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Exchange Interaction and Energy Transfer for $3d^3$ Ions: $^4A_2$-^2E Transition for KMgF$_3$:V^{2+}†

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The energy levels of exchange-coupled pairs of $3d^3$ ions, each in the $^4A_2$ or ^2E state, are derived, taking into account the orbitally anisotropic nature of the exchange interaction. Specific analysis is made of the spectrum of collinear pairs of vanadium ions in a KMgF$_3$ host. It is found that the Davydov-type splittings in the excited levels of the pairs, which are caused by the exchange orbital anisotropy, are 2–6 times greater than the ground-state–ground-state exchange matrix elements. Using a semiquantitative method for estimating the diminution of exchange as one increases the number of ligand linkages between the magnetic ions, the magnitude of energy-transfer integrals for V^{2+} ions separated by three F$^-$ ions is found sufficient to cause rapid single-ion–single-ion energy transfer (~1 μsec). This result indirectly supports the argument that the Davydov-like terms for weakly coupled Cr^{3+} pairs are responsible for energy transfer in dilute ruby.

I. INTRODUCTION

RECENTLY, a number of authors have demonstrated[1,2] that exchange, acting between the ground and excited magnetic levels in concentrated magnetic materials, can give rise to large (comparable or greater than the ground-state splitting) Davydov splittings of the $\mathbf{k}=0$ exciton band. In addition, several authors[3–5] have considered equivalent terms in the energy matrix for pairs of exchange-coupled Cr^{3+} ions in Al$_2$O$_3$ and found large values for these quantities. Numerical estimates of the magnitude of the Davydov-type exchange terms for the ^2E and $^4A_2$ levels [$^4A_2(a)$, $^2E(b) \rightarrow {}^2E(a)$, $^4A_2(b)$, where the two ions are labeled a and b, respectively] are terribly involved for Cr$_2$O$_3$. Not only are the overlap and transfer integrals complicated because of noncollinear Cr^{3+}-O^{2-}-Cr^{3+} bonds, but also no adequate wave functions are available for the O^{2-} in a trivalent "Madelung cage." This is a serious difficulty; experience in other contexts[6] has demonstrated factors of nearly 5 errors in overlap and transfer parameters when using available[7] O^{2-} wave functions computed for divalent Madelung cages, in a trivalent environment.

For these reasons, and because all the relevant one- and two-electron integrals have already been computed[8] for V^{2+} in KMgF$_3$, we have analyzed the $^4A_2$, ^2E spectrum for collinear pairs of vanadium ions in this (cubic) host. In brief, we find the exchange terms which would lead to a Davydov splitting in the concentrated material to be large (2–6 times the ground-state–ground-state exchange matrix elements). In addition, the simplicity of cubic surroundings greatly simplifies the pair energy matrix, so that the form of the results is interesting in itself. Finally, quantitative arguments are given which enable us to correlate rather directly the magnitude of the Davydov-like pair terms with the ground-state–ground-state exchange.

It should be noted that, as Birgeneau[5] has pointed out, the Davydov-like terms for weakly coupled pairs are probably responsible for energy transfer in dilute ruby. Our numerical results verify his conjecture, and yield a semiquantitative method for estimating the diminution of exchange as one increases the number of ligand linkages between magnetic ions. For our model system, we are able to demonstrate sufficient magnitude for the energy-transfer integrals for V^{2+} ions separated by three F$^-$ ions to enable rapid single-ion–single-ion

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energy transfer (~1 μsec) to obtain. We are aware that the system we are considering may not, in fact, be very useful to study in this context, since it is not even sure if the ^2E level lies below the $^4T_2$ in dilute $KMgF_3$.[9] Nevertheless, arguing by analogy, our results do demonstrate that in ruby, where an enormous (~60) number of Al^{3+} sites are available within a distance separated by three oxygen links, exchange is potent enough to do the job.

II. ENERGY LEVELS OF EXCHANGE COUPLED PAIRS

The $^4A_2$ and ^2E states for a d^3 ion in a cubic environment can be written as[10]

$$\begin{aligned} &{}^4A_2(M_S=\tfrac{3}{2})=(\xi\eta\zeta)\,, \\ &{}^2E_\theta(M_S=\tfrac{1}{2})=[(\xi\bar{\eta}\zeta)-(\bar{\xi}\eta\zeta)]/\sqrt{2}\,, \\ &{}^2E_\epsilon(M_S=\tfrac{1}{2})=[2(\xi\eta\bar{\zeta})-(\xi\bar{\eta}\zeta)-(\bar{\xi}\eta\zeta)]/\sqrt{6}\,, \end{aligned} \tag{1}$$

where

$$|\xi\rangle=(i/\sqrt{2})(|l=2,\,m_l=1\rangle+|l=2,\,m_l=-1\rangle)\cdot|m_S=\tfrac{1}{2}\rangle\,,$$

$$|\eta\rangle=-(1/\sqrt{2})(|l=2,\,m_l=1\rangle \\ -|l=2,\,m_l=-1\rangle)\cdot|m_S=\tfrac{1}{2}\rangle\,,$$

and

$$|\bar{\zeta}\rangle=(-i/\sqrt{2})(|l=2,\,m_l=2\rangle \\ -|l=2,\,m_l=-2\rangle)\cdot|m_S=-\tfrac{1}{2}\rangle\,, \quad \text{etc.}$$

We shall ignore the admixing of $^4T_2$ into $^4A_2$ and ^2E by the spin-orbit coupling since its contribution to the energy of the exchange-coupled pair will be negligible. Note that in both $^4A_2$ and ^2E states, each of the three t_{2g} orbitals is singly occupied. Consequently, we can adopt the following simple expression for the exchange[11]:

$$\mathcal{H}_{\text{ex}}=-2\sum_{i,j=1}^{3}J_{ij}\mathbf{s}_i{}^a\cdot\mathbf{s}_j{}^b\,. \tag{2}$$

When both ions are in the ground state $^4A_2$, which posseses the maximum spin multiplicity and no orbital moment, Eq. (2) reduces to the conventional form

$$\mathcal{H}_{\text{ex}}(^4A_2,{}^4A_2)=-(2/9)\Big(\sum_{i,j=1}^{3}J_{ij}\Big)\mathbf{S}^a\cdot\mathbf{S}^b\equiv-2J\mathbf{S}^a\cdot\mathbf{S}^b\,. \tag{3}$$

Note that the exchange integral J entering in the above expression is just the average of J_{ij}. When one ion is in the excited state ^2E, it becomes necessary to use the general exchange Hamiltonian (2) rather than (3) because J_{ij} depends on the angular distribution of the electrons.[12] The exchange Hamiltonian given by (2) possesses the important property that it does not commute with $\mathbf{S}^a$ or $\mathbf{S}^b$. As a result, Eq. (2) interconnects $^4A_2$ and ^2E states, whereas Eq. (3) does not. This property demonstrates why Pryce[3] and Kisliuk *et al.*[4] find that Eq. (2) rather than Eq. (3) must be used in assigning the observed pair spectra in ruby to the theoretical values, and why Refs. 1 and 2 found it necessary to use (2) in order to explain the splitting of the $\mathbf{k}=0$ exciton band in concentrated magnetic materials (MnF_2 and Cr_2O_3, respectively). The noncommutivity also shows that the exchange interaction can be utilized as a mechanism for the single ion-pair energy transfer as discussed by Birgeneau.[5]

We shall consider the cases where both ions are in $^4A_2$; one in $^4A_2$, the other in ^2E; and both in ^2E. The allowed values for the *total* spin of the pair are then given by $S=0$, 1, 2, and 3. Since the exchange Hamiltonian (2) commutes with total (pair) $\mathbf{S}$, S is a good quantum number as long as we ignore spin-orbit coupling. Hence, we shall diagonalize $\mathcal{H}_{\text{ex}}$ by using the pair wave functions which are constructed to be the eigenstates of S^2. For the purpose of observing the important features of the energy matrix of $\mathcal{H}_{\text{ex}}$, we shall consider the case $S=2$ in detail in the following. The energy matrices for $S=0$, 1, and 3 are given in the Appendix.

The eigenfunctions of S^2 corresponding to $S=2$ and $M_S=2$ are given by

$$\begin{aligned} \varphi_1&=(A^a{}_{3/2}A^b{}_{1/2}-A^a{}_{1/2}A^b{}_{3/2})/\sqrt{2}\,, \\ \varphi_2&=E^a{}_{\theta,1/2}A^b{}_{3/2}\,, \\ \varphi_3&=E^a{}_{\epsilon,1/2}A^b{}_{3/2}\,, \\ \varphi_4&=A^a{}_{3/2}E^b{}_{\theta,1/2}\,, \\ \varphi_5&=A^a{}_{3/2}E^b{}_{\epsilon,1/2}\,, \end{aligned} \tag{4}$$

where $A^a{}_{3/2}={}^4A^a{}_2(M_S=\frac{3}{2})$ and $E^a{}_{\theta,1/2}={}^2E^a{}_\theta(M_S=\frac{1}{2})$, etc. Using Eqs. (1) and (4), it is straightforward but laborious to compute the matrix elements of $\mathcal{H}_{\text{ex}}$. We find

$$\begin{array}{cccccc} & \varphi_1 & \varphi_2 & \varphi_3 & \varphi_4 & \varphi_5 \\ \varphi_1 & 3J/2 & \sum(J_{1j}-J_{2j})/\sqrt{3} & \frac{1}{3}\sum(J_{1j}+J_{2j}-2J_{3j}) & \sum(J_{j2}-J_{j1})/\sqrt{3} & \frac{1}{3}\sum(2J_{j3}-J_{j2}-J_{j1}) \\ \varphi_2 & & R-\frac{1}{2}\sum J_{3j} & \sum(J_{1j}-J_{2j})/2\sqrt{3} & \frac{1}{2}(J_{12}+J_{21}-J_{11}-J_{22}) & (2J_{13}-2J_{33}+J_{21}+J_{22}-J_{11}-J_{12})/2\sqrt{3} \\ \varphi_3 & & & R-\frac{1}{6}\sum(2J_{1j}+2J_{2j}-J_{3j}) & (2J_{31}-2J_{32}+J_{12}+J_{22}-J_{11}-J_{21})/2\sqrt{3} & \frac{1}{6}(2J_{13}+2J_{23}+2J_{31}+2J_{32}-J_{11}-J_{22}-J_{21}-J_{12}-4J_{33}) \\ \varphi_4 & & & & R-\frac{1}{2}\sum J_{j3} & \sum(J_{j1}-J_{j2})/2\sqrt{2} \\ \varphi_5 & & & & & R-\frac{1}{6}\sum(2J_{j1}+2J_{j2}-J_{j3}) \end{array}\,, \tag{5}$$

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[9] The $^4A_2\rightarrow{}^4T_2$ excitations in dilute $KMgF_3:V^{2+}$ will be discussed in a separate paper. Energy transfer between these two states is of interest because the excitation-transfer integrals involve vibrational overlaps which would effectively reduce the "bare" exciton transfer rate given by the interionic exchange. It has been pointed out to the author that M. D. Sturge (unpublished) has found $^4T_2$ to be the first excited state in $KMgF:V^{2+}$.

[10] J. S. Griffith, *The Theory of Transition-Metal Ions* (Cambridge University Press, London, 1964), p. 406.

[11] The criteria for applying Eq. (2) simultaneously to interactions involving excited and ground multiplets have been discussed in detail by S. Freeman in Ref. 1. For the case of $KMgF_3:V^{2+}$, the anion-cation and cation-cation transfer energies have been estimated (see Ref. 8) to be ~21 eV and 17 eV, respectively, whereas the intra-atomic exchange is of the order of 1 eV. Hence, the error involved in applying Eq. (2) to both the ground and excited multiplets is roughly 6%.

[12] J. H. Van Vleck, Rev. Univ. Tucuman A (Argentina) **14**, 189 (1962).

where R denotes the energy difference between ${}^2E$ and ${}^4A_2$ in a single ion, and the summation runs over $j=1$, 2, and 3. The elements which are not given explicitly can be obtained from $\langle\varphi_i|\mathcal{H}_{\rm ex}|\varphi_j\rangle=\langle\varphi_j|\mathcal{H}_{\rm ex}|\varphi_i\rangle$. Note that if there were no orbital anisotropy in the exchange, i.e., if the J_{ij}'s were all the same and Eq. (2) became the same as Eq. (3), the off-diagonal terms in the energy matrix (5) would have vanished. The presence of the off-diagonal terms has the following effects: (1) It gives rise to various Davydov splitting of from 13 to 40°K in KMgF$_3$:V^{2+}, as we shall see below. Such splittings are obviously essential to the assignment of the observed optical spectra. (2) It demonstrates that the exchange interaction given by Eq. (2) provides a mechanism for the single-ion-pair energy transfer. The latter property follows from the fact that in (5), off-diagonal elements of the form $\langle{}^4A_2{}^a,{}^2E^b|\mathcal{H}_{\rm ex}|{}^2E^a,{}^4A_2{}^b\rangle$ exist. These have the effect of simultaneously exciting ion b from ${}^4A_2$ to ${}^2E$ and deexciting ion a from ${}^2E$ to ${}^4A_2$, resulting in an energy transfer between the two ions. The strength of these terms will be estimated later.

One might question the possibilities of replacing Eq. (2) by an expression involving the two *ionic* spins. It turns out that, although such an expression could yield the correct energies, by defining an "effective" ionic spin and appropriate coupling constants, it is actually useless since it will not interconnect ${}^2E$ and ${}^4A_2$. One might also expect that the isotropic exchange given by Eq. (3) should be applicable to the calculation of the diagonal elements of (5). This is apparently not true in our case because of the specific forms of the ${}^2E_\theta$ and ${}^2E_\epsilon$ wave functions that we have chosen. As a result, $\langle{}^2E_{\theta,\epsilon}|\mathbf{s}_i|{}^2E_{\theta,\epsilon}\rangle$ is not independent of i in our notation. In fact, applying an appropriate unitary transformation to our ${}^2E_\theta$ and ${}^2E_\epsilon$ wave functions, we find that Eq. (3) can indeed be used to compute the diagonal matrix elements[13] (only).

The above considerations are entirely general for a pair of d^3 ions, each in the ${}^4A_2$ or ${}^2E$ state. Let us now consider the example of KMgF$_3$:V^{2+}. For the case where two V ions are along a cubic axis which is chosen to be the z axis, the cubic symmetry leads to the following relations: $J_{13}=J_{23}=J_{31}=J_{32}$, $J_{12}=J_{21}$, and $J_{11}=J_{22}$. Here, we have assigned the indices 1, 2, and 3 to the orbitals $\xi(\sim yz)$, $\eta(\sim xz)$, and $\zeta(\sim xy)$, respectively. Furthermore, using the method of configuration interaction, it is found[8] that $J_{11}\cong-31$°K, $J_{12}\simeq J_{13}\simeq1$°K, and $J_{33}\cong0$°K. These lead to a value of -6°K for J, whereas the experimental value for J determined by Smith and Owen,[14] from a measurement of the ground-state pair spectra, is -4.4°K. Although the theoretical calculation is not in excellent agreement with the experiment (owing to difficulties similar to those involved in estimating the amount of charge transfer in weakly covalent crystals), yet it shows that among the J_{ij}, J_{11} is by far the dominant term. This is in qualitative agreement with the fact that $d_{yz}{}^a$ and $d_{yz}{}^b$ (or $d_{xz}{}^a$ and $d_{xz}{}^b$) *both* overlap with the ligand orbital p_y (or p_x). (Such a situation is not appropriate to Cr^{3+}:Al$_2$O$_3$, of course, since the bonding is by no means collinear.) Hence there exists a strong superexchange interaction between these d orbitals. Making the approximation of retaining J_{11} $(=J_{22})$ and ignoring the others, we find

$$J_{11}\simeq\tfrac{9}{2}J=-19.8\text{°K}. \tag{6}$$

In this approximation, the pair energy levels, the matrix element of $\mathcal{H}_{\rm ex}$ entering in the rate of energy transfer, and the Davydov splittings, all take simple forms, as we shall see in the following.

In order to solve for the eigenvalues of (5), we form the symmetric and antisymmetric combinations of the φ_i's to reduce the matrix into block form. Using (6), we find the energies of the pair corresponding to the symmetric and the antisymmetric states to be

$$\begin{aligned} S=2:\quad & \tfrac{3}{2}J,\ R-\tfrac{3}{2}J,\ R+\tfrac{9}{2}J \quad && \text{(antisym.)} \\ & R-\tfrac{9}{2}J,\ R-\tfrac{9}{2}J && \text{(sym.)}, \end{aligned} \tag{7}$$

where we have only retained terms of the order J/R as compared with R. In a similar manner, from the energy matrices given in the Appendix, we find the pair energies corresponding to $S=0$, 1, and 3 to be

$$\begin{aligned} S=0:\quad & \tfrac{15}{2}J,\ 2R+\tfrac{3}{2}(2\pm\sqrt{5})J && \text{(antisym.)} \\ & 2R\pm\tfrac{9}{2}J && \text{(sym.)}, \end{aligned} \tag{8}$$

$$\begin{aligned} S=1:\quad & R-\tfrac{3}{2}J,\ R+\tfrac{9}{2}J,\ 2R+\tfrac{3}{2}J && \text{(antisym.)} \\ & \tfrac{11}{2}J,\ R+\tfrac{3}{2}J,\ R+\tfrac{11}{2}J,\ 2R-\tfrac{3}{2}J, \\ & \qquad 2R-J\pm\tfrac{1}{2}(13)^{1/2}J && \text{(sym.)}, \end{aligned} \tag{9}$$

$$S=3:\quad -\tfrac{9}{2}J \qquad \text{(sym.)}. \tag{10}$$

For the case of two nearest neighbors with $S=2$, using (7), the Davydov splittings are found to be

$$\begin{aligned} &E[(\varphi_3-\varphi_5)/\sqrt{2}]-E[(\varphi_3+\varphi_5)/\sqrt{2}] \\ &\qquad\qquad =3J=-13.2\text{°K}, \\ &E[(\varphi_2-\varphi_4)/\sqrt{2}]-E[(\varphi_2+\varphi_4)/\sqrt{2}] \\ &\qquad\qquad =9J=-39.6\text{°K}, \end{aligned} \tag{11}$$

where $(\varphi_i+\varphi_j)/\sqrt{2}$ and $(\varphi_i-\varphi_j)/\sqrt{2}$ correspond to the symmetric and the antisymmetric state, respectively. Note that these splittings are 2–6 times greater than the ground-state–ground-state exchange splitting $\frac{3}{2}J$ given in (7). The matrix elements entering in the rate of energy transfer are found to be

$$\begin{aligned} \langle{}^2E_\theta{}^a,{}^4A_2{}^b|\mathcal{H}_{\rm ex}|{}^4A_2{}^a,{}^2E_\theta{}^b\rangle &=-\tfrac{9}{2}J=19.8\text{°K}, \\ \langle{}^2E_\epsilon{}^a,{}^4A_2{}^b|\mathcal{H}_{\rm ex}|{}^4A_2{}^a,{}^2E_\epsilon{}^b\rangle &=-\tfrac{3}{2}J=6.6\text{°K}. \end{aligned} \tag{12}$$

Expressions similar to Eqs. (11) and (12) also obtain for the case $S=1$.

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[13] The unitary transformation required is given by

$$\frac{1}{\sqrt{2}}\begin{pmatrix}-i & 1\\ i & 1\end{pmatrix}.$$

Using $(E_\epsilon\pm iE_\theta)/\sqrt{2}$ as the new basis set for ${}^2E$, we find that the diagonal matrix elements of Eq. (2) are the same as those of the isotropic exchange (3).

[14] S. R. P. Smith and J. Owen (unpublished).

III. CONCLUSION

We have demonstrated above the importance of the orbitally anisotropic nature of exchange integrals. In the case of 1% ruby, using the observed single-ion-pair transfer rate and a theoretical estimate for the convolution of the no-phone line and the phonon density of states, Birgeneau[5] found that

$$|\langle {}^4A_2{}^a, {}^2E^b|\mathcal{H}_{\text{int}}|{}^2E^a, {}^4A_2{}^b\rangle|$$

for single-ion-single-ion transitions needs to be $\sim 2.5\times 10^{-3}$ cm^{-1}. He also found that the electric or magnetic multipole interactions are roughly three orders of magnitude too small, as compared with this value, and concluded that orbitally anisotropic exchange is the mechanism for the energy transfer in ruby. For the case of two nearest V neighbors in KMgF_3, we found in Eq. (12) that $\langle {}^4A_2{}^a, {}^2E^b|\mathcal{H}_{\text{ex}}|{}^2E^a, {}^4A_2{}^b\rangle$ is of the order of 10°K. This value should be reduced roughly by a factor S^2 ($\sim 10^{-2}$) for each additional ligand which sits along the path of the superexchange interaction between the magnetic ions. Here S is the overlap integral between two neighboring F^- ions. Hence, very roughly, we would get a value of 10^{-3} °K for the above matrix element corresponding to the case of two V^{2+} ions separated by three F^- ions. Thus, even for exchange paths containing three ligand linkages, there is sufficient magnitude for rapid single–ion–single-ion energy transfer.

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APPENDIX

The wave functions and the matrix elements of Eq. (2) corresponding to $S=0$, 1, and 3 are given below. We need to consider only wave functions having the maximum value of M_S, since $\mathcal{H}_{\text{ex}}$ is invariant under rotations in spin space.

(i) $S=0$:

$$\begin{aligned}
\psi_1 &= \tfrac{1}{2}(A^a{}_{3/2}A^b{}_{-3/2} - A^a{}_{1/2}A^b{}_{-1/2} \\
&\qquad + A^a{}_{-1/2}A^b{}_{1/2} - A^a{}_{-3/2}A^b{}_{3/2}),\\
\psi_2 &= (E^a{}_{\theta,1/2}E^b{}_{\theta,-1/2} - E^a{}_{\theta,-1/2}E^b{}_{\theta,1/2})/\sqrt{2},\\
\psi_3 &= (E^a{}_{\epsilon,1/2}E^b{}_{\theta,-1/2} - E^a{}_{\epsilon,-1/2}E^b{}_{\theta,1/2})/\sqrt{2},\\
\psi_4 &= (E^a{}_{\theta,1/2}E^b{}_{\epsilon,-1/2} - E^a{}_{\theta,-1/2}E^b{}_{\epsilon,1/2})/\sqrt{2},\\
\psi_5 &= (E^a{}_{\epsilon,1/2}E^b{}_{\epsilon,-1/2} - E^a{}_{\epsilon,-1/2}E^b{}_{\epsilon,1/2})/\sqrt{2}.
\end{aligned}$$

The matrix elements of $\mathcal{H}_{\text{ex}}$ are found to be

$$\begin{aligned}
\langle\psi_1|\mathcal{H}_{\text{ex}}|\psi_1\rangle &= \tfrac{15}{2}J,\\
\langle\psi_1|\mathcal{H}_{\text{ex}}|\psi_2\rangle &= (J_{11}+J_{22}-J_{12}-J_{21})/\sqrt{2},\\
\langle\psi_1|\mathcal{H}_{\text{ex}}|\psi_3\rangle &= (J_{11}-J_{12}+J_{21}-J_{22}-2J_{31}+2J_{32})/\sqrt{6},\\
\langle\psi_1|\mathcal{H}_{\text{ex}}|\psi_4\rangle &= (J_{11}-J_{21}+J_{12}-J_{22}-2J_{13}+2J_{23})/\sqrt{6},\\
\langle\psi_1|\mathcal{H}_{\text{ex}}|\psi_5\rangle &= (4J_{33}-2J_{32}-2J_{31}-2J_{13}-2J_{23}\\
&\qquad +J_{22}+J_{21}+J_{12}+J_{11})/3\sqrt{2},\\
\langle\psi_2|\mathcal{H}_{\text{ex}}|\psi_2\rangle &= 2R+\tfrac{3}{2}J_{33},\\
\langle\psi_2|\mathcal{H}_{\text{ex}}|\psi_3\rangle &= \tfrac{3}{2}(J_{23}-J_{13}),\\
\langle\psi_2|\mathcal{H}_{\text{ex}}|\psi_4\rangle &= \tfrac{3}{2}(J_{32}-J_{31}),\\
\langle\psi_2|\mathcal{H}_{\text{ex}}|\psi_5\rangle &= \tfrac{1}{2}(J_{11}+J_{22}-J_{12}-J_{21}) = \langle\psi_3|\mathcal{H}_{\text{ex}}|\psi_4\rangle,\\
\langle\psi_3|\mathcal{H}_{\text{ex}}|\psi_3\rangle &= 2R+J_{13}+J_{23}-\tfrac{1}{2}J_{33},\\
\langle\psi_3|\mathcal{H}_{\text{ex}}|\psi_5\rangle &= (2J_{12}-2J_{11}+2J_{22}-2J_{21}+J_{31}-J_{32})/2\sqrt{3},\\
\langle\psi_4|\mathcal{H}_{\text{ex}}|\psi_4\rangle &= 2R+J_{31}+J_{32}-\tfrac{1}{2}J_{33},\\
\langle\psi_4|\mathcal{H}_{\text{ex}}|\psi_5\rangle &= (2J_{21}-2J_{11}+2J_{22}-2J_{12}+J_{13}-J_{23})/2\sqrt{3},\\
\langle\psi_5|\mathcal{H}_{\text{ex}}|\psi_5\rangle &= 2R+\tfrac{1}{6}(4J_{11}+4J_{12}-2J_{13}+4J_{21}+4J_{22}\\
&\qquad -2J_{23}-2J_{31}-2J_{32}+J_{33}).
\end{aligned}$$

(ii) $S=1$, $M_S=1$:

$$\begin{aligned}
u_1 &= (\sqrt{\tfrac{3}{10}})A^a{}_{3/2}A^b{}_{-1/2} - (\sqrt{\tfrac{2}{5}})A^a{}_{1/2}A^b{}_{1/2}\\
&\qquad + (\sqrt{\tfrac{3}{10}})A^a{}_{-1/2}A^b{}_{3/2},\\
u_2 &= \tfrac{1}{2}(\sqrt{3}E^a{}_{\theta,-1/2}A^b{}_{3/2} - E^a{}_{\theta,1/2}A^b{}_{1/2}),\\
u_3 &= \tfrac{1}{2}(\sqrt{3}E^a{}_{\epsilon,-1/2}A^b{}_{3/2} - E^a{}_{\epsilon,1/2}A^b{}_{1/2}),\\
u_4 &= \tfrac{1}{2}(\sqrt{3}A^a{}_{3/2}E^b{}_{\theta,-1/2} - A^a{}_{1/2}E^b{}_{\theta,1/2}),\\
u_5 &= \tfrac{1}{2}(\sqrt{3}A^a{}_{3/2}E^b{}_{\epsilon,-1/2} - A^a{}_{1/2}E^b{}_{\epsilon,1/2}),\\
u_6 &= E^a{}_{\theta,1/2}E^b{}_{\theta,1/2},\\
u_7 &= E^a{}_{\epsilon,1/2}E^b{}_{\theta,1/2},\\
u_8 &= E^a{}_{\theta,1/2}E^b{}_{\epsilon,1/2},\\
u_9 &= E^a{}_{\epsilon,1/2}E^b{}_{\epsilon,1/2}.
\end{aligned}$$

The matrix elements of $\mathcal{H}_{\text{ex}}$ are found to be

$$\begin{aligned}
\langle u_1|\mathcal{H}_{\text{ex}}|u_1\rangle &= \tfrac{11}{2}J,\\
\langle u_1|\mathcal{H}_{\text{ex}}|u_2\rangle &= (\sqrt{5})\textstyle\sum(J_{2j}-J_{1j})/3\sqrt{3}\\
&= (2/\sqrt{5})\langle u_2|\mathcal{H}_{\text{ex}}|u_3\rangle,\\
\langle u_1|\mathcal{H}_{\text{ex}}|u_3\rangle &= \tfrac{1}{9}(\sqrt{5})\textstyle\sum(2J_{3j}-J_{1j}-J_{2j}),\\
\langle u_1|\mathcal{H}_{\text{ex}}|u_4\rangle &= (\sqrt{5})\textstyle\sum(J_{j2}-J_{j1})/3\sqrt{3}\\
&= (2/\sqrt{5})\langle u_4|\mathcal{H}_{\text{ex}}|u_5\rangle,\\
\langle u_1|\mathcal{H}_{\text{ex}}|u_5\rangle &= \tfrac{1}{9}(\sqrt{5})\textstyle\sum(2J_{j3}-J_{j1}-J_{j2}),\\
\langle u_1|\mathcal{H}_{\text{ex}}|u_6\rangle &= \tfrac{1}{6}(\sqrt{10})(J_{11}+J_{22}-J_{12}-J_{21})\\
&= -(\tfrac{1}{2}\sqrt{5})\langle u_2|\mathcal{H}_{\text{ex}}|u_7\rangle\\
&= -(\tfrac{1}{2}\sqrt{5})\langle u_3|\mathcal{H}_{\text{ex}}|u_6\rangle\\
&= -(\tfrac{1}{2}\sqrt{5})\langle u_4|\mathcal{H}_{\text{ex}}|u_8\rangle\\
&= -(\tfrac{1}{2}\sqrt{5})\langle u_5|\mathcal{H}_{\text{ex}}|u_6\rangle\\
&= (\sqrt{10})\langle u_2|\mathcal{H}_{\text{ex}}|u_4\rangle = -(\sqrt{10})\langle u_6|\mathcal{H}_{\text{ex}}|u_9\rangle\\
&= -(\sqrt{10})\langle u_7|\mathcal{H}_{\text{ex}}|u_8\rangle,
\end{aligned}$$

$$\begin{aligned}\langle u_1|\mathcal{H}_{\mathrm{ex}}|u_7\rangle &= (\surd 5)\\ &\quad\times(2J_{32}-2J_{31}+J_{21}-J_{12}+J_{11}-J_{22})/3\surd 6\\ &=(\surd 10)\langle u_3|\mathcal{H}_{\mathrm{ex}}|u_4\rangle\\ &=-(\tfrac{1}{2}\surd 5)\langle u_4|\mathcal{H}_{\mathrm{ex}}|u_9\rangle\\ &=-(\tfrac{1}{2}\surd 5)\langle u_5|\mathcal{H}_{\mathrm{ex}}|u_7\rangle,\end{aligned}$$

$$\begin{aligned}\langle u_1|\mathcal{H}_{\mathrm{ex}}|u_8\rangle &= (\surd 5)(2J_{23}-2J_{13}+J_{12}\\ &\qquad -J_{21}+J_{11}-J_{22})/3\surd 6\\ &=-(\tfrac{1}{2}\surd 5)\langle u_2|\mathcal{H}_{\mathrm{ex}}|u_9\rangle\\ &=-(\tfrac{1}{2}\surd 5)\langle u_3|\mathcal{H}_{\mathrm{ex}}|u_8\rangle=(\surd 10)\langle u_2|\mathcal{H}_{\mathrm{ex}}|u_5\rangle,\end{aligned}$$

$$\begin{aligned}\langle u_1|\mathcal{H}_{\mathrm{ex}}|u_9\rangle &= (\surd 5)(4J_{33}-2J_{32}-2J_{31}-2J_{23}+J_{22}\\ &\qquad +J_{21}-2J_{13}+J_{12}+J_{11})/9\sqrt{2}\\ &=(\surd 10)\langle u_3|\mathcal{H}_{\mathrm{ex}}|u_5\rangle,\end{aligned}$$

$$\langle u_2|\mathcal{H}_{\mathrm{ex}}|u_2\rangle=\tfrac{5}{6}\sum J_{3j},$$

$$\langle u_2|\mathcal{H}_{\mathrm{ex}}|u_6\rangle=\sqrt{2}(J_{31}-J_{32})/\sqrt{3}=2\sqrt{2}\langle u_6|\mathcal{H}_{\mathrm{ex}}|u_8\rangle,$$

$$\langle u_2|\mathcal{H}_{\mathrm{ex}}|u_8\rangle=\tfrac{1}{3}\sqrt{2}(J_{31}+J_{32}-2J_{33}),$$

$$\langle u_3|\mathcal{H}_{\mathrm{ex}}|u_3\rangle=(5/18)\sum(2J_{1j}+2J_{2j}-J_{3j}),$$

$$\begin{aligned}\langle u_3|\mathcal{H}_{\mathrm{ex}}|u_7\rangle &= \sqrt{2}(2J_{11}-2J_{22}-2J_{12}\\ &\qquad +2J_{21}+J_{32}-J_{31})/3\sqrt{3}\\ &=2\sqrt{2}\langle u_7|\mathcal{H}_{\mathrm{ex}}|u_9\rangle,\end{aligned}$$

$$\begin{aligned}\langle u_3|\mathcal{H}_{\mathrm{ex}}|u_9\rangle &= \tfrac{1}{9}\sqrt{2}(2J_{11}+2J_{12}-4J_{13}+2J_{21}+2J_{22}\\ &\qquad -4J_{23}-J_{31}-J_{32}+2J_{33}),\end{aligned}$$

$$\langle u_4|\mathcal{H}_{\mathrm{ex}}|u_4\rangle=\tfrac{5}{6}\sum J_{j3},$$

$$\langle u_4|\mathcal{H}_{\mathrm{ex}}|u_6\rangle=\sqrt{2}(J_{13}-J_{23})/\sqrt{3}=2\sqrt{2}\langle u_6|\mathcal{H}_{\mathrm{ex}}|u_7\rangle,$$

$$\langle u_4|\mathcal{H}_{\mathrm{ex}}|u_7\rangle=\tfrac{1}{3}\sqrt{2}(J_{13}+J_{23}-2J_{33}),$$

$$\langle u_5|\mathcal{H}_{\mathrm{ex}}|u_5\rangle=(5/18)\sum(2J_{j1}+2J_{j2}-J_{j3}),$$

$$\begin{aligned}\langle u_5|\mathcal{H}_{\mathrm{ex}}|u_8\rangle &= \sqrt{2}(2J_{11}-2J_{22}-2J_{21}\\ &\qquad +2J_{12}+J_{23}-J_{13})/3\sqrt{3}\\ &=2\sqrt{2}\langle u_8|\mathcal{H}_{\mathrm{ex}}|u_9\rangle,\end{aligned}$$

$$\begin{aligned}\langle u_5|\mathcal{H}_{\mathrm{ex}}|u_9\rangle &= \tfrac{1}{9}\sqrt{2}(2J_{11}+2J_{21}-4J_{31}+2J_{12}+2J_{22}\\ &\qquad -4J_{32}-J_{13}-J_{23}+2J_{33}),\end{aligned}$$

$$\langle u_6|\mathcal{H}_{\mathrm{ex}}|u_6\rangle=-\tfrac{1}{2}J_{33},$$

$$\langle u_7|\mathcal{H}_{\mathrm{ex}}|u_7\rangle=\tfrac{1}{6}(J_{33}-2J_{13}-2J_{23}),$$

$$\langle u_8|\mathcal{H}_{\mathrm{ex}}|u_8\rangle=\tfrac{1}{6}(J_{33}-2J_{31}-2J_{32}),$$

$$\begin{aligned}\langle u_9|\mathcal{H}_{\mathrm{ex}}|u_9\rangle &= (1/18)(-4J_{11}-4J_{12}+2J_{13}-4J_{21}-4J_{22}\\ &\qquad +2J_{23}+2J_{31}+2J_{32}-J_{33}).\end{aligned}$$

(iii) $S=3$, $M_S=3$:

$$v=A^{a}{}_{3/2}A^{b}{}_{3/2}$$

$$\langle v|\mathcal{H}_{\mathrm{ex}}|v\rangle=-\tfrac{9}{2}J.$$