

# Magnetic parameters of $p^{2,4}$ , $dt_2^{2,4}$ , and $d^2$ configurations in axial symmetric crystal fields

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(Received 12 February 1974)

The energies and wavefunctions of a  $p^{2,4}$  configuration under the influence of a crystal field possessing axial symmetry are calculated. If the crystal field parameter  $\Delta$  is smaller than, or of the order of, the Slater-Condon parameter  $F_2$ , the  ${}^3P$  wavefunctions have the lowest energies. In that case one finds, depending on the sign of  $\Delta$ , that either an orbital doublet or an orbital singlet has the lowest energy. For the latter, the fine structure parameters, the  $g$  values, and the hyperfine parameters are calculated. Using an irreducible tensor formalism, it is shown that the results for  $p^{2,4}$  can be used to find the interactions within  $dt_2^{2,4}$ . Tetragonal as well as trigonal symmetry are treated and it is found that the hyperfine interactions differ substantially for both cases. Finally, the interactions within  ${}^3F(d^2)$  under the influence of a crystal field possessing tetragonal symmetry are treated.

## I. INTRODUCTION

Crystal field theory and its more extended form, ligand field theory, can explain many spectroscopic properties of a variety of complexes. In the course of the theoretical developments, two approaches emerged—the weak field coupling scheme and the strong field coupling scheme.

The weak field approach is appealing since it permits the use of simple operator equivalents and so reduces the labor involved in calculating the necessary matrix elements. The classic paper of Abragam and Pryce<sup>1</sup> is still a good illustration of the power of the weak field theory.

For many transition ions, however, the strong field coupling scheme gives better results. The theory can easily be extended to include chemical bonding, but the drawback is that one is not permitted to use the simple operator equivalents (functions of  $\mathbf{L}$  and  $\mathbf{S}$ ).

It is the purpose of this paper to show that it is still possible to use the simple operator equivalents for  $dt_2^{2,4}$  if one takes advantage of the  ${}^2p^n-dt_2^n$  isomorphism. That is to say, the interactions within  $p^{2,4}$  configurations are calculated and the results are used to calculate the magnetic parameters for the  $dt_2^{2,4}$  configurations. The  $p^{2,4}$  configurations themselves are also very interesting since complexes have already been found which can be described as  ${}^3p^4$ , and more data on  $p^n$  systems can be expected.

The  ${}^3F(d^2)$  term has been treated by Abragam and Pryce<sup>1</sup>; however, their results only apply to crystal fields having trigonal symmetry. The interactions which depend on bilinear combinations of  $\mathbf{L}$  (e.g.,  $L_xL_y + L_yL_x$ ) should differ for trigonal and tetragonal symmetry, since the classification of the states as eigenstates of the fictitious orbital momentum  $\bar{\mathbf{L}}$  is not enough to calculate the necessary matrix elements.<sup>4</sup>

Some numerical solutions of  $dt_2^4$  systems in axial fields and crystal fields of lower symmetry have been reported recently by Oosterhuis and Lang.<sup>5</sup> Our solutions are analytical and are thus preferable. However, there are also some discrepancies with their work and they

will be discussed.

## II. $p^{2,4}$ AND $dt_2^{2,4}$ IN CRYSTAL FIELDS OF AXIAL SYMMETRY.

In order to treat a crystal field of tetragonal symmetry, we have to know the different irreducible components of a tetragonal field. The irreducible components of the cubic group which span the unit representation of  $D_4$  are  ${}^2E\Theta$  and  $A_1a_1$ . The  $A_1a_1$  component displaces only the center of gravity of  $T_1$  or  $T_2$  states, but does not alter the relative energies; therefore, we neglect it. The crystal field operator, which is a one-electron operator, can then be written as

$$C_{\Theta}^E = \sum_i C_{\Theta}^E(i), \quad (1)$$

in which the summation is over the valence electrons. The complex  $p$  orbitals ( $p_1, p_0, p_{-1}$ ), which form a basis for  $T_1$ , diagonalize the  $C_{\Theta}^E$  matrix because<sup>6</sup>

$$\langle p_i | C_{\Theta}^E | p_j \rangle = -R(-1)^i V \begin{pmatrix} T_1 & T_1 & E \\ -i & j & \Theta \end{pmatrix}, \quad i, j = 0, \pm 1, \quad (2)$$

in which  $R$  is a reduced matrix element independent of  $i$  and  $j$ .  $V$  is a Clebsch-Gordan coefficient of the cubic group in the complex tetragonal system.  $V = \frac{1}{8}\sqrt{3}$  when  $i = j = \pm 1$ ,  $V = \frac{1}{3}\sqrt{3}$  when  $i = j = 0$ , and  $V = 0$  otherwise. The splitting of the  $p$  orbitals is  $E(p_{\pm 1}) - E(p_0) = \frac{1}{2}\sqrt{3}R = \Delta$ .

From the atomic  $p^2$  configuration, three terms can be built:  ${}^3P$ ,  ${}^1S$ , and  ${}^1D$ . To obtain the energies and wavefunctions under the influence of the crystal field, we diagonalize the matrix of  $\sum_i C_{\Theta}^E(i) + \sum_{i,j} (e^2/r_{ij})$  within the terms. In Table I, the result is given in terms of the crystal field splitting  $\Delta$  and the Slater-Condon parameters  $F_0$  and  $F_2$  (the same was done for a crystal field of low symmetry in Ref. 3), and the result is plotted in Fig. 1.

If we consider the  $p^4$  configuration as two holes<sup>2</sup> in the  $p$  shell, we can use the results of the  $p^2$  configuration.  $C_{\Theta}^E$  is an operator that is invariant under Kramers's star operator ("time even"). This means that all off-diagonal elements change sign on going from  $p^2$  to  $p^4$ . The diagonal elements also change sign on going from  $p^2$  to  $p^4$  apart from a constant diagonal energy common to all states. It can be shown that the two-

TABLE I. Matrix elements of  $\sum_{i<j}(e^2/r_{ij})$  (Column a) and  $\sum_i C_{ij}^2(i)$  (Column b) within a  $p^2$  configuration.<sup>a</sup>

	(a)	(b)
$ {}^1E\epsilon^1B_1b_1\rangle$	$F_0 + F_2$	$\frac{2}{3}\Delta$
$ {}^1T_{2g}^1B_2b_2\rangle$	$F_0 + F_2$	$\frac{2}{3}\Delta$
$ {}^1T_{2x,-2y}^1E_{x,y}\rangle$	$F_0 + F_2$	$-\frac{1}{3}\Delta$
$ {}^3T_{1g}^3A_2a_2\rangle$	$F_0 - 5F_2$	$\frac{2}{3}\Delta$
$ {}^3T_{1x,1y}^3E_{x,y}\rangle$	$F_0 - 5F_2$	$-\frac{1}{3}\Delta$
$ {}^1E\theta^1A_1a_1\rangle$	$F_0 + F_2$	$-\frac{2}{3}\Delta$
$ {}^1A_1a_1^1A_1a_1\rangle$	$F_0 + 10F_2$	0

<sup>a</sup>The only off-diagonal matrix element is  $\langle{}^1E\theta^1A_1a_1|3C|{}^1A_1a_1^1A_1a_1\rangle = \frac{2}{3}\sqrt{2}\Delta$ .

electron operator  $\sum_{i<j}(e^2/r_{ij})$  has identical matrices within  $p^2$  and  $p^4$ , apart from an added constant in the diagonal elements, which does not alter the relative energies. We conclude that the results for  $p^2$  are carried over to  $p^4$  just by replacing  $\Delta$  by  $-\Delta$ . This means that the plot for  $p^2$  (Fig. 1) should be mirrored with respect to the  $E/F_2$  axis.

Adopting the following notations for the  $dt_2$  orbitals,

$$\begin{aligned} |dt_2, 1\rangle &= |2, -1\rangle \sim |1, 1\rangle \\ |dt_2, 0\rangle &= \frac{1}{\sqrt{2}}(|2, 2\rangle - |2, -2\rangle) \sim |1, 0\rangle \\ |dt_2, -1\rangle &= -|2, 1\rangle \sim |1, -1\rangle, \end{aligned} \quad (3)$$

and letting them correspond to the  $p$  orbitals as indicated, it can be shown that the wavefunctions of the  $dt_2^n$  configurations in cubic symmetry correspond to the  $p^n$  configurations in spherical (or cubic) symmetry.<sup>2</sup> This isomorphism has already been used<sup>7</sup> by applying the well-known results for the  $p^n$  atoms to the  $dt_2^n$  systems. The close relationship between  $dt_2^n$  and  $p^n$  is recognized on inspecting the  $V$  coefficients of the cubic group. We notice that

$$V \begin{pmatrix} T_1 & T_1 & \Gamma \\ a & b & M_\Gamma \end{pmatrix} = V \begin{pmatrix} T_2 & T_2 & \Gamma \\ a & b & M_\Gamma \end{pmatrix}. \quad (4)$$

This means that every irreducible tensor operator has matrix elements within a  $T_1$  triplet which are proportional to the matrix elements within a  $T_2$  triplet. A well-known example is the orbital angular momentum operator  $\mathbf{l}$ , having a proportionality constant of  $-1$  when  $p$  orbitals are compared with  $dt_2$  orbitals.

A way of calculating matrix elements of a one-electron operator within  $dt_2$  states is to first calculate the proportionality constant of the operator on going from  $dt_2^{2,4}$  to  $p^{2,4}$  and to calculate the matrix elements within  $p^{2,4}$  next, which is often much easier than direct calculation, as will be shown in the next section.

The plot of Fig. 1 also applies to  $dt_2^{2,4}$  in tetragonal symmetry, provided we associate  $F_0$  with  $A + \frac{5}{3}C$  and  $F_2$  with  $B + \frac{1}{3}C$  ( $A$ ,  $B$ , and  $C$  are Racah parameters).<sup>2</sup>

The case of trigonal symmetry is easily included. As

a starting point for  $p^{2,4}$ , we take the complex orbitals quantized along a trigonal axis.<sup>6</sup> The same results are obtained as in the case of a tetragonal crystal field, apart from a change in some symmetry labels. If we take as a starting point for  $dt_2^{2,4}$  the trigonal  $dt_2$  orbitals<sup>8</sup>

$$\begin{aligned} -|dt_2, \pm 1\rangle &= \sqrt{1/3}|2, \pm 1\rangle \pm \sqrt{2/3}|2, \mp 2\rangle, \\ |dt_2, 0\rangle &= |2, 0\rangle, \end{aligned} \quad (5)$$

then the same results are again obtained.

### III. MAGNETIC INTERACTIONS AND QUADRUPOLE COUPLING.

We will discuss the interactions in the spin triplet orbital singlet ground state of  $p^{2,4}$  and  $dt_2^{2,4}$ , and we will assume that the  ${}^3P$  term is isolated well enough from other terms that only the nine wavefunctions built from this orbital triplet have to be considered (cf. Fig. 1). The interactions that will be considered are spin-orbit coupling, hyperfine interaction (including the isotropic, the dipole-dipole, and the electron orbit-nuclear spin interaction), quadrupole interaction, and coupling with an external magnetic field. The dipole-dipole interaction and the quadrupole interaction are the most difficult. We will start with them.

Both interactions are closely related to the quantity  $W$  defined by<sup>6</sup>

$$W = \sum_{k=1}^5 V_k(\mathbf{A}, \mathbf{A}) \overline{V_k(\mathbf{B}, \mathbf{C})}. \quad (6)$$

$\mathbf{A}$  is a spatial operator (orbital angular momentum in our case), and  $\mathbf{B}$  and  $\mathbf{C}$  are spin operators. The definition of  $V_k$  is (in the complex tetragonal system)

$$\begin{aligned} V_1(\boldsymbol{\alpha}, \boldsymbol{\beta}) &= -\sqrt{2}(\boldsymbol{\alpha} \times \boldsymbol{\beta})_z^2, \\ V_2(\boldsymbol{\alpha}, \boldsymbol{\beta}) &= -\sqrt{2}(\boldsymbol{\alpha} \times \boldsymbol{\beta})_x^2, \\ V_{3,4,5}(\boldsymbol{\alpha}, \boldsymbol{\beta}) &= -\sqrt{2}(\boldsymbol{\alpha} \times \boldsymbol{\beta})_{1,0,-1}^2. \end{aligned} \quad (7)$$

The quantity  $W$ , a scalar, remains unchanged by an orthogonal transformation. A transformation to the trigonal system will be considered at the end of this section.

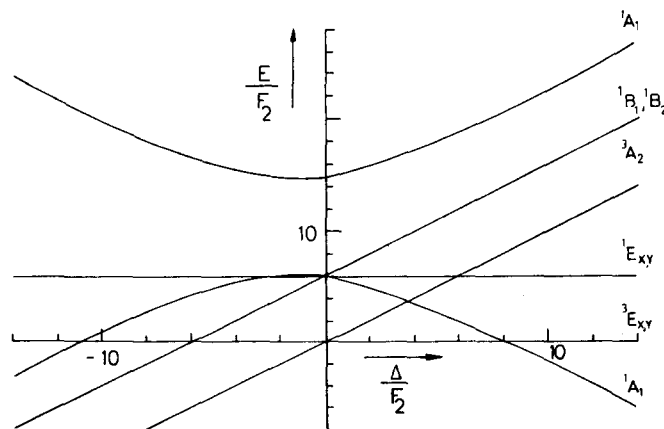


FIG. 1. The energy levels of  $p^2$  under the influence of a crystal field having tetragonal symmetry as function of reduced variables relative to the  ${}^3E_{x,y}$  states.

The hyperfine dipole-dipole coupling written in this way yields<sup>2</sup>

$$H_{hf}^d = \frac{3}{2} g_e g_N \beta_e \beta_N \sum_{\lambda} \gamma_{\lambda}^{-5} \sum_k V_k(\mathbf{r}_{\lambda}, \mathbf{r}_{\lambda}) \overline{V_k(\mathbf{S}_{\lambda}, \mathbf{I})}. \quad (8)$$

The summation  $\lambda$  is over the electrons. An operator equivalent to this operator is<sup>2</sup>

$$H_{hf}^d = -\frac{3}{2} \eta P \sum_{\lambda, k} V_k(\mathbf{1}_{\lambda}, \mathbf{1}_{\lambda}) \overline{V_k(\mathbf{S}_{\lambda}, \mathbf{I})}; \quad (9)$$

$\eta = \frac{2}{5}$  for  $p$  electrons and  $\frac{2}{21}$  for  $d$  electrons, and  $P = g_N g_e \beta_N \beta_e \langle r^{-3} \rangle$ . If all states that are considered belong to one  $^{2S+1}L$  term, a considerable simplification of Eq. (9) is obtained, since the following operator equivalent can be used:

$$-\frac{3}{2} \eta' P \sum_k V_k(\mathbf{L}, \mathbf{L}) \overline{V_k(\mathbf{S}, \mathbf{I})}; \quad (10)$$

$\eta' = -\frac{1}{5}$  for the ground term  $^3P(p^2)$ . For  $dt_2^{2,4}$ , this replacement is not justified. The use of an operator equivalent simpler than Eq. (9) will be demonstrated: The  $(p^{2,4}; ^3P)$  functions are denoted by  $|m_1, m_S, m_I\rangle$  and the corresponding  $dt_2^{2,4}$  states are denoted by  $|\hat{m}_1, m_S, m_I\rangle$ . The following matrix element is pertinent:

$$\begin{aligned} & \langle \hat{m}_1, m_S, m_I | \sum_{\lambda, k} V_k(\mathbf{1}_{\lambda}, \mathbf{1}_{\lambda}) \overline{V_k(\mathbf{S}_{\lambda}, \mathbf{I})} | \hat{m}'_1, m'_S, m'_I \rangle \\ & \equiv 0(m_1, m'_1, m_S, m'_S, m_I, m'_I) \\ & = \sum_{\lambda, k} \langle \hat{m}_1, m_S, m_I | V_k(\mathbf{1}_{\lambda}, \mathbf{1}_{\lambda}) | \hat{m}'_1, m'_S, m'_I \rangle \\ & \quad \langle \hat{m}'_1, m'_S, m'_I | \overline{V_k(\mathbf{S}_{\lambda}, \mathbf{I})} | \hat{m}_1, m_S, m_I \rangle. \end{aligned} \quad (11)$$

As the application to the ground term of  $p^{2,4}$ ,  $dt_2^{2,4}$  was already in mind, a sum over  $|\hat{m}'_1, m'_S, m'_I\rangle$  states has not been included. Since only spin functions are involved,  $\langle \hat{m}'_1, m'_S, m'_I | V_k(\mathbf{S}_{\lambda}, \mathbf{I}) | \hat{m}'_1, m'_S, m'_I \rangle$  can be replaced by  $\langle m'_1, m'_S, m'_I | V_k(\mathbf{S}_{\lambda}, \mathbf{I}) | m'_1, m'_S, m'_I \rangle$ , and since the  $V_k$ 's are irreducible tensor operators [cf. Eq. (4)],  $\langle \hat{m}_1, m_S, m_I | V_k(\mathbf{1}_{\lambda}, \mathbf{1}_{\lambda}) | \hat{m}_1, m_S, m_I \rangle$  can be replaced by  $\alpha_k \langle m_1, m_S, m_I | V_k(\mathbf{1}_{\lambda}, \mathbf{1}_{\lambda}) | m'_1, m'_S, m'_I \rangle$ , for which  $\alpha_k = -3$  for  $k=1, 2$ ,  $\alpha_k = +3$  for  $k=3, 4, 5$  (tetragonal symmetry).<sup>9</sup>

As a final result, we have

$$\begin{aligned} & 0(m_1, m'_1, m_S, m'_S, m_I, m'_I) \\ & = \sum_{\lambda, k} \{ \alpha_k \langle m_1, m_S, m_I | V_k(\mathbf{1}_{\lambda}, \mathbf{1}_{\lambda}) | m'_1, m'_S, m'_I \rangle \\ & \quad \times \langle m'_1, m'_S, m'_I | \overline{V_k(\mathbf{S}_{\lambda}, \mathbf{I})} | m_1, m_S, m_I \rangle \}. \end{aligned} \quad (12)$$

However, the rhs of Eq. (12) can be replaced by operators of the total angular momentum, since now only

$^3P$  states are involved:

$$\begin{aligned} & 0(m_1, m'_1, m_S, m'_S, m_I, m'_I) \\ & = -\frac{1}{2} \sum_k \{ \alpha_k \langle m_1, m_S, m_I | V_k(\mathbf{L}, \mathbf{L}) | m'_1, m'_S, m'_I \rangle \\ & \quad \times \langle m'_1, m'_S, m'_I | \overline{V_k(\mathbf{S}, \mathbf{I})} | m_1, m_S, m_I \rangle \}, \end{aligned} \quad (13)$$

which is the desired result.

For the  $dt_2^{2,4}$ , Eq. (13) means

$$\begin{aligned} & \langle \hat{m}_1, m_S, m_I | H_{hf}^d | \hat{m}'_1, m'_S, m'_I \rangle \\ & = \frac{1}{14} P 0(m_1, m'_1, m_S, m'_S, m_I, m'_I). \end{aligned} \quad (14)$$

The quadrupole interaction can be written as<sup>2</sup>

$$H_Q = \frac{3}{2} \eta q' \sum_{\lambda, k} V_k(\mathbf{1}_{\lambda}, \mathbf{1}_{\lambda}) \overline{V_k(\mathbf{I}, \mathbf{I})}, \quad (15)$$

with

$$q' = \frac{e^2 q \langle r^{-3} \rangle}{2I(2I-1)},$$

and where  $q$  is the nuclear quadrupole moment. Within  $^{2S+1}L$ , this can be replaced by

$$\frac{3}{2} \eta' q' \sum_k V_k(\mathbf{L}, \mathbf{L}) \overline{V_k(\mathbf{I}, \mathbf{I})}. \quad (16)$$

$\eta' = \pm 2S\eta'$  for a ground term of  $l^n$ . The negative sign applies if the shell is more than half filled.

A reasoning analogous to the one that led to Eq. (14) gives

$$\begin{aligned} & \langle \hat{m}_1, m_S, m_I | H_Q | \hat{m}'_1, m'_S, m'_I \rangle \\ & = -\frac{1}{7} q' \sum_k \alpha_k \langle m_1, m_S, m_I | V_k(\mathbf{L}, \mathbf{L}) \overline{V_k(\mathbf{I}, \mathbf{I})} | m'_1, m'_S, m'_I \rangle, \end{aligned} \quad (17)$$

which again connects the matrix elements of  $dt_2^{2,4}$  with  $p^{2,4}$ .

In the case of trigonal symmetry, we have to use the  $V$  coefficient in a trigonal system, and we choose the complex trigonal system. The remaining interactions are simpler. The isotropic hyperfine interaction is included as  $-\kappa \mathbf{S} \cdot \mathbf{I}$ . On going from  $p^{2,4}$  to  $dt_2^{2,4}$ ,  $\mathbf{L}$  should be replaced by  $-\mathbf{L}$ , irrespective of the type of axial crystal field.

The framework is now complete; within ( $^3P, p^2$ ) the spin-orbit coupling and crystal field are diagonalized, and then the interactions like hyperfine interactions are calculated for the ground state and, if possible, the result is fitted into a spin Hamiltonian with  $\mathbf{S}' = 1$ .

#### IV. $p^{2,4}$ IN TETRAGONAL SYMMETRY.

We use as basis  $|m_1, m_S\rangle$  and an additional quantum number<sup>1</sup>  $m = 1_x + s_x$  (the nuclear spin state indication will be dropped).

The results for  $p^2$  are

$$\begin{aligned} m = \pm 2: & E = -\frac{1}{3} \Delta + \lambda & \Psi_1 = |1, 1\rangle & \Psi_2 = |-1, -1\rangle \\ m = \pm 1: & E = \frac{1}{6} \Delta + \frac{1}{2} S_1 & \Psi_3 = a |0, 1\rangle + b |1, 0\rangle \\ & E = \frac{1}{6} \Delta - \frac{1}{2} S_1 & \Psi_4 = b |0, 1\rangle - a |1, 0\rangle \end{aligned}$$

and similar functions  $\Psi_5$  and  $\Psi_6$  with  $m = -1$

$$\begin{aligned}
 m=0: E &= -\frac{1}{3}\Delta - \lambda & \Psi_7 &= \frac{1}{\sqrt{2}}(|1, -1\rangle - |-1, 1\rangle) \\
 E &= \frac{1}{6}\Delta - \frac{1}{2}\lambda + \frac{1}{2}S_0 & \Psi_8 &= c|0, 0\rangle + \frac{d}{\sqrt{2}}(|1, -1\rangle + |-1, 1\rangle) \\
 E &= \frac{1}{6}\Delta - \frac{1}{2}\lambda - \frac{1}{2}S_0 & \Psi_9 &= d|0, 0\rangle - \frac{c}{\sqrt{2}}(|1, -1\rangle + |-1, 1\rangle)
 \end{aligned}$$

in which

$$\begin{aligned}
 S_1 &= (\Delta^2 + 4\lambda^2)^{1/2} & S_0 &= (\Delta^2 + 2\lambda\Delta + 9\lambda^2)^{1/2} \\
 a &= \left\{ \frac{1}{2} \left( 1 + \frac{\Delta}{S_1} \right) \right\}^{1/2} & b &= +\{1 - a^2\}^{1/2} \\
 c &= \left\{ \frac{1}{2} \left( 1 + \frac{\Delta + \lambda}{S_0} \right) \right\}^{1/2} & d &= +\{1 - c^2\}^{1/2}.
 \end{aligned} \tag{18}$$

The results are plotted in Fig. 2. If  $\Delta < 0$ , we have, irrespective of the relative magnitude of  $\lambda$ , the following ground state triplet:

$$\begin{aligned}
 \Psi_{\pm 1} &= b|0, \pm 1\rangle - a|\pm 1, 0\rangle \\
 \Psi_0 &= d|0, 0\rangle - \frac{c}{\sqrt{2}}(|1, -1\rangle + |-1, 1\rangle).
 \end{aligned} \tag{19}$$

Griffith defined a "Kramers triplet" in the following way<sup>2</sup>: Three functions  $\Psi_a, \Psi_b,$  and  $\Psi_c$  form a Kramers triplet if the following relation holds:

$$\Psi_i^* = \sum_{j=a} c_{ji} \Psi_j, \quad i, j = a, b, \text{ or } c. \tag{20}$$

This relation holds for our ground triplet since  $\Psi_0^* = \Psi_0$  and  $\Psi_{\pm 1}^* = -\Psi_{\mp 1}$ . For a Kramers triplet, it can be proved that all interactions already mentioned, except the quadrupole interaction, can be fitted into a spin Hamiltonian with  $S' = 1$ :

$$\begin{aligned}
 \mathcal{H}_s &= g_{\parallel} \beta_e H_{\parallel} S_{\parallel} + \frac{1}{2} g_{\perp} \beta_e (H^+ S^- + H^- S^+) + D[S_z^2 - \frac{1}{3} S(S+1)] + \\
 &+ A_{\parallel} S_z I_z + \frac{1}{2} A_{\perp} (S^+ I^- + S^- I^+) + g_N \beta_N \mathbf{H} \cdot \mathbf{I},
 \end{aligned} \tag{21}$$

with the following spin-Hamiltonian parameters:

$$\begin{aligned}
 D &= \frac{1}{2}\lambda + \frac{1}{2}S_0 - \frac{1}{2}S_1 \approx -\frac{\lambda^2}{\Delta}, \\
 g_{\parallel} &= g_e b^2 + a^2 \approx 2 - \frac{\lambda^2}{\Delta^2},
 \end{aligned}$$

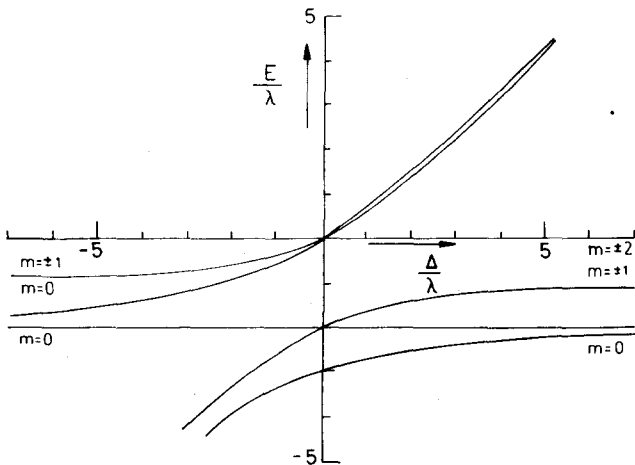


FIG. 2. The energy levels of  ${}^3P(p^2)$  under the influence of an axial symmetric crystal field and the spin-orbit coupling relative to the  $m = \pm 2$  states. Again, reduced variables are used.

$$\begin{aligned}
 g_1 &= g_e b d + \frac{g_{\parallel}}{\sqrt{2}} a c - \frac{bc}{\sqrt{2}} - a d \approx 2 + \frac{2\lambda}{\Delta} - \frac{\lambda^2}{\Delta^2}, \\
 \frac{A_{\parallel}}{P} &= -\frac{2}{5} b^2 - \kappa b^2 - \frac{3}{5} a b + a^2 \approx -\frac{2}{5} - \kappa \left( 1 - \frac{\lambda^2}{\Delta^2} \right) + \frac{3}{5} \frac{\lambda}{\Delta} + \frac{7}{5} \frac{\lambda^2}{\Delta^2}, \\
 \frac{A_{\perp}}{P} &= \frac{1}{5} b d - \kappa b d - \frac{\kappa}{\sqrt{2}} a c - \frac{7}{10\sqrt{2}} b c \\
 &+ \frac{1}{2\sqrt{2}} a c - a d \approx \frac{1}{5} - \kappa \left( 1 - \frac{\lambda^2}{2\Delta^2} \right) + \frac{17\lambda}{10\Delta} + \frac{1}{5} \frac{\lambda^2}{\Delta^2}.
 \end{aligned} \tag{22}$$

Also, the perturbation limits are given ( $|\lambda/\Delta| \ll 1$ ) to second order. If the nucleus has a quadrupole moment, this gives a complication. The expectation value of  $3L_z^2 - L(L+1)$  should be the same for the three states. This is only true if  $\lambda/\Delta \ll 1$  and, in that case, the interaction can be included by adding to Eq. (21) the term  $Q[I_x^2 - \frac{1}{3} I(I+1)]$  with

$$Q = \frac{3e^2 q \langle r^{-3} \rangle}{5I(2I-1)}. \tag{23}$$

As was discussed in Sec. III, the interactions within  $p^4$  can easily be found from the results of  $p^2$ . We have to make the following changes:

$$\begin{aligned}
 \Delta &\rightarrow -\Delta, \\
 \lambda &\rightarrow -\lambda.
 \end{aligned} \tag{24}$$

The new coefficients  $a', b', c',$  and  $d'$  are

$$\begin{aligned}
 a' &= \left\{ \frac{1}{2} \left( 1 - \frac{\Delta}{S_1} \right) \right\}^{1/2}, & b' &= -(1 - a'^2)^{1/2}, \\
 c' &= \left\{ \frac{1}{2} \left( 1 - \frac{\Delta + \lambda}{S_0} \right) \right\}^{1/2}, & d' &= -(1 - c'^2)^{1/2}.
 \end{aligned} \tag{25}$$

For an orbital singlet to lie lowest,  $\Delta$  should now be positive. The diagram of Fig. 2 should be mirrored with respect to the  $\Delta/\lambda$  axis.

The results for the ground triplet can be fitted with the spin Hamiltonian of Eq. (21) with the following parameters:

$$\begin{aligned}
 D &= -\frac{1}{2}\lambda + \frac{1}{2}S_0 - \frac{1}{2}S_1 \approx \frac{\lambda^2}{\Delta}, \\
 Q &= -\frac{3e^2 q \langle r^{-3} \rangle}{5I(2I-1)}.
 \end{aligned} \tag{26}$$

The other parameters are obtained from Eq. (22) by replacing  $a, b, c,$  and  $d$  by  $a', b', c',$  and  $d'$ , respectively. The perturbation limits remain the same.

### V. $dt_2^{2,4}$ IN TETRAGONAL SYMMETRY.

With the help of the formulas derived in Sec. III we calculate the spin-Hamiltonian parameters. The reason we retained  $g_e$  instead of 2 in the preceding section is that terms that originate from  $\mathbf{S}$  can easily be traced now.

The eigenvalues of Eq. (18) are valid for  $dt_2^{2,4}$  provided we replace  $\lambda \rightarrow -\lambda$ . This is only a formal replacement because the one-electron spin-orbit parameters are different:  $\zeta_d \neq \zeta_p$ . The plot of Fig. 2 is valid provided we mirror twice—with respect to the  $E/\lambda$  axis and with respect to the  $\Delta/\lambda$  axis. If  $\Delta < 0$ , a Kramers triplet forms the ground state and the same effective Hamiltonian as expressed by Eq. (21) can be used with

$$D = -\frac{1}{2}\lambda + \frac{1}{2}S'_0 - \frac{1}{2}S_1 \approx \frac{-\lambda^2}{\Delta},$$

$$g_J = g_e \beta^2 - \alpha^2 \approx 2 - \frac{3\lambda^2}{\Delta^2},$$

$$g_1 = g_e \beta \delta + \frac{g_e}{\sqrt{2}} \alpha \gamma + \frac{\beta \gamma}{\sqrt{2}} + \alpha \delta \approx 2 + \frac{2\lambda}{\Delta} - \frac{\lambda^2}{\Delta^2}.$$

$A_J$ ,  $A_1$ , and  $Q$  are calculated with the help of Eqs. (14) and (17):

$$\frac{A_J}{P} = \frac{2}{7}\beta^2 - \frac{3}{7}\beta\alpha - \alpha^2 - \kappa\beta^2 \approx \frac{2}{7} - \frac{3\lambda}{7\Delta} - \frac{9\lambda^2}{7\Delta^2} - \kappa \left(1 - \frac{\lambda^2}{\Delta^2}\right),$$

$$\frac{A_1}{P} = -\frac{1}{7}\beta\delta + \frac{1}{14\sqrt{2}}\alpha\gamma + \frac{17}{14\sqrt{2}}\beta\gamma + \alpha\delta - \kappa\beta\delta - \frac{\kappa\alpha\gamma}{\sqrt{2}} \quad (27)$$

$$\approx -\frac{1}{7} + \frac{31\lambda}{14\Delta} + \frac{2\lambda^2}{7\Delta^2} - \kappa \left(1 - \frac{\lambda^2}{2\Delta^2}\right),$$

$$Q = -\frac{3e^2q\langle r^{-3} \rangle}{7I(2I-1)}.$$

$\alpha, \beta, \gamma, \delta$ , and  $S'_0$  are to be obtained from  $a', b', c', d'$ , and  $S_0$ , respectively, by replacing  $\Delta$  by  $-\Delta$ .

For  $dt_2^{2,4}$ , Eqs. (18) are valid provided we change  $\Delta$  in  $-\Delta$ . The plot of Fig. 2 should be mirrored with respect to the  $\Delta/\lambda$  axis. If  $\Delta > 0$ , an orbital singlet-spin triplet lies lowest, and again the  $S' = 1$  spin Hamiltonian can be used.

The coefficients are  $\alpha', \beta', \gamma'$ , and  $\delta'$  and are to be obtained from  $a, b, c$ , and  $d$ , respectively, by replacing  $\Delta$  by  $-\Delta$ ;

$$D = \frac{1}{2}\lambda + \frac{1}{2}S'_0 - \frac{1}{2}S_1 \approx \frac{\lambda^2}{\Delta}. \quad (28)$$

$Q$  changes sign as compared to  $dt_2^{2,4}$ , and the other parameters are found by attaching a prime to coefficients in Eqs. (27)

### VI. $p^{2,4}$ AND $dt_2^{2,4}$ IN TRIGONAL SYMMETRY

The  $p$  orbitals quantized along a tetragonal axis have the same functional dependence on  $x, y$ , and  $z$  as the  $p$  orbitals quantized along a trigonal axis on  $\rho, \sigma$ , and  $\tau$ . This means that the results for  $p^{2,4}$  in trigonal and tetragonal symmetry should be indistinguishable. How-

ever, this is not true for  $dt_2^{2,4}$ , so we still have to calculate the interactions for  $p^{2,4}$  in trigonal symmetry and then use Eqs. (14) and (17).

The energy levels of  $dt_2^{2,4}$  are the same in either tetragonal or trigonal symmetry. However, the hyperfine parameters differ substantially. For  $dt_2^{2,4}$ , if  $\Delta < 0$ , the ground triplet can be described by the  $S' = 1$  spin Hamiltonian with  $D, g_J$  and  $g_1$  the same as in the tetragonal case, but

$$\frac{A_J}{P} = -\frac{2}{7}\beta^2 + \frac{1}{7}\alpha\beta - \alpha^2 - \kappa\beta^2 \approx -\frac{2}{7} + \frac{1\lambda}{7\Delta} - \frac{5\lambda^2}{7\Delta^2} - \kappa \left(1 - \frac{\lambda^2}{\Delta^2}\right),$$

$$\frac{A_1}{P} = \frac{1}{7}\beta\delta - \frac{15}{14\sqrt{2}}\beta\gamma - \frac{1}{14\sqrt{2}}\alpha\gamma + \alpha\delta - \kappa\beta\delta - \frac{\kappa\alpha\gamma}{\sqrt{2}} \quad (29)$$

$$\approx \frac{1}{7} + \frac{27\lambda}{14\Delta} - \frac{1\lambda^2}{7\Delta^2} - \kappa \left(1 - \frac{\lambda^2}{2\Delta^2}\right),$$

$$Q(\text{trigonal}) = -Q(\text{tetragonal}).$$

The hyperfine interaction changes sign compared to the tetragonal case.

For  $dt_2^{2,4}$  in trigonal symmetry, we again have  $D, g_J$ , and  $g_1$  being the same as in the tetragonal case and that  $Q$  changing sign. The hyperfine parameters can be obtained by replacing  $\alpha, \beta, \gamma$ , and  $\delta$  by  $\alpha', \beta', \gamma'$ , and  $\delta'$ , respectively, in Eq. (29).

### VII. ( $d^2; {}^3F$ ) IN TETRAGONAL SYMMETRY.

The tetragonal crystal fields splits  ${}^3F$  into a singlet ( ${}^3A_2$ ) and two triplets ( ${}^3T_1$  and  ${}^3T_2$ ). If  $B_4$  is negative,  ${}^3T_1$  lies lowest. The groundstates are<sup>10</sup>

$$-|30\rangle \equiv |\bar{0}\rangle, \quad (30)$$

$$\sqrt{\frac{3}{8}}|3, \pm 1\rangle + \sqrt{\frac{5}{8}}|\mp 3\rangle \equiv |\pm 1\rangle.$$

The three states can be described as eigenfunctions of the fictitious orbital momentum  $\bar{I}$  ( $\bar{I} = 1$ ) with orbital Landé factor  $\alpha = -\frac{3}{2}$ . The effect of  $C_0^2$  and  $\alpha\lambda\bar{I} \cdot \mathbf{S}$  is to split the ninefold level in three  $m = 0$  states, in two  $m = \pm 1$  doublets, and in an  $m = \pm 2$  doublet. The eigenvalues are the same in tetragonal and trigonal symmetry and have been reported in Ref. 1. However, the expressions for the hyperfine interactions differ substantially. If  $\Delta$  is negative, we have a ground triplet that can be described with a  $S' = 1$  spin Hamiltonian with the following parameters:

$$\frac{A_J}{P} = \frac{4}{35}B^2 - \frac{3}{70}AB - \frac{3}{2}A^2 - \kappa B^2 \approx \frac{4}{35} - \frac{9}{140\Delta} - \frac{1017\lambda^2}{280\Delta^2} - \kappa \left(1 - \frac{9}{4}\frac{\lambda^2}{\Delta^2}\right),$$

$$\frac{A_1}{P} = -\frac{2}{35}BD - \frac{1}{28\sqrt{2}}AC + \frac{213}{140\sqrt{2}}BC + \frac{3}{2}AD - \kappa \left(BD + \frac{AC}{\sqrt{2}}\right)$$

$$\approx -\frac{2}{35} + \frac{1269\lambda}{280\Delta} + \frac{9}{80}\frac{\lambda^2}{\Delta^2} - \kappa \left(1 - \frac{9}{8}\frac{\lambda^2}{\Delta^2}\right),$$

$$Q = \frac{6e^2q\langle r^{-3} \rangle}{35I(I-1)}, \quad (31)$$

$$A = \left(\frac{1}{2} + \frac{1}{2}\frac{\Delta}{S'_1}\right)^{1/2}, \quad B = -(1 - A^2)^{1/2}$$

$$C = \left\{ \frac{1}{2} + \frac{\frac{1}{2}(\Delta - \frac{3}{2}\lambda)}{S_0''} \right\}^{1/2}, \quad D = -(1 - C^2)^{1/2},$$

$$S'' = (\Delta^2 + 9\lambda^2)^{1/2}, \quad S_0'' = (\Delta^2 - 3\lambda\Delta + \frac{9}{4}\lambda^2)^{1/2}.$$

### VIII. MISCELLANEOUS

The electron spin–electron spin interaction was neglected in the preceding sections. The reason is that it is known that only in cases where the symmetry deviates very strongly from cubic or tetrahedral symmetry the contribution of the spin–spin interaction to, e.g., the zero field splitting cannot be neglected. This is at least true for  $d^n$  (or  $dt_2^n$ ) states. It is not known for  $p^n$ , and we will investigate it. The spin–spin splitting can be presented within  $^{2S+1}L$  by the equivalent Hamiltonian

$$H_{ss} = -\frac{1}{2}\rho \sum_{k=1}^5 V_k(\mathbf{L}, \mathbf{L}) \overline{V_k(\mathbf{S}, \mathbf{S})}. \quad (32)$$

For the  $^3P(p^{2,4})$  state, this means a zero field splitting of  $\frac{1}{2}\rho$ ;  $\rho$  is connected with the following integral:

$$\int_0^\infty p(1)p(1) dr_1 \int_{r_1}^\infty r_2^3 p(2)p(2) dr_2 \equiv J.$$

$J$  was evaluated by Kayama and Bourd<sup>11</sup> for C, N, O, S, and Se and was always at least two orders of magnitude smaller than the spin–orbit coupling parameter. Only in extreme axial fields should this contribution also be considered.

The extension to more adjustable parameters can readily be done within this framework—for instance, by introduction of orbital Landé parameters and holding  $\alpha_k$  as a parameter.

Relevant to our calculations is the work of Oosterhuis and Lang.<sup>5</sup> They numerically calculated the parameters for  $\text{Fe}^{3+}$  low spin. Their approach is somewhat different from ours because they also include the Zeeman interaction in the zeroth order Hamiltonian. This is only necessary for high magnetic fields and/or very small axial splittings. This interaction can be included in our framework with the help of simple perturbation theory because only one state not belonging to the ground triplet is important.

Oosterhuis and Lang<sup>5</sup> also derived perturbation for-

mulas that can be compared with our expansions to second order in  $\lambda/\Delta$ . However, their results do not wholly agree with ours. This is largely caused by the fact that Oosterhuis and Lang did not renormalize their wavefunctions. This is absolutely necessary because the corrections are of order  $\lambda^2/\Delta^2$  which is the order one still wants to represent correctly. In our results, this problem does not arise because the exact results were expanded in  $\lambda/\Delta$ .

### IX. CONCLUSION

The interactions in the magnetic ground state of  $p^{2,4}$  and  $dt_2^{2,4}$  in crystal fields possessing axial symmetry have been calculated.

The  $p^n$ – $dt_2^n$  isomorphism has been used to derive, in a straightforward and convenient way, the results of  $dt_2^n$  from the results of  $p^n$ .

For completeness, the results for ( $d^2$ ;  $^3F$ ) in tetragonal symmetry have also been given.

### ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Professor D. Schoemaker for his interest in the work and his valuable suggestions. This work is part of the research program of E.S.I.S. International Centre for Theoretical Solid State Physics in Belgium.

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