Zero-Field Splitting of S-State Ions. I. Point-Multipole Model*

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The zero-field splitting terms in the spin Hamiltonian for an S-state ion, $D[3S_z^2-S(S+1)]$ and $E(S_x^2-S_y^2)$, are computed using a point-multipole model. Various contributions to D and E are considered and quantitative results are given for the most important mechanisms. Specific application is made to Mn^{2+}: ZnF_2 and MnF_2, where accurate values for D and E are known from electron-spin-resonance experiments. The most important contribution for these cases comes from the "Blume-Orbach" mechanism involving the first-order matrix element of the axial and rhombic fields between excited quartet states which have been admixed into one another by the cubic component of the crystalline field. This term contributes results of the correct sign, and of nearly the correct magnitude, to explain the entirety of the axial and rhombic field splitting of Mn^{2+} in these hosts. The next most important contribution arises from the spin-spin interaction (the "Pryce" mechanism) involving again the first-order matrix element of the crystalline field, but this time between an excited configuration and the ground state. Instead of the usual perturbation approach, the Schrödinger equation containing the crystal-field potential is integrated numerically. It is found that the term considered by Pryce, the $d\rightarrow s$ admixture, is small, and of the opposite sign from the more important contribution of the $d\rightarrow d$ admixture. The net contribution from the spin-spin mechanism yields results for D of the wrong sign and of roughly one-third the magnitude of the Blume-Orbach term, and for E a constribution of the correct sign but an order of magnitude smaller than the Blume-Orbach term. The configuration-interaction contribution of Orbach, Das, and Sharma is shown to be next in decreasing order of importance, followed by the contribution originally computed by Watanabe.

I. INTRODUCTION

THE origin of the axial field splitting of S-state ions was first discussed in a qualitative manner by Van Vleck and Penney[1] in 1934. The vanishing of the diagonal matrix element of an electric operator in a half-filled shell led them to the consideration of high-order admixtures involving the spin-orbit coupling and the axial field. Pryce[2] in 1950, however, showed that one could obtain a finite contribution in relatively low order by the use of the spin-spin interaction and the admixture of states outside the ground configuration. The Pryce mechanism for the $3d^5$ ions (Mn^{2+}, Fe^{3+}) involved the matrix element of the spin-spin interaction Hamiltonian $\mathcal{H}_{ss}$ between the $^6S(3d^5)$ and $^6D(3d^44s)$ states, and the matrix element of the axial field potential $\mathcal{H}_{ax}$ between the $^6D(3d^44s)$ and the $^6S(3d^5)$ states. Thus,

$$D_P \propto \frac{\langle {}^6S(3d^5)|\mathcal{H}_{ax}|{}^6D(3d^44s)\rangle\langle {}^6D(3d^44s)|\mathcal{H}_{ss}|{}^6S(3d^5)\rangle}{E({}^6S(3d^5))-E({}^6D(3d^44s))}. \quad (1)$$

Watanabe[3] in 1957 performed the first quantitative calculation of both the spin-orbit and spin-spin (Pryce) contributions. In additon to the Pryce term, Watanabe also considered the admixture of the excited $|{}^4P\rangle$ into the ground $|{}^6S\rangle$ state by the spin-orbit coupling $\mathcal{H}_{so}$. The matrix element of the axial field potential was then taken between the $|{}^4P\rangle$ admixed into the ground level and the $|{}^4D\rangle$ excited level.

Thus,

$$D_W \propto \frac{\langle {}^6S|\mathcal{H}_{so}|{}^4P\rangle\langle {}^4P|\mathcal{H}_{ax}|{}^4D\rangle\langle {}^4D|\mathcal{H}_{ax}|{}^4P\rangle\langle {}^4P|\mathcal{H}_{so}|{}^6S\rangle}{[E({}^6S)-E({}^4P)]^2[E({}^6S)-E({}^4D)]}. \quad (2)$$

It is understood in (2) that all the term values are constructed from the $3d^5$ configuration alone. Watanabe's results appeared to be considerably smaller than the values measured experimentally and Kondo[4] suggested in 1960 that anisotropic covalent admixtures might remove the discrepancy. In this and a subsequent paper[5] Kondo computed the covalent contributions to the axial field splitting of Mn^{2+} in MnF_2 and strained MgO. He fitted his formulas to the observed experimental results obtaining a (small) value for γ_σ, the electron transfer coefficient for σ-type bonding orbitals. He considered both spin-spin and spin-orbit contributions to D and E. Because agreement was obtained using a small value for the electron transfer, it appeared that the overlap contribution to the axial field splitting was dominant. Subsequently, Blume and Orbach[6] (BO)

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[1] J. M. Van Vleck and W. G. Penney, Phil. Mag. **17**, 961 (1939).
[2] M. H. L. Pryce, Phys. Rev. **80**, 1107 (1950).
[3] H. Watanabe, Progr. Theoret. Phys. (Kyoto) **18**, 405 (1957).
[4] J. Kondo, Progr. Theoret. Phys. (Kyoto) **23**, 106 (1960).
[5] J. Kondo, Progr. Theoret. Phys. (Kyoto) **28**, 1026 (1962).
[6] M. Blume and R. Orbach, Phys. Rev. **127**, 1587 (1962).

considered the axial field splitting of S-state ions in a deformed cubic host. They proposed a mechanism involving the spin-orbit admixture of the excited $|{}^4P\rangle$ into the ground $|{}^6S\rangle$ and the first-order matrix element of the axial and rhombic fields. Normally such terms would vanish but in this case a nonzero result obtained because of mixing of the excited quartet states by the cubic crystalline field. More specifically, the ${}^4\Gamma_4$ component of the $|{}^4P\rangle$ is strongly admixed with the ${}^4\Gamma_4$ components of the $|{}^4G\rangle$ and $|{}^4F\rangle$ states by the cubic crystalline field. Nonvanishing first-order matrix elements of the axial and rhombic field potentials exist between the $|{}^4P\rangle$, $|{}^4F\rangle$, and the $|{}^4G\rangle$ components of the admixed excited ${}^4\Gamma_4$ level. Thus,

$$D_{\mathrm{BO}} \propto \frac{\langle {}^6S|\mathcal{H}_{\mathrm{so}}|{}^4\Gamma_4\rangle\langle {}^4\Gamma_4|\mathcal{H}_{\mathrm{ax}}|{}^4\Gamma_4\rangle\langle {}^4\Gamma_4|\mathcal{H}_{\mathrm{so}}|{}^6S\rangle}{[E({}^4\Gamma_4)-E({}^6S)]^2}. \quad (3)$$

Notice that treatment of the cubic field by conventional perturbation theory would result in an extra factor in (3) of $\mathcal{H}_{\mathrm{cubic}}/[E({}^6S)-E({}^4G)]$, which would considerably reduce the value of D. Such a procedure is not appropriate, however, when the cubic field potential is of the same order as the ${}^4P$, ${}^4G$, ${}^4F$ free-ion energy separations. It is necessary to first diagonalize the quartet ${}^4\Gamma_4$ matrix in a cubic crystalline field and then use perturbation theory to consider the effects of the spin-orbit coupling and axial and rhombic fields. The values obtained by BO for the spin-Hamiltonian coefficients in a deformed crystal were of the same magnitude but opposite in sign to the experimental values obtained by Watkins and Feher,[7] Shiren,[8] and Feher.[9] Unfortunately the sign of their result was wrong because of an incorrect choice of phase for the ${}^4G$ state. A subsequent calculation by the authors[10] will consider this question in more detail. Another attempt to fit the axial field splitting of S-state ions was made by Orbach, Das, and Sharma[11] (ODS) using a method due to Sternheimer.[12] They added the axial field potential to the Hartree-Fock potential derived from Watson's[13] $3d$ functions and integrated the one-electron Schrödinger equation numerically to obtain s-, d-, and g-like admixtures to the unperturbed functions. The term value determinants were then constructed using the perturbed orbitals, and the matrix element of the axial field perturbation was taken between the perturbed states. Denoting the configurationally admixed states by a prime, this leads to an axial field splitting

$$D_{\mathrm{DOS}} \sim \frac{\langle {}^6S|\mathcal{H}_{\mathrm{so}}|{}^4\Gamma_4'\rangle\langle {}^4\Gamma_4'|\mathcal{H}_{\mathrm{ax}}|{}^4\Gamma_4'\rangle\langle {}^4\Gamma_4'|\mathcal{H}_{\mathrm{so}}|{}^6S\rangle}{[E({}^6S)-E({}^4\Gamma_4')]^2}, \quad (4)$$

a result of very much the same form as D_{BO}. A direct comparison showed this result to dominate that computed by Watanabe, but to still fall somewhat short of the experimental values.

This paper presents a comprehensive treatment of the axial field splitting of Mn^{2+} ions in the point-multipole approximation. All the preceding mechanisms, with the exception of Kondo's covalent contribution, are computed using axial rhombic and cubic potentials appropriate to Mn^{2+} in ZnF_2 and MnF_2. It will be shown that very close agreement is obtained with the experimental values of D and E in these two salts. In a subsequent paper, the covalent terms considered by Kondo will be re-examined and computed in considerable detail. It will be shown that covalent contributions to D and E are smaller than the point-multipole contributions by, in some cases, an order of magnitude. The origin of the discrepancy between our covalent estimates of D and E and those of Kondo seems to lie in some approximations which Kondo was forced to make in order to evaluate some two-center integrals appearing in his final expressions for D and E. A third paper will discuss the axial splitting of Mn^{2+} ions in a strained cubic host. Specific application will be made to MgO to facilitate comparison with experiment.[7–9]

In the next section, the wave functions of a ${}^6S$, $3d^5$ ion are obtained in a cubic crystalline field, perturbed by axial and rhombic potentials and the spin-orbit coupling. The resulting wave functions are used to compute: Sec. III, the Watanabe contribution; Sec. IV, the BO contribution; Sec. V, the ODS contribution; and Sec. VI, the spin-spin (Pryce) contribution to D and E. In Sec. VII, the explicit expressions for the crystalline electric fields are derived and a specific evaluation is made for the cases of Mn^{2+}: ZnF_2 and MnF_2.

In Sec. VIII the results are discussed and compared with the experimental values.

II. S-STATE ION WAVE FUNCTION IN AN AXIAL FIELD

The Hamiltonian governing the $3d$ functions is

$$\mathcal{H} = -\sum_i (\hbar^2/2m)\nabla_i^2 - \sum_i (Ze^2/r_{iN}) + \sum_{i<j} e^2/r_{ij} + \mathcal{H}_c + \mathcal{H}_{\mathrm{so}} + \mathcal{H}_{\mathrm{ss}} + V_2^0 + V_2^2 + V_4 + V_4^2. \quad (5)$$

[7] G. D. Watkins and E. Feher, Bull. Am. Phys. Soc. **7**, 29 (1962).
[8] N. S. Shiren, Bull. Am. Phys. Soc. **7**, 29 (1962).
[9] E. Feher, Phys. Rev. **136**, A145 (1964).
[10] R. R. Sharma, T. P. Das, and R. Orbach (to be published).
[11] R. Orbach, T. P. Das, and R. R. Sharma, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and the Physical Society, London, 1965), p. 330.

It is appropriate to point out some numerical corrections in this earlier publication on the configuration-interaction mechanism. The right-hand side of Eq. (15) in this reference should read $(-17.82/R^3)$. Equations (17) and (19) should be replaced, respectively, by

$$D = +0.0007\ \mathrm{cm}^{-1},$$

and

$$D_W = -0.0005\ \mathrm{cm}^{-1}.$$

Equation (21) suffers from some algebraic errors and should be replaced by Eq. (52) of this paper with $B_2^0 = 2/R^3$.

[12] R. M. Sternheimer and H. Foley, Phys. Rev. **102**, 961 (1965).
[13] R. E. Watson, Phys. Rev. **118**, 1036 (1960).

The first three terms in (5) represent the free-ion Hamiltonian for the $3d$ electrons. We shall assume that these terms are not modified upon going from the free ion to the solid. The fourth term is the cubic crystalline field

$$\mathcal{H}_c = B_4^0 \sum_i r_i^4 \{ Y_4^0(i) + (5/14)^{1/2} [Y_4^4(i) + Y_4^{-4}(i)] \}, \quad (6)$$

and the fifth, the spin-orbit coupling

$$\mathcal{H}_{so} = \sum_i \zeta(r_i) \mathbf{l}_i \cdot \mathbf{s}_i. \quad (7)$$

In this paper we shall take the free-ion value for $\zeta(r_i)$. In a subsequent paper treating covalent effects it will be necessary to use the more correct operator form for $\zeta_{OP}(r_i) = (e\hbar^2/2m^2c^2)(1/r)dV(i)/dr$. The sixth term in (4) is the spin-spin interaction,

$$\mathcal{H}_{ss} = \frac{g^2\beta^2}{a_0^3} \sum_{i<j} \left[\frac{\mathbf{s}_i \cdot \mathbf{s}_j}{r_{ij}^3} - \frac{3(\mathbf{s}_i \cdot \mathbf{r}_{ij})(\mathbf{s}_j \cdot \mathbf{r}_{ij})}{r_{ij}^5} \right], \quad (8)$$

and the seventh and eighth terms are the axial and rhombic potentials, respectively,

$$V_2^0 = -B_2^0 (4\pi/5)^{1/2} \sum_i r_i^2 Y_2^0(i), \quad (9a)$$

$$V_2^2 = -B_2^2 (4\pi/5)^{1/2} \sum_i r_i^2 [Y_2^2(i) + Y_2^{-2}(i)]. \quad (9b)$$

The ninth term is the so-called "unbalanced" axial component of the $l=4$ terms in the crystalline field potential. That is, V_4 represents the remainder of the potential,

$$V_4 = -B_4^{0\prime} (4\pi/9)^{1/2} \sum_i r_i^4 Y_4^0(i), \quad (10a)$$

after the cubic component (5) has been subtracted. Finally V_4^2 represents the fourth-order rhombic field,

$$V_4^2 = -B_4^2 (4\pi/9)^{1/2} \sum_i r_i^4 [Y_4^2(i) + Y_4^{-2}(i)]. \quad (10b)$$

The low-lying eigenstates of the free-ion Hamiltonian (in the absence of V_{so}) are shown on the left of Fig. 1. The ground level ^6S is the only sextet in the d^5 configuration and is an orbital singlet. Because we need to compute the matrix elements of orbital operators [Eqs. (8)–(10)] it is clear that we must consider admixtures of excited states with orbital moment into the ground level. This necessitates the use of the spin-orbit coupling (7). Using the fact that $\mathbf{l}(r_i)$ transforms as Γ_4 of the cubic group, and the orbital part of the ground ^6S level as Γ_1, only excited $^4\Gamma_4$ levels can be admixed by $\mathcal{H}_{so}$. The only excited quartets which contain Γ_4 character are the ^4P, ^4F, and ^4G. The triangle rule assures that only the ^4P will be admixed by $\mathcal{H}_{so}$ into the ^6S. However, as Blume and Orbach[6] point out, the cubic crystalline field (6) admixes the three $^4\Gamma_4$ levels into one another. The size of the cubic field is

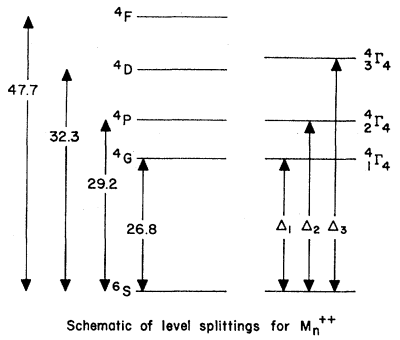

FIG. 1. Schematic of level splittings for Mn^{2+}. The atomic energy levels for the free $3d^5$—Mn^{2+} ion are indicated on the left while on the right the levels appropriate to a cubic field are shown. The numbers in the figure give the energies of the levels relative to ^6S in units of 10^3 cm^{-1}.

comparable in magnitude to the relative splitting of ^4P, ^4F, and ^4G. Hence it is necessary to first diagonalize the $^4\Gamma_4$ matrix in the presence of the cubic field. Defining the phases of the quartet states for which $M_L = L$, $M_S = S$ by

$$\begin{aligned}
&|{}^4G, M_L=4\rangle = |2^+2^-1^+0^+-1^+\rangle, \\
&|{}^4F, M_L=3\rangle = (1/\sqrt{2})[|2^+1^+1^-0^+-1^+\rangle \\
&\qquad\qquad + |2^+2^-1^+0^+-2^+\rangle], \\
&|{}^4P, M_L=1\rangle = (1/\sqrt{5})[|2^+1^+0^+-1^+-1^-\rangle \\
&\qquad + (\sqrt{\tfrac{3}{2}})|2^+1^+0^+0^--2^+\rangle \\
&\qquad + (\sqrt{\tfrac{3}{2}})|2^+1^+1^--1^+-2^+\rangle \\
&\qquad\qquad + |2^+2^-0^+-1^+-2^+\rangle],
\end{aligned} \quad (11)$$

the three eigenfunctions of $\mathcal{H}_c$ which transform as $^4\Gamma_4$ can be written as

$$|{}^4\Gamma_4 M_\Gamma\rangle = [\alpha_i |P^4\Gamma_4 M_\Gamma\rangle + \beta_i |F^4\Gamma_4 M_\Gamma\rangle + \gamma_i |G^4\Gamma_4 M_\Gamma\rangle], \quad (12)$$

where M_Γ denotes one of the three subvectors of the Γ_4 representation which we label by -1, 0, $+1$. The coefficients α_i, β_i, and γ_i are determined from the secular determinant of $\mathcal{H}_c$. Using the free-ion splittings,[14]

$$\begin{aligned}
E(^4P) - E(^4G) &= 2357.5 \text{ cm}^{-1}, \\
E(^4F) - E(^4G) &= 16\,782.6 \text{ cm}^{-1}, \\
E(^4G) - E(^6S) &= 26\,800.0 \text{ cm}^{-1},
\end{aligned} \quad (13)$$

and values of $\mathcal{H}_c$ appropriate to $10Dq = 9000$ cm^{-1}, 10 000 cm^{-1}, and 11 000 cm^{-1}, the eigenfunctions and eigenvalues (Δ_i) of the cubic secular determinant were computed and listed in Table I. It will be seen that a similar table in the Blume-Orbach[6] paper apparently gives the same signs for the γ_i as found in Table I. However BO should really have found a value for γ_i of opposite sign because the phase factors chosen for the ^4G state here and that adopted by Blume and Orbach differ by a negative sign.

[14] Charlotte E. Moore, *Atomic Energy Levels*, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Publishing and Printing Office, Washington, D. C., 1949).

TABLE I. Values of α_i, β_i, γ_i, and Δ_i for the Mn^{+2} ion.

i	α_i	β_i	γ_i	Δ_i (cm^{-1}) measured from ^6S
		$10Dq=9000\ cm^{-1}$		
1	0.633	−0.127	0.763	19 501
2	0.761	0.285	−0.583	35 380
3	0.143	−0.950	−0.277	44 805
		$10Dq=10\,000\ cm^{-1}$		
1	0.637	−0.135	0.759	18 546
2	0.751	0.334	−0.570	36 001
3	0.176	−0.933	−0.314	45 138
		$10Dq=11\,000\ cm^{-1}$		
1	0.640	−0.143	0.755	17 588
2	0.739	0.385	−0.553	36 569
3	0.212	−0.912	−0.352	45 529

The spin-orbit coupling can now couple the $|{}_i{}^4\Gamma_4, M_\Gamma\rangle$ to the ^6S ground level. To first order, the admixed wave functions are

$$|{}^6SM_S\rangle' = |{}^6SM_S\rangle - \sum_{i=1}^{3} \frac{\alpha_i}{\Delta_i}\zeta[a(M_S)\,|{}_i{}^4\Gamma_4 1, M_S-1\rangle + b(M_S)\,|{}_i{}^4\Gamma_4 -1, M_S+1\rangle + c(M_S)\,|{}_i{}^4\Gamma_4 0, M_S\rangle], \quad (14)$$

where

$$\begin{aligned}
&|{}_i{}^4\Gamma_4 1 M_S\rangle \\
&\quad = \{\alpha_i|P1\rangle + \beta_i[(\sqrt{\tfrac{3}{8}})|F1\rangle + (\sqrt{\tfrac{5}{8}})|F-3\rangle] \\
&\qquad -\gamma_i[(\sqrt{\tfrac{7}{8}})|G1\rangle + (\sqrt{\tfrac{1}{8}})|G-3\rangle]\}\cdot|\tfrac{3}{2}M_S\rangle; \\
&|{}_i{}^4\Gamma_4 0 M_S\rangle \\
&\quad = \{\alpha_i|P0\rangle + \beta_i|F0\rangle + \gamma_i[-(1/\sqrt{2})|G4\rangle \\
&\qquad + (1/\sqrt{2})|G-4\rangle]\}\cdot|\tfrac{3}{2}M_S\rangle; \qquad (15) \\
&|{}_i{}^4\Gamma_4 -1 M_S\rangle \\
&\quad = \{\alpha_i|P-1\rangle + \beta_i[(\sqrt{\tfrac{5}{8}})|F3\rangle + (\sqrt{\tfrac{3}{8}})|F-1\rangle] \\
&\qquad + \gamma_i[-(1/\sqrt{8})|G3\rangle + (\sqrt{\tfrac{7}{8}})|G-1\rangle]\}\cdot|\tfrac{3}{2}, M_S\rangle;
\end{aligned}$$

and $a(M_S)$, $b(M_S)$, $c(M_S)$ are defined by

$$\begin{aligned}
a(M_S) &= \tfrac{1}{2}\langle {}^4P1M_S-1|\sum_j l_j{}^+ s_j{}^-|{}^6SM_S\rangle; \\
b(M_S) &= \tfrac{1}{2}\langle {}^4P-1M_S+1|\sum_j l_j{}^- s_j{}^+|{}^6SM_S\rangle; \qquad (16) \\
c(M_S) &= \langle {}^4P0M_S|\sum_j l_j{}^z s_j{}^z|{}^6SM_S\rangle;
\end{aligned}$$

and $|{}^4PM_LM_S\rangle = |{}^4PM_L\rangle\cdot|S=\tfrac{3}{2}, M_S\rangle$. The quantities (16) are listed in Table II.

So far the above states have been constructed implicitly out of $3d$ functions. The presence of an axial field will alter (14) in two ways. The first involves admixture of other $3d^5$ states, the second admixtures of excited configurations into the $3d$ shell. The former will be considered in Secs. III and IV, the latter in Secs. V and VI. Concerning configurational admixtures,

TABLE II. List of $a(M_S)$, $b(M_S)$, and $c(M_S)$ describing the spin-orbit effect.

M_S	$\frac{5}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$	$-\frac{5}{2}$
$a(M_S)$	$+\sqrt{5}$	$+\sqrt{3}$	$+\frac{1}{2}\sqrt{6}$	$+\frac{1}{2}\sqrt{2}$	0	0
$b(M_S)$	0	0	$+\frac{1}{2}\sqrt{2}$	$+\frac{1}{2}\sqrt{6}$	$+\sqrt{3}$	$+\sqrt{5}$
$c(M_S)$	0	$-\sqrt{2}$	$+\sqrt{3}$	$+\sqrt{3}$	$+\sqrt{2}$	0

apparently only those involving $3d \rightarrow 4s$ have previously been considered. Because these admixtures will be proportional to

$$\langle ns|\mathcal{H}_{ax}|3d\rangle/[E(3d)-E(ns)],$$

where $\mathcal{H}_{ax}$ is the axial or rhombic perturbation, not only will $4s$ admixtures be important but also $5s$, $6s$, $\cdots$, $4d$, $5d$, $\cdots$, and $4g$, $5g$ $\cdots$. This occurs because the $3d$ function, when weighted by r^2 or r^4, has significant overlap with a large number of excited configurations, and the energy denominators do not increase rapidly enough to overcome the sizeable matrix elements of $\mathcal{H}_{ax}$. This difficulty is one often encountered in shielding problems and was first treated in detail by Sternheimer[12] and subsequently by Das, Bersohn, and Wikner,[15] Dalgarno,[16] Khubchandani, Sharma, and Das.[17] To the unperturbed one-electron Hamiltonian $\mathcal{H}_i{}^0$ for the ith electron with wave function $\psi^0(i)$ and energy $\epsilon_i{}^0$ is added a perturbing potential h_1. The first-order change in wave function $\delta\psi_i$ is determined from[16]

$$(\mathcal{H}_i{}^0-\epsilon_i{}^0)\delta\psi_i - \sum_j(\epsilon_j{}^0-\epsilon_i{}^0)\langle\psi^0(j)\,|\,\delta\psi_i\rangle\psi^0(j) = -h_1\psi^0(i)+\sum_j\langle\psi^0(j)|h_1|\psi^0(i)\rangle\psi^0(j). \quad (17)$$

The presence of the second term on the left makes (17) an integral-differential equation and complicates the solution greatly. It has been shown[17] that its omission will not lead to error of more than ~15%. We thus consider the simpler differential equation

$$(\mathcal{H}_i{}^0-\epsilon_i{}^0)\delta\psi_i = -h_1\psi^0(i)+\sum_j\langle\psi^0(j)|h_1|\psi^0(i)\rangle\psi^0(j). \quad (18)$$

The functions $\psi^0(i)$ represent one-electron d orbitals of the form

$$\psi_m{}^0(i) = [u_d{}^0(r)/r]Y_2{}^m. \quad (19)$$

To find the perturbed wave function $\delta\psi_m(i)$, consider a perturbation of the type

$$h_1 = -p_k{}^{mk}r^k Y_k{}^{mk}, \quad (20)$$

where $p_k{}^m$ is a constant defining the required potential.

[15] T. P. Das and R. Bersohn, Phys. Rev. **102**, 733 (1956); E. G. Wikner and T. P. Das, *ibid.* **109**, 360 (1958).
[16] A. Dalgarno, Proc. Roy. Soc. (London) **A251**, 282 (1959).
[17] R. G. Khubchandam, R. R. Sharma, and T. P. Das, Phys. Rev. **126**, 594 (1962).

TABLE III. Table of $(4\pi/5)^{1/2}F_{2,4}{}^{m,m_k}(l')$ for $k=2$.

m \ m_k	2	1	0	−1	−2
4	$\sqrt{(2/35)}$	$1/(\sqrt{35})$	$\sqrt{3}/7(\sqrt{5})$	$1/7(\sqrt{5})$	$1/35$
2	0	0	$-2/7(\sqrt{5})$	$-(\sqrt{6})/7(\sqrt{5})$	$-2/7(\sqrt{5})$
0	0	0	0	0	$1/5$
		$2\sqrt{2}/7(\sqrt{5})$	$(\sqrt{6})/7(\sqrt{5})$	$4/35$	$1/7(\sqrt{5})$
1		$(\sqrt{6})/7(\sqrt{5})$	$1/7(\sqrt{5})$	$-1/7(\sqrt{5})$	$-(1/7)(\sqrt{6})/(\sqrt{5})$
		0	0	$-1/5$	0
			$6/35$	$(\sqrt{6})/7(\sqrt{5})$	$\sqrt{3}/7(\sqrt{5})$
0			$2/7(\sqrt{5})$	$1/7(\sqrt{5})$	$-2/7(\sqrt{5})$
			$1/5$	0	0
				$2\sqrt{2}/7(\sqrt{5})$	$1/(\sqrt{35})$
−1				$(\sqrt{6})/7(\sqrt{5})$	0
				0	0
					$\sqrt{(2/35)}$
−2					0
					0

The product

$$h_1\psi_m{}^0(i)=-p_k{}^{m_k}r^kY_k{}^{m_k}[u_d{}^0(r)/r]Y_2{}^m$$
$$\equiv -p_k{}^{m_k}r^k[u_d{}^0(r)/r]\times\sum_{l'}F_{2,k}{}^{m,m_k}(l')Y_{l'}{}^{m+m_k}, \quad (21)$$

defines the quantities $F_{2,k}{}^{m,m_k}(l')$ tabulated in Tables III and IV for appropriate values of k, m, m_k, and l'. The form of (21) suggests that we can write

$$\delta\psi_i=p_k{}^{m_k}\sum_{l'=|2-k|}^{2+k}\frac{u_{d\to k}{}^{l'(1)}(r)}{r}F_{2,k}{}^{m,m_k}(l')Y_{l'}{}^{m+m_k}. \quad (22)$$

Taking $k=2$, appropriate to the axial and rhombic potentials (9), l' in (22) can assume the values 0, 2, 4 representing the admixture of s-, d-, and g-like functions into $\psi_m{}^0(i)$. Inserting (22) and (21) in (18) results in the three differential equations,

$$-\frac{d^2u_{d\to^2s}{}^{(1)}}{dr^2}-\frac{6}{r^2}u_{d\to^2s}{}^{(1)}+\frac{u_{d\to^2s}{}^{(1)}}{u_d{}^0}\frac{d^2u_d{}^0}{dr^2}=r^2u_d{}^0; \quad (23)$$

$$-\frac{d^2u_{d\to^2d}{}^{(1)}}{dr^2}+\frac{u_{d\to^2d}{}^{(1)}}{u_d{}^0}\frac{d^2u_d{}^0}{dr^2}=r^2u_d{}^0-\langle u_d{}^0|r^2|u_d{}^0\rangle u_d{}^0; \quad (24)$$

$$-\frac{d^2u_{d\to^2g}{}^{(1)}}{dr^2}+\frac{14}{r^2}u_{d\to^2g}{}^{(1)}+\frac{u_{d\to^2g}{}^{(1)}}{u_d{}^0}\frac{d^2u_d{}^0}{dr^2}=r^2u_d{}^0. \quad (25)$$

These equations were solved for Mn^{++} using Numerov's numerical integration procedure and Watson's[13] analytical solutions of the Hartree-Fock equation. The solutions $u_{d\to^2s}{}^{(1)}$, $u_{d\to^2d}{}^{(1)}$, and $u_{d\to^2g}{}^{(1)}$ are displayed graphically in Fig. 2 for Mn^{++} and will be used in the evaluation of the spin-spin contribution to D and E in Sec. VI and in the less important excited configuration spin-orbit contribution (ODS) to be considered in Sec. V.

III. THE WATANABE MECHANISM

The contribution to the axial field splitting from a mechanism considered by Watanabe[3] has already been outlined in the Introduction and displayed in Eq. (2). It will be shown in Sec. VIII that the contribution to D from this term will be small for reasonable values of the electric field gradient and will be nearly cancelled by the contribution from configuration interaction (ODS) considered in Sec. V. We include a discussion of (2) here for completeness and to demonstrate the role of the cubic crystalline field. Watanabe found

$$D_W=-\frac{1}{70}\frac{\zeta^2}{\Delta_{DS}}\frac{\langle r^2\rangle^2}{(\Delta_{PS})^2}(B_2{}^0)^2, \quad (26)$$

where $B_2{}^0$ measures the strength of the axial field (9a)

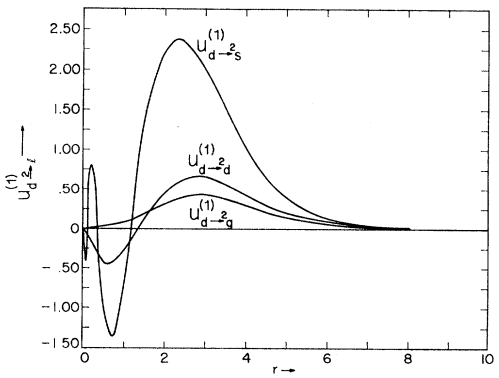

FIG. 2. Plot of $u_{d\to^2s}{}^{(1)}$, $u_{d\to^2d}{}^{(1)}$, $u_{d\to^2g}{}^{(1)}$ for Mn^{2+}. All quantities are in atomic units.

TABLE IV. Values of $(4\pi)^{1/2}F_{2,4}{}^{m,m_k}(l')$ for $k=4$.

m \ m_k	4	3	2	1	0	−1	−2	−3	−4
6	$15/(\sqrt{11.13})$	$5(\sqrt{6})/(\sqrt{11.13})$	$5(\sqrt{42})/11(\sqrt{13})$	$3(\sqrt{70})/11(\sqrt{13})$	$5(\sqrt{14})/11(\sqrt{13})$	$5(\sqrt{7})/11(\sqrt{13})$	$5(\sqrt{3})/11(\sqrt{13})$	$5/11(\sqrt{13})$	$(\sqrt{5})/11(\sqrt{13})$
2 4	0	0	$-2(\sqrt{30})/11(\sqrt{7})$	$-3(\sqrt{30})/11(\sqrt{7})$	$-30(\sqrt{3})/77$	$-10(\sqrt{30})/77$	$-30(\sqrt{3})/77$	$-3(\sqrt{30})/11(\sqrt{7})$	$-2(\sqrt{30})/11(\sqrt{7})$
2	0	0	0	0	1/7	$(\sqrt{5})/7$	$(\sqrt{15})/7$	$(\sqrt{5})/(\sqrt{7})$	$(\sqrt{10})/(\sqrt{7})$
	$5(\sqrt{3})/(\sqrt{11.13})$	$20(\sqrt{3})/11(\sqrt{13})$	$6(\sqrt{35})/11(\sqrt{13})$	$4(\sqrt{70})/11(\sqrt{13})$	$5(\sqrt{35})/11(\sqrt{13})$	$10(\sqrt{6})/11(\sqrt{13})$	$5(\sqrt{14})/11(\sqrt{13})$	$4(\sqrt{10})/11(\sqrt{13})$	$3(\sqrt{5})/11(\sqrt{13})$
1	0	$2(\sqrt{15})/11$	$5(\sqrt{15})/11(\sqrt{7})$	$9(\sqrt{15})/77$	$5(\sqrt{6})/77$	$-5(\sqrt{6})/77$	$-9(\sqrt{15})/77$	$-5(\sqrt{15})/11(\sqrt{7})$	$-2(\sqrt{15})/11$
	0	0	0	$-55/7$	$-4/7$	$-(\sqrt{30})/7$	$-2(\sqrt{10})/7$	$-(\sqrt{5})/(\sqrt{7})$	0
	15/11(√13)	$6(\sqrt{15})/11(\sqrt{13})$	$2(\sqrt{210})/11(\sqrt{13})$	$5(\sqrt{42})/11(\sqrt{13})$	$15(\sqrt{5})/11(\sqrt{13})$	$5(\sqrt{42})/11(\sqrt{13})$	$2(\sqrt{210})/11(\sqrt{13})$	$5(\sqrt{15})/11(\sqrt{13})$	15/11(√13)
0	$-4(\sqrt{5})/11$	$-(\sqrt{5})/11$	$8(\sqrt{5})/77$	$17(\sqrt{5})/77$	$20(\sqrt{5})/77$	17(5)/77	$8(\sqrt{5})/77$	$-(\sqrt{5})/11$	$-4(\sqrt{5})/11$
	0	0	$(\sqrt{15})/7$	$(\sqrt{30})/7$	6/7	$(\sqrt{30})/7$	$(\sqrt{15})/7$	0	0
	$3(\sqrt{5})/11(\sqrt{13})$	$4(\sqrt{10})/11(\sqrt{13})$	$5(\sqrt{14})/11(\sqrt{13})$	$10(\sqrt{6})/11(\sqrt{13})$	$5(\sqrt{35})/11(\sqrt{13})$	$4(\sqrt{70})/11(\sqrt{13})$	$6(\sqrt{35})/11(\sqrt{13})$	$20(\sqrt{3})/11(\sqrt{13})$	$5(\sqrt{3})/(\sqrt{11.13})$
−1	$-2(\sqrt{15})/11$	$-5(\sqrt{15})/11(\sqrt{7})$	$-9(\sqrt{15})/77$	$-5(\sqrt{6})/77$	$5(\sqrt{6})/77$	$9(\sqrt{15})/77$	$5(\sqrt{15})/11(\sqrt{7})$	$2(\sqrt{15})/11$	0
	0	$-(\sqrt{5})/(\sqrt{7})$	$-2(\sqrt{10})/7$	$-(\sqrt{30})/7$	$-4/7$	$-(\sqrt{5})/7$	0	0	0
	$(\sqrt{5})/11(\sqrt{13})$	$5/11(\sqrt{13})$	$5(\sqrt{3})/11(\sqrt{13})$	$5(\sqrt{7})/11(\sqrt{13})$	$5(\sqrt{14})/11(\sqrt{13})$	$3(\sqrt{70})/11(\sqrt{13})$	$5(\sqrt{42})/11(\sqrt{13})$	$5(\sqrt{6})/(\sqrt{11.13})$	$15/(\sqrt{11.13})$
−2	$-2(\sqrt{30})/11(\sqrt{7})$	$-3(\sqrt{30})/11(\sqrt{7})$	$-30(\sqrt{3})/77$	$-10(\sqrt{30})/77$	$-30(\sqrt{3})/77$	$-3(\sqrt{30})/11(\sqrt{7})$	$-2(\sqrt{30})/11(\sqrt{7})$	0	0
	$(\sqrt{10})/(\sqrt{7})$	$(\sqrt{5})/(\sqrt{7})$	$(\sqrt{15})/7$	$(\sqrt{5})/7$	1/7	0	0	0	0

and Δ_{DS}, Δ_{PS} are the energy differences $E(^4D)-E(^6S)$, $E(^4P)-E(^6S)$, respectively.

The presence of the cubic field will alter somewhat the value obtained for D_W in (26) because the ^4P state will not be "pure" but will contain admixtures from the ^4F and ^4G states as shown by (12). These admixtures will result in changes of the energy denominators and contributions to the matrix elements from the admixed states. We find

$$D_{WC}=-\frac{1}{70}\frac{\zeta^2}{\Delta_{DS}}\langle r^2\rangle^2(B_2{}^0)^2\left|p_{\alpha\alpha}+\frac{4}{7}p_{\alpha\beta}\right|^2, \tag{27}$$

where

$$p_{\alpha\alpha}=\sum_{i=1}^{3}\alpha_i{}^2/\Delta_i,$$
$$p_{\alpha\beta}=\sum_{i=1}^{3}\alpha_i\beta_i/\Delta_i. \tag{28}$$

The α_i, β_i, and Δ_i are listed in Table I. The expression (27) is the correct one to use for the case of a weak axial perturbation superimposed upon a strong cubic crystalline field. Evaluation of $p_{\alpha\alpha}$ and $p_{\alpha\beta}$ for $10Dq=10\,000$ cm^{-1} shows that D_{WC} exceeds D_W by a factor of 1.6. Hence the presence of the cubic field causes an enhancement of the Watanabe contribution to the axial field splitting.

It is also possible to compute the rhombic splitting E using the Watanabe and configuration-interaction mechanisms for E. Such contributions would arise out of second-order effects involving $V_2{}^0$ and $V_2{}^2$. One could derive expressions for E resembling Eqs. (27) and (39) following essentially identical procedures as for D. However, as we shall see in Sec. VIII, where numerical results for various mechanisms will be considered, the Watanabe and configuration-interaction mechanisms both yield rather small contributions as compared to the spin-spin and Blume-Orbach mechanisms. In addition, the signs of the Watanabe and configuration interaction results are opposite, and nearly cancel one another. Thus, we shall not give expressions here for E_W and E_{ODS}.

IV. THE BLUME–ORBACH MECHANISM

The next contribution to D and E we shall consider was first proposed by Blume and Orbach.[6] The mechanism has been outlined in the Introduction and the form of the result given in Eq. (3). In addition to the $l=2$ terms (9a) and (9b), the BO mechanism also allows the $l=4$ terms (10a) and (10b) to contribute to D and E. These additional terms do not contribute to D_W because the triangle rule causes their matrix elements to vanish between the ^4P and ^4D states. They can, however, connect ^4P and ^4F with ^4G states in a d^5 configuration.[18] The contribution of the axial and rhombic crystalline

[18] S. R. Polo, RCA Laboratories (unpublished).

fields to D and E is found using the spin-orbit-perturbed cubic wave functions (14). The energy shift for a particular ground M_S level is found from

$$\Delta E(M_S)=\langle {}^6SM_S|\mathcal{H}_{ax}|{}^6SM_S\rangle'. \tag{29}$$

The value for D is then

$$D_{BO}=\tfrac{1}{12}[\Delta E(\tfrac{5}{2})-\Delta E(\tfrac{3}{2})]. \tag{30}$$

It turns out that the matrix element of Y_2^0 in (29) vanishes so that only (10a) contributes to D. Inserting (14) and (10a) into (29), we find

$$\Delta E(M_S)=-\tfrac{1}{6}(\sqrt{5})(B_4^0)'\langle r^4\rangle[a^2(M_S)+b^2(M_S)]\times[\zeta^2 p_{\alpha\gamma}(2p_{\alpha\alpha}-p_{\alpha\beta})], \tag{31}$$

to second order in Y_2^0. Here $p_{\alpha\alpha}$ and $p_{\alpha\beta}$ are as defined in (28) and $p_{\alpha\gamma}=\sum_{i=1}^{3}\alpha_i\gamma_i/\Delta_i$. Using the values of $a(M_S)$ and $b(M_S)$ given in Table II and (30), we find

$$D_{BO}=-(B_4^0)'[(\sqrt{5}/36]\langle r^4\rangle[\zeta^2 p_{\alpha\gamma}(2p_{\alpha\alpha}-p_{\alpha\beta})]. \tag{32}$$

The BO contribution to E is found in an analagous manner. The matrix elements of the rhombic terms (9b) and (10b) are taken between the states (14) with differing M_S values and compared with the matrix elements of $E(S_x^2-S_y^2)$ between the same $S=\frac{5}{2}$ spin-Hamiltonian states. Again, the matrix element of the $l=2$ rhombic component vanishes so that only (10b) contributes. We find

$$E_{BO}=-B_4^2(\sqrt{2}/6)\langle r^4\rangle[\zeta^2 p_{\alpha\gamma}(2p_{\alpha\alpha}-p_{\alpha\beta})]. \tag{33}$$

It is interesting to note that

$$E_{BO}/D_{BO}=6(\sqrt{\tfrac{2}{5}})B_4^2/(B_4^0)', \tag{34}$$

independent of the strength of the cubic admixtures of the excited quarted states. This ratio will serve as a useful check on the numerical estimates of D and E to be given in Secs. VII and VIII.

V. THE ORBACH, DAS, AND SHARMA MECHANISM

In this section, we make use of the configurational mixing discussed in Sec. II brought about by the presence of the axial and rhombic fields. To the individual $3d$ wave functions $\psi_m^0(i)$, a perturbed quantity $\delta\psi_{m,i}$ as defined by (22) is added. The individual term functions ${}^4P$, ${}^4F$, and ${}^4G$ are then constructed using the perturbed one-electron wave functions $\psi_m(i)+\delta\psi_m(i)$. Then, exactly as in Sec. IV, the matrix elements of $\mathcal{H}_{ax}$ are taken between the spin-orbit perturbed cubic wave functions (14) composed now, however, out of the configurationally admixed one-electron wave functions. It is found that

$$D_{ODS}=(B_2^0)^2[(\sqrt{5})/192\pi][\zeta^2 p_{\alpha\gamma}(2p_{\alpha\alpha}-p_{\alpha\beta})]\times(M_2-4M_1+3M_0), \tag{35}$$

where

$$M_m=\sum_{l=0,2,4} a_{ml}\langle u_d^0|r^2|u_{d\to^2 l}^{(1)}\rangle. \tag{36}$$

The a_{ml} are components of the matrix

$$\mathbf{a}=\begin{pmatrix} 0 & 4/49 & 3/49 \\ 0 & 1/49 & 6/49 \\ \frac{1}{5} & 4/49 & 36/245 \end{pmatrix}. \tag{37}$$

The matrix elements of r^2 contained in (36) have been computed numerically using the perturbed wave functions found in Sec. II and displayed in Fig. 2. We find:

$$\begin{aligned}\langle u_d^0|r^2|u_{d\to^2 s}^{(1)}\rangle&=6.70,\\ \langle u_d^0|r^2|u_{d\to^2 d}^{(1)}\rangle&=1.70,\\ \langle u_d^0|r^2|u_{d\to^2 g}^{(1)}\rangle&=1.38,\end{aligned} \tag{38}$$

in atomic units. These lead to

$$D_{ODS}=2.1044(B_2^0)^2, \tag{39}$$

where B_2^0 is expressed in units of $e^2/2a_0^3$. This contribution is proportional to the square of B_2^0, as is the Watanabe contribution (27). However (39) is opposite in sign to (27).

The magnitude of (39) will be shown to be nearly equal to (27) in Sec. VII so that a nearly complete cancellation of D_{WC} and D_{ODS} obtains. The same result occurs for the rhombic terms and is the reason for the omission of explicit expressions for E in Secs. III and V.

In addition to the quadratic effects in V_2^0 one might expect to find excited configuration contributions to D_{ODS} from either V_4 acting twice or V_4 and V_2^0 each acting once. These contributions may be termed D_{EC}. Expressions for D_{EC} due to these latter mechanisms can be derived following the procedure in this section. We have made rough estimates of D_{EC} from these mechanisms and find results an order of magnitude smaller than D_{ODS} computed in this section. One can therefore neglect these contributions, as well as similar Watanabe-type contributions, to D.

VI. THE SPIN–SPIN MECHANISM

The use of spin-spin coupling (8) to admix an excited $4s$ configuration into the $3d^5$ configuration was first proposed by Pryce.[2] His paper represents the first meaningful quantitative treatment of the axial field splitting of S-state ions. Pryce did not perform the detailed atomic calculations necessary to find the magnitude of D but rather relied on an extraction of the strength of the spin-spin interaction from free-ion excited-state splittings. His approach has been criticized by Blume and Watson[19] and by Leushin.[20] These criticisms take note of the importance of other interactions which shift the free-ion excited levels (e.g. spin-other orbit) and which may be wrongly included in an estimate of the strength of the spin-spin interaction. Blume and Watson actually calculate the $4s$ spin-spin admixture and find it much smaller than estimated by

[19] M. Blume and R. E. Watson, Phys. Rev. **139**, A1209 (1965).
[20] A. M. Leushin, Fiz. Tverd. Tela **5**, 2352 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1711 (1964)].

Pryce. In this section we shall not make use of conventional perturbation theory to treat configurational mixtures but rather rely on the Sternheimer[12] method outlined in Sec. II. It will be shown that d-like admixtures are more important than s-like admixtures and yield an axial field splitting of opposite sign. Hence, the results of previous treatments considering only $4s$ admixtures and using conventional perturbation theory (e.g., Watanabe,[3] Leushin[20]) *cannot* yield a result of the correct magnitude and sign.

At this point we should mention the work of Chakravarty[21] who also attempted to determine the spin-spin contribution to the axial field splitting of S-state ions. He used the same approach as we shall make use of in this section, except that he employed analytic Slater rather than Hartree-Fock orbitals. The inaccuracy of Slater orbitals leaves Chakravarty's results open to serious question quantitatively, though he did also find d-like admixtures more important than s-like admixtures. Our numerical results differ substantially from his; the source of this difference appears to lie in the difference between the wave functions used and also in some numerical errors in Chakravarty's formalism.

In order to detail the method of computation of the spin-spin contribution to the axial and rhombic field splitting it is necessary to expand the spin-spin interaction (7) in the following way:

$$\begin{aligned}\mathcal{H}_{ss}=&-\frac{1}{2}\frac{g^2\beta^2}{a_0^3}\sum_{i<j} r_{ij}^{-5}[(3z_{ij}^2-r_{ij}^2)(3s_i^zs_j^z-\mathbf{s}_i\cdot\mathbf{s}_j)\\&+3(x_{ij}^2-y_{ij}^2)(s_i^xs_j^x-s_i^ys_j^y)\\&+6(s_i^xs_j^y+s_i^ys_j^x)x_{ij}y_{ij}\\&+6(s_i^ys_j^z+s_i^zs_j^y)y_{ij}z_{ij}\\&+6(s_i^zs_j^x+s_i^xs_j^z)z_{ij}x_{ij}].\end{aligned}\tag{40}$$

The first term in (40) contributes to D, the second to E.

Our method of calculation is somewhat similar to Sec. V. We construct the ^6S ground determinant out of the perturbed one-electron orbitals $\psi_m{}^0(i)+\delta\psi_{m,i}$ given by (22). The matrix element of the spin-spin interaction (40) between the perturbed S, M_S ground levels is then

$$\begin{aligned}W_{ss}(M_S',M_S)&=\langle{}'{}^6S,M_S'|\mathcal{H}_{ss}|{}^6S,M_S\rangle'\\&=2\langle{}^6S,M_S'|\mathcal{H}_{ss}|{}^6S,M_S\rangle'.\end{aligned}\tag{41}$$

The prime in (41) indicates the use of perturbed one-electron orbitals in constructing the ground Slater determinant. Thus,

$$\begin{aligned}|{}^6S,M_S\rangle'=&[1/(\sqrt{5!})]\epsilon_{\alpha,\beta,\gamma,\delta,\epsilon}\\&\times\psi_\alpha(1)^{(1)}\psi_\beta(2)^{(1)}\psi_\gamma(3)^{(1)}\psi_\delta(4)^{(1)}\psi_\epsilon(5)^{(1)},\end{aligned}\tag{42}$$

$$\begin{aligned}|{}^6S,M_S\rangle=&[1/(\sqrt{5!})]\epsilon_{\alpha,\beta,\gamma,\delta,\epsilon}\\&\times\psi_\alpha(1)^0\psi_\beta(2)^0\psi_\gamma(3)^0\psi_\delta(4)^0\psi_\epsilon(5)^0.\end{aligned}$$

[21] A. S. Chakravarty, J. Chem. Phys. 39, 1004 (1963).

Here

$$\psi_m(i)^{(1)}=\psi_m(i)^0+\delta\psi_m(i).$$

Then,

$$\begin{aligned}D_{ss}&=\tfrac{1}{12}[W_{ss}(\tfrac{5}{2},\tfrac{5}{2})-W_{ss}(\tfrac{3}{2},\tfrac{3}{2})],\\E_{ss}&=[1/(\sqrt{10})]W_{ss}(\tfrac{5}{2},\tfrac{1}{2}).\end{aligned}\tag{43}$$

Inserting (40) into (41), and using (42) and (43), we obtain

$$\begin{aligned}D_{ss}&=-\frac{g^2\beta^2}{20a_0}\langle{}^6S|\sum_{i<j}\frac{3(z_{ij}^2-r_{ij}^2)}{r_{ij}^5}|{}^6S\rangle',\\E_{ss}&=-\frac{g^2\beta^2}{20a_0}\langle{}^6S|\sum_{i<j}\frac{3(x_{ij}^2-y_{ij}^2)}{r_{ij}^5}|{}^6S\rangle',\end{aligned}\tag{44}$$

where the matrix elements of the spin functions have already been evaluated. Thus, states appearing in (44) are solely orbital and of the same form as (42). This is permissible because of the half-filled character of the d^5 configuration and the spin independence of $\mathcal{H}_{ax}$. We now adopt the same technique used in Sec. II to write $V_{cryst}=\sum_{k,m_k}V_k{}^{m_k}$ where [see Eq. (20)]

$$V_k{}^{m_k}=-p_k{}^{m_k}\sum_i r_i{}^kY_k{}^{m_k}(i).\tag{45}$$

For an axial field only $m_k=0$ terms are present while for a rhombic field $m_k=\pm2$ terms can also be present.

For simplicity we shall first evaluate the axial term in (44). Using (22) we find

$$D_{ss}=\sum_{l'=|2-k|}^{2+k}D_{ss}(d\rightarrow l'),\tag{46}$$

where

$$D^{55}(d\rightarrow l')=-\frac{g^2\beta^2}{20a_0^3}\frac{p_k{}^0}{2}\sum_{l''}f_{d\rightarrow k l'}{}^{l''-1,l''+2}D_{k,l'}{}^{l''}.\tag{47}$$

In (47) we have introduced the symbols

$$f_{d\rightarrow k l}{}^{n,m}=\int\int(u_d{}^0(1))^2\frac{r_>{}^n}{r_>{}^m}u_d{}^0(2)u_{d\rightarrow k l}{}^{(1)}(2)d\mathbf{r}_1d\mathbf{r}_2,\tag{48}$$

and

$$\begin{aligned}D_{k,l'}{}^{l''}=&\sum_{\alpha\neq\beta=-2}^{2}F_{2,k}{}^{0,\alpha}(l')\{C_{l',0}(-1)^{\alpha+\beta}\\&\times[F_{2,l'}{}^{-\alpha,-\alpha}(l''-1)F_{2,2}{}^{-\beta,\beta}(l''+1)\\&+F_{2,l'}{}^{-\alpha,\alpha}(l''+1)F_{2,2}{}^{-\beta,\beta}(l''-1)]\\&-C_{l'',\alpha-\beta}[F_{2,2}{}^{-\alpha,\beta}(l''-1)F_{2,l'}{}^{-\beta,\alpha}(l''+1)\\&+F_{2,2}{}^{-\alpha,\beta}(l''+1)F_{2,l'}{}^{-\beta,\alpha}(l''-1)]\}.\end{aligned}\tag{49}$$

We have used the quantity $F_{2,k}{}^{m,m_k}(l')$ in (49), defined by (21) and tabulated in Tables III and IV, as well as

the normalization coefficient

$$C_{l',m'}=\frac{4\pi}{[(2l'+1)(2l'+3)]^{1/2}}\times\left[\frac{(l'-m'+1)!(l'+m'+1)!}{(l'+m'-1)!(l'-m'-1)!}\right]^{1/2}. \quad (50)$$

The coefficient $C_{l'm'}$ occurs in the expansion

$$\frac{Y_2^0(1'2)}{r_{12}^3}=\sum_{l',m'}\frac{r_1^{l'-1}}{r_2^{l'+2}}Y_{l'-1}^{m'}(1)Y_{l'+1}^{m'*}(2),$$

which is true for $r_1<r_2$. For $r_1>r_2$ one should interchange 1 and 2 (both radial and angular variables). Using the numerical values found in Tables III and IV and Eq. (50), (46) reduces to

$$D_{ss}=D_{ss}(d\rightarrow s)+D_{ss}(d\rightarrow d)+D_{ss}(d\rightarrow g), \quad (51)$$

where

$$\begin{aligned}D_{ss}(d\rightarrow s)&=-\frac{g^2\beta^2}{40(\sqrt{5})}B_2^0[3.58f_{d\rightarrow 2s}{}^{0,3}-5.37f_{d\rightarrow 2s}{}^{2,5}],\\ D_{ss}(d\rightarrow d)&=-\frac{g^2\beta^2}{40(\sqrt{5})}B_2^0[3.83f_{d\rightarrow 2d}{}^{0,3}-4.38f_{d\rightarrow 2d}{}^{2,5}],\\ D_{ss}(d\rightarrow g)&=-\frac{g^2\beta^2}{40(\sqrt{5})}B_2^0[9.20f_{d\rightarrow 2g}{}^{0,3}\\ &\quad -5.59f_{d\rightarrow 2g}{}^{2,5}-19.17f_{d\rightarrow 2g}{}^{4,7}].\end{aligned} \quad (52)$$

The two-electron integrals $f_{d\rightarrow 2l'}{}^{l'',l''+2}$ appearing in (52) can be evaluated using Watsonls[13] Mn^{++} analytic functions for $u_d{}^{(0)}$ and the values of $u_{d\rightarrow 2l}{}^{(1)}$ found in Sec. II. These integrals are tabulated in Table V for Mn^{2+}. Our result $D_{ss}(d\rightarrow s)$ agrees with D_P [Eq. (1)] if conventional first-order perturbation theory is used to admix the $4s$ configuration by the axial field. In particular, one can obtain Pryce's result by setting

$$u_{d\rightarrow 2s}{}^{(1)}=u_{4s}{}^0\frac{\langle u_{3d}{}^0|\mathcal{H}_{ax}|u_{4s}{}^0\rangle}{\Delta_{ds}}, \quad (53)$$

where Δ_{ds} is the $3d\rightarrow 4s$ promotion energy. Using Table V we find (52) reduces to

$$\begin{aligned}D_{ss}(d\rightarrow s)&=-0.01915B_2^0\ \text{cm}^{-1},\\ D_{ss}(d\rightarrow d)&=\ \ 0.0707\ B_2^0\ \text{cm}^{-1},\\ D_{ss}(d\rightarrow g)&=-0.0068\ B_2^0\ \text{cm}^{-1}.\end{aligned} \quad (54)$$

The total spin-spin contribution to the axial field splitting (51) becomes

$$D_{ss}=0.0447B_2^0\ \text{cm}^{-1}, \quad (55)$$

where B_2^0 is again expressed in units of $e^2/2a_0^3$. The method of computation for E_{ss} follows the computation of D_{ss} in an analagous manner. Using again the quantity (48),

$$E_{ss}=-\frac{g^2\beta^2}{20a_0^3}\frac{p_k{}^{m_k}}{2}\sum_{l''}f_{d\rightarrow k l'}{}^{l'',l''+2}\times\tfrac{1}{2}(E_{k,l',l''}{}^{m_k}(1)\delta_{m_k,-2}+E_{k,l',l''}{}^{m_k}(2)\delta_{m_k,2}), \quad (56)$$

where

$$\begin{aligned}&E_{k,l',l''}{}^{m_k}(1)\\ &=\sum_{\alpha\neq\beta=-2}^{2}F_{k,2}{}^{m_k,\alpha}(l')\{(-1)^{\alpha+\beta}\\ &\quad\times[C_{l'',-1}{}'F_{2,l'}{}^{-\alpha,\alpha+m_k}(l''-1)F_{2,2}{}^{-\beta,\beta}(l''+1)\\ &\quad+C_{l'',1}{}'F_{2,2}{}^{-\beta,\beta}(l''-1)F_{2,l'}{}^{-\alpha,\alpha+m_k}(l''+1)]\\ &\quad-[C_{l'',\beta-\alpha}{}'F_{2,2}{}^{-\alpha,\beta}(l''-1)F_{2,l'}{}^{-\beta,\alpha+m_k}(l''+1)\\ &\quad+C_{l'',\alpha-\beta-1}{}'F_{2,l'}{}^{-\beta,\alpha+m_k}(l''-1)F_{2,2}{}^{-\alpha,\beta}(l''+1)]\}.\end{aligned} \quad (57)$$

Here

$$C_{l'',m'}{}'=\frac{4\pi}{[(2l'-1)(2l'+3)]^{1/2}}\left[\frac{(l'+m'+2)!}{(l'+m'-2)!}\right]^{1/2}. \quad (58)$$

The quantity $E_{k,l',l''}{}^{m_k}(2)$ can be obtained from $E_{k,l',l''}{}^{m_k}(1)$ by interchanging α and β in $C_{l'',\beta-\alpha+1}{}'$ and $C_{l'',\beta-\alpha-1}{}'$. We identify (9b) as the form for the rhombic field, so that $B_2^2=(p_2^2+p_2^{-2})/[2(4\pi/5)^{1/2}]$. Then, using Tables III and IV and (58) to evaluate (57), and inserting into (56), we find

$$E_{ss}=E_{ss}(d\rightarrow s)+E_{ss}(d\rightarrow d)+E_{ss}(d\rightarrow g), \quad (59)$$

where

$$\begin{aligned}E_{ss}(d\rightarrow s)&=-(g^2\beta^2/40)B_2^2\\ &\quad\times[8.76f_{d\rightarrow 2s}{}^{0,3}-13.15f_{d\rightarrow 2s}{}^{2,5}],\\ E_{ss}(d\rightarrow d)&=-(g^2\beta^2/40)B_2^2\\ &\quad[9.38f_{d\rightarrow 2d}{}^{0,3}-10.73f_{d\rightarrow 2d}{}^{2,5}],\\ E_{ss}(d\rightarrow g)&=-(g^2\beta^2/40)B_2^2[22.53f_{d\rightarrow 2g}{}^{0,3}\\ &\quad-13.68f_{d\rightarrow 2g}{}^{2,5}-46.95f_{d\rightarrow 2g}{}^{4,7}].\end{aligned} \quad (60)$$

As before, using Table V for the $f_{d\rightarrow 2l'}{}^{l'',l''+2}$, we

TABLE V. Table of two-electron integrals $f_{d\rightarrow kl'}{}^{l'',l''+2}$ appearing in (52).

l'' \ l'	0	2	4
1	−0.522343	−0.403704	0.065059
3	−0.375473	−0.230164	0.030665
5	...	...	0.019571

evaluate (60) to yield

$$E_{ss}(d\rightarrow s)=-0.0475B_2^2\ \text{cm}^{-1},$$
$$E_{ss}(d\rightarrow d)=\ \ 0.1735B_2^2\ \text{cm}^{-1}, \quad (61)$$
$$E_{ss}(d\rightarrow g)=-0.0168B_2^2\ \text{cm}^{-1},$$

where B_2^2 is expressed in units of $e^2/2a_0^3$. Combining, we find finally that

$$E_{ss}=0.1092B_2^2\ \text{cm}^{-1}. \quad (62)$$

Again we see that $d\rightarrow d$ admixtures give contributions to E of greater magnitude and of opposite sign than contributions from $d\rightarrow s$ admixtures.

One might also expect first-order contributions to D and E from the crystal-field components V_4^0 and V_4^2 in combination separately with the spin-spin interaction. These contributions can be shown to vanish identically from the properties of the rotation-group matrix elements. We shall demonstrate this briefly for the case of D. Following the same procedure as in Sec. II we can write

$$D_{ss}=\sum_{l_2=2,4,6} D_{ss}(d\rightarrow {}^4l_2), \quad (63)$$

since, using the form (10a) for V_4^0, one can show that the perturbed d orbitals involve d-, g-, and i-type admixtures. The number 4 on l_2 in Eq. (63) indicates the effect of the V_4 potential. The quantity $D_{ss}(d\rightarrow {}^4l_2)$ can be expressed as

$$D_{ss}(d\rightarrow {}^4l_2)=-(g^2\beta^2/20a_0^3)(B_4^0)'\sum_{i=1,3,5} f_{d\rightarrow {}^4l_2}{}^{l'-1,l'+2}D_{4,l_2}{}^{l'}, \quad (64)$$

where $f_{d\rightarrow {}^4l_2}{}^{l'-1,l'+2}$ can be obtained from the expression (48). The quantity $D_{4,l_2}{}^{l'}$ can be expressed as a sum of two parts, one of which is given by

$$D_{4,l_2}{}^{l'}(1)=\sum_{\alpha\neq\beta=-2}^{2} F_{4,2}{}^{0,\alpha}(l_2)\times[C_{l',0}(-1)^{\alpha+\beta}F_{2,l_2}{}^{-\alpha,\alpha}(l'-1)F_{2,2}{}^{-\beta,\beta}(l'+1)-C_{l',\alpha-\beta}F_{2,2}{}^{-\alpha,\beta}(l'-1)F_{2,l_2}{}^{-\beta,\alpha}(l'+1)]. \quad (65)$$

The second part of $D_{4,l_2}{}^{l'}(2)$ can be obtained from the first by interchanging $l'-1$ and $l'+1$ in the arguments of the quantities F inside the square brackets. Using Eqs. (50) and Tables III and IV one finds that

$$D_{4,l_2}{}^{l'}(1)=-D_{4,l_2}{}^{l'}(2), \quad (66)$$

so that these contributions to D_{ss} identically vanish.

In concluding our discussion of the various mechanisms responsible for D and E, we should point out that when the paramagnetic ion is not at a site possessing symmetry, odd crystal-field components $V_{2n+1}{}^0$ are present. One has terms of the form, for example,

$$V_{2n+1}{}^0=-p_{2n+1}{}^0\sum_i r_i{}^{2n+1}Y_{2n+1}{}^0(i). \quad (67)$$

One can work out the first-order contributions to D via the spin-spin and Blume-Orbach mechanisms following exactly the same procedures as in the present section and in Sec. IV, respectively. Consideration of the pertinent matrix elements involved in the expressions analogous to (47) and (30) shows that D_{ss} and D_{BO} by first-order mechanisms involving the odd crystal-field components exactly vanish.

Second-order effects of the odd crystal-field components via the spin-orbit interaction lead to expressions for D_{DOS} entirely analogous to Eq. (35) with

$$M_m=-(p_{2n+1}{}^0)^2\sum_{l'}\langle u_d{}^0|r^{2n+1}|u_{d\rightarrow 2^{m+1}l'}\rangle \times F_{2,2n+1}{}^{m,0}(l')F_{2,2n+1}{}^{-m,0}(l'). \quad (68)$$

In the crystal Mn^{+2}:ZnF_2 and MnF_2, the Mn^{2+} ion occupies a site with inversion symmetry so that the odd components of the crystalline field vanish. In other cases, as in ruby,[22,23] or in solid solutions of Mn^{+2} in the alkali halides,[24] one can expect to find finite odd crystalline-field components so that it is necessary to evaluate the matrix elements (68). However, since D_{ODS} and D_W, through the even crystal-field components, are found to be much smaller than D_{BO} and D_{ss}, we expect the second-order effects of the odd crystalline-field components to be also be negligible.

VII. CALCULATION OF CRYSTALLINE FIELDS

An important ingredient in these calculations is the crystalline field as described by its components V_2^0, V_4^0, V_2^2, and V_4^2 defined by Eqs. (9a), (9b), (10a), and (10b) in Sec. II.

If B_2^0, as defined by (9), is produced by external point charges $g_j|e|$ situated at (R_j,Θ_j,Φ_j) with resepect to an origin taken at the site of the paramagnetic ion, then B_2^0 is given by

$$B_2^0=\sum_j q_j(3\cos^2\Theta_j-1)/R_j^3, \quad (69)$$

where R_j is in units of a_0 and B_2^0 in units of $e^2/2a_0^3$. This then yields V_2^0 in rydbergs ($e^2/2a_0$). The quantity B_2^2, as defined by (9b), can be expressed in terms of a lattice summation paralleling (71),

$$B_2^2=(\sqrt{\tfrac{3}{2}})\sum_j q_j\sin^2\Theta_j\cos 2\Phi_j/R_j^3. \quad (70)$$

The crystal-field potential B_4^2 which shall be useful for the expressions (10b) and (33) is

$$B_4^2=\tfrac{1}{2}(\sqrt{10})\sum_j q_j(\sin^2\Theta_j)(7\cos^2\Theta_j-1)\cos 2\Phi_j. \quad (71)$$

[22] R. R. Sharma and T. P. Das, J. Chem. Phys. **41**, 3581 (1964); D. S. McClure, *ibid.* **36**, 2757 (1962); **38**, 2289 (1963).
[23] J. O. Artman and J. C. Murphy, Phys. Rev. **135**, A1622 (1964).
[24] G. D. Watkins, Phys. Rev. **113**, 79 (1959).

We shall next consider the axial potential that originates from the unbalanced part of the cubic potential V_4^0 in Eq. (9b). For cubic symmetry, the cubic potential is expressed as

$$\mathcal{H}_c=(4\pi/9)^{1/2}(B_4^0)\sum_i r_i^4 Y_4^0(i) + (4\pi/9)^{1/2}B_4^4\sum_i r_i(Y_4^4+Y_4^{-4}). \quad (72)$$

If $\mathcal{H}_c$ is expressed in rydbergs $e^2/2a_0$, then, for the point-charge model

$$(B_4^0)_c=\tfrac{1}{4}\sum_j^c q_j(35\cos^4\Theta_j-30\cos^2\Theta_j+3)/R_j^5, \quad (73)$$

and

$$(B_4^4)_c=\left(\frac{35}{32}\right)^{1/2}\sum_j^c q_j\sin^4\Theta_j\cos^4\Phi_j/R_j^5. \quad (74)$$

It is well known that there exists a constant ratio between $(B_4^0)_c$ and $(B_4^4)_c$. Let this ratio be denoted by

$$\alpha=(B_4^0)_c/(B_4^4)_c. \quad (75)$$

Thus at a perfect cubic site in a crystal $(B_4^0)_c-\alpha(B_4^4)_c$ vanishes. If the cubic symmetry at the site is destroyed, the new noncubic potential V_{nc} is given by

$$V_{nc}=(B_4^0)_{nc}(4\pi/9)^{1/2}\sum_i r_i^4 Y_4^0(i) + (B_4^4)_{nc}(4\pi/9)^{1/2}\sum_i r_i^4[Y_4^4(i)+Y_4^{-4}(i)]. \quad (76)$$

Then $(B_4^0)_{nc}-\alpha(B_4^4)_{nc}$ is no longer zero. We shall denote this difference by $(B_4^0)_{nc}'$.

$$(B_4^0)_{nc}'=(B_4^0)_{nc}-\alpha(B_4^4)_{nc}. \quad (77)$$

For the point-charge model, the quantities $(B_4^0)_{nc}$ and $(B_4^4)_{nc}$ can be expressed as

$$(B_4^0)_{nc}=\tfrac{1}{4}\sum_j q_j(35\cos^4\Theta_j-30\cos^2\Theta_j+3)/R_j^5, \quad (78)$$

and

$$(B_4^4)_{nc}=\tfrac{1}{8}(\sqrt{70})\sum_j q_j\sin^4\Theta_j\cos 4\Phi_j/R_j^5. \quad (79)$$

In view of Eqs. (76) and (77), the crystal-field component $(B_4^0)'$ used in (10a) can now be defined in terms of the crystal-field components $(B_4^0)_{nc}$ and $(B_4^4)_{nc}$ as follows:

$$(B_4^0)'=(B_4^0)_{nc}'=(B_4^0)_{nc}-\alpha(B_4^4)_{nc}. \quad (80)$$

The quantity $(B_4^0)'$ is the appropriate coefficient to use in the expression (32).

We have evaluated B_2^0, B_2^2, $(B_4^0)_{nc}$, and $(B_4^4)_{nc}$ by both the direct lattice summation[22] and the Nijboer and deWette[25] methods.

It is worth pointing out that in this investigation we have not considered the effect of the induced dipoles in the computation of the crystal fields B_2^0, B_2^2, B_4^2, and $(B_4^0)'$. This can be done very easily following the procedure used by Taylor and Das[26] or Artman and Murphy.[23] Because, however, the F^- ions are much less deformable than O^{--}, the dipolar contributions to the crystalline fields will be much less significant for MnF_2 and ZnF_2 than for corundum.

VIII. RESULTS AND DISCUSSION

The results for D will now be evaluated using the expressions developed in Secs. II through VI. To fix our ideas and to make a reasonable comparison with experiment, we shall consider three specific cases. First, we use as a model a unit charge $(+e)$ totally external to the Mn^{++} ion and a distance $R=4.78a_0$ away. The second and third cases will be those of MnF_2 and Mn^{2+} in ZnF_2, respectively.

A. Single-Charge Model

For the hypothetical single-charge model, the crystal-field components are supposed to be produced by a unit positive charge on the Z axis at a distance R from the Mn^{++} ion. We have chosen R to correspond to a typical field gradient $B_2^0=(0.0184)e^2/2a_0^3$ which, for example, is found in the corundum-type lattice. This leads to $R=4.78a_0$. In this case, since $(B_4^4)_{nc}$ as given by (81) vanishes, we obtain from (80) and (81),

$$(B_4^0)'=8.047\times10^{-4}. \quad (81)$$

Using B_2^0 as given by (69) for the evaluation of (27), (39), (54), and (55), and using $(B_4^0)'$ from (81) for the evaluation of (32), we obtain the values of D for the different mechanisms discussed in Secs. III to VI. These calculated values are listed in Table VI. Since a unit charge on the Z axis produces only an axial field B_2^0, the rhombic crystal fields B_2^2 and B_4^2 are absent and therefore E vanishes.

On analyzing Table VI we find that the contribution to D through configuration interaction, which we denoted by D_{ODS}, is small compared with D_{ss}, and is very small compared with D_{BO}. It also appears that D_W is nearly equal to D_{ODS} in magnitude but differs in sign. As a result, the combined effects of D_W and D_{ODS} add up to a negligible quantity. Watanabe did not consider the effect of the cubic field in his calculations. When the effect of the cubic field is taken into account, the resulting contribution, denoted by D_{WC}, is found to be $1.6D_W$ and is listed in Table VI.

We should like to analyze why D_{BO} gives the most important contribution to D. Substituting $(B_4^0)'$ from (81) in terms of R and comparing the resulting equation with $D(C)=D_{ODS}+D_{WC}$ and D_{ss} as given by (39),

[25] B. R. A. Nijboer and F. W. deWette, Physica 23, 309 (1957).

[26] T. T. Taylor and T. P. Das, Phys. Rev. 133, A1327 (1964); see also Ref. 22.

TABLE VI. Various contributions to D and E in the three cases (a) single-point-charge model, (b) MnF_2, and (c) Mn^{+2}:ZnF_2. The D and E are all expressed in units of 10^{-4} cm^{-1}. ζ has been taken equal to 300 cm^{-1}.

Mechanisms		MnF_2-Mn^{+2} D	MnF_2-Mn^{+2} E	ZnF_2-Mn^{+2} D	ZnF_2-Mn^{+2} E	Single-point-charge model D
Spin-orbit	ODS	+1.06	···	+1.59	···	+7.09
	$d \rightarrow s$	+1.36	+2.26	+1.66	+1.38	−3.52
Spin-spin	$d \rightarrow d$	−5.01	−8.26	−6.14	−5.04	+12.97
	$d \rightarrow g$	+0.48	+0.79	+0.59	+0.49	−1.25
	Total	−3.17	−5.21	−3.88	−3.17	+8.20
Spin-orbit	Watanabe	−0.68	···	−1.01	···	−4.53
	WC	−0.88	···	−1.31	···	−5.86
	ODS+WC	+0.18	···	+0.28	···	+1.23
	B-O	+10.66	−97.40	+27.51	−99.25	+34.93
Total		+7.70	−102.61	+24.01	−102.32	+44.36
Experiment		+11.5	−121.5	+10.5	−113.5	

(27), and (35), we have

$$D(C):D_{ss}:D_{BO}=1.45/R^6:0.09/R^3:8.68/R^5. \quad (82)$$

The magnitude of D_{BO} is larger than $D(C)$ for two reasons. First, the numerical coefficient for D_{BO} is about six times larger than that for $D(C)$ (this is because $\langle r^4\rangle$ occurring in D_{BO} is larger than $\langle r^2\rangle^2$ occurring in the other two mechanisms) and secondly in D_{BO} the negative power of R is less by one than that occurring in $D(C)$, which makes it another factor of 5 larger. These considerations together thus explain why D_{BO} is almost 30 times larger than $D(C)$. If we compare D_{BO} with D_{ss}, we find that through the dependence on powers of $1/R$, D_{BO} would be expected to be smaller by a factor of 1/25 as compared to D_{ss}. However, the numerical coefficient for D_{BO} is about one hundred times larger than that for D_{ss} which makes D_{BO} altogether about four times larger than D_{ss}, as may be seen from Table VI.

Watkins[24] has mentioned that by comparing experimental results with Pryce's expression[2] he has obtained the correct sign for the axial field parameter D. However, we notice from Table VI that $D_{ss}(d \rightarrow d)$ is larger than $D_{ss}(d \rightarrow s)$ and of opposite sign. Watkins' conclusions about D_P are therefore erroneous.

B. Case of Mn^{+2} in MnF_2

The crystal of MnF_2 has a rutile structure with its unit cell tetragonal. However, the environment around each Mn^{2+} ion has only orthorhombic symmetry. The lattice parameters and the coordinates of the ions inside the unit cell as determined by Baur[27] are given in Table VII. We have used Baur's data for the calculation of the crystal-field components as defined by the Eqs. (69)–(71) and (78)–(80). The coordinates of the ions listed in Table VII are expressed with respect to the crystal axes (X_c,Y_c,Z_c) as shown in Fig. 3. To compute the crystalline fields, we transform the coordinates of the ions from the crystal axes (X_c,Y_c,Z_c) system to the system of axes (X,Y,Z) shown in Fig. 3. This will be a more convenient set of axes to use. The Z axis in Fig. 3 is perpendicular to the planar rectangle formed by the four F ions. The X axis is assumed to be parallel to the longer side of the rectangle.

TABLE VII. Crystal structure data for MnF_2 and ZnF_2.

Crystal MX_2	a (Å)	c (Å)	x	Coordinates of M	Coordinates of X
ZnF_2	4.7034	3.1335	0.303	(0,0,0)	$(x,x,0)$ $(\bar{x},\bar{x},0)$
MnF_2	4.8734	3.3099	0.305	$(\frac{1}{2},\frac{1}{2},\frac{1}{2})$	$(\frac{1}{2}+x,\frac{1}{2}-x,\frac{1}{2})$ $(\frac{1}{2}-x,\frac{1}{2}+x,\frac{1}{2})$

The crystalline-field components B_2^0, B_2^2, B_4^2, $(B_4^0)_{nc}$ were computed by the Nijboer-deWette method assuming 2 units of positive charge on the Mn^{++} and one unit of negative charge on the F^- sites. These values are tabulated in Table VIII. These same crystal-field components were computed for ZnF_2 by two different methods, the direct method of lattice summation[22] and the Nijboer-deWette method.[25] It is reassuring that the values obtained by the two methods are in very good agreement with each other.

The constant α appearing in $(B_4^0)'$, defined by (77), can be evaluated using (73), (76), and (77). One finds $\alpha=-(14/5)^{1/2}$. Inserting this result into Eq. (80), employing the lattice constants in Table VII, and the

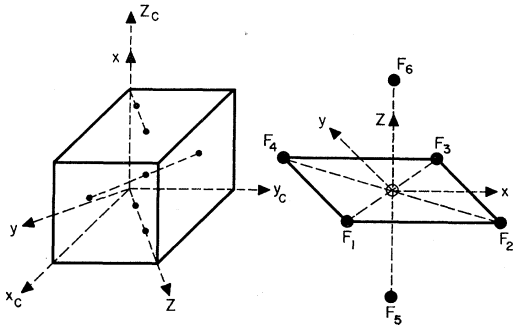

FIG. 3. Positions of the nearest-neighbor F^- ions around a Mn^{++} ion and relative dispositions of X, Y, Z and X_c, Y_c, Z_c axes.

[27] V. W. H. Baur, Acta Cryst. 11, 488 (1958).

TABLE VIII. Crystalline-field components B_l^m for MnF_2 and ZnF_2 in units of $e^2/2a^{l+1}$ when a is lattice constant in atomic units.[a]

Crystal MX_2[b]	Method	B_2^0	B_2^2	B_4^2	$(B_4^0)_{nc}$	$(B_4^4)_{nc}$	B_4^0
ZnF_2	Direct summation	−6.095392	−2.038725	66.965694	−412.970720	267.79	35.127643
	Nijboer-deWette	−6.103556	−2.043104	66.955049	−413.071264	267.902036	35.214571
MnF_2	Nijboer-deWette	−5.542414	−3.728737	79.768149	−401.492368	249.702084	16.339123

[a] The various B_l^m components are defined in Sec. II.
[b] We have taken two units of positive charge on M and one unit of negative charge on X.

crystal-field components in Table VIII, one finds for MnF_2,

$$(B_4^0)' = 2.462\times10^{-4} e^2/2a_0^5. \tag{83}$$

In the similar units $e^2/2a_0^{l+1}$ one obtains the following values for the other crystal-field components:

$$\begin{aligned} B_4^2 &= 6.011\times10^{-4}, \\ B_2^2 &= -47.69\times10^{-4}, \\ B_2^0 &= -70.89\times10^{-4}. \end{aligned} \tag{84}$$

We insert the values into the various contributions to D and E derived in Secs. III to VI and list the results in Table VI. We again observe the same features concerning the relative importance of D_{ss}, D_{BO}, D_{ODS}, and D_{WC}. We have not calculated the contributions to E from the Watanabe and the configuration-interaction mechanisms, because, as pointed out in Sec. III, we expect these to be of minor importance.

Our results, when compared with the experimental values of D and E as found by Tinkham[28] and listed in Table VI, demonstrate that the point-charge model is able to account for the majority of the axial and rhombic field splitting in MnF_2.

C. Case of ZnF_2-Mn^{+2}

The crystal structure of ZnF_2 is similar to that of MnF_2. Baur's crystal-structure data are also tabulated for ZnF_2 in Table VII and the crystal-field components calculated by the direct lattice summation method as well as by the Nijboer-deWette method are both listed in Table VII. Following the same procedure as for MnF_2,

$$\begin{aligned} B_2^0 &= -86.84\times10^{-4}, \\ B_2^2 &= -29.01\times10^{-4}, \\ (B_4^0)' &= 6.338\times10^{-4}, \\ B_4^2 &= 6.025\times10^{-4}. \end{aligned} \tag{85}$$

The various contributions to D and E in this case are listed in Table VI. The relative importance of the various mechanisms for D and E are again of the same nature as for the use of MnF_2.

[28] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 (1956).

The agreement between our theoretical predictions from the point-charge model and experimental results is a little worse for Mn^{++}:ZnF_2 than for MnF_2. The reason for this discrepancy may be the neglect of lattice distortions[29] produced by the presence of Mn^{++} in ZnF_2.

IX. CONCLUSION

We have examined quantitatively various mechanisms which contribute to D and E from first principles using a strictly external point-charge point-multipole model. It has been our primary aim to judge the relative importance of the various mechanisms rather than attempt an absolute comparison between theory and experiment. We have tried to minimize the number of approximations in order to arrive at some realistic estimates of the various contributions. Our results for Mn^{+2} in MnF_2 and ZnF_2 show that the point-charge model is able to produce results in reasonable agreement with observed axial and rhombic terms in the spin-Hamiltonian. An analysis of overlap and charge-transfer effects will be presented in a subsequent paper[10] though, on the basis of comments contained in the Introduction, we expect the effects of such terms to be small. We should, however, like to comment on the error that one makes in treating the nearest-neighbor ions as point charges rather than as extended charge distributions. To correct for the effect of this one would have to use expressions for B_n^m appropriate to the case where the electron is internal to the source density producing the field.[30,31] Such correction terms in the crystal fields will involve negative powers of r, instead of positive powers which obtain when the source charges are completely external. We believe, however, that because charge transfer is directly related to this penetration effect, and there is widespread evidence that charge-transfer effects for the Mn^{+2} ion are unimportant, the correction due to penetration in the specific cases we have treated will not be very important.

[29] T. P. Das, Phys. Rev. **140**, A1957 (1965).
[30] R. M. Stenheimer, Phys. Rev. **132**, 1637 (1963).
[31] G. Burns, J. Chem. Phys. **31**, 1253 (1959).