepsilon | P \rangle^{-1} \) and treating the term linear in \( \varepsilon \) as an overlap matrix. Obviously, since the NMTO set is exact at \( N+1 \) energy points, it is more accurate.

Our present NMTO code is however not yet self-consistent, so we used the current Stuttgart tight-binding version of the linear-muffin-tin-orbital (TB-LMTO) code within the atomic sphere approximation (ASA) to generate the LDA potentials. Despite this shape approximation for the potential, the NMTO bands used in the present paper are more accurate than LMTO bands, first of all because the NMTOs do not use the zero-energy approximation in the interstitial region and, secondly, because we use \( N > 1 \).

**APPENDIX B: COMPUTATIONAL DETAILS**

As mentioned in Appendix A, our present NMTO code is not self-consistent, we therefore used the current Stuttgart TB-LMTO-ASA code to generate the LDA potentials. Such a potential in the atomic-spheres approximation is an overlapping MT-potential, like the one handled by the NMTO method, but with the relative overlaps,

\[ \omega_{RR'} \equiv \frac{s_R + s_{R'}}{|\vec{R} - \vec{R}'|} - 1, \]

limited to about 20%. This limitation comes from the LMTO-ASA+cc method, which solves Schrödinger’s equation by treating the overlap as a perturbation (the so called combined-correction term, cc) \textit{and} uses screened spherical waves of zero kinetic energy in the \( s \)-interstitial. Poisson’s equation is solved for the output charge density, spherically symmetrized inside the \textit{same} atomic \( s \)-spheres.

We now specify our computational set-up. The radii of the potential spheres, \( s_R \), were dictated by our use of the LMTO-ASA method to generate the LDA potentials. In order to limit the overlaps defined by equation (B1), \textit{interstitial} \textbf{or} \textit{empty} \textbf{spheres} \( (E) \) were inserted in the non-cubic structures. Table [V] gives the radii of the potential spheres. As a result, the overlap between atomic spheres was <16%, between atomic and empty spheres <18%, and between empty spheres <20%. We used the guidance given by the current version of the code in choosing the potential spheres appropriately.

**TABLE V: Radii \( s_R \) of potential spheres in Bohr atomic units.**

|   | V | O1 | O2 | E | E1 | E2 | E3 | E4 | E5 |
|---|---|----|----|---|----|----|----|----|----|
| PM | 2.46 | 1.88 | 2.36 | 1.80 |
| PI | 2.46 | 1.88 | 2.36 | 1.80 |
| AFI | 2.46 | 1.88 | 1.88 | 2.36 | 2.36 | 1.80 | 1.80 | 1.80 | 1.80 |

**TABLE VI: LMTO basis sets used in the self-consistent calculation of LDA potential.** \( (l) \) means that the \( l \)-partial waves were downfolded within in the LMTO-ASA+cc.

|   | V | O1 | O2 | E | E1 | E2 | E3 | E4 | E5 |
|---|---|----|----|---|----|----|----|----|----|
| PM | spd | sp(d) | s(pd) | s(p) |
| PI | spd | sp(d) | s(pd) | s(p) |
| AFI | spd | sp(d) | s(pd) | s(pd) | s(p) | s(p) | s(p) | s(p) |

The self-consistent valence-electron densities were calculated with the LMTO bases listed in Table [VI]. We found it important to downfold the oxygen \( d \) partial waves, rather than to neglect them \textit{(i.e. to approximate them by spherical Bessel functions when solving Schrödinger’s equation, and to neglect them in the charge...}
density). Since the LMTO calculations were used to produce the self-consistent charge densities, the energies, $\epsilon_{Ri}$, for the linear $\phi_{pj}, \phi_{Ri}$ expansions were chosen at the centers of gravity of the occupied parts of the respective DOS $R_i$-projections.

Finally, in the NMTO calculations, the hard-sphere radii, $a_R$, for the active channels were chosen as $0.7s_R$.

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In Matteheiss’s paper the bands were plotted along the symmetry directions of the hexagonal BZ, where in the present paper they have been plotted along the symmetry directions of the rhombohedral BZ. We have also plotted the LMTO bands in the symmetry directions of the hexagonal BZ and they have been found to be in good agreement with that obtained by LAPW calculation of Matteheiss.

The rather high contour chosen in the figure tend to mask the antibonding \( \langle p_1, d_4 \rangle \) and \( \langle d_1, p_4 \rangle \) hopping paths and one erroneously focuses on the bonding \( \langle d_1, d_4 \rangle \) and \( \langle p_1, p_4 \rangle \) hopping paths. However, the \( \langle p_1, d_4 \rangle \) and \( \langle d_1, p_4 \rangle \) gives larger contribution than \( \langle p_1, p_4 \rangle \), and \( \langle p_1, d_4 \rangle + \langle d_1, p_4 \rangle \) is antibonding (blue \( p_1 \) lob overlap with red \( d_4 \) lob and blue \( p_4 \) lob overlap with red \( d_1 \) lob).

In the correndum structure, the octahedral environment of the cation sites within a layer are equivalent, which does not change the wavefunctions. However, those belonging to the next two adjacent layers (e.g. that at site V4) are obtained by application of rotation by angle \( \pi \) around the \( y \)-axis followed by translation, if necessary. This, for example, introduces a negative sign for the \( e^{g}_{1}, 1 \) wavefunction at site V4 compared to that at site V1. In CNR paper, they introduced a further sign to overcome this while we kept the original convention. This results into a sign change of the \( e^{g}_{1}, 1 - e^{g}_{1}, 1 \), \( e^{g}_{2}, 2 - e^{g}_{2}, 1 \) and \( a_{1g} - e^{g}_{1}, 1 \) hoppings in the directions 4, 5, 5, 6, \( 5, 6, 5, 6 \) in our calculation compared to CNR’s convention.

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