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Anisotropy in Two-Center Exchange Interactions*

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The exchange interaction between electrons on two different centers is developed in a bipolar series of angular momentum operators. In contrast to the isotropic Hamiltonian commonly used to represent this interaction, we find that all forms of anisotropic terms are needed, antisymmetric as well as symmetric ones. The degrees of the anisotropy assume all values commensurate with the angular momenta of the electrons. Beside the Dzyaloshinsky-Moriya term $\mathbf{S}_1\times\mathbf{S}_2$, two-center exchange interactions contain antisymmetric anisotropies of higher degrees. For ions with strong orbital contributions to their magnetic moments, anisotropic exchange does not enter merely as a perturbation, and we find that the magnitudes of the symmetric and antisymmetric anisotropies are as large as the isotropic part of the exchange interaction. Explicit expressions containing radial integrals are derived for the coefficients representing the anisotropy in the exchange interaction. These anisotropy coefficients are related to the more conventional exchange constants; we also find the number of independent parameters needed to describe two-center exchange interactions for various situations. The coefficients of anisotropy representing the exchange interaction between ions with N equivalent electrons are related to the coefficients for the interaction between ions with one electron. Although anisotropic superexchange is not considered in detail, both the form of the Hamiltonian representing this interaction, and also the number of independent parameters in the Hamiltonian, immediately follow from the Hamiltonian for the two-center exchange interaction.

I. INTRODUCTION

IN the original derivation of the exchange forces between electrons, Heisenberg considered only the case of orbitally nondegenerate s-state electrons.[1] Dirac[2] showed that this interaction, although electrostatic in origin, could be written as a scalar product of the spin variables of the two electrons $J_{12}\mathbf{S}_1\cdot\mathbf{S}_2$. This interaction was readily extended and applied by Van Vleck[3] to exchange interactions between atoms in molecules and solids. It was realized that in cases of orbital degeneracy the Dirac–Van Vleck form $J_{12}\mathbf{S}_1\cdot\mathbf{S}_2$ is incomplete and that the spin-orbit coupling of an electron gives additional anisotropic contributions to the exchange interaction.[4] In most of the situations analyzed, the orbital angular momentum of the electrons was partially or totally quenched; in these cases anisotropic contributions to the exchange Hamiltonian are very small compared to the isotropic term and the degree of the anisotropy is low, like dipolar or quadrupolar anisotropy.

However, more recent studies have concentrated on the exchange interactions between ions with strong orbital contributions to their magnetic moments. For these ions, orbital degeneracy remains; the spins are coupled to the orbit, and major deviations from the simple Dirac-Van Vleck Hamiltonian are to be expected. The possibility that orbital degeneracy could create *highly* anisotropic interactions was mentioned by Wolf,[5] and a striking illustration of this effect was soon provided by Wickershiem and White[6] from the anisotropy of the exchange splittings of the lowest doublets of the $^2F_{5/2}$ and $^2F_{7/2}$ states of ytterbium (Yb^{3+}) in ytterbium iron garnet (YbIG). Also, Baker *et al.*[7] have recently found direct evidence of strong highly anisotropic interactions between cerium ions in the lanthanum trihalides.

The idea that different orbital states have different exchange constants was used by Van Vleck[8] to show that the exchange interaction between s and p electrons on different centers is anisotropic, and that the strength of the anisotropy is proportional to the difference in the exchange constants for the different orbital states. This concept was applied by Levy[9] and Koster and Statz[10] to extend Van Vleck's example to rare-earth–iron exchange in the garnets. More recently, Elliott and Thorpe[11] discussed the form of the exchange interaction when both electrons are in orbitally degenerate states. They used symmetry arguments to find the appropriate form of the anisotropic exchange Hamiltonian. Also, Hartmann-Boutron[12] has recently made an explicit calculation of the anisotropic superexchange interaction between two d^1 configuration ions in octahedral environments.

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[11] R. J. Elliott and M. F. Thorpe, J. Appl. Phys. **39**, 802 (1968).

[12] F. Hartmann-Boutron, J. Phys. (Paris) **29**, 212 (1968).

We do not find in any previous treatments of *direct* two-center exchange an *ab initio* development of the exchange integral J_{12}, in terms of orbital angular momentum operators, which explicitly gives the dependence of the interaction on the orientation of the electron orbitals relative to the line joining their centers.[13] Exactly this expansion was given by Racah[14] for the exchange interaction between two atomic electrons on one center. For atoms, the total orbital angular momentum of the electrons is conserved and the exchange Hamiltonian is a scalar product of orbital operators[15]:

$$\mathcal{H}_{ex} \doteq -\sum_k G^k(n_a l_a, n_b l_b)(l_a \| C^{[k]} \| l_b)^2$$
$$\times \sum_r [r]^{3/2} \bar{W}(l_a l_a r / l_b l_b k)[U^{[r]}(1) \times U^{[r]}(2)]^{[0]}$$
$$\times (\tfrac{1}{2} + 2\mathbf{s}_1 \cdot \mathbf{s}_2) \quad (1)$$

[The dot over the equal sign means that the equality only holds for a restricted set of states, e.g., in Eq. (1) for states in the manifolds $n_a l_a$ and $n_b l_a$.]

In this paper, we derive an analog of Racah's expansion for two centers. For one center the orbitals described by spherical harmonics are orthonormal; however, they are not naturally orthonormal when referred to two different centers. To simplify our derivation, we consider the electrons in orthogonalized orbitals. This simplification in no way alters any of our results concerning the form of the anisotropy; however, it does not give good results for the magnitude and sign of the exchange integral.[16] We overcome the major difficulty in extending Eq. (1) to two centers by using an expansion which expresses the orbitals on the second center in a complete set of orbitals referred to the first center. After finding the expansion of the exchange interaction for two electrons we derive the Hamiltonian for any number of *equivalent* electrons per ion.

In previous work on this problem,[9–11] the form of the exchange interaction was found by symmetry arguments. Our derivation provides an expression for the anisotropy coefficients which could, in principle, be evaluated if one solved for the radial integrals involved. In the analysis which follows, we show that when we consider the angular momentum l of each electron constant, the two-body electrostatic exchange interaction contains only *symmetric* exchange. However, the generality of our expansion allows us to show that when crystal-field effects are important, antisymmetric exchange is also present. We derive formulas for the number of independent coefficients in the exchange interaction, and we find the relation between these coefficients and the exchange constants like J_{12}. We consider in detail some very simple cases of anisotropic exchange, in order to show explicitly the form of the anisotropy present in these interactions. Finally, we note that the *form* of the expression for two-electron two-center exchange can be applied to cases where superexchange is the dominant mechanism. In these cases the coefficients are no longer given explicitly; they must be determined empirically.

We demonstrate that it is a gross oversimplification to represent the exchange interaction between two ions with orbital degeneracy in the form of an isotropic interaction. Nonetheless, when we consider the staggering number of independent parameters necessary to describe these interactions faithfully, we understand why such an approximation has become so commonplace. A summary of our results has been published.[17] In a future paper we will consider the application of our expansion to exchange interactions in magnetic insulators.

II. DERIVATION OF OPERATOR FOR EXCHANGE INTERACTION

Consider two one-electron ions a distance R apart. When we use properly antisymmetrized wave functions for the two-electron system, we find that the average value of the Coulomb interaction energy of the two electrons e^2/r_{12} has a direct and an exchange term. The direct contribution

$$(\psi_a'(1)\psi_b'(2)|e^2/r_{12}|\psi_a(1)\psi_b(2)) \quad (2)$$

corresponds to the interaction energy of two charge clouds; the exchange term is written as

$$-(\psi_a'(1)\psi_b'(2)|e^2/r_{12}|\psi_b(1)\psi_a(2)), \quad (3)$$

where

$$\psi_\alpha(\mathbf{r}_i,\mathbf{s}_i) \equiv R_{n_\alpha l_\alpha}(r_i) Y_{l_\alpha m_\alpha}(\Omega_i) \chi_{m_{s\alpha}}(s_i)$$
$$\equiv R_{n_\alpha l_\alpha} \phi_\alpha(\Omega_i,\mathbf{s}_i),$$

$\Omega_i \equiv \theta_i$, and ϕ_i are the polar angles of the ith electron. As a further simplification we have neglected the small orthogonalization terms in the wave function ψ_α. The R_{nl}'s represent the radial part of the wave function, and the spherical harmonics Y_{lm} are normalized according to the convention of Fano and Racah,[18] i.e., $Y_{lm}^* = (-)^{l-m} Y_{l-m}$. The minus sign in front of the exchange integral enters because the wave function of the two electron system is antisymmetric with respect to the interchange of the two electrons. The label $\alpha = a, b$ refers

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[13] The exchange integral for *indirect* exchange via s electrons has been discussed by T. A. Kaplan and D. H. Lyons, Phys. Rev. **129**, 2072 (1963); T. Kasuya and D. H. Lyons, J. Phys. Soc. (Japan) **21**, 287 (1966); and Yu P. Irkhin, Zh. Eksperim. i Teor Fiz. **23**, 379 (1966) [English transl.: Soviet Phys.—JETP **23**, 253 (1966)]. V. V. Druzhinin, Fiz. Tverd. Tela **9**, 2463 (1967) [English transl.: Soviet Phys.—Solid State **9**, 1938 (1968)], calculates the reduction in the Slater integral F^k due to the direct exchange interaction between electrons on an impurity ion and the surrounding ligands, and does include the anisotropy in the exchange interaction.

[14] G. Racah, Phys. Rev. **62**, 438 (1942).

[15] The meaning of the terms in Eq. (1) will be defined in Sec. II.

[16] For a good discussion of the exchange integral for nonorthogonal orbitals see P. O. Löwdin, Rev. Mod. Phys. **34**, 80 (1962).

[17] P. M. Levy, Phys. Rev. Letters **20**, 1366 (1968).

[18] U. Fano and G. Racah, *Irreducible Tensorial Sets* (Academic Press Inc., New York, 1959). The phase convention for the spherical harmonics is given on pp. 24–26.

to the center to which the wave function is referred, and $i=1, 2$ refers to the electron.

There are two ways of evaluating this integral. One can expand the operator $1/r_{12}$ in a bipolar series; in this case the coordinates of one electron are referred to center A while the coordinates of the other electron are referred to center B [see Fig. 1]. The bipolar expansion appropriate for overlapping charge distributions is given by Buehler and Hirschfelder[19] for $\Theta_{ab}=\phi_{ab}=0°$ (see Fig. 1):

$$\frac{1}{r_{12}}=\sum_{n_1n_2m} B_{n_1n_2}{}^{|m|}(r_1r_2;\, R_{ab})P_{n_1}{}^{|m|}(\cos\theta_1) \times P_{n_2}{}^{|m|}(\cos\theta_2)e^{im(\phi_2-\phi_1)}.$$

The $P_n{}^m$ are Legendre polynomials, and the expansion coefficients $B_{n_1n_2}{}^{|m|}$ for overlapping charge distributions are very complex functions of n_1, n_2, and m. The radial integrals in these coefficients depend on the spatial quantum number m; this dependence prevents us from finding a closed expression for the angular part of the Coulomb interaction. There is no particular advantage in using the bipolar expansion to derive the dependence of the exchange integral on the angular variables, because the integrals over the angular variables contain wave functions that are not referred to the same center, e.g.,

$$(\psi_a'(1)\,|\,B_{n_1n_2}{}^{|m|}(r_1r_2;\, R_{ab})P_{n_1}{}^{|m|}(\cos\theta_1)e^{-im\phi_1}\,|\,\psi_b(1)).$$

To evaluate this integral it is necessary to expand the orbital ψ_b in a series of harmonics referred to center A.

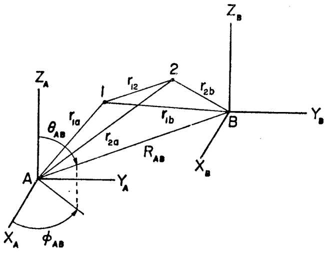

FIG. 1. Orientation of coordinate axes about the two centers A and B.

For exchange integrals it is always necessary to expand the orbitals about another center; therefore the second, and simpler, method is to refer all wave functions to a common center and to use the one-center expansion

$$\frac{1}{r_{12}}=\sum_{k=0}^{\infty}\frac{r_<{}^k}{r_>{}^{k+1}}\mathbf{C}^{[k]}(1)\cdot\mathbf{C}^{[k]}(2), \tag{4}$$

where

$$C_q{}^{[k]}(i)=[4\pi/(2k+1)]^{1/2}Y_{kq}(\Omega_i)$$

and $r_<$ is the lesser and $r_>$ the greater of r_1 and r_2.

The objective of our derivation is to rewrite the exchange integral Eq. (3) so that the operators and wave functions involving an electron are all referred to the same center

$$(\psi_a'(1)\psi_b'(2)\,|\,-e^2/r_{12}P_{12}\,|\,\psi_a(1)\psi_b(2)), \tag{5}$$

where P_{12} is the operator which interchanges electrons 1 and 2 amongst the orbitals ψ_a and ψ_b. By placing the one-center expansion for $1/r_{12}$, Eq. (4), in the exchange integral Eq. (3), we find

$$-e^2\sum_{k=0}^{\infty}\sum_{q=-k}^{k}(-)^{k+q}(\psi_a'(1)\psi_b'(2)\,|\,[r_<{}^k/r_>{}^{k+1}]C_q{}^{[k]}(1)C_{-q}{}^{[k]}(2)\,|\,\psi_b(1)\psi_a(2)). \tag{6}$$

To evaluate this integral we do not take advantage of the fact that the expansion of $1/r_{12}$ is in terms of scalar invariants of the two-electron system. For one center, this could be used to evaluate the exchange integral in a representation LM_L in which the orbital angular momenta of the electrons are coupled.[20] However, for a two-center problem the total angular momentum of the two electrons $L(L+1)$ is not conserved, and it is somewhat meaningless to evaluate the exchange integral in this composite representation.

If we assume that the expansion of $1/r_{12}$ is given in terms of operators referred to center A, it is necessary to reexpress the wave functions about center B, in terms of harmonics referred to center A. This expansion has been given recently by Silverstone[21]:

$$\psi(\mathbf{r}_{ib})=R_{nL}(r_{ib})Y_{LM}(\Omega_{ib})=\sum_{l=0}^{\infty}\sum_{\lambda=|L-l|}^{L+l}\mathcal{V}'_{l\lambda nL}(r_{ia},R_{ab})([l][\lambda]/4\pi)^{1/2}\bar{V}(lL\lambda;\,000)[\mathbf{Y}^{[\lambda]}(\Omega_{ab})\times\mathbf{Y}^{[l]}(\Omega_{ia})]_M{}^{[L]},$$

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[19] R. J. Buehler and J. O. Hirschfelder, Phys. Rev. **83**, 628 (1951). The expansion coefficients, in the region of overlap that we consider, are given in an addendum, *ibid.* **85**, 149 (1952).

[20] See Ref. 18, pp. 91–94.

[21] H. J. Silverstone, J. Chem. Phys. **47**, 537 (1967); see Eq. (20). We have rewritten the expansion so as to make it clear that the composite symmetry of the two harmonics $Y_{\lambda m_\lambda}(\Omega_{ab})$ and $Y_{lm}(\Omega_{ia})$ is still given by $Y_{LM}(\Omega_{ib})$.

where

$$\mathbf{r}_{ib}=\mathbf{r}_{ia}-\mathbf{R}_{ab},$$

$$\mathcal{V}'_{l\lambda nL}(r_{ia},R_{ab})\equiv\frac{1}{\pi}\int_{-\infty}^{\infty}j_\lambda(kR_{ab})j_l(kr_{ia})\bar{\psi}(k)k^2dk, \tag{7}$$

and

$$\bar{\psi}(k)\equiv4\pi\int_0^\infty R_{nL}(r_{ib})j_L(kr_{ib})r_{ib}^2dr_{ib}.$$

The $\bar{V}$ symbols are defined by Fano and Racah and are similar to Wigner 3-j symbols. The $j_\lambda(kR)$ are spherical Bessel functions, the spherical harmonics follow the convention of Fano and Racah,[18] and $[l]\equiv2l+1$. By using this expansion for the wave functions referred to center B we find that the exchange integral Eq. (3) is written as

$$-\frac{e^2}{4\pi}\sum_{k=0}^{\infty}\sum_{q=-k}^{k}(-)^{k+q}\sum_{l,l'=0}^{\infty}\sum_{\lambda=|l_b-l|}^{l_b+l}\sum_{\lambda'=|l_b'-l'|}^{l_b'+l'}([l'][l][\lambda'][\lambda])^{1/2}\bar{V}(l_bl\lambda;000)\bar{V}(l_b'l'\lambda';000)$$
$$\times\left\{\iint_0^\infty\frac{r_<^k}{r_>^{k+1}}R_{n_a'l_a'}(r_{1a})\mathcal{V}'_{l\lambda n_bl_b}(r_{1a},R_{ab})R_{n_al_a}(r_{2a})\mathcal{V}'_{l'\lambda'n_b'l_b'}(r_{2a},R_{ab})r_{1a}^2r_{2a}^2dr_{1a}dr_{2a}\right\}$$
$$\times\left\{\int_{\Omega_1}Y_{l_a'm_a'}{}^*(1)C_q{}^{[k]}(1)[\mathbf{Y}^{[\lambda]}(\Omega_{ab})\times\mathbf{Y}^{[l]}(\Omega_1)]_{m_b}{}^{[l_b]}d\Omega_1\int_{\Omega_2}[\mathbf{Y}^{[\lambda']}(\Omega_{ab})\times\mathbf{Y}^{[l']}(\Omega_2)]_{m_b'}{}^{[l_b']*}C_{-q}{}^{[k]}(2)Y_{l_am_a}(2)d\Omega_2\right\}$$
$$\times(\tfrac{1}{2}m_{sa}'\tfrac{1}{2}m_{sb}'|\tfrac{1}{2}m_{sb}\tfrac{1}{2}m_{sa}). \tag{8}$$

To evaluate the integrals over the angles Ω_1 and Ω_2, it is necessary first to decompose the irreducible products as follows:

$$[\mathbf{Y}^{[\lambda]}\times\mathbf{Y}^{[l]}]_{m_b}{}^{[l_b]}=\sum_{m=-l}^{l}\sum_{m_\lambda=-\lambda}^{\lambda}(-)^{l_b-m_b}[l_b]^{1/2}V(\lambda ll_b;m_\lambda m-m_b)Y_{\lambda m_\lambda}Y_{lm},$$

where

$$[l_b]\equiv2l_b+1.$$

The two integrals over the angular variables are rewritten as

$$\sum_{mm_\lambda}\sum_{m'm_\lambda'}(-)^{l_b-m_b+l_b'-m_b'}([l_b][l_b'])^{1/2}\bar{V}(\lambda ll_b;m_\lambda m-m_b)\bar{V}(\lambda'l'l_b';m_\lambda'm'-m_b')$$
$$\times Y_{\lambda m_\lambda}(\Omega_{ab})Y_{\lambda'm_\lambda'}{}^*(\Omega_{ab})(l_a'm_a'|C_q{}^{[k]}|lm)(l'm'|C_{-q}{}^{[k]}|l_am_a). \tag{9}$$

The two spherical harmonics in the variables Ω_{AB} can be combined and expressed as follows[22]:

$$Y_{\lambda m_\lambda}Y_{\lambda'm_\lambda'}{}^*=(-)^{\lambda-m_\lambda}\sum_{\lambda''=|\lambda-\lambda'|}^{\lambda+\lambda'}\sum_{m_\lambda''=-\lambda''}^{\lambda''}([\lambda][\lambda'][\lambda'']/4\pi)^{1/2}\bar{V}(\lambda\lambda'\lambda'';000)\bar{V}(\lambda\lambda'\lambda'';-m_\lambda m_\lambda'm_\lambda'')Y_{\lambda''m_\lambda''}.$$

The matrix elements in Eq. (9) are integrals over three spherical harmonics[23]

$$(l_a'm_a'|C_q{}^{[k]}|lm)=(-1)^{\frac{1}{2}(l_a'+l+k)}(-)^{l_a'-m_a'}([l_a'][l])^{\frac{1}{2}}\bar{V}(l_a'lk;000)\bar{V}(kll_a';qm-m_a').$$

Combining terms, we find that the integrals over the angular variables, Eq. (9), are

$$\sum_{\lambda''m_\lambda''}\sum_{mm_\lambda}\sum_{m'm_\lambda'}(-)^{l_b+l_b'+l_a'+l'+\lambda-(m_b+m_b'+m_a'+m'+m_\lambda)+\frac{1}{2}(\lambda+\lambda'+\lambda''+l_a'+l+k+l'+l_a+k)}$$
$$\times([l_a'][l_a][l_b'][l_b][l][l'][\lambda][\lambda'][\lambda'']/4\pi)^{1/2}\bar{V}(l_a'lk;000)\bar{V}(l'l_ak;000)\bar{V}(\lambda\lambda'\lambda'';000)\bar{V}(\lambda ll_b;m_\lambda m-m_b)$$
$$\times\bar{V}(\lambda'l'l_b';m_\lambda'm'-m_b')\bar{V}(\lambda\lambda'\lambda'';-m_\lambda m_\lambda'm_\lambda'')\bar{V}(kll_a';qm-m_a')\bar{V}(kl_al';-qm_a-m')Y_{\lambda''m_\lambda''}(\Omega_{ab}). \tag{10}$$

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[22] Ref. 18, p. 164, Eq. (J.10), and A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N. J., 1957), p. 63.

[23] See Ref. 18, Eq. (14.10). The $\bar{V}$ symbol $\bar{V}(l_a'lk;000)$ and the matrix elements vanish if the sum $l_a'+l+k$ is odd.

To rearrange the terms entering the $\bar{V}$ symbols so that orbitals referring to the same center are together, we must perform two recouplings. The simpler one involves the orbitals on center A, and is equivalent to a recoupling of four angular momenta which form a scalar invariant[24]:

$$\sum_{q}(-)^{q}\bar{V}(ll_a'k;\,m-m_a'q)\bar{V}(l_al'k;\,m_a-m'-q)$$

$$=\sum_{k_1=|l_a'-l_a|}^{l_a'+l_a}\ \sum_{q_1=-k_1}^{k_1}(-)^{k_1+k-m-m'}[k_1]\bar{\bar{W}}(l_al_a'k_1/ll'k)\bar{V}(l_al_a'k_1;\,m_a-m_a'q_1)\bar{V}(ll'k_1;\,m-m'-q_1)\,.$$

The $\bar{\bar{W}}$ symbol is a symmetrized Racah coefficient.[25] The recoupling of the orbitals about center B is equivalent to one involving four angular momenta which do not form a scalar[26]:

$$\sum_{m_\lambda m_\lambda' mm'}\bar{V}(\lambda ll_b;\,m_\lambda m-m_b)\bar{V}(\lambda'l'l'_b;\,m_\lambda'm'-m_b')\bar{V}(\lambda\lambda'\lambda'';\,-m_\lambda m_\lambda'm_\lambda'')\bar{V}(ll'k_1;\,m-m'-q_1)$$

$$=(-)^{\lambda'+\lambda''+l+l_b}\sum_{k_2=|l_b'-l_b|}^{l_b'+l_b}\ \sum_{q_2=-k_2}^{k_2}[k_2]X(\lambda''k_2k_1/\lambda l_bl/\lambda'l'_bl')\bar{V}(k_1k_2\lambda'';\,q_1q_2m_\lambda'')\bar{V}(l_b'l_bk_2;\,-m_b'm_bq_2)\,.$$

The $X(\ /\ /\ )$ is a 9-j symbol.[27] We now express the $\bar{V}$ symbols containing the orbitals $l_\alpha(\alpha=a,b)$ as matrix elements of new operators by using the Wigner-Eckart theorem[28]

$$\bar{V}(l_\alpha'l_\alpha k_i;\,-m_\alpha'm_\alpha q_i)=(-)^{l_\alpha'-m_\alpha'}(l_\alpha'm_\alpha'|u_{q_i}^{[k_i]}|l_\alpha m_\alpha)/(l_\alpha'\|\mathbf{u}^{[k_i]}\|l_\alpha)\,,$$

where $i=1,2$. We define these operators by specifying that their reduced matrix elements are[29]

$$(l_\alpha'\|\mathbf{u}^{[k_i]}\|l_\alpha)\equiv(-1)^{\frac{1}{2}(l_\alpha'-l_\alpha-k_i)}\,. \tag{11}$$

Upon placing the recoupled $\bar{V}$ symbols and the operator equivalents in Eq. (10), we find that we can write the integral over the angular variables as

$$(1/4\pi)\sum_{k_1k_2\lambda''}(-)^{l_b'-l_b+l_a'-l_a+\lambda+k+\frac{1}{2}(k_1+k_2+\lambda'')}([l_a'][l_a][l_b'][l_b][l][l'][\lambda][\lambda'])^{1/2}[k_1][k_2][\lambda'']$$
$$\times\bar{V}(l_a'lk;\,000)\bar{V}(l'l_ak;\,000)\bar{V}(\lambda\lambda'\lambda'';\,000)\bar{\bar{W}}(l_al_a'k_1/ll'k)X(\lambda''k_2k_1/\lambda l_bl/\lambda'l_b'l')$$
$$\times(l_a'm_a'l_b'm_b'|[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)\times\mathbf{C}^{[\lambda'']}(\Omega_{ab})]^{[0]}|l_am_al_bm_b)\,. \tag{12}$$

To demonstrate the symmetry of the interaction, we have written the triple product of the two operators $u_{q_i}^{[k_i]}$ and the spherical harmonic as an invariant[30]:

$$\sum_{q_1q_2m''}u_{q_1}^{[k_1]}u_{q_2}^{[k_2]}C_{m_\lambda''}^{[\lambda'']}\bar{V}(k_1k_2\lambda'';\,q_1q_2m_\lambda'')=[\mathbf{u}^{[k_1]}\times\mathbf{u}^{[k_2]}\times\mathbf{C}^{[\lambda'']}]^{[0]}\,. \tag{13}$$

The matrix element over the spin variables in Eq. (8) can be written as

$$(m_{sa}'m_{sb}'|(\tfrac{1}{2}+2\mathbf{s}_1\cdot\mathbf{s}_2)|m_{sa}m_{sb}) \tag{14}$$

by using the well-known Dirac identity.[2] When we replace the transformed matrix elements Eqs. (12) and (14) in Eq. (8) and compare the result with the desired form of the matrix element, Eq. (5), we write the entire exchange integral as

$$(\phi_a'(1)\phi_b'(2)|\sum_{k_1=|l_a'-l_a|}^{l_a'+l_a}\ \sum_{k_2=|l_b'-l_b|}^{l_b'+l_b}\ \sum_{\Lambda=|k_1-k_2|}^{k_1+k_2}-\Gamma_{k_1k_2\Lambda}(n_a'l_a'n_b'l_b',n_al_an_bl_b)$$
$$\times[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}(\tfrac{1}{2}+2\mathbf{s}_1\cdot\mathbf{s}_2)|\phi_a(1)\phi_b(2))\,, \tag{15}$$

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[24] See Ref. 18, Eq. (11.18).

[25] See Ref. 18, Chap. 11.

[26] D. M. Brink and G. R. Satchler, *Angular Momentum* (The Clarendon Press, Oxford, 1962), p. 119. We have rewritten the expression, given in terms of 3-j symbols, in terms of $\bar{V}$ symbols.

[27] See Ref. 18, Chap. 12.

[28] See Ref. 18, pp. 76–79.

[29] This definition assures us that the operator $u_{q_i}^{[k_i]}$ has the proper transformation properties under complex conjugation. See Ref. 18, p. 80. It should be noted that for $l_\alpha'\neq l_\alpha$ $(u_{q_i}^{[k_i]})^{+}=(-)^{l_\alpha'-l_\alpha-k_i-q_i}u_{-q_i}^{[k_i]}$.

[30] See Ref. 18, pp. 48–50.

where, from Eq. (3), $\phi_\alpha(i) \equiv |l_\alpha m_\alpha)|\frac{1}{2} m_{s\alpha})$, and

$$\Gamma_{k_1k_2\Lambda} \equiv (-)^{l_a+l_b'+\frac{1}{2}(k_1+k_2+\Lambda)}(e/4\pi)^2[k_1][k_2][\Lambda]([l_a'][l_a][l_b'][l_b])^{1/2}$$

$$\times \sum_{k,l,l'=0}^{\infty} \sum_{\lambda=|l_b-l|}^{l_b+l} \sum_{\lambda'=|l_b'-l'|}^{l_b'+l'} (-)^k[l][l'][\lambda][\lambda']\bar{V}(l_a'lk;\,000)\bar{V}(l'l_ak;\,000)\bar{V}(l_bl\lambda;\,000)\bar{V}(l'l_b'\lambda';\,000)\bar{V}(\lambda\lambda'\Lambda;\,000)$$

$$\times \bar{W}(l_al_a'k_1/ll'k)X(\Lambda k_2k_1/\lambda l_bl/\lambda'l_b'l') \int\int_0^\infty \frac{r_<^k}{r_>^{k+1}} R_{n_a'l_a'}(r_1)\mathcal{V}'_{l\lambda n_bl_b}(r_1,R_{ab})R_{n_al_a}(r_2)\mathcal{V}'_{l'\lambda'n_b'l_b'}(r_2,R_{ab})r_1^2r_2^2dr_1dr_2.$$

This equation is our main result. By comparing it with Racah's result for one center, Eq. (1), we find that in contrast to the one-center problem, where angular momentum is conserved and the product of the two operators is a scalar invariant, the spherical harmonic in the triple product of the two-center expansion requires that the irreducible products of these operators be nonscalar. Therefore, the expansion contains anisotropic as well as isotropic terms. The terms of rank Λ greater than zero represent the orbital anisotropy present in the two-center exchange interaction. The radial integrals in the coefficient $\Gamma_{k_1k_2\Lambda}$ are the analog of the Slater G^k integrals for one center. Once these coefficients are evaluated, our result, Eq. (15), gives the matrix element of the exchange interaction for any spatial orientation of the electron orbitals ϕ_α.

Our result also can be written in forms more amenable to direct evaluation by decoupling the triple product in Eq. (15). The orbital part of the exchange operator[31] is written as

$$\sum_{k_1k_2\Lambda m} -\Gamma_m^{[\Lambda]}(1,2)[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)]_m^{[\Lambda]}, \qquad (15')$$

where

$$\Gamma_m^{[\Lambda]}(1,2) \equiv [\Lambda]^{-1/2}\Gamma_{k_1k_2\Lambda}C_m^{[\Lambda]*},$$

and as

$$\sum_{k_1k_2q_1q_2} -\Gamma_{q_1q_2}^{k_1k_2}u_{q_1}^{[k_1]}(1)u_{q_2}^{[k_2]}(2), \qquad (15'')$$

where

$$\Gamma_{q_1q_2}^{k_1k_2} \equiv \sum_{\Lambda,m} \Gamma_{k_1k_2\Lambda}C_m^{[\Lambda]}\bar{V}(k_1k_2\Lambda;\,q_1q_2m).$$

In our derivation of the expansion of the orbital part of the exchange integral, we assumed the coordinate systems to be parallel (see Fig. 1). However, there are cases when *other* interactions must be taken into account, e.g., crystal-field. In these cases it is either inconvenient or impossible to have both coordinate systems parallel. To obtain an expression that is valid under these conditions, we must rotate through the Eulerian angles $\psi\theta\phi$[32] the coordinate axes to which one of the orbital operators $u_{q_i}^{[k_i]}(i)$ is referred. The irreducible-tensor operators $u_{q_2}^{[k_2]}(2)$ are related by rotation matrices[32] to the operators $u_{q_2'}^{[k_2]}(2')$ referred to axes at angles $\psi\theta\phi$ with respect to the original;

$$u_{q_2}^{[k_2]}(2) = \sum_{q_2'} \mathfrak{D}_{q_2q_2'}^{[k_2]}(\psi\theta\phi)u_{q_2'}^{[k_2]}(2').$$

By placing this operator in Eq. (15′) we find that the orbital part of the exchange operator appropriate for nonparallel coordinate systems is

$$\sum_{k_1k_2\Lambda'm'} -\Gamma_{m'}^{[\Lambda']}(1,2')[u^{[k_1]}(1)\times u^{[k_2]}(2')]_{m'}^{[\Lambda']}, \qquad (16)$$

where

$$\Gamma_{m'}^{[\Lambda']}(1,2') \equiv \sum_{\Lambda m} ([\Lambda'][\Lambda])^{1/2}\Gamma_m^{[\Lambda]}(1,2')$$
$$\times \sum_{q_1q_2q_2'} \bar{V}(k_1k_2\Lambda;\,q_1q_2m)\mathfrak{D}_{q_2q_2'}^{[k_2]*}(\psi\theta\phi)$$
$$\times \bar{V}(k_1k_2\Lambda';\,q_1q_2'm').$$

The expression for the rotated spin operators is readily found from the above formula by setting $\Gamma_{k_1k_2\Lambda} = \sqrt{3}$, $k_1 = k_2 = 1$, and $\Lambda = m = 0$:

$$\mathbf{s}_1\cdot\mathbf{s}_2 = \sqrt{3}[\mathbf{s}^{[1]}(1)\times\mathbf{s}^{[1]}(2)]^{[0]}$$
$$= \sum_{\Lambda'=0,1,2} \sum_{m'} \Delta_{m'}^{[\Lambda']}[\mathbf{s}^{[1]}(1)\times\mathbf{s}^{[1]}(2')]_{m'}^{[\Lambda']},$$

where

$$\Delta_{m'}^{[\Lambda']} \equiv [\Lambda']^{1/2} \sum_{q_1q_2} (-)^{1-q_2}\mathfrak{D}_{q_1q_2}^{[1]}\bar{V}(11\Lambda';\,q_1-q_2m').$$

It is immediately apparent that, where other interactions require us to use nonparallel coordinate systems, the form of the exchange interaction is changed, e.g., the product of the spin operators is no longer a scalar, but contains first- and second-rank irreducible tensor products ($\Lambda' = 1$, 2) representing antisymmetric and pseudodipolar anisotropies, respectively.

For situations in which it is best to work in a jm_j representation, we couple together the spin and orbital angular momentum operators in Eq. (15):

$$[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)\times\mathbf{C}^{[\Lambda]}]^{[0]}\mathbf{s}(1)\cdot\mathbf{s}(2) = \sqrt{3}[\Lambda]^{-1/2}\sum_m C_m^{[\Lambda]*}[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)]_m^{[\Lambda]}[\mathbf{s}^{[1]}(1)\times\mathbf{s}^{[1]}(2)]^{[0]}.$$

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[31] The expression inside the matrix element in Eq. (15) is called the exchange operator.

[32] See Ref. 18, pp. 21–23 and 29–30.

Therefore, this coupling is equivalent to a recoupling of four angular momenta[33]

$$\sqrt{3}[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)]_m{}^{[\Lambda]}[\mathbf{s}^{[1]}(1)\times\mathbf{s}^{[1]}(2)]^{[0]}$$

$$=\sqrt{3}\sum_{r_1=|k_1-1|}^{k_1+1}\sum_{r_2=|k_2-1|}^{k_2+1}([\Lambda][r_1][r_2])^{1/2}X(k_1k_2\Lambda/110/r_1r_2\Lambda)[[\mathbf{U}^{[k_1]}(1)\times\mathbf{s}^{[1]}(1)]^{[r_1]}\times[\mathbf{U}^{[k_2]}(2)\times\mathbf{s}^{[1]}(2)]^{[r_2]}]_m{}^{[\Lambda]}$$

$$=\sum_{r_1r_2}(-)^{k_1+r_2+\Lambda+1}([r_1][r_2])^{1/2}\bar{W}(k_1k_2\Lambda/r_2r_11)[\mathfrak{j}^{[r_1]}(1)\times\mathfrak{j}^{[r_2]}(2)]_m{}^{[\Lambda]},$$

where

$$\mathfrak{j}_{m_i}{}^{[r_i]}\equiv[\mathbf{u}^{[k_i]}\times\mathbf{s}^{[1]}]_{m_i}{}^{[r_i]}.$$

In the coupled jm_j representation the *spin-dependent* part of the exchange integral, Eq. (15), is written as[34]

$$(\phi_{j_a}{}'\phi_{j_b}{}'|\sum_{k_1k_2\Lambda}\sum_{r_1r_2}-\Gamma_{k_1k_2\Lambda}{}^{r_1r_2}[\mathfrak{j}^{[r_1]}(1)\times\mathfrak{j}^{[r_2]}(2)\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}|\phi_{j_a}\phi_{j_b}),\tag{17}$$

where

$$\Gamma_{k_1k_2\Lambda}{}^{r_1r_2}\equiv(-)^{k_1+r_2+\Lambda+1}2([r_1][r_2])^{1/2}\bar{W}(k_1k_2\Lambda/r_2r_11)\Gamma_{k_1k_2\Lambda}$$

and $\phi_{j_\alpha}\equiv|j_\alpha m_{j_\alpha})$. The spin-independent term is the same as in Eq. (15).

When we decouple the triple product, this operator can be rewritten as

$$-\sum_{k_1k_2}\sum_{r_1r_2m_1m_2}\Gamma_{m_1m_2}{}^{r_1r_2}(k_1k_2)\mathfrak{j}_{m_1}{}^{[r_1]}(1)\mathfrak{j}_{m_2}{}^{[r_2]}(2),\tag{17$'$}$$

where

$$\Gamma_{m_1m_2}{}^{r_1r_2}(k_1k_2)\equiv\sum_{\Lambda m}\Gamma_{k_1k_2\Lambda}{}^{r_1r_2}C_m{}^{[\Lambda]}\bar{V}(r_1r_2\Lambda;\,m_1m_2m).$$

When it is necessary to refer the exchange interaction to nonparallel coordinate systems, we follow the same procedure used to arrive at Eq. (16); we find that the *spin-dependent* part of the exchange integral is written as

$$-\sum_{r_1r_2}\sum_{k_1k_2\Lambda'm'}\bar{\Gamma}_{m'}{}^{[\Lambda']}(1,2')[\mathfrak{j}^{[r_1]}(1)\times\mathfrak{j}^{[r_2]}(2')]_{m'}{}^{[\Lambda']},\tag{18}$$

where

$$\bar{\Gamma}_{m'}{}^{[\Lambda']}(1,2')\equiv\sum_{\Lambda m}([\Lambda'][\Lambda])^{1/2}\bar{\Gamma}_m{}^{[\Lambda]}(1,2)$$

$$\times\sum_{m_1m_2m_2'}\bar{V}(r_1r_2\Lambda;\,m_1m_2m)\mathfrak{D}_{m_2m_2'}{}^{[r_2]*}(\psi\theta\phi)$$

$$\times\bar{V}(r_1r_2\Lambda;\,m_1m_2'm'),$$

and

$$\bar{\Gamma}_m{}^{[\Lambda]}(1,2)\equiv[\Lambda]^{-1/2}\Gamma_{k_1k_2\Lambda}{}^{r_1r_2}C_m{}^{[\Lambda]*}(\Omega_{ab}).\tag{18$'$}$$

This completes the derivation of the various expansions for the two-center two-electron exchange integral. We now proceed to discuss some properties of these expansions and relate the expansion coefficients $\Gamma_{k_1k_2\Lambda}$ to the matrix elements of the exchange interaction, i.e., to the exchange constants $J(m_a'm_b',m_am_b)$.

III. PROPERTIES OF TWO-CENTER EXCHANGE INTERACTIONS

We now use the explicit operator expressions Eqs. (15)–(18) to discuss the properties of two-center exchange interactions. In the most general situation possible, we have off-diagonal matrix elements between states whose orbital angular momenta l_α differ, i.e., $l_\alpha'\neq l_\alpha$.[35] For this case, the only restrictions on the ranks of the operators entering Eq. (15) are that their magnitudes are limited by the angular momenta of the states

$$|l_\alpha'-l_\alpha|\leqslant k_i\leqslant l_\alpha'+l_\alpha\tag{19}$$

and

$$|k_1-k_2|\leqslant\Lambda\leqslant k_1+k_2.$$

The label α refers to the quantum numbers specifying the wave function of the electron, and the label i refers to the electron.

The matrix elements of the exchange interaction form a Hermitian matrix, as can be seen by taking the transposed complex conjugate of the matrix element, Eq. (8). However, the operator in Eq. (15) is *not* Hermitian in the manifold of states spanned by the orbitals ϕ_α.

The Hermitian adjoint of the triple product follows from the definitions of the operators $u_{q_i}{}^{[k_i]}$, Eq. (11), and the spherical harmonic $C_m{}^{[\Lambda]}$ (see Refs. 18, 29):

$$[\mathbf{u}^{[k_1]}\times\mathbf{u}^{[k_2]}\times\mathbf{C}^{[\Lambda]}]^{[0]\dagger}$$

$$=(-)^{l_a'-l_a+l_b'-l_b}[\mathbf{u}^{[k_1]}\times\mathbf{u}^{[k_2]}\times\mathbf{C}^{[\Lambda]}]^{[0]}.\tag{20a}$$

The complex conjugate of the coefficient $\Gamma_{k_1k_2\Lambda}$, Eq. (15), is

$$\Gamma_{k_1k_2\Lambda}{}^*(n_a'l_a'n_b'l_b',n_al_an_bl_b)$$

$$=(-)^{k_1+k_2+\Lambda}\Gamma_{k_1k_2\Lambda}(n_a'l_a'n_b'l_b',n_al_an_bl_b).\tag{20b}$$

Combining these two parts, we see that the operator in Eq. (15) is not Hermitian. But this is to be expected because the coefficients $\Gamma_{k_1k_2\Lambda}$ depend on the radial part

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[33] See Ref. 18, Eq. (12.11).

[34] In the definition of the coefficient $C_m{}^{[l]}(l_1l_2,j_1j_2,\hat{R})$ in Ref. 17, the phase factor $(-)^{l_1+j_2+l+1}$ was erroneously omitted. We are indebted to Dr. G. M. Copland for pointing this out to us.

[35] It is sufficient that $l_\alpha'\neq l_\alpha$, but it is also possible for the principal quantum numbers to differ.

of the wave functions. If, in addition, we take the "*transpose*" of the coefficient $\Gamma_{k_1k_2\Lambda}$, we find

$$\Gamma_{k_1k_2\Lambda}(n_a'l_a'n_b'l_b',n_al_an_bl_b) \\ =(-)^{l_a'-l_a+l_b'-l_b+k_1+k_2+\Lambda}\Gamma_{k_1k_2\Lambda} \\ \times(n_al_an_bl_b,n_a'l_a'n_b'l_b'). \quad (20c)$$

Combining the three operations in Eqs. (20a)–(20c), we find that the operator expression in Eq. (15) is Hermitian for manifolds spanned by the wave functions ψ_α, Eq. (3), but not for the orbitals ϕ_α. For this reason, we refrain from calling the operator in Eq. (15) for $l_\alpha'\neq l_\alpha$ a Hamiltonian.

An operator is time-even or time-odd according to whether the time-reversal transformation gives the Hermitian adjoint of the operator or its negative.[36] The time-reverse of the operator $u_q^{[k]}$ is[37]

$$\theta^{-1}u_q^{[k]}\theta=(-)^q u_{-q}^{[k]}=(-)^{l_\alpha'-l_\alpha-k}u_q^{[k]\dagger}, \quad (21a)$$

and that for the spherical harmonic $C_m^{[\Lambda]}$ is

$$\theta^{-1}C_m^{[\Lambda]}\theta=(-)^m C_{-m}^{[\Lambda]}=(-)^\Lambda C_m^{[\Lambda]*}. \quad (21b)$$

By using these relations we find that the time-reverse of the exchange operator Eq. (15) is equal to its Hermitian adjoint. Therefore, the operator and the exchange interaction are invariant under time reversal, as all electrostatic interactions should be.

So that we can discuss the nature of the anisotropy present in two-center exchange interactions, we give the following definitions. When the rank Λ is zero, the ranks of the operators representing the anisotropy k_1 and k_2 are equal, and the interaction is *isotropic*. This is exactly the *form* of Racah's result for the one-center exchange interaction, see Eq. (1). When Λ is nonzero the interaction is *anisotropic*. When the ranks k_1 and k_2 are equal, the anisotropy is symmetric or antisymmetric depending on whether the rank Λ is even or odd;[38] when the ranks are not equal, we define the anisotropy as asymmetric.[39] For the case considered above $l_\alpha'\neq l_\alpha$, the three types of anisotropy are present.

When we consider a manifold for which the orbitals for the two electrons are identical, i.e., $n_a'l_a'=n_b'l_b'$ and $n_al_a=n_bl_b$, the two-electron system has a center of inversion, and we find that only *even* values of the rank Λ are possible. This restriction arises from the properties of the $\bar{V}$ symbols in $\Gamma_{k_1k_2\Lambda}$, Eq. (15), so that they do not vanish.[23] In addition, when the ions are identical the coefficients $\Gamma_{k_1k_2\Lambda}$ and $\Gamma_{k_2k_1\Lambda}$ are related. It is difficult to ascertain the relation from Eq. (15) because in the expansion of the exchange integral [see Eqs. (6) and (8)] the two centers are not treated on an equal basis. However, we arrive at the relation by equating two indistinguishable matrix elements:

$$J_{k_1k_2\Lambda}(\phi_a'\phi_a)\equiv(\phi_a'(1)\phi_a'(2) \\ \times|\Gamma_{k_1k_2\Lambda}[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}|\phi_a(1)\phi_a(2))$$

and a similar expression for $J_{k_2k_1\Lambda}$. The two matrix elements are equal, and by using the definition of the triple product, Eq. (13), we find the desired relation between coefficients

$$\Gamma_{k_2k_1\Lambda}=(-)^{k_1+k_2+\Lambda}\Gamma_{k_1k_2\Lambda} \\ =(-)^{k_1+k_2}\Gamma_{k_1k_2\Lambda} \quad (\Lambda\text{ even}). \quad (22)$$

The condition that Λ must be even rules out antisymmetric exchange interactions ($k_1=k_2$, $k_1+k_2+\Lambda=\text{odd}$), as can be seen from Eq. (15′). However, if other interactions are present and must be taken into account, the sites occupied by the two electrons may not be equivalent.[40] No simple relation between the Γ's exists and now, when the exchange integral Eq. (15) is written in the coordinate axes suitable to other interactions, antisymmetric exchange is possible because the rank Λ' in Eq. (16) need not be even.

If we confine Eq. (15) to situations in which interatomic forces are small compared to the intra-atomic forces, e.g., in the rare-earth salts, only one l,s manifold need be considered, so that $n_\alpha'l_\alpha'=n_\alpha l_\alpha$. The conditions on the ranks in the $\bar{V}$ symbols in $\Gamma_{k_1k_2\Lambda}$ require that the allowable values of the rank Λ be even. Another condition is obtained by setting $n_\alpha'l_\alpha'=n_\alpha l_\alpha$ in Eq. (20c); we find that the sum of the ranks $k_1+k_2+\Lambda$ must be even so that the coefficient $\Gamma_{k_1k_2\Lambda}$ does not vanish. Under these conditions, the operator in Eq. (15) is Hermitian [see Eqs. (20)] and the coefficients $\Gamma_{k_1k_2\Lambda}$ are *real*. Only symmetric exchange is possible under these conditions [see Eq. (15′)]. However, if other interactions require us to choose coordinate axes for the two electrons which are not parallel to one another, we see from Eq. (16) that antisymmetric exchange enters even when each electron is in a definite orbital ($l_\alpha'=l_\alpha$).

When we consider ions for which the states of the electrons are described in a jm_j representation, we ascertain from the conditions already determined for the ranks k_1 and k_2 what the conditions will be on the ranks r_1 and r_2 entering Eq. (17). For $l_\alpha'=l_\alpha$, but for different *total* angular momentum of the states of each ion $j_\alpha'\neq j_\alpha$, there are no conditions on the ranks of the operators representing the anisotropy r_1 and r_2. When we confine our attention to one j manifold for each ion, i.e., $j_\alpha'=j_\alpha$, the matrix elements of the operator $\mathbf{j}^{[r_i]}$ vanish unless the sum k_i+r_i+1 is even.[41] As the sum of the ranks k_1 and k_2 must be even, this condition on the r_i

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[36] See Ref. 26, pp. 59–63, and A. Abragam, lecture notes on the use of angular momentum operators in crystal-field theory (unpublished).

[37] See Eq. (11), and Ref. 9, Eq. (B3).

[38] The definitions of symmetric and antisymmetric exchange follow from the change in sign of the triple product Eq. (13), used to represent the anisotropy, when the two operators are interchanged. See Ref. 18, p. 51.

[39] All asymmetric exchange can be classified as symmetric or antisymmetric; therefore, this category does not define a new symmetry class.

[40] When other interactions are taken into account we no longer have true two-center exchange. However, the form of the exchange operator Eq. (16) is still valid. Only the coefficients $\Gamma_m^{[\Lambda]}$ are changed; they are not related to the radial integrals as in Eq. (15).

[41] This condition is arrived at by evaluating the reduced matrix element of the operator $\mathbf{j}^{[r]}\equiv[\mathbf{u}^{[k]}\times\mathbf{s}^{[1]}]^{[r]}$ in a j state. See Ref. 18, Eq. (15.4), $(lsj\|[\mathbf{u}^{[k]}\times\mathbf{s}^{[1]}]^{[r]}\|lsj)=[j][r]^{1/2}(l\|\mathbf{u}^{[k]}\|l)(\frac{1}{2}\|\mathbf{s}^{[1]}\|\frac{1}{2})\times X(llk/\frac{1}{2}\frac{1}{2}1/jjr)$. By permuting the two identical columns, we find that the 9-j symbol vanishes unless $k+r+1$ is even.

requires that the sum of the ranks r_1+r_2 be even. Together with the condition that the rank Λ must be even, only symmetric exchange is possible. When other interactions require us to choose nonparallel coordinate axes, we see from Eq. (18) that the rank Λ' is not restricted to even values and that antisymmetric exchange is possible, even when the electrons are in definite j states.

So far we have given the matrix elements of the two-center exchange interaction, Eq. (2), in terms of the coefficients $\Gamma_{k_1k_2\Lambda}$. For these coefficients to be of maximum usefulness, it is necessary to relate them to the conventional exchange constants, which we define as the matrix elements of the *orbital* part of the exchange interaction in Eq. (15)

$$J(\psi_a'\psi_b';\psi_a\psi_b)\equiv(\phi_a'(1)\phi_b'(2)|\sum_{k_1k_2\Lambda}\Gamma_{k_1k_2\Lambda}(n_a'l_a'n_b'l_b',n_al_an_bl_b)[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}|\phi_a(1)\phi_b(2)). \quad (23)$$

In the present context, $\psi_\alpha\equiv n_\alpha l_\alpha m_\alpha$ and $\phi_\alpha\equiv l_\alpha m_\alpha$. Hereafter, we suppress the labels $n_\alpha l_\alpha$ in designating the exchange constant J. By using this definition, we can write the exchange interaction in a more conventional form as

$$-J(m_a'm_b',m_am_b)(\tfrac{1}{2}+2\mathbf{s}_1\cdot\mathbf{s}_2). \quad (24)$$

Most of the work on two-center exchange integrals is presented in the form of exchange constants. To find the value of the coefficients $\Gamma_{k_1k_2\Lambda}$ from these constants, we have to invert the relation between the two, Eq. (23). We start by uncoupling the triple product and by evaluating the matrix elements of the operators $u_{q_i}^{[k_i]}$. Then we use the unitary transformation properties of the $\bar{V}$ symbols in the form[42]

$$\sum_{q_1q_2}\bar{V}(k_1k_2l;\,q_1q_2m)\bar{V}(k_1k_2l';\,q_1q_2m')=[l]^{-1}\delta_{ll'}\delta_{mm'} \quad (25)$$

and the sum rule for spherical harmonics[43]

$$\sum_m|C_m^{[\Lambda]}|^2=1.$$

The resulting expression is recoupled into a triple product, and we find that the coefficients are given in terms of the exchange constants by the following relation:

$$\Gamma_{k_1k_2\Lambda}(n_a'l_a'n_b'l_b',n_al_an_bl_b)=[k_1][k_2][\Lambda]$$
$$\times\sum_{m_a'm_b'm_am_b}J(m_a'm_b',m_am_b)$$
$$\times(\phi_a'\phi_b'|[\mathbf{u}^{[k_1]}\times\mathbf{u}^{[k_2]}\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}|\phi_a\phi_b)^*. \quad (26)$$

Now the preceeding discussion of the properties of the coefficients Γ can be used to determine the properties of the exchange constants J. Most important, we can obtain from the above relations the number of independent parameters necessary to describe a two-center exchange interaction.[44] The relations Eqs. (23) and (26) provide a one-to-one correspondence between the coefficients $\Gamma_{k_1k_2\Lambda}$ and the constants $J(m_a'm_b',m_am_b)$; therefore, *the number of independent constants J equals the number of different coefficients* Γ. This number is readily found by counting the different combinations of the three ranks of the operators in Eq. (15) subject to the conditions given in Eq. (19) and any further restrictions when the interaction is evaluated in certain manifolds.

In the most general case of two-center exchange where the angular momenta of each of the electron states differ, i.e., $l_\alpha'\neq l_\alpha$, the number of coefficients is

$$N(l_a'l_b',l_al_b)=\sum_{k_1=\delta_a}^{\sigma_a}\sum_{k_2=\delta_b}^{\sigma_b}\sum_{\Lambda=|k_1-k_2|}^{k_1+k_2}1$$
$$=\tfrac{1}{3}\delta_a(\delta_a-1)(\delta_a-3\sigma_b-2)+\tfrac{1}{3}\sigma_b(\sigma_b+1)(3\sigma_a-\sigma_b+1)$$
$$+(\sigma_a-\delta_a+1)(\sigma_b-\delta_b^2+1), \quad (27)$$

provided the ranks k_1 and k_2 have some values in common, and $l_a^>$ is greater than or equal to $l_b^>$. In this formula $\delta_\alpha\equiv l_\alpha^>-l_\alpha^<$, $\sigma_\alpha\equiv l_\alpha^>+l_\alpha^<$; $l_\alpha^>$ is the larger of the angular momenta l_α' and l_α of the states of the ion α, and $l_\alpha^<$ is the smaller of the two. If the angular momentum $l_b^>$ is greater than $l_a^>$ we reverse the labels on the δ's and σ's in Eq. (27). If the angular momenta of the states are such that the ranks k_1 and k_2 have no values in common, and if $l_a^>\geqslant l_b^>$, the number of coefficients is

$$N(l_a'l_b',l_al_b)=(\sigma_a-\delta_a+1)(\sigma_b^2-\delta_b^2+2\sigma_b+1). \quad (27')$$

For $l_a^><l_b^>$, the labels on the δ's and σ's are reversed. The total number of exchange constants J is found by counting the different combinations of the four spatial quantum numbers m_a', m_b', m_a, and m_b. This number is simply

$$\sum_{m_a'=-l_a'}^{l_a'}\sum_{m_b'=-l_b'}^{l_b'}\sum_{m_a=-l_a}^{l_a}\sum_{m_b=-l_b}^{l_a}1=[l_a'][l_b'][l_a][l_b]. \quad (28)$$

When we actually evaluate these numbers, Eqs. (27) and (28), for several cases, we are readily convinced that the number of coefficients—and hence the number of independent exchange constants—necessary for two-center exchange, Eqs. (27), is considerably less than the

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[42] See Ref. 18, Eq. (10.17).

[43] See A. R. Edmonds, Ref. 22, p. 63. The above sum rule is derived from Eq. (4.6.7) for $\theta=\theta'$ and $\phi=\phi'$, so that $\cos\omega=1$ and $P_l(1)=1$. This sum rule has the same form in the phase conventions of both Edmonds, and Fano and Racah.

[44] If we evaluate the radial integrals in the coefficients $\Gamma_{k_1k_2\Lambda}$ [see Eq. (15)] there are no undetermined parameters. However, unless nonorthogonal orbitals are used it is unrealistic to evaluate the exchange coefficients from Eq. (15). Therefore, we consider the different coefficients as *independent* parameters to be empirically determined.

number given by Eq. (28). As we will see in the last section, by relating the exchange constants $J(m_a'm_b',m_am_b)$ to the coefficients $\Gamma_{k_1k_2\Lambda}$ we considerably reduce the number of constants necessary to describe an exchange interaction.

When we confine the states of each ion to one l manifold so that $l_\alpha'=l_\alpha$, the rank Λ and the sum of the ranks k_1 and k_2 must be even. Under these conditions the number of coefficients is:

$$N(l_al_b)=\sum_{k_1=0}^{2l_a}\sum_{k_2=0}^{2l_b}\sum_{\Lambda=|k_1-k_2|}^{k_1+k_2} 1 \quad k_1+k_2=\text{even},\quad \Lambda=\text{even}$$

$$=l_>(l_<+1)(2l_<+1)-\tfrac{1}{3}l_<(2l_<^2-5)+1\,, \qquad (29)$$

where $l_>$ is the greater of the angular momenta l_a and l_b, and $l_<$ is the smaller of the two. If the ions are *identical* so that $l_a=l_b$, the number given by Eq. (29) is further reduced because $\Gamma_{k_1k_2\Lambda}=\Gamma_{k_2k_1\Lambda}$, see Eq. (22) ($k_1+k_2$ is even for this case). When other interactions are taken into account cases may arise in which the ions are identical, $l_a=l_b$ but the sites are inequivalent so that $\Gamma_{k_1k_2\Lambda}\neq\Gamma_{k_2k_1\Lambda}$ and there is no further reduction of the number given by Eq. (29).

IV. HAMILTONIAN FOR *N*-ELECTRON EXCHANGE INTERACTION

It was Dirac[2] who first showed that when we calculate the perturbation due to Coulomb forces the whole perturbation matrix, including the permutation degeneracy of the electrons $(P_a\Psi|V|P_b\Psi)$, is equal to the matrix of the operator $\sum_P V_PP$.[45] The summation is over the $n!$ permutations P of the n electrons amongst the orbitals of the unperturbed system. In a manifold spanned by these orbitals the perturbation V can be written as

$$V\doteq\sum_P V_PP=V_1+\sum_{r<s} V_{rs}P_{rs}$$
$$+\text{higher-order permutations}, \qquad (30)$$

where the operator P_{rs} interchanges a single pair of electrons amongst the available orbitals. If the orbitals are orthogonal, all higher-order permutations give zero matrix elements because the Coulomb interaction is a two-particle interaction.[45] However, for nonorthogonal orbitals the magnitudes of the matrix elements of the Coulomb interaction for the higher-order permutations are proportional to the overlap of the orbitals containing the interchanged electrons.[46] For materials in which the magnetic ions are well separated, the overlap of the orbitals is small. Therefore, Eq. (30) can be viewed as a perturbation expansion where overlap is the small parameter, and we approximate the true Coulomb interaction between electrons on well-separated ions by including only the identity and single-pair permutations[46]

$$V\cong V_1+\sum_{r<s} V_{rs}P_{rs}\,, \qquad (30')$$

where

$$P_{rs}=-\{\tfrac{1}{2}+2\mathbf{s}_1\cdot\mathbf{s}_2\}\,.$$

The first term V_1 gives rise to the direct Coulomb interaction, while the second term is the conventional exchange interaction.

When we have only one electron per ion, Eq. (30) terminates because it is impossible to interchange more than one pair of electrons; for this case the above expression Eq. (30′) is exact. However, for N electrons per ion the conventional exchange interaction is an *approximation* which is valid for systems where the overlap between the orbitals is small.

Derivation

In the approximation where we neglect both higher-order permutations, and the nonorthogonality of the electron orbitals, the Coulomb exchange interaction between the electrons on different ions is[47]

$$\mathcal{H}_{ex}=-\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}\frac{e^2}{r_{ij}}P_{ij}\,. \qquad (31)$$

Since we are interested in the interatomic exchange interaction, we are evaluating the exchange energy between states $\Psi_\alpha(i)$ that have been properly antisymmetrized with respect to the N_α *equivalent* electrons on the ion. Also, since we assume that overlap is negligible, the interatomic forces are small compared to the intra-atomic forces, and we confine our derivation to one orbital configuration, i.e., $l_\alpha'=l_\alpha$ for all N_α electrons. In the following derivation, we only consider cases where intra-atomic electrostatic interactions are greater than the spin-orbit couplings of the electrons so that the Russell-Saunders coupling scheme is valid, i.e., the total orbital angular momentum $\sum_i \mathbf{l}_i=\mathbf{L}$ and the total spin $\sum_i \mathbf{s}_i=\mathbf{S}$ are good quantum numbers. With this condition, and the assumption of negligible overlap, it is unnecessary to consider the matrix elements of the exchange interaction between atomic states of different $\mathbf{L}_\alpha$ and $\mathbf{S}_\alpha$; however, we will do so in the derivation so that our results are complete.

The exchange integral we consider is

$$\left(\Psi_a'(1)\Psi_b'(2)\left|-\sum_{i=1}^{N_a}\sum_{j=1}^{N_b}\frac{e^2}{r_{ij}}P_{ij}\right|\Psi_a(1)\Psi_b(2)\right), \qquad (32)$$

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[45] The extension of Dirac's result to several orbital configurations is given by R. Serber, Phys. Rev. **45**, 461 (1943).

[46] See article by C. Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York. 1966), Vol. IIB, Secs. II and III.

[47] There is no need to restrict the sums over the electrons because the field of numbers $\{i\}$ which refer to electrons on ion A, does not overlap with the set $\{j\}$, which refers to electrons on ion B. Also, we now call the operator expression, Eq. (31), a Hamiltonian, because we are restricting its use to manifolds of definite orbital angular momentum, i.e., $l_\alpha'=l_\alpha$. The operator is Hermitian in these manifolds.

where

$$\Psi_\alpha \equiv \left(\prod_{i=1}^{N_\alpha} R_{n_\alpha l_\alpha}(r_i) \right) \Phi_\alpha$$

and

$$\Phi_\alpha \equiv \rrbracket l_\alpha{}^{N_\alpha} L_\alpha M_{L_\alpha} S_\alpha M_{S_\alpha} \rangle .$$

This wave function is centered about ion α and is antisymmetrized with respect to the N_α equivalent electrons on the ion. Although the operator e^2/r_{ij} is a two-electron operator, it operates on two different antisymmetrized sets of states. Therefore, with respect to each ion, the interatomic exchange operator is a one-electron operator. A method has been developed by Racah[48] for evaluating the matrix elements of one-electron operators in antisymmetrized states of N equivalent electrons. The idea behind his method is to fractionate one electron from the total wave function for the N_α electrons and then to evaluate the matrix element of the operator Eq. (31) between the fractionated states. By following this approach, the wave function Φ_α is written as

$$\rrbracket l_\alpha{}^{N_\alpha} L_\alpha M_{L_\alpha} S M_{S_\alpha} \rangle = \sum_{L_\alpha' S_\alpha'} (l_\alpha{}^{N_\alpha - 1}(L_\alpha' S_\alpha'), l_\alpha L_\alpha S_\alpha \rrbracket l_\alpha{}^{N_\alpha} L_\alpha S_\alpha) \quad \rrbracket l_\alpha{}^{N_\alpha - 1}(L_\alpha' S_\alpha'), l_\alpha L_\alpha M_{L_\alpha} S_\alpha M_{S_\alpha} \rangle , \tag{33}$$

where $(l_\alpha{}^{N_\alpha - 1}(L_\alpha' S_\alpha'), l_\alpha L_\alpha S_\alpha \rrbracket l_\alpha{}^{N_\alpha} L_\alpha S_\alpha)$ is a coefficient of fractional parentage. The state

$$\rrbracket l_\alpha{}^{N_\alpha - 1}(L_\alpha' S_\alpha'), l_\alpha L_\alpha M_{L_\alpha} S_\alpha M_{S_\alpha} \rangle$$

is antisymmetrized with respect to the $N_\alpha - 1$ electrons; the last electron is coupled to the $N_\alpha - 1$ electrons to form $L_\alpha S_\alpha$, but it is *not* antisymmetrized. The matrix element of the exchange interaction between the fractionated states is exactly that given by Eq. (15), where *now* $n_\alpha' l_\alpha' = n_\alpha l_\alpha$. Therefore, by following Racah's procedure we find that the matrix element of the exchange interaction Eq. (32) can be rewritten as

$$\left(\Psi_a' \Psi_b' \left| \sum_{i=1}^{N_a} \sum_{j=1}^{N_b} -\frac{e^2}{r_{ij}} P_{ij} \right| \Psi_a \Psi_b \right)$$

$$= \left(\Phi_a' \Phi_b' \left| \sum_{i,j=1}^{N_a \; N_b} \sum_{k_1 k_2 \Lambda} -\Gamma_{k_1 k_2 \Lambda}(n_a l_a, n_b l_b) [\mathbf{u}^{[k_1]}(i) \times \mathbf{u}^{[k_2]}(j) \times \mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]} \times (\tfrac{1}{2} \times 2\sqrt{3} [\mathbf{s}^{[1]}(i) \times \mathbf{s}^{[1]}(j)]^{[0]}) \right| \Phi_a \Phi_b \right) . \tag{34}$$

The coefficients $\Gamma_{k_1 k_2 \Lambda}(n_a l_a, n_b l_b)$ are the *same* for all N_α equivalent electrons, and the operators in this matrix element act on one of the electrons in the multielectron wave functions. We want to rewrite Eq. (34) in terms of operators of the same rank and component as the one-electron operators, but which act on the entire antisymmetrized and coupled multielectron wave functions. The relation between the two operators is found by using the Wigner-Eckart theorem for double tensors[49]

$$\sum_{i=1}^{N_\alpha} u_q{}^{[k]}(i) s_{m_s}{}^{[K]}(i) \doteq \frac{(l_\alpha{}^{N_\alpha} L_\alpha' S_\alpha' \| \sum_i \mathbf{u}^{[k]}(i) \mathbf{s}^{[K]}(i) \| l_\alpha{}^{N_\alpha} L_\alpha S_\alpha)}{(L_\alpha' S_\alpha' \| \mathbf{U}^{[k]} \mathfrak{S}^{[K]} \| L_\alpha S_\alpha)} U_q{}^{[k]}(\alpha) \mathfrak{S}_{m_s}{}^{[K]}(\alpha) , \tag{35}$$

where $K = 0, 1$. The operators $\mathbf{s}^{[0]}$ and $\mathfrak{S}^{[0]}$ are defined by their reduced matrix elements $[S_\alpha]^{1/2} \delta_{S_\alpha' S_\alpha}$. The operator $\mathfrak{S}_{m_s}{}^{[1]}$ is the same as the conventional spin operator when $S_\alpha' = S_\alpha$, but, for off-diagonal elements in which $S_\alpha' \neq S_\alpha$, we define the operator by its reduced matrix element

$$(S_\alpha' \| \mathfrak{S}^{[1]} \| S_\alpha) = (-1)^{\frac{1}{2}(S_\alpha' - S_\alpha - 1)} . \tag{36}$$

The operator $U_q{}^{[k]}$ is defined in the same way as the operator $u_q{}^{[k]}$ [see Eq. (11)]. Although the orbital and spin angular momenta are not coupled together in the sense of an irreducible product, they are related by the antisymmetrization of the multielectron wave functions. Therefore, it is not possible to factorize the reduced matrix element

$$(l^N L' S' \| \sum_i \mathbf{u}^{[k]}(i) \mathbf{s}^{[K]}(i) \| l^N L S) \tag{37}$$

into separate orbital and spin reduced matrix elements. However the reduced matrix element in the denominator of Eq. (35) can be factorized immediately because the operators $\mathbf{U}(\alpha)^{[k]}$ and $\mathfrak{S}(\alpha)^{[K]}$ act on the *total* orbital and spin angular momenta.[50] By using the Wigner-Eckart theorem in the form of Eq. (35) we can write the exchange

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[48] G. Racah, Phys. Rev. **63**, 367 (1943); **76**, 1352 (1949).

[49] The concept of double tensors was introduced by G. Racah, see Ref. 14.

[50] To these operators the composition of a state is immaterial; only the total orbital and total spin angular momenta determine the value of their matrix elements.

integral Eq. (34) as[51]

$$(\Phi_a'\Phi_b'|-\sum_{k_1k_2\Lambda}\sum_{K=0,1}\Gamma_{k_1k_2\Lambda}{}^{(K)}(L_a'S_a'L_b'S_b',L_aS_aL_bS_b)[\mathbf{U}(a)^{[k_1]}\times\mathbf{U}(b)^{[k_2]}\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}$$
$$\times(\tfrac{1}{2}\delta_{K0}+2\delta_{K1}\mathfrak{S}(a)\cdot\mathfrak{S}(b))\,|\,\Phi_a\Phi_b)\,, \quad (38)$$

where

$$\Gamma_{k_1k_2\Lambda}{}^{(K)}\equiv\Gamma_{k_1k_2\Lambda}\prod_{\alpha=a,b}\frac{(l_\alpha{}^{N_\alpha}L_\alpha'S_\alpha'\|\sum_i{}^{N_\alpha}\mathbf{u}(i)^{[k_\alpha]}\mathbf{s}(i)^{[K]}\|l_\alpha{}^{N_\alpha}L_\alpha S_\alpha)}{(L_\alpha'S_\alpha'\|\mathbf{U}^{[k_\alpha]}\mathfrak{S}^{[K]}\|L_\alpha S_\alpha)}$$

and $k_\alpha=k_1$ for $\alpha=a$, and k_2 for $\alpha=b$. If we consider states still within the Russell-Saunders coupling scheme for which the spin-orbit coupling is appreciable, it is best to couple the operators $\mathbf{U}^{[k_\alpha]}(\alpha)$ and $\mathfrak{S}^{[K]}(\alpha)$ in Eq. (38) as we did in Eq. (17). In the LSJM$_J$ representation the exchange integral is written as

$$\left(\Phi_{J_a}{}'\Phi_{J_b}{}'\left|-\sum_{k_1k_2\Lambda r_1r_2}\sum_{K}\Gamma_{k_1k_2\Lambda}{}^{r_1r_2K}[\mathfrak{J}(K,a)^{[r_1]}\times\mathfrak{J}(K,b)^{[r_2]}\times C^{[\Lambda]}(\Omega_{ab})]^{[0]}\right|\Phi_{J_a}\Phi_{J_b}\right), \quad (39)$$

or, in an equivalent form,

$$-\sum_{k_1k_2K}\sum_{r_1r_2m_1m_2}\Gamma_{m_1m_2}{}^{r_1r_2K}(k_1k_2)\mathfrak{J}_{m_1}{}^{[r_1]}(K,a)\mathfrak{J}_{m_2}{}^{[r_2]}(K,b)\,. \quad (39')$$

The wave function $\Phi_{J_\alpha}\equiv|J_\alpha M_{J_\alpha}\rangle$, the coefficient

$$\Gamma_{k_1k_2\Lambda}{}^{r_1r_2K}\equiv(-)^{k_1+k_2+\Lambda+K}(\tfrac{1}{2}\delta_{K0}+2\delta_{K1})([r_1][r_2])^{1/2}\overline{W}(k_1k_2\Lambda/r_2r_1K)\Gamma_{k_1k_2\Lambda}{}^{(K)}\,,$$

the coefficient

$$\Gamma_{m_1m_2}{}^{r_1r_2K}(k_1k_2)\equiv\sum_{\Lambda m}\Gamma_{k_1k_2\Lambda}{}^{r_1r_2K}C_m{}^{[\Lambda]}(\Omega_{ab})\overline{V}(r_1r_2\Lambda;\,m_1m_2m)\,,$$

and

$$\mathfrak{J}_{m_\alpha}{}^{[r_\alpha]}(K,\alpha)\equiv[\mathbf{U}^{[k_\alpha]}(\alpha)\times\mathbf{S}^{[K]}(\alpha)]_{m_\alpha}{}^{[r_\alpha]}\,.$$

The reduced matrix elements are evaluated by the methods outlined in an earlier paper.[9,52] The result is

$$(l^NL'S'\|\sum_1^N{}_i\mathbf{u}^{[k]}(i)\mathbf{s}^{[K]}(i)\|l^NLS)=(-)^{L'+S'+l+\frac{1}{2}+k+K}N\sum_{\bar{\theta}}(-)^{\bar{L}+\bar{S}}(\theta\{|\bar{\theta})(\bar{\theta}|\}\theta')([L'][L][S'][S])^{1/2}$$
$$\times(l\|\mathbf{u}^{[k]}\|l)(\tfrac{1}{2}\|\mathbf{s}^{[K]}\|\tfrac{1}{2})\overline{W}(L'Lk/ll\bar{L})\overline{W}(S'SK/\tfrac{1}{2}\tfrac{1}{2}\bar{S})\,, \quad (37')$$

where

$$\theta\equiv l^NLS,\quad \theta'\equiv l^NL'S',\quad \bar{\theta}\equiv l^N\bar{L}\bar{S}\,.$$

The coefficients of fractional parentage $(\theta\{|\bar{\theta})$ for all d^N configurations have been tabulated by Racah[53] and those for f^N configurations by Nielson and Koster.[54] Racah[55] has also related the reduced matrix elements Eq. (37) of ions with more than half-filled shells to those for ions with less than half-filled shells.[56]

By collecting the results for the reduced matrix elements in Eq. (35) we obtain explicit expressions for the coefficients $\Gamma_{k_1k_2\Lambda}{}^{(K)}$. When we consider matrix elements of the exchange interaction between states of different orbital and spin angular momenta, we find

$$\Gamma_{k_1k_2\Lambda}{}^{(K)}=-(\tfrac{1}{2}\|\mathbf{s}^{[K]}\|\tfrac{1}{2})^2\Gamma_{k_1k_2\Lambda}\prod_{\alpha=a,b}(-)^{\frac{1}{2}(L_\alpha'+L_\alpha)+l_\alpha+S_\alpha'}N_\alpha([L_\alpha'][L_\alpha][S_\alpha'][S_\alpha])^{1/2}(S_\alpha'\|\mathfrak{S}^{[K]}\|S_\alpha)^{-1}$$
$$\times\sum_{\bar{\theta}_\alpha}(-)^{\bar{L}_\alpha+\bar{S}_\alpha}(\theta_\alpha\{|\bar{\theta}_\alpha)(\bar{\theta}_\alpha|\}\theta_\alpha')\overline{W}(L_\alpha'L_\alpha K_\alpha/l_\alpha l_\alpha\bar{L}_\alpha)\overline{W}(S_\alpha'S_\alpha K/\tfrac{1}{2}\tfrac{1}{2}\bar{S}_\alpha)\,, \quad (40)$$

where $k_\alpha=k_1$ for $\alpha=a$, and k_2 for $\alpha=b$. For matrix elements between states in an LS manifold we can replace the operators $U_{q_\alpha}{}^{[k_\alpha]}(\alpha)$ by angular momentum operators which transform in the same way as the irreducible tensors

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[51] Only the spin-dependent part of the exchange interaction Eq. (34) is relevant for strong crystal fields; however, when spin-orbit coupling is strong this is no longer true.

[52] Also see B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Co., New York, 1963), Chaps. 7 and 8.

[53] G. Racah (1943), see Ref. 48.

[54] C. W. Nielson and G. F. Koster, *Spectroscopic Coefficients for the p^n, d^n and f^n Configurations* (MIT Press, Cambridge, Mass., 1963); also G. Racah (1949), see Ref. 48.

[55] G. Racah (1942), see Ref. 14.

[56] Other relations among the reduced matrix elements have been given by P. M. Levy, see Ref. 9; and by B. R. Judd, see Ref. 52, Chap. 8.

$U_{q_\alpha}{}^{[k_\alpha]}$. These are called operator equivalents, and have been tabulated by Smith and Thornley.[57] In terms of operator equivalents, the *spin-dependent* part of the N-electron exchange Hamiltonian [see Eqs. (31) and (38)] takes the form

$$-\sum_{k_1k_2\Lambda} \Gamma_{k_1k_2\Lambda}{}^{(1)}(L_aS_a,L_bS_b)[\mathbf{O}^{[k_1]}(L_a)\times\mathbf{O}^{[k_2]}(L_b)\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}\mathbf{S}(a)\cdot\mathbf{S}(b)\,, \tag{41}$$

where now

$$\Gamma_{k_1k_2\Lambda}{}^{(1)}\equiv-\tfrac{3}{2}\Gamma_{k_1k_2\Lambda}\prod_{\alpha=a,b}(-)^{(L_\alpha+l_\alpha+k_\alpha+S_\alpha)}2^{k_\alpha}N_\alpha[L_\alpha]\{(2L_\alpha-k_\alpha)!(2S_\alpha+1)/(2L_\alpha+k_\alpha+1)!S_\alpha(S_\alpha+1)\}^{1/2}$$
$$\times\sum_{\bar\theta_\alpha}(-)^{\bar L_\alpha+\bar S_\alpha}|(\theta_\alpha[\![\bar\theta_\alpha)|^2\bar W(L_\alpha L_\alpha k_\alpha/l_\alpha l_\alpha\bar L_\alpha)\bar W(S_\alpha S_\alpha 1/\tfrac{1}{2}\tfrac{1}{2}\bar S_\alpha)\,.$$

The operator equivalent $O_{q_i}{}^{[k_i]}(L)$ is defined by its reduced matrix element [57]

$$(L\|\mathbf{O}^{[k_\alpha]}\|L)=\frac{(-)^{-\frac{1}{2}k_\alpha}}{2^{k_\alpha}}\left\{\frac{(2L+k_\alpha+1)!}{(2L-k_\alpha)!}\right\}^{\frac{1}{2}}\,. \tag{42}$$

When we confine our attention to the matrix elements of the exchange interaction between states having the same total angular momentum J, we replace the operators $\mathfrak{J}^{[r_\alpha]}$ by the operator equivalents $\mathbf{O}^{[r_\alpha]}(J_\alpha)$ and Eq. (39) is written in the following form:

$$\sum_{r_1r_2\Lambda}-\bar\Gamma_{r_1r_2\Lambda}[\mathbf{O}^{[r_1]}(J_a)\times\mathbf{O}^{[r_2]}(J_b)\times\mathbf{C}^{[\Lambda]}(\Omega_{ab})]^{[0]}\,, \tag{43}$$

where

$$\bar\Gamma_{r_1r_2\Lambda}\equiv\sum_{K=0,1}(\tfrac{1}{2}\delta_{K0}+2\delta_{K1})\sum_{k_1=|r_1-K|}^{r_1+K}\ \sum_{\substack{k_2=|r_2-K|\\ k_1+k_2=\text{even}}}^{r_2+K}(-)^{k_1+r_2+\Lambda+1}[r_1][r_2](\tfrac{1}{2}\|\mathbf{s}^{[K]}\|\tfrac{1}{2})^2\bar W(k_1k_2\Lambda/r_2r_1K)$$
$$\times\Gamma_{k_1k_2\Lambda}(n_al_a,n_bl_b)\prod_{\alpha=a,b}(-)^{\frac{1}{2}(k_\alpha+r_\alpha+K)}(-)^{(L_\alpha+S_\alpha+l_\alpha)}2^{r_\alpha}N_\alpha[L_\alpha][S_\alpha][J_\alpha]\{(2J_\alpha-r_\alpha)!/(2J_\alpha+r_\alpha+1)!\}^{1/2}$$
$$\times X(L_\alpha L_\alpha k_\alpha/S_\alpha S_\alpha K/J_\alpha J_\alpha r_\alpha)\sum_{\theta_\alpha}(-)^{\bar L_\alpha+\bar S_\alpha}|(\theta_\alpha[\![\bar\theta_\alpha)|^2\bar W(L_\alpha L_\alpha k_\alpha/l_\alpha l_\alpha\bar L_\alpha)\bar W(S_\alpha S_\alpha K/\tfrac{1}{2}\tfrac{1}{2}\bar S_\alpha)\,.$$

Only those operator equivalents enter whose ranks r_α are such that the sum $k_\alpha+r_\alpha+K$ is even; this can be seen by interchanging the two identical columns in the 9-j symbol and noting that the sign of the 9-j symbol is the negative of itself when $k_\alpha+r_\alpha+K$ is odd.

This completes our discussion of the appropriate Hamiltonians which are used to represent two-center exchange interactions for various conditions on the orbital and spin angular momentum manifolds. In this derivation we assumed that the radial integrals are identical for all N_α equivalent electrons. Consequently no new parameters enter over those in the two-electron exchange interaction Eq. (15), i.e., the $\Gamma_{k_1k_2\Lambda}$, and all the properties of the two-electron exchange interaction discussed in Sec. III, also apply to the N-electron interaction. For example, the number of independent parameters in the N-electron exchange interaction is still that given by Eqs. (27) and (29).

V. CONCLUSIONS AND DISCUSSION OF RESULTS

To obtain an idea of the anisotropy present in exchange interactions we evaluate our result, Eq. (15), for several cases. The simplest case possible is the one considered by Van Vleck,[8] that of the exchange between an s and p electron on different centers. The s electron is on the center B $l_b'=l_b=0$, and the p electron is on center A $l_a'=l_a=1$. The only operator that can fit in the manifold $l_b'=l_b=0$ is one of rank zero. Therefore, $k_2=0$. Similarly, the operator of rank k_1 must fit in the manifold $l_a'=l_a=1$. Therefore, $k_1=0$, 1, 2. In order that the triple product in Eq. (15) form a scalar invariant, the rank of the sperhical harmonic Λ must equal k_1. As $l\alpha'=l_\alpha$, we have the further condition that the rank k_1 must be even, and there are only two coefficients Γ_{000} and Γ_{202}.[58] The Hamiltonian for the *spin-dependent* part of this exchange interaction is[59]

$$\mathcal{H}_{\text{ex}}=-2\sum_{k=0,2}\Gamma_{k0k}(p,s)[\mathbf{u}^{[k]}(a)\times\mathbf{C}^{[k]}(\Omega_{ab})]^{[0]}\mathbf{s}_a\cdot\mathbf{s}_b\,, \tag{44}$$

or

$$\mathcal{H}_{\text{ex}}=-2\sum_{kq}\Gamma_q{}^{[k]}u_q{}^{[k]}(a)\mathbf{s}_a\cdot\mathbf{s}_b\,,$$

where

$$\Gamma_q{}^{[k]}\equiv[k]^{-1/2}\Gamma_{k0k}C_q{}^{[k]*}(\Omega_{ab})\,.$$

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[57] D. Smith and J. H. M. Thornley, Proc. Phys. Soc. (London) **89**, 779 (1966). To conform to the conventions adopted by Fano and Racah, see Ref. 18, the reduced matrix elements of the operator equivalents $O_q{}^{[k]}$ must be defined with a phase factor $(-1)^{-(1/2)k}$. Therefore the operator equivalents given by Smith and Thornley should be multiplied by $(-1)^{(1/2)k}$.

[58] We could also arrive at this number of coefficients by using Eq. (29).

[59] The spin-independent term will not give rise to a coupling of the magnetic momenta for s-p exchange. Therefore it is not further considered.

When all other interactions are neglected, we can choose the orientation of the coordinate axes so that the Hamiltonian is in its simplest form. For this, we choose $\theta_{ab}=0°$ [see Fig. 1], because $C_q^{[k]*}(0,\phi)=(-)^k \times\delta(q0)$.[60] The operators $u_q^{[k]}$ can be written in terms of the operator equivalents of Smith and Thornley[61] by using the Wigner-Eckart theorem[28]:

$$\mathbf{u}^{[0]}=(1/3)^{\frac{1}{2}}\mathbf{O}^{[0]}=(\tfrac{1}{3})^{1/2},$$

$$u_q^{[2]}=-[2/(30)^{\frac{1}{2}}]O_q^{[2]},$$

and specifically, for $l_a=1$,

$$u_0^{[2]}=-(30)^{-1/2}(3l_z^2-2).$$

With these operator equivalents we can write the Hamiltonian in its simplest form ($\theta_{ab}=0°$) as

$$\mathcal{H}_{\mathrm{ex}}=-(2/\sqrt{3})\times[\Gamma_{000}-(1/5\sqrt{2})(3l_z^2(a)-2)\Gamma_{202}]\mathbf{s}_a\cdot\mathbf{s}_b. \qquad (44')$$

The two coefficients could be explicitly evaluated from the expression in Eq. (15). However, the true wave functions for ions in solids are not accurately known, and also the calculated values of the coefficients would be unrealistic because only orthogonalized orbitals were considered. Therefore we consider these coefficients as parameters to be determined empirically. As the exchange constants $J(m_a'm_b',m_am_b)$ are usually quoted rather than the coefficients $\Gamma_{\epsilon_1\epsilon_2\Omega}$, we relate the two by using Eq. (26). For the *s-p* exchange interaction, we find

$$\begin{aligned}\Gamma_{000}&=(1/\sqrt{3})[J(00,00)+2J(10,10)],\\ \Gamma_{202}&=(10/\sqrt{6})[J(00,00)-J(10,10)].\end{aligned} \qquad (45)$$

To arrive at these relations, we use the condition that, for two-center exchange,

$$J(-10,\,-10)=J(10,10).$$

Written in terms of the exchange constants the *s-p* exchange interaction, Eq. (44′), is

$$\mathcal{H}_{\mathrm{ex}}=-2\{\tfrac{1}{3}[J(00,00)+2J(10,10)] -\tfrac{1}{3}[J(00,00)-J(10,10)](3l_z^2(a)-2)\}\mathbf{s}_a\cdot\mathbf{s}_b. \qquad (44'')$$

The validity of this expression is immediately verified. For $m_a=0$, we find

$$-2J(00,00)\mathbf{s}_a\cdot\mathbf{s}_b,$$

while for $m_a=\pm1$ we find

$$-2J(10,10)\mathbf{s}_a\cdot\mathbf{s}_b.$$

We note that the isotropic term is the mean value of the different exchange constants, and the coefficient representing the anisotropy depends on the difference between the exchange constants. As Van Vleck[4,8] mentions, anisotropy in two-center exchange interactions occurs because the overlap of orbital charge densities depends on the relative orientation of the charge densities with respect to the interatomic axis. This dependence accounts for the difference in the two exchange constants in Eq. (44″).

If the direct Coulomb interaction, Eq. (2), between the *s* and *p* electron is much greater than the spin-orbit coupling of the *p* electron, or if other electrostatic interactions, e.g., crystalline field, cause one orbital configuration of the *s-p* molecule to be much lower in energy than the other (compared to the spin-orbit splitting), the exchange will be nearly isotropic. In these cases the effective exchange constant is the expectation value of the orbital part of the Hamiltonian, Eq. (44″) evaluated in the state of lowest energy, as determined by these interactions. Anisotropy enters as a perturbation only when we consider the effect of the intra-atomic spin-orbit interaction in coupling the orbital ground state to the excited ones. Therefore, in this limit anisotropic exchange is small compared to the isotropic part of the exchange interaction.

If, however, the intra-atomic spin-orbit coupling is much greater than the direct Coulomb and other electrostatic interactions, the orbital and spin angular momenta are strongly coupled and we rewrite Eq. (44) in a jm_j representation as in Eq. (17):

$$\mathcal{H}_{\mathrm{ex}}=-\sum_{k=0,2}\ \sum_{r=|k-1|}^{k+1}\Gamma_{k0k}^{r1}\times[[\mathbf{u}^{[k]}(a)\times\mathbf{s}^{[1]}(a)]^{[r]}\times\mathbf{s}^{[1]}(b)\times\mathbf{C}^{[k]}(\Omega_{ab})]^{[0]}, \qquad (46)$$

where

$$\Gamma_{k0k}^{r1}=(-)^{k+r+1}2([r]/[k])^{1/2}\Gamma_{k0k}.$$

Since $k_2=0$ is the only allowed rank for an orbital operator representing an *s* electron, $r_2=1$. The values of r_1 range from $|k-1|$ to $k+1$, which for a *p* electron ($k=0$, 2) gives $r=1$ for $k=0$ and $r=1$, 2, 3 for $k=2$. If we restrict the Hamiltonian to a manifold where the total angular momentum J is a good quantum number, the sum of the ranks k_i+r_i+1 must be even. For our case, this condition restricts the values of r to be odd because k is even. If we further confine our attention to the ${}^2P_{1/2}$ state of the *p* electron, the only operators that can act on the manifold $j_a'=j_a=\frac{1}{2}$ are those of rank $r=1$.[62] For this state we can write the operator $\mathfrak{j}^{[r]}$ in terms of the total angular momentum operator $\mathbf{j}^{[r]}$ defined by Levy,[9] by using the Wigner-Eckart theorem[63]:

$$[\mathbf{u}^{[0]}\times\mathbf{s}^{[1]}]^{[1]}\doteq-(1/3\sqrt{3})j^{[1]}$$

and

$$[\mathbf{u}^{[2]}\times\mathbf{s}^{[1]}]^{[1]}\doteq-(2/3\sqrt{3})j^{[1]}.$$

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[60] See Ref. 26, p. 19, Eq. (2.11). In accordance with the conventions of Fano and Racah, a factor $(-1)^{\frac{1}{2}k}$ is added to the spherical harmonics. This accounts for the factor of $(-1)^k$.

[61] Here, the phase factor of $(-1)^{(1/2)k}$ has been absorbed in the numerical coefficients; the operator equivalents are *as given* by Smith and Thornley, see Ref. 57.

[62] Operators of rank $r=0$ could also act on this manifold; however, for the case under consideration they are excluded by the requirement that r be odd.

[63] To arrive at these "operator equivalents" we have to evaluate the reduced matrix element of $\mathfrak{j}^{[r]}$. See Ref. 18, Eq. (15.4).

The Hamiltonian for $^2S_{1/2}$-$^2P_{1/2}$ exchange in its simplest form $[\theta_{AB}=0°, C_q^{[k]*}=(-)^k\delta(q0)]$ is written as

$$\mathcal{H}_{\mathrm{ex}} \doteq \tfrac{2}{3}\Gamma_{000}[\mathbf{j}^{[1]}(a)\times\mathbf{s}^{[1]}(b)]^{[0]} + (4/15)\Gamma_{202}[\mathbf{j}^{[1]}(a)\times\mathbf{s}^{[1]}(b)]_0^{[2]}. \quad (46')$$

The irreducible products can be expressed in terms of conventional angular momentum operators by using the definition of these products[64]:

$$[\mathbf{j}^{[1]}\times\mathbf{s}^{[1]}]^{[0]}=(1/\sqrt{3})\mathbf{j}\cdot\mathbf{s}$$

and

$$[\mathbf{j}^{[1]}\times\mathbf{s}^{[1]}]_0^{[2]}=(1/\sqrt{6})(\mathbf{j}\cdot\mathbf{s}-3j_zs_z).$$

Also, the coefficients Γ_{k0k} are related to the exchange constants as in Eq. (45). With these substitutions, the exchange Hamiltonian assumes a form similar to the one first given by Van Vleck[8]:

$$\mathcal{H}_{\mathrm{ex}} \doteq (2/9)[J(00,00)+2J(10,10)]\mathbf{j}_a\cdot\mathbf{s}_b + (4/9)[J(00,00)-J(10,10)] \times(\mathbf{j}_a\cdot\mathbf{s}_b-3j_z(a)s_z(b)). \quad (46'')$$

From this example, we conclude that anisotropic exchange does not enter as a perturbation when spin-orbit forces are greater than the electrostatic forces. The magnitude of the anisotropy is proportional to the difference between the exchange constants, and it can be as large as the isotropic part of the exchange interaction. Therefore we expect that exchange interactions between ions with strong orbital contributions to their magnetic momenta will be highly anisotropic.

In the above example we find only symmetric exchange. For the $^2P_{3/2}$ state, asymmetric exchange $[\mathbf{j}^{[3]}(a)\times\mathbf{s}^{[1]}(b)]^{[2]}$ is present, as well as the symmetric exchange $[\mathbf{j}^{[1]}(a)\times\mathbf{s}^{[1]}(b)]^{[k]}$. However, it is not possible to obtain antisymmetric exchange for $r_1=r_2$, as was done in Eqs. (16) and (18) by rotating the axes of quantization, because one of the electrons has no orbital moment and therefore no preferred set of axes of quantization. The lack of an orbital moment for one of the electrons does produce this essential qualitative difference between exchange interactions in which both electrons have orbital moments and those in which one electron is in an s state.

Situations do exist in which the crystal field is much greater than the exchange interaction but less than the spin-orbit coupling of the electron, e.g., rare-earth–iron exchange in the garnets. In these cases, antisymmetric exchange does exist and it can be as large as symmetric exchange.[65] To account for the effects of the strong crystal field, it is necessary to project the exchange Hamiltonian Eq. (46) onto a crystal-field level, and to rewrite the resultant Hamiltonian in terms of fictitious angular momenta. The study of exchange interactions in crystal-field states (where one or both electrons have orbital moments) for cases of strong spin-orbit coupling will be discussed in a future paper.

The above example is the simplest one possible, and it is not necessary to use Racah's algebra to arrive at the results Eqs. (44) and (46). However, in more realistic situations when we have d or f electrons, and in cases where both electrons have orbital angular momentum, it is very difficult to arrive at the proper form of the exchange interaction, Eqs. (15) and (17) without employing the techniques developed by Racah and used in this paper. To illustrate the usefulness of this technique, let us consider the exchange interaction between two p electrons. In this case, $l_a'=l_a=l_b'=l_b=1$, $k_1, k_2=0, 1, 2$, $\Lambda=0, 2, 4$ (only even values of Λ and of the sum k_1+k_2 are allowed), and the exchange interaction Eq. (15′) in its simplest form ($\theta_{ab}=0°$) is

$$\mathcal{H}_{\mathrm{ex}}=-\sum_{k_1=0}^{2}\sum_{k_1+k_2=\mathit{even}}\sum_{k_2=0}^{2}\sum_{\Lambda=0}^{4}\sum_{\Lambda=\mathit{even}}[\Lambda]^{-1/2}\Gamma_{k_1k_2\Lambda} \times[\mathbf{u}^{[k_1]}(a)\times\mathbf{u}^{[k_2]}(b)]_0^{[\Lambda]}(\tfrac{1}{2}+2\mathbf{s}_a\cdot\mathbf{s}_b). \quad (47)$$

When we go over to a jm_j representation the possible values for r_1 and r_2, Eq. (17), are $r_1, r_2=0, 1, 2, 3$. When we want matrix elements between states of different total angular momentum j, there are no other restrictions on the ranks r_1 and r_2.

$$\mathcal{H}_{\mathrm{ex}}=\sum_{k_1k_2\Lambda}\sum_{r_1,r_2=0}^{3}\sum_{K=0}^{1}(-)^{k_1+r_2}(-\tfrac{1}{2}\delta_{K0}+2\delta_{K1}) \times([r_1][r_2]/[\Lambda])^{1/2}\overline{W}(k_1k_2\Lambda/r_2r_1K)\Gamma_{k_1k_2\Lambda} \times[[\mathbf{u}^{[k_1]}\times\mathbf{s}^{[K]}]^{[r_1]}\times[\mathbf{u}^{[k_2]}\times\mathbf{s}^{[K]}]^{[r_2]}]_0^{[\Lambda]}. \quad (47')$$

However, within a state of definite j value the restriction is that k_i+r_i+K must be even. When both electrons are in definite j states, the foregoing restrictions lead to the extra condition that the sum r_1+r_2 must be even.

When we consider exchange between p electrons only in $^2P_{1/2}$ states, we find that the *form* of the anisotropy is the same as that for the $^2S_{1/2}$-$^2P_{1/2}$ exchange interaction Eq. (46″). As in the former case, no antisymmetric exchange is possible for $^2P_{1/2}$-$^2P_{1/2}$ exchange. As we have considered a case where $l_\alpha'=l_\alpha$, only even-rank operators can describe the direct Coulomb interaction or crystal field. The degeneracy in the $^2P_{1/2}$ state is not split by these interactions, and the orientation of the coordinate axes is arbitrary. Therefore, we cannot have any antisymmetric exchange as in Eq. (18). The same holds true when only one electron is in a $^2P_{3/2}$ state. However, when both p electrons are in $^2P_{3/2}$ states we can have antisymmetric exchange if the other interactions, which must be taken into account, have nonparallel coordinate axes at centers A and B.[66] When the exchange interaction is much greater than the other interactions, but still less than the spin-orbit coupling, the zeroth-order Hamiltonian is Eq. (47′), and antisymmetric exchange enters only as a perturbation. However, when

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[64] See Ref. 18, Eq. (7.10).

[65] K. W. H. Stevens, Rev. Mod. Phys. **25**, 166 (1953); R. M. White and R. L. White, Phys. Rev. Letters **20**, 62 (1968); P. M. Levy, *ibid.* **20**, 1366 (1968).

other interactions are stronger, the zeroth-order Hamiltonian is like Eq. (18) but includes the spin-independent term, and antisymmetric exchange is of the same order of magnitude as the other anisotropies.[67]

The total number of exchange constants is given by Eq. (28) and for p electrons ($l_\alpha'=l_\alpha=1$) this gives 81. Of these, many are equal to one another as we have shown for the s-p exchange constants. Whereas there were only nine possible constants for s-p exchange, we see that as the angular momenta of the states increases, the number of these constants rapidly rises. For this reason it is very helpful to use the one-to-one correspondence between these constants and the coefficients $\Gamma_{k_1k_2\Lambda}$, Eqs. (23) and (26). The number of these coefficients is invariably much less than the total number of constants, Eq. (28), and it also represents the minimum[68] number of *different* exchange constants. For two-center exchange between two p electrons, the number of different coefficients as given by Eq. (29) for $l_> = l_< = 1$ is eight. If, however, the two p electrons are on identical sites, the coefficients Γ_{022} and Γ_{202} are equal, and there are seven *different* coefficients. If we treat these coefficients as empirical parameters, we notice that even for the case of two p electrons we have considerably more unknowns (7) than for isotropic exchange (1). As there are seven different coefficients, we know immediately that only seven of the 81 exchange constants are different for two-center exchange. These seven are, for $\theta_{ab}=0°$ (see Fig. 1)

$$J(00,00)\,,$$

$$J(11,11)=J(-1-1,\,-1-1)\,,$$

$$J(10,10)=J(01,01)=J(-10,\,-10)=J(0-1,\,0-1)\,,$$

$$J(1-1,\,1-1)=J(-11,\,-11)\,,$$

$$J(1-1,\,00)=J(-11,\,00)=J(00,\,1-1)=J(00,\,-11)\,,$$

$$J(10,01)=J(01,10)=J(-10,\,0-1)=J(0-1,\,-10)\,,$$

$$J(1-1,\,-11)=J(-11,\,1-1)\,.$$

By our choice of $\theta_{ab}=0°$ we have eliminated 62 of the 81 matrix elements for which $\Delta m\equiv m_a'+m_b'-m_a-m_b$ is nonzero. Of the remaining 19, only 7 are different.[69] From the definition of the exchange constants Eq. (23), and from the complex conjugation properties of the coefficients Γ and the triple product Eqs. (20), we verify that the $J(m_a'm_b',m_am_b)$ are real for $\theta_{ab}=0°$ as long as we consider orbital states within a manifold of definite angular momentum, i.e., $l_\alpha'=l_\alpha$.[70]

When the exchange interaction between magnetic ions in a solid is direct, we can apply the above formulas. However, most exchange interactions between magnetic ions in insulators are not direct, but take place through the intervening nominally nonmagnetic ions. Our derivation does not apply to these multicenter exchange, or superexchange, interactions. Nonetheless, we know the form of the Hamiltonian for the most general superexchange interaction just from considering the spatial and time symmetry requirements of this interaction.[9–11] Provided that we consider only single pair interchanges between ions,[46] the *form* of the anisotropic superexchange Hamiltonian is identical to the operators Eqs. (15′) and (17′) for direct two-center exchange.[71] The difference is that for superexchange interactions we consider coefficients like

$$\Gamma_m^{[\Lambda]}(k_1k_2;\,n_a'l_a'n_b'l_b',n_al_an_bl_b)$$

and

$$\bar{\Gamma}_m^{[\Lambda]}(k_1k_2,r_1r_2)$$

as empirical parameters, whereas for two-center exchange we can evaluate them in terms of radial integrals by using the definitions of $\Gamma_m^{[\Lambda]}$ and $\Gamma_{k_1k_2\Lambda}$ [see Eqs. (15), (15′), and (18′)]. The properties of these parameters for superexchange are readily derived from those already determined for the coefficients $\Gamma_{k_1k_2\Lambda}$ by using the definition of $\Gamma_m^{[\Lambda]}$, Eq. (15′). For example, if we consider matrix elements only for $l_\alpha'=l_\alpha$, the complex conjugate of the parameters follows from Eq. (20b) and the phase convention of Fano and Racah for the spherical harmonics,[18] and we find

$$\Gamma_m^{[\Lambda]*}=(-)^{\Lambda-m}\Gamma_{-m}^{[\Lambda]}\,. \tag{48}$$

Also, the relation between the parameters $\Gamma_m^{[\Lambda]}$ and $J(m_a'm_b',m_am_b)$ is found from Eq. (26);

$$\begin{aligned}\Gamma_m^{[\Lambda]}(k_1k_2;\,n_a'l_a'n_b'l_b',n_al_an_bl_b)&\\ =[k_1][k_2]\sum_{m_a'm_b'm_am_b}&J(m_a'm_b',m_am_b)\\ &\times(\phi_a'\phi_b'|[\mathbf{u}^{[k_1]}(1)\times\mathbf{u}^{[k_2]}(2)]_m^{[\Lambda]}|\phi_a\phi_b)^*.\end{aligned} \tag{49}$$

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[66] We could express the exchange Hamiltonian for ${}^2P_{1/2}-{}^2P_{3/2}$ and ${}^2P_{3/2}-{}^2P_{3/2}$ exchange in terms of the conventional total angular momentum operators, as we did for the ${}^2S_{1/2}-{}^2P_{1/2}$ interaction. However, due to the high rank of the irreducible products that enter, e.g., $[\mathbf{j}^{[3]}(a)\times\mathbf{j}^{[3]}(b)]_0^{[4]}$, the expressions would be long and not very informative.

[67] Moriya considered the case where the crystal field was much greater than the exchange and spin-orbit interactions. He found, by using second-order perturbation theory, that the first anisotropic exchange term is antisymmetric. Our results are an extension of his calculations to cases where spin-orbit coupling is large compared to the exchange interaction and crystal field. See T. Moriya, Phys. Rev. Letters **4**, 228 (1960); Phys. Rev. **120**, 91 (1960).

[68] Two-center exchange interactions are described by a minimum number of coefficients. As soon as we consider superexchange, the number of coefficients increases; however, the number is still considerably less than the total number of exchange constants, Eq. (28).

[69] We arrive at the number 19, which is the maximum number of parameters for axial exchange for p electrons, by placing $l_\alpha^> = l_\alpha^< = 1$ in Eq. (27). This is the number we obtain when there are no restrictions on the ranks k_1, k_2 and Λ, other than those given by Eq. (19).

[70] For $\theta_{ab}\neq 0°$, the spherical harmonics introduce a complex phase factor into the expression for the exchange constants; see Eq. (23).

[71] The superexchange interaction as represented in the form Eq. (15″), is essentially the same as the expression given by R. J. Elliott and M. F. Thorpe (see Ref. 11).

Although our formalism does not provide explicit expressions of the coefficients $\Gamma_m^{[\Lambda]}$ for superexchange interactions, it does tell us how many independent parameters are needed to describe fully the interaction, i.e., the number of different coefficients $\Gamma_m^{[\Lambda]}(k_1k_2)$. In general, when the angular momentum of each magnetic ion changes, i.e., $l_\alpha' \neq l_\alpha$, and when we do not consider any restrictions on the spatial quantum number m due to symmetry about the pair axis, the number of parameters is

$$N(l_a'l_b',l_al_b)=\sum_{k_1k_2\Lambda}\sum_m 1=[l_a'][l_a][l_b'][l_b]. \tag{50}$$

This equals the total number of exchange constants J. Therefore, when no symmetry exists about the axis connecting the two magnetic ions, we have the maximum number of independent parameters for the superexchange interaction. Usually some symmetry does exist about the pair axis, some values of m are not allowed, and the number of independent parameters is reduced.

When we confine the angular momentum states of each ion to one l manifold, so that $l_\alpha'=l_\alpha$, the sum of the ranks k_1 and k_2 must be even. If we do not consider any further restrictions on the spatial quantum number m, the number of independent parameters is

$$\begin{aligned} N(l_al_b)&=\sum_{k_1k_2\Lambda}\sum_m 1 \quad k_1+k_2=\text{even} \\ &=2l_>(l_>+1)[l_<]^2+\tfrac{1}{2}([l_>]+[l_<])[l_<], \end{aligned} \tag{51}$$

where $l_>$ and $l_<$ have the same meaning as in Eq. (29). If a center of inversion exists between the two magnetic ions, antisymmetric exchange is ruled out,[72] and only even values of the rank Λ are possible. The number of independent parameters for this case is

$$\begin{aligned} N(l_al_b)&=\sum_{k_1k_2\Lambda}\sum_m 1 \quad k_1+k_2=\text{even}, \quad \Lambda=\text{even} \\ &=2l_>(l_>+1)(l_<+1)(2l_<+1)+l_>(l_<+1) \\ &\qquad +\tfrac{1}{3}l_<(2l_<^2+6l_<+7)+1. \end{aligned} \tag{52}$$

Again, there are fewer parameters if some symmetry exists about the pair axis. Also, if the electrons ($l_a=l_b$) and the two sites are identical, we can reduce the number of parameters by noting that the following relation exists between the coefficients:

$$\Gamma_m^{[\Lambda]}(k_1k_2)=\Gamma_m^{[\Lambda]}(k_2k_1). \tag{53}$$

This relation is found by using arguments similar to those used to arrive at Eq. (22).

For superexchange interactions involving two p electrons $l_>=l_<=1$, the number of independent parameters in the absence of any symmetry is 45 [Eq. (51)]. If the two sites containing the p electrons are identical, we use the above relations, Eqs. (52) and (53), to find that there are now only 27 independent parameters. When the pair axis has C_2, or higher, symmetry there are even fewer parameters. For example, when there is axial symmetry about the pair axis, as in two-center exchange, only $m=0$ is allowed, and there are only seven independent parameters. For superexchange interactions involving d electrons $l_>=l_<=2$; there are at most 325 parameters, Eq. (51), and at least 22.[73] For f electrons ($l_>=l_<=3$) there are at most 1225 parameters, and at least 50.[73] From these illustrations we conclude that the necessary number of parameters to describe fully exchange interactions between ions in solids is very large. Nevertheless, there are situations for which one can make further approximations to reduce the number to as few as one. We will consider this in greater detail in a future paper.

We can say, in summing up, that contrary to the common assumption of isotropy, all forms of anisotropy are present in two-center exchange interactions; antisymmetric exchange occurs as well as the more common symmetric exchange. The degrees of the anisotropies are limited only by the angular momenta of the magnetic electrons. Besides the Dzyaloshinsky-Moriya term $\mathbf{S}_a\times\mathbf{S}_b([\mathfrak{J}^{[1]}(a)\times\mathfrak{J}^{[1]}(b)]_m{}^{[1]})$, higher-degree antisymmetric exchange interactions are also present. For ions with strong spin-orbit coupling, anisotropic exchange does not enter as a perturbation, and the symmetric and antisymmetric anisotropies are of the same magnitude as the isotropic component of the interaction. The number of independent parameters needed to describe these exchange interactions is prohibitively large; approximations must be made which drastically reduce the number to be commensurate with the available empirical data. The coefficients for interactions involving any number of equivalent electrons are related to those for two-electrons, so that no new parameters are needed. Although anisotropic superexchange was not considered in detail, we have been able to predict both the forms of the anisotropy present in these interactions, and also the number of independent parameters needed in the Hamiltonian to represent the interaction. Applications which illustrate the usefulness of these results will be made in subsequent papers.

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[72] I. Dzyaloshinsky, J. Phys. Chem. Solids 4, 241 (1958); T. Moriya, see Ref. 67.

[73] This number is arrived at by using Eq. (29) and the relation $\Gamma_{k_1k_2\Lambda}=\Gamma_{k_2k_1\Lambda}$ for equivalent sites.