

Zero-Field Splitting of S-State Ions. II. Overlap and Covalency Model*

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A general formulation including both overlap and charge-transfer covalency effects is developed for the parameters D and E in the spin Hamiltonian $\mathcal{H}_S = D(3S_z^2 - S(S+1)) + E(S_x^2 - S_y^2)$ for a 6S ion surrounded by six singly charged negative closed-shell ions. The contributions to D and E arise in second order from the spin-orbit interaction and in first order from the spin-spin interaction. These contributions can be broken down into three categories: local, nonlocal, and distant, depending on whether the ligand orbitals are involved not at all, once, or twice. Specific application is made to the case of a Mn^{2+} ion surrounded by six F^- ions ($\text{Mn}^{2+}:\text{ZnF}_2$). The calculations are performed for the recent crystal-structure parameters given by Baur. We find, on the one hand, that for the spin-spin interaction, the nonlocal terms predominate over the local and distant terms, and are of the same sign. On the other hand, for the spin-orbit interaction, the local and distant terms predominate over the nonlocal terms, and are of opposite sign, though similar in magnitude. The total (overlap only) contribution to D is found to be $-10.94 \times 10^{-4} \text{ cm}^{-1}$, which is comparable and of opposite sign to the point-charge contribution $24.01 \times 10^{-4} \text{ cm}^{-1}$ calculated in our earlier publication on this problem. The sum of the two contributions (point charge and overlap) is found to be $13.07 \times 10^{-4} \text{ cm}^{-1}$, very close to the experimental value of $+10.5 \times 10^{-4} \text{ cm}^{-1}$. The overlap contribution to E is found to be $-19.77 \times 10^{-4} \text{ cm}^{-1}$, which is rather smaller than the point-charge contribution of $-102.32 \times 10^{-4} \text{ cm}^{-1}$. The combined result, $E = -122.09 \times 10^{-4} \text{ cm}^{-1}$, is also close to the experimental value of $-113.5 \times 10^{-4} \text{ cm}^{-1}$.

I. INTRODUCTION

IN an earlier paper¹ (to be referred to as I), we discussed the zero-field splitting of an S -state ion, specifically Mn^{2+} , using an external point-charge and point-multipole model. We found values for D and E in MnF_2 and $\text{Mn}^{2+}:\text{ZnF}_2$ of the same sign and order of magnitude as those observed experimentally.^{2,3} This result is in contradiction with previous point-charge estimates. In order to remedy this supposed "deficiency" of the point-multipole model, Kondo⁴ had earlier developed an approximate theory relating D and E to overlap and charge transfer in number of different environments. Unfortunately, we shall show that Kondo's calculations were quite approximate and in fact cannot account for the observed values of D and E for $\text{Mn}^{2+}:\text{ZnF}_2$.

We construct in this paper a general formulation for D and E for S -state ions surrounded by ligand ion orbitals which overlap and take part in covalent binding. All the relevant two-electron terms are retained up to second order in overlap and charge-transfer coefficients. The resulting expressions are then evaluated using Hartree-Fock wave functions and Löwdin's α -function

technique whenever more than one-center integrals are involved.

In Sec. II we outline the method we have used for the inclusion of overlap and charge transfer by introducing a simple three-electron-two-atom model. For convenience of calculation and interpretation, a separation is made into local, nonlocal, and distant terms when taking expectation values of relevant operators. The distinction between these three terms is whether the ligand orbitals are involved not at all, once, or twice. In Sec. III the orbitals for a $\text{Mn}^{2+}-\text{F}_6^-$ complex ($\text{Mn}^{2+}:\text{ZnF}_2$) are formulated, after incorporating overlap and charge transfer. The local, nonlocal, and distant contributions to D and E via the spin-spin interaction are considered in Sec. IV. In Sec. V, the local, nonlocal, and distant contributions from the spin-orbit interaction (in second order) are analyzed. A comparison of our work with the earlier results is made in both these sections. Finally, in Sec. VI we discuss the over-all results and speculate on directions for future improvements.

There are two sets of crystal-structure data available for ZnF_2 . One set was used by Mukherji and Das,⁵ Tinkham,² and Kondo.⁴ The other set of data was determined recently by Baur.⁶ The parameters for both determinations are listed in Table I. We have used Baur's data for the calculation of D and E in order to compare the results obtained here with experiment. The older set of data leads to a slightly larger over-all value for E and a value for D of half the magnitude and of opposite sign to that found using Baur's data.

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¹ R. R. Sharma, T. P. Das, and R. Orbach, *Phys. Rev.*, **149**, 257 (1966).

² M. Tinkham, *Proc. Roy. Soc. (London)* **A236**, 535 (1956).

³ A. M. Clogston, J. P. Gordon, V. Jaccarino, M. Peter, and L. R. Walker, *Phys. Rev.* **117**, 1222 (1960).

⁴ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **23**, 106 (1960).

⁵ A. Mukherji and T. P. Das, *Phys. Rev.* **111**, 1479 (1958).

⁶ W. H. Baur, *Acta Cryst.* **11**, 488 (1958). An earlier determination, which differs slightly from Baur's, was made by J. W. Stout and S. A. Reed, *J. Am. Chem. Soc.* **5**, 5279 (1954).

TABLE I. The lattice parameters for the ZnF_2 lattice as determined at room temperature by Baur and by Sout and Reed (Ref. 6). Referring to Fig. 1, the parameters $a(\text{Mn}^{2+}\text{-F}_1)$, $a(\text{Mn}^{2+}\text{-F}_2)$, $a(\text{F}_1\text{-F}_2)$, and $a(\text{F}_1\text{-F}_4)$ are the distances between, respectively, the central Mn^{2+} ion and F ion 1, the central Mn^{2+} ion and F ion 5, the F's numbered 1 and 2 and the F's numbered 1 and 4. $\cos(2\beta)$ is the cosine of the angle between the diagonals $\text{F}_1\text{-F}_3$ and $\text{F}_2\text{-F}_4$.

		$a(\text{Mn}^{2+}\text{-F}_1)$ Å	$a(\text{Mn}^{2+}\text{-F}_5)$ Å	$a(\text{F}_1\text{-F}_2)$ Å	$a(\text{F}_1\text{-F}_4)$ Å	$\cos 2\beta$
Baur	ZnF_2	2.04	2.01	3.13	2.62	0.1769
Stout	ZnF_2	2.03	2.04	3.13	2.59	0.1871

II. TWO-ATOM FRAGMENT MODEL FOR INCLUSION OF OVERLAP AND CHARGE TRANSFER

Before discussing the effects of overlap and covalency on D and E , it is important to clarify the terminology and notation. To retain continuity with the literature, we shall use a notation similar to that adopted by Shulman and Sugano,⁷ Watson and Freeman,⁸ and Simánek and Sroubek.⁹

For simplicity, we shall consider in this section a three-electron molecular fragment made up of two atoms, A and B . The proximity of the two atoms is assumed to be great enough so that the electronic cloud of one perturbs the other. This perturbation can arise in three ways. First, there can be an electrostatic deformation due to the potential produced by the charge distribution on the neighboring atom. This effect has already been dealt with in our earlier paper,¹ neglecting the effects of overlap on the potential. A second effect can arise out of a charge transfer between the atoms leading to partial formation of the fragment A^+-B^- (or A^--B^+). Finally, because of overlap between the ions, the Pauli principle necessitates either, (1) use of a determinant wave function in which the nonorthogonality of the wave functions is automatically taken into account, or (2) use of the orthogonalized atomic orbital (OAO) formalism developed by Löwdin.¹⁰ In our consideration of the overlap effect we would like to work with orthogonal one-electron wave functions and graft onto the atomic wave functions the effects of overlap and charge transfer. In effect, then, we shall use the molecular orbital (MO) approach, identical with the OAO in the absence of charge transfer.

Let the unperturbed wave function of the electron on atom A be ϕ_A and that on the atom B be χ_B . We can form two molecular orbitals, bonding and antibonding, by combining ϕ_A and χ_B with the help of the mixing parameters γ and λ . We denote the antibonding orbital

by ϕ_a' and the bonding orbital by χ_b' . We have

$$\phi_a' = N^a(\phi_A - \lambda\chi_B) \quad (1)$$

and

$$\chi_b' = N^b(\chi_B + \gamma\phi_A), \quad (2)$$

where λ and γ are the mixing parameters for the antibonding and bonding orbitals, respectively. The normalization constants N^a and N^b are given by,

$$N^a = [1 + |\lambda|^2 - (\lambda S_{AB}^* + \lambda^* S_{AB})]^{-1/2} \quad (3)$$

and

$$N^b = [1 + |\gamma|^2 + (\gamma S_{AB}^* + \gamma^* S_{AB})]^{-1/2}, \quad (4)$$

where S_{AB} is the overlap integral,

$$S_{AB} = \langle \chi_B | \phi_A \rangle. \quad (5)$$

Since there are three electrons, two of them pair up and occupy the lower-energy bonding orbitals while the other one is unpaired and occupies the antibonding orbital. In the one-electron MO theory, the bonding and antibonding orbitals are orthogonal; that is,

$$\langle \phi_a' | \chi_b' \rangle = 0. \quad (6)$$

To lowest order (6) leads to the following relation between the mixing parameters λ and γ ,

$$\lambda = \gamma^* + S_{AB}. \quad (7)$$

The quantity S_{AB} in (5) will be referred to hereafter as the "overlap parameter" and γ the "charge-transfer" or "covalency" parameter. The relative magnitudes of γ and S_{AB} determine whether charge transfer predominates over overlap or vice versa. Taking the expectation value h of an operator, $h(\text{op})$, between the antibonding wave functions (1) then leads to,

$$h = \langle \phi_a' | h(\text{op}) | \phi_a' \rangle = h(l) + h(nl) + h(d), \quad (8)$$

where

$$h(l) = |N^a|^2 \langle \phi_A | h(\text{op}) | \phi_A \rangle \\ \cong \{1 - [|\lambda|^2 - (\lambda S_{AB}^* + \lambda^* S_{AB})]\} \\ \times \langle \phi_A | h(\text{op}) | \phi_A \rangle, \quad (9)$$

$$h(nl) = -|N^a|^2 [\lambda^* \langle \chi_B | h(\text{op}) | \phi_A \rangle + \lambda \langle \phi_A | h(\text{op}) | \chi_B \rangle] \\ \cong -[1 - |\lambda|^2 + (\lambda S_{AB}^* + \lambda^* S_{AB})] \\ \times [\lambda^* \langle \chi_B | h(\text{op}) | \phi_A \rangle + \lambda \langle \phi_A | h(\text{op}) | \chi_B \rangle], \quad (10)$$

and

$$h(d) = |N^a|^2 |\lambda|^2 \langle \chi_B | h(\text{op}) | \chi_B \rangle \\ \cong |\lambda|^2 \langle \chi_B | h(\text{op}) | \chi_B \rangle. \quad (11)$$

In (8) to (11), $h(l)$, $h(nl)$, and $h(d)$ are referred to as "local," "nonlocal," and "distant" contributions, respectively. Equations (9), (10), and (11) are obtained by retaining terms up to third order in the mixing parameters λ and S_{AB} . We are specifically interested in two types of operators, the spin-spin and spin-orbit interactions. The spin-spin interaction operator does not specifically refer to any center because it is a function of only the interelectronic separation \mathbf{r}_{12} . The non-

⁷ R. G. Shulman and S. Sugano, Phys. Rev. **130**, 506 (1963); K. Knox, R. G. Shulman and S. Sugano, *ibid.* **130**, 512 (1963); S. Sugano and R. G. Shulman, *ibid.* **130**, 517 (1963).

⁸ R. E. Watson and A. J. Freeman, Phys. Rev. **134**, A1526 (1964).

⁹ E. Simánek and Z. Sroubek, Phys. Status Solidi **4**, 251 (1964).

¹⁰ Per-Olov Löwdin, Advan. Phys. **5**, No. 17, (1956).

local spin-spin term will turn out to yield a larger contribution than the local term.

The situation is quite different for the spin-orbit operator. Because the spin-orbit interaction arises from the orbital motion of the electrons around the nuclei, both atoms A and B contribute. The nonlocal term will turn out to be small because the largest part of its contribution arises from the region in which both ϕ_A and χ_B are appreciable. In this region the spin-orbit Hamiltonian due to either A or B is quite small. The local term will be proportional to the spin-orbit interaction on atom A itself, while the distant contribution will be proportional to the spin-orbit interaction on atom B .

III. WAVE FUNCTION OF THE $Mn^{2+}-F_6^-$ CLUSTER INCLUDING OVERLAP AND CHARGE TRANSFER

In Fig. 1 the arrangement of the six ligand F^- ions surrounding a Mn^{2+} in $Mn^{2+}:ZnF_2$ is pictured. The four F^- ions in the plane, (F_1, F_2, F_3, F_4), are equivalent to one another but distinct from the two, (F_5, F_6), lying on the axis perpendicular to the plane. The point-group symmetry at the Mn^{2+} site is orthorhombic. The Z axis will be chosen to lie along the pair of ions F_5 and F_6 , the x axis is taken parallel to the longer side of the rectangle formed by F_1, F_2, F_3 , and F_4 , and the y axis is parallel to the shorter side of the rectangle. Let the unperturbed unoccupied orbitals $3d_{\pm 2}, 3d_{\pm 1}, 3d_0$ of the Mn^{2+} ion, quantized along the Z axis, be denoted by $\psi_{\alpha^0}(\alpha=0, \pm 1, \pm 2)$. Using (1), we write the perturbed $3d$ orbital $\psi_{\alpha}^{(1)}$ as

$$\psi_{\alpha}^{(1)} = N_{\alpha} [\psi_{\alpha^0} - \sum_{FLM} \lambda_{LM\alpha^F} \psi_{FLM}], \quad (12)$$

where ψ_{FLM} is the F^- wave function for a fluorine ion F in the state L, M . The parameter $\lambda_{LM\alpha^F}$ is the combined overlap and charge-transfer mixing parameter analogous to that found in (1) and (7), and N_{α} is the normalization constant. The summation in (12) extends over all the $2s$ and $2p$ orbitals of the ligand F^- ions. The axes of quantization for the orbitals on the ligand F^- ions can be chosen arbitrarily. For computational convenience, we shall choose a different axis of quantization for each of the ligand ions; namely, the line joining the ligand ion of interest to the Mn^{2+} ion.

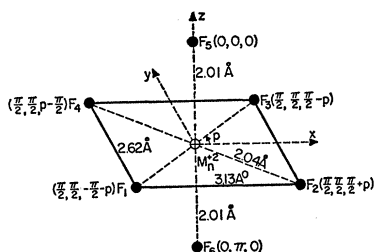


FIG. 1. A schematic showing the immediate neighborhood of a Mn^{2+} ion in ZnF_2 . The F^- 's numbered 1, 2, 3, and 4 lie in a plane at right angles to the line joining the F^- 's 5 and 6.

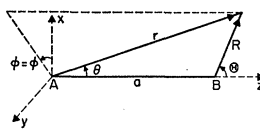


FIG. 2. The definition of the polar angles used in the text for the $Mn^{2+}-F_6^-$ complex.

One can in a similar manner define the doubly occupied bonding orbitals, $\psi_{FLM}^{(1)}$, as in (2),

$$\psi_{FLM}^{(1)} = N_{FLM} [\psi_{FLM} + \sum_{\alpha'} \gamma_{LM\alpha^F} \psi_{\alpha^0}], \quad (13)$$

where N_{FLM} is the normalization constant and $\gamma_{LM\alpha^F}$ represents the appropriate covalency parameter. The orthogonality condition between the antibonding and bonding orbitals yields, to lowest order in λ and γ ,

$$\lambda_{LM\alpha^F} = S_{LM\alpha^F} + \gamma_{LM\alpha^F}, \quad (14)$$

where $S_{LM\alpha^F}$ is the overlap between the wave functions ψ_{α^0} of Mn^{2+} and ψ_{FLM} of a F^- ion:

$$S_{LM\alpha^F} = \langle \psi_{FLM} | \psi_{\alpha^0} \rangle. \quad (15)$$

Using (14), the normalization constant N_{α} appearing in (12) can be shown to be,

$$N_{\alpha} = \{1 + \sum_{FLM} [(\gamma_{LM\alpha^F})^2 - |S_{LM\alpha^F}|^2]\}^{-1/2}. \quad (16)$$

If the polar axis is chosen as the line joining the Mn^{2+} and a particular F^- ion (Fig. 2), the the F^- wave functions can be expanded about the Mn^{2+} site as follows,¹⁰

$$\psi_{FLM} = \sum_{l_2=0}^{\infty} \frac{\alpha_{l_2}(FLM|ar)}{r} Y_{l_2}^M(\theta, \phi). \quad (17)$$

The polar coordinates (r, θ, ϕ) are referred to the Mn^{2+} ion as origin. Analytical integral forms have been derived for the α functions appearing in (17) by Löwdin¹⁰ for a few values of L and l_2 . A general analytic form applicable to all values of L and l_2 has been derived by one of the authors (RRS) and is presented in Appendix A. One can transform the above system of axes to that shown in Fig. 1 by making use of the relation

$$Y_{l_2}^M(\theta, \phi) = \sum_{m_2} b_{l_2, M, m_2}(F) Y_{l_2}^{m_2}(\theta, \phi). \quad (18)$$

In (18), $b_{l_2, M, m_2}(F)$ are the requisite rotation group elements and θ, ϕ are the polar and azimuthal angles in the coordinate system defined by Fig. 1. The rotation group elements are usually expressed in terms of the Eulerian angles $(\alpha_F, \beta_F, \gamma_F)$ required for the transformation. Thus, if we define

$$b_{l_2, M, m_2}(F) = (-i)^{M-m_2} e^{im_2\gamma_F} e^{iM\alpha_F} B_{l_2, M, m_2}(-\beta_F) \quad (19)$$

then the $B_{l_2, M, m_2}(\beta_F)$ are real and given by

$$B_{l_2, M, m_2}(\beta_F) = \sum_t (-1)^t \frac{[(l_2+M)!(l_2-M)!(l_2+m_2)!(l_2-m_2)!]^{1/2}}{(l_2-M-t)!(l_2+m_2-t)!(t+M-m_2)!} \times \cos^{2l_2-M-m_2-2t}(\beta_F/2) \sin^{M-m_2+2t}(\beta_F/2). \quad (20)$$

TABLE II. Tables of values for $B_{l_2, M, m_2}(-\pi/2)$ defined in (20) for $l_2=0, 2$, and 4.

$B_{0, M, m}(-\pi/2)$				$B_{2, M, m}(-\pi/2)$					
$M \backslash m$	-1	0	1	$M \backslash m$	-2	-1	0	1	2
-1	1/2	1/√2	1/2	-2	0.25	0.5	0.61237	0.5	0.25
0	-1/√2	0	1/√2	-1	-0.5	-0.5	0	0.5	0.5
1	1/2	-1/√2	1/2	0	0.61237	0	-0.5	0	0.61237
				1	-0.5	0.5	0	-0.5	0.5
				2	0.25	-0.5	0.61237	-0.5	0.25

$B_{4, M, m}(-\pi/2)$									
$M \backslash m$	-4	-3	-2	-1	0	1	2	3	4
-4	0.0625	0.1768	0.3307	0.4677	0.5229	0.4677	0.3307	0.1768	0.0625
-3	-0.1768	-0.375	-0.4677	-0.3307	0	0.3307	0.4677	0.375	0.1768
-2	0.3307	0.4677	0.25	-0.1768	-0.3953	-0.1768	0.25	0.4677	0.3307
-1	-0.4677	-0.3307	0.1768	0.375	0	-0.375	-0.1768	0.3307	0.4677
0	0.5229	0	-0.3953	0	0.375	0	-0.3953	0	0.5229
1	-0.4677	0.3307	0.1768	-0.375	0	0.375	-0.1768	-0.3307	0.4677
2	0.3307	-0.4677	0.25	0.1768	-0.3953	0.1768	0.25	-0.4677	0.3307
3	-0.1768	0.375	-0.4677	0.3307	0	-0.3307	0.4677	-0.375	0.1768
4	0.0625	-0.1768	0.3307	-0.4677	0.5229	-0.4677	0.3307	-0.1768	0.0625

We have listed in Table II values of $B_{l_2, M, m_2}(-\pi/2)$ for the relevant l_2, M, m_2 which occur in Secs. IV and V. On substituting expression (18) for $Y_{l_2}^M$ in (17) one obtains

$$\psi_{FLM} = \sum_{l_2, m_2} \frac{1}{r} \alpha_{l_2}(FLM|ar) b_{l_2, M, m_2}(F) Y_{l_2}^{m_2}(\theta, \phi). \quad (21)$$

Using Eq. (21), Eq. (12) can then be reduced to the form

$$\psi_{\alpha}^{(1)} = \psi_{\alpha} + \delta\psi_{\alpha}, \quad (22)$$

where

$$\psi_{\alpha} = N_{\alpha} \psi_{\alpha}^0 \quad (23)$$

and

$$\delta\psi_{\alpha} = -N_{\alpha} \sum_{FLM} \sum_{l_2, m_2} \lambda_{LM\alpha}^F b_{l_2, M, m_2}(F) \times \frac{\alpha_{l_2}(FLM|ar)}{r} Y_{l_2}^{m_2}(\theta, \phi). \quad (24)$$

In keeping with our convention for "local," "non-local," and "distant" terms as discussed in Sec. II, we shall denote those terms which contribute to D and E and depend only on ψ_{α} but not on $\delta\psi_{\alpha}$ as the "local" contribution. Those terms that depend on $\delta\psi_{\alpha}$ only once will be termed the "nonlocal" contribution and those terms that involve $\delta\psi_{\alpha}$ twice will be called the "distant" contribution.

The overlap integrals $S_{LM\alpha}^F$ can be simplified by substituting (21) for ψ_{FLM} in (15). One obtains,

$$S_{LM\alpha}^F = b_{2, M, \alpha}^*(F) M_{3d, 2}^{L, M}(F), \quad (25)$$

where $b_{2, M, \alpha}^*(F)$ is the complex conjugate of (19) and $M_{3d, 2}^{L, M}(F)$ is a radial integral defined by

$$M_{3d, 2}^{L, M}(F) = \langle u_{3d}^0 | \alpha_2(FLM|ar) \rangle. \quad (26)$$

In (26), u_{3d}^0 denotes the radial part of the Mn^{2+} wave functions defined by,

$$\psi_{\alpha}^0 = (u_{3d}^0/r) Y_{2}^{\alpha} \quad (\alpha = \pm 2, \pm 1, 0). \quad (27)$$

The overlap integrals (26) can be correlated with the more commonly used $s, \sigma,$ and π overlaps as follows,

$$\begin{aligned} S_s(F_1) &= M_{3d, 2}^{0, 0}(F_1), \\ S_{\sigma}(F_1) &= M_{3d, 2}^{1, 0}(F_1), \\ S_{\pi}(F_1) &= M_{3d, 2}^{1, 1}(F_1), \end{aligned} \quad (28)$$

with similar expressions for the other five F^- ions.

IV. SPIN-SPIN CONTRIBUTIONS TO D AND E

In our earlier paper, we defined the spin-spin contributions to D and E using the following expressions,

$$D_{SS} = \frac{1}{2} D_0 \langle \psi^{(1)} | \sum_{i < j} (3z_{ij}^2 - r_{ij}^2)/r_{ij}^5 | \psi^{(1)} \rangle, \quad (29)$$

and

$$E_{SS} = \frac{1}{2} E_0 \langle \psi^{(1)} | \sum_{i < j} 3(x_{ij}^2 - y_{ij}^2)/r_{ij}^5 | \psi^{(1)} \rangle, \quad (30)$$

where

$$D_0 = E_0 = -g^2 \beta^2 / 20 a_0^3.$$

In these equations the many-particle wave function $\psi^{(1)}$ is defined by

$$\begin{aligned} \psi^{(1)} &= \frac{1}{\sqrt{5!}} \epsilon_{\alpha, \beta, \gamma, \delta, \epsilon} \psi_{\alpha}^{(1)}(1) \psi_{\beta}^{(1)}(2) \\ &\quad \times \psi_{\gamma}^{(1)}(3) \psi_{\delta}^{(1)}(4) \psi_{\epsilon}^{(1)}(5), \end{aligned} \quad (31)$$

and we sum over repeated indices.

In order to evaluate D_{SS} and E_{SS} we use the one-electron expansion for the operators $(3z_{ij}^2 - r_{ij}^2)/r_{ij}^5$

and $(x_{ij}^2 - y_{ij}^2)/r_{ij}^5$ given by Watson and Blume¹¹ and by Pitzer and Lipscomb¹²:

$$(3z_{ij}^2 - r_{ij}^2)/r_{ij}^5 = \sum_{\nu, m'} c_{\nu, m'} \frac{r_i^{\nu-1}}{r_j^{\nu+2}} \times Y_{\nu-1}^{m'}(i) Y_{\nu+1}^{m'+1}(j), \quad (32)$$

$$3(x_{ij}^2 - y_{ij}^2)/r_{ij}^5 = \text{Re} \sum_{\nu, m'} c'_{\nu, m'} \frac{r_i^{\nu-1}}{r_j^{\nu+2}} \times Y_{\nu-1}^{m'-1}(i) Y_{\nu+1}^{m'+1}(j), \quad (33)$$

where

$$c_{\nu, m'} = 4\pi \left[\frac{(\nu - m' + 1)!(\nu + m' + 1)!}{(2\nu - 1)(2\nu + 3)(\nu + m' - 1)!(\nu - m' - 1)!} \right]^{1/2}, \quad (34)$$

and

$$c'_{\nu, m'} = 4\pi \left[\frac{(\nu + m' + 2)!}{(2\nu - 1)(2\nu + 3)(\nu + m' - 2)!} \right]^{1/2}. \quad (35)$$

The expressions (32) and (33) are valid for $r_i < r_j$. If $r_i > r_j$, the indices i and j should be interchanged throughout. In the following subsections, we shall evaluate (29) and (30) in detail.

A. Local Spin-Spin Contribution, D_{SS}^l

Substituting (32) into (29), and collecting all the local terms, we obtain

$$D_{SS}^l = \frac{D_0}{2} \sum_{\nu=1,3} f_{d,d}^{\nu-1, \nu+2} \sum_{\alpha, \beta} (\mu_\alpha + \mu_\beta) \times [c_{\nu,0} F_{2,2}^{-\alpha, \alpha} (\nu-1) F_{2,2}^{-\beta, \beta} (\nu+1) (-1)^{\alpha+\beta} - c_{\nu, \alpha-\beta} F_{2,2}^{-\alpha, \beta} (\nu-1) F_{2,2}^{-\beta, \alpha} (\nu+1)], \quad (36)$$

where the $F_{2,k}^{m, m_k}(l)$ are defined and tabulated in Table III of I, and are simply coefficients for combining spherical harmonics. The quantities $f_{d,d}^{\alpha, \beta}$ and μ_α are defined by the equations,

$$f_{d,d}^{\alpha, \beta} = \int \int u_{3d}^{\alpha}(1) u_{3d}^{\beta}(2) \frac{r_1 < r_2}{r_1 > r_2} u_{3d}^{\alpha}(1) u_{3d}^{\beta}(2) dr_1 dr_2 \quad (37)$$

and

$$\mu_\alpha = 1 - N_\alpha. \quad (38)$$

Expanding (16) and retaining only terms second order in λ and S , we obtain from (38)

$$\mu_\alpha = \frac{1}{2} \sum_{FLM} [|S_{LM\alpha}^F|^2 - (\gamma_{LM\alpha}^F)^2]. \quad (39)$$

One can express μ_α in terms of the integrals $M_{3d,2}^{L,M}(F)$

defined in (26), the quantities $B_{2,M,m}(\beta_F)$ defined in (20), and the Eulerian angles appropriate to a particular F^- ion, displayed in Fig. 1.

$$\mu_\alpha = \sum_{L,M} \mu_\alpha^{L,M} = \sum_{L,M} [2[B_{2,M,\alpha}(-\pi/2)]^2 \times \{[M_{3d,2}^{L,M}(F_1)]^2 - [\gamma^{L,M}(F_1)]^2\} + \frac{1}{2}[M_{3d,2}^{L,M}(F_5)]^2(\delta_{M,\alpha} + \delta_{M,-\alpha})]. \quad (40)$$

The overlap integrals $M_{3d,2}^{L,M}(F)$ in (40) can be evaluated using (26) once the requisite α functions are known. It turns out that, for each of the s , σ , or π orbitals on the F^- ions, we need only two types of α functions, one corresponding to any of the four F^- ions F_1, F_2, F_3, F_4 and the other to either of the ions F_5 or F_6 .

Substituting (40) into (36) and making use of Table III in I for $F_{l_1, l_2}^{m_1, m_2}(l_3)$ and Table II of this paper for $B_{2,M,m}(-\pi/2)$, we find,

$$D_{SS}^l = D_{SS}^l(L=0, M=0) + D_{SS}^l(L=1, M=0) + D_{SS}^l(L=1, M=1) + D_{SS}^l(L=1, M=-1), \quad (41)$$

where

$$D_{SS}^l(L=0, M=0) = (6/7)D_0\{[S_s^2(F_5) - \gamma_s^2(F_5)] - [S_s^2(F_1) - \gamma_s^2(F_1)]\}[f_{d,d}^{\alpha,0,3} - (8/7)f_{d,d}^{\alpha,2,5}], \quad (42a)$$

$$D_{SS}^l(L=1, M=0) = (6/7)D_0\{[S_\sigma^2(F_5) - \gamma_\sigma^2(F_5)] - [S_\sigma^2(F_1) - \gamma_\sigma^2(F_1)]\}[f_{d,d}^{\alpha,0,3} - (8/7)f_{d,d}^{\alpha,2,5}], \quad (42b)$$

$$D_{SS}^l(L=1, M=1) = D_{SS}^l(L=1, M=-1) = (3/7)D_0\{[S_\pi^2(F_5) - \gamma_\pi^2(F_5)] - [S_\pi^2(F_1) - \gamma_\pi^2(F_1)]\}[f_{d,d}^{\alpha,0,3} - (8/7)f_{d,d}^{\alpha,2,5}]. \quad (42c)$$

Here, the charge-transfer coefficients are defined in a manner analogous to the definition of the overlap integrals (28). Using Watson's analytic expressions¹³ for the $3d$ wave functions, we find from (37)

$$f_{d,d}^{\alpha,0,3} = 0.9799, \quad (43)$$

$$f_{d,d}^{\alpha,2,5} = 0.5353,$$

in atomic units. In addition, using Watson's analytical expressions¹³ for the $F^- 2s$ and $2p$ functions, the expressions (A1) to (A13) for the α functions, and the interatomic distances given in Table I, we find,

$$S_s(F) = M_{3d,2}^{0,0}(F) = -0.0671 \quad \text{for } F = F_1$$

$$= -0.0708 \quad \text{for } F = F_5,$$

$$S_\sigma(F) = M_{3d,2}^{1,0}(F) = 0.0785 \quad \text{for } F = F_1 \quad (44)$$

$$= 0.0818 \quad \text{for } F = F_5,$$

$$S_\pi(F) = M_{3d,2}^{1,1}(F) = 0.0504 \quad \text{for } F = F_1$$

$$= 0.0532 \quad \text{for } F = F_5.$$

Because of the great uncertainty in the charge-transfer coefficients γ and their expected smallness for

¹¹ R. E. Watson and M. Blume, Phys. Rev. **139**, A1209 (1965).

¹² R. M. Pitzer and W. N. Lipscomb, J. Chem. Phys. **39**, 1995 (1963).

¹³ R. E. Watson, MIT Solid State Molecular Group Technical Report No. 12, 1959 (unpublished), and private communication.

$\text{Mn}^{2+}:\text{ZnF}_2$, we evaluate (42) taking only overlap into account. We find

$$\begin{aligned} D_{\text{SS}}^l(L=0, M=0) &= -0.95 \times 10^{-4} \text{ cm}^{-1}, \\ D_{\text{SS}}^l(L=1, M=0) &= -1.00 \times 10^{-4} \text{ cm}^{-1}, \\ D_{\text{SS}}^l(L=1, M=\pm 1) &= -0.28 \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (45)$$

Adding the various contributions we find,

$$D_{\text{SS}}^l = -2.51 \times 10^{-4} \text{ cm}^{-1}. \quad (46)$$

Kondo⁴ neglected the $L=0, M=0$, and $L=1, M=\pm 1$ contributions to D_{SS}^l . It is clear from (45) that this neglect is in error by almost a factor of 2. In addition, he neglected completely the nonlocal contribution to D_{SS} which we shall show in the next subsection to, in fact, be larger than the local contribution (46).

B. Nonlocal Spin-Spin Contribution, D_{SS}^{nl}

The nonlocal contribution to D can be obtained from (29) together with Eqs. (22) and (24) by retaining those terms which arise out of the $\delta\psi_\alpha$ part of $\psi_\alpha^{(1)}$, and are second order in overlap and charge transfer. Using (32) we obtain,

$$D_{\text{SS}}^{nl} = -\frac{D_0}{2} \sum_{FLM, l_2, m_2} b_{l_2, M, m_2}(\text{F}) \times D_{L, l_2}^{M, m_2}(\text{F}) \lambda_{LM m_2}^{\text{F}}, \quad (47)$$

where

$$D_{L, l_2}^{M, m_2}(\text{F}) = \sum_{l'} f_{d, l_2}^{l'-1, l'+2}(\text{FLM}) N_{l_2, m_2}^{l'} \quad (48)$$

$$\begin{aligned} P_{L, l_2}^{M, m_2}(l') &= 4B_{l_2, M, m_2}(-\pi/2) B_{2, M, m_2}(-\pi/2) [M_{3d, 2}^{L, M}(\text{F}_1) + \gamma^{L, M}(\text{F}_1)] f_{d, l_2}^{l'-1, l'+2}(\text{F}_1 \text{LM}) \\ &\quad + M_{3d, 2}^{L, M}(\text{F}_5) f_{d, l_2}^{l'-1, l'+2}(\text{F}_5 \text{LM}) [B_{l_2, M, m_2}(0) B_{2, M, m_2}(0) + B_{l_2, M, m_2}(-\pi) B_{2, M, m_2}(-\pi)]. \end{aligned} \quad (53)$$

The properties of the quantities $F_{l_2, l_2}^{m, n_2}(l_3)$ in (50) limit the summation over l' in (47) to the values $l'=1, 3$, and 5, and l_2 to the values 0, 2, 4, 6, and 8. For compactness, we define the quantities:

$$R_{l_2, M}^{l'}(1) = \sum_{m_2} B_{l_2, M, m_2}(-\pi/2) B_{2, M, m_2}(-\pi/2) N_{l_2, m_2}^{l'} \quad (54)$$

and

$$R_{l_2, M}^{l'}(2) = \sum_{m_2} N_{l_2, m_2}^{l'} [B_{l_2, M, m_2}(0) B_{2, M, m_2}(0) + B_{l_2, M, m_2}(-\pi) B_{2, M, m_2}(-\pi)]. \quad (55)$$

One can then rewrite (52) as

$$\begin{aligned} D_{\text{SS}}^{nl} &= -\frac{D_0}{2} \left\{ 4 \sum_{LM} [M_{3d, 2}^{L, M}(\text{F}_1) + \gamma^{L, M}(\text{F}_1)] \sum_{\substack{l'=1, 3, 5 \\ l_2=0, 2, 4, 6, 8}} [f_{d, l_2}^{l'-1, l'+2}(\text{F}_1 \text{LM}) R_{l_2, M}^{l'}(1)] \right. \\ &\quad \left. + \sum_{LM} [M_{3d, 2}^{L, M}(\text{F}_5) + \gamma^{L, M}(\text{F}_5)] \sum_{\substack{l'=1, 3, 5 \\ l_2=0, 2, 4, 6, 8}} [f_{d, l_2}^{l'-1, l'+2}(\text{F}_5 \text{LM}) R_{l_2, M}^{l'}(2)] \right\}. \end{aligned} \quad (56)$$

Going through the same steps that led to (41) and (42) for the local contribution, we find (56) reduces to,

$$D_{\text{SS}}^{nl} = D_{\text{SS}}^{nl}(L=0, M=0) + D_{\text{SS}}^{nl}(L=1, M=0) + D_{\text{SS}}^{nl}(L=1, M=1) + D_{\text{SS}}^{nl}(L=1, M=-1), \quad (57)$$

where

$$\begin{aligned} D_{\text{SS}}^{nl}(L=0, M=0) &= -2D_0 \{ [S_s(\text{F}_1) + \gamma_s(\text{F}_1)] [-1.7889 f_0^{0,3}(\text{F}_{1s}) + 2.6833 f_0^{2,5}(\text{F}_{1s}) \\ &\quad - 0.8571 f_2^{0,3}(\text{F}_{1s}) + 0.9796 f_2^{2,5}(\text{F}_{1s}) - 1.5333 f_4^{0,3}(\text{F}_{1s}) + 0.9309 f_4^{2,5}(\text{F}_{1s}) + 3.1943 f_4^{4,7}(\text{F}_{1s})] \\ &\quad - [S_s(\text{F}_5) + \gamma_s(\text{F}_5)] [-1.7889 f_0^{0,3}(\text{F}_{5s}) + 2.6833 f_0^{2,5}(\text{F}_{5s}) - 0.8571 f_2^{0,3}(\text{F}_{5s}) + 0.9796 f_2^{2,5}(\text{F}_{5s}) \\ &\quad - 1.5333 f_4^{0,3}(\text{F}_{5s}) + 0.9309 f_4^{2,5}(\text{F}_{5s}) + 3.1943 f_4^{4,7}(\text{F}_{5s})] \}, \end{aligned} \quad (58a)$$

$$N_{l_2, m_2}^{l'} = N_{l_2, m_2}^{l'}(1) + N_{l_2, m_2}^{l'}(2), \quad (49)$$

$$N_{l_2, m_2}^{l'}(1) = c_{l', 0} \left[(-1)^{m_2} F_{2, l_2}^{-m_2, m_2}(l'+1) \frac{5}{\sqrt{4\pi}} \delta_{l', 1} \right.$$

$$\left. - F_{2, 2}^{-m_2, m_2}(l'-1) F_{2, l_2}^{-m_2, m_2}(l'+1) \right] - \sum_{\alpha \neq m_2} c_{l', \alpha - m_2}$$

$$\times F_{2, l_2}^{-\alpha, m_2}(l'-1) F_{2, 2}^{-m_2, \alpha}(l'+1), \quad (50a)$$

$$\begin{aligned} N_{l_2, m_2}^{l'}(2) &= -c_{l', 0} F_{2, l_2}^{-m_2, m_2}(l'-1) F_{2, 2}^{-m_2, m_2}(l'+1) \\ &\quad - \sum_{\beta \neq m_2} c_{l', m_2 - \beta} F_{2, 2}^{-m_2, \beta}(l'-1) F_{2, l_2}^{-\beta, m_2}(l'+1), \end{aligned} \quad (50b)$$

and finally,

$$\begin{aligned} f_{d, l_2}^{n, m}(\text{FLM}) &= \int \int u_d^0(1) u_d^0(2) \frac{r^{<n}}{r^{>m}} \\ &\quad \times \alpha_{l_2}(\text{FLM} | ar_2) u_d^0(1) dr_1 dr_2. \end{aligned} \quad (51)$$

The summation in (47) over the F^- ions can be performed with the help of (19), (25), and the Eulerian angles defined in Fig. 1. We find,

$$D_{\text{SS}}^{nl} = -\frac{D_0}{2} \sum_{l_2, L, M} \sum_{m_2, l'} N_{l_2, m_2}^{l'} P_{L, l_2}^{M, m_2}(l'), \quad (52)$$

where

TABLE III. Table of values for $f_{3d, l_2}^{n, n+3}(FLM)$ defined in (51) for the various values of separation a defined in Fig. 1 and appropriate to ZnF_2 .

$a(\text{\AA})$	l_2, L, M	0	$\frac{n}{2}$	4	$a(\text{\AA})$	l_2, L, M	0	$\frac{n}{2}$	4
2.04	0,0,0	0.011399	0.005409	0.003329	2.03	0,0,0	0.011721	0.005565	0.003422
	2,0,0	-0.005723	-0.002103	-0.001232		2,0,0	-0.005884	-0.002166	-0.001270
	4,0,0	0.002066	0.000548	0.000250		4,0,0	0.002159	0.000549	0.000259
	0,1,0	-0.056983	-0.029031	-0.017822		0,1,0	-0.05793	-0.029521	-0.018209
	2,1,0	0.011507	0.004767	0.002875		2,1,0	0.011745	0.004870	0.002934
	4,1,0	-0.002679	-0.000869	-0.000172		4,1,0	-0.002282	-0.000244	-0.000111
	2,1,1	0.005356	0.002132	0.001286		2,1,1	0.005482	0.002184	0.001271
	4,1,1	-0.002203	-0.000530	-0.000049		4,1,1	-0.002500	-0.000115	-0.000088

$$D_{SS}^{nl}(L=1, M=0) = -2D_0\{[S_\sigma(F_1) + \gamma_\sigma(F_1)][-1.7889f_0^{0,3}(F_1\sigma) + 2.6833f_0^{2,5}(F_1\sigma) - 0.8571f_2^{0,3}(F_1\sigma) + 0.9796f_2^{2,5}(F_1\sigma) - 1.5333f_4^{0,3}(F_1\sigma) + 0.9309f_4^{2,5}(F_1\sigma) + 3.1943f_4^{4,7}(F_1\sigma)] - [S_\sigma(F_5) + \gamma_\sigma(F_5)][-1.7889f_0^{0,3}(F_5\sigma) + 2.6833f_0^{2,5}(F_5\sigma) - 0.8571f_2^{0,3}(F_5\sigma) + 0.9796f_2^{2,5}(F_5\sigma) - 1.5333f_4^{0,3}(F_5\sigma) + 0.9309f_4^{2,5}(F_5\sigma) + 3.1943f_4^{4,7}(F_5\sigma)]\}, \quad (58b)$$

$$D_{SS}^{nl}(L=1, M=1) = D_{SS}^{nl}(L=1, M=-1) = -D_0\{[S_\pi(F_1) + \gamma_\pi(F_1)][-0.8571f_2^{0,3}(F_1\pi) + 0.9796f_2^{2,5}(F_1\pi) - 2.7994f_4^{0,3}(F_1\pi) + 1.6996f_4^{2,5}(F_1\pi) + 5.8322f_4^{4,7}(F_1\pi)] - [S_\pi(F_5) + \gamma_\pi(F_5)][-0.8571f_2^{0,3}(F_5\pi) + 0.9796f_2^{2,5}(F_5\pi) - 2.7994f_4^{0,3}(F_5\pi) + 1.6996f_4^{2,5}(F_5\pi) + 5.8322f_4^{4,7}(F_5\pi)]\}. \quad (58c)$$

These equations neglect terms corresponding to $l_2=6$ and $l_2=8$ in (56) because the $f_{d, l_2}^{n, n+3}(FLM)$ become very small as l_2 becomes large

The overlap integrals appearing in (58) are tabulated in (44), the $f_{3d, l_2}^{n, n+3}(FLM)$ in Tables III and IV. We again neglect the charge-transfer coefficients to find

$$\begin{aligned} D_{SS}^{nl}(L=0, M=0) &= -0.51 \times 10^{-4} \text{ cm}^{-1}, \\ D_{SS}^{nl}(L=1, M=0) &= -1.31 \times 10^{-4} \text{ cm}^{-1}, \\ D_{SS}^{nl}(L=1, M=\pm 1) &= -0.67 \times 10^{-4} \text{ cm}^{-1}, \end{aligned} \quad (59)$$

so that, combining,

$$D_{SS}^{nl} = -3.16 \times 10^{-4} \text{ cm}^{-1}. \quad (60)$$

C. Local Spin-Spin Contribution, E_{SS}^l

In order to obtain the local contribution to E , E_{SS}^l , we make use of (30) and the expansion (33) for $3(x_{ij}^2 - y_{ij}^2)/r_{ij}^5$. We obtain, after some simplification,

$$E_{SS}^l = \frac{E_0}{2} \sum_{\alpha, \beta} (\mu_\alpha + \mu_\beta) \sum_{l', m'} c'_{l', m'} f_{d, d}^{l', l'+2} (-1)^{\alpha+\beta} \times [F_{2,2}^{-\alpha, \alpha}(l'-1)F_{2,2}^{-\beta, \beta}(l'+1)\delta_{m', 1}\delta_{m', -1} - F_{2,2}^{-\alpha, \beta}(l'-1)F_{2,2}^{-\beta, \alpha}(l'+1)\delta_{m'-1, \alpha-\beta}\delta_{m'+1, \alpha-\beta}] \equiv 0. \quad (61)$$

The zero result follows because the quantities inside the square brackets vanish as a consequence of the Kronecker- δ functions.

TABLE IV. Table of values for $f_{3d, l_2}^{n, n+3}(FLM)$ and $M_{3d, 2}^{L, M}(F)$ [defined in (26)] for the separation a defined in Fig. 1 and appropriate to ZnF_2 .

$a(\text{\AA})$	l_2, l, M	$M_{3d, 2}^{L, M}(F)$	$f_{3d, l_2}^{0,3}(FLM)$	$f_{3d, l_2}^{2,5}(FLM)$	$f_{3d, l_2}^{4,7}(FLM)$
2.01	0,0,0	...	0.012392	0.005890	0.003644
	2,0,0	-0.070807	-0.006221	-0.002299	-0.001356
	4,0,0	...	0.002224	0.000602	0.000278
	0,1,0	...	-0.059884	-0.030521	-0.019807
	2,1,0	0.081851	0.012225	0.005084	0.003092
	4,1,0	...	-0.003122	-0.000948	-0.000478
	2,1,1	0.053231	0.005743	0.002291	0.001323
	4,1,1	...	-0.002147	-0.000854	0.000290

D. Nonlocal Spin-Spin Contribution, E_{SS}^{nl}

The procedure for deriving the nonlocal contribution to E is similar to that employed for D_{SS}^{nl} , only one starts from expressions (30) and (33). Thus, with the help of the (22), (23), (24), and (31), retaining only nonlocal terms, one finds after some manipulation:

$$E_{SS}^{nl} = -\frac{E_0}{2} \sum_{F, L, M, l_2, m_2} b_{l_2, M, m_2}(F) E_{L, l_2}^{M, m_2}(F) \lambda_{L, M, m_2-2}^F, \quad (62)$$

where

$$E_{L, l_2}^{M, m_2}(F) = \sum_{l'} f_{d, l_2}^{l'-1, l'+2}(FLM) G_{l_2, m_2}^{l'-1}, \quad (63)$$

and

$$G_{l_2, m_2}^{l'-1} = G_{l_2, m_2}^{l'-1}(1) + G_{l_2, m_2}^{l'-1}(2). \quad (64)$$

Here,

$$G_{l_2, m_2}^{l'-1}(1) = c'_{l', 1} \left[\delta_{l', 1} \frac{5}{\sqrt{4\pi}} (-1)^{m_2} - F_{2, 2}^{2-m_2, m_2-2}(l'-1) \right] F_{2, l_2}^{2-m_2, \alpha}(l'+1) \\ + (\delta_{l', 5} - 1) \sum_{\alpha \neq m_2-2} c'_{l', \alpha-m_2+1} F_{2, l_2}^{-\alpha, m_2}(l'-1) F_{2, 2}^{2-m_2, \alpha}(l'+1) \quad (65a)$$

and

$$G_{l_2, m_2}^{l'-1}(2) = \sum_{\beta \neq m_2-2} [c'_{l', -1} (-1)^{m_2+\beta} F_{2, l_2}^{-m_2+2, m_2}(l'-1) F_{2, 2}^{-\beta, \beta}(l'+1) \\ - c'_{l', m_2-1-\beta} F_{2, 2}^{-m_2+2, \beta}(l'-1) F_{2, l_2}^{-\beta, m_2}(l'+1)]. \quad (65b)$$

The summation over the F^- ions in (62) can be accomplished as before by making use of (19) and the Eulerian angles $(\alpha_F, \beta_F, \gamma_F)$ indicated in Fig. 1. Equation (62) can then be rewritten in the form,

$$E_{SS}^{nl} = -2E_0 \cos 2p \sum_{LM} [M_{3d, 2}^{L, M}(F_1) + \gamma^{L, M}(F_1)] \sum_{\substack{l'=1, 3, 5 \\ l_2=0, 2, 4, 6, 8}} f_{d, l_2}^{l'-1, l'+2}(F_1 LM) H_{l_2, M}^{l'-1}, \quad (66)$$

where

$$H_{l_2, M}^{l'-1} = \sum_{m_2} G_{l_2, m_2}^{l'-1} B_{l_2, M, m_2}(-\pi/2) B_{2, M, m_2-2}(-\pi/2). \quad (67)$$

We notice from these equations that the F^- ions 5 and 6 lying on the z axis do not contribute to E . This is to be expected because they can produce only axial distortions of the Mn^{2+} ion's charge distribution. Retaining only terms for $l_2=0, 2$, and 4 for the same reason as in IV B, we find,

$$E_{SS}^{nl} = E_{SS}^{nl}(L=0, M=0) + E_{SS}^{nl}(L=1, M=0) + E_{SS}^{nl}(L=1, M=1) + E_{SS}^{nl}(L=1, M=-1), \quad (68)$$

where

$$E_{SS}^{nl}(L=0, M=0) = -2E_0 \cos 2p [S_s(F_1) + \gamma_s(F_1)] [5.3666 f_0^{0,3}(F_{1s}) - 8.0498 f_0^{2,5}(F_{1s}) \\ + 2.5714 f_2^{0,3}(F_{1s}) - 2.9388 f_2^{2,5}(F_{1s}) + 4.5999 f_4^{0,3}(F_{1s}) - 2.7928 f_4^{2,5}(F_{1s}) - 9.5831 f_4^{4,7}(F_{1s})], \quad (69a)$$

$$E_{SS}^{nl}(L=1, M=0) = -2E_0 \cos 2p [S_\sigma(F_1) + \gamma_\sigma(F_1)] [5.3666 f_0^{0,3}(F_{1\sigma}) - 8.0498 f_0^{2,5}(F_{1\sigma}) \\ + 2.5714 f_2^{0,3}(F_{1\sigma}) - 2.9388 f_2^{2,5}(F_{1\sigma}) + 4.5999 f_4^{0,3}(F_{1\sigma}) - 2.7928 f_4^{2,5}(F_{1\sigma}) - 9.5831 f_4^{4,7}(F_{1\sigma})], \quad (69b)$$

$$E_{SS}^{nl}(L=1, M=1) = E_{SS}^{nl}(L=1, M=-1) = -2E_0 \cos 2p [S_\pi(F_1) + \gamma_\pi(F_1)] \\ \times [2.5714 f_2^{0,3}(F_{1\pi}) - 2.9388 f_2^{2,5}(F_{1\pi}) + 8.3982 f_4^{0,3}(F_{1\pi}) - 5.0990 f_4^{2,5}(F_{1\pi}) - 17.4964 f_4^{4,7}(F_{1\pi})]. \quad (69c)$$

In (69), p is the angle measuring the departure of the surroundings of the Mn^{2+} ion from cylindrical symmetry, as shown in Fig. 1. We evaluate (69) using the same tables referred to previously for the evaluation of D . For $Mn^{2+}:ZnF_2$, $\cos 2p=0.1769$ so that we find

$$E_{SS}^{nl}(L=0, M=0) = -2.53 \times 10^{-4} \text{ cm}^{-1}, \\ E_{SS}^{nl}(L=1, M=0) = -10.55 \times 10^{-4} \text{ cm}^{-1}, \\ E_{SS}^{nl}(L=1, M=\pm 1) = -0.68 \times 10^{-4} \text{ cm}^{-1}. \quad (70)$$

Summing, we find,

$$E_{SS}^{nl} = -14.43 \times 10^{-4} \text{ cm}^{-1}. \quad (71)$$

Our result at first sight appears similar to Kondo's⁴. However, Kondo was forced to make a number of numerical approximations which considerably altered his value of E_{SS}^{n1} . In essence, they consisted of approximating the α function $\alpha_{i_2}(F_{10}|ar)$ appearing in the integrals $f_{a,i_2}^{n,m}(FLM)$, (51), by $S_\sigma(F_1)u_a^0(r)$. This replacement leads to serious numerical errors in the calculation of the two-center integrals which occur in (69).¹⁴ In addition, Kondo⁴ neglected the $L=0, M=0$, and $L=1, M=\pm 1$ contributions, as pointed out in our calculation of D_{SS} . Finally we make the somewhat trivial remark that he attributed the spin-spin contribution to E as arising from local terms through, as we have shown, they in fact arise from nonlocal terms.

V. SPIN-ORBIT CONTRIBUTION TO D AND E

The first-order change in energy of the electrons due to the spin-orbit interaction vanishes for Mn^{2+} because of the absence of orbital moment in the half filled shell. We shall therefore use second-order perturbation theory, in conjunction with the wave functions perturbed by overlap and charge transfer that were defined in Sec. III. The second-order energy using conventional perturbation theory is given by

$$W_{SO} = -\sum_n \frac{\langle \Psi_G | V_{SO} | \Psi_n \rangle \langle \Psi_n | V_{SO} | \Psi_G \rangle}{\Delta_n}, \quad (72)$$

where the Ψ_n represent the excited-state wave functions, Δ_n is the energy difference between the ground state and the n th excited state, and the prime restricts n from denoting the ground state. In order to calculate this energy one needs a knowledge of the wave functions and energies of those excited states connected to the ground term value by the spin-orbit coupling. These levels must be of 4P character.¹ To simplify our analysis we shall use an average energy denominator Δ to denote these excited-state splittings. This should not be a serious approximation since there is only a single 4P term in the d^5 configuration, and the cubic field admixtures of other quartet states causes energy shifts which are small compared to the difference in energy between the 4P level and the ground 6S level. Thus,

$$W_{SO} = -\frac{1}{\Delta} \langle \Psi_G | (V_{SO})^2 | \Psi_G \rangle. \quad (73)$$

The Hamiltonian for the spin-orbit interaction may be written as

$$V_{SO} = \sum_i \zeta(r_i) \mathbf{l}_i \cdot \mathbf{s}_i, \quad (74)$$

where \mathbf{l}_i and \mathbf{s}_i are the orbital and spin angular momenta for the i th electron and $\zeta(r_i)$ is the spin-orbit coupling constant. Taking the square of (74),

$$(V_{SO})^2 = \sum_i \zeta^2(r_i) (\mathbf{l}_i \cdot \mathbf{s}_i)^2 + \sum_{i \neq j} \zeta(r_i) \zeta(r_j) (\mathbf{l}_i \cdot \mathbf{s}_i) (\mathbf{l}_j \cdot \mathbf{s}_j). \quad (75)$$

It can be shown by inspection that the first term in (75) cannot lead to a tensor term in the spin-Hamiltonian which is quadratic in the components of the total spin.

Therefore, it is necessary to use the second term in order to obtain a contribution to D and E .

In the spin-Hamiltonian, D and E occur in the form

$$\mathcal{H}_S = D[3S_z^2 - S(S+1)] + E(S_x^2 - S_y^2). \quad (76)$$

It is trivially shown that,

$$D = -\frac{1}{12\Delta} [\langle \Psi_G(\frac{5}{2}, \frac{5}{2}) | (V_{SO})^2 | \Psi_G(\frac{5}{2}, \frac{5}{2}) \rangle - \langle \Psi_G(\frac{5}{2}, \frac{3}{2}) | (V_{SO})^2 | \Psi_G(\frac{5}{2}, \frac{3}{2}) \rangle] \quad (77)$$

and

$$E = -\frac{1}{(10)^{1/2}\Delta} \langle \Psi_G(\frac{5}{2}, \frac{5}{2}) | (V_{SO})^2 | \Psi_G(\frac{5}{2}, \frac{1}{2}) \rangle, \quad (78)$$

where the ground-state wave functions, $\Psi_G(S, M_s)$ are characterized by total spin S and projection M_s . To include explicitly the effects of overlap and charge transfer we write,

$$\Psi_G(S, M_s) = \Psi^{(1)} | S, M_s \rangle, \quad (79)$$

where $\Psi^{(1)}$ is defined in (31) and $| S, M_s \rangle$ is the appropriate spin function for the five electrons of Mn^{2+} . One should remark that a separation into orbital and spin parts, as in (79), greatly simplifies the calculation, and is only possible for the 6S level.

It is helpful to re-express (75) in terms of the components of the one-electron orbital and spin operators. Thus, we define,

$$(V_{SO})^2 = (V_{SO})^2_D + (V_{SO})^2_E, \quad (80)$$

where

$$(V_{SO})^2_D = \sum_{i \neq j} \zeta(r_i) \zeta(r_j) [s_{iz} s_{jz} l_{iz} l_{jz} + \frac{1}{4} (l_i^+ l_j^- s_i^- s_j^+ + l_i^- l_j^+ s_i^+ s_j^-)], \quad (81)$$

and

$$(V_{SO})^2_E = \frac{1}{4} \sum_{i \neq j} \zeta(r_i) \zeta(r_j) (l_i^+ l_j^+ s_i^- s_j^- + l_i^- l_j^- s_i^+ s_j^+). \quad (82)$$

The first term of (75), and some additional components, such as $l_{iz} l_j^+ s_{iz} s_j^- \dots$ which do not contribute to the matrix elements in (77) and (78), have been omitted from (81) and (82). The expression $(V_{SO})^2_D$ contributes only to the expression (77) for D , while the expression $(V_{SO})^2_E$ contributes only to (78) for E .

A. Local Spin-Orbit Contribution, D_{SO}^l

To evaluate the local spin-orbit contribution D_{SO}^l , we substitute (81) into (77) and expand in terms of one-

¹⁴ Dennis Ikenberry and T. P. Das, Phys. Rev. **138**, A822 (1965).

electron integrals. We retain only those terms which do *not* involve ligand orbitals to obtain the local contribution. For ease of manipulation, it is helpful to handle the expectation value of the space and spin parts of the many-electron wave functions separately. We find,

$$\langle \Psi^{(1)} | (V_{\text{SO}})_D^2 | \Psi^{(1)} \rangle_{\text{loc}} = \frac{1}{2} (\zeta_{d,d})^2 \left[-s_{1z} s_{2z} \sum_{\alpha=-2}^{+2} \alpha^2 \mu_{\alpha} - \frac{1}{4} s_1^+ s_2^- \sum_{\alpha=-2}^{+2} \mu_{\alpha} q_{2,\alpha} - \frac{1}{4} s_1^- s_2^+ \sum_{\alpha=-2}^{+2} \mu_{\alpha} q_{2,-\alpha} \right], \quad (83)$$

where

$$q_{l,m} = [(l-m)(l+m+1)]^{1/2}, \quad (84)$$

$$\zeta_{d,d} = \int u_d^0 \zeta(r) u_d^0 dr,$$

and μ_{α} is defined in (40). Taking the expectation value of (83) over the spin functions $|SM_s\rangle$, the local contribution to D becomes

$$D_{\text{SO}}^l = \frac{(\zeta_{d,d})^2}{20\Delta} \sum_{\alpha=-2}^{+2} \mu_{\alpha} (\alpha^2 - 2). \quad (85)$$

Equation (85) can be conveniently split up in terms of ligand L, M contributions, as done in Sec. IV for D . We have

$$D_{\text{SO}}^l = D_{\text{SO}}^l(L=0, M=0) + D_{\text{SO}}^l(L=1, M=0) + D_{\text{SO}}^l(L=1, M=1) + D_{\text{SO}}^l(L=1, M=-1), \quad (86)$$

where

$$D_{\text{SO}}^l(L=0, M=0) = \frac{(\zeta_{d,d})^2}{10\Delta} \{ [S_s^2(F_1) - \gamma_s^2(F_1)] - [S_s^2(F_5) - \gamma_s^2(F_5)] \}, \quad (87a)$$

$$D_{\text{SO}}^l(L=1, M=0) = \frac{(\zeta_{d,d})^2}{10\Delta} \{ [S_{\sigma}^2(F_1) - \gamma_{\sigma}^2(F_1)] - [S_{\sigma}^2(F_5) - \gamma_{\sigma}^2(F_5)] \}, \quad (87b)$$

and

$$D_{\text{SO}}^l(L=1, M=1) = D_{\text{SO}}^l(L=1, M=-1) = \frac{(\zeta_{d,d})^2}{20\Delta} \times \{ [S_{\pi}^2(F_1) - \gamma_{\pi}^2(F_1)] - [S_{\pi}^2(F_5) - \gamma_{\pi}^2(F_5)] \}. \quad (87c)$$

To evaluate D_{SO}^l for Mn^{2+} , we set $\zeta_{dd} = 300 \text{ cm}^{-1}$, and $\Delta = 2.93 + 10^4 \text{ cm}^{-1}$, the same values employed in I and by Kondo,⁴ respectively. If charge transfer is ignored, then, using the values for the overlap integrals given in (44), one obtains the following results:

$$\begin{aligned} D_{\text{SO}}^l(L=0, M=0) &= -1.56 \times 10^{-4} \text{ cm}^{-1}, \\ D_{\text{SO}}^l(L=1, M=0) &= -1.66 \times 10^{-4} \text{ cm}^{-1}, \\ D_{\text{SO}}^l(L=1, M=\pm 1) &= -0.50 \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (88)$$

Adding the individual contributions, we find

$$D_{\text{SO}}^l = -4.22 \times 10^{-4} \text{ cm}^{-1}. \quad (89)$$

The expression (87b) for $L=1, M=0$, agrees exactly with Kondo's⁴ expression for D_{SO}^l . The other terms, corresponding to the remaining L, M values, which Kondo omitted, also contribute and from (88) are seen to be as large as the single term he considered.

B. Nonlocal Spin-Orbit Contribution, D_{SO}^{nl}

To obtain the nonlocal contribution to D one must again use (77), but now retain those one-electron integrals which involve the ligand orbitals only once. It is helpful once more to work with the space and spin parts of the wave functions in successive steps. Thus, using (31) and (81), one obtains,

$$\langle \Psi^{(1)} | (V_{\text{SO}})_D | \Psi^{(1)} \rangle_{\text{nonloc}} = \sum_{\substack{FLM \\ l_2, m_2}} \delta_{l_2, 2} Q'_{l_2, m_2}(s_1, s_2) A_{L, l_2}^{M, m_2}, \quad (90)$$

where

$$Q'_{l_2, m_2}(s_1, s_2) = s_{1z} s_{2z} m_2^2 + \frac{1}{4} s_1^- s_2^+ q_{l_2, m_2} q_{2, -m_2-1} + \frac{1}{4} s_1^+ s_2^- q_{l_2, -m_2} q_{2, m_2-1}, \quad (91)$$

and

$$A_{L, l_2}^{M, m_2} = \sum_{\text{F}} b_{l_2, M, m_2}(\text{F}) g_{d, l_2}(\zeta_1, \zeta_2, FLM) \lambda_{L, M, m_2}^{\text{F}}. \quad (92)$$

Here, the $b_{l_2, M, m_2}(\text{F})$ and $\lambda_{L, M, m_2}^{\text{F}}$ have been defined previously in (19) and (14), respectively, while,

$$g_{d, l_2}(\zeta_1, \zeta_2, FLM) = \zeta_{d,d} \zeta_{d, l_2}(FLM), \quad (93)$$

where

$$\zeta_{d, l_2}(FLM) = \int u_{3d}^0 \zeta(r) \alpha_{l_2}(FLM | ar) dr. \quad (94)$$

On taking the expectation values of (90) over spin functions, (77) and (90) lead to

$$D_{\text{SO}}^{nl} = \frac{1}{120\Delta} \sum_{L, M, m_2} Q_{m_2} A_{L, 2}^{M, m_2}. \quad (95)$$

Here, the Q_{m_2} are given by

$$Q_{m_2} = -4m_2^2 + q_{2, m_2} q_{2, -m_2-1} + q_{2, -m_2} q_{2, m_2-1}. \quad (96)$$

We can simplify $A_{L, 2}^{M, m_2}$ in (95) by substituting (14), (19), and (93) into (92). We find,

$$\begin{aligned} A_{L, 2}^{M, m_2} &= \zeta_{d,d} \zeta_{d, 2}(FLM) [4\{M_{3d, 2}^{L, M}(F_1) + \gamma^{L, M}(F_1)\} \\ &\quad \times [B_{2, M, m_2}(-\pi/2)]^2 + \{M_{3d, 2}^{L, M}(F_5) + \gamma^{L, M}(F_5)\} \\ &\quad \times \{[B_{2, M, m_2}(0)]^2 + [B_{2, M, m_2}(-\pi/2)]^2\}]. \end{aligned} \quad (97)$$

The various contributions to D_{SO}^{nl} can then be separated into the following four parts:

$$D_{\text{SO}}^{nl} = D_{\text{SO}}^{nl}(L=0, M=0) + D_{\text{SO}}^{nl}(L=1, M=0) + D_{\text{SO}}^{nl}(L=1, M=1) + D_{\text{SO}}^{nl}(L=1, M=-1), \quad (98)$$

where

$$D_{\text{SO}}^{nl}(L=0, M=0) = -\frac{1}{5} \frac{\zeta_{d,d}}{\Delta} \{ \zeta_{d,2}(\text{F}_100) [S_s(\text{F}_1) + \gamma_s(\text{F}_1)] - \zeta_{d,2}(\text{F}_500) [S_s(\text{F}_5) + \gamma_s(\text{F}_5)] \}, \quad (99a)$$

$$D_{\text{SO}}^{nl}(L=1, M=0) = -\frac{1}{5} \frac{\zeta_{d,d}}{\Delta} \{ \zeta_{d,2}(\text{F}_110) [S_\sigma(\text{F}_1) + \gamma_\sigma(\text{F}_1)] - \zeta_{d,2}(\text{F}_510) [S_\sigma(\text{F}_5) + \gamma_\sigma(\text{F}_5)] \}, \quad (99b)$$

$$D_{\text{SO}}^{nl}(L=1, M=1) = D_{\text{SO}}^{nl}(L=1, M=-1) = -\frac{1}{10} \frac{\zeta_{d,d}}{\Delta} \{ \zeta_{d,2}(\text{F}_111) [S_\pi(\text{F}_1) + \gamma_\pi(\text{F}_1)] - \zeta_{d,2}(\text{F}_511) [S_\pi(\text{F}_5) + \gamma_\pi(\text{F}_5)] \}. \quad (99c)$$

To evaluate (99) we need $\zeta_{d,2}(FLM)$ for $L=0, M=0$, and $L=1, M=0, \pm 1$. We have calculated the pertinent $\zeta_{d,2}(FLM)$ using the usual expression for $\zeta(r)$,

$$\zeta(r) = \frac{e^2 \hbar^2}{4m^2 c^2 a_0^3} \frac{1}{r} \frac{dV}{dr}, \quad (100)$$

where r and V are in units of a_0 and $e^2/2a_0$, respectively. The potential function $V(r)$ in (100) is obtained by using the commonly adopted technique of writing,

$$V(r) = \left(\frac{d^2 u_{d^0}}{dr^2} / u_{d^0} \right) - \frac{6}{r^2}. \quad (101)$$

We find,

$$\begin{aligned} \zeta_{d,2}(\text{F}_100) &= -0.43 \text{ cm}^{-1}, \\ \zeta_{d,2}(\text{F}_110) &= 0.75 \text{ cm}^{-1}, \\ \zeta_{d,2}(\text{F}_111) &= 0.35 \text{ cm}^{-1}. \end{aligned} \quad (102)$$

Evaluating (99) we obtain,

$$\begin{aligned} D_{\text{SO}}^{nl}(L=0, M=0) &= 0.03 \times 10^{-4} \text{ cm}^{-1}, \\ D_{\text{SO}}^{nl}(L=1, M=0) &= 0.05 \times 10^{-4} \text{ cm}^{-1}, \\ D_{\text{SO}}^{nl}(L=1, M=\pm 1) &= 0.01 \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (103)$$

The total nonlocal contribution to D is thereby given by

$$D_{\text{SO}}^{nl} = +0.10 \times 10^{-4} \text{ cm}^{-1}. \quad (104)$$

Comparing (104) with (89) we see that the nonlocal spin-orbit contribution to D is a factor of 40 times smaller than the local contribution, and of opposite sign.

C. Distant Spin-Orbit Contribution, D_{SO}^d

To obtain the distant contribution D_{SO}^d , we must collect the terms in (77) which involve the ligand orbitals twice. We find

$$\langle \Psi^{(1)} | (V_{\text{SO}}^2)_D | \Psi^{(1)} \rangle_{\text{dist}} = 2\zeta_{d,d} \sum_{L,M,M',m,\alpha} \zeta_{L,L}(\text{F}^-) \times [T_{LMM'm\alpha}(1) s_{1z} s_{2z} + T_{LMM'm\alpha}(2) s_{1-} s_{2+} + T_{LMM'm\alpha}(3) s_{1+} s_{2-}], \quad (105)$$

where

$$T_{LMM'm\alpha}(1) = -\alpha m \{ 4\lambda^{L,M}(\text{F}_1) \lambda^{L,M'}(\text{F}_1) B_{2,M,\alpha}(-\pi/2) B_{2,M',\alpha}(-\pi/2) B_{L,M,m}(-\pi/2) B_{L,M',m}(-\pi/2) + \lambda^{L,M}(\text{F}_5) \lambda^{L,M'}(\text{F}_5) [\delta_{M,\alpha} \delta_{M',\alpha} \delta_{M,m} \delta_{M',m} + \delta_{M,-\alpha} \delta_{M',-\alpha} \delta_{M,-m} \delta_{M',-m}] \}. \quad (106a)$$

$$T_{LMM'm\alpha}(2) = -\frac{1}{4} q_{2,\alpha-1} q_{L,-m-1} \{ 4\lambda^{L,M}(\text{F}_1) \lambda^{L,M'}(\text{F}_1) B_{2,M,\alpha-1}(-\pi/2) B_{2,M',\alpha-1}(-\pi/2) B_{L,M,m}(-\pi/2) \times B_{L,M',m+1}(-\pi/2) + \lambda^{L,M}(\text{F}_5) \lambda^{L,M'}(\text{F}_5) [\delta_{M,\alpha-1} \delta_{M',\alpha-1} \delta_{M,m} \delta_{M',m+1} + \delta_{M,-\alpha+1} \delta_{M',-\alpha+1} \delta_{M,-m} \delta_{M',-m-1}] \}, \quad (106b)$$

and

$$T_{LMM'm\alpha}(3) = -\frac{1}{4} q_{2,-\alpha-1} q_{L,m-1} \{ 4\lambda^{L,M}(\text{F}_1) \lambda^{L,M'}(\text{F}_1) B_{2,M,\alpha+1}(-\pi/2) B_{2,M',\alpha+1}(-\pi/2) B_{L,M,m-1}(-\pi/2) \times B_{L,M,m}(-\pi/2) + \lambda^{L,M}(\text{F}_5) \lambda^{L,M'}(\text{F}_5) [\delta_{M,\alpha+1} \delta_{M',\alpha+1} \delta_{M,m-1} \delta_{M',m} + \delta_{M,-\alpha-1} \delta_{M',-\alpha-1} \delta_{M,-m+1} \delta_{M',-m}] \}. \quad (106c)$$

In (106), $\lambda^{L,M}(\text{F})$ is connected to $\lambda_{LM\alpha}^{\text{F}}$ by the relation

$$\lambda_{LM\alpha}^{\text{F}} = b^*_{2,M} M_{\alpha}(\text{F}) \lambda^{L,M}(\text{F}). \quad (107)$$

Thus,

$$\lambda^{L,M}(\text{F}) = M_{3d,2}^{L,M}(\text{F}) + \gamma^{L,M}(\text{F}), \quad (108)$$

and

$$\zeta_{L,L}(\text{F}^-) = \int u_L^0(\text{F}^-) \zeta(r) u_L^0(\text{F}^-) dr, \quad (109)$$

where $u_L^0(\text{F}^-)$ is r times the radial wave function associated with angular momentum L for a $n=2$ F^- ion orbital.

On taking the requisite expectation values of (106) over spin states, one obtains

$$D_{\text{SO}}^d = -\frac{2}{15\Delta} \zeta_{d,d} \zeta_{p,p}(\text{F}^-) \{ [\lambda_{\pi}(\text{F}_1)]^2 - [\lambda_{\pi}(\text{F}_5)]^2 - \sqrt{3} [\lambda_{\sigma}(\text{F}_1) \lambda_{\pi}(\text{F}_1) - \lambda_{\sigma}(\text{F}_5) \lambda_{\pi}(\text{F}_5)] \}, \quad (110)$$

where, as usual

$$\lambda_{\sigma}(\text{F}) = S_{\sigma}(\text{F}) + \gamma_{\sigma}(\text{F}), \quad (111)$$

$$\lambda_{\pi}(\text{F}) = S_{\pi}(\text{F}) + \gamma_{\pi}(\text{F}).$$

Most of the quantities appearing in (110) have already

been evaluated in the course of this paper. The only parameter left to determine is the spin-orbit parameter $\zeta_{p,p}(F^-)$ for the $2p$ states of the F^- ion. We have evaluated $\zeta_{p,p}(F^-)$ using (101) and the definition (109), together with Watson's Hartree-Fock wave functions for the F^- ion.¹³ We obtain,

$$\zeta_{p,p}(F^-) = 207 \text{ cm}^{-1}, \quad (112)$$

which is near the value of 223 cm^{-1} determined from spectroscopic data for the neutral F atom. We evaluate (110) to find

$$D_{\text{SO}}^d = -1.15 \times 10^{-4} \text{ cm}^{-1}. \quad (113)$$

On comparing D_{SO}^d with D_{SO}^l , [(89) with (113)], we find the distant contribution to be one-fourth of the local contribution. This result could be anticipated since the expressions (87) and (110) resemble each other closely, except for the replacement of one $\zeta_{d,d}$ by $\zeta_{p,p}(F^-)$.

D. Local Spin-Orbit Contribution, E_{SO}^l

After manipulating Eq. (78) in exactly the same manner as was done for D_{SO}^l , we find a vanishing result.

E. Nonlocal Spin-Orbit Contribution, E_{SF}^{nl}

The nonlocal contribution to E arising from spin-orbit effects can be obtained in the same manner as D_{SO}^{nl} . Using Eqs. (78) and (82), one obtains,

$$\langle \Psi^{(1)} | (V_{\text{SO}}^2)_E | \Psi^{(1)} \rangle_{\text{nonloc}} = -2 \sum_{F,L,M,l_2,m_2} b_{l_2,M,m_2}(F) \epsilon_{L,l_2}^{M,m_2}(F), \quad (114)$$

where

$$\epsilon_{L,l_2}^{M,m_2}(F) = -\frac{1}{4} \delta_{l_2,2} \zeta_{d,d} \zeta_{d,l_2}(FLM) \times [a_- (\lambda_{L,M,m_2+2}^F - \lambda_{L,M,m_2+1}^F) + a_+ (\lambda_{L,M,m_2-2}^F - \lambda_{L,M,m_2-1}^F)], \quad (115)$$

and,

$$a_- = q_{l_2,-m_2} q_{2,m_2+1} s_1^- s_2^-, \quad (116)$$

$$a_+ = q_{l_2,m_2} q_{2,-m_2+1} s_1^+ s_2^+.$$

Substituting these expressions in (78) one obtains the nonlocal contribution to E ,

$$E_{\text{SO}}^{nl} = -\frac{1}{20\Delta} \sum_{F,L,M,l_2,m_2} [\delta_{l_2,2} b_{l_2,M,m_2}(F) \times \zeta_{d,d} \zeta_{d,l_2}(FLM) q_{l_2,-m_2} q_{2,-m_2+1} (\lambda_{L,M,m_2-2}^F - \lambda_{L,M,m_2-1}^F)]. \quad (117)$$

This expression can be simplified further using (14), (19), and (25);

$$E_{\text{SO}}^{nl} = -\frac{\zeta_{d,d} \cos 2p}{5\Delta} \sum_{L,M,m_2} \{ \zeta_{d,d}(F_1LM) \times B_{2,M,m_2}(-\pi/2) B_{2,M,m_2-2}(-\pi/2) q_{2,m_2} q_{2,m_2-1} \times [M^{L,M} \zeta_{3d,2}(F_1) + \gamma^{L,M} \zeta_{3d,2}(F_1)] \}, \quad (118)$$

where the sum over m_2 runs from -2 to $+2$ and over M from $-L$ to $+L$. Making use of Table II, one obtains, after considerable algebra,

$$E_{\text{SO}}^{nl} = E_{\text{SO}}^{nl}(L=0, M=0) + E_{\text{SO}}^{nl}(L=1, M=0) + E_{\text{SO}}^{nl}(L=1, M=1) + E_{\text{SO}}^{nl}(L=1, M=-1), \quad (119)$$

where

$$E_{\text{SO}}^{nl}(L=0, M=0) = \frac{3}{5} \frac{\zeta_{d,d}}{\Delta} (\cos 2p) \zeta_{d,2}(F_100) \times [S_s(F_1) + \gamma_s(F_1)], \quad (120a)$$

$$E_{\text{SO}}^{nl}(L=1, M=0) = \frac{3}{5} \frac{\zeta_{d,d}}{\Delta} (\cos 2p) \zeta_{d,2}(F_110) \times [S_\sigma(F_1) + \gamma_\sigma(F_1)], \quad (120b)$$

$$E_{\text{SO}}^{nl}(L=1, M=+1) = E_{\text{SO}}^{nl}(L=1, M=-1) = \frac{3}{10} \frac{\zeta_{d,d}}{\Delta} (\cos 2p) \zeta_{d,2}(F_111) [S_\pi(F_1) + \gamma_\pi(F_1)]. \quad (120c)$$

Again, our expressions for E_{SO}^{nl} differ from those of Kondo⁴ because of a numerical approximation he was forced to make, and because he omitted the $L=0, M=0$, and $L=0, M=\pm 1$ terms in (120). The specific approximation he made was to set

$$(\text{Kondo}) \quad \zeta_{d,2}(F_110) \sim \zeta_{d,d} S_\sigma(F_1). \quad (121)$$

We find this approximation to be *very* poor; explicit calculations show

$$\zeta_{d,2}(F_110) = (1/40) \zeta_{d,d} S_\sigma(F_1). \quad (122)$$

Hence, Kondo's calculated value E_{SO}^{nl} is too large by a factor of roughly 40. This, in large part, explains his ability to fit the experimental values of E for $\text{Mn}^{2+}:\text{ZnF}_2$ using the overlap model. We shall show that, to the contrary, overlap contributions to E are significantly smaller than those obtained in Paper I. Evaluating (120), we find

$$E_{\text{SO}}^{nl}(L=0, M=0) = 0.31 \times 10^{-4} \text{ cm}^{-1},$$

$$E_{\text{SO}}^{nl}(L=1, M=0) = 0.64 \times 10^{-4} \text{ cm}^{-1}, \quad (123)$$

$$E_{\text{SO}}^{nl}(L=1, M=\pm 1) = 0.09 \times 10^{-4} \text{ cm}^{-1},$$

so that

$$E_{\text{SO}}^{nl} = 1.13 \times 10^{-4} \text{ cm}^{-1}. \quad (124)$$

F. Distant Spin-Orbit Contribution, E_{SO}^d

The distant contribution to E can be obtained in a similar manner as D_{SO}^d (110). After considerable algebra, one obtains

$$E_{\text{SO}}^d = -\frac{2 \cos 2p}{5 \Delta} \zeta_{d,d} \zeta_{p,p}(F^-) \{ [S_\pi(F_1) + \gamma_\pi(F_1)]^2 - \sqrt{3} [S_\pi(F_1) + \gamma_\pi(F_1)] [S_\sigma(F_1) + \gamma_\sigma(F_1)] \}. \quad (125)$$

Using the values $\zeta_{p,p}(F^-) = 207 \text{ cm}^{-1}$ and $\zeta_{d,d} = 300 \text{ cm}^{-1}$, we obtain

$$E_{SO}^{d=} = -6.47 \times 10^{-4} \text{ cm}^{-1}. \quad (126)$$

It is interesting to note that the distant contribution to E is about five times larger than the nonlocal contribution (124) to E and of opposite sign.

VI. DISCUSSION

The goal of these papers is the calculation of the spin-Hamiltonian parameters D and E for an S -state ion, specifically $\text{Mn}^{2+}:\text{ZnF}_2$. We have treated in this paper the effects of overlap and charge transfer. Unfortunately, the lack of a detailed knowledge of the charge-transfer coefficients prevented us from including them in our quantitative estimations for D and E . However, there exists evidence from other sources (transferred hyperfine interactions and g shifts) that charge-transfer effects may not be very important for the Mn^{2+} ion. In any case, our formalism does allow for charge transfer, and can be used for quantitative estimates when such parameters are available.

We summarize the results of Secs. IV and V in Table

TABLE V. Overlap contribution to the spin-Hamiltonian parameters D and E for $\text{Mn}^{2+}:\text{ZnF}_2$, in units of 10^{-4} cm^{-1} .

	D			E		
	Local	Nonlocal	Distant	Local	Nonlocal	Distant
Spin-Spin	-2.51	-3.16	...	0	-14.43	...
Spin-Orbit	-4.22	+0.10	-1.15	0	+1.13	-6.47
Total		-10.94			-19.77	

V. The sum of the overlap contribution computed in this paper and of the point-charge model from I (for Baur's crystal parameters) are compared with the experimental results of Tinkham² in Table VI. From this table it is clear that the point-charge mechanism and overlap effects lead to contributions of nearly the same magnitude as experiment. This conclusion should be contrasted with that of Kondo,⁴ who argued for the dominance of overlap terms. In fact, the contribution to E from overlap effects ($-19.77 \times 10^{-4} \text{ cm}^{-1}$) is considerably smaller in magnitude than the point-charge contribution ($-102.32 \times 10^{-4} \text{ cm}^{-1}$). The sum of the two contributions to E , $-122.09 \times 10^{-4} \text{ cm}^{-1}$, is remarkably close to Tinkham's² experimental value of $-113.50 \times 10^{-4} \text{ cm}^{-1}$.

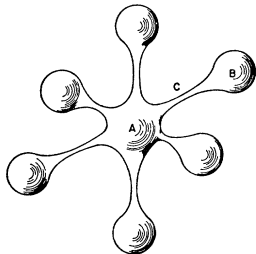


FIG. 3. A very pictorial view of the charge distribution appropriate to the $\text{Mn}^{2+}:\text{F}_6^-$ cluster.

TABLE VI. Compilation of results for D and E appropriate to $\text{Mn}^{2+}:\text{ZnF}_2$ from I and this paper, in units of 10^{-4} cm^{-1} .

	D	E
Point-Multipole Model	+24.01	-102.32
Overlap Model	-10.94	-19.77
Total	+13.07	-122.09
Experimental (Ref. 2)	+10.50	-113.50

The overlap contribution to D is seen to be opposite in sign to the point-charge contribution so that a partial cancellation occurs. The net result, $13.07 \times 10^{-4} \text{ cm}^{-1}$, is also close to Tinkham's value of $10.50 \times 10^{-4} \text{ cm}^{-1}$.

It is of interest to note that for both D and E : (i) nonlocal terms dominate for spin-spin interactions, (ii) the nonlocal terms play a negligible role in the case of spin-orbit interaction, and (iii) the relative signs of local and nonlocal terms for the spin-orbit mechanism are different while the relative signs of the local and distant terms are the same. One can construct physical arguments for these results from a consideration of the schematic diagram, Fig. 3, representing the distribution of charge density in the $\text{Mn}^{2+}:\text{F}_6^-$ cluster. It is convenient to divide the regions of the cluster into three parts; A, B, and C. Region A represents the immediate vicinity of the central ion, region B the immediate vicinity of the ligand F^- ions, and C the intermediate or "neck regions." The contributions to D and E are finite only when the charge distribution around the central ion deviates from cubic symmetry. The relative contributions to D and E from regions A and B as compared to C will depend on the extent of the departure from cubic symmetry in these regions. It is evident that the charge density in region C is strong nonspherical compared to A and B. This argument then explains the predominance of the nonlocal terms over the local in the case of spin-spin interaction. One might attempt to apply the same argument to the spin-orbit interaction but, as we have shown already in Sec. V, the nonlocal spin-orbit coupling constants $\zeta_{d,2}(FLM)$ are more than a factor of 260 smaller than $\zeta_{d,d}$ or $\zeta_{p,p}(F^-)$. As a result, the nonlocal contribution to D and E is vanishingly small. As regards the third observation, we note that, because of overlap effects, the charge density of the electrons surrounding the central and ligand ions (regions A and B) will increase as the electron density accumulates in the regions A and B by migration from the region C as a consequence of the Pauli correlation. An increase of electron density means an increase of negative-charge density while a decrease of electron density can be thought of as an increase of positive-charge density. Thus, in the regions A and B, an effective negative perturbed charge density is present while, in region C, a positive perturbed charge density is present. Because the orbital moment has opposite sign for positive and negative charge, the sign of the spin-orbit interaction

(but not of the spin-spin interaction) will depend on the sign of the charge. Thus, the sign of the perturbed charge in regions A and B is effectively opposite to that in the region C and we expect that the local and distant contributions should have the same relative sign but that both should be opposite to that of the nonlocal contribution.

It is also of interest to predict the over-all signs of D and E on the basis of overlap model. For this purpose one must analyze the various expressions derived in Secs. IV and V. An examination of our results demonstrates that the sign of D and E depends on the following quantities:

$$D \sim [S_i^2(F_1) - S_i^2(F_5)] \quad (127)$$

and

$$E \sim -(\cos 2\phi) S_i^2(F_1). \quad (128)$$

Thus, if the distance between the central ion and the ligand ion F_5 is larger than the distance between the central ion and ligand ion F_1 , the sign of D due to overlap is positive. The value of D vanishes if these two distances are equal. The sign of E, however, will be negative if the angle 2ϕ between the diagonals is less than $\pi/2$, otherwise it is positive. E is zero if ϕ becomes equal to $\pi/4$.

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APPENDIX

We are interested in this Appendix in deriving an explicit form for the α functions defined in Eq. (17). Löwdin¹⁰ has derived a few of these expressions for small l , L , and M , but to our knowledge no general formula for the α functions has yet been given. These functions are found to be quite useful for a variety of problems. For example, we have made use of them in the calculation of the overlap integrals (26) and (28), the double integrals (51), and the nonlocal spin-orbit coupling constants (94). A detailed derivation of the results presented in this Appendix will be given by one of the authors (RRS) elsewhere.¹⁵

According to our definition of the α function, we write

$$\Phi(NLM | R, \Theta, \Phi) = \sum_{l=0}^{\infty} \frac{1}{r} \alpha_l(NLM | ar) Y_l^m(\theta, \phi), \quad (A1)$$

where $\Phi(NLM | R, \Theta, \Phi)$ is the wave function centered at the site B to be expanded about the center A which lies a distance a away, as in Fig. 2. The polar coordinates (r, θ, ϕ) are the coordinates with respect to the center A, and R, Θ, Φ are those with respect to center B.

According to Löwdin's definition of α function which we denote by $\alpha_l^0(NLM | ar)$, we have

$$\Phi(NLM | R, \Theta, \Phi) = k_{LM} \sum_{l=0}^{\infty} \alpha_l^0(NLM | ar) P_L^M(\cos \theta) \begin{pmatrix} \cos m\phi \\ \sin m\phi \end{pmatrix}, \quad (A2)$$

where

$$k_{LM} = \left[\epsilon_M \left(\frac{2L+1}{4\pi} \right) \frac{(L-M)!}{(L+M)!} \right]^{1/2}, \quad (A3)$$

and

$$\epsilon_0 = 1, \quad \epsilon_\mu = 2 \quad (\nu \geq 1). \quad (A4)$$

It is clear from (A2) that Löwdin used real spherical harmonics instead of the complex expressions Y_l^m which we employ. One can relate our α functions to his, α_l and α_l^0 , by the simple relation

$$\alpha_l(FLM | ar) = \left[\frac{(2L+1)(L-M)!(L+M)!}{(2l+1)(l+M)!(L+M)!} \right]^{1/2} r \alpha_l^0(NLM | ar). \quad (A5)$$

In the paper by RRS,¹⁵ a general and explicit form for α_l^0 is derived. He finds,

$$\alpha_l^0(NLM | ar) = B_{LMl}(ar) \sum_{s=0}^{l+L} H_{L,l}^{M,s}(ar) \int_{|a-r|}^{|a+r|} f_{NLM}(R) R^{-L+2s} dR, \quad (A6)$$

¹⁵ R. R. Sharma, J. Math. Phys. (to be published).

where

$$B_{LMl}(ar) = \frac{(2l+1)(-1)^L [\cos \frac{1}{2}(l+M)\pi](l+M-1)!}{a^{2-L} 2^{2L+l-M} [\frac{1}{2}(l+M)]! [\frac{1}{2}(l+M)-1]!} \left(\frac{r}{a}\right)^{M-1} \frac{(l-M)!}{(l+M)!}, \quad l+M \text{ an even integer} \quad (\text{A7})$$

$$= \frac{(2l+1)(-1)^L [\sin \frac{1}{2}(l+M)\pi](l-M)!}{a^{2-L} 2^{2L+l-M} [\frac{1}{2}(l-M-1)]! [\frac{1}{2}(l+M-1)]!} \left(\frac{r}{a}\right)^{M-2} \left(1 + \frac{r^2}{a^2}\right), \quad l+M \text{ an odd integer}$$

and

$$H_{L,l}^{M,s}(ar) = \frac{1}{a^{2s}} \sum_{n,r',q'=0}^{n_0, r_0', q_0'} c c' \left(1 - \frac{r^2}{a^2}\right)^{L-r'-M-s+q'} \frac{(1+r^2/a^2)^{2n-q'}}{(r/a)^{2n}} \quad (\text{A8})$$

with $n_0 =$ quotient of $\frac{1}{2}(l+M)$ (for example quotient of $\frac{3}{2}$ is 1 and quotient of $\frac{1}{2}$ is 0),

$r_0' =$ quotient of $\frac{1}{2}(L-M)$, $q_0' = (2n)$ or $(2n+1)$ according as $l+M$ is even or odd,

and

$$c = \frac{(-1)^{r'+q'} (2n)! (2L-2r')!}{n! q! (2n+1-q)! (s-q-r')! (L-r'-M-s+q)! (L-r')! r'! 2^{2n-2r'}}, \quad (\text{A9})$$

$$c' = \begin{cases} \left(\frac{l}{2} \frac{M}{2}\right)_n \left(\frac{1}{2} + \frac{l}{2} \frac{M}{2}\right)_n \frac{2n-q'+1}{(\frac{1}{2})_n}, & \text{if } l+M = \text{even integer} \\ \left(\frac{1}{2} \frac{l}{2} \frac{M}{2}\right)_n \left(1 + \frac{l}{2} \frac{M}{2}\right)_n (2n+1), & \text{if } l+M = \text{odd integer.} \end{cases} \quad (\text{A10})$$

The function $f(R)$ occurring in (A6) is R times the radial part of the wave function $\Phi(NLM | R\Theta\Phi)$. That is,

$$\Phi(NLM | R\Theta\Phi) = [f_{NL}(R)/R] Y_L^M(\Theta, \Phi). \quad (\text{A11})$$

The notations $(b)_n$ used in (A10) is defined by

$$(b)_n = 1 \quad \text{for } n=0, \quad (b)_n = \frac{\Gamma(b+n)}{\Gamma(b)} = b(b+1)\cdots(b+n-1) \quad \text{for } n=1, 2, \dots \quad (\text{A12})$$

Equations (A6) to (A12) give explicit forms for the α functions α_l^0 as defined by Löwdin (A2), which are applicable for all values of l , L , and M .

An asymptotic form for the α functions for small r can be derived as follows. For small values of r the integral appearing in (A6) can be replaced by

$$\int_{|a-r|}^{a+r} f_{NL}(R) R^{-L+2s} dR = f_{NL}(a) \times \frac{(a+r)^{-L+2s+1} - (|a-r|)^{-L+2s+1}}{-L+2s+1} \quad \text{for } L-2s \neq 1 \quad (\text{A13})$$

$$\times \ln\left(\frac{a+r}{|a-r|}\right) \quad \text{for } L-2s = 1.$$

Using (A13), the value of the α function for small values of r can be obtained directly from (A6). For $r=0$, we find

$$\alpha_l^0(NLM | a0) = \frac{f_{NLM}(a)}{a} (-1)^L \delta_{l,0} \delta_{M,0}. \quad (\text{A14})$$