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Exchange Interaction between Nearest-Neighbor Ion Pairs. II. V^{2+} in MgO*

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The configuration-interaction method is applied to the (right-angle) exchange interaction between nearest-neighbor V^{2+} ion pairs in MgO. Specific configurations under consideration are the ionic configuration, all allowed anion-to-cation charge-transfer configurations, and the most important cation-to-cation charge-transfer configuration. Numerical calculations are performed for the exchange interactions between individual 3*d*-electron pairs. The exchange coupling constant J_{AB} associated with the exchange energy $-2J_{AB}\mathbf{S}_A\cdot\mathbf{S}_B$ between total spins of two V^{2+} ions is deduced by projecting the single electronic spin onto the total spin. Its value is found to be 8.2°K (ferromagnetic). The lack of orthogonality between neighboring cation 3*d* orbitals is shown to be very important for the exchange coupling between two magnetic ions at right angles to an intervening anion. The sign of the contribution to the exchange integral arising from this nonorthogonality depends on the symmetry of electron orbitals. For the specific cases under consideration, these contributions are found to be of overriding numerical importance.

I. INTRODUCTION

IN our previous paper[1] (hereafter referred to as I) we applied the method of configuration interaction to investigate the exchange interaction between nearest-neighbor V^{2+} ion pairs in $KMgF_3$ and noted the importance of taking into account the overlap integral between neighboring free-ion *d* orbitals and the cation → cation charge-transfer excitations resulting from this nonorthogonality. The primary objective of this paper is to study the sign of the exchange interaction between nearest-neighboring V^{2+} ions and the relative importance of various charge-transfer excitations for V^{2+}:MgO, using the same approach as adopted in I. For the present case, the two V^{2+} ions are at right angles with respect to an intervening oxygen ion and are separated from one another by 2.97 Å only, as compared to a nearest cation-cation separation of 4.00 Å in V^{2+}:$KMgF_3$. Consequently, nonorthogonality between the cation *d* orbitals plays a very important role for the exchange interaction in the present case.

From the symmetry of electron orbitals, Kanamori[2] has shown that, in the anhydrous chlorides where the cations within a layer normal to the principal axis are nearly at right angles with respect to an intervening anion, the exchange interaction between two magnetic ions of d^3 configuration is ferromagnetic. He further pointed out that in the monoxides, direct interaction and electron-transfer excitation between the cations are important and that the latter will give rise to an antiferromagnetic interaction. Up to now no experiment has analyzed the exchange interaction between two nearest d^3 ions in the NaCl type of structure. However, the intralayer exchange in $CrBr_2$, where the Cr–Br–Cr bond is nearly a right angle, is in fact found to be +5.44°K (ferromagnetic) by Gossard *et al.*[3] Also, Baltzer *et al.*[4] recently reported that the exchange interaction between nearest Cr^{3+} neighbors in the chromium chalcogenide spinels (the Cr-anion-Cr bond is a right angle) is ferromagnetic, varying from 11.8°K ($CdCr_2S_4$) to 15.8°K ($HgCr_2Se_4$).

We shall consider the perturbation on the ionic configuration caused by the anion→cation and the cation→cation charge-transfer excitations. Since these processes are allowed only between the nonorthogonal orbitals, it is necessary to observe first what these orbitals are. Consider two V^{2+} ions and an intervening oxygen ion in the *xz* plane as shown in Fig. 1. Using the symmetry properties, we list in Tables I and II the nonorthogonal 2*p*-3*d* orbitals and the 3*d*-3*d* orbitals, respectively. From Table I we note that the anion→cation charge transfer processes are allowed for the configurations shown in Figs. 2(a) and 2(b). In the former case, an electron can be transferred from the $2p_x$ (or $2p_z$) orbital to the unoccupied $V^{2+}-d_{xz}$ orbital at center *A* (or center *B*), while in Fig. 2(b) electron transfer is allowed from $2p_y$ orbital to the unoccupied d_{yz} orbital at center *A* or to the d_{xy} orbital at center *B*. The cation →cation charge transfer takes place from the d_{xz} orbital at one center to the d_{xz}, d_{z^2}, or $d_{x^2-y^2}$ orbitals at the other, also from the d_{xy} (or d_{yz}) orbital at one center to the d_{xy} and d_{yz} orbitals at the other. Since the t_{2g} orbitals are half-filled for a V^{2+} ion in the ground state in an octahedral crystal field and the e_g orbitals are empty, it is clear that the electron transfer from d_{xz} to d_{z^2} or $d_{x^2-y^2}$ will result in a ferromagnetic interaction due to the Hund's rule, whereas the other cation→cation transfers will give rise to an antiferromagnetic coupling. In the following sections we shall consider all the previously mentioned anion→cation transfer processes. As to the cation→cation transfers, only the

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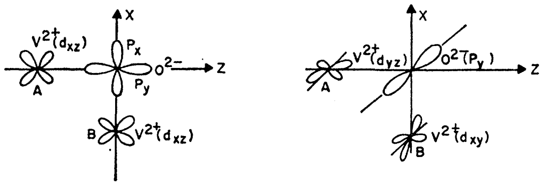
TABLE I. The anion $2p$ and cation $3d$ (centered at site A or B) orbitals which are nonorthogonal.

O^{2-}	$3d$ orbitals centered at cation A or B
$2p_x$	$d_{xz}(A), d_{x^2}(B)$
$2p_y$	$d_{yz}(A), d_{xy}(B)$
$2p_z$	$d_{z^2}(A), d_{xz}(B)$



(a) (b)

FIG. 2. (a) Configuration in which the charge transfer from anion $2p_x$ or $2p_z$ to cation is allowed. (b) Configuration in which the charge transfer from anion $2p_y$ to cation is allowed.

transfer between two d_{xz} orbitals will be considered. The significance of the other processes will be discussed in Sec. IV.

Since the electronic orbitals involved explicitly in the charge-transfer excitations in Fig. 2(a) are different from those in Fig. 2(b), we can treat these two cases separately to a good approximation. Moreover, we found in I that the interaction between the anion→cation and cation→cation charge-transfer excitations is numerically unimportant, so that we assume here that we can consider these two kinds of excitations independently. We therefore solve the configuration interaction problem for the following three excitations separately: (i) charge transfer from the anion $2p_x$ and $2p_z$ orbitals to the cations, (ii) charge transfer from the anion $2p_y$ orbital to the cations, and (iii) charge transfer between the cation d_{xz} orbitals. A brief account of the method of permutation degeneracy is given in Sec. II. Expressions for the exchange integral between two individual d electrons arising from each of the above mentioned cases and the numerical estimates are given in Sec. III A–C. Projection of the spin of a single electron onto the total spin of the ion and estimate for the exchange coupling constant between the total spins of the V^{2+} ions are given in Sec. III D.

II. THE METHOD OF PERMUTATION DEGENERACY

We use the Dirac–Van Vleck–Serberper mutation degeneracy method[5–7] to solve for the spin-dependent part of the perturbed ground-configuration energy. The wave function describing a configuration is taken to be the product of atomic orbitals and the exclusion principle is taken into account by using only the physically allowed spin states in constructing the matrix representation of the permutation operators. The matrix element which connects configuration R_i to R_j is expanded into the matrix representation of the permutation operators as follows:

$$(\mathcal{H}-W)^{R_iR_j} = \sqrt{2}^{\,r_i-r_j}\sum_P{}'(\mathcal{H}-W)_P{}^{R_iR_j}\wp^{R_iR_j} \qquad (r_i \geq r_j), \quad (1)$$

where $\mathcal{H}$ is the sum of the total kinetic energy of the electrons, the electron-nuclear potential energy, and the Coulomb interaction energy between the electrons, W is the unknown energy to be solved for in the secular equation, r_i equals the number of pairs of filled orbitals in configuration R_i, and the sum is carried over the $n!/2^{r_i}$ permutations which differ by more than an interchange of identical orbitals in R_i (n = number of electrons under consideration). It can be shown[7] that the coefficient $(\mathcal{H}-W)_P{}^{R_iR_j}$ of the matrix representation of the permutation operator P is given by the expression

$$(\mathcal{H}-W)_P{}^{R_iR_j} = \langle P\psi^{R_i}|\mathcal{H}-W|\psi^{R_j}\rangle \equiv \mathcal{H}_P{}^{R_iR_j} - W\langle P\psi^{R_i}|\psi^{R_j}\rangle, \quad (2)$$

where

$$\psi^{R_i} \equiv \varphi_1{}^i(\mathbf{r}_1)\varphi_2{}^i(\mathbf{r}_2)\cdots\varphi_n{}^i(\mathbf{r}_n) \quad (3)$$

is the product of the one-electron orbitals specifying configuration R_i.

The construction of the matrix representation of the permutation operators will be demonstrated in Sec. III for our specific case. Obviously, such construction depends upon the relative spin orientation of the d electrons. Hence by using (1) and (2) to set up the secular equation for the energy eigenvalues, we are able to solve for the strength of the interionic exchange interaction.

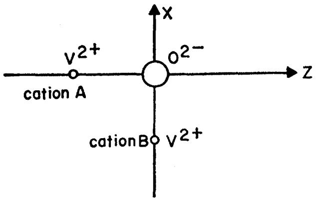


FIG. 1. Positions of the cations and anion under consideration.

TABLE II. The nonorthogonal $3d$ orbitals centered at cation A and B.

$3d$ orbitals centered at cation A	$3d$ orbitals centered at cation B
$d_{xz}, d_{z^2}, d_{x^2-y^2}$	$d_{xz}, d_{x^2}, d_{y^2-z^2}$
d_{xy}, d_{yz}	d_{xy}, d_{yz}

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III. CONTRIBUTION TO THE EXCHANGE INTERACTION VIA THE ANION→CATION AND CATION→CATION CHARGE-TRANSFER EXCITATIONS

A. Charge-Transfer Excitations from the $2p_x$ and $2p_z$ Orbitals to the Cations

The configurations under consideration are shown in Fig. 3, where A is the ionic configuration, B and B' are the excited configurations in which an electron is transferred from the anion $2p_x$ and $2p_z$ orbitals to the e_g orbital of cation A and B, respectively, and C and C' are the excited configurations in which an electron is transferred from the $2p_x$ and $2p_z$ orbitals to the d_{xz} orbital at center A and B, respectively. Clearly, since the ionic configuration is even, it connects only with the following even combinations of the excited configurations:

$$\psi_{G_1} \simeq (1/\sqrt{2})(\psi^B + \psi^{B'}),$$

$$\psi_{G_2} \simeq (1/\sqrt{2})(\psi^C + \psi^{C'}). \tag{4}$$

The energy matrix to be solved is then given by

$$\begin{vmatrix} (\mathcal{H}-W)^{AA} & (\mathcal{H}-W)^{G_1A} & (\mathcal{H}-W)^{G_2A} \\ (\mathcal{H}-W)^{AG_1} & (\mathcal{H}-W)^{G_1G_1} & (\mathcal{H}-W)^{G_2G_1} \\ (\mathcal{H}-W)^{AG_2} & (\mathcal{H}-W)^{G_1G_2} & (\mathcal{H}-W)^{G_2G_2} \end{vmatrix} = 0, \tag{5}$$

Using symmetry properties we can show that

$$(\mathcal{H}-W)^{G_1G_1} = (\mathcal{H}-W)^{BB} + (\mathcal{H}-W)^{BB'},$$

$$(\mathcal{H}-W)^{G_2G_2} = (\mathcal{H}-W)^{CC} + (\mathcal{H}-W)^{CC'},$$

$$(\mathcal{H}-W)^{G_1G_2} = (\mathcal{H}-W)^{BC} + (\mathcal{H}-W)^{BC'}. \tag{6}$$

Detailed calculation indicates that the exchange interaction between two d electrons belonging to two neighboring cations contains, to the lowest order in overlap integrals, only the parts in $\mathcal{H}^{G_1G_1}$, $\mathcal{H}^{G_2G_2}$, and $\mathcal{H}^{G_1G_2}$ which depend upon the relative spin orientation of these two electrons. We find that the dominant terms of such spin-dependent parts are contained in $(\mathcal{H}-W)^{BB}$, $(\mathcal{H}-W)^{CC}$, and $(\mathcal{H}-W)^{BC}$; hence we can ignore the elements $(\mathcal{H}-W)^{BB'}$, $(\mathcal{H}-W)^{CC'}$, and $(\mathcal{H}-W)^{BC'}$. Accordingly, only the electron on the $2p_z$ orbital takes part in the charge transfer, and the six-electron model shown in Fig. 3 can then be replaced by a four-electron one. In other words, we shall consider those two electrons belonging to the $2p_x$ orbitals implicitly by choosing a proper effective nuclear charge in solving for the interaction between configurations A, B, and C.

Construction of the Matrix Representation of the Permutation Operators

The eigenfunctions for the total spin of a four-electron system consist of a quintet state, three triplet states, and two singlet states. However, because of the presence of identical orbitals in configurations A and C, the exclusion principle restricts the spin $\mathbf{s}_1$ associated with the electron on the orbital a_1 (or c_1) to be antiparallel to the spin $\mathbf{s}_2$ associated with the electron on the orbital a_2 (or c_2). In configuration B, the electron being transferred from the anion to the cation cannot change the direction of its spin, because our Hamiltonian is taken to be spin-independent. Thus we have again $\mathbf{s}_1$ antiparallel to $\mathbf{s}_2$ for this configuration. This requirement turns out to be consistent only with one of the three triplet states and one of the two singlet states for all three configurations A, B, and C. The quintet state is clearly inconsistent with the above requirement. Accordingly, the matrix representation $\mathcal{P}^{R_iR_j}$ is independent of the configuration indices R_i and R_j. Moreover, since any permutation operator P_{ij} is related to the

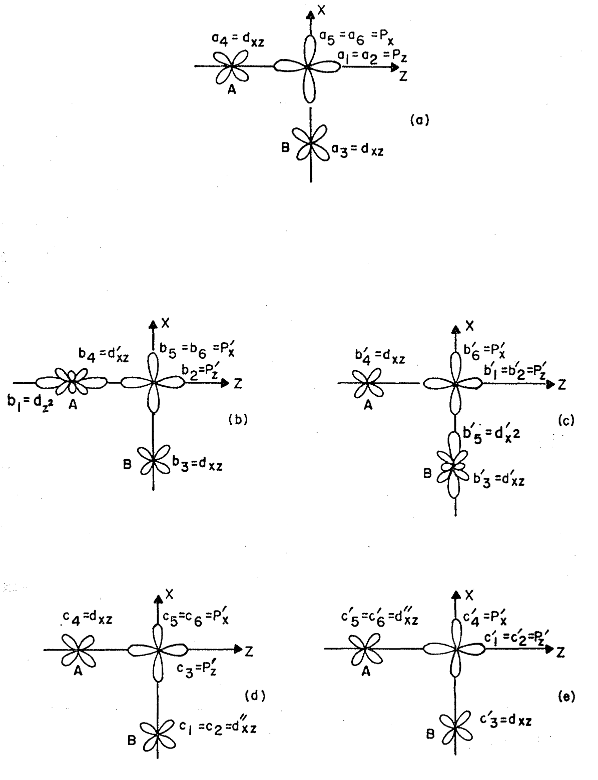

FIG. 3. (a) Ionic configuration A is considered in Sec. III A. (b) Excited configuration B in which an electron is transferred from $2p_z$ to the $3d_{z2}$ orbital of cation A. (c) Excited configuration B' in which an electron is transferred from $2p_x$ to the $3d_{x2}$ orbital of cation B. (d) Excited configuration C in which an electron is transferred from $2p_z$ to the $3d_{xz}$ orbital of cation B. (e) Excited configuration C' in which an electron is transferred from $2p_x$ to the $3d_{xz}$ orbital of cation A.

spin variables by the expression[5]

$$P_{ij}=-\tfrac{1}{2}(1+4\mathbf{s}_i\cdot\mathbf{s}_j), \tag{7}$$

which is obviously invariant under a rotation of the spin axes and commutes with the total spin, the permutation operators then have no matrix elements between states of different total spin S or M_S. Furthermore, for each value of S, we obtain a representation of P which is independent of M_S, as pointed out by Serber.[7] Therefore, the $\mathcal{P}$'s are one-dimensional for $S=1$ or $S=0$.

Demanding that $\mathbf{s}_1$ to be antiparallel to $\mathbf{s}_2$, the physically allowed eigenstates of the total spin are found to be

$$\psi_1=(1/\sqrt{2})(\alpha_1\beta_2-\beta_1\alpha_2)\alpha_3\alpha_4$$

for

$$S=1 \quad \text{and} \quad M_S=1 \tag{8a}$$

and

$$\psi_0=\tfrac{1}{2}(\alpha_1\beta_2-\beta_1\alpha_2)(\alpha_3\beta_4-\beta_3\alpha_4), \qquad \text{for } S=0. \tag{8b}$$

Thus the $\mathcal{P}$'s are simply given by

$$\mathcal{P}=\langle\psi_1|P|\psi_1\rangle \qquad \text{for } S=1, \tag{9a}$$

$$=\langle\psi_0|P|\psi_0\rangle \qquad \text{for } S=0. \tag{9b}$$

One way to determine the exchange coupling constant J between two d electrons belonging to two cations is to solve for the energies E_s and E_t for the singlet and triplet state, respectively, and then calculate J from $J=\frac{1}{2}(E_s-E_t)$. An equivalent, but more convenient, method is to determine the $\mathcal{P}$'s using only the singlet state for $\mathbf{s}_1$ and $\mathbf{s}_2$ and leave the directions of $\mathbf{s}_3$ and $\mathbf{s}_4$ completely unspecified. The solution to the secular equation is then expressed in terms of the inner product $\mathbf{s}_3\cdot\mathbf{s}_4$, and J is determined. The latter procedure is adopted in this section. Decomposing the permutation operators involving more than two indices into products of P_{ij}'s and using (7), (8), and (9), we obtain the following expressions for the $\mathcal{P}$'s:

$$\begin{aligned}
&\mathcal{P}_I=1,\\
&\mathcal{P}_{13}=\mathcal{P}_{23}=\mathcal{P}_{14}=\mathcal{P}_{24}=-\tfrac{1}{2},\\
&\mathcal{P}_{134}=\mathcal{P}_{234}=\mathcal{P}_{143}=\mathcal{P}_{243}=-\tfrac{1}{2}\mathcal{P}_{34},\\
&\mathcal{P}_{13,24}=\mathcal{P}_{14,23}=\tfrac{1}{2}(1+\mathcal{P}_{34}),
\end{aligned} \tag{10a}$$

and

$$\begin{aligned}
&\mathcal{P}_{12}=1,\\
&\mathcal{P}_{123}=\mathcal{P}_{124}=\mathcal{P}_{132}=\mathcal{P}_{142}=-\tfrac{1}{2},\\
&\mathcal{P}_{12,34}=\mathcal{P}_{34},\\
&\mathcal{P}_{1234}=\mathcal{P}_{1243}=\mathcal{P}_{1342}=\mathcal{P}_{1432}=-\tfrac{1}{2}\mathcal{P}_{34},\\
&\mathcal{P}_{1324}=\mathcal{P}_{1423}=\tfrac{1}{2}(1+\mathcal{P}_{34}),
\end{aligned} \tag{10b}$$

where the first group, given in (10a), is for the twelve permutations which differ by more than an interchange of orbitals "1" and "2," while the twelve $\mathcal{P}$'s in (10b) correspond to the permutation operators which are related to the first twelve by a multiplication of P_{12}.

Solution to the Secular Equation

We define the following overlap integrals:

$$S_\pi=\langle P_z|d_{xz}(B)\rangle, \qquad S_\sigma=\langle p_z|d_{z^2}(A)\rangle,$$

$$T_1=\langle d_{xz}(A)|d_{xz}(B)\rangle, \qquad T_2=\langle d_{z^2}(A)|d_{xz}(B)\rangle, \tag{11}$$

and approximate the orbitals d_{xz}', d_{xz}'', and p_z' shown in Fig. 3 by d_{xz} and p_z (i.e., we take $a_1=b_2=c_3$, $a_3=b_3=c_1$, and $a_4=b_4=c_4$) because the high-frequency character of the virtual excitations prevents the charge redistribution to be fully developed, as discussed by Šimánek and Tachiki.[8] According to (1) we need to consider the 4! permutations entered in (10a) and (10b) for the expansion of $(\mathcal{H}-W)^{BB}$ in terms of the $\mathcal{P}$'s, while for the other matrix elements only the twelve $\mathcal{P}$'s in (10a) are required. Upon substituting (2), (3), (10), and (11) into (1), we obtain

$$(\mathcal{H}-W)^{AA}=(\mathcal{H}_I{}^{AA}-W)-(\mathcal{H}_{13}{}^{AA}-WS_\pi{}^2)-\mathcal{H}_{14}{}^{AA}+\mathcal{H}_{13,24}{}^{AA}+\mathcal{P}_{34}[(\mathcal{H}_{34}{}^{AA}-WT_1{}^2)-(\mathcal{H}_{134}{}^{AA}+\mathcal{H}_{143}{}^{AA})+\mathcal{H}_{13,24}{}^{AA}], \tag{12a}$$

$$\begin{aligned}
(\mathcal{H}-W)^{BB}=(\mathcal{H}_I{}^{BB}-W)&-\tfrac{1}{2}(\mathcal{H}_{13}{}^{BB}-WT_2{}^2+\mathcal{H}_{14}{}^{BB}+\mathcal{H}_{23}{}^{BB}-WS_\pi{}^2+\mathcal{H}_{24}{}^{BB})\\
&+(\mathcal{H}_{12}{}^{BB}-WS_\sigma{}^2)+\tfrac{1}{2}(\mathcal{H}_{13,24}{}^{BB}+\mathcal{H}_{14,23}{}^{BB}+\mathcal{H}_{1324}{}^{BB}+\mathcal{H}_{1423}{}^{BB})\\
&-\tfrac{1}{2}(\mathcal{H}_{132}{}^{BB}+\mathcal{H}_{142}{}^{BB}+\mathcal{H}_{123}{}^{BB}+\mathcal{H}_{124}{}^{BB}-2WS_\sigma S_\pi T_2{}^2)\\
&+\mathcal{P}_{34}[(\mathcal{H}_{34}{}^{BB}-WT_1{}^2)+(\mathcal{H}_{12,34}{}^{BB}-WS_\sigma{}^2T_1{}^2)\\
&-\tfrac{1}{2}(\mathcal{H}_{134}{}^{BB}+\mathcal{H}_{143}{}^{BB}+\mathcal{H}_{234}{}^{BB}+\mathcal{H}_{243}{}^{BB}+\mathcal{H}_{1342}{}^{BB}+\mathcal{H}_{1432}{}^{BB})\\
&-\tfrac{1}{2}(\mathcal{H}_{1234}{}^{BB}+\mathcal{H}_{1243}{}^{BB}-\mathcal{H}_{13,24}{}^{BB}-\mathcal{H}_{14,23}{}^{BB}-\mathcal{H}_{1324}{}^{BB}-\mathcal{H}_{1423}{}^{BB})],
\end{aligned} \tag{12b}$$

$$\begin{aligned}
(\mathcal{H}-W)^{CC}=(\mathcal{H}_I{}^{CC}-W)&-(\mathcal{H}_{13}{}^{CC}-WS_\pi{}^2)-(\mathcal{H}_{14}{}^{CC}-WT_1{}^2)+(\mathcal{H}_{13,24}{}^{CC}-WS_\pi{}^2T_1{}^2)\\
&+\mathcal{P}_{34}[\mathcal{H}_{34}{}^{CC}-\mathcal{H}_{134}{}^{CC}-\mathcal{H}_{143}{}^{CC}+(\mathcal{H}_{13,24}{}^{CC}-WS_\pi{}^2T_1{}^2)],
\end{aligned} \tag{12c}$$

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[8] E. Šimánek and M. Tachiki, Phys. Letters **21**, 625 (1966).

$$
\begin{aligned}
(\mathcal{H}-W)^{AB}=\sqrt{2}[&(\mathcal{H}_I{}^{AB}-WS_\sigma)-\tfrac{1}{2}(\mathcal{H}_{13}{}^{AB}-WS_\pi T_2)-\tfrac{1}{2}(\mathcal{H}_{23}{}^{AB}-WS_\sigma S_\pi{}^2)\\
&+\tfrac{1}{2}(\mathcal{H}_{13,24}{}^{AB}+\mathcal{H}_{14,23}{}^{AB}-\mathcal{H}_{14}{}^{AB}-\mathcal{H}_{24}{}^{AB})]\\
&+\sqrt{2}\mathcal{P}_{34}[(\mathcal{H}_{34}{}^{AB}-WS_\sigma T_1{}^2)+\tfrac{1}{2}(\mathcal{H}_{13,24}{}^{AB}+\mathcal{H}_{14,23}{}^{AB})-\tfrac{1}{2}(\mathcal{H}_{134}{}^{AB}+\mathcal{H}_{143}{}^{AB}+\mathcal{H}_{234}{}^{AB}+\mathcal{H}_{243}{}^{AB})], \qquad \text{(12d)}
\end{aligned}
$$

$$
\begin{aligned}
(\mathcal{H}-W)^{AC}=&(\mathcal{H}_I{}^{AC}-WS_\pi{}^3)-(\mathcal{H}_{13}{}^{AC}-WS_\pi)-\mathcal{H}_{14}{}^{AC}+\mathcal{H}_{13,24}{}^{AC}\\
&+\mathcal{P}_{34}[\mathcal{H}_{34}{}^{AC}-\mathcal{H}_{134}{}^{AC}+\mathcal{H}_{13,24}{}^{AC}-(\mathcal{H}_{143}{}^{AC}-WS_\pi T_1{}^2)], \qquad \text{(12e)}
\end{aligned}
$$

$$
\begin{aligned}
(\mathcal{H}-W)^{BC}=\sqrt{2}[&(\mathcal{H}_I{}^{BC}-WS_\pi{}^2T_2)-\tfrac{1}{2}(\mathcal{H}_{13}{}^{BC}-WS_\sigma S_\pi)-\tfrac{1}{2}(\mathcal{H}_{23}{}^{BC}-WT_2{}^2)\\
&-\tfrac{1}{2}(\mathcal{H}_{14}{}^{BC}+\mathcal{H}_{24}{}^{BC}-\mathcal{H}_{13,24}{}^{BC}-\mathcal{H}_{14,23}{}^{BC})]\\
&+\sqrt{2}\mathcal{P}_{34}[\mathcal{H}_{34}{}^{BC}-\tfrac{1}{2}(\mathcal{H}_{134}{}^{BC}+\mathcal{H}_{234}{}^{BC}-\mathcal{H}_{13,24}{}^{BC}-\mathcal{H}_{14,23}{}^{BC})\\
&-\tfrac{1}{2}(\mathcal{H}_{143}{}^{BC}-WS_\pi S_\sigma T_1{}^2)-\tfrac{1}{2}(\mathcal{H}_{243}{}^{BC}-WT_1{}^2T_2)]. \qquad \text{(12f)}
\end{aligned}
$$

The secular determinant (5) involves a cubic equation in W. In order to simplify the algebra, we use the same procedure adopted by Keffer and Oguchi[9] by replacing W everywhere except in the term $\mathcal{H}_I{}^{AA}-W$ by its zeroth order approximation $\mathcal{H}_I{}^{AA}$. This is adequate since we are only interested in the perturbed energy of the ionic configuration involving the $\mathbf{s}_3\cdot\mathbf{s}_4$ terms. Thus we find,

$$
\begin{aligned}
W=&\mathcal{H}_I{}^{AA}-(\mathcal{H}_{13}{}^{AA}-\mathcal{H}_I{}^{AA}S_\pi{}^2)-\mathcal{H}_{14}{}^{AA}+\mathcal{H}_{13,24}{}^{AA}+\mathcal{P}_{34}[(\mathcal{H}_{34}{}^{AA}-\mathcal{H}_I{}^{AA}T_1{}^2)-\mathcal{H}_{134}{}^{AA}-\mathcal{H}_{143}{}^{AA}+\mathcal{H}_{13,24}{}^{AA}]\\
&+\frac{2(\mathcal{H}-\mathcal{H}_I{}^{AA})^{AB}[(\mathcal{H}-\mathcal{H}_I{}^{AA})^{AB}(\mathcal{H}-\mathcal{H}_I{}^{AA})^{CC}-2(\mathcal{H}-\mathcal{H}_I{}^{AA})^{AC}(\mathcal{H}-\mathcal{H}_I{}^{AA})^{BC}]+2(\mathcal{H}-\mathcal{H}_I{}^{AA})^{BB}[(\mathcal{H}-\mathcal{H}_I{}^{AA})^{AC}]^2}{[(\mathcal{H}-\mathcal{H}_I{}^{AA})^{BC}]^2-(\mathcal{H}-\mathcal{H}_I{}^{AA})^{BB}(\mathcal{H}-\mathcal{H}_I{}^{AA})^{CC}},
\end{aligned}
\qquad \text{(13)}
$$

where the matrix elements contained in the last line are given by (12) with W to be replaced by $\mathcal{H}_I{}^{AA}$. Expanding the denominator into power series in the overlap integrals, we find that the dominant terms for the spin-dependent part of W are

$$
\begin{aligned}
\Delta W=-2\mathbf{s}_3\cdot\mathbf{s}_4\Big\{&(\mathcal{H}_{34}{}^{AA}-\mathcal{H}_I{}^{AA}T_1{}^2)-\mathcal{H}_{134}{}^{AA}-\mathcal{H}_{143}{}^{AA}+\mathcal{H}_{13,24}{}^{AA}\\
&+\frac{4(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\pi)}{\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA}}[\mathcal{H}_{13,24}{}^{AC}-\mathcal{H}_{134}{}^{AC}+\mathcal{H}_{34}{}^{AC}-(\mathcal{H}_{143}{}^{AC}-\mathcal{H}_I{}^{AA}S_\pi T_1{}^2)]\\
&-\frac{8(\mathcal{H}_I{}^{AB}-\mathcal{H}_I{}^{AA}S_\sigma)}{\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}}[(\mathcal{H}_{34}{}^{AB}-\mathcal{H}_I{}^{AA}S_\sigma T_1{}^2)-\tfrac{1}{2}\mathcal{H}_{143}{}^{AB}+\tfrac{1}{2}\mathcal{H}_{14,23}{}^{AB}]\\
&+\frac{2(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\pi)^2}{(\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA})^2}\mathcal{H}_{34}{}^{CC}\\
&+\frac{4(\mathcal{H}_I{}^{AB}-\mathcal{H}_I{}^{AA}S_\sigma)^2}{(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^2}[(\mathcal{H}_{34}{}^{BB}-\mathcal{H}_I{}^{AA}T_1{}^2)+\tfrac{1}{2}\mathcal{H}_{14,23}{}^{BB}]\\
&+\frac{4(\mathcal{H}_I{}^{AB}-\mathcal{H}_I{}^{AA}S_\sigma)(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\pi)(\mathcal{H}_{134}{}^{BC}-\mathcal{H}_{14,23}{}^{BC})}{(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})(\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA})}\Big\}\\
\equiv-2J_{34}{}'\mathbf{s}_3\cdot\mathbf{s}_4.&
\end{aligned}
\qquad \text{(14)}
$$

The exchange integral, J_{34}', between the electrons occupying the d_{xz} orbitals at center A and B due to the anion→cation charge transfers is then given by the terms in the curly brackets of (14). We note that the ionic configuration alone contributes to the superexchange interaction also, because of the lack of orthogonality of the electron orbitals, as pointed out by Yamashita and Kondo.[10]

We shall evaluate the matrix elements in (14) by following the procedures adopted in I and in the calculation for the cation $(3d)$→cation $(4s)$ transfer integral for $\mathrm{KMnF_3}$ and MnO.[11] Consider the spin-independent Hamiltonian

$$
\begin{aligned}
\mathcal{H}&=\sum_i-(\hbar^2/2m)\nabla_i{}^2-\sum_{i,g}(Z_ge^2/r_{ig})+\sum_{i>j}(e^2/r_{ij})\\
&\equiv\sum_i\mathcal{H}_i+\sum_{i>j}(e^2/r_{ij}),
\end{aligned}
\qquad \text{(15)}
$$

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[9] F. Keffer and T. Oguchi, Phys. Rev. **115**, 1428 (1959).

[10] J. Yamashita and J. Kondo, Phys. Rev. **109**, 730 (1958).

[11] Nai Li Huang, R. Orbach, E. Šimánek, J. Owen, and D. R. Taylor (to be published).

where Z_g is the atomic number of the nucleus at the point g and $\mathcal{H}_i$ the one-electron part of the Hamiltonian. Using (2), (3), and (15), the matrix elements in (14) are written in terms of the one-electron and two-electron integrals in Appendix A. Observing these expressions, one can interpret some of the terms in (14) as follows. Comparing the expression given by (A1) in Appendix A with the exchange integral for a H_2 molecule,[12] we identify $\mathcal{H}_{34}{}^{AA}-\mathcal{H}_I{}^{AA}T_1{}^2$ as the direct exchange integral between two electrons on the $3d_{xz}(A)$ and $3d_{xz}(B)$ orbitals in the presence of an O^{2-} ion. Contributions of configurations A and C, which involve only the p_z orbitals and are independent of the cation-cation overlap effects, are given in (14) by the following terms:

$$J_{43}'(AC)=\mathcal{H}_{13,24}{}^{AA}-\frac{2(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\pi)}{\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA}}\mathcal{H}_{134}{}^{AC}+\frac{(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\pi)^2}{(\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA})^2}\mathcal{H}_{34}{}^{CC}. \quad (14')$$

From the expression (A4), we identify

$$(\mathcal{H}_{13}{}^{AC}-\mathcal{H}_I{}^{AA}S_\pi)(\mathcal{H}_I{}^{AA}-\mathcal{H}_I{}^{CC})^{-1}$$

as the covalency parameter B_π[13–15] entering in the bonding orbital $p_z(\downarrow)-B_\pi d_{xz}(B)\downarrow$ (we assign a spin direction $\uparrow$ to the electron on the occupied d_{xz} orbital of cation B). Using (A3), (A6), and (A13), we reduce (14′) into the simple form,

$$\begin{aligned}J_{34}'(AC)&=(B_\pi+S_\pi)^2\langle a_4a_1\|a_1a_4\rangle\\&=f_\pi\langle a_4a_1\|a_1a_4\rangle,\end{aligned}$$

where f_π is the unpaired spin density of the anion coming from the overlap and charge transfer effects between p_z and $d_{xz}(B)$ orbitals.[13–15] Thus (14′) represents the superexchange interaction arising from the direct exchange between the electron on the $d_{xz}(A)$ orbital and the unpaired spin density f_π on the p_z orbital.

Numerical Estimates

Using the O^{2-} $2p$ orbitals[16] and the V^{2+} $3d$ orbitals[17] calculated by Watson, the one-center and two-center two-electron integrals in Appendix A can be accurately evaluated using the modified version of the Switendick-Carbato MIDIAT program,[18] whereas the three-center integrals are roughly estimated by using an overlap charge model. It is important to point out that a rotation of coordinate axes by $\pi/4$ is necessary in computing the two-center integrals which involve *both* cations, because these ions are aligned off a symmetry axis of the cubic crystal field by $\pi/4$. This rotation mixes the e_g orbitals with the t_{2g} orbitals and complicates the evaluation of the two-electron integrals to a great extent. The values of the two-electron integrals are listed in Table III.

TABLE III. The two-electron integrals

$$\langle\phi_1\phi_2\|\phi_3\phi_4\rangle\equiv\langle\phi_1\phi_2|e^2/r_{ij}|\phi_3\phi_4\rangle$$

involved in Appendix A. The values are given in atomic units.

$\langle a_1a_1\|a_1a_1\rangle=0.63901$
$\langle a_1a_3\|a_1a_3\rangle=0.24371$
$\langle a_1a_4\|a_1a_4\rangle=0.27035$
$\langle a_4a_1\|a_1a_4\rangle=0.00360$
$\langle a_3a_1\|a_3a_3\rangle=0.03171$
$\langle a_1a_1\|a_3a_1\rangle=0.03418$
$\langle a_3a_4\|a_3a_4\rangle=0.17130$
$\langle a_3a_4\|a_4a_3\rangle=0.00042$
$\langle a_1a_1\|b_1a_1\rangle=-0.06283$
$\langle a_1a_4\|b_1a_4\rangle=-0.04996$
$\langle a_1a_4\|a_4b_1\rangle=-0.00379$
$\langle b_1a_1\|b_1a_1\rangle=0.27670$
$\langle a_4b_1\|b_1a_4\rangle=0.02102$
$\langle a_3b_1\|a_3a_4\rangle=0.00097$
$\langle a_4b_1\|a_3b_1\rangle=0.00820$
$\langle a_4b_1\|a_3a_4\rangle=0.00035$

$\langle a_1a_3\|a_1a_4\rangle\simeq0.008$
$\langle a_3a_1\|a_1a_4\rangle\simeq0.0003$
$\langle a_4a_1\|a_3a_4\rangle\simeq0.0001$
$\langle a_1a_4\|a_3a_4\rangle\simeq0.02$
$\langle a_3a_1\|a_3a_4\rangle\simeq0.002$
$\langle a_4a_1\|a_3a_3\rangle\simeq0.001$
$\langle a_1a_4\|b_1a_3\rangle\simeq-0.001$
$\langle a_4a_1\|b_1a_3\rangle\simeq0.003$

The effects of the electrons other than those considered in the four-electron model can be approximately taken into account by assuming the following one-electron Hamiltonian to be used in (A1)–(A17):

$$\mathcal{H}_1=-(\hbar^2/2m)\nabla_1{}^2+V_A(V^{3+})+V_B(V^{3+})+V(O), \quad (16)$$

where $V_A(V^{3+})$, $V_B(V^{3+})$ and $V(O)$ are the effective one-electron potential energies arising from the V^{3+} ion at cation A site, the V^{3+} ion at cation B site and the O atom, respectively. The ionicities are chosen in the above manner such that the interactions between the four electrons under our explicit consideration are not doubly counted in our Hamiltonian (15). Evaluation of the one-electron matrix elements in Appendix A is carried out by following the same procedures used in our previous calculations.[1,11] We list the results in Table IV, where we also list the values of the overlap integrals defined by (11).

Using the values listed in Tables III and IV, the matrix elements entered in (14) for the exchange integral are evaluated. Their values are listed in Table V. The denominators $\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}$ and $\mathcal{H}_I{}^{CC}-\mathcal{H}_I{}^{AA}$ entered in (14) are the energies required for the virtual process of transferring an electron from the $O^{2-}-2p$ orbital to the $V^{2+}-3d_{z^2}$ and $3d_{xz}$ orbital, respectively. Various contributions to these transfer energies have been discussed in our previous calculations.[1,11] Follow-

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[12] W. Heitler and F. London, Z. Physik **44**, 455 (1927).

[13] S. Sugano and R. G. Shulman, Phys. Rev. **130**, 517 (1963).

[14] E. Šimánek and Z. Šroubek, Phys. Status Solidi **4**, 251 (1964).

[15] R. E. Watson and A. J. Freeman, Phys. Rev. **134**, A1526 (1964).

[16] R. E. Watson, Phys. Rev. **111**, 1108 (1958).

[17] R. E. Watson, MIT SSMTG Technical Report No. 12, 1959 (unpublished).

[18] A. C. Switendick and J. J. Carbato, MIT SSMTG Quarterly Progress Report No. 34, 1959 (unpublished).

TABLE IV. The one-electron integrals entered in Appendix A in atomic units. The overlap integrals defined by (11) are also listed.

$\langle a_1 \mid \mathcal{H}_1 \mid a_1 \rangle = -2.25381$	$S_\pi = 0.08202$
$\langle a_3 \mid \mathcal{H}_1 \mid a_4 \rangle = -0.05568$	$S_\sigma = -0.10426$
$\langle a_3 \mid \mathcal{H}_1 \mid a_3 \rangle = -1.61690$	$T_1 = 0.02300$
$\langle a_1 \mid \mathcal{H}_1 \mid a_3 \rangle = -0.20609$	$T_2 = 0.00588$
$\langle a_1 \mid \mathcal{H}_1 \mid b_1 \rangle = 0.32035$	
$\langle a_4 \mid \mathcal{H}_1 \mid b_1 \rangle = 0.00307$	
$\langle b_1 \mid \mathcal{H}_1 \mid b_1 \rangle = -1.61340$	
$\langle a_1 \mid \mathcal{H}_1 \mid a_4 \rangle \simeq -10^{-4}$ [a]	

[a] Since a_1 and a_4 are orthogonal, $\langle a_1 \mid \mathcal{H}_1 \mid a_4 \rangle$ reduces to $\langle a_1 \mid V_B(\mathrm{V}^{3+}) \mid a_4 \rangle$. We are unable to estimate this matrix element, but we believe it is of the order of -10^{-4} a.u.

ing the identical procedures, we find

$$\mathcal{H}_I^{BB} - \mathcal{H}_I^{AA} = 0.59 \text{ a.u.},$$

$$\mathcal{H}_I^{CC} - \mathcal{H}_I^{AA} = 0.69 \text{ a.u.} \qquad (17)$$

Substitution of (17) and the values listed in Table V into (14) yields the exchange integral arising from the direct exchange interaction between two cations and the superexchange interaction via *one* of the two intervening anions (cf., Fig. 3). However, the other intervening anion plays an identical role to the superexchange coupling; hence the anion-dependent terms in (14) should be multiplied by a factor of 2, whereas the direct exchange coupling, given by the terms which depend only on the cations in (A1), enters only once. In this manner we obtain

$$J_{34}' = 91.8°\mathrm{K}. \qquad (18)$$

In arriving at this result, we note that a contribution of $-163.8°$K comes from the direct exchange between the electrons on the $d_{xz}(A)$ and $d_{xz}(B)$ orbitals, and 255.6°K from superexchange interactions via the anions. The strong *antiferromagnetic* direct exchange coupling is a result of using nonorthogonal cation orbitals in our formulation. This nonorthogonality allows for the attractive nuclear potential to contribute, in addition to the ferromagnetic Heisenberg exchange integral, $\langle \phi_i \phi_j | e^2/r_{12} | \phi_j \phi_i \rangle$. It should be emphasized that J_{34}' is the strength of the exchange interaction between two electrons, each occupying the d_{xz} orbital of the cation A or B. To determine the coupling constant between the total spins of cation A and cation B, it is necessary to project the individual spins onto the total spin of a cation. This process will be discussed in Sec. III D.

TABLE V. Values of the matrix elements, in atomic units, entered in (14) for the exchange integral.

$$\mathcal{H}_{34}^{AA} - \mathcal{H}_I^{AA} T_1^2 = -0.00031$$
$$\mathcal{H}_{134}^{AA} = \mathcal{H}_{143}^{AA} = 0.00002$$
$$\mathcal{H}_{13,24}^{AA} = 0.00002$$
$$\mathcal{H}_{13}^{AC} - \mathcal{H}_I^{AA} S_\pi = -0.03210$$
$$\mathcal{H}_{13,24}^{AC} = 0.00017$$
$$\mathcal{H}_{134}^{AC} = 0.00030$$
$$\mathcal{H}_{34}^{AC} \simeq 0.000002$$
$$\mathcal{H}_{143}^{AC} - \mathcal{H}_I^{AA} S_\pi T_1^2 = -0.00005$$
$$\mathcal{H}_I^{AB} - \mathcal{H}_I^{AA} S_\sigma = 0.07021$$
$$\mathcal{H}_{34}^{AB} - \mathcal{H}_I^{AA} S_\sigma T_1^2 = 0.00006$$
$$\mathcal{H}_{143}^{AB} = 0.00008$$
$$\mathcal{H}_{14,23}^{AB} = -0.00003$$
$$\mathcal{H}_{34}^{CC} = 0.00360$$
$$\mathcal{H}_{34}^{BB} - \mathcal{H}_I^{AA} T_1^2 = -0.00590$$
$$\mathcal{H}_{14,23}^{BB} = 0.00014$$
$$\mathcal{H}_{134}^{BC} = -0.00031$$
$$\mathcal{H}_{14,23}^{BC} = 0.00045$$

B. Charge-Transfer Excitations from the $2p_y$ Orbital to the Cations

The configurations under consideration are shown in Fig. 4. A is the ionic configuration, B and C are the excited configurations in which an electron is transferred from the $2p_y$ orbital to cation A and B, respectively. As far as the symmetry of the electron orbitals is concerned, our present problem is identical to the anion→cation charge-transfer excitations that we studied in I. Namely, we consider, in the ionic configuration, two anion orbitals which are symmetric with respect to the d orbital on each cation site. Charge-transfer excitation occurs from the anion orbital to either cation. Keffer and Oguchi[9] solved a similar problem for the exchange coupling between the next-nearest Mn neighbors in MnO. They neglected the overlap integral between the $3d$ orbitals and found that the contributions to the exchange integral arising from the ionic configuration as well as its interactions with the anion→cation charge transfer excitations are all antiferromagnetic. In our previous calculation for KMgF$_3$:V^{2+}, we allowed for the d–d overlap integral and found that it yielded a ferromagnetic contribution, although the net exchange

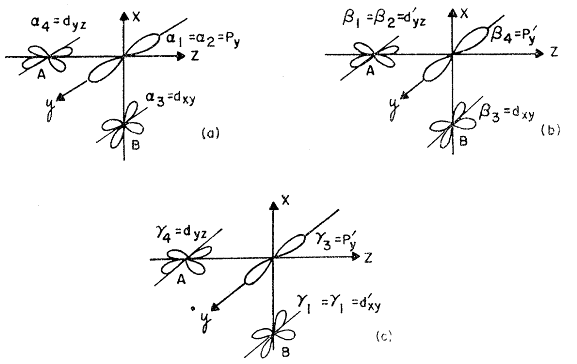

FIG. 4. (a) Ionic configuration A considered in Sec. III B. (b) Excited configuration B in which an electron is transferred from $2p_y$ to the $3d_{yz}$ orbital of cation A. (c) Excited configuration C in which an electron is transferred from $2p_y$ to the $3d_{xy}$ orbital of cation B.

interaction due to the anion→cation transfer was still antiferromagnetic. In the present case, because of the larger value for the *d–d* overlap integral, as compared to the corresponding value in $\mathrm{KMgF_3{:}V^{2+}}$, the contribution to the exchange integral involving the *d–d* overlap integral can overcome that involving merely the *p–d* overlap integral and lead to a net *ferromagnetic* interaction. In fact this will be shown to be the case.

The expression for the exchange integral is given by $J_{\mathrm{ion}}+J_{\mathrm{ac}}$ derived in I. We have

$$\begin{aligned} J_{34}'' = {} & \mathcal{H}_{34}{}^{AA}-\mathcal{H}_I{}^{AA}T_3{}^2-2(\mathcal{H}_{134}{}^{AA}-\mathcal{H}_I{}^{AA}S_\pi{}^2T_3)+(\mathcal{H}_{13,24}{}^{AA}-\mathcal{H}_I{}^{AA}S_\pi{}^4) \\ & +\frac{4(\mathcal{H}_{14}{}^{AB}-\mathcal{H}_I{}^{AA}S_\pi)}{\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}}[-(\mathcal{H}_{143}{}^{AB}-\mathcal{H}_I{}^{AA}S_\pi{}^3)+(\mathcal{H}_{13,24}{}^{AB}-\mathcal{H}_I{}^{AA}S_\pi T_3)] \\ & +\frac{2(\mathcal{H}_{14}{}^{AB}-S_\pi\mathcal{H}_I{}^{AA})^2}{(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA})^2}[(\mathcal{H}_{34}{}^{BB}-S_\pi{}^2\mathcal{H}_I{}^{AA})-(\mathcal{H}_{13,24}{}^{BC}-\mathcal{H}_I{}^{AA}S_\pi{}^2)+(\mathcal{H}_{134}{}^{BC}-\mathcal{H}_I{}^{AA}T_3)], \end{aligned} \tag{19}$$

where S_π is the same integral $\langle p_z|d_{xz}(B)\rangle$ defined in (11) and $T_3\equiv\langle d_{yz}(A)|d_{xy}(B)\rangle$. Using (2), (10a), and (15), we express, in Appendix B, the matrix elements in (19) in terms of the one-electron and two-electron integrals. Numerical computations for these integrals and the resulting values for $\mathcal{H}_p{}^{R_iR_j}$ are listed in Tables VI, VII, and VIII. Direct evaluation of J_{34}'' indicates that the sum of the terms in (19) which do not contain the nonorthogonal effects between the *d* orbitals is antiferromagnetic (−93°K), whereas the terms arising from the cation–cation nonorthogonality (these terms are, for example, $\mathcal{H}_{34}{}^{AA}-T_3{}^2\mathcal{H}_I{}^{AA}$, $\mathcal{H}_{134}{}^{AA}-S_\pi{}^2T_3\mathcal{H}_I{}^{AA}$, etc.) yield a ferromagnetic interaction of 108°K. Thus we obtain a net ferromagnetic coupling of $J_{34}''=15$°K.

There is an interaction identical to the one we have just considered via the other intervening anion, i.e., the exchange coupling between the d_{xy} orbital at center *A* and the d_{yz} orbital at center *B* via an intervening anion, as shown in Fig. 5. For this case the strength of exchange coupling is also 15°K.

C. Charge-Transfer Excitations between the d_{xz} Orbitals of Two Nearest $\mathrm{V^{2+}}$ Neighbors

We consider the ionic configuration *A*, the excited configuration *B* in which an electron is transferred from the d_{xz} orbital at cation *A* to the d_{xz} orbital at cation *B*, and the excited configuration *C* in which charge transfer occurs from cation *B* to cation *A*. These configurations are shown schematically in Fig. 6. Obviously, these charge-transfer processes are allowed only for the case of $\mathbf{s}_3$ antiparallel to $\mathbf{s}_4$. The ground configuration is only connected with the following even combination of the excited configurations:

$$\psi_G\simeq(1/\sqrt{2})(\psi_B+\psi_C). \tag{20}$$

The secular equation to be solved for the perturbed energy of the ground singlet is given by

$$\begin{vmatrix} (\mathcal{H}-W)^{AA} & (\mathcal{H}-W)^{AG} \\ (\mathcal{H}-W)^{GA} & (\mathcal{H}-W)^{GG} \end{vmatrix}=0, \tag{21}$$

in which each matrix element is given by (1) and (10a) with $\mathcal{P}_{34}=1$, a relation appropriate to the case for $\mathbf{s}_3$ and $\mathbf{s}_4$ in a singlet state. The interaction between configurations *A* and *G* is given, to the lowest order in the overlap integral, by

$$\Delta W=-4(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}T_1)^2/(\mathcal{H}_I{}^{BB}-\mathcal{H}_I{}^{AA}), \tag{22}$$

where T_1 is defined in (11). Assuming a four-electron model, we find

$$\begin{aligned} \mathcal{H}_I{}^{BA}-\mathcal{H}_I{}^{AA}T_1 = {} & \langle a_3|\mathcal{H}_1|a_4\rangle-\langle a_3|\mathcal{H}_1|a_3\rangle T_1 \\ & +2\langle a_1a_3||a_1a_4\rangle+\langle a_3a_3||a_3a_4\rangle \\ & -(2\langle a_1a_4||a_1a_4\rangle+\langle a_3a_4||a_3a_4\rangle)T_1, \end{aligned} \tag{23}$$

where $\langle a_ia_j||a_ka_l\rangle\equiv\langle a_ia_j|e^2/r_{12}|a_ka_l\rangle$. From Tables III and IV and, in addition, using the value $\langle a_3a_3||a_3a_4\rangle=0.00908$, we obtain $\mathcal{H}_I{}^{BA}-\mathcal{H}_I{}^{AA}T_1=-0.010$. It is necessary to consider also the contribution of the other intervening anion which plays a role identical to the one shown in Fig. 6. This contribution is taken into account by doubling the terms in (23) involving the anion. Doing this, we find $\mathcal{H}_I{}^{BA}-\mathcal{H}_I{}^{AA}T_1=-0.006$. The energy denominator in (22) is estimated to be 0.47 a.u., following the same procedures adopted before.[1,11] We thus find $\Delta W=-30.8\times10^{-5}$ a.u. This is the amount of energy of the singlet ground state lowered by the cation→cation charge-transfer excitations. The corresponding value for the exchange inter-

TABLE VI. The two-electron integrals entered in Appendix B. The values are given in atomic units.

$\langle\alpha_1\alpha_1||\alpha_1\alpha_1\rangle=0.63901$
$\langle\alpha_1\alpha_3||\alpha_1\alpha_3\rangle=0.24371$
$\langle\alpha_1\alpha_3||\alpha_3\alpha_1\rangle=0.00333$
$\langle\alpha_1\alpha_1||\alpha_1\alpha_4\rangle=0.03418$
$\langle\alpha_1\alpha_4||\alpha_4\alpha_4\rangle=0.03171$
$\langle\alpha_3\alpha_4||\alpha_3\alpha_4\rangle=0.17538$
$\langle\alpha_3\alpha_4||\alpha_4\alpha_3\rangle=0.00006$
$\langle\alpha_4\alpha_4||\alpha_4\alpha_4\rangle=0.76501$
$\langle\alpha_3\alpha_4||\alpha_3\alpha_3\rangle=0.00204$
$\langle\alpha_1\alpha_1||\alpha_3\alpha_4\rangle\simeq0.002$
$\langle\alpha_1\alpha_3||\alpha_4\alpha_1\rangle\simeq0.002$
$\langle\alpha_1\alpha_3||\alpha_1\alpha_4\rangle\simeq0.003$
$\langle\alpha_4\alpha_3||\alpha_4\alpha_1\rangle\simeq0.02$
$\langle\alpha_1\alpha_3||\alpha_3\alpha_4\rangle\simeq0.0004$

TABLE VII. The one-electron integrals entered in Appendix B. The value for the overlap integral $T_3=\langle d_{yz}(A)\mid d_{xy}(B)\rangle$ is also listed.

$\langle\alpha_1\mid\mathcal{H}_1\mid\alpha_3\rangle=-0.20609$ $T_3=0.00971$

$\langle\alpha_1\mid\mathcal{H}_1\mid\alpha_1\rangle=-2.25381$

$\langle\alpha_3\mid\mathcal{H}_1\mid\alpha_3\rangle=-1.61690$

$\langle\alpha_3\mid\mathcal{H}_1\mid\alpha_4\rangle=-0.02129$

action is -15.4×10^{-5} a.u., or -48.2°K. Combining this with the value of $J_{34}'=91.8$°K, estimated in Sec. III A, coming from the ionic configuration and the anion→cation charge-transfer excitations, we obtain a net coupling of 43.6°K between two electrons on the orbitals $d_{xz}(A)$ and $d_{xz}(B)$.

D. Exchange Coupling between Total Spins of Two V^{2+} Ions

We have estimated the strength of exchange coupling between pairs of individual d electrons. The exchange energy coupling two ions is given by the sum of the coupling energies between all pairs of electrons (the two electrons in a pair belong to two different cations), i.e., we have

$$W_{AB}=-2\sum_{i=1}^{n_A}\sum_{j=1}^{n_B}J_{ij}\mathbf{s}_i\cdot\mathbf{s}_j, \tag{24}$$

where n_A and n_B are, respectively, the number of unpaired spins for cation A and B, and J_{ij} is the exchange-coupling constant between the ith unpaired spin of one cation and the jth unpaired spin of the other cation. However, the quantity of interest to us is the coupling constant J_{AB} associated with the exchange energy $-2J_{AB}\mathbf{S}_A\cdot\mathbf{S}_B$, where $\mathbf{S}_A$ and $\mathbf{S}_B$ are the total spins of cation A and B, respectively. For the case of half-filled shells and also for ions with d^3 or d^8 configurations in an octahedral field, Van Vleck[19] has shown that

$$-2\sum_{i=1}^{n}\sum_{j=1}^{n}J_{ij}\mathbf{s}_i\cdot\mathbf{s}_j=-\frac{2}{n_An_B}\mathbf{S}_A\cdot\mathbf{S}_B\sum_{i=1}^{n_A}\sum_{j=1}^{n_B}J_{ij} \tag{25}$$
$$\equiv-2J_{AB}\mathbf{S}_A\cdot\mathbf{S}_B,$$

assuming the intraionic couplings to be small compared to the Russell-Saunders energies of individual ions.

Hence, summing over our previously estimated couplings, we obtain a ferromagnetic interaction between the total spins with a strength of

$$J_{AB}=8.2\text{°K}. \tag{26}$$

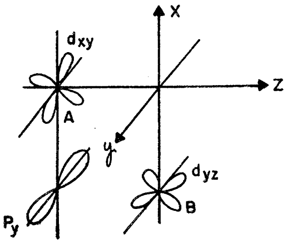

FIG. 5. A four-electron model which leads to an exchange interaction identical to the one arising from Fig. 4.

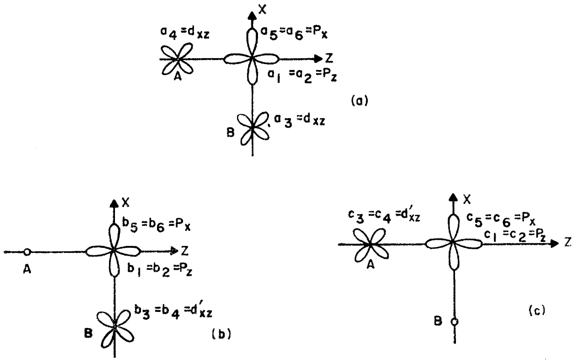

FIG. 6. (a) Ionic configuration A considered in Sec. III C. (b) Excited configuration B in which an electron is transferred from the $3d_{xz}(A)$ to the $3d_{xz}(B)$ orbital. (c) Excited configuration C in which an electron is transferred from the $3d_{xz}(B)$ to the $3d_{xz}(A)$ orbital.

IV. DISCUSSION

We believe that we have demonstrated in this paper the important one-electron transfer excitations for the exchange coupling between two nearest V^{2+} ions. Our estimate of $J_{AB}=8.2$°K seems to have the correct order of magnitude, although there is no measurement to be compared with. Clearly, our accuracy is restricted by the following approximations: (i) We have neglected the crystal surroundings of two V^{2+} ions and two intervening anions in evaluating the matrix elements in the exchange integrals (but the whole crystal is taken into account in estimating the transfer energies). (ii) Rough estimates have been made for the three-center integrals. (iii) We have assumed that no charge redistribution occurs in the excited configurations. Improvements to these approximations require difficult numerical work. This is even further complicated since the electronic states which result upon charge transfer are not known quantitatively at the present time. Nevertheless, we believe that the following features dis-

TABLE VIII. Values of the matrix elements entered in (19), in atomic units.

$\mathcal{H}_{34}{}^{AA}-T_3{}^2\mathcal{H}_I{}^{AA}=-0.00003$

$\mathcal{H}_{134}{}^{AA}-S_\pi{}^2T_3\mathcal{H}_I{}^{AA}=-0.00007$

$\mathcal{H}_{13,24}{}^{AA}-S_\pi{}^4\mathcal{H}_I{}^{AA}=-0.00009$

$\mathcal{H}_{14}{}^{AB}-S_\pi\mathcal{H}_I{}^{AA}=-0.03696$

$\mathcal{H}_{143}{}^{AB}-S_\pi{}^3\mathcal{H}_I{}^{AA}=-0.00077$

$\mathcal{H}_{13,24}{}^{AB}-S_\pi T_3\mathcal{H}_I{}^{AA}=-0.00100$

$\mathcal{H}_{34}{}^{BB}-S_\pi{}^2\mathcal{H}_I{}^{AA}=-0.00233$

$\mathcal{H}_{13,24}{}^{BC}-S_\pi{}^2\mathcal{H}_I{}^{AA}=-0.00498$

$\mathcal{H}_{134}{}^{BC}-T_3\mathcal{H}_I{}^{AA}=-0.00371$

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[19] J. H. Van Vleck, Rev. Univ. Nac. Tucuman, Ser. A 14, 189 (1962).

played in our estimates are correct: (i) The direct exchange interaction between two electrons on the $d_{xz}(A)$ and $d_{xz}(B)$ orbitals and the charge-transfer excitation between them both give rise to antiferromagnetic coupling. (ii) The superexchange interaction between these electrons is strongly ferromagnetic, because the presence of two intervening anions provides two "paths" for superexchange coupling. A net ferromagnetic interaction is thus obtained. (iii) The superexchange interaction between electrons on the $d_{yz}(A)$ and $d_{xy}(B)$ orbitals is ferromagnetic because of a rather significant overlap between these orbitals. Ignoring this overlap would lead to an antiferromagnetic coupling.

In our estimate of J_{AB} we have ignored charge transfers from the d_{xz} orbital at one center to the empty e_g states at the other. These excitations give rise to a ferromagnetic interaction, for reasons pointed out in Sec. I, but they are diminished by roughly a factor of $J_{\text{intra}}/\Delta E \sim 0.1$ [here J_{intra} is the intra-atomic exchange integral between the cation t_{2g} and e_g orbitals and ΔE is the energy required to transfer an electron from the $d_{xz}(B)$ orbital to the empty $d_{z^2}(A)$ orbital] as compared to the excitation from the $d_{xz}(A)$ to the $d_{xz}(B)$ orbitals. The other direct transfers, for example, between $d_{xy}(A)$ and $d_{xy}(B)$ orbitals or $d_{xy}(A)$ and $d_{yz}(B)$ orbitals, are also unimportant because of the relatively small overlap integrals as compared to the overlap between $d_{xz}(A)$ and $d_{xz}(B)$ orbitals. The $2s$ electrons of the oxygen ion play an insignificant role to the superexchange because they are orthogonal to the t_{2g} orbitals.

We conclude that it is necessary to consider the overlap integrals between the cation d orbitals in solving the exchange coupling between nearest neighbors in NaCl type of structures. The charge-transfer excitations that we considered in Sec. III together with the ionic configuration contribute probably the majority of the exchange interaction.

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APPENDIX A

In this Appendix we express the matrix elements in (14) in terms of the one-electron and two-electron integrals. Using (2), (3), and (15), we obtain

$$\mathcal{H}_{34}{}^{AA}-\mathcal{H}_{I}{}^{AA}T_1{}^2=2\langle a_3|\mathcal{H}_1|a_4\rangle T_1-2\langle a_3|\mathcal{H}_1|a_3\rangle T_1{}^2+4\langle a_1a_3||a_1a_4\rangle T_1-2\langle a_1a_3||a_1a_3\rangle T_1{}^2 -2\langle a_1a_4||a_1a_4\rangle T_1{}^2+\langle a_3a_4||a_4a_3\rangle-\langle a_3a_4||a_3a_4\rangle T_1{}^2, \tag{A1}$$

$$\mathcal{H}_{134}{}^{AA}=\mathcal{H}_{143}{}^{AA}=\langle a_1|\mathcal{H}_1|a_4\rangle S_\pi T_1+\langle a_3a_1||a_1a_4\rangle T_1+\langle a_4a_1||a_3a_4\rangle S_\pi, \tag{A2}$$

$$\mathcal{H}_{13,24}{}^{AA}=\langle a_4a_1||a_1a_4\rangle S_\pi{}^2, \tag{A3}$$

$$\mathcal{H}_{13}{}^{AC}-\mathcal{H}_{I}{}^{AA}S_\pi=\langle a_1|\mathcal{H}_1|a_3\rangle-\langle a_1|\mathcal{H}_1|a_1\rangle S_\pi+\langle a_3a_1||a_3a_3\rangle+\langle a_1a_1||a_3a_1\rangle +\langle a_1a_4||a_3a_4\rangle-S_\pi\langle a_1a_1||a_1a_1\rangle-S_\pi\langle a_1a_3||a_1a_3\rangle-S_\pi\langle a_1a_4||a_1a_4\rangle, \tag{A4}$$

$$\mathcal{H}_{13,24}{}^{AC}=\langle a_1|\mathcal{H}_1|a_4\rangle T_1+\langle a_3a_1||a_3a_4\rangle T_1+\langle a_4a_1||a_3a_4\rangle, \tag{A5}$$

$$\mathcal{H}_{134}{}^{AC}=\langle a_4a_1||a_1a_4\rangle S_\pi, \tag{A6}$$

$$\mathcal{H}_{34}{}^{AC}=\langle a_1|\mathcal{H}_1|a_4\rangle S_\pi{}^2T_1+\langle a_4a_3||a_1a_4\rangle S_\pi{}^2+2\langle a_1a_4||a_3a_1\rangle S_\pi T_1, \tag{A7}$$

$$\mathcal{H}_{143}{}^{AC}-\mathcal{H}_{I}{}^{AA}S_\pi T_1{}^2=2\langle a_4|\mathcal{H}_1|a_3\rangle S_\pi T_1+\langle a_1|\mathcal{H}_1|a_3\rangle T_1{}^2-(\langle a_1|\mathcal{H}_1|a_1\rangle+2\langle a_3|\mathcal{H}_1|a_3\rangle)S_\pi T_1{}^2 +2\langle a_4a_1||a_3a_3\rangle T_1+2\langle a_4a_1||a_3a_1\rangle S_\pi T_1+\langle a_4a_3||a_3a_4\rangle S_\pi+\langle a_1a_1||a_3a_1\rangle T_1{}^2, \tag{A8}$$

$$\mathcal{H}_{I}{}^{AB}-\mathcal{H}_{I}{}^{AA}S_\sigma=\langle a_1|\mathcal{H}_1|b_1\rangle-\langle a_1|\mathcal{H}_1|a_1\rangle S_\sigma+\langle a_1a_1||b_1a_1\rangle+\langle a_1a_3||b_1a_3\rangle +\langle a_1a_4||b_1a_4\rangle-\langle a_1a_1||a_1a_1\rangle-\langle a_1a_3||a_1a_3\rangle-\langle a_1a_4||a_1a_4\rangle, \tag{A9}$$

$$\mathcal{H}_{34}{}^{AB}-\mathcal{H}_{I}{}^{AA}S_\sigma T_1{}^2=\langle a_1|\mathcal{H}_1|b_1\rangle T_1{}^2+2\langle a_3|\mathcal{H}_1|a_4\rangle S_\sigma T_1-(\langle a_1|\mathcal{H}_1|a_1\rangle+2\langle a_3|\mathcal{H}_1|a_3\rangle)S_\sigma T_1{}^2 +\langle a_1a_1||b_1a_1\rangle T_1{}^2+2\langle a_1a_4||b_1a_3\rangle T_1+2\langle a_1a_3||a_1a_4\rangle S_\sigma T_1+\langle a_4a_3||a_3a_4\rangle S_\sigma -(\langle a_1a_1||a_1a_1\rangle+\langle a_3a_4||a_3a_4\rangle+2\langle a_1a_3||a_1a_3\rangle+2\langle a_1a_4||a_1a_4\rangle)S_\sigma T_1{}^2, \tag{A10}$$

$$\mathcal{H}_{143}{}^{AB}=\langle a_4|\mathcal{H}_1|b_1\rangle S_\pi T_1+\langle a_4a_3||b_1a_4\rangle S_\pi+\langle a_4a_1||b_1a_3\rangle T_1, \tag{A11}$$

$$\mathcal{H}_{14,23}{}^{AB}=\langle a_4a_1||b_1a_4\rangle S_\pi{}^2, \tag{A12}$$

$$\mathcal{H}_{34}{}^{CC}=\langle a_4a_1||a_1a_4\rangle, \tag{A13}$$

$$\begin{aligned}\mathcal{H}_{34}{}^{BB}-\mathcal{H}_I{}^{AA}T_1{}^2={}&\langle b_1\,|\,\mathcal{H}_1\,|\,b_1\rangle T_1{}^2+2\langle a_3\,|\,\mathcal{H}_1\,|\,a_4\rangle T_1-(\langle a_1\,|\,\mathcal{H}_1\,|\,a_1\rangle+2\langle a_3\,|\,\mathcal{H}_1\,|\,a_3\rangle)T_1{}^2\\&+\langle b_1a_1\,||\,b_1a_1\rangle T_1{}^2+2\langle b_1a_3\,||\,b_1a_4\rangle T_1+2\langle a_1a_3\,||\,a_1a_4\rangle T_1+\langle a_4a_3\,||\,a_3a_4\rangle\\&-(\langle a_3a_4\,||\,a_3a_4\rangle+2\langle a_1a_3\,||\,a_1a_3\rangle+2\langle a_1a_4\,||\,a_1a_4\rangle)T_1{}^2,\end{aligned}\tag{A14}$$

$$\mathcal{H}_{14,23}{}^{BB}=\langle a_4b_1\,||\,b_1a_4\rangle S_\pi{}^2,\tag{A15}$$

$$\mathcal{H}_{134}{}^{BC}=\langle a_4a_1\,||\,b_1a_4\rangle S_\pi,\tag{A16}$$

$$\mathcal{H}_{14,23}{}^{BC}=\langle b_1\,|\,\mathcal{H}_1\,|\,a_4\rangle T_1+\langle a_4b_1\,||\,a_3a_4\rangle+\langle a_3b_1\,||\,a_3a_4\rangle T_1.\tag{A17}$$

APPENDIX B

The matrix elements in (19) are written in terms of the one-electron and two-electron integrals in the following:

$$\begin{aligned}\mathcal{H}_{34}{}^{AA}-\mathcal{H}_I{}^{AA}T_3{}^2={}&2\langle\alpha_3\,|\,\mathcal{H}_1\,|\,\alpha_4\rangle T_3-2\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_1\rangle T_3{}^2+4\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_4\rangle T_3-4\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle T_3{}^2\\&+\langle\alpha_3\alpha_4\,||\,\alpha_4\alpha_3\rangle-\langle\alpha_3\alpha_4\,||\,\alpha_3\alpha_4\rangle T_3{}^2,\end{aligned}\tag{B1}$$

$$\begin{aligned}\mathcal{H}_{134}{}^{AA}-\mathcal{H}_I{}^{AA}S_\pi{}^2T_3={}&\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi T_3+\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_4\rangle S_\pi T_3+\langle\alpha_3\,|\,\mathcal{H}_1\,|\,\alpha_4\rangle S_\pi{}^2-\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_1\rangle S_\pi{}^2T_3\\&-2\langle\alpha_3\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi{}^2T_3+2\langle\alpha_1\alpha_1\,||\,\alpha_3\alpha_1\rangle S_\pi T_3+2\langle\alpha_1\alpha_3\,||\,\alpha_3\alpha_4\rangle S_\pi+\langle\alpha_1\alpha_4\,||\,\alpha_3\alpha_1\rangle T_3\\&+\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_4\rangle S_\pi{}^2-\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_1\rangle S_\pi{}^2T_3-\langle\alpha_3\alpha_4\,||\,\alpha_3\alpha_4\rangle S_\pi{}^2T_3-4\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle S_\pi{}^2T_3,\end{aligned}\tag{B2}$$

$$\begin{aligned}\mathcal{H}_{13,24}{}^{AA}-\mathcal{H}_I{}^{AA}S_\pi{}^4={}&4\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi{}^2-2\langle\alpha_4\,|\,\mathcal{H}\,|\,\alpha_4\rangle S_\pi{}^4-2\langle\alpha_3\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi{}^4+2\langle\alpha_1\alpha_3\,||\,\alpha_3\alpha_1\rangle S_\pi{}^2\\&+2\langle\alpha_1\alpha_1\,||\,\alpha_3\alpha_4\rangle S_\pi{}^2+2\langle\alpha_1\alpha_3\,||\,\alpha_4\alpha_1\rangle S_\pi{}^2-\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_1\rangle S_\pi{}^4-\langle\alpha_3\alpha_4\,||\,\alpha_3\alpha_4\rangle S_\pi{}^4-4\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle S_\pi{}^4,\end{aligned}\tag{B3}$$

$$\begin{aligned}\mathcal{H}_{14}{}^{AB}-\mathcal{H}_I{}^{AA}S_\pi={}&\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_4\rangle-\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_1\rangle S_\pi+\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_4\rangle+\langle\alpha_1\alpha_4\,||\,\alpha_4\alpha_4\rangle\\&+\langle\alpha_1\alpha_3\,||\,\alpha_4\alpha_3\rangle-\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_1\rangle S_\pi-2\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle S_\pi,\end{aligned}\tag{B4}$$

$$\begin{aligned}\mathcal{H}_{143}{}^{AB}-S_\pi{}^3\mathcal{H}_I{}^{AA}={}&3\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi{}^2-2\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_1\rangle S_\pi{}^3-\langle\alpha_3\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi{}^3+2\langle\alpha_1\alpha_4\,||\,\alpha_3\alpha_4\rangle S_\pi{}^2\\&+2\langle\alpha_3\alpha_4\,||\,\alpha_1\alpha_1\rangle S_\pi+\langle\alpha_3\alpha_1\,||\,\alpha_1\alpha_3\rangle S_\pi+\langle\alpha_4\alpha_4\,||\,\alpha_1\alpha_4\rangle S_\pi{}^2-\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_1\rangle S_\pi{}^3\\&-\langle\alpha_3\alpha_4\,||\,\alpha_3\alpha_4\rangle S_\pi{}^3-4\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle S_\pi{}^3,\end{aligned}\tag{B5}$$

$$\begin{aligned}\mathcal{H}_{13,24}{}^{AB}-\mathcal{H}_I{}^{AA}S_\pi T_3={}&\langle\alpha_3\,|\,\mathcal{H}_1\,|\,\alpha_4\rangle S_\pi+\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle T_3-\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_1\rangle S_\pi T_3-\langle\alpha_3\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi T_3\\&+\langle\alpha_3\alpha_4\,||\,\alpha_4\alpha_4\rangle S_\pi+\langle\alpha_3\alpha_1\,||\,\alpha_4\alpha_3\rangle+\langle\alpha_3\alpha_1\,||\,\alpha_4\alpha_1\rangle S_\pi+\langle\alpha_4\alpha_1\,||\,\alpha_4\alpha_3\rangle T_3\\&+\langle\alpha_1\alpha_1\,||\,\alpha_3\alpha_1\rangle T_3-\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_1\rangle S_\pi T_3-\langle\alpha_3\alpha_4\,||\,\alpha_3\alpha_4\rangle S_\pi T_3-3\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle S_\pi T_3,\end{aligned}\tag{B6}$$

$$\begin{aligned}\mathcal{H}_{34}{}^{BB}-\mathcal{H}_I{}^{AA}S_\pi{}^2={}&2\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi-2\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_1\rangle S_\pi{}^2+\langle\alpha_4\alpha_4\,||\,\alpha_4\alpha_4\rangle S_\pi{}^2+4\langle\alpha_4\alpha_3\,||\,\alpha_4\alpha_1\rangle S_\pi\\&+\langle\alpha_3\alpha_1\,||\,\alpha_1\alpha_3\rangle-\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_1\rangle S_\pi{}^2-\langle\alpha_3\alpha_4\,||\,\alpha_3\alpha_4\rangle S_\pi{}^2-4\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle S_\pi{}^2,\end{aligned}\tag{B7}$$

$$\begin{aligned}\mathcal{H}_{13,24}{}^{BC}-\mathcal{H}_I{}^{AA}S_\pi{}^2={}&2\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_3\rangle S_\pi-2\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_1\rangle S_\pi{}^2+2\langle\alpha_1\alpha_4\,||\,\alpha_4\alpha_4\rangle S_\pi+2\langle\alpha_1\alpha_3\,||\,\alpha_4\alpha_3\rangle S_\pi\\&+\langle\alpha_1\alpha_3\,||\,\alpha_4\alpha_1\rangle-\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_1\rangle S_\pi{}^2-4\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle S_\pi{}^2,\end{aligned}\tag{B8}$$

$$\begin{aligned}\mathcal{H}_{134}{}^{BC}-\mathcal{H}_I{}^{AA}T_3={}&\langle\alpha_3\,|\,\mathcal{H}_1\,|\,\alpha_4\rangle-\langle\alpha_1\,|\,\mathcal{H}_1\,|\,\alpha_1\rangle T_3+2\langle\alpha_3\alpha_4\,||\,\alpha_3\alpha_3\rangle+\langle\alpha_4\alpha_1\,||\,\alpha_3\alpha_1\rangle\\&-\langle\alpha_1\alpha_1\,||\,\alpha_1\alpha_1\rangle T_3-2\langle\alpha_1\alpha_3\,||\,\alpha_1\alpha_3\rangle T_3.\end{aligned}\tag{B9}$$