PHYSICAL REVIEW B VOLUME 18, NUMBER 9 1 NOVEMBER 1978

Magnetic structure of V_2O_3 in the insulating phase

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(Received 14 June 1977)

A phase diagram for all the possible collinear spin arrangements for V_2O_3 is derived within the atomic limit. Due to the fact that the a_{1g} electrons of the V atoms form a diamagnetic bond for the vertical pairs of V atoms, the magnetic structure of V_2O_3 can be considered to be essentially determined by the remaining one electron per V atom in a twofold degenerate e_g level. Depending on only two parameters: t_{ij}^{11}/t_{ij}^{22}, the ratio of the hopping integrals within the two orbital states 1 and 2 and between a certain pair (i,j) of V atoms in the basal plane, and J/U, the ratio of the exchange constant to Hubbard's U, the regions of stability for a particular magnetic and orbital order are determined. The experimentally observed magnetic order falls into a region of values of these parameters which are expected for V_2O_3.

I. INTRODUCTION

Of all the transition-metal oxides which exhibit a metal-to-insulator transition (MIT), the most extensively studied in recent years has been V_2O_3, both from the experimental point of view (done to a large extent by McWhan and co-workers[1]) and from a theoretical point of view (mainly by Rice and Weger and collaborators[2]). Yet the mechanism of the first-order transition at 150°K has remained up to now a controversial matter if not an unresolved one. Issues like the singular magnetic structure among the corundum type of compounds (Fe_2O_3, Cr_2O_3) in the insulating phase,[3,4] the rather unexpected number of Bohr magnetons per site (1.2 μB) for a V^{3+} configuration,[4] and the peculiar lattice distortion taking place at the transition,[5] are all phenomena which as yet have received no explanation. Equally lacking is a consistent interpretation of the metallic phase, both under pressure at zero temperature and at the transition temperature at atmospheric pressure, and one is looking for a realistic calculation that might give preference to a certain model over another one. Some very interesting suggestions have already appeared in the literature[3,6-8] which throw some light onto this almost classical problem.

This is the first of a three-paper series (Papers I, II, and III, hereafter referred to as I, II, and III, respectively) in which we attempt to paint a more consistent picture of the MIT problem in V_2O_3, providing a unified and consistent point of view on all the issues we have mentioned above. In II,[9] realistic calculations which explain the rather singular magnetic sturcutre of V_2O_3 are done for the antiferromagnetic insulating phase with a fairly good degree of reliability. Less realistic calculations, although sufficiently indicative, are carried out for the metallic phase which will enable us to discriminate among various possible interpretations of this phase and to support one in particular. Finally, in III,[10] a conclusive interpretation of the mechanism of the two transitions (at 150 and 500 °K) is attempted, although due to the complexity of the system, the last word in favor or against our interpretation must be left to certain specific experiments which we suggest in order to verify our interpretation.

Our first aim is to understand the insulating phase of V_2O_3 and notably the unique antiferromagnetic structure. A Luttinger-Tizsa method (or an equivalent alternative method[11]) has previously been applied to an Heisenberg Hamiltonian for a corundum type of structure with isotropic exchange constants $J(\rho)$ up to fifth neighbors [isotropic in the sense that $J(\rho)$ is assumed to be equal for neighbors of the same distance] which has provided all the possible solutions for colinear spin structures in a corundum lattice. Their domain of stability was delimited on the basis of inequality relations among the exchange constants but not a single one of them described the magnetic colinear spin structure experimentally observed in V_2O_3.[4] Obviously, some basic assumptions must not be satisfied in this type of approach. If we think of an Heisenberg Hamiltonian as an effective Hamiltonian derived from a Hubbard model in the atomic limit ($W/U \to 0$, where W is the bandwidth and U the Coulomb repulsion for two electrons on the same site), then the isotropy of $J(\rho)$ means that the magnetic electrons are assumed to belong to a nondegenerate atomic state. A closer inspection of the atomic structure of V_2O_3, as explained in Sec. II and from a band point of view in II, forces us to abandon this assumption and to consider a generalized Hubbard model for electrons in a doubly-degenerate atomic state.

Although the real situation of electrons in V_2O_3

is far from being near the atomic limit ($W/U \simeq 1$ as will become more apparent in II), we choose, in I, to study this limit for the following reasons. Firstly, we are not aware of any previously reported general and complete derivation of an effective Hamiltonian from a generalized Hubbard model with two degenerate atomic states per site, nor of an application of the result to a corundum type of structure. We hope to fill a gap in the information urgently needed as far as the orbital degeneracy is concerned in determining the magnetic structure. Our derivation will parallel that of Cyrot and Lyon-Caen.[12] Secondly, it will turn out that, due to the complexity of the V_2O_3 structure, this preliminary study is essential for determining the type of symmetry-breaking solutions, in a realistic unrestricted Hartree-Fock calculation, that will be attempted in II. In other words, we believe that the kind of instability against certain symmetry-breaking operations which already show up for our degenerate-band Hubbard model in the atomic limit persist with varying W/U ratio until the real situation ($W/U \simeq 1$) is reached. The actual calculation in II bears this out. A somewhat different approach has been followed by Kubo and Inakaki[13] for the special case of a cubic lattice (with mixed transfer integral between band 1 and 2 being equal to zero) which consists in studying within the RPA the response functions for the order-parameter operators relative to certain broken symmetries and in looking for the instability condition when varying the parameters of the Hamiltonian. Unfortunately, this method can only be applied when the crystal structure of the system under consideration is simple enough or severe simplifying assumptions are made so that an analytical calculation is possible. For our case of a corundum structure, this method becomes prohibitive.

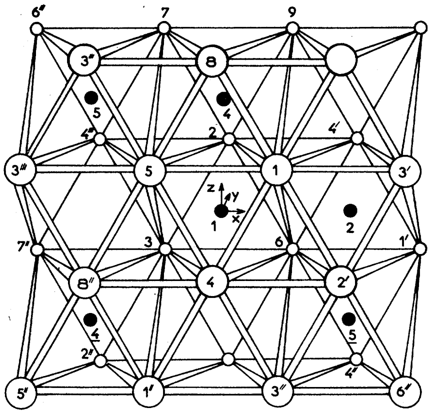


FIG. 1. Arrangement of metal atoms (full circles) and oxygen atoms (open circles) in the corundum structure.

II. CHOICE OF THE MODEL HAMILTONIAN

The arrangement of cations and anions in the corundum structure is shown in Fig. 1. Although the immediate surrounding of metal ions has an almost octahedral type of symmetry with point group O_h, a slight trigonal distortion and the influence of more distant cations in the lattice reduces the point group symmetry to D_{3d}, lifting the degeneracy of the three T_{2g} orbital in cubic environment (Fig. 2). In this way, we obtain a higher, simply-degenerate a_{1g} orbital and a lower, doubly-degenerate e_g orbital. Since three electrons are already engaged in forming more or less covalent bonds with the $2p$ states of the oxygens (this statement will be elaborated in II), we are left with two magnetic electrons for each cation. Moreover, the fact that the trigonal field splitting of the simply degenerate T_{2g} level is much smaller than the cubic splitting between T_{2g} and E_g levels per-

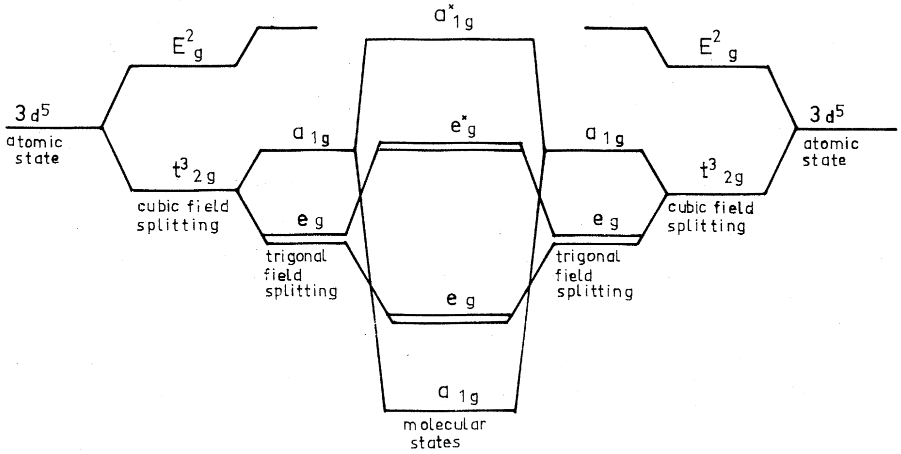


FIG. 2. Schematic energy splitting of the $3d$ level in the corundum structure and formation of a stable bond between the a_{1g} orbitals of a vertical pair of cations.

mits us to take, as the Hilbert subspace in which to diagonalize our Hamiltonian, the space spanned by the two e_g orbitals and the a_{1g} orbital for each cation. In other words, our fields operator $\psi_\sigma(\vec{x})$ is expanded in terms of a complete set of Wannier functions of a_{1g} and e_g symmetry (complete in our Hilbert subspace chosen):

$$\psi_\sigma(\vec{x})=\sum_{m=1}^{3}\sum_{j} w_j^m(\vec{x})c_{jm\sigma}\,, \tag{2.1}$$

where j runs over all the cation sites, $w_j^m(\vec{x})$ being the Wannier function centered on site j, of symmetry type m. Henceforth $m=1,2$ will indicate the two Wannier functions of e_g-symmetry type, whereas $m=3$ will denote the Wannier function of a_{1g} type.

In the spirit of a Hubbard type of approximation (that is to say by retaining in the interaction part only the terms on the same lattice site) the general Hamiltonian

$$H=\sum_{\sigma}\psi_\sigma^\dagger(\vec{x})\left[-\frac{\hbar^2}{2m}\nabla^2+V(\vec{x})\right]\psi(\vec{x})d^3x$$
$$+\tfrac{1}{2}\sum_{\sigma}\psi_\sigma^\dagger(\vec{x})\psi_{\sigma'}^\dagger(\vec{x}\,')V(\vec{x}-\vec{x}\,')\psi_{\sigma'}(\vec{x}\,')\psi_\sigma(\vec{x})d^3x\,d^3x' \tag{2.2}$$

becomes

$$H=\sum_{jj'}\sum_{mm'\sigma}t_{jj'}^{mm'}c_{jm\sigma}^\dagger c_{j'm'\sigma}+\frac{1}{2}\sum_{j}\sum_{mm'}\sum_{\sigma\sigma'}\left[(1-\delta_{mm'}\delta_{\sigma\sigma'})U_{mm'}n_{jm\sigma}n_{jm'\sigma'}-\delta_{\sigma\sigma'}(1-\delta_{mm'})J_{mm'}n_{jm\sigma}n_{jm'\sigma}\right.$$
$$-(1-\delta_{mm'})(1-\delta_{\sigma\sigma'})J_{mm'}c_{jm\sigma}^\dagger c_{jm\sigma'}c_{jm'\sigma'}^\dagger c_{jm'\sigma}$$
$$\left.+(1-\delta_{mm'})(1-\delta_{\sigma\sigma'})I_{mm'}c_{jm'\sigma'}^\dagger c_{jm'\sigma}^\dagger c_{jm\sigma}c_{jm\sigma'}\right]. \tag{2.3}$$

Since we can choose our Wannier functions to be real we have

$$t_{jj'}^{mm'}=\int w_j^m(\vec{x})H_0(\vec{x})w_{j'}^{m'}(\vec{x})\,d^3x\,, \tag{2.4}$$

where $H_0=-(\hbar^2/2m)\nabla^2+V(\vec{x})$ and $V(\vec{x})$ is some crystal potential having the symmetry of the lattice, and

$$U_{mm'}=\int |w_j^m(\vec{x})|^2V(\mathrm{x}-\mathrm{x}')|w_j^{m'}(\vec{x}\,')|^2d^3x\,d^3x'\,, \tag{2.5}$$

$$J_{mm'}=I_{mm'}=\int w_j^m(\vec{x})w_j^{m'}(\vec{x})V(\vec{x}-\vec{x}\,')$$
$$\times w_j^m(\vec{x}\,')w_j^{m'}(\vec{x}\,')\,d^3x\,d^3x'\,, \tag{2.6}$$

where $V(\vec{x}-\vec{x}\,')$ is taken to be a screened Coulomb potential having the property that for any rotation R,

$$V(R\vec{x}-R\vec{x}\,')=V(\vec{x}-\vec{x}\,')\,. \tag{2.7}$$

In deriving Eq. (2.3) from Eq. (2.2), we have used the fact that all the terms in the interaction part in (2.2) containing an odd number of functions of a certain symmetry type vanish. This property follows from the fact that our basis Wannier functions can be obtained by means of a real symmetric transformation $\underline{T}$ from a basis transforming like the xy, xz, and yz three-dimensional functions of symmetry type T_{2g}. (This latter property will be shown to hold in II.) Indeed, it is well known[14] that in this latter basis ϕ_m ($m=1,3$) we have

$$U_{ab;cd}=\int\phi_a^\dagger(\vec{x})\phi_b^\dagger(\vec{x}\,')V(\vec{x}-\vec{x}\,')\phi_c(\vec{x}\,')$$
$$\times\phi_d(\vec{x})d^3x\,d^3x'$$
$$=U_1\delta_{ab}\delta_{cd}\delta_{ac}+U_2\delta_{ad}\delta_{bc}(1-\delta_{ab})$$
$$+J[\delta_{ab}\delta_{cd}(1-\delta_{ac})+\delta_{ac}\delta_{bd}(1-\delta_{ab})\}\,, \tag{2.8}$$

where we have indicated for later convenience the complex conjugate despite the reality of the basis. Moreover, the three parameters in (2.8) are not independent, since

$$U_1=U_2+2J\,. \tag{2.9}$$

This can easily be verified by performing an arbitrary rotation R on the integration coordinates x and x', taking into account the transformation properties of the basis under rotation and noticing that the integral remains unchanged by this operation. As a consequence, Eq. (2.8) can be rewritten as

$$U_{ab;cd}=U_2\delta_{ad}\delta_{bc}+J(\delta_{ac}\delta_{bd}+\delta_{ab}\delta_{cd})\,. \tag{2.10}$$

If we now go over to another basis $f_m=\sum_{m'}D_{mm'}\phi_{m'}$ (where for the moment we take the matrix $\underline{T}$ to be unitary: $\sum_l D_{il}^\dagger D_{jl}=\delta_{ij}$), we find for the corresponding quantities in (2.8)

$$
\begin{aligned}
U'_{ab;cd} &= \int f_a^\dagger(\vec{x}) f_b^\dagger(\vec{x}') V(\vec{x}-\vec{x}') f_c(\vec{x}') f_d(\vec{x}) d^3x\, d^3x' \\
&= \sum_{\alpha\beta\gamma\delta} D^\dagger_{a\alpha} D^\dagger_{b\beta} D_{c\gamma} D_{d\delta} U_{\alpha\beta;\gamma\delta} \\
&= U_2 \delta_{ad}\delta_{bc} + J\delta_{ac}\delta_{bd} \\
&\quad + J \sum_{\alpha\beta} D^*_{a\alpha} D^*_{b\alpha} D_{c\beta} D_{d\beta} \,. \qquad (2.11)
\end{aligned}
$$

Hence, we see that we recover the previous formula (2.10) if the transformation matrix is real since in this case the unitary relation becomes simply $\sum_l D_{il} D_{jl} = \delta_{ij}$. This discussion points out that there are actually two independent parameters in the interaction Hamiltonian (2.3), a fact that will prove very useful in the following, since we shall be able to estimate with rather reasonable accuracy the transfer integrals (2.4) at least in the trigonal metallic phase. In a problem of such a complexity, a minimal number of parameters is essential to give a minimum of credibility to the eventual conclusions.

As already pointed out in the introduction, we want to study the atomic limit of (2.3), that is to say $\lim(W/U) \to 0$ where U is the smallest of the quantities $U_{mm'}$ and W is the bandwidth as obtained by the diagonalization of the kinetic part of (2.3). In this limit, the unperturbed Hamiltonian H_0 is taken to be the interaction part of (2.3), the kinetic perturbation lifting the spin and orbital degeneracy of the ground state of H_0. This arises from the fact that we can arrange the orbital and spin occupancy of the two electrons independently of each other in the three atomic states at each site. Even in the atomic limit this problem would be quite complicated to treat in full generality if some simplifications were not possible. A hint comes from the experimentally observed number of Bohr magnetons per site: 1.2 μB. This fact and the consideration of the corundum structure which favors pairings of the cations along the z axis, strongly suggests, as already anticipated by several authors,[15,16] that one a_{1g} electron per site is engaged in forming a more or less covalent nonmagnetic bond between the vertical cations pairs. This bond is enlarged into a band by interaction with neighboring pairs (Fig. 2). This leaves the remaining electron in a doubly-degenerate band to determine the magnetic structure experimentally observed. A covalency-enhancement mechanism and an exchange polarization of the a_{1g} electron can then be invoked as discussed at length in II, to account for the rather unusual amount of 1.2 μ_B per site.

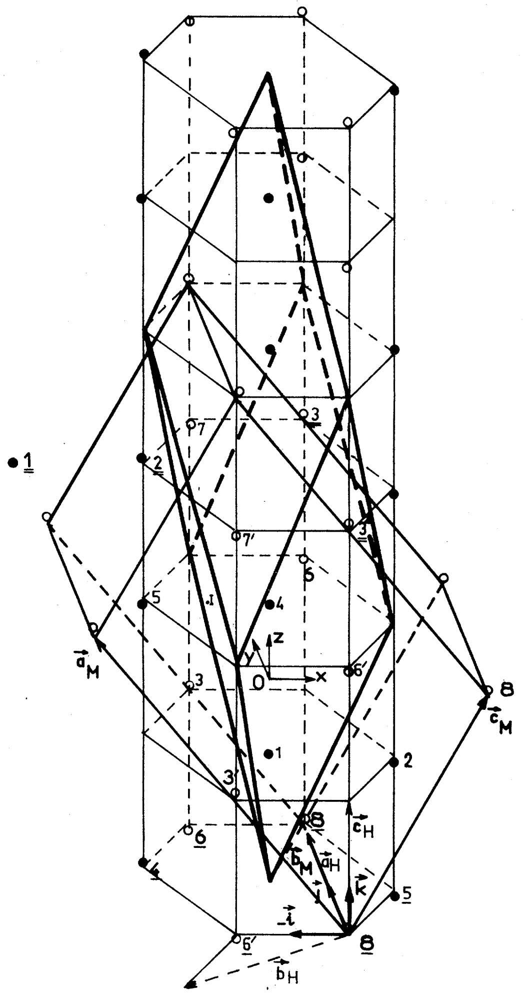


FIG. 3. Corundum structure together with the unit cells for the trigonal and monoclinic phase, respectively. Only cations are shown (black circles: spin up; white circles: spin down). 0 is the origin of the xyz reference (oriented as in Fig. 1) placed midway between atoms 1 and 4, while I is the inversion center midway between atoms 4 and 5.

Other possible interpretations are to be ruled out on the basis of the following consideration: The observed magnetic structure cannot be exclusively determined by the a_{1g} electrons. Neglecting for the moment the presence of the other electrons on each site, an a_{1g} electron per site would be described by an Hubbard Hamiltonian for a nondegenerate band, leading, as is well known, to an antiferromagnetic coupling with the immediate neighbors, contrary to what is observed. Moreover, the observed magnetic breaking of the trigonal symmetry would be inexplicable in such a situation. In fact, in the atomic limit, the magnetic system would be described by the Heisenberg Hamiltonian

$$
H_{\text{exch}} = \sum_{ij} \frac{(t^{33}_{ij})^2}{U_{33}} (2\vec{S}_i \cdot \vec{S}_j - \tfrac{1}{2}), \qquad (2.12)
$$

where

$$t_{ij}^{33}=\int w_i^3(\vec{x})H_0(\vec{x})w_j^3(\vec{x})\,d^3x\,. \tag{2.13}$$

By the trigonal symmetry and the invariance of w_j^3 under C_3 $[w_j^3(C_3\vec{x})=w_{C_3j}^3(\vec{x})]$, the value of t_{ij}^{33} [and consequently of the exchange constant $(t_{ij}^{33})^2/U_{33}$] would be the same for all the three basal-plane neighbors of a central cation (in Fig. 3, $t_{12}^{33}=t_{13}^{33}=t_{13'}^{33}$).

On the other hand, we run into the same kind of difficulties if we think of putting the two electrons per site in the doubly degenerate e_g states. Since by Hunds Rule they should occupy an orbital, each with parallel spin, the situation, as far as the magnetic structure is concerned, would be exactly analogous to the case of one electron per site in a single band. This leaves us the first possibility so that in Sec. III, we shall take as our model Hamiltonian the expression (2.3) where the sum over m is to be understood to range from 1 to 2 and the "unperturbed" ground state containing one electron per site.

III. EFFECTIVE HAMILTONIAN IN THE ATOMIC LIMIT

Under the assumption of Sec. II, the ground state of the unperturbed Hamiltonian in Eq. (2.3) is 2^{2N}-fold degenerate, N being the number of sites. Denoting by α and α' two particular ground states and by β one of the excited states (we shall neglect the excited states with more than two electrons per site), second-order perturbation theory gives the eigenvalue equation

$$\left|\sum_{\beta}\frac{\langle\alpha|H'|\beta\rangle\langle\beta|H'|\alpha'\rangle}{E_\alpha-E_\beta}-E\delta_{\alpha\alpha'}\right|=0 \tag{3.1}$$

for the lifting of the degeneracy by the perturbation

$$H'=\sum_{jj'}\sum_{mm'}\sum_{\sigma}t_{jj'}^{mm'}c_{jm\sigma}^{\dagger}c_{j'm'\sigma}\,. \tag{3.2}$$

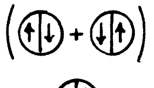
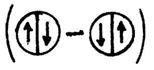
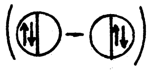
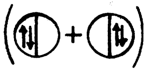
In (3.1) $E_\alpha=E_{\alpha'}$ (for every α and α') is the ground-state energy common to all the 2^{2N} degenerate states, whereas E_β is the energy of the intermediate excited configuration. For each site, there are six such configurations given in Table I, where as usual in the literature, to visualize the electron occupancy on a site, we have used a circle divided into halves indicating the two orbitals: orbital 1 (left half), orbital 2 (right half). The state $|0\rangle$ is the vacuum state. It follows that the operator

$$\sum_j\sum_{\lambda=1}^{6}\frac{|\beta_{j\lambda}\rangle\langle\beta_{j\lambda}|}{(E_\alpha-E_\beta)} \tag{3.3}$$

when acting on the state $H'|\alpha\rangle$ is given by $\underline{X}=\sum_j\underline{X}_j$ where

$$-\underline{X}_j=\frac{1}{U_{12}-J}\sum_{\sigma}n_{j1\sigma}n_{j2\sigma}+\frac{1}{U_{12}^2-J^2}\Big(U_{12}\sum_{m\neq m'}n_{jm\uparrow}n_{jm'\downarrow}+J\sum_{m\neq m'}c_{jm\uparrow}^{\dagger}c_{jm\downarrow}c_{jm'\downarrow}^{\dagger}c_{jm'\uparrow}\Big)$$
$$+\frac{1}{U_{11}^2-J^2}\Big(U_{11}\sum_{m}n_{jm\uparrow}n_{jm\downarrow}-J\sum_{m\neq m'}c_{jm\uparrow}^{\dagger}c_{jm\downarrow}^{\dagger}c_{jm'\downarrow}c_{jm'\uparrow}\Big)\,. \tag{3.4}$$

TABLE I. Six excited states $|\beta_i\rangle$ $(i=1,6)$ together with their energy $E_{\beta_i}-E_\alpha$ which determine the effective Hamiltonian in second-order perturbation theory.

		$E_\beta-E_\alpha=$
$|\beta_1\rangle=c_{1\uparrow}^{\dagger}c_{2\uparrow}^{\dagger}|0\rangle=$		$U_{12}-J$
$|\beta_2\rangle=(1/\sqrt{2})(c_{1\uparrow}^{\dagger}c_{2\downarrow}^{\dagger}+c_{1\downarrow}^{\dagger}c_{2\uparrow}^{\dagger})|0\rangle=\frac{1}{\sqrt{2}}$		$U_{12}-J$
$|\beta_3\rangle=c_{1\downarrow}^{\dagger}c_{2\downarrow}^{\dagger}|0\rangle=$		$U_{12}-J$
$|\beta_4\rangle=(1/\sqrt{2})(c_{1\uparrow}^{\dagger}c_{2\downarrow}^{\dagger}-c_{1\downarrow}^{\dagger}c_{2\uparrow}^{\dagger})|0\rangle=\frac{1}{\sqrt{2}}$		$U_{12}+J$
$|\beta_5\rangle=(1/\sqrt{2})(c_{1\uparrow}^{\dagger}c_{1\downarrow}^{\dagger}-c_{2\uparrow}^{\dagger}c_{2\downarrow}^{\dagger})|0\rangle=\frac{1}{\sqrt{2}}$		$U_{11}-J$
$|\beta_6\rangle=(1/\sqrt{2})(c_{1\uparrow}^{\dagger}c_{1\downarrow}^{\dagger}+c_{2\uparrow}^{\dagger}c_{2\downarrow}^{\dagger})|0\rangle=\frac{1}{\sqrt{2}}$		$U_{11}+J$

We have eliminated the operator $|0\rangle\langle 0|$ by replacing it with the complete set $\sum_n |n\rangle\langle n|$ (equal to the identity operator) since the states other than $\langle 0|$ cannot contribute to the sum because of the particle-number conservation. Also, we have written $J_{12}=J$ for simplicity.

Coming back to the expression (3.1), we see that in the Hilbert subspace spanned by the states $|\alpha\rangle$, we have to diagonalize the effective Hamiltonian

$$H_{\text{eff}}=H'\underline{X}H'\,. \tag{3.5}$$

Moreover in this subspace, only terms of the kind

$$t_{ij}^{nm}t_{ji}^{m'n'}c_{in\sigma}^{\dagger}c_{jm\sigma}\underline{X}_j c_{jm'\sigma'}^{\dagger}c_{in'\sigma'} \tag{3.6}$$

can contribute. In this same subspace, the operator $c_{jm\sigma}\underline{X}_j c_{jm'\sigma'}^{\dagger}$ when applied to the states $c_{in'\sigma'}|\alpha\rangle$ is equivalent to

$$\begin{aligned} c_{jm\sigma}\underline{X}_j c_{jm'\sigma'}^{\dagger} &= c_{jm\sigma}[\underline{X}_j, c_{jm'\sigma'}^{\dagger}] \\ &= -[\underline{X}_j, c_{jm'\sigma'}^{\dagger}]c_{jm\sigma}+\{c_{jm\sigma}, [\underline{X}_j, c_{jm'\sigma'}^{\dagger}]\} \\ &= \{c_{jm\sigma}, [\underline{X}_j, c_{jm'\sigma'}^{\dagger}]\}, \end{aligned} \tag{3.7}$$

where $[A, B]$ indicates the commutator between two operators A and B, and $\{A, B\}$ their anticommutator.

The use of the usual anticommutation rules between the c fermion operators leads to the following ($-\sigma$ indicating the spin orientation opposite to σ):

$$\begin{aligned} -\left\{c_{jm\sigma}, \left[\underline{X}_j, c_{jm'\sigma'}^{\dagger}\right]\right\} = {} & \frac{1}{U_{11}^2-J^2}\,[U_{11}\delta_{mm'}(n_{jm\,-\sigma}\delta_{\sigma\sigma'}-c_{jm\,-\sigma}^{\dagger}c_{jm\sigma}\delta_{\sigma\,-\sigma})-J(1-\delta_{mm'}) \\ & \times(c_{jm\,-\sigma}^{\dagger}c_{jm'\,-\sigma}\delta_{\sigma\sigma'}-c_{jm\,-\sigma}^{\dagger}c_{jm'\sigma}\delta_{\sigma\,-\sigma'})] \\ & +\frac{1}{U_{12}^2-J^2}\left[U_{12}\sum_{m''\neq m'}(\delta_{mm'}\delta_{\sigma\sigma'}n_{jm''\,-\sigma}-\delta_{\sigma\,-\sigma'}\delta_{mm''}c_{jm'\,-\sigma}^{\dagger}c_{jm\sigma})\right. \\ & \left.+J\sum_{m''\neq m'}(\delta_{mm'}\delta_{\sigma\,-\sigma'}c_{jm''\,-\sigma}^{\dagger}c_{jm''\sigma}-\delta_{mm''}\delta_{\sigma\sigma'}c_{jm'\,-\sigma}^{\dagger}c_{jm\,-\sigma})\right] \\ & +\frac{1}{U_{12}-J}\left[\sum_{m''\neq m'}(\delta_{mm'}\delta_{\sigma\sigma'}n_{jm\sigma}-\delta_{mm''}\delta_{\sigma\sigma'}c_{jm'\sigma}^{\dagger}c_{jm\sigma})\right]. \end{aligned} \tag{3.8}$$

Hence, upon introduction of the symbol $-m$ to indicate the orbital other than m and suitable grouping of the various terms, we can write the effective Hamiltonian

$$H_{\text{eff}}=\sum_{ij}\sum_{nn'}\sum_{mm'}\sum_{\sigma}c_{in\sigma}^{\dagger}\{c_{jm\sigma}, [\underline{X}, c_{jm'\sigma'}^{\dagger}]\} \times c_{in'\sigma'}t_{ij}^{nm}t_{ij}^{n'm'} \tag{3.9}$$

in the following form:

$$\begin{aligned} H_{\text{eff}} = {} & -\sum_{ij}\sum_{nn'm}\sum_{\sigma}t_{ij}^{nm}t_{ij}^{n'm}c_{in\sigma}^{\dagger}c_{in'\sigma}\left(\frac{U_{11}}{U_{11}^2-J^2}\,n_{jm\,-\sigma}+\frac{U_{12}}{U_{12}^2-J^2}\,n_{j\,-m\,-\sigma}+\frac{1}{U_{12}-J}\,n_{j\,-m\sigma}\right) \\ & -\sum_{ij}\sum_{nn'm}\sum_{\sigma}t_{ij}^{nm}t_{ij}^{n'm}c_{in\sigma}^{\dagger}c_{in'\,-\sigma}\left(-\frac{U_{11}}{U_{11}^2-J^2}\,c_{jm\,-\sigma}^{\dagger}c_{jm\sigma}+\frac{J}{U_{12}^2-J^2}\,c_{j\,-m\,-\sigma}^{\dagger}c_{j\,-m\sigma}\right) \\ & -\sum_{ij}\sum_{nn'm}\sum_{\sigma}t_{ij}^{nm}t_{ij}^{n'\,-m}c_{in\sigma}^{\dagger}c_{in'\sigma}\left(-\frac{J}{U_{11}^2-J^2}\,c_{jm\,-\sigma}^{\dagger}c_{j\,-m\,-\sigma}-\frac{J}{U_{12}^2-J^2}\,c_{j\,-m\,-\sigma}^{\dagger}c_{jm\,-\sigma}-\frac{1}{U_{12}-J}\,c_{j\,-m\sigma}^{\dagger}c_{jm\sigma}\right) \\ & -\sum_{ij}\sum_{nn'm}\sum_{\sigma}t_{ij}^{nm}t_{ij}^{n'\,m}c_{in\sigma}^{\dagger}c_{in'\,-\sigma}\left(\frac{J}{U_{11}^2-J^2}\,c_{jm\,-\sigma}^{\dagger}c_{j\,-m\sigma}-\frac{U_{12}}{U_{12}^2-J^2}\,c_{j\,-m\,-\sigma}^{\dagger}c_{jm\sigma}\right). \end{aligned} \tag{3.10}$$

Now let us turn our attention to the states $|\alpha\rangle$. These states can be represented as $\Pi_j c^\dagger_{jm_js_j}|0\rangle$ where m_j can take up two values (1, 2) per site j and similarly for the spin s_j. Hence, the state of our electron localized at the site j can be characterized by two quantum numbers: the spin s and the number of the occupied orbital. In our case of twofold degeneracy, it is convenient to describe the orbital state by means of the "pseudospin" operator τ with properties that are exactly analogous to the properties of the usual spin operator s. Then a value $\tau^z = \frac{1}{2}$ will correspond to the occupied orbital $m = 1$, whereas $\tau^z = -\frac{1}{2}$ will indicate the orbital $m = 2$. Correspondingly, the state $|\alpha\rangle$ can be represented as $\Pi_j |\tau^z_j; s^z_j\rangle$, the state $|\tau^z, s^z\rangle$ being an eigenstate of the product $\tau^z s^z$. (Notice that the axes in the τ space are independent from those in s space, although we shall continue to use the same notation for convenience.)

Moreover, it is straightforward to check that the operators $c^\dagger_{in\sigma}c_{in'\sigma'}$ acting onto the states $|\alpha\rangle = \Pi_j c^\dagger_{jm_js_j}|0\rangle$ (which describe a charge in the orbital and/or spin quantum number) can be set in a one-to-one correspondence (depending on the indices n, n' and σ, σ') with the product τs acting onto $|\alpha\rangle = \Pi_j |\tau_j; s_j\rangle$ in accordance with the following rules:

$$(n=1, n'=1) \rightarrow \tfrac{1}{2} + \tau^z, \quad (2,2) \rightarrow \tfrac{1}{2} - \tau^z, \quad (1,2) \rightarrow \tau^+, \quad (2,1) \rightarrow \tau^-$$

$$(\sigma = \uparrow, \sigma' = \uparrow) \rightarrow \tfrac{1}{2} + S^z,$$

$$(\downarrow, \downarrow) \rightarrow \tfrac{1}{2} - S^z, \quad (\uparrow, \downarrow) \rightarrow S^+, \quad (\downarrow, \uparrow) \rightarrow S^-, \tag{3.11}$$

where, as usual, we have defined

$$\tau^\pm = \tau^x \pm i\tau^y \text{ and } S^\pm = S^x \pm iS^y.$$

Hence, as an example, the operator $c^\dagger_{i1\uparrow}c_{i1\downarrow}$ is represented by $(\frac{1}{2} + \tau^z_i)S^+_i$ and the operator $c^\dagger_{i2\downarrow}c_{i1\downarrow}$ by $\tau^-_i(\frac{1}{2} - S^z_i)$. A straightforward but nevertheless tedious algebra leads to the following expression for H_{eff} in (3.10):

$$\begin{aligned}
-H_{\text{eff}} = \sum_{ij} \Bigg\{ & -\frac{1}{U_{12} - J}\,[A_{ij}(\vec\tau) - \tfrac{1}{2}B_{ij}(\vec\tau) + C_{ij}(\vec\tau) + D_{ij}(\vec\tau)](2\vec{S}_i \cdot \vec{S}_j + \tfrac{1}{2}) \\
& + \Bigg[[A_{ij}(\vec\tau) + C_{ij}(\vec\tau)]\left(\frac{J}{U_{12}^2 - J^2} + \frac{J}{U_{11}^2 - J^2}\right) \\
& - \tfrac{1}{2}\left(\frac{U_{12}}{U_{12}^2 - J^2} + \frac{U_{11}}{U_{11}^2 - J^2}\right)B_{ij}(\vec\tau) + D'_{ij'}(\vec\tau)\Bigg](2\vec{S}_i \cdot \vec{S}_j - \tfrac{1}{2})\Bigg\},
\end{aligned} \tag{3.12}$$

where

$$\begin{aligned}
A_{ij}(\vec\tau) &= \{[(t^{11}_{ij})^2 - (t^{12}_{ij})^2](\tfrac{1}{2} + \tau^z_i) + (t^{11}_{ij}t^{21}_{ij} - t^{12}_{ij}t^{22}_{ij})(\tau^+_i + \tau^-_i) + [(t^{12}_{ij})^2 - (t^{22}_{ij})^2](\tfrac{1}{2} - \tau^z_i)\}\tau^z_j, \\
B_{ij}(\vec\tau) &= \{[(t^{11}_{ij})^2 + (t^{12}_{ij})^2](\tfrac{1}{2} + \tau^z_i) + (t^{11}_{ij}t^{21}_{ij} + t^{12}_{ij}t^{22}_{ij})(\tau^+_i + \tau^-_i) + [(t^{12}_{ij})^2 + (t^{22}_{ij})^2](\tfrac{1}{2} - \tau^z_i)\}, \\
C_{ij}(\vec\tau) &= [t^{11}_{ij}t^{12}_{ij}(\tfrac{1}{2} + \tau^z_i) + t^{21}_{ij}t^{22}_{ij}(\tfrac{1}{2} - \tau^z_i)](\tau^+_j + \tau^-_j), \\
D_{ij}(\vec\tau) &= [(t^{11}_{ij}t^{22}_{ij}\tau^+_i + t^{21}_{ij}t^{12}_{ij}\tau^-_i)\tau^-_j + (t^{11}_{ij}t^{22}_{ij}\tau^-_i + t^{21}_{ij}t^{12}_{ij}\tau^+_i)\tau^+_j], \\
D'_{ij}(\vec\tau) &= \Bigg[(t^{11}_{ij}t^{22}_{ij}\tau^+_i + t^{21}_{ij}t^{12}_{ij}\tau^-_i)\left(\frac{J}{U_{11}^2 - J^2}\tau^+_j + \frac{J}{U_{12}^2 - J^2}\tau^-_j\right) + (t^{11}_{ij}t^{22}_{ij}\tau^-_i + t^{21}_{ij}t^{12}_{ij}\tau^+_i) \\
&\quad \times \left(\frac{J}{U_{11}^2 - J^2}\tau^-_j + \frac{J}{U_{12}^2 - J^2}\tau^+_j\right)\Bigg].
\end{aligned} \tag{3.13}$$

The usual Heisenberg Hamiltonian for electrons in a nondegenerate band is recovered by putting

$$\tau^z = \tfrac{1}{2}, \quad t^{12} = t^{22} = J = 0, \quad U_{11} = U_{12} = U.$$

Before going on to discuss the orbital and spin ground-state configuration (for our case of interest), we want to treat the case of the diatomic molecule with one electron per site in a doubly-degenerate Wannier state. The exact eigenstates and eigenvalues (exact in the Hilbert subspace spanned by the four Wannier orbitals) can be easily found and are given in Appendix A. This discussion will enable us to check the correctness of (3.13) in this particular case and what is more important, to have an insight into the structure of the ground state and the low-lying excited states. Let us indicate with a and b the two sites, that is to say the two atoms constituting the molecule; and let the four real Wannier functions be $w_a^1(\vec{x})$, $w_a^2(\vec{x})$, $w_b^1(\vec{x})$, and $w_b^2(\vec{x})$. Since the axis joing the two atoms is a symmetry axis for rotation $R(\theta)$ of any angle θ, we must have

$$\begin{aligned} R(\theta)w^1_{a(b)}(\vec{x}) &= w^1_{a(b)}(R(\theta)\vec{x}) = \cos l\theta\, w^1_{a(b)}(\vec{x}) + \sin l\theta\, w^2_{a(b)}(\vec{x}) , \\ R(\theta)w^2_{a(b)}(\vec{x}) &= w^2_{a(b)}(R(\theta)\vec{x}) = -\sin l\theta\, w^1_{a(b)}(\vec{x}) + \cos l\theta\, w^2_{a(b)}(\vec{x}) \end{aligned} \tag{3.14}$$

since the combination $w^1 + iw^2$ must transform

$$R(\theta)(w^1 + iw^2) = (e^{-i\theta})^l (w^1 + iw^2)$$

in the E_l representation ($l = 1, 2, \ldots$) of the group ∞/mm. As usual we have indicated by $R(\theta)\vec{x}$ a rotation of the coordinates about the symmetry axis taken as z axis. Moreover, since the one body potential $V(\vec{x})$ is invariant under $R(\theta)$, we have

$$\begin{aligned} t^{11}_{ab}(\theta) &= \int w^1_a(R(\theta)\vec{x})\, V(R(\theta)\vec{x})\, w^1_b(R(\theta)\vec{x})\, dx = \int d^3x\, w^1_a(\vec{x}) V(\vec{x}) w^1_b(\vec{x}) = t^{11}_{ab} \\ &= \cos^2 l\theta\, t^{11}_{ab} + \sin^2 l\theta\, t^{22}_{ab} + \cos l\theta \sin l\theta (t^{12}_{ab} + t^{21}_{ab}) , \\ t^{22}_{ab}(\theta) &= t^{22}_{ab} = \sin^2 l\theta\, t^{11}_{ab} + \cos^2 l\theta\, t^{22}_{ab} - \sin l\theta \cos l\theta (t^{12}_{ab} + t^{21}_{ab}) , \\ t^{12}_{ab}(\theta) &= t^{12}_{ab} = \cos l\theta \sin l\theta (t^{22}_{ab} - t^{11}_{ab}) + \cos^2 l\theta\, t^{12}_{ab} - \sin^2 l\theta\, t^{21}_{ab} , \\ t^{21}_{ab}(\theta) &= t^{21}_{ab} = \cos l\theta \sin l\theta (t^{22}_{ab} - t^{11}_{ab}) + \cos^2 l\theta\, t^{21}_{ab} - \sin^2 l\theta\, t^{21}_{ab} , \end{aligned} \tag{3.15}$$

implying that $t^{11}_{ab} = t^{22}_{ab} = t$ and $t^{12}_{ab} = t^{21}_{ab} = 0$ (all this will also apply for particular values of θ $(= \pm\frac{2}{3}\pi)$ and $l = 1$ to any particular pair of cations along the z axis (three-fold rotation C_3 axis) in V_2O_3. Moreover, we shall put without loss of generality $t^{mm}_{aa} = t^{mm}_{bb} = 0$ $(m = 1, 2)$. Defining the functions $\mu(x) = [x - (x^2 + 16t^2)^{1/2}]/4t$ and $\epsilon(x) = \frac{1}{2}(x - [x^2 + 16t^2]^{1/2})$ it is shown in Appendix A that the ground state of the molecule is given by

$$\begin{aligned} &[(c^\dagger_{a1\uparrow} c^\dagger_{b2\uparrow} - c^\dagger_{a2\uparrow} c^\dagger_{b1\uparrow}) \\ &+ \mu(U_{12} - T)(c^\dagger_{a1\uparrow} c^\dagger_{a2\uparrow} + c^\dagger_{b1\uparrow} c^\dagger_{b2\uparrow})]|0\rangle \end{aligned} \tag{3.16}$$

with an energy $\epsilon(U_{12} - J)$. In the atomic limit $[4t/(U_{12} - J) \ll 1]$ we find

$$\epsilon(U_{12} - J) \to -4t^2/(U_{12} - J)$$

and

$$\mu(U_{12} - J) \to -2t/(U_{12} - J).$$

In the τs space, the nonpolar part of the state (3.16) becomes

$$\begin{aligned} |\Psi_s\rangle|\phi_t\rangle = (1/\sqrt{2})[\,|a{:}\tau^z = \tfrac{1}{2}\rangle|b{:}\tau^z = -\tfrac{1}{2}\rangle - |a{:}\tau^z \\ = -\tfrac{1}{2}\rangle|b{:}\tau^z = \tfrac{1}{2}\rangle]|a{:}s^z = \tfrac{1}{2}\rangle|b{:}s^z = \tfrac{1}{2}\rangle , \end{aligned} \tag{3.17}$$

where we have used the convention that the first ket of the Kronecker product refers to the orbital part (s indicating a singlet state in τ space) whereas the second ket refers to the spin part (t indicating a triplet state in spin space). Then it is easy to verify that

$$\begin{aligned} &\langle\Psi_s|A_{ab}(\vec{\tau})|\Psi_s\rangle = -\tfrac{1}{2}t^2 , \\ &\langle\Psi_s| -\tfrac{1}{2}B_{ab}(\vec{\tau})|\Psi_s\rangle = -\tfrac{1}{2}t^2 , \\ &\langle\Psi_s|C_{ab}(\vec{\tau})|\Psi_s\rangle = 0 \\ &\langle\Psi_s|D_{ab}(\vec{\tau})|\Psi_s\rangle = -t^2 , \\ &\langle\phi_t|(2\vec{S}_a \cdot \vec{S}_b + \tfrac{1}{2})|\phi_t\rangle = 1 , \\ &\langle\phi_t|(2\vec{S}_a \cdot \vec{S}_b - \tfrac{1}{2})|\phi_t\rangle = 0 , \end{aligned}$$

so that

$$\langle\phi_t|(\Psi_s|H_{\text{eff}}|\Psi_s)|\phi_t\rangle = -4t^2/(U_{12} - J) , \tag{3.18}$$

as it should (the extra factor of two is coming from the $\sum_{ab}$ in H_{eff}). Actually

$$H_{\text{eff}}\,|\Psi_s\rangle|\phi_t\rangle=-[4t^2/(U_{12}-J)]|\psi_s\rangle|\phi_t\rangle$$

that is $|\Psi_s\rangle|\phi_t\rangle$ is an eigenstate of H_{eff}. The perturbed ground state turns out to be

$$|\Psi_s\rangle|\phi_t\rangle-\frac{2t}{U_{12}-J}\,\frac{1}{\sqrt{2}}\,[|a{:}\tau^z=\tfrac{1}{2},s^z=\tfrac{1}{2}\rangle|a{:}\tau^z=-\tfrac{1}{2},s^z=\tfrac{1}{2}\rangle+|b:\tau^z=\tfrac{1}{2},s^z=\tfrac{1}{2}\rangle|b{:}\tau^z=-\tfrac{1}{2},s^z=\tfrac{1}{2}\rangle], \tag{3.19}$$

which is the atomic limit of (3.16).

From (3.19) and (3.16) it is apparent that the electrons in the ground state assume a singlet orbital and a triplet spin configuration as a consequence of the fact that in their virtual jumps on the same atom, they want to pay the minimum of repulsive Coulomb energy possible, i.e., $U_{12}-J$. This is the reason why the vertical pairs in the antiferromagnetic-insulating phase of V_2O_3 are ferromagnetically coupled. Exciting the orbital state to a triplet configuration,

$$|\Psi_t\rangle=(1/\sqrt{2})[|a{:}\tfrac{1}{2}\rangle|b{:}-\tfrac{1}{2}\rangle+|a{:}-\tfrac{1}{2}\rangle|b{:}\tfrac{1}{2}\rangle], \tag{3.20}$$

we find, taking into account that $\langle\Psi_t|A_{ab}(\vec{\tau})|\Psi_t\rangle=-\frac{1}{2}t^2$,

$$\begin{aligned}&\langle\Psi_t|-\tfrac{1}{2}B_{ab}(\vec{\tau})|\Psi_t\rangle=-\tfrac{1}{2}t^2,\\&\langle\Psi_t|C_{ab}(\vec{\tau})|\Psi_t\rangle=0\\&\langle\Psi_t|D_{ab}(\vec{\tau})|\Psi_t\rangle=t^2,\\&\langle\phi_t|\langle\Psi_t|H_{\text{eff}}|\Psi_t\rangle|\phi_t\rangle=0,\end{aligned} \tag{3.21}$$

which corresponds to the "exact" eigenstate

$$H(c^\dagger_{a1\uparrow}c^\dagger_{b2\uparrow}+c^\dagger_{a2\uparrow}c^\dagger_{b1\uparrow})|0\rangle=0. \tag{3.22}$$

In this configuration, the electrons cannot gain kinetic energy by jumping onto the same site since this is forbidden by the Pauli principle. Hence, the excitation energy connected to this orbital excitation leaving the spin configuration unchanged is given by

$$-\epsilon(U_{12}-J)\xrightarrow[\text{atom lim}]{}4t^2/(U_{12}-J). \tag{3.23}$$

A lower excitation energy is found if we change simultaneously the spin and orbital configuration; that is to say, we consider the state

$$\begin{aligned}|\Psi_t\rangle|\phi_s\rangle=(1/\sqrt{2})&[|a{:}\tfrac{1}{2}\rangle|b{:}-\tfrac{1}{2}\rangle+|a{:}-\tfrac{1}{2}\rangle|b{:}\tfrac{1}{2}\rangle]\\&\times(1/\sqrt{2})[|a{:}s^z=\tfrac{1}{2}\rangle|b{:}s^z=-\tfrac{1}{2}\rangle\\&\qquad-|a{:}s^z=-\tfrac{1}{2}\rangle|b{:}s^z=\tfrac{1}{2}\rangle].\end{aligned} \tag{3.24}$$

Since $\langle\phi_s|(2\mathrm{S}_a\cdot\mathrm{S}_b+\frac{1}{2})|\phi_s\rangle=-1$ and $\langle\phi_s|(2\mathrm{S}_a\cdot\mathrm{S}_b-\frac{1}{2})|\phi_s\rangle=-2$, we have still to evaluate

$$\begin{aligned}&\langle\Psi_t|D'_{ab}(\vec{\tau})|\Psi_t\rangle\\&=\langle\Psi_t|t^2\tau_a^+\left(\frac{J}{U_{11}^2-J^2}\tau_b^++\frac{J}{U_{12}^2-J^2}\tau_b^-\right)+\text{H.c.}|\Psi_t\rangle\\&=t^2\frac{J}{U_{12}^2-J^2}.\end{aligned}$$

Summing up the various contributions, we find

$$\begin{aligned}&\langle\phi_s|\langle\Psi_t|H_{\text{eff}}|\Psi_t\rangle|\phi_s\rangle\\&=-\frac{1}{U_{12}-J}(-2t^2+2t^2)\\&\quad+2\left[-t^2\left(\frac{J}{U_{12}^2-J^2}+\frac{J}{U_{11}^2-J^2}\right)\right.\\&\quad\left.-t^2\left(\frac{U_{12}}{U_{12}^2-J^2}+\frac{U_{11}}{U_{11}^2-J^2}\right)+2t^2\frac{J}{U_{12}^2-J^2}\right]\\&=-\frac{4t^2}{U_{12}+J},\end{aligned} \tag{3.25}$$

which is the atomic limit of the energy $\epsilon(U_{12}+J)$ relative to the exact excited state

$$\begin{aligned}&[(c^\dagger_{a1\uparrow}c^\dagger_{b2\downarrow}-c^\dagger_{a1\downarrow}c^\dagger_{b2\uparrow}+c^\dagger_{a2\uparrow}c^\dagger_{b1\downarrow}-c^\dagger_{a2\downarrow}c^\dagger_{b1\uparrow})\\&\quad+\mu(U_{12}+J)(c^\dagger_{a1\uparrow}c^\dagger_{a2\downarrow}-c^\dagger_{a1\downarrow}c^\dagger_{a2\uparrow}\\&\qquad+c^\dagger_{b1\uparrow}c^\dagger_{b2\downarrow}-c^\dagger_{b1\downarrow}c^\dagger_{b2\uparrow})]|0\rangle.\end{aligned} \tag{3.26}$$

The excitation energy of this state relative to the ground state is given by

$$\begin{aligned}\epsilon(U_{12}+J)-\epsilon(U_{12}-J)\xrightarrow[\text{atom lim}]{}&-\frac{4t^2}{U_{12}+J}+\frac{4t^2}{U_{12}-J}\\&=\frac{8t^2J}{U_{12}^2-J^2},\end{aligned} \tag{3.27}$$

which is much lower than (3.23).

Similarly, for the state $|\Psi_s\rangle|\phi_s\rangle$ corresponding to the exact eigenstate

$$\begin{aligned}&H(c^\dagger_{a1\uparrow}c^\dagger_{b2\downarrow}-c^\dagger_{a1\downarrow}c^\dagger_{b2\uparrow}\\&\quad-c^\dagger_{a2\uparrow}c^\dagger_{b1\downarrow}+c^\dagger_{a2\downarrow}c^\dagger_{b1\uparrow})|0\rangle=0,\end{aligned}$$

we find

$$\langle\phi_s|\langle\Psi_s|H_{\text{eff}}|\Psi_s\rangle|\phi_s\rangle=0$$

since

$$\langle\Psi_s|D'_{ab}(\vec{\tau})|\Psi_s\rangle=-t^2J/(U_{12}^2-J^2).$$

The excitation energy relative to the ground state is given by (3.23), the Pauli principle again preventing two electrons from jumping onto the same site. Hence, we see that the pure spin excitations or the pure orbital excitations would have in the atomic limit a critical temperature of the order of $[4t^2/(U_{12}-J)]/k_B$, whereas for the combined orbital and spin excitations we would get a critical temperature of the order of $[8Jt^2/(U_{12}^2-J^2)]/k_B$.[12]

Other excited states have an excitation energy relative to the ground state comparable to the one in (3.27). These states take advantage of the last term in the Hamiltonian (2.3) by having the two electrons on the same orbital with antiparallel spin when they jump on the same site. Since the last term in (2.3) does not conserve the total z component of the orbital spin $\tau^z=\tau_a^z+\tau_b^z$, the nonpolar part of the states is not an eigenstate of τ_{tot}^z although it is still an eigenstate of $(\vec{\tau}_a+\vec{\tau}_b)^2$. From Appendix A, we derive that one of these states is given by

$$\begin{aligned}[](c_{a1\uparrow}^\dagger c_{b1\downarrow}^\dagger - c_{a1\downarrow}^\dagger c_{b1\uparrow}^\dagger - c_{a2\uparrow}^\dagger c_{b2\downarrow}^\dagger + c_{a2\downarrow}^\dagger c_{b2\uparrow}^\dagger)\\ +\mu(U_{11}-J)(c_{a1\uparrow}^\dagger c_{a1\downarrow}^\dagger - c_{a2\uparrow}^\dagger c_{a2\downarrow}^\dagger\\ + c_{b1\uparrow}^\dagger c_{b1\downarrow}^\dagger - c_{b2\uparrow}^\dagger c_{b2\downarrow}^\dagger)]\,|0\rangle\,, \qquad (3.28)\end{aligned}$$

with eigenvalue

$$\epsilon(U_{11}-J)\xrightarrow[\text{atom lim}]{}-4t^2/(U_{11}-J)\,, \qquad (3.29)$$

remembering that $U_{11}=U_{12}+2J$ is the same as (3.25).

The corresponding state in τs space is given by

$$|\chi^-\rangle|\phi_s\rangle=(1/\sqrt{2})[|a{:}\tfrac12\rangle|b{:}\tfrac12\rangle-|a{:}-\tfrac12\rangle|b{:}-\tfrac12\rangle]|\phi_s\rangle\,, \qquad (3.30)$$

where we have indicated the new orbital part by $|\chi^-\rangle$ and used the same symbol for the spin singlet state. As seen from (3.30)

$$|\chi^-\rangle=(1/\sqrt{2})(|\Psi_t,\tau_{\text{tot}}^z=1\rangle-|\Psi_t,\tau_{\text{tot}}^z=-1\rangle)$$

is a mixture of states with different τ_{tot}^z.

Since one finds

$$\langle\chi^-|A_{ab}(\vec{\tau})|\chi^-\rangle=\tfrac12 t^2,\quad \langle\chi^-|-\tfrac12 B_{ab}(\vec{\tau})|\chi^-\rangle=-\tfrac12 t^2,$$

$$\langle\chi^-|D_{ab}(\vec{\tau})|\chi^-\rangle=0,\quad \langle\chi^-|D'_{ab}(\vec{\tau})|\chi\rangle=-Jt^2/(U_{11}^2-J^2),$$

$$\langle\chi^-|C_{ab}(\vec{\tau})|\chi^-\rangle=0$$

one can easily verify that

$$\langle\phi_s|\langle\chi^-|H_{\text{eff}}|\chi^-\rangle|\phi_s\rangle=-4t^2/(U_{11}-J)\,, \qquad (3.31)$$

as it should.

A nearby lying level is given by the state

$$\begin{aligned}[](c_{a1\uparrow}^\dagger c_{b1\downarrow}^\dagger - c_{a1\downarrow}^\dagger c_{b1\uparrow}^\dagger + c_{a2\uparrow}^\dagger c_{b2\downarrow}^\dagger - c_{a2\downarrow}^\dagger c_{b2\uparrow}^\dagger)\\ +\mu(U_{11}+J)(c_{a1\uparrow}^\dagger c_{a1\downarrow}^\dagger + c_{a2\uparrow}^\dagger c_{a2\downarrow}^\dagger + c_{b1\uparrow}^\dagger c_{b1\downarrow}^\dagger\\ + c_{b2\uparrow}^\dagger c_{b2\downarrow}^\dagger)]\,|0\rangle\,, \qquad (3.32)\end{aligned}$$

with energy

$$\epsilon(U_{11}+J)\xrightarrow[\text{atom lim}]{}-4t^2/(U_{11}+J)\,.$$

For the corresponding state in τs space, we find

$$|\chi^+\rangle|\phi_s\rangle=(1/\sqrt{2})[|a{:}\tfrac12\rangle|b{:}\tfrac12\rangle+|a{:}-\tfrac12\rangle|b{:}-\tfrac12\rangle]|\phi_s\rangle\,,$$

for which it is easy to check that

$$\langle\phi_s|\langle\chi^+|H_{\text{eff}}|\chi^+\rangle|\phi_s\rangle=-4t^2/(U_{11}+J)$$

with an excitation energy relative to the ground state of

$$\begin{aligned}&\epsilon(U_{11}+J)-\epsilon(U_{12}-J)\\ &\quad=\epsilon(U_{12}+3J)-\epsilon(U_{12}-J)\xrightarrow[\text{atom lim}]{}\frac{4t^2 4J}{(U_{12}-J)(U_{12}+3J)}\,.\end{aligned} \qquad (3.33)$$

Finally, it is straightforward to check that

$$\langle\phi_t|\langle\chi^\pm|H_{\text{eff}}|\chi^\pm\rangle|\phi_t\rangle=0\,,$$

corresponding to the exact eigenstates

$$H(c_{a1\uparrow}^\dagger c_{b1\uparrow}^\dagger \pm c_{a2\uparrow}^\dagger c_{b2\uparrow}^\dagger)|0\rangle=0\,, \qquad (3.34)$$

where again the Pauli principle prevents electrons from jumping onto the same site. Throughout the previous discussion, there is a threefold degeneracy associated with the spin-triplet states which must be taken into account when counting the number of independent states. The conclusive and interesting picture stemming from this discussion relative to the diatomic molecule is that there are two groups of excited states well separated from each other; one being quite near to the ground state with an excitation energy ΔE of order of t^2J/U_{12}^2 in the atomic limit, while the other has a ΔE of about t^2/U_{12} (we have been considering that $J/U_{12}\lesssim 0.1$ to 0.2 as known from atomic calculation). This fact will be of interest when discussing the properties of V_2O_3.

IV. SYMMETRY CONSIDERATIONS

To apply the effective Hamiltonian (3.13) to our case of interest we have to specialize the values of the relevant transfer integrals. To limit the number of parameters in our discussion, we shall consider only nearest and next-nearest neighbors interaction so that one atom interacts with only four neighboring atoms. Since our aim is to study the symmetry-breaking solutions of the Hamiltonian (3.13), we shall assume this latter to be invariant under the space group of V_2O_3 in the metallic state, i.e., the group $D_{3d}^6(R\bar{3}c)$. This space group has the following generators: (a) C_3: Rotation by $\frac23\pi$ around the corundum c axis (z axis in Fig. 1),

$$c_3(x,y,z)=(-\tfrac12 x-\tfrac12\sqrt{3}\,y,\ \tfrac12\sqrt{3}\,x-\tfrac12 y,\ z)\,;$$

(b) C_2: Rotation by π around the y axis,

$$C_2(x,y,z)=(-x,y,-z)\,;$$

(c) C: A glide plane consisting of a translation in the xz plane by half a unit cell in the x and z direction followed by a reflection in the xz plane,

$$C(x,y,z)=(x-(a/\sqrt{3}),\,-y,\,z+\tfrac{1}{6}c)\,.$$

All 12 operations of the group are products of these three generators. In particular $C_2C=I$, the inversion with respect to the center between atoms 4 and 5 (Fig. 3).

There are four vanadium atoms per unit cell (1, 2, 4, and 5) in the trigonal phase, and eight (1, 2, 3, 4, 5, 6, 7, and 8) in the monoclinic unit cell. The above symmetry operations transform them as follows

$$\begin{aligned} &C_3(R_1,R_2,R_4,R_5)=(R_1,R_3,R_4,R_{6'})\,,\\ &C_2(R_1,R_2,R_4,R_5)=(R_4,R_5,R_1,R_2)\,, \qquad (4.1)\\ &C\,(R_1,R_2,R_4,R_5)=(R_5,R_4,R_2'',R_1'')\,. \end{aligned}$$

In particular

$$I(R_1,R_2,R_4,R_5)=(R_2'',R_1'',R_5,R_4)\,. \qquad (4.2)$$

R''; indicates the doubly underlined positions i in Fig. 3. It will be shown in II that our basis wave functions $w^1_{R_i}(\vec{x}),w^2_{R_i}(\vec{x})$ transform under these operations as follows

$$\begin{aligned} C_3[w^1_{R_i}(\vec{x}),w^2_{R_i}(\vec{x})]&=[w^1_{C_3R_i}(C_3(\vec{x}),w^2_{C_3R_i}(C_3(\vec{x})]\\ &=[-\tfrac{1}{2}w^1_{C_3R_i}(\vec{x})+\tfrac{1}{2}\sqrt{3}\,w^2_{C_3R_i}(\vec{x}),\\ &\qquad -\tfrac{1}{2}\sqrt{3}\,w^1_{C_3R_i}(\vec{x})-\tfrac{1}{2}w^2_{C_3R_i}(\vec{x})], \end{aligned} \qquad (4.3a)$$

$$C_2[w^1_{R_i}(\vec{x}),w^2_{R_i}(\vec{x})]=[-w^1_{C_2R_i}(\vec{x}),w^2_{C_2R_i}(\vec{x})], \qquad (4.3b)$$

$$C[w^1_{R_i}(\vec{x}),w^2_{R_i}(\vec{x})]=[-w^1_{CR_i}(\vec{x}),w^2_{CR_i}(\vec{x})], \qquad (4.3c)$$

$$I[w^1_{R_i}(\vec{x}),w^2_{R_i}(\vec{x})]=[w^1_{IR_i}(\vec{x}),w^2_{IR_i}(\vec{x})], \qquad (4.3d)$$

where the result of the operations $C_{(3,2)}R_i$ or IR_i is given in (4.1) and (4.2) for $i=1,2,4,5$. Moreover, the one-particle Hamiltonian $H_0(\vec{x})$ in (2.5) is assumed to be invariant under the group generators (hence under the whole group)

$$H_0(C_{(3,2)}\vec{x})=H_0(\vec{x})\,. \qquad (4.4)$$

An immediate application of the Eqs. (4.2) and (4.3d) is to show that $t^{12}_{ij}=t^{21}_{ij}$ for ij nearest neighbors in the basal plane. In fact, remembering the definition of these quantities in (2.4), we have

$$\begin{aligned} t^{12}_{R_1R_2}&=\int w^1_{R_2}(\vec{x})H_0(\vec{x})w^2_{R_2}(\vec{x})\,d^3x\\ &=\int w^1_{IR_1}(I\vec{x})H_0\,(I\vec{x})\,w^2_{IR_2}(I\vec{x})\,d^3x\\ &=\int w^1_{IR_1}(\vec{x})H_0(\vec{x})w^2_{IR_2}(\vec{x})\,d^3x\\ &=\int w^1_{R_2}(\vec{x})H_0(\vec{x})w^2_{R_1}(\vec{x})\,d^3x=t^{12}_{R_2R_1}=t^{21}_{R_1R_2}\,, \end{aligned} \qquad (4.5)$$

the last step being a consequence of the fact that our Wannier functions are real. This is also sufficient to establish that $t^{12}_{R_4R_5}=t^{21}_{R_4R_5}$, since by application of C_2 we have

$$\begin{aligned} t^{12}_{R_4R_5}&=\int w^1_{R_4}(\vec{x})H_0(\vec{x})w^2_{R_5}(\vec{x})\,d^3x\\ &=-\int w^1_{C_2R_4}(\vec{x})H_0(\vec{x})w^2_{C_2R_5}(\vec{x})d^3x\\ &=-\int w^1_{R_1}(\vec{x})H_0(\vec{x})w^2_{R_2}(\vec{x})\,d^3x=-t^{12}_{R_1R_2}\,, \end{aligned} \qquad (4.6)$$

(remembering that $C_2^{-1}=C_2$). Similarly one obtains $t^{21}_{R_4R_5}=-t^{21}_{R_1R_2}$. For more distant pairs in the system R_i,R_j, the equality $t^{12}_{R_iR_j}=t^{21}_{R_iR_j}$ is in general not true. We shall see an example of this later on. Making full use of the symmetry properties allows us to express all the relevant transfer integrals in terms of the following four, which we denote using the same notations of Nebenzahl and Weger[17]:

$$\begin{aligned} &\int w^1_{R_1}(\vec{x})H_0(\vec{x})w^1_{R_2}(\vec{x})\,d^3x=-\alpha,\\ &\int w^1_{R_1}(\vec{x})H_0(\vec{x})w^2_{R_2}(\vec{x})\,d^3x=\chi\,,\\ &\int w^2_{R_1}(\vec{x})H_0(\vec{x})w^2_{R_2}(\vec{x})\,d^3x=\beta\,,\\ &\int w^1_{R_1}(\vec{x})H_0(\vec{x})w^1_{R_4}(\vec{x})\,d^3x=\mu\,. \end{aligned} \qquad (4.7)$$

Then, denoting by $t^{mm'}_{\vec{\delta}}$ the transfer integrals $t^{mm'}_{ij}$ relative to the two Wannier functions centered at the two ends of the vector $\vec{\delta}=\vec{R}_j-\vec{R}_i$ and making reference to Fig. 4, all the relevant transfer integrals are given in Table II, where it is apparent that $t^{mm'}_{\vec{\delta}_1}$ is related to $t^{mm'}_{\vec{\delta}_2}$ ($t^{mm'}_{\vec{\delta}_3}$) by C_3 (C_3^{-1}),

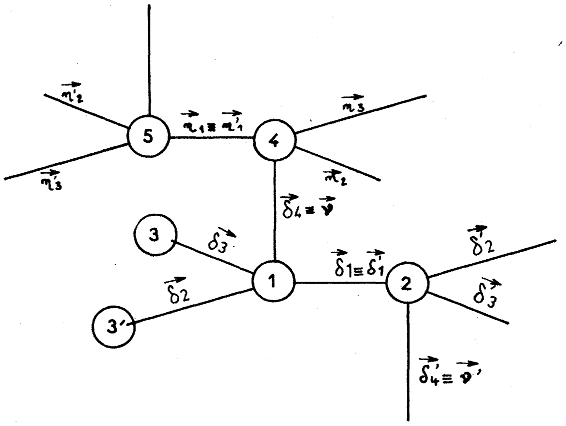


FIG. 4. Nearest-neighbors of atoms 1, 2, 4, and 5 needed for the calculation of the transfer integrals relevant to our problem.

TABLE II. Transfer integrals for electron hopping between the two e_g states and along the directions $\vec{\delta}_i$, $\vec{\eta}_i\,(i=1,3)$ and $\vec{\delta}_4, \vec{\delta}'_4$.

$t^{11}_{\vec{\delta}_1}=-\alpha$	$t^{11}_{\vec{\delta}_2}=-\frac{1}{4}\alpha+\frac{3}{4}\beta+\frac{1}{2}\sqrt{3}\chi$	$t^{11}_{\vec{\delta}_3}=-\frac{1}{4}\alpha+\frac{3}{4}\beta-\frac{1}{2}\sqrt{3}\chi$	$t^{11}_{\vec{\delta}_4}=\mu$
$t^{22}_{\vec{\delta}_1}=\beta$	$t^{22}_{\vec{\delta}_2}=-\frac{3}{4}\alpha+\frac{1}{4}\beta-\frac{1}{2}\sqrt{3}\chi$	$t^{22}_{\vec{\delta}_3}=-\frac{3}{4}\alpha+\frac{1}{4}\beta+\frac{1}{2}\sqrt{3}\chi$	$t^{22}_{\vec{\delta}_4}=\mu$
$t^{12}_{\vec{\delta}_1}=\chi$	$t^{12}_{\vec{\delta}_2}=\frac{1}{4}\sqrt{3}(\alpha+\beta)-\frac{1}{2}\chi$	$t^{12}_{\vec{\delta}_3}=-\frac{1}{4}\sqrt{3}(\alpha+\beta)-\frac{1}{2}\chi$	$t^{12}_{\vec{\delta}_4}=0$
$t^{11}_{\vec{\eta}_1}=-\alpha$	$t^{11}_{\vec{\eta}_2}=-\frac{1}{4}\alpha+\frac{3}{4}\beta+\frac{1}{2}\sqrt{3}\chi$	$t^{11}_{\vec{\eta}_3}=-\frac{1}{4}\alpha+\frac{3}{4}\beta-\frac{1}{2}\sqrt{3}\chi$	$t^{11}_{\vec{\delta}'_4}=\mu$
$t^{22}_{\vec{\eta}'1}=\beta$	$t^{22}_{\vec{\eta}_2}=-\frac{3}{4}\alpha+\frac{1}{4}\beta-\frac{1}{2}\sqrt{3}\chi$	$t^{22}_{\vec{\eta}_3}=-\frac{3}{4}\alpha+\frac{1}{4}\beta+\frac{1}{2}\sqrt{3}\chi$	$t^{22}_{\vec{\delta}'_4}=\mu$
$t^{12}_{\vec{\eta}'1}=-\chi$	$t^{12}_{\vec{\eta}_2}=-\frac{1}{4}\sqrt{3}(\alpha+\beta)+\frac{1}{2}\chi$	$t^{12}_{\vec{\eta}_3}=\frac{1}{4}\sqrt{3}(\alpha+\beta)+\frac{1}{2}\chi$	$t^{12}_{\vec{\delta}'_4}=0$

as, for example,

$$
\begin{aligned}
t^{11}_{\vec{\delta}_2}=t^{11}_{R_1R_3}&=\int w^1_{R_1}(\vec{x})H_0(\vec{x})w^1_{R_3}(\vec{x})\,d^3x\\
&=\int w^1_{C_3^{-1}R_1}(C_3^{-1}\vec{x})H_0(C_3^{-1}\vec{x})w^1_{C_3^{-1}R_3}(C_3^{-1}\vec{x})\,d^3x\\
&=\int[-\tfrac{1}{2}w^1_{R_1}(\vec{x})-\tfrac{1}{2}\sqrt{3}\,w^2_{R_1}(\vec{x})]H_0(x)[-\tfrac{1}{2}w^1_{R_2}(\vec{x})-\tfrac{1}{2}\sqrt{3}\,w^2_{R_2}(\vec{x})]\,d^3x=-\tfrac{1}{4}\alpha+\tfrac{3}{4}\beta+\tfrac{1}{2}\sqrt{3}\,\chi\,,
\end{aligned}
\tag{4.8}
$$

and that

$$t^{mm'}_{\vec{\eta}_i}=(-1)^{m+m'}t^{mm'}_{\vec{\delta}_i}\quad(i=1,2,3)\ \text{by}\ C_2$$

and

$$t^{mm'}_{\vec{v}}=t^{mm'}_{\vec{v}'}\ \text{by}\ I\,.$$

Notice that the last column of Table II follows from the same consideration already used for the diatomic molecule (unvariance of the transfer integrals under the particular rotation C_3). Moreover, again with reference to Fig. 4, we easily derive that $t^{mm'}_{\vec{\eta}_i}=t^{mm'}_{\vec{\eta}'_i}$ $(i=2,3)$ by I, and $t^{mm'}_{\vec{\delta}_i}=t^{mm'}_{\vec{\delta}'_i}$ $(i=2,3)$ by $C_2'IC_2$.

We are now in a position to discuss the symmetry properties of the Hamiltonian (2.3) and of the effective Hamiltonian (3.9)–(3.10). [For completeness we shall also consider the state $a_{1g}(m=3)$, which is shown to be invariant under D^6_{3d} in II.] The invariance of these two Hamiltonians under the D^6_{3d} group is easily verified if we show that they are invariant under the group generators. In so far as the trigonal rotation C_3 is concerned, the $c_{jm\sigma}$ operators are transformed the following way:

$$
C_3\begin{bmatrix}c_{j1\sigma}\\ c_{j2\sigma}\\ c_{j3\sigma}\end{bmatrix}=\begin{bmatrix}\cos\frac{2}{3}\pi\,c_{C_3j1\sigma}+\sin\frac{2}{3}\pi\,c_{C_3j2\sigma}\\ -\sin\frac{2}{3}\pi\,c_{C_3j1\sigma}+\cos\frac{2}{3}\pi\,c_{C_3j2\sigma}\\ c_{C_3j3\sigma}\end{bmatrix}
=\underline{D}\begin{bmatrix}c_{C_3j1\sigma}\\ c_{C_3j2\sigma}\\ c_{C_3j3\sigma}\end{bmatrix}
=\begin{bmatrix}\cos\frac{2}{3}\pi & \sin\frac{2}{3}\pi & 0\\ -\sin\frac{2}{3}\pi & \cos\frac{2}{3}\pi & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}c_{C_3j1\sigma}\\ c_{C_3j2\sigma}\\ c_{C_3j3\sigma}\end{bmatrix},
\tag{4.9}
$$

where C_3j is the site obtained from the site j under the C_3 transformation. The interaction part of the Hamiltonian (2.3) is then invariant under the transformation (4.9) because of (2.11). For the kinetic-energy part

$$\sum_{ij}\sum_{mm'\sigma}t^{mm'}_{ij}c^\dagger_{im\sigma}c_{jm'\sigma}\tag{4.10}$$

(which can also be formally written as

$$\sum_{ij} (c^{\dagger}_{i1\sigma} c^{\dagger}_{i2\sigma} c^{\dagger}_{i3\sigma}) T_{ij} \begin{bmatrix} c_{j1\sigma} \\ c_{j2\sigma} \\ c_{j3\sigma} \end{bmatrix} ,$$

where $T_{ij} = (t^{mn}_{ij})$ is the 3×3 matrix of the transfer integrals between sites i and j) the operation (4.9) gives as a result

$$\sum_{ij} (c^{\dagger}_{C_3 i1\sigma} c^{\dagger}_{C_3 i2\sigma} c^{\dagger}_{C_3 i3\sigma}) \underline{D}^T T_{ij} \underline{D} \begin{bmatrix} c_{C_3 j1\sigma} \\ c_{C_3 j2\sigma} \\ c_{C_3 j3\sigma} \end{bmatrix} , \qquad (4.11)$$

$\underline{D}^T$ being the transposed matrix of $\underline{D}$. Now, it follows from (4.8) that

$$\underline{D}^T T_{ij} \underline{D} = T_{C_3 i C_3 j} , \qquad (4.12)$$

so that the expression (4.11) is identical with the one in (4.10). The proof of the invariance of the Hamiltonian (2.3) under C_2 and C follows the same lines as for C_3 if account is taken of the transformation properties (4.3) together with the fact already used that for any operation D of the D^6_{3d} group, $Dc_{j3\sigma} = c_{Dj3\sigma}$.

The question of the invariance of the effective Hamiltonian (3.9) is now easily set up, since from Eqs. (3.5) and (3.6) it appears to be a product of two kinetic-energy operators times the $\underline{X}$ operator defined in Eq. (3.4). Hence, its invariance under D^6_{3d} can be verified if we show the invariance of $\underline{X}$. We now remember that

$$\underline{X} = \sum_j \underline{X}_j = \sum_j \sum_\lambda \frac{|\beta_{j\lambda}\rangle\langle\beta_{j\lambda}|}{E_\alpha - E_\lambda}$$

and that the states $|\beta_{j\lambda}\rangle$ in Eq. (3.3) are eigenstates of the interaction part of the Hamiltonian (2.3) (where now the sum over m is to be understood over orbitals 1 and 2). Hence, if they are nondegenerate, they are left unchanged by any transformation D of the group D^6_{3d}; that is to say from the fact that $H_0|\beta_{j\lambda}\rangle = E_\lambda|\beta_{j\lambda}\rangle$ and $D^\dagger H_0 D = H_0$ it follows that $D|\beta_{j\lambda}\rangle = |\beta_{Dj\lambda}\rangle$, so that $\sum_j |\beta_{j\lambda}\rangle\langle\beta_{j\lambda}| / (E_\alpha - E_\lambda)$ is invariant. If there are states degenerate in energy, like $|\beta_{j4}\rangle$ and $|\beta_{j5}\rangle$ in Eq. (3.3.), then one has $D|\beta_{j\lambda}\rangle = \sum_{\lambda'} D_{\lambda\lambda'} |\beta_{Dj\lambda'}\rangle$ and the matrix $D_{\lambda\lambda'}$ is unitary. Again, we have

$$\sum_{j\lambda} \frac{D|\beta_{j\lambda}\rangle\langle\beta_{j\lambda}|D^\dagger}{E_\alpha - E_\lambda} = \sum_{j\lambda} \sum_{\lambda'\lambda''} \frac{D_{\lambda\lambda'}|\beta_{Dj\lambda'}\rangle\langle\beta_{Dj\lambda''}|D^\dagger_{\lambda\lambda''}}{E_\alpha - E_\lambda}$$

$$= \sum_j \sum_{\lambda'} \frac{|\beta_{Dj\lambda'}\rangle\langle\beta_{Dj\lambda'}|}{E_\alpha - E_\lambda}$$

$$= \sum_{j\lambda} \frac{|\beta_{j\lambda}\rangle\langle\beta_{j\lambda}|}{E_\alpha - E_\lambda} ,$$

exploiting the unitary of the $D_{\lambda\lambda'}$ matrix together with the fact that the sum over λ is to be understood over states which are degenerate in energy. The proof of the invariance of the effective Hamiltonian (3.9) is now completed and we can turn in Sec. V to the search of the possible types of spin and orbital configuration.

V. POSSIBLE GROUND-STATE CONFIGURATIONS FOR THE EFFECTIVE HAMILTONIAN

The problem of finding all the possible ground-state orbital and magnetic structures would be best discussed in all its generality by use of a convenient generalization of the Luttinger-Tizsa method. However, since we have restricted ourselves to first- and second-neighbor interactions, we do not expect noncollinear solutions for spin and orbital order. This fact allows us to use a simpler and more direct method. We shall use a variational procedure taking a trial wave function of the type

$$|\Psi\rangle = \prod_j |\psi_j\rangle|\phi_j\rangle , \qquad (5.1)$$

where the state $|\psi_j\rangle$ refers to orbital occupancy on site j and it is acted on by the $\vec{\tau}_j$ operators in the effective Hamiltonian (3.12), whereas the state $|\phi_j\rangle$ refers to spin occupancy on site j, and it is acted upon by the spin operators $\vec{S}_j$.

Quite generally, we can choose

$$\begin{aligned} |\psi_j\rangle &= \cos\psi_j|\tau^z = \tfrac{1}{2}\rangle + \sin\psi_j|\tau^z = -\tfrac{1}{2}\rangle, \\ |\phi_j\rangle &= \cos\phi_j|s^z = \tfrac{1}{2}\rangle + \sin\phi_j|s^z = -\tfrac{1}{2}\rangle , \end{aligned} \qquad (5.2)$$

and then minimize the average value of the Hamiltonian in the state (5.1) with respect to ψ_j and ϕ_j. Since the effective Hamiltonian acts only onto two sites at a time and it can be factored in the orbital and spin variables, we need only to calculate averages of the type

$$\langle\psi_i|\langle\psi_j|H^o_{ij}|\psi_j\rangle|\psi_i\rangle ,$$

and (5.3)

$$\langle\phi_i|\langle\phi_j|H^s_{ij}|\phi_j\rangle|\phi_i\rangle$$

where $H^{o(s)}_{ij}$ is the ij term in the effective Hamiltonian (3.12) referring to orbital (spin) variables. The second average in (5.3) is straightforward whereas for the first term, we find after some algebric exercise

$$\langle\psi_i|\langle\psi_j|c[A_{ij}+A_{ji}-\tfrac{1}{2}(B_{ij}+B_{ji})+C_{ij}+C_{ji}+D_{ij}+D_{ji}]|\psi_j\rangle|\psi_i\rangle$$
$$=c[-(T^2_{ij}-2S_{ij})\sin^2(\psi_i+\psi_j)+\tfrac{1}{2}T^2_{ij}\sin2\psi_i\sin2\psi_j-2(t^{12}_{ij})^2\cos2(\psi_i+\psi_j)+t^{12}_{ij}(t^{12}_{ij}-t^{22}_{ij})\sin2(\psi_i+\psi_j)],\quad(5.4)$$

$$\langle\psi_i|\langle\psi_j|[(A_{ij}+A_{ji}+\tfrac{1}{2}B_{ij}+\tfrac{1}{2}B_{ji}+C_{ij}+C_{ji})a-(B_{ij}+B_{ji})b+D'_{ij}+D'_{ji}]|\psi_j\rangle|\psi_i\rangle$$
$$=2a[t^{11}_{ij}\cos\psi_i\cos\psi_j+t^{22}_{ij}\sin\psi_i\sin\psi_j+t^{12}_{ij}\sin(\psi_i+\psi_j)]^2$$
$$-b\{[(t^{12}_{ij})^2+(t^{11}_{ij})^2](\cos^2\psi_i+\cos^2\psi_j)+[(t^{22}_{ij})^2+(t^{12}_{ij})^2](\sin^2\psi_i+\sin^2\psi_j)+t^{12}_{ij}T_{ij}(\sin2\psi_i+\sin2\psi_j)\},\quad(5.5)$$

where we denote for sake of convenience

$$c=1/(U_{12}-J),\quad b=U_{12}/(U^2_{12}-J^2),$$
$$a=J/(U^2_{12}-J^2)+J/(U^2_{11}-J^2),\quad(5.6)$$

and

$$T_{ij}=t^{11}_{ij}+t^{22}_{ij},\quad S_{ij}=t^{11}_{ij}t^{22}_{ij}-(t^{12}_{ij})^2.\quad(5.7)$$

In specializing to the corundum structure, it is useful to take advantage of the symmetry properties of the effective Hamiltonian in evaluating the expressions (5.4) and (5.5). In our case, it will be most convenient to exploit the trigonal symmetry. Indeed, if we know, for example, the matrix element (5.4) along the pair $i1-j2$ of Fig. 3, then for the same matrix element along the pair $i1-j3'$, we find

$$\langle\psi_{i1}|\langle\psi_{j3'}|H_{i1j3'}|\psi_{j3'}\rangle|\psi_{i1}\rangle$$
$$=\langle\psi_{i1}|\langle\psi_{j3'}|C_3^\dagger H_{i1j2}C_3|\psi_{j3'}\rangle|\psi_{i1}\rangle$$
$$=\langle\psi_1+\tfrac{2}{3}\pi|\langle\psi_2+\tfrac{2}{3}\pi|H_{12}|\psi_2+\tfrac{2}{3}\pi\rangle|\psi_1+\tfrac{2}{3}\pi\rangle\quad(5.8)$$

since from (5.2) and the transformation properties (4.39) of the orbitals 1 and 2, we derive

$$C_3|\psi_{j3'}\rangle=C_3[\cos\psi_{3'}w^1_{3'}(\vec{x})+\sin\psi_{3'}w^2_{3'}(\vec{x})]$$
$$=\cos(\psi_2+\tfrac{2}{3}\pi)w^1_2(\vec{x})+\sin(\psi_2+\tfrac{2}{3}\pi)w^2_2(\vec{x})$$
$$=|\psi_2+\tfrac{2}{3}\pi\rangle,\quad(5.9)$$

$$C_3|\psi_{j1})=C_3[\cos\psi_1w^1_1(\vec{x})+\sin\psi_1w^2_1(\vec{x})]$$
$$=\cos(\psi_1+\tfrac{2}{3}\pi)w^1_1(\vec{x})+\sin(\psi_1+\tfrac{2}{3}\pi)w^2_1(\vec{x})$$
$$=|\psi_1+\tfrac{2}{3}\pi\rangle.\quad(5.10)$$

The same relation as for (5.8) holds for the pair along $i1$-$j3$ with $-\frac{2}{3}\pi$. One can directly check the validity of (5.8) from the general expressions (5.4) and (5.5), respectively, evaluated for the two directions.

One more simplification is achieved if we take in Table II $t^{12}_{\delta}=\chi=0$ as will turn out in II. In this way, two consecutive basal planes in the corundum structure are translationally equivalent. Use of the transfer integrals in Table II and of the Eq. (5.8) gives the following expression for the average value of the Hamiltonian (3.12) in the trial wave function (5.1):

$$-\langle\Psi|H_{\rm eff}|\Psi\rangle=\frac{1}{2}\sum_{\langle ij\rangle}^{i=1,4}\langle\phi_i|(2\vec{S}_i\cdot\vec{S}_j+\tfrac{1}{2})|\phi_j\rangle\Big((1-\delta_{i4})\{\tfrac{1}{2}u[1-\cos2(\psi_j+\gamma_i)\cos2(\psi_i+\gamma_i)]$$
$$+\tfrac{1}{2}(u-2v)\sin2(\psi_j+\gamma_i)\sin2(\psi_i+\gamma_i)\}+w\delta_{i4}\sin^2(\psi_j-\psi_i)\Big)$$
$$+\frac{1}{2}\sum_{\langle ij\rangle}^{i=1,4}\langle\phi_i|(\tfrac{1}{2}-(2\vec{S}_i\cdot\vec{S}_j)|\phi_j\rangle\Big((1-\delta_{i4})\{(b-\tfrac{1}{2}a)\frac{u}{c}-r\cos2(\psi_j+\gamma_i)\cos2(\psi_i+\gamma_i)$$
$$+s[\cos2(\psi_i+\gamma_i)+\cos2(\psi_j+\gamma_i)]+t\sin2(\psi_i+\gamma_i)\sin2(\psi_j+\gamma_i)\}$$
$$+\frac{w}{c}\delta_{i4}[b-a\cos^2(\psi_j-\psi_i)]\Big),\quad(5.11)$$

where we have introduced the quantities

$$u=(\alpha^2+\beta^2)c,\quad v=\tfrac{1}{2}(\alpha-\beta)^2c,\quad w=2\mu^2c,$$
$$r=\tfrac{1}{2}a(\alpha^2+\beta^2),\quad s=\tfrac{1}{2}(b-a)(\alpha^2-\beta^2),\quad t=a\alpha\beta,\quad(5.12)$$

and used the convention that the symbol $\sum_{\langle ij\rangle}^{i=1,4}$ means summation over all the four nearest neighbors i of all the sites j in the lattice; i indicating the site at the end of the vector $\vec{\delta}_i$ in Fig. 4 if the site j is the site number 1 in Fig. 3. If this latter is the site 2 of Fig. 3, the association is $i\rightarrow\vec{\delta}'_i$ in

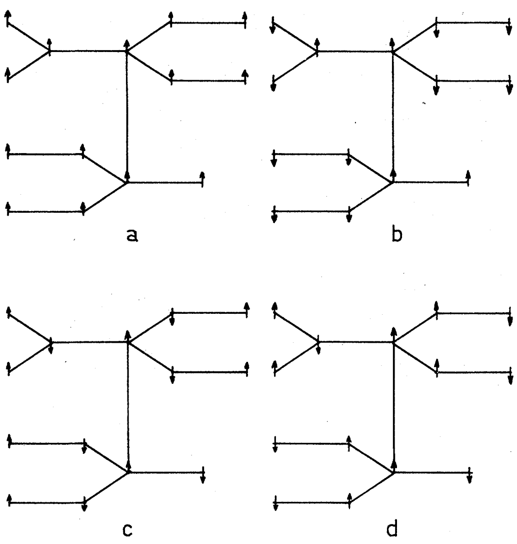


FIG. 5. Possible spin orderings in the corundum structure.

Fig. 4. With this assumption,

$$\gamma_1 = 0\,, \quad \gamma_2 = +\tfrac{2}{3}\pi\,, \quad \gamma_3 = -\tfrac{2}{3}\pi\,. \tag{5.13}$$

Notice that either from (5.2) or from (5.11), we see that the range of variation of ψ_i and ψ_j is between 0 and π since $|\psi+\pi\rangle = -|\psi\rangle$. Since we are interested in the possible ground-state configurations for certain range of variation of the parameters in our effective Hamiltonian, we immediately see from (5.11) that the coupling along the vertical direction δ_4 must be ferromagnetic and such that $\psi_j = \psi_4 + \frac{1}{2}\pi$. In such a case, the term proportional to s in the second term of (5.11) never contributes to the ground-state energy since given the corundum structure each site j will have a vertical nearest neighbor with an orbital occupation out of phase of $\frac{1}{2}\pi$.

This contraint on the vertical pairs restricts us to the consideration of collinear spin structures such as shown in Fig. 5. The possible associated orbital ordering is derived by minimizing with respect to the angles ψ_j and $\psi_{j'}$ of the vertical nearest-neighbors sites j and j'. This will give some conditions for the orbital occupancy of their nearest neighbors in their respective basal planes and a solution of the variational problem will be found by consistently filling out the whole lattice with these particular solutions (where by "consistently," we mean that the solutions for the orbital occupancy relative to a site j with its four neighbors must match those centered on any other neighboring site).

The minimizing equations for the orbital occupancy are derived from (5.11) to be

$$\begin{aligned}\frac{\partial}{\partial\psi_j}\langle\Psi|H_{\text{eff}}|\Psi\rangle = w\sin 2(\psi_j-\psi_{j'}) &\\ +\sum_{i=1}^{3}[\alpha_i\sin 2(\psi_j+\gamma_i)\cos 2(\psi_i+\gamma_i) &\\ +\beta_i\cos 2(\psi_j+\gamma_i)\sin 2(\psi_i+\gamma_i)] = 0\,, &\end{aligned} \tag{5.14a}$$

$$\begin{aligned}\frac{\partial}{\partial\psi_{j'}}\langle\Psi|H_{\text{eff}}|\Psi\rangle = -w\sin 2(\psi_j-\psi_{j'}) &\\ +\sum_{i'=1}^{3}[\alpha_{i'}\sin 2(\psi_{j'}+\gamma_{i'})\cos 2(\psi_{i'}+\gamma_{i'}) &\\ +\beta_{i'}\cos 2(\psi_{j'}+\gamma_{i'})\sin 2(\psi_{i'}+\gamma_{i'})] = 0\,, &\end{aligned} \tag{5.14b}$$

where the indices ij and $i'j'$ refer to adjacent basal planes and the coefficients α_i and β_i are easily derived from (5.11) taking into account the fact that a ferromagnetic spin coupling along a certain direction picks out the first term in (5.11), whereas an antiferromagnetic spin coupling picks out the second. Since we have

$$\begin{aligned}\sin 2(\psi_j+\gamma_i)\cos 2(\psi_i+\gamma_i) = \sin 2\psi_i\cos 2\psi_i\cos^2 2\gamma_i &\\ +\sin 2\psi_i\cos 2\psi_j\sin^2 2\gamma_i &\\ +\cos 4(\psi_i+\psi_j)\tfrac{1}{4}\sin 4\gamma_i\,, &\end{aligned} \tag{5.15}$$

we see that we can achieve a solution of (5.14), whatever α_i and β_i are, provided we take $\psi_2 = \psi_3$, $\psi_j - \psi_{j'} = \frac{1}{2}\pi$ (the solution $\psi_j - \psi_{j'} = 0$ is to be discarded since it leads to a maximum) and we take

$$\begin{cases}\sin 2\psi_j\cos 2\psi_i = 0\,,\\ \cos 2\psi_j\sin 2\psi_i = 0\,,\end{cases}$$
$$\begin{cases}\sin 2\psi_{j'}\cos 2\psi_{i'} = 0\,,\\ \cos 2\psi_{j'}\sin 2\psi_{i'} = 0\,,\end{cases} \quad (i, i' = 1, 2, 3) \tag{5.16}$$

to be satisfied simultaneously.

This leads to the set of solutions for each plane given in Table III together with the condition $\psi_j - \psi_{j'} = \frac{1}{2}\pi$ for adjacent basal planes. This means that we want to match solutions of set I with set II in the adjacent plane, and similarly set III with set IV. As a consequence, the only possible orbital structures are those given in Fig. 6 and those obtained by increasing all the angles in Fig. 6 by $\frac{1}{4}\pi$.

We are now in a position to derive a general phase diagram for our system, that is to say a plot of the regions of stability of a certain orbital and spin structure for definite ranges of the parameters appearing in the effective Hamiltonian. For this purpose, we rewrite Eq. (5.11) as follows:

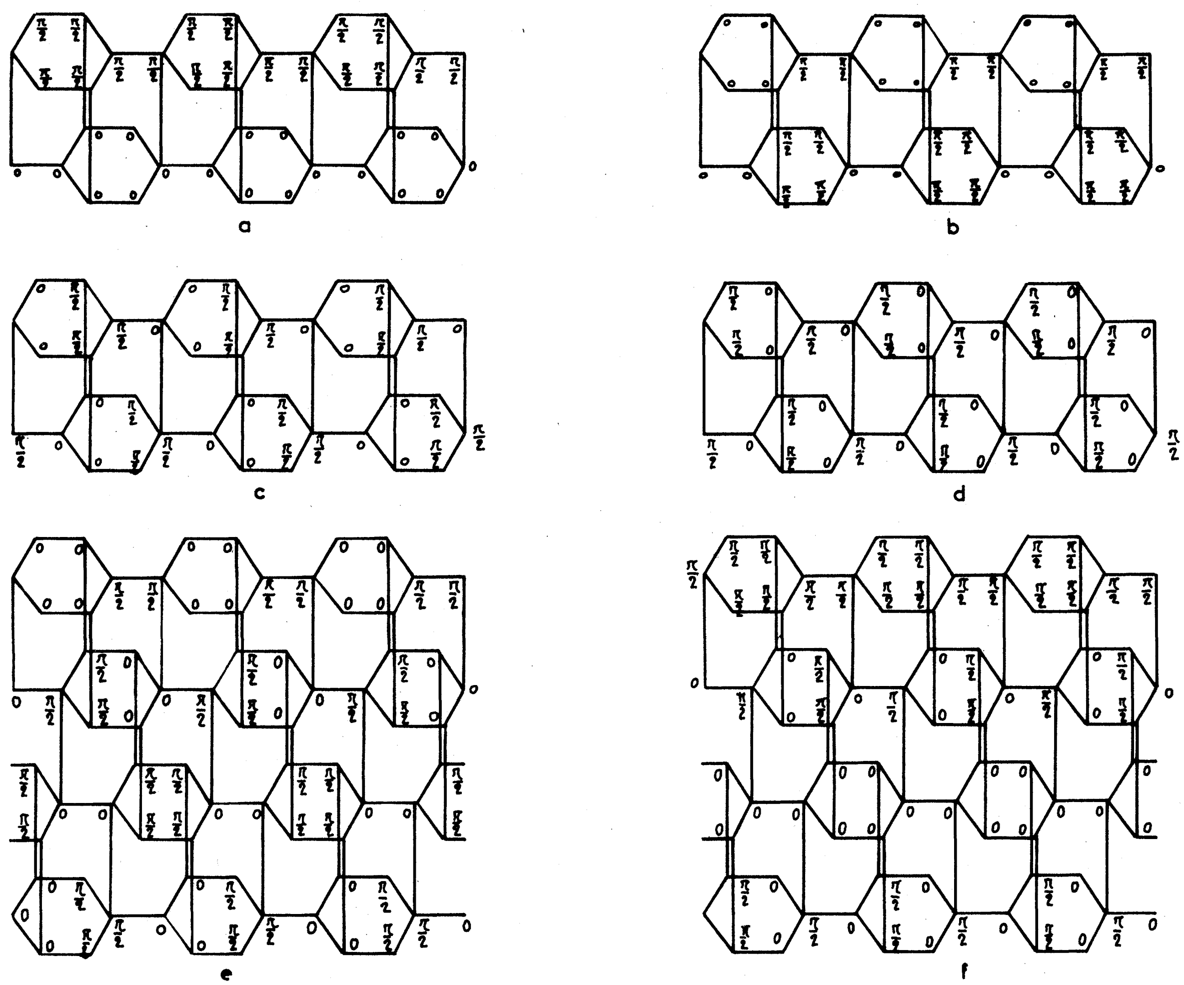


FIG. 6. Possible orderings in the corundum structure. The angles indicate the orbital occupancy according to Eq. (5.2).

$$-(\Psi|H_{\mathrm{eff}}|\Psi)=\frac{1}{2}\sum_{\langle ij\rangle}^{i=1,4}\left[J^{f}(i,j)\langle\phi_i|2\vec{S}_i\cdot\vec{S}_j+\tfrac{1}{2}|\phi_j\rangle + J^{a}(i,j)\langle\phi_i|\tfrac{1}{2}-2\vec{S}_i\cdot\vec{S}_j|\phi_i\rangle\right], \qquad (5.17)$$

where $J^f(i,j)$ and $J^a(i,j)$ represent, respectively, the exchange contribution to the ground states from a ferromagnetic or antiferromagnetic spin coupling along the direction *ij*. Their explicit expression is easily written as follows:

TABLE III. Four possible configurations for orbital occupancy of the two degenerate e_g states per V atom in the basal plane.

I	ψ_j	ψ_1	$\psi_{2=3}$	II	ψ_j	ψ_1	$\psi_{2=3}$	III	ψ_j	ψ_1	$\psi_{2=3}$	IV	ψ_j	ψ_1	$\psi_{2=3}$
1	0	0	0	5	$\frac{1}{2}\pi$	0	0	9	$\frac{1}{4}\pi$	$\frac{1}{4}\pi$	$\frac{1}{4}\pi$	13	$\frac{3}{4}\pi$	$\frac{1}{4}\pi$	$\frac{1}{4}\pi$
2	0	0	$\frac{1}{2}\pi$	6	$\frac{1}{2}\pi$	0	$\frac{1}{2}\pi$	10	$\frac{1}{4}\pi$	$\frac{1}{4}\pi$	$\frac{3}{4}\pi$	14	$\frac{3}{4}\pi$	$\frac{1}{4}\pi$	$\frac{3}{4}\pi$
3	0	$\frac{1}{2}\pi$	0	7	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	0	11	$\frac{1}{4}\pi$	$\frac{3}{4}\pi$	$\frac{1}{4}\pi$	15	$\frac{3}{4}\pi$	$\frac{3}{4}\pi$	$\frac{1}{4}\pi$
4	0	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	8	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	$\frac{1}{2}\pi$	12	$\frac{1}{4}\pi$	$\frac{3}{4}\pi$	$\frac{3}{4}\pi$	16	$\frac{3}{4}\pi$	$\frac{3}{4}\pi$	$\frac{3}{4}\pi$

$$\begin{aligned}
J^f(1,j) &= \tfrac{1}{2}[u(1-\cos 2\psi_j \cos 2\psi_1) + (u-2v)\sin 2\psi_j \sin 2\psi_1],\\
J^f(2,j) &= \tfrac{1}{2}[u+\tfrac{1}{2}(u-3v)\cos 2\psi_j \cos 2\psi_2 - \tfrac{1}{2}(u+v)\sin 2\psi_j \sin 2\psi_2 + \tfrac{1}{2}\sqrt{3}(u-v)\sin 2(\psi_j+\psi_2)],\\
J^f(3,j) &= \tfrac{1}{2}[u+\tfrac{1}{2}(u-3v)\cos 2\psi_j \cos 2\psi_3 - \tfrac{1}{2}(u+v)\sin 2\psi_j \sin 2\psi_3 - \tfrac{1}{2}\sqrt{3}(u-v)\sin 2(\psi_j+\psi_3)],\\
J^f(4,j) &= w\sin^2(\psi_j-\psi_4),\\
J^a(1,j) &= (1/c)(b-\tfrac{1}{2}a)u - r\cos 2\psi_j \cos 2\psi_1 + t\sin 2\psi_j \sin 2\psi_1 + s(\cos 2\psi_j + \cos 2\psi_1),\\
J^a(2,j) &= (1/c)(b-\tfrac{1}{2}a)u - \tfrac{1}{4}(r-3t)\cos 2\psi_j \cos 2\psi_2 - \tfrac{1}{4}(3r-t)\sin 2\psi_j \sin 2\psi_2\\
&\quad - \tfrac{1}{4}\sqrt{3}(r+t)\sin 2(\psi_j+\psi_2) - \tfrac{1}{2}s(\cos 2\psi_j + \cos 2\psi_2) + \tfrac{1}{2}\sqrt{3}\,s(\sin 2\psi_j + \sin 2\psi_2),\\
J^a(3,j) &= (1/c)(b-\tfrac{1}{2}a)u - \tfrac{1}{4}(r-3t)\cos 2\psi_j \cos 2\psi_3 - \tfrac{1}{4}(3r-t)\sin 2\psi_j \sin 2\psi_3\\
&\quad + \tfrac{1}{4}\sqrt{3}(r+t)\sin 2(\psi_j+\psi_3) - \tfrac{1}{2}s(\cos 2\psi_j + \cos 2\psi_3) + \tfrac{1}{2}\sqrt{3}\,s(\sin 2\psi_j + \sin 2\psi_3),\\
J^a(4,j) &= (w/c)[b-a\cos^2(\psi_j-\psi_4)].
\end{aligned} \tag{5.18}$$

The ground-state energy for a particular orbital and spin structure is then easily obtained from (5.17) and (5.18) by picking out for each pair the appropriate $J^{f\,(a)}(ij)$ contribution and then summing over all the sites of the relative unit cell.

The following Table IV giving the quantities $J^{f(a)}_{ij}(\psi_i, \psi_j)$ for all the possible orbital occupancies given in Table III is of some help in this computation.

Notice that we have introduced the quantity $2\mathcal{J}^{f(a)}_{2j}(\psi_i\psi_j) = J^{f(a)}_{2j}(\psi_i\psi_j) + J^{f(a)}_{3j}(\psi_i\psi_j)$ since the sites 2 and 3 are always translationally equivalent for all structures considered.

Use of this table allows us to readily construct Table V giving the ground-state energies for the orbital and spin structures most relevant to our purposes, that is to say the ones which have lowest energy.

In Table V the column heading refers to the spin structure on each basal plane (the coupling between planes being always ferromagnetic); FS, AS, and RS, indicating, respectively, a ferromagnetic, a antiferromagnetic, and a "real" spin structure. Moreover, "real" refers to the actual spin configuration realized in V_2O_3, namely a ferromagnetic coupling along the vertical pair and one pair in the basal plane, the other two pairs in the basal plane being coupled antiferromagnetically.

The row heading $a(1), b(1), c(1), d(1), e(1), f(1)$ refer to the orbital structures represented in Fig. 6. The row headings $a(2), b(2), c(2), d(2), e(2), f(2)$ refer to an arrangement which is obtained from Fig. 6 after changing each angle ψ_i into $\psi_i + \frac{1}{4}\pi$. The quantity at each crossing of a column (spin structure) and a row (orbital structure) represents

TABLE IV. Various orbital-dependent terms of the effective Hamiltonian expressed in terms of the matrix elements of the trial wave function (5.2).

$J^f_{1j}(0,0)=0$	$J^a_{1j}(0,0)=(1/c)(b-\frac{1}{2}a)u-r+2s$
$2\mathcal{J}^f_{2j}(0,0)=\frac{3}{2}(u-v)$	$2\mathcal{J}^a_{2j}(0,0)=(2/c)(b-\frac{1}{2}a)u-\frac{1}{2}(r-3t)-2s$
$J^f_{1j}(\frac{1}{2}\pi,\frac{1}{2}\pi)=0$	$J^a_{1j}(\frac{1}{2}\pi,\frac{1}{2}\pi)=(1/c)(b-\frac{1}{2}a)u-v-2s$
$2\mathcal{J}^f_{2j}(\frac{1}{2}\pi,\frac{1}{2}\pi)=\frac{3}{2}(u-v)$	$2\mathcal{J}^a_{2j}(\frac{1}{2}\pi,\frac{1}{2}\pi)=(2/c)(b-\frac{1}{2}a)u-\frac{1}{2}(r-3t)+2s$
$J^f_{1j}(0,\frac{1}{2}\pi)=u$	$J^a_{1j}(0,\frac{1}{2}\pi)=(1/c)(b-\frac{1}{2}a)u+r$
$2\mathcal{J}^f_{2j}(0,\frac{1}{2}\pi)=\frac{1}{2}(u+3v)$	$2\mathcal{J}^a_{2j}(0,\frac{1}{2}\pi)=(2/c)(b-\frac{1}{2}a)u+\frac{1}{2}(r-3t)$
$J^f_{1j}(\frac{1}{4}\pi,\frac{1}{4}\pi)=u-v$	$J^a_{1j}(\frac{1}{4}\pi,\frac{1}{4}\pi)=(1/c)(b-\frac{1}{2}a)u+t$
$2\mathcal{J}^f_{2j}(\frac{1}{4}\pi,\frac{1}{4}\pi)=\frac{1}{2}(u-v)$	$2\mathcal{J}^a_{2j}(\frac{1}{4}\pi,\frac{1}{4}\pi)=(2/c)(b-\frac{1}{2}a)u-\frac{1}{2}(3r-t)$
$J^f_{1j}(\frac{3}{4}\pi,\frac{3}{4}\pi)=u-v$	$J^a_{1j}(\frac{3}{4}\pi,\frac{3}{4}\pi)=(1/c)(b-\frac{1}{2}a)u+t$
$2\mathcal{J}^f_{2j}(\frac{3}{4}\pi,\frac{3}{4}\pi)=\frac{1}{2}(u-v)$	$2\mathcal{J}^a_{2j}(\frac{3}{4}\pi,\frac{3}{4}\pi)=(2/c)(b-\frac{1}{2}a)u-\frac{1}{2}(3r-t)$
$J^f_{1j}(\frac{1}{4}\pi,\frac{3}{4}\pi)=v$	$J^a_{1j}(\frac{1}{4}\pi,\frac{3}{4}\pi)=(1/c)(b-\frac{1}{2}a)u-t$
$2\mathcal{J}^f_{2j}(\frac{1}{4}\pi,\frac{3}{4}\pi)=\frac{1}{2}(3u+v)$	$2\mathcal{J}^a_{2j}(\frac{1}{4}\pi,\frac{3}{4}\pi)=(2/c)(b-\frac{1}{2}a)u+\frac{1}{2}(3r-t)$

TABLE V. Variational ground-state energies for the three spin structures FS, RS, and AS and various orbital structures.

	FS	RS	AS
$a(1)$ FO(1)	$4[\frac{3}{2}(u-v)+w]$	$4[2(b-\frac{1}{2}a)(u/c)-\frac{1}{2}(r-3t)+w]$	$4[3(b-\frac{1}{2}a)(u/c)-\frac{3}{2}(r-t)+w]$
$a(2)$ FO(2)	$4[\frac{3}{2}(u-v)+w]$	$4[(u-v)+2(b-\frac{1}{2}a)(u/c)-\frac{1}{2}(3r-t)+w]$	$4[3(b-\frac{1}{2}a)(u/c)-\frac{3}{2}(r-t)+w]$
$b(1)$ RO(1)	$4[\frac{1}{2}(u+3v)+w]$	$4[2(b-\frac{1}{2}a)(u/c)+\frac{1}{2}(r-3t)+w]$	$4[3(b-\frac{1}{2}a)(u/c)-\frac{1}{2}(r+3t)+w]$
$b(2)$ RO(2)	$4[\frac{1}{2}(5u-v)+w]$	$4[(u-v)+2(b-\frac{1}{2}a)(u/c)+\frac{1}{2}(3r-t)+w]$	$4[3(b-\frac{1}{2}a)(u/c)+\frac{1}{2}(3r+t)+w]$
$c(1)$	$4[\frac{1}{2}(5u-v)+w]$	$4[u+2(b-\frac{1}{2}a)(u/c)-\frac{1}{2}(r-3t)+w]$	$4[3(b-\frac{1}{2}a)(u/c)+\frac{1}{2}(r+3t)+w]$
$c(2)$	$4[\frac{1}{2}(u+v)+w]$	$4[v+2(b-\frac{1}{2}a)(u/c)-\frac{1}{2}(3r-t)+w]$	$4[3(b-\frac{1}{2}a)(u/c)-\frac{1}{2}(3r+t)+w]$
$d(1)$ AO(1)	$4[\frac{3}{2}(u+v)+w]$	$4[u+2(b-\frac{1}{2}a)(u/c)+\frac{1}{2}(r-3t)+w]$	$4[3(b-\frac{1}{2}a)(u/c)+\frac{3}{2}(r-t)+w]$
$d(2)$ AO(2)	$4[\frac{3}{2}(u+v)+w]$	$4[v+2(b-\frac{1}{2}a)(u/c)+\frac{1}{2}(3r-t)+w]$	$4[3(b-\frac{1}{2}a)(u/c)+\frac{3}{2}(r-t)+w]$
$e(1)$	$4(\frac{3}{2}u+w)$	$4[\frac{1}{2}u+2(b-\frac{1}{2}a)(u/c)+w]$	$4[3(b-\frac{1}{2}a)(u/c)+w]$
$e(2)$	$4(\frac{3}{2}u+w)$	$4[\frac{1}{2}u+2(b-\frac{1}{2}a)(u/c)+w]$	$4[3(b-\frac{1}{2}a)(u/c)+w]$
$f(1)$	$4(\frac{3}{2}u+w)$	$4[\frac{1}{2}u+2(b-\frac{1}{2}a)(u/c)+w]$	$4[3(b-\frac{1}{2}a)(u/c)+w]$
$f(2)$	$4(\frac{3}{2}u+w)$	$4[\frac{1}{2}u+2(b-\frac{1}{2}a)(u/c)+w]$	$4[3(b-\frac{1}{2}a)(u/c)+w]$

the ground-state energy per monoclinic unit cell (8 vanadium atoms, Fig. 3) corresponding to this orbital and spin ordering.

A glance at Table V and at the definitions (5.12) shows that the differences between ground-state energies depend within a factor α^2/U_{12} only upon the ratios β/α and J/U_{12}, the dependence on α and β being symmetric. Hence, the phase diagram of Fig. 7 is easily drawn. Here, the y axis refers to the ratio β/α ranging in the interval $(-1, 1)$ and the x axis to the ratio J/U_{12} ranging from 0 to less than 1. We see that there is a reasonably large range of the physical parameters β/α and J/U_{12} for which the RS spin structure is stable. Moreover, the competition is always between two ferromagnetic spin states RO(2) – FS, AO(1) – FS or AO(2) – FS and two "real" spin ordering states RO(2) – RS or AO(1) – RS. AO(1) and AO(2) stand for antiferromagnetic orbital order corresponding to configurations in Fig. 6(d) and Fig. 6(d) on replacing $(0, \frac{1}{2}\pi)$ by $(\frac{1}{4}\pi, \frac{3}{4}\pi)$. RO(2) stands for real orbital order and corresponds to the configuration Fig. 6(b) on replacing $(0, \frac{1}{2}\pi)$ by $(\frac{1}{4}\pi, \frac{3}{4}\pi)$. All the other orbital and spin configurations are higher in energy in the whole range of variation of the physical parameters. In particular the AS states (complete antiferromagnetic coupling in the basal plane) lie always higher than the RS states, being degenerate with them only for $J = 0$. All the other spin structures which are not mentioned in Table V have been found to have higher ground-state energy.

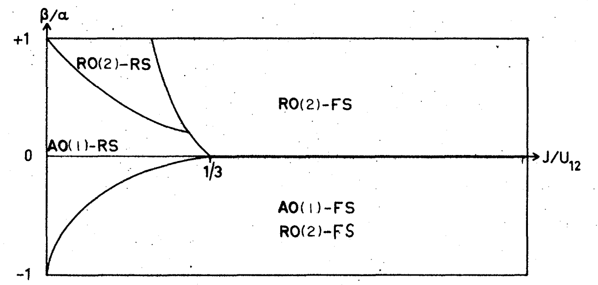


FIG. 7. Phase diagram for the orbital and spin ordering in the corundum structures in the atomic limit for first- and second-nearest neighbors interactions.

So starting from a Hamiltonian invariant under C_3, we have found a stable ground-state orbital and spin ordering which breaks this symmetry. Looking at Fig. 8, where the RO(2) – RS and AO(1) – RS configurations are drawn, and remembering Table II, the reason for this is not difficult to understand. The coupling along the vertical pair is always ferromagnetic in the spin and antiferromagnetic in the orbital occupancy, since along this direction $t_{12} = 0$ because of C_3, so that there is no transfer between orbitals 1 and 2. The electrons can in this way achieve the maximum of kinetic-energy lowering and at the same time take full advantage of the exchange energy give up as little repulsive energy as possible $(U_{12} - J)$ when being

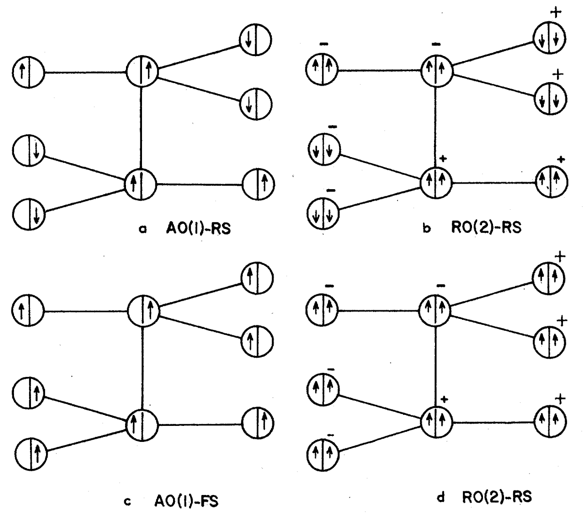


FIG. 8. Orbital and spin ordered solutions of phase diagram in Fig. 7 depicted in form of clusters representing the corundum lattice. The left and right halfs of the circles represent orbital 1 and 2, respecttively. The ± signs above each circle in configurations *b*, *d* indicate orbital occupancy for the wave function $(1/\sqrt{2})\,(w^1 \pm w^2)$, each arrow representing, in this case, half spin.

on the same site. In the basal plane, this situation is again met along the direction $\vec{\delta}_1$, since we have taken $t^{12}_{\delta_1} = \chi = 0$ (actually, even if the chosen Wannier functions were not already such that the interband transfer integral $t^{12}_{\vec{\delta}_1}$ is zero, we could always choose a Wannier basis in which this is the case. Obviously, in such a new basis $t^{12}_{\vec{\delta}_4}$ would still be zero).

Along $\vec{\delta}_2$ and $\vec{\delta}_3$ however, C_3 symmetry demands that $t^{12}_{\vec{\delta}_2}, t^{12}_{\vec{\delta}_3}$ be comparable, or even bigger than, the corresponding $t^{11}_{\vec{\delta}_{2,3}}, t^{22}_{\vec{\delta}_{2,3}}$. As a result, an antiferromagnetic spin coupling is preferred to achieve the maximum lowering of kinetic energy compatible with the necessity of giving up as little repulsive energy as possible when two electrons happen to occupy the same site. Notice that if $\beta/\alpha \simeq 0$, this situation is achieved with complete antiferromagnetic orbital ordering for the Wannier functions $w^1(\vec{x})$ and $w^2(\vec{x})$. When $\beta/\alpha \simeq 1$, the orbital ordering becomes RO(2), that is to say an ordering similar to the spin order for the Wannier functions $(1/\sqrt{2})[w^1(\vec{x}) \pm w^2(\vec{x})]$. Notice that in this latter basis $t^{11}_{\vec{\delta}_1} = t^{22}_{\vec{\delta}_1} = \frac{1}{2}(\beta - \alpha) \sim 0$ whereas $t^{12}_{\vec{\delta}_1} = -(\alpha + \beta) \sim -2\alpha$, so that the ferromagnetic orbital ordering along $\vec{\delta}_1$ is justified. In the vertical direction instead, we still have $t^{11}_{\vec{\delta}_4} - t^{22}_{\vec{\delta}_4} = \mu$ and $t^{12}_{\vec{\delta}_4} = 0$ so that the orbit and spin ordering does not change. We then see that relative magntiude of the various transfer integrals may be essential to determine the actual orbital and spin ordering in the corundum lattice (and in general in every lattice).

This fact raises the question whether inclusion of the transfer integrals up to the nine third neighbors of a vanadium atom (Fig. 9) (we shall see in II that they might not be negligible due mainly to covalency effect) does not affect the conclusions we have drawn up to now. As far as the possible orbital and spin structures are concerned, there is no change in the conclusions. Quite generally, we can see from expressions (5.4) and (5.5) that our new transfer integral can bring about in the minimizing equations (5.14) only new terms of the type

$$\sum_{i=1}^{3} \epsilon_i \sin 4(\psi_j + \psi_i), \quad \sum_{i=1}^{3} \epsilon_i' \sin 2(\psi_j + \psi_i)$$

or

$$\sum_{i=1}^{3} \epsilon_i'' \sin 4\psi_j \cos\psi_i .$$

These terms are always zero when evaluated for the solutions in Table III. However, inclusion of new transfer integral can modify the phase diagram in Fig. 7. In fact, if we introduce the transfer integrals $t^{11}_{j_1 j_5}, t^{22}_{j_1 j_5}$, and $t^{12}_{j_1 j_5} = -t^{21}_{j_1 j_5}$ between sites 1 and 5 in Fig. 9 (all the other ones needed can be derived by symmetry operations from these) and define the quantities

$$(t^{11}_{j_1 j_5})^2 b = p, \quad (t^{12}_{j_1 j_5})^2 c = q, \tag{5.19}$$

(from II, it will turn out that $t^{22}_{j_1 j_5} \simeq 0$) the ground-

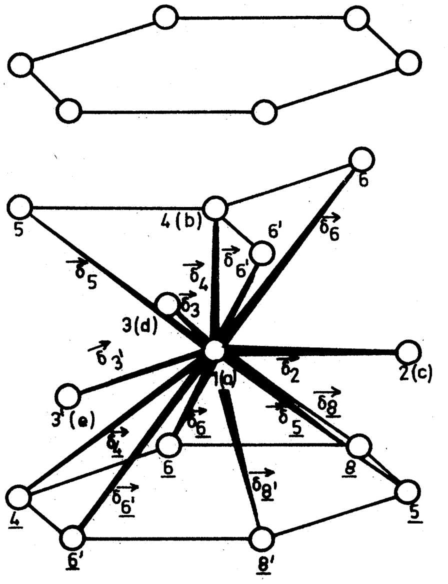


FIG. 9. Nine third nearest neighbors of a certain in the corundum structure. Numbering of the cations is the same as in Fig. 3.

state energies for the four most relevant states mentioned above become

$$
\begin{aligned}
&E_G(\mathrm{RO}(2)-\mathrm{FS})=4[\tfrac{1}{2}(5u-v)+15q+\tfrac{9}{4}p],\\
&E_G(\mathrm{AO}(1)-\mathrm{FS})=4[\tfrac{3}{2}(u+v)+w+8q+\tfrac{13}{4}p],\\
&E_G(\mathrm{RO}(2)-\mathrm{RS})=4[(u-v)+2(b-\tfrac{1}{2}a)u/c+\tfrac{1}{2}(3r-t)+w+6q(1+2b/c-3a/c)+p(\tfrac{3}{2}+6b/c)-\tfrac{15}{4}a/c)],\\
&E_G(\mathrm{AO}(1)-\mathrm{RS})=4[u+2(b-\tfrac{1}{2}a)u/c+\tfrac{1}{2}(r-3t)+w+6q(\tfrac{2}{3}+2b/c-7a/c)+p(1+6b/c-\tfrac{5}{4}a/c)].
\end{aligned}
\tag{5.20}
$$

Hence, if the new transfer integrals are a substantial fraction of α and β in Table II, the configuration RO(2) – RS at least for positive β can cover the whole stability domain of the real spin configuration. Moreover, the boundary of this latter domain can be altered according to the relative weight of q and p. It will turn out in II that these latter values are such as not to disturb too much the picture of the phase diagram given in Fig. 7.

Up to now, we have been concerned with the ground-state configuration of our system. However, its orbital spin excitations according to the effective Hamiltonian (3.12) are interesting phenomena to discuss and to compare with what has been found for the diatomic molecule.

The spin excitation for a given orbital configuration is easily obtained from (5.17) by dropping the spin averages and the constant terms. The resulting Hamiltonian $H_{\mathrm{eff}}^{\mathrm{ex}}$ is

$$-H_{\mathrm{eff}}^{\mathrm{ex}}=\sum_{\langle ij\rangle}^{i=1,4}[J^f(i,j)-J^a(i,j)]\vec{S}_i\cdot\vec{S}_j\,, \tag{5.21}$$

where the effective exchange constants are to be evaluated from expression (5.18) for the particular orbital configuration under study. As an instructive example also useful for later purposes, we discuss the spin excitations for the orbital structures RO(2) and AO(1). Since in these (actually in all orbital) configurations, the ordering for the orbital occupancy for the vertical pair along $\vec{\delta}_4$ is always antiferromagnetic ($\psi_j-\psi_{i=4}=\frac{1}{2}\pi$), we find from expression (5.18) that

$$
\begin{aligned}
J^f(4,j)-J^a(4,j)&=w-\frac{w}{c}\,b\\
&=2\mu^2\left(\frac{1}{U_{12}-J}-\frac{U_{12}}{U_{12}^2-J^2}\right)\\
&=2\mu^2\,\frac{J}{U_{12}^2-J^2}\sim\frac{2\mu^2}{U_{12}}\,\frac{J}{U_{12}}\,;
\end{aligned}
$$

that is to say, a weak ferromagnetic exchange [remember the minus sign in (5.21)] relative to a hopping from a full to an empty orbital, in accordance with the Goodenough-Kanamori-Anderson rules[7,18,19] since the transfer integral $t^{12}_{\vec{\nu}}$ between occupied orbitals is zero.

The situation along the direction $\vec{\delta}_1$ can be different according to the orbital structures. In the AO(1) ordering, we find from Table IV that

$$
\begin{aligned}
J^f(1,j)-J^a(1,j)&=u-\frac{1}{c}\,(b-\tfrac{1}{2}a)u-r\\
&=(\alpha^2+\beta^2)\left(\frac{1}{U_{12}-J}-\frac{U_{12}}{U_{12}^2-J^2}\right)\\
&=(\alpha^2+\beta^2)\,\frac{J}{U_{12}^2-J^2}\,;
\end{aligned}
$$

that is to say again, a weak ferromagnetic exchange, since we have put from the outset the transfer integral $t^{12}_{\vec{\delta}_1}=\chi$ relative to the occupied orbitals equal to zero. In the RO(2) ordering however, Table IV gives an exchange

$$
\begin{aligned}
J^f(1,j)-J^a(1,j)&=u-v-\frac{1}{c}\,(b-\tfrac{1}{2}a)u-t\\
&=(\alpha^2+\beta^2)\,\frac{J}{U_{12}^2-J^2}-\tfrac{1}{2}(\alpha-\beta)^2\\
&\quad\times\left[\frac{U_{12}}{U_{12}^2-J^2}+\frac{J}{U_{11}^2-J^2}\right],
\end{aligned}
$$

which can be positive (ferro-) or negative (antiferromagnetic) according to the spin and the magnitude of β. When $\alpha=\beta$ we find the usual weak ferromagnetic exchange between an empty and a full orbital. In this latter case in fact, since the occupied orbital on each site is $(1/\sqrt{2})(w^1+w^2)$, whereas the other $(1/\sqrt{2})(w^1-w^2)$ is empty, we have

$$\int\frac{1}{2}\,(w^1\pm w^2)H_0(w^1\pm w^2)=t^{11'}_{\vec{\delta}_1}=t^{22'}_{\vec{\delta}_1}=\tfrac{1}{2}(\beta-\alpha)=0$$

and

$$\int\frac{1}{2}\,(w^1\pm w^2)H_0(w^1\mp w^2)=t^{12'}_{\vec{\delta}_1}=t^{21'}_{\vec{\delta}_1}=-\tfrac{1}{2}(\alpha+\beta)\,,$$

so that there is only transfer to an empty orbital.

Departure from the relation $\alpha = \beta$ introduces more and more transfer between occupied orbitals, finally making the net exchange antiferromagnetic,

$$\sim -\tfrac{1}{2}(\alpha - \beta)^2/(U_{12} - J).$$

Along the other two direction $\vec{\delta}_2$ and $\vec{\delta}_3$, we can easily check from Table IV that the net coupling is always antiferromagnetic (for the orbital structures under consideration

$$J^{f(a)}(2, j) = J^{f(a)}(3, j) = \mathcal{J}_{2j}^{f(a)}),$$

transfer between occupied orbitals always prevails over the empty ones. For the AO(1) structure, we find

$$J^f(2, j) - J^a(2, j) = \tfrac{1}{4}(u + 3v) - (1/c)(b - \tfrac{1}{2}a)u \\ - \tfrac{1}{4}(r - 3t) \propto -\tfrac{3}{4}(\alpha^2 + \beta^2)/(U_{12} - J),$$

whereas in the RO(2) case, the exchange is

$$J^f(2, j) - J^a(2, j) = \tfrac{1}{4}(3u + v) - (1/c)(b - \tfrac{1}{2}a)u \\ + \tfrac{1}{4}(3r - t) \propto -\tfrac{1}{4}(\alpha^2 + \beta^2)/(U_{12} - J).$$

All the above exchange constants represent the energy needed to turn a spin *in situ* and the results of the previous discussion parallel those we have found in the case of the diatomic molecule although in the case of the lattice, the Pauli principle is less effective and we can have spin excitations requiring an energy $\propto t^2/(U_{12} - J)$ without having to change the orbital order.

The orbital excitations for a given spin configuration and the orbital and spin excitation are easily obtained from Table V or expression (5.18).

It is to be noticed that up to now, we have been talking of orbital and spin excitations of the Ising type. In the lattice, the proper excitations would be orbital and spin waves for the description of which the effective Hamiltonian (3.12) should be considered and the usual techniques used. We are not interested in this aspect of the problem for our purposes.

APPENDIX

The exact eigenstates for a diatomic molecule with one electron per site in degenerate atomic levels are easily found if one uses the following procedure. Since the Hamiltonian is the sum

$$H = H' + H_0 \tag{A1}$$

of a kinetic-energy part H' transferring electrons from site to site and an interaction part H_0 which operates within the sites, we choose right away eigenstates of H_0 which can be constructed by taking linear combinations over the two sites a and b of the molecule of the "polar" states in (3.3). For example, let us take

$$(1/\sqrt{2})(c_{a1\uparrow}^\dagger c_{a2\uparrow}^\dagger + c_{b1\uparrow}^\dagger c_{b2\uparrow}^\dagger)|0\rangle = |S_P\rangle.$$

Application of the Hamiltonian (A1) onto these states results in a nonpolar state easily derived since

$$\begin{aligned} H|S_P\rangle &= (U_{12} - J)|S_P\rangle + H'|S_P\rangle \\ &= (U_{12} - J)|S_P\rangle + [H', (1/\sqrt{2})(c_{a1\uparrow}^\dagger c_{a2\uparrow}^\dagger \\ &\qquad + c_{b1\uparrow}^\dagger c_{b2\uparrow}^\dagger)]|0\rangle. \end{aligned} \tag{A2}$$

But quite generally, since $H' = \sum t_{ab}^{mm'} c_{am\sigma}^\dagger c_{bm\sigma}$ and $t_{ab}^{mm'} = 0$ $(m \neq m')$ in our case, we obtain

$$[H', c_{am\sigma}^\dagger c_{am'\sigma'}^\dagger] = t(c_{bm\sigma}^\dagger c_{am'\sigma'}^\dagger + c_{am\sigma}^\dagger c_{bm'\sigma'}^\dagger). \tag{A3}$$

Hence,

$$H'|S_P\rangle = 2t(1/\sqrt{2})(c_{b1\uparrow}^\dagger c_{a2\uparrow}^\dagger + c_{a1\uparrow}^\dagger c_{b2\uparrow}^\dagger)|0\rangle = 2t|S_{NP}\rangle.$$

The result of this application of H onto the nonpolar state $|S_{NP}\rangle$ is now immediate, since $H_0|S_{NP}\rangle = 0$ and obviously $H'|S_{NP}\rangle = 2t|S_P\rangle$ because

$$[H', c_{am\sigma}^\dagger c_{bm'\sigma'}^\dagger] = t(c_{bm\sigma}^\dagger c_{bm'\sigma'}^\dagger + c_{am\sigma}^\dagger c_{am'\sigma'}^\dagger). \tag{A4}$$

Collecting all the previous results, the matrix to be diagonalized is

$$\begin{aligned} H|S_P\rangle &= (U_{12} - J)|S_P\rangle + 2t|S_{NP}\rangle, \\ H|S_{NP}\rangle &= 2t|S_P\rangle, \end{aligned} \tag{A5}$$

which leads immediately to the eigenstate (3.16) and to the eigenvalue $\epsilon(U_{12} - J)$ of the text. It goes without saying that the combination of the polar states on site a and b must be such that the corresponding nonpolar state is different from zero. In such a way, we can easily obtain all the states for which the Pauli principle does not prevent the electrons from jumping from one site to another. It is easily recognized that the states given in Sec. III exhaust this class apart from spin degeneracy.

The nonpolar states for which the Pauli principle prevents jumping of the electrons on the same site are then immediately found by inspection from the ones already found since they must be antisymmetric under interchange of the sites a and b. For example, from $(1/\sqrt{2})(c_{a1\uparrow}^\dagger c_{b2\uparrow}^\dagger - c_{a2\uparrow}^\dagger c_{b1\uparrow}^\dagger)|0\rangle$ which is symmetric under this operation, one immediately finds $(1/\sqrt{2})(c_{a1\uparrow}^\dagger c_{b2\uparrow}^\dagger + c_{a2\uparrow}^\dagger c_{b1\uparrow}^\dagger)|0\rangle$ which is antisymmetric under the same operation and such as to give zero when operated upon by H'.

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