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Technical Report

AN MO THEORY OF THE CUBIC FIELD SPLITTING OF $3d^5$ ^6S IONS IN II-VI COMPOUNDS OF T_d SYMMETRY

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ABSTRACT

Molecular orbital techniques have been employed to find the cubic field splitting 3a of $(3d)^5\ {}^6S$ ions in II-VI compounds of T_d symmetry. The parameter 3a is calculated by perturbation analysis, through spin-orbit interaction $\sum_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i$ between the ground state $t_a^3\ e_a^2\ {}^6A_1$ and excited states $|t_a^p\ S_1\ h_1\ e_a^{4-p}\ S_2\ h_2,\ \gamma\ S_3\ h_3,\ S\ h >$. Here t_a, e_a are the antibonding orbitals of the complex composed of the $(3d)^5\ {}^6S$ ion and its four nearest ligands and p and 4-p are the hole configurations of orbitals t_a and e_a, respectively.

The perturbation calculations have been carried out up to the fourth order which is the lowest order necessary for the splitting 3a to occur. Moreover, these calculations have been limited to the very small number of states which arise exclusively from those initial states $t_a^p\ S_1\ h_1,\ e_a^{4-p}\ S_2\ h_2$ .... with S_1, S_2 ... having their maximum value. The analytical result is found as

$$3a = \sum_{i=o}^{4} C_i\ \zeta_d^{4-i}\ \zeta_p^{\ i}$$

where ζ_d and ζ_p are spin-orbit parameters of the d-orbitals of $(3d)^5\ {}^6S$ ion and p orbitals of the ligands respectively. The coefficients C_i are functions of coefficients of linear combinations of d and p orbitals which give rise to the molecular orbitals t_a, e_a and γ. They are also functions of energies E_{jk} required for promotion of a hole from a state $|\chi_j\ S_j\ h_j >$ to another state $|\chi_k\ S_k\ h_k >$. The χ_j and χ_k in above states describe the hole configurations of orbitals t_a, e_a, γ and their coupling scheme.

Numerical results, obtained for states $|\chi S = 5/2\ h>$ of Fe^{3+} in the series of ZnS, ZnSe and ZnTe compounds with a reasonable set of coefficients of linear combination of atomic orbitals and an average promotion energy of 32000 cm^{-1}, indicate that the term $C_4\ \zeta_p{}^4$ contributes a large negative value to 3a in agreement with experimentally determined 3a of Fe^{3+} in ZnTe.

CHAPTER I

INTRODUCTION

The importance of the concept of spin Hamiltonian in electron spin resonance (ESR) is very well known.* The techniques of the measurement of the parameters in this Hamiltonian are also well developed. However, the attempts to interpret the measured values of the parameters have met with partial degree of success.

A particularly puzzling discrepancy has been the ground state splitting of the iron group S-state ions in II-VI compounds of T_d symmetry. The first ESR measurement of this splitting was made on ZnS:Mn by Matarrese and Kikuchi.[1] This was followed by Watanabe's theory+ which predicted the 3a of a given S-state ion, in several compounds with the same formal charge, should decrease as the metal-ligand distance, R, increases. Predictions of this theory were given support by the measured 3a in II-VI compounds with O_h symmetry. Subsequent measurements showed that such is not always the case for every compound such as CdS:Mn and CdTe:Mn[2]. The 3a in CdTe:Mn was larger than that in CdS:Mn. This observation indicated that the point charge model is not adequate for the explanation of 3a in covalent II-VI compounds and the covalency effects should also be taken into account.

The purpose of this work is to explore the contributions to 3a caused by the above covalency effects present in such compounds such as CdTe by invoking the molecular orbital theory instead of the above-mentioned point charge model. In order to obtain an insight into the sources of such contribution to 3a, as well as to the mechanisms causing

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*A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. A, 205, 135 (1951). Ibid, 206, 164. Ibid, 206, 173 (1951).

+See Reference 5.

the splitting to occur, a brief introduction to calculations based on the point charge model should be very helpful. Therefore, we proceed by giving a review of the previous work on 3a first, and then, we arrive at the possible covalency phenomena affecting this parameter.

The ground state of the free ions Cr^{+}, Mn^{2+} and Fe^{3+} is six fold degenerate with the spectroscopic classification of $(3d)^5\ {}^6S_{5/2}$. Substituting such an ion in the metal site of cubic II-VI compounds, such as Mn^{2+} in the Zn^{2+} site of ZnS, one finds from electron spin resonance (ESR) spectra of the system ZnS:Mn[1,2], that the ground state of the S-state ion splits into a spin quartet U' and a spin doublet E". This splitting is called the cubic field splitting of a $(3d)^5\ {}^6S_{5/2}$ ion and is denoted by the parameter 3a = E(U') - E(E") with E(U') and E(E") as the lowest energy values of levels of symmetries U' and E", respectively.

The crystalline cubic field can be expressed as:[2] $V = a\,(15)^{-1}\,(T_0^{\ 4} + (5/14)^{1/2}\,(T_4^{\ 4} + T^4_{\ -4}))$. The matrix elements of tensors $T_q^{(k)}$ of V for two states $|\gamma\ L\ M_L>$ and $|\gamma'\ L'\ M'_L>$ are:*

$$<\gamma\ L\ M_L|\ T_q^{(k)}\,|\gamma'\ L'\ M'_L> = (-1)^{L-M_L}\begin{pmatrix} L & k & L' \\ -M_L & q & M'_L \end{pmatrix}$$

$$(x)\ \ (\gamma\ L||T^{(k)}||\gamma'\ L') \equiv 0, \qquad \text{for } L = L' = 0;\ k = 4$$

This result indicates that the ground state ${}^6S_{5/2}$ is not split by a cubic field but that the splitting is caused from admixture of the ground state by excited states through perturbation by spin orbit coupling, spin-spin interaction, etc.

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*B. R. Judd, "Operator Techniques in Atomic Spectroscopy," McGraw-Hill Book Company, Incorporated, New York, (1963), p. 42

A similar ground state splitting was manifested in an observation of the anisotropy of the magnetic susceptibility of paramagnetic crystals containing Mn^{2+} such as $Mn\ (NH_4)_2\ (SO_4)_2\ 6H_2O$. To explain this, Van Vleck and Penney (1934)[3] considered various higher order processes involving the cubic field V and the spin orbit interaction, $H_p = \sum_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i$ through intermediate excited states using the order of magnitude argument to estimate the resulting splitting. Later Pryce (1950),[4] in explaining the same splitting for Fe^{3+}, pointed out the inadequacy of mechanisms proposed by Van Vleck[3] and attributed the cubic ground state splitting of Fe^{3+} to a fifth order perturbation quartic in H_p and linear in V. The work by Pryce was followed by Watanabe (1957),[5] who based his calculations of the cubic splitting on the complimentary theorem in the crystalline field splitting of the transition ions. He argued that two ions with complementary electronic configurations, such as Ti^{3+} and Cu^{2+} whose ground level can be split by the first power of V, have always inverted splitting patterns with respect to each other when placed under the same crystalline environment. Based on this theorem, he concluded that a $3d^5$ ion is its own complementary and that any splitting arising from the first power of V should be both positive and negative, and hence identically zero. Proving, in this way, that linear contributions of the cubic field cannot contribute to the splitting, he extended the fifth order perturbation suggested by Pryce to the sixth order so that the crystal field contribution could appear in the second power and spin orbit interaction in the fourth power. In addition, he included contributions from fourth and fifth order perturbations by cubic field, spin orbit and spin-spin interaction. In these calculations, the excited states considered were spin quartets; ^4P, ^4D, ^4F and ^4G of the $(3d)^5$ configuration with excited energies in the range of 30 to 50 x 10^4 cm^{-1}. The splitting 3a obtained from these calculations is positive, and varies from about 10^{-3} to 10^{-4} cm^{-1}. It seems to satisfy the scant experimental data available at the time. (See Table 1, Ref. 5.)

Upon comparing the excited state energies of 5×10^4 cm^{-1} and the cubic field splitting 3a of the order of 10^{-3} cm^{-1} obtained from fifth and sixth order perturbations, there is an indication that none of the contributions which might arise from other excited multiplets of $(3d)^5$ configuration can, a priori, be ignored. Indeed, there are spin doublets; ^2S, ^2P, $^2D(3)$, $^2F(2)$, $^2G(2)$, ^2H and ^2I lying in the region of 45 to 100×10^3 cm^{-1}. Some of these such as ^2I and ^2H may be in the vicinity of ^4D and ^4F and can contribute to the splitting. Powell et al (1960)[6] took all of the doublets ^2S..... ^2I into account and carried out sixth order perturbation calculations with and without spin-spin interaction. They found that the inclusion of doublets increases the predicted splitting by one to two orders of magnitude as compared to the predicted splitting arising from spin quartets alone. Their calculated results, for the particular case of MgO:Mn^{2+}, agrees with experiments, provided that the spin orbit interaction constant, ζ_d of Mn^{2+}, is taken as 400 cm^{-1} and the cubic field strength, 10Dq of MgO, as 10500 cm^{-1}. Both of these are unreasonably high. Low and Rosengarten (1963, 1964)[7,8] carried out calculations similar to that of Powell et al without spin-spin interaction but they included the orbital polarization factor α, called Tree's correction factor.[9] Their conclusion was that crystal field analysis is relatively successful in explaining the position of energy levels of the d^5 manifold, but it is not capable of explaining the finer parameters such as the cubic field splitting, 3a, and the spectroscopic factor, g, both measured from ESR spectra of $3d^5$ ^6S ions.

A comparison of the above theories with ESR measurements on Mn^{2+} in several compounds was made by Hall et al (1961).[10] They observed that their measured 3a for Mn^{2+}, in a number of fluorides and chlorides, could be accounted for by Powell's theory, whereas the agreement for ZnO got worse. For very covalent compounds, CdTe[2] and ZnTe,[11] a discrepancy of almost one to two orders of magnitude can be found. This indicates the inadequacy of Powell's purely ionic model for covalent systems. Another area in which both Powell's and Low's theories have failed is the spectroscopic g value. These theories predict a g value, for an S-state ion such as Fe^{3+}, as less than the $g_e = 2.0023$ of the free electron, in complete contradiction to experimental observations that the g parameter of Fe^{3+} is larger than 2.0023. Most of these investigators have attributed these irreconcilable discrepancies to the ligand-to-metal charge transfer processes such as those suggested by Fidone and Stevens[12] and by Watanabe [13-14] for the evaluation of $\Delta g = g - g_e$. An initial study for the determination of the charge transfer contribution to 3a, patterned after Watanabe's work, was carried out by Azarbayejani et al.[15]

These calculations included the construction of appropriate molecular orbital (MO) wavefunctions and the allowance of ligand-to-metal electron transfer. In constructing the MO wavefunction, σ-bonding approximation was invoked and the cubic field splitting was obtained by a fourth order spin-orbit perturbation calculation.

It was found[15] that $3a \sim 3a_1 = 0.1728\ \lambda^4\ \beta^6\ (1 - \varepsilon_{11}/\delta_1)\ \delta_1^{-3}$, where $\lambda = \zeta_d$ is the single electron spin orbit parameter, $\beta^2 = 1 - \alpha^2$ is the covalency of the d orbitals of $3d^5\ {}^6S$ ion and ε_{11} and δ_1 are related to ligand-to-metal electron transfer energy. From free ion optical spectra (Ref. 16, p. 437), an approximate value of $\zeta_d = 350\ cm^{-1}$ may be taken, and from a comparison of the hyperfine structure constant in crystals to that of the free ion,[17] β^2 may be estimated. For the particular case of ZnS:Mn where $\zeta_d = 350\ cm^{-1}$, $\beta^2 = 0.22$ energies δ_1 of the order of 8000 to 10000 cm^{-1} give qualitative agreements with the measured 3a. The most encouraging aspect of these 3a results is their correct trend for Mn^{2+} in going from ZnS to ZnTe because δ_1 is expected to decrease as one goes from ZnS to ZnTe in accordance with Bube's conclusions on acceptor levels in II-VI compounds.*

In the present work, we have extended our previous analysis[15] to include π-orbitals in addition to the σ-orbitals. This has introduced

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*R. H. Bube, "Photoconductivity of Solids," J. Wiley and Sons, Inc., New York (1960), p. 171 (Fig. 6.4-12).

extra orbitals in the charge transfer wavefunctions. Most of the desired spin orbit matrix elements for the determination of 3a arise from the above wavefunctions and contain three or four orbitals. Since no expression for the evaluation of these matrix elements is available in the literature, general formulae for obtaining such matrix elements have been found first, and then, 3a has been calculated.

A brief introduction to the method of measuring 3a and the values of 3a for both the octahedral and tetrahedral II-VI compounds is given in II. Spin orbit matrix elements between excited spin multiplets is considered in III. The cubic field splitting 3a from these charge transfer states, $t_2^p e^{4-p}\gamma$,is obtained in IV and is discussed in V. Concluding remarks are given in VI.

CHAPTER II

EXPERIMENTAL DETERMINATION OF THE CUBIC FIELD SPLITTING OF THE $3d^5$ S-STATE IONS

The purpose of this chapter is to give a brief introduction to the method of measuring the cubic field splitting, 3a, of the S-state ions such as Cr^+, Mn^{2+} and Fe^{3+}.

The equipment employed consists of an electron spin resonance spectrometer such as the Varian V4502 EPR spectrometer in a 12-inch rotating electromagnet. Most of the measurements have been carried out at 4.2 and 77°K with a few being performed at 300°K. The magnetic field, associated with a spectral line, has been obtained by first tuning a Varian F-8 Fluxmeter for the proton resonance at that field and then measuring of the proton resonance frequency by a Beckman 7370 electronic counter. The frequency of the microwave source used in the experiment was determined by first finding one of its subharmonics through Beckman transfer oscillator and then measuring the frequency of that subharmonic by the above mentioned counter.

The ESR spectra of Mn^{2+} in CaO and ZnTe are given in order to serve as representatives of ESR spectra of $3d^5\ {}^6S$ ions in octahedral and tetrahedral II-VI compounds.

In the octahedral case (O_h), the paramagnetic $3d^5\ {}^6S$ ion is surrounded by six ligands or nonmetal nearest neighbors as shown in Fig. 2.1. These lie along the six crystallographic directions [100], [010], [001], $[\bar{1}00]$, $[0\bar{1}0]$ and $[00\bar{1}]$ with the paramagnetic ion at the origin of the coordinate system.

On the other hand, in the tetrahedral case (T_d), the paramagnetic $3d^5\ {}^6S$ ion is surrounded by four nearest neighbors lying along the four crystallographic directions [111], $[\bar{1}\bar{1}1]$, $[\bar{1}1\bar{1}]$ and $[1\bar{1}\bar{1}]$ as shown in Fig. 2.2.

The expression for the crystalline field of these ligands of the central ion is the same for both cases, provided the coordinate system is chosen as shown in Figs. 2.1 and 2.2.

Denoting the angle between the d.c. magnetic field and one of the coordinate axes such as z by θ, we have shown the spectra at $\theta = 0$ for Mn^{2+} in CaO (Fig. 2.3) and ZnTe (Fig. 2.4). As mentioned above, the

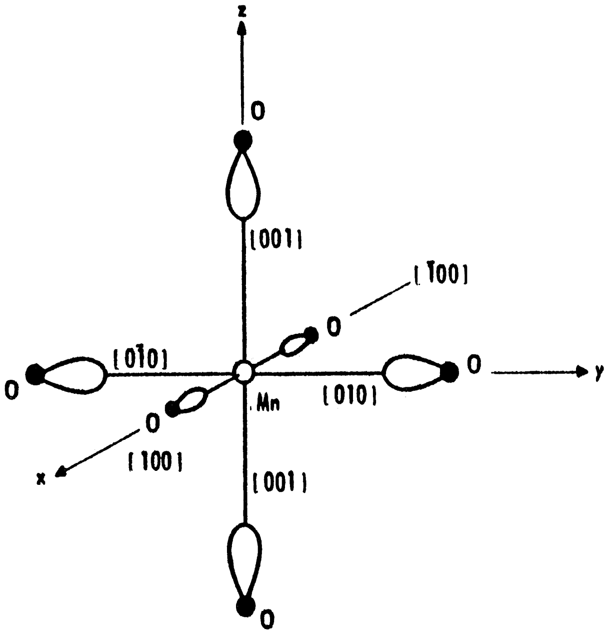

Fig. 2.1. The octahedral coordination in cubic II-VI compounds (CaO:Mn).

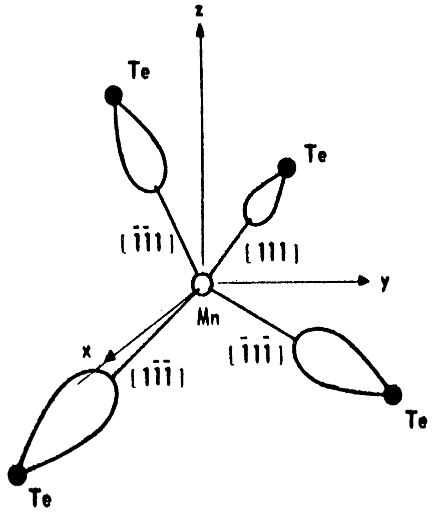

Fig. 2.2. The tetrahedral coordination in cubic II-VI compounds (ZnTe:Mn).

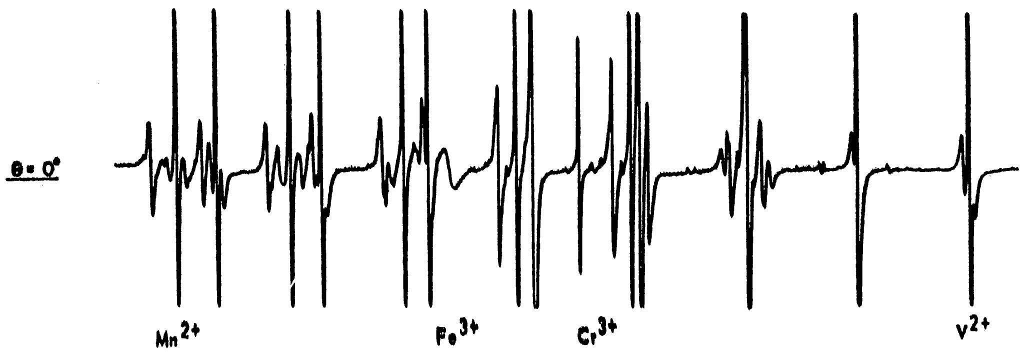

Fig. 2.3. ESR spectra of V^{2+}, Cr^{3+}, Mn^{2+} and Fe^{3+} in a single crystal of CaO at $\theta = H \wedge [100] = 0$ and $T = 300°K$

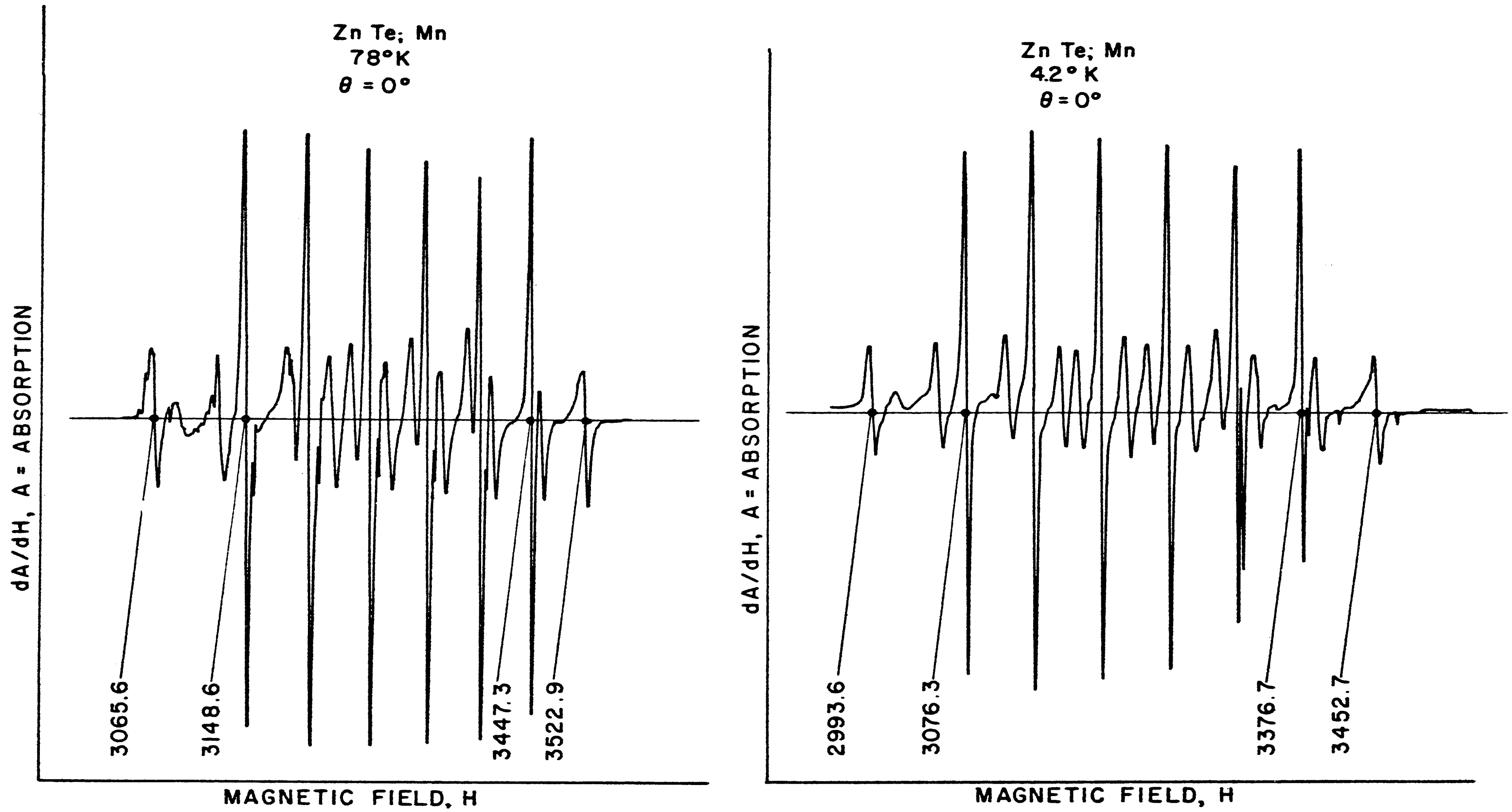

Fig. 2.4. Differentiation of ESR absorption spectra in ZnTe:Mn

proper choice of the coordinate system has allowed us to analyze the spectra in both 0_h and T_d cases by means of the same spin-Hamiltonian:*

$$H_s = g\,\beta_e\,\underline{H}\cdot S + A\underline{I}\cdot\underline{S} + a\,(S_x^{\,4} + S_y^{\,4} + S_z^{\,4})/6 + \sum_n \underline{I}^n\cdot A'_n\cdot\underline{S} - g_N\,\beta_N\,\underline{H}\cdot\underline{I} \tag{2.1}$$

Here, g is the spectroscopic g factor, A, the hyperfine structure constant, 3a the cubic crystalline field splitting, A'_n is the super-hyperfine coupling coefficient and the last term is the nuclear Zeeman effect. The brief reports on the measurements of g, A and 3a of ZnTe:Mn and CaO:Mn obtained by using (2.1) are made previously. A brief introduction to the calculation of these parameters from the spin-Hamiltonian in (2.1) is as follows:

For θ = 0, the spin-Hamiltonian of (2.1) may be rewritten as

$$H_s(\theta = 0) = g\,\beta_e\,HS_Z + A\underline{I}\cdot\underline{S} + a\left(T_{40} + \sqrt{5/14}\,(T_{44} + T_{4-4})\right)/15 \tag{2.2}$$

in which

$$T_{40} = \left[35\,S_Z^{\,4} - 30S^{*2}\,S_Z^{\,2} + 25\,S_Z^{\,2} - 6S^{*2} + 3S^{*4}\right]/8 \tag{2.3}$$

and

$$T_{4\underline{+}4} = \sqrt{70}\,S_{\underline{+}}^{\,4}/16;\quad S^{*2} = S(S+1),\ S_{\underline{+}} = (S_x \pm iS_y)/\sqrt{2} \tag{2.4}$$

The H_s in (2.1) can be expressed as

$$H_s = H_s^{fs} + H_s^{hfs}$$

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*B. Bleaney and K. W. H. Stevens "Paramagnetic Resonance" Repts. Prog. Phys. 16, 108 (1953) p. 137.

where

$$H_s^{fs} = g\,\beta_e\,HS_Z + a\left[T_{40} + \sqrt{5/14}\,(T_{44} + T_{4-4})\right]/15 \qquad (2.5)$$

and

$$H_s^{hfs} = A\underline{I}\cdot\underline{S} \qquad (2.6)$$

The energy of each M_S level can be obtained by solving the secular equation corresponding to the fine structure Hamiltonian H^{fs} given in (2.5)

$$\|\,(H_s^{fs})_{MM'} - E\,\delta_{MM'}\,\| = o \qquad (2.7)$$

where

$$(H_s^{fs})_{MM'} = X\,\delta_{MM'} + y\,\delta_{MM'\,\underline{+}4}$$

$$X = [2M\varepsilon + a\,(14M^4 - 95M^2 + 184)/48]$$

$$y = \sqrt{5a}/2$$

and

$$\varepsilon = g\,\beta_e\,H/2$$

Substituting for (2.7) one finds:

$$E\,(M_S = \underline{+}\,1/2) = \underline{+}\,\varepsilon + a$$

$$E\,(M_S = \underline{+}\,3/2) = \underline{+}\,3\varepsilon - 3a/2\,\underline{+}\,5a^2/32\varepsilon \qquad (2.8)$$

$$E\,(M_S = \underline{+}\,5/2) = \underline{+}\,5\varepsilon + a/2\,\underline{+}\,5a^2/32$$

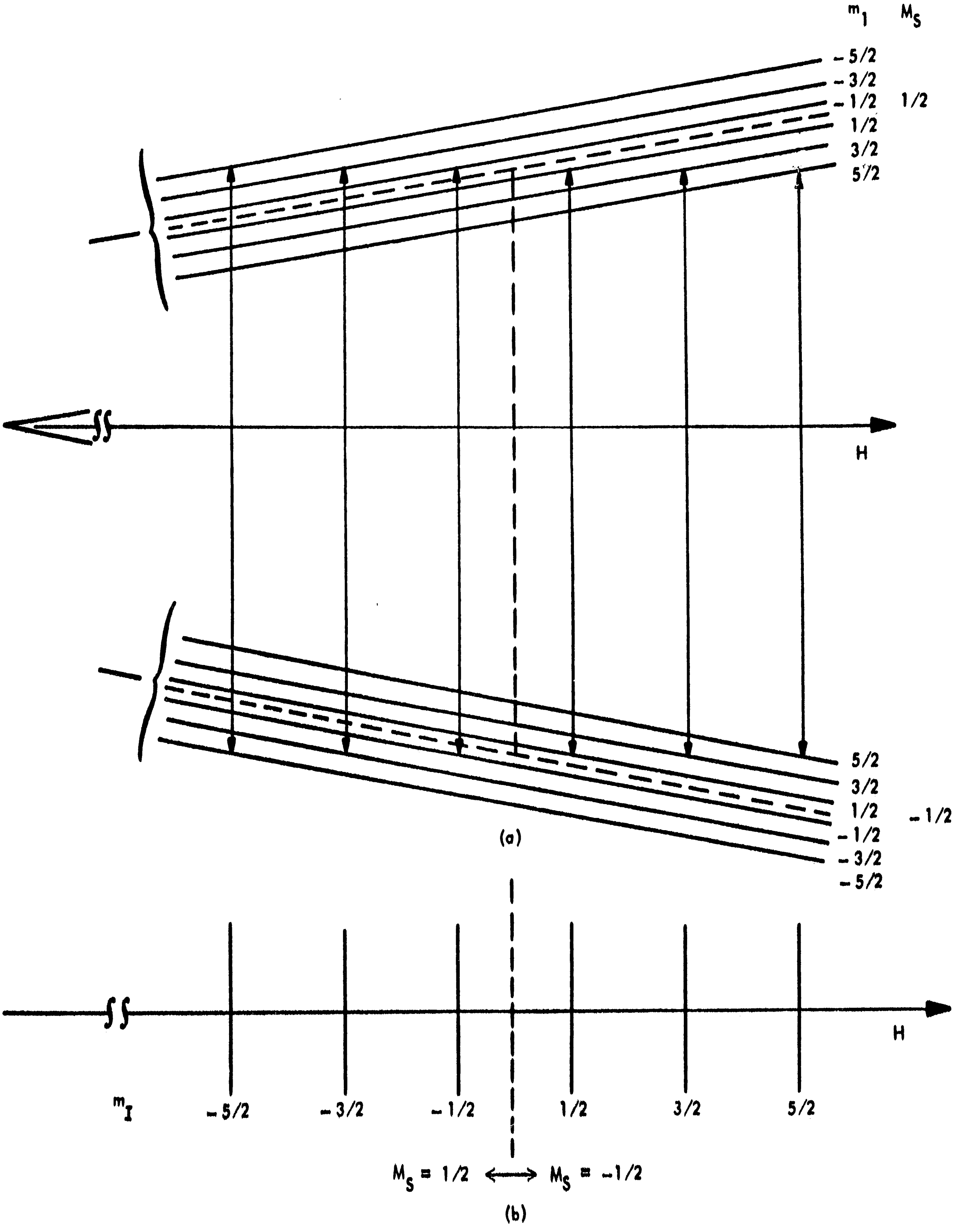

Fig. 2.5. (a) The splittings of $M_S = \frac{1}{2}$ and $-\frac{1}{2}$ levels into six close lying levels and (b) the splitting of the $M_S = \frac{1}{2} \leftrightarrow M_S = -\frac{1}{2}$ transition into six approximately equally spaced transitions.

For many cases where the microwave frequency ν_0, used for ESR measurements is about 10 KMC and a II-VI compound is the host material, the ratio $\varepsilon/a = 0.01 - 0.1$ for $3d^5\ {}^6S$ ions Cr^+, Mn^{2+} and Fe^{3+}. In such cases, one is able to use $A\underline{I}\cdot\underline{S}$ as a perturbation on the first term of (2.5) which causes each M_S level to split into six close lying levels. As an example, the splittings of the $M_S = 1/2$ and $-1/2$ levels are given in Fig. 2.5. For the allowed ESR transitions ($\Delta M_S = \pm 1$, $\Delta m_I = 0$) each $M_S - 1 \leftrightarrow M_S$ transition will split in $2I + 1$ transitions. The number of $M_S - 1 \leftrightarrow M_S$ transitions which can be observed distinctly is 2S, provided that the parameter A in (2.8) is large enough to offset the effect of the line broadening.

The energy diagram of the M_S levels of a $3d^5\ {}^6S$ ion at $\theta = 0$ is obtained as a function of $\rho = g\ \beta H/2a$ (Table 2.1 and Fig. 2.6). The numbers identify the upper M_S values. Thus, the five transitions $M_S = -5/2 \leftrightarrow M_S = -3/2 \ldots\ldots M_S = 3/2 \leftrightarrow = 5/2$ are designated by $-3/2$, $-1/2 \ldots\ldots 5/2$, respectively. When the lines are well resolved one expects to observe $2S(2I + 1)$ lines. This number for Mn^{2+} with $S = 5/2$ and $I = 5/2$ is 30 (Figs. 2.3 and 2.7). These lines can be identified with the electronic and nuclear magnetic quantum numbers M_S and m_I by considering the fact that the intensity of the five lines $3/2 \ldots\ldots 5/2$ belonging to any of the $2I + 1$ quintets should vary as 5:8:9:8:5. Therefore, the following assignments are possible for both octahedral and tetrahedral cases (Fig. 2.7).

$$\alpha_i,\ \lambda_i \ \text{correspond to}\ M_S = \pm 3/2 \leftrightarrow \pm 1/2$$

$$\beta_i,\ \delta_i \ \text{correspond to}\ M_S = \pm 5/2 \leftrightarrow \pm 3/2$$

and

$$\gamma_i \ \text{correspond to}\ M_S = \pm 1/2 \leftrightarrow \pm 1/2$$

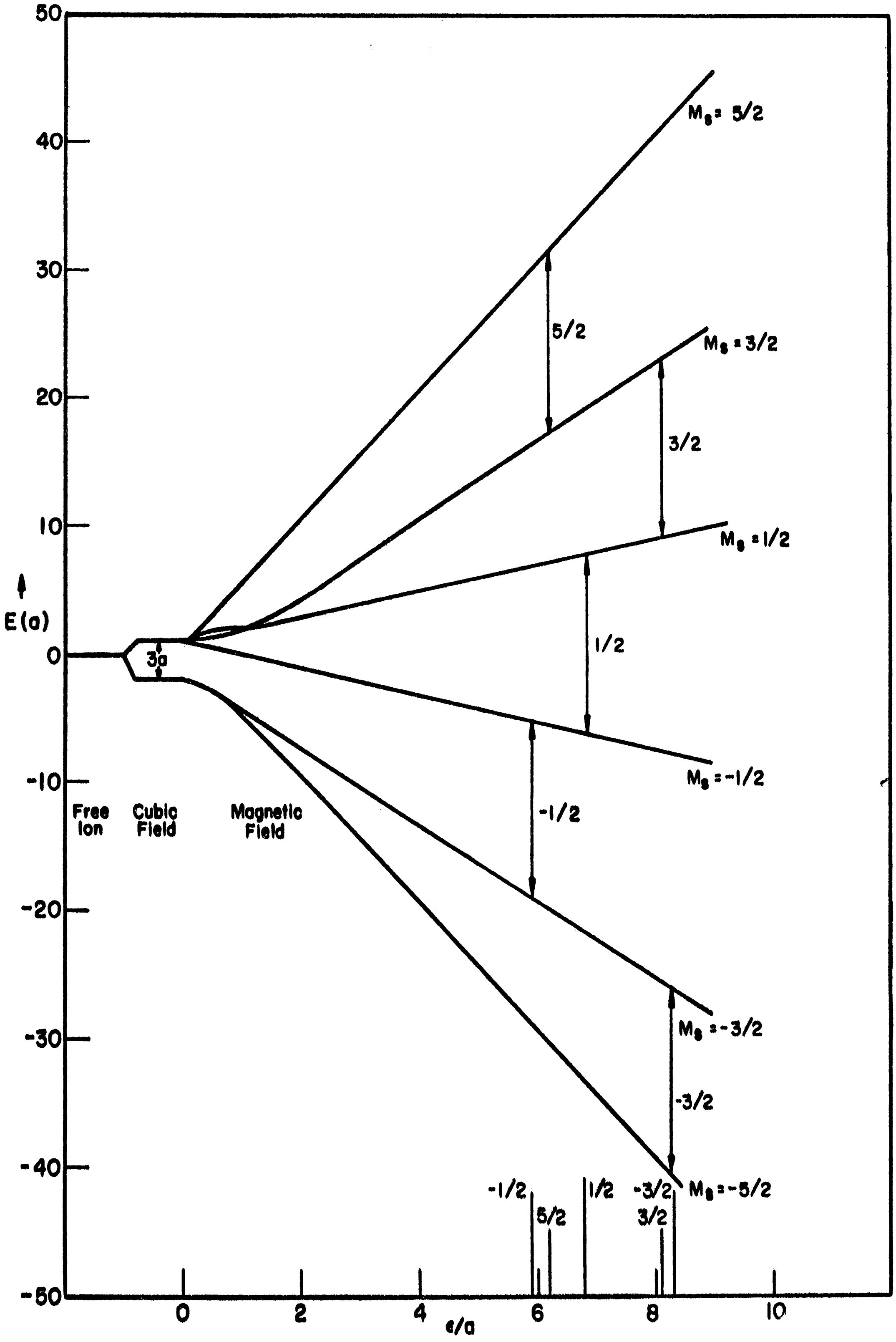

Fig. 2.6. Energy level scheme of $3d^5\ {}^6S_{5/2}$ (Mn^{2+}) in a tetrahedral field at $\theta = 0$.

Table 2.1. Variation of separation of Mn^{++} ESR fine-structure components at $\theta = 0$ as a function of $\rho = g\beta H/2a = \varepsilon/a$

ρ	$E_{-5/2}-E_F$	$E_{-3/2}-E_F$	$E_{-1/2}-E_F$	$E_{1/2}-E_F$	$E_{3/2}-E_F$	$E_{5/2}-E_F$
0	-2.00	-2.00	1.00	1.00	1.00	1.00
1	-4.71	-4.62	0.00	2.00	1.71	5.62
2	-9.59	-7.57	-1	3	4.59	10.57
3	-14.56	-10.55	-2	4	7.05	15.55
4	-19.54	-13.54	-3	5	10.54	20.54
5	-24.53	-16.53	-4	6	13.53	25.54
6	-29.52	-19.53	-5	7	16.53	30.52
7	-34.52	-22.52	-6	8	19.52	35.52
10	-49.52	-31.51	-9	11	28.51	50.5
100	-499.5	-301.50	-99	101	298.5	500.5

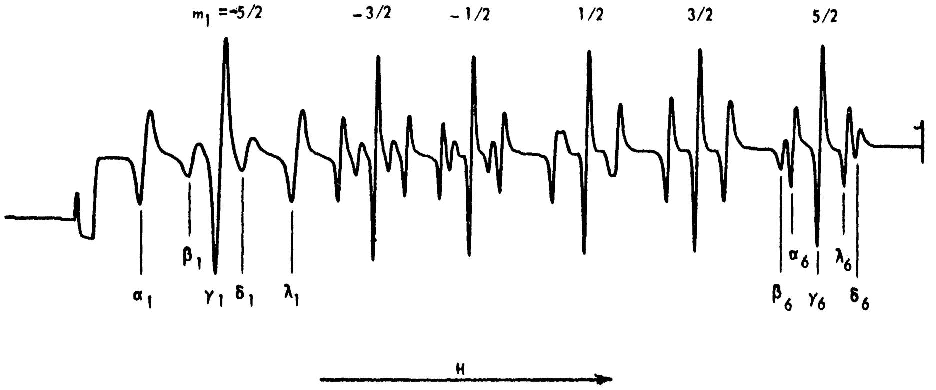

Fig. 2.7. Assignment of ESR spectra of Mn^{2+} in both O_h and T_d cases: (The spectrum belongs to Mn^{2+} in cubic ZnS)

The next step to consider is the determination of the spin-Hamiltonian coefficients g, A and a of (2). For a fixed microwave frequency ν_o, these coefficients can be measured as follows:

$$g = h\nu_o/\beta_e \, [(H_{\gamma 1} + H_{\gamma 6})]/2$$

$$|A| = g\,\beta_e \, [(H_{\gamma 6} - H_{\gamma 1})]/5 \qquad (2.9)$$

and

$$|a| \cong g\,\beta_e\,[(H_{\gamma 1} - H_{\alpha 1}) + (H_{\lambda 6} - H_{\gamma 6})]/5$$

The signs of A and a can be determined relative to each other with the sign of a being determined independently by its measurement at low temperatures. The results of such measurements are given in Table 2.2 and 3a and g are compared with predictions of the present theories of these parameters in Table 2.3 and Fig. 2.8. The agreement is generally satisfactory for the case of MgO, CaO and SrS, whereas disagreement is observed for zinc and cadmium chalcogendies. These deviations from ionic theory which arise from larger covalency existing in the latter group compared to the former, have emphasized the need of a more

Table 2.2. ESR results of S-state ions in II-VI compounds

Material	Symmetry	Coordination	R-X (A°)	Cr^+			Mn^{++}			Fe^{+++}		
				A $10^{-4}cm^{-1}$	g	3a $10^{-4}cm^{-1}$	A $10^{-4}cm^{-1}$	g	3a $10^{-4}cm^{-1}$	A	g	3a $10^{-4}cm^{-1}$
MgO	O_h^7	6	2.12	--	--	--	-81.0	2.0014	55		2.0037	615
CaO	O_h^7	6	2.40	--	--	--	-80.7	2.0009	17.7		2.0052	191
SrS	O_h^7	6	3.05	--	--	--	-77	2.0009	4.2		--	--
ZnO	C_{6v}^4	4	1.95	--	--	--	-74	2.0016	18		2.006	123
ZnS	T_d^2	4	2.36	13.4	1.9995	12	-64.9	2.0025	23.7		2.019	382
ZnS	C_{6v}^4	4	--	--	--	--	--	--	--		2.018	384
ZnSe	T_d^2	4	2.45	13.3	2.0016	16.05	--	--	--		--	144.9
ZnSe	C_{6v}^4	4	--	--	--	--	-61.7	2.0055	52.1		--	--
ZnTe	T_d^2	4	2.66	12.4	2.0023	19.80	-56.5	2.0075	88.9		2.09	-7800
CdS	C_{6v}^4	4	2.52	--	--	--	-65.3	2.003	11.7		2.01	285
CdSe	C_{6v}^4	4	2.64	--	--	--	-62.7	2.005	4.3		--	--
CdTe	T_d^2	4	2.80	12.8	1.9997	9.3	-55	2.0078	83.1		--	--

Table 2.3.* Comparison of ESR results with predictions of ionic theory

Material	Sym	r_T	r_E			Δg_T	Δg_E		
			Cr^+	Mn^{++}	Fe^{+++}		Cr^+	Mn^{++}	Fe^{+++}
MgO	O_h	1.000		1.000	1.000	<0		<0	>0
CaO	O_h	0.287		0.32	0.311	<0		<0	>0
SrS	O_h	0.026		0.07		<0		<0	
ZnO	C_{6v}^4	6.635		0.76	0.316	<0		<0	>0
ZnS	C_{6v}^4 & T_d^2	1.000	1.000	1.000	1.000	<0	<0	∿0	>0
ZnSe	C_{6v}^4 & T_d^2	0.685	1.34	2.198	0.38	<0	<0	>0	>0
ZnTe	T_d^2	0.301	1.65	3.751	-20	<0	∿0	0	>0
CdS	C_{6v}^4	1.000		1.000		<0		0	>0
CdSe	C_{6v}^4	0.624		3.67		<0		0	
CdTe	T_d^2	0.345		7.02		<0	<0	0	

*The r_T and r_E are the theoretical and experimental ratios of 3a respectively and $\Delta g = g-2.0023$. The ratio $r_T(i,j) = 3a^i:3a^j = (a_o^j : a_o^i)^{10}$ with a_o being the lattice constant.

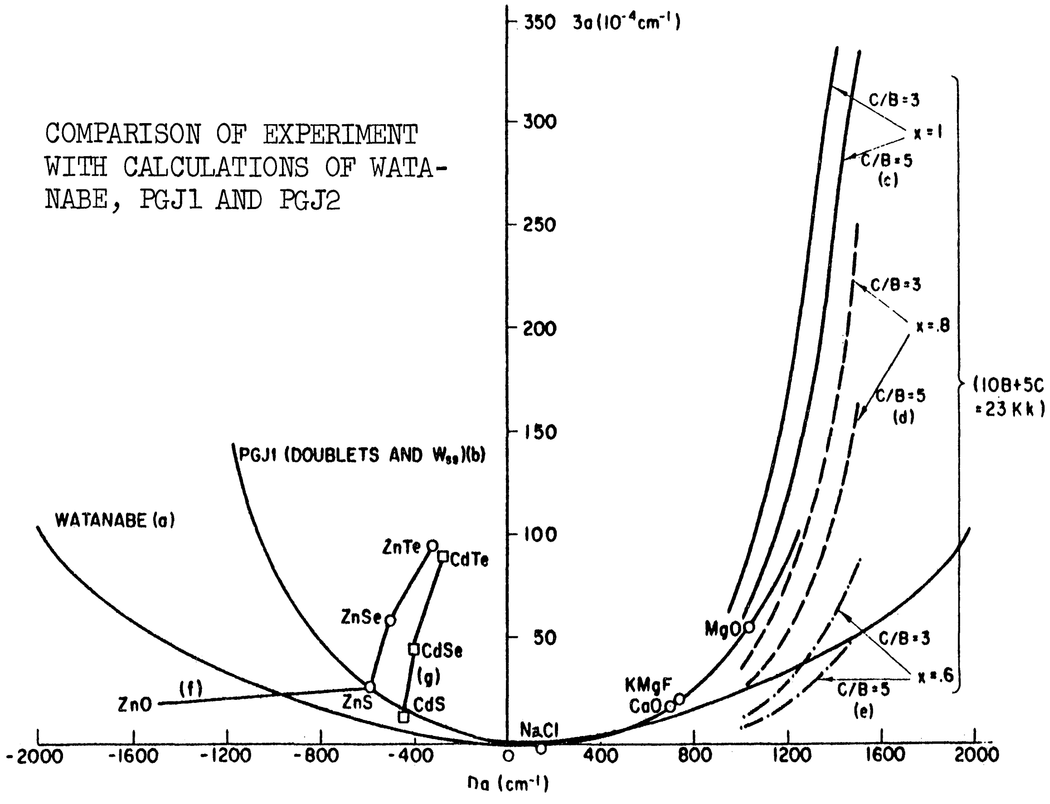

Fig. 2.8. Comparison of experimental and theoretical values of 3a.

realistic theory which takes these covalency effects into account. In the next few chapters the dependence on the covalency of the parameters given in (9) is pursued with a greater emphasis on calculations related to the cubic field splitting 3a.

CHAPTER III

THEORETICAL

As mentioned in the last section, we intend to obtain the cubic field splitting 3a by using the linear combination of atomic orbital molecular orbital (LCAO-MO) techniques. The wavefunctions constructed from these LCAO-MO's in a certain manner,[*] serve as excited states which admix to the ground state wavefunction through spin orbit interaction and cause a contribution to the cubic splitting 3a.

From this brief introduction, it is immediately evident that our task is twofold: (1) to construct the LCAO-MO (henceforth denoted by MO) and the desired wavefunctions and (2) to develop appropriate expressions for the matrix elements of the spin orbit interaction in the MO scheme.

Since we are primarily concerned with the cubic field splitting, 3a, in compounds of T_d symmetry, our effort will be directed toward the determination of the matrix elements of spin orbit interaction, $H_p = \sum_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i$, between various wavefunctions of a complex, $[\Sigma\ \Lambda_4]^{-n'}$, consisting of a $3d^5\ {}^6S$ ion[**] Σ and four ligands, $\Lambda_1 \ldots\ldots \Lambda_4$, the whole complex being located in a cubic crystal $B\Lambda$. For example, in the case of manganese doped zinc sulfide, (ZnS:Mn), Zn = B, S = Λ, Mn = Σ, $n' = 6$ and the complex is $[MnS_4]^{-6}$.

In order to limit our analysis to those formulae affecting just 3a, we proceed by defining the cubic field splitting and the symmetry of the levels which give rise to that splitting.

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[*] The excited wavefunctions considered here, are those obtained from an electron transfer from the ligand to the metal ion.

[**] A summary of the symbols is given in Appendix A.

1. CUBIC FIELD SPLITTING

The following is a brief elaboration of the symmetry group of the states into which the ground state of the complex, $(\Sigma\ \Lambda_4)^{-n'}$ splits (Σ = Cr^+, Mn^{2+}, Fe^{3+}, Λ = S^{--}, .. Te^{--}).

The symmetry[*] of the ground state of the above complex is of A_1 and has a total spin S = 5/2. Thus, the ground state may be given as $\left[[\Sigma\ \Lambda_4]^{-n'}\ A_1\ S = 5/2\right\rangle]$ or more simply by $|\chi_o\ {}^6A_1\rangle$ where χ_o denotes the MO's giving rise to the ${}^6A_1$ state, their electronic configuration and finally, the total spin values and the irreducible representations, $S_i h_i$, of each of these MO which comprise χ_o.

The symmetry group of the total Hamiltonian of the complex is $0 \times U_2$ where 0 is the group of symmetry operations of a cube in orbital space and U_2 is the group of rotation in spin space. The representation of ${}^6A_1$, in the full rotation double group, $G' = R_3 \times U_2$, is J = 5/2. The irreducible representations of J = 5/2 in $G = 0 \times U_2$ are E'' + U'.

According to the irreducibility principle,[†] the maximum number of levels created by the perturbation of $|A_1\ S = 5/2\rangle = |{}^6A_1\rangle$ will be the number of irreducible representations of J = 5/2 in G which is two levels.

The cubic field splitting is defined as the energy separation of these two levels:

$$3a = E(U') - E(E'') \qquad (3.1)$$

where

$$E\ (\Gamma') = E^{(0)}\ (\Gamma') + E^{(1)}\ (\Gamma') +....+ E^{(4)}\ (\Gamma');\quad \Gamma' = U' \text{ or } E'' \qquad (3.2)$$

---

[*] Mulliken's notation (see Ref. 22) is used for all cases except when mentioned otherwise. The state symmetries and energy terms are identified by the irreducible representations A_1, A_2, E, T_1, T_2, E', E'' and U' of the cubic double group where the molecular orbitals are denoted by the small letters a_1, a_2, t_1 and t_2.

[†] V. Heine, "Group Theory in Quantum Mechanics," University of Cambridge Press, 1960, p. 45.

Here, $E^{(n)}(\Gamma')$ (n = 0, 1..., 4...) are the n^{th} order contribution to $E(\Gamma')$. The 3a will be positive or negative depending on the relative magnitudes of E(U') and E(E'').

The Hamiltonians giving $E^{(n)}(\Gamma)$ will be examined in the next section.

2. HAMILTONIANS

We wish to consider a Hamiltonian of the complex, $[\Sigma\ \Lambda_4]^{-n'}$, which includes a $zero^{th}$ order Hamiltonian, H_0, satisfying $H_0\psi_n = E_n\psi_n$ and a perturbation Hamiltonain, H_p, from whose matrix elements M_{mn} between ψ_m and ψ_n, the corrections $E^{(n)}(\Gamma)$ may be obtained. Denoting the above Hamiltonian by H_0', one has

$$H_0' = H_0 + H_p \tag{3.3}$$

In the present work, we limit out perturbation analysis to spin orbit interaction. Thus,*

$$H_p = \sum_{i}^{n''} \zeta_i\ \underline{\ell}^i \cdot \underline{s}^i \tag{3.4}$$

and the $zero^{th}$ order Hamiltonian, H_0 is:

$$H_o = \sum_{i=1}^{n''} \left(P_i^2/2m_i - Z\ e^2\ r_i^{-1} \right) + \sum_{i>j}^{n''} e^2\ r_{ij}^{-1} + \sum_{k=1}^{4} \sum_{i=1}^{n''} V(\underline{r}_{ik}) \tag{3.5}$$

where n'' = 37, refers to the sum of the 32 valence electrons in the molecular orbitals of the complex, $(\Sigma\Lambda_4)^{-n'}$, and the 5 electrons located in the d orbitals of the central ion Σ. The first term in (3.5), represents the kinetic and potential energies, the second one gives the

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[*] ζ_i acts as an operator, being ζ_d when operating on d parts of the i^{th} orbital and ζ_p when operating on the p part of the i^{th} orbital. (Appendix B)

Coulomb and exchange energies and the last term gives the effect of four ligands, k, separated from the central ion by r_k. Z_α in (3.5) refers to the effective charge of the central ion. The eigenfunctions and eigenvalues of (3.5) are usually obtained by approximate techniques. One of these is known as the self-consistent charge configuration (SCCC) method. Ballhausen[23] used this last technique to construct the eigenvalues and eigenvectors belonging to the $[MnO_4]^{-1}$ complex and very recently Basch et al[24] extended the same method to the 32 complexes of transition ions in compounds with O_h or T_d symmetries. The latter authors give an energy diagram for the $[FeCl_4]^{-2}$ complex. The levels lie from -220 x 10^3 cm^{-1} to about 90 x 10^3 cm^{-1} and they are classified according to their symmetry as follows:

$$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4(3t_2)^6(t_1)^6(2e)^2(4t_2)^4(5t_2)^0(3a_1)^0 \qquad (3.6)$$

where the superscripts are the electronic configurations and $1a_1$, $1t_2$.. ..$3a_1$ have the symmetry A_1, T_2....A_1 of the cubic point group. The MO configuration for Fe^{3+}, in tetrahedral complexes as well as Mn^{2+} and Cr^+ in such complexes will be the same as in (3.6) except the configuration of $(4t_2)$ reduces from 4 to 3. The orbitals we plan to use for the construction of the excited wavefunctions are 1e, $3t_2$, t_1, 2e and $4t_2$. To simplify the notation, we label them e_b, t_b, t_1, e_a and t_a, respectively. Here, the subscript b points out that e_b and t_b are bonding orbitals with E and T_2 symmetries, respectively. Similarly, those with the subscript a are the antibonding orbitals, whereas t_1, which does not have any subscript, is a nonbonding orbital. A schematic energy diagram associated with the above five orbitals; t_b, e_b, t_1, e_a and t_a and their corresponding electronic configurations characteristic of $[\Sigma\ \Lambda_4]^{-n'}$ is given in Fig. 3.1.

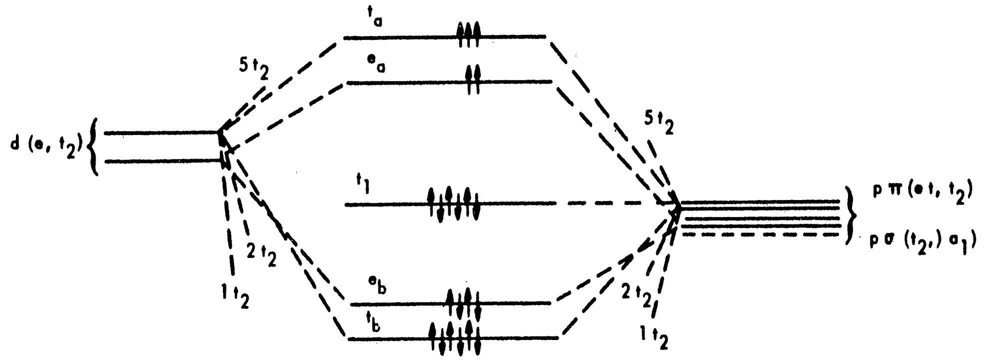

Fig. 3.1. A schematic energy diagram of $\left\{[\Sigma\Lambda_4]^{-n'},\ {}^6A_1\right\}$complex.

The $p\pi$ in Fig. 3.1 are linear combinations of the components of ligand p orbitals which are perpendicular to the interionic distance. The $p\sigma$ are the part of the p orbital projected along the interionic axis. Having defined the nature of the orbitals involved, we now proceed to construct the wavefunctions.

3. WAVEFUNCTIONS

We want to describe the spin values S_i and the irreducible representations, h_i, of the individual molecular orbitals (MO) giving rise to the ground state and excited states. A knowledge of these is necessary for the determination of spin-orbit matrix elements as will be seen later (see 4). Therefore, we first consider the ground state and then, discuss the excited ones.

3.1 Ground State Wavefunction

A description of the ground state wavefunction is being sought which emphasizes the symmetry, spin and irreducible representation of the molecular orbitals which constitute it.

The radial part of the individual wavefunction will not be included for simplicity and the spin orbit interaction parameter, $\zeta_i(r)$ of (3.4) will be considered as ζ_d for the d orbitals of ion Σ and ζ_p for the p orbitals of ligands Λ_i in the complex $[\Sigma\ \Lambda_4]^{-n'}$ (Σ = Cr^+, Mn^{2+}, Fe^{3+}, Λ_i = O^{--}, ... T_e^{--}).

The orbital part of the ground state wavefunction can be deduced from Fig. 3.1, in the following form:

$$|\chi_o^{e}\ {}^6A_1\rangle = \left\{\left[(\Sigma\Lambda_4)^{-n'},\ c\ t_b^{6} e_a^{4} t_1^{6} e_a^{2} t_a^{3} ; {}^6A_1\right\rangle\right\} \rightarrow |t_b^{6} e_a^{4} t_1^{6} e_a^{2} t_a^{3}\ {}^6A_1\rangle \tag{3.7}$$

where

$$\chi_o^{e} = t_b^{6} e_a^{4} t_1^{6} e_a^{2} t_a^{3} \text{ is electron configuration} \tag{3.8a}$$

or

$$\chi_o^{h} = t_b^{o} e_b^{o} t_1^{o} e_a^{2} t_a^{3} \text{ is hole configuration} \tag{3.8b}$$

The irreducible representations of the molecular orbitals t_b, e_b... in (3.7) - (3.8b) are

$$\Gamma\ (t_b) = \Gamma\ (t_a) = T_2$$

$$\Gamma\ (e_b) = \Gamma\ (e_a) = E$$

$$\Gamma\ (t_1) = \qquad T_1 \tag{3.9}$$

The symmetry of the irreducible representations T_2, E and T_1 of T_d group can be deduced from the character table of this group (Ref. 25, p. 383) given in Table 3.1.

The group classes C_2, C_3, σ_d and S_4 of Table 3.1 are classes of symmetry elements of a tetrahedron as shown in Figure 3.2.

3.2 Excited State Wavefunctions - Charge Transfer Wavefunctions

We wish to describe here, the excited states created exclusively by the process of promoting one electron from one of the three orbitals t_b, e_b or t_1 of χ_o^{e} in (3.8a) to any of the two orbitals e_a and

Table 3.1. Double Valued Character Table of Group T_d

Bethe	Mulliken	1	R	$8C_3$	$8C_3R$	$6C_2$	$12\sigma_d$	$6S_4$	$6S_4R$
Γ_1	A_1	1	1	1	1	1	1	1	1
Γ_2	A_2	1	1	1	1	1	-1	-1	-1
Γ_3	E	2	2	-1	-1	2	0	0	0
Γ_4	T_1	3	3	0	0	-1	-1	1	1
Γ_5	T_2	3	3	0	0	-1	1	-1	-1
Γ_6	E'	2	-2	1	-1	0	0	$\sqrt{2}$	$-\sqrt{2}$
Γ_7	E''	2	-2	1	-1	0	0	$-\sqrt{2}$	$\sqrt{2}$
Γ_8	U'	4	-4	-1	1	0	0	0	0

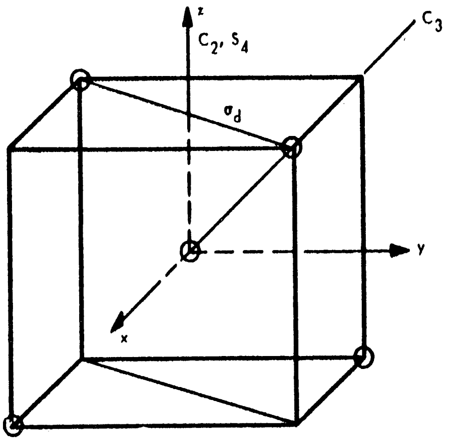

Fig. 3.2. Symmetry elements of a tetrahedron

t_a in χ_o^e. All other excited wavefunctions arising either from multiple charge transfer or from the irreducible representations, h_i, of terms of t_a^p and e_a^{5-p} which belong to spin values of $S_i = p/2 - 1$ and $1/2\ (5-p)-1$ are ignored. A similar restriction is imposed upon h_i after charge transfer (hole transfer) occurs, and, as a result of this, all excited states arising from $t_a^{p'}$ and $e_a^{4-p'}$ (after hole transfer, the sum of the hole configuration of t_a and e_a will be 4) which belong respectively to spin values of $S_i = p'/2 - 1$ or $(4-p')/2 - 1$, are ignored. For example, a hole transfer from t_a^3 in (3.8b) gives t_a^2 as a new hole configuration for this orbital. The irreducible representations, (IR) of t_a^2 are

$$\Gamma\ (t_a^{\ 2}) = {}^3T_1 + {}^1A_1 + {}^1E + {}^1T_2 \tag{3.10a}$$

and similarly,

$$\Gamma\ (e_a^{\ 2}) = {}^3A_2 + {}^1A_1 + {}^1E \tag{3.10b}$$

From the IR's (3.10a - 3.10b) only those with the maximum spin of these two shells, namely,

$$\Gamma_{max}\ (t_a^{\ 2}) = {}^3T_1$$

and

$$\Gamma_{max}\ (e_a^{\ 2}) = {}^3A_2 \tag{3.11}$$

are considered and all the remaining spin singlets are ignored. The electronic configurations of the complex, after charge transfer, and their corresponding terms constructed in the above scheme are given in Table 3.2.

Now we consider the determination of the spin orbit matrix elements between spin sextets ${}^6A_1$ of the ground state and the excited spin sextets and quartets given in Table 3.2.

4. MATRIX ELEMENTS OF SPIN ORBIT INTERACTION

The matrix elements of the spin orbit Hamiltonian, $H_p = \sum_i \zeta_i \underline{\ell}^i \cdot \underline{s}$, will be discussed in this section and Section 5.

A few initial comments are necessary to point out the need for the development of new formulae for evaluations of the desired matrix elements. Considering Table 3.2, it is evident that a matrix element between the

Table 3.2. Charge transfer configurations and terms

Hole	Configuration [*]					Spin Sextet			Spin Quartet [+]		
No.	t_a	e_a	t_1	e_b	t_b	E	T_1	T_2	E_1	T_1	T_2
2	2	2	1	0	0	1	1	1	1	1	1
3	2	2	0	1	0		1	1		1	1
4	2	2	0	0	1	1	1	1	1	1	1
5	3	1	1	0	0		1	1		1	1
6	3	1	0	1	0	1			1		
7	3	1	0	0	1		1	1		1	1

[+] These are the spin quartets obtained from the spin sectets by allowing its total spin to add up to 3/2 instead of 5/2

[*] The MO's t_a----t_b are linear combinations of atomic orbitals as will be seen later (Sec. IV).

spin sextet of E symmetry from configuration 4 and the spin sextet of T_1 symmetry from configuration 3 contain the four different orbitals, t_a, e_a, t_1 and e_b, which participate in the construction of ^6E and $^6T_1$. Therefore, the final matrix elements depend on the coupling scheme of the above four orbitals in ^6E and $^6T_1$. The behavior of the sublevels, S_ih_i, arising from $t_a^{p'}$, $e_a^{4-p'}$ and other orbitals t_1, e_b and t_b is unique for spin sextets, but varies for quartets and doublets which in turn gives rise to several hundred spin quartets and doublets. The best technique for the determination of matrix elements of any operator between a huge number of states with the same spin S and IR, h, but with different configurations is the method of Reduced Matrix Elements.

Griffith[26] has applied this technique to calculate the matrix elements of the spin orbit interaction between various, S_ih_i of the cubic group. Our analysis follows his very closely and gives rise to new formulae for determination of the spin-orbit matrix elements between pairs of the spin sextuplets arising from coupling of three or four orbits.*

As in Griffith (p. 82), the matrix elements of spin orbit interaction, $\sum_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i$, from a pair of states $|\chi\ S\ h\ J\ t\ \tau >$ and $|\chi' S' h' J' t\ \tau >$ can be given as:

$$\langle \chi\ S\ h\ J\ t\ \tau | \sum_i \zeta_i\ \underline{\ell}^i \cdot \underline{s}^i | \chi' S' h' J' t\ \tau \rangle = \sum_{\substack{M\ M' \\ \theta\ \theta'}} \langle \chi\ S\ h\ J\ t\ \tau | \chi\ S\ h\ M\ \theta \rangle$$

$$(x) \langle \chi\ S\ h\ M\ \theta | \sum_i \zeta_i\ \underline{\ell}^i \cdot \underline{s}^i | \chi' S' h' M' \theta' \rangle \langle \chi' S' h' M' \theta' | \chi' S' h' J' t\ \tau \rangle \quad (3.12)$$

$$\equiv \langle \chi\ S\ h || \sum_i \zeta_i\ \underline{\ell}^i \cdot \underline{s}^i || \chi' S' h' \rangle\, K_{JJ'} \begin{pmatrix} S & S' & T_1 \\ h' & h & t \end{pmatrix} \quad (3.13)$$

where S and h are the spin and irreducible representation (IR) of the state $|\chi Sh>$; M and θ are, respectively the components of S and h, t is an IR of the system in the cubic double group belonging to the resultant of the coupling of S and h; J is an identification number used wherever there are more than one t are, finally τ is one of the components of t. The first term in (3.13) is the reduced matrix of $\sum_i \zeta_i\ \underline{\ell}^i \cdot \underline{s}^i$ from states $|\chi\ S\ h >$ and $|\chi' S' h' >$ and the second one** is the coupling coefficient which is independent of χ and χ'. The study of the coupling coefficient will be reserved for Section 5. The reduced matrix elements will be elaborated further in the next subsection and new results, not found in the literature will be tabulated.

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*Griffith[26] has given all the formulae needed, for evaluation of the reduced matrix elements of spin orbit interaction, arising from two orbits t_2 and e of cubic group. As a result of this, his book contains tables for spin quartets only (see Ref. 26 p. 126)

**$K_{JJ'}$ is exactly the same as the Ω_{JJ}' defined by Griffith (p. 82)

4.1 Reduced Matrix Elements

Here, the reduced matrix elements (RME),

$$\left\langle \chi\ S\ h \| \sum_i \zeta_i\, \underline{\ell}^i \cdot s^i \| \chi' S' h' \right\rangle \tag{3.14}$$

of (3.13), will be discussed further with particular attention to the effect of χ and χ' on RME. There are three classes of RME depending on the nature of configurations χ and χ':

(1) Both χ and χ' include three orbitals with the same configurations.

(2) Both χ and χ' include three orbitals with different configurations.

(3) χ and χ' include four orbitals with different configurations.

The formulae for obtaining the reduced matrix elements, (RME), associated with these three classes of configuration are given in Sections 4, 5 and 6 of the Appendix C respectively. The numerical results are given here in Tables 3.3 through 3.5.

Table 3.3. Reduced matrix elements[†] $|\langle\chi_1 Sh\|\Sigma_i\zeta_i\underline{\ell}^i\cdot\underline{s}^i\|\chi_1' S'h'\rangle|^2$

$\chi_1 = \chi_1'$	$Sh-S'h'$ aa	$^6T_1-^6T_2$	$^6T_1-^4T_2$	$^6T_1-^6E$	$^6T_1-^4E$	$^4T_1-^6T_2$	$^4T_1-^4T_2$	$^4T_1-^6E$	$^4T_1-^4E$
$t_a^3\ ^4A_2\ (e_at_b)\ ^3T_2$	t_bt_b	21/20	6/5*	---	---	6/5	3/10*	---	---
$t_a^2\ ^3T_1\ (e_a^2t_b)\ ^4T_1$	t_bt_b	7/20*	2/5	7/30*	8/30	2/5*	1/10	8/30*	2/30
	t_at_a	7/20*	1/40*	7/30*	1/60*	1/40	9/40*	1/60	3/20*
$t_a^2\ ^3T_1\ (e_a^2e_b)\ ^4E$	t_at_a	21/20	3/40	---	---	3/40*	27/40	---	---
$t_a^3\ ^4A_2\ (e_at_1)\ ^3T_2$	t_1t_1	21/20*	6/5	---	---	6/5*	3/10	---	---
$t_a^2\ ^3T_1\ (e_a^2t_1)\ ^4T_2$	t_at_a	7/20	1/40	7/10	1/20	1/40*	9/40	1/20*	9/20
	t_1t_1	7/20	2/5*	7/10*	4/5	2/5	1/10*	4/5*	1/5

*The sign of the square root of the numbers with asterisk is negative

[†] $aa = \langle 1/2a\|\zeta\underline{\ell}\cdot\underline{s}\|1/2a\rangle$

Table 3.4. Reduced matrix elements $|\langle \chi_2 Sh || \sum_i \zeta_i\ \underline{\ell}^i \cdot \underline{s}^i || \chi'_2 S'h' \rangle|^2$

$\chi_2 - \chi'_2$	$< 1/2\ b || \zeta\ \underline{\ell}\cdot\underline{s} || 1/2\ c >$ = bc	Sh - S'h'							
		${}^6A_1 - {}^6T_1$	${}^6A_1 - {}^4T_1$						
$t_a^3\ {}^4A_2\ e_a^2\ {}^3A_2 : {}^6A_1 — t_a^3\ {}^4A_2\ (e_a t_b)\ {}^3T_2$	$e_a t_b$	7/5*	9/40						
$t_a^3\ {}^4A_2\ e_a^2\ {}^3A_2 : {}^6A_1 — t_a^2\ {}^3T_1\ (e_a^2 T_b)\ {}^4T_1$	$t_a t_b$	7/5*	2/45						
$t_a^3\ {}^4A_2\ e_a^2\ {}^3A_2 : {}^6A_1 — t_a^2\ {}^3T_1\ (e_a^2 e_b)\ {}^4E$	$t_a e_b$	7/5	2/45*						
$t_a^3\ {}^4A_2\ e_a^2\ {}^3A_2 : {}^6A_1 — t_a^3\ {}^4A_2\ (e_a t_1)\ {}^3T_2$	$e_a t_1$	7/5*	9/40						
$t_a^3\ {}^4A_2\ e_a^2\ {}^3A_2 : {}^6A_1 — t_a^2\ {}^3T_1\ (e_a^2 t_1)\ {}^4T_2$	$t_a t_1$	7/5*	2/45						
		${}^6T_1 - {}^6T_2$	${}^6T_1 - {}^4T_2$	${}^6T_1 - {}^6E$	${}^6T_1 - {}^4E$	${}^4T_1 - {}^6T_2$	${}^4T_2 - {}^4T_2$	${}^4T_1 - {}^6E$	${}^4T_1 - {}^4E$
$t_a^3\ {}^4A_2\ (e_a t_b)\ {}^3T_2 — t_a^2\ {}^3T_1\ (e_a^2 t_b)\ {}^4E$	$t_a e_a$	7/20	1/40	14/15*	1/15*	1/40*	9/40	1/15	3/5*
$t_a^2\ {}^3T_1\ (e_a^2 t_b)\ {}^4T_1 — t_a^3\ {}^4A_2\ (e_a t_b)\ {}^3T_2$	$e_a t_a$	21/20	2/40	—	—	3/40*	27/40	—	—
$t_a^2\ {}^3T_1\ (e_a^2 e_b)\ {}^4E — t_a^3\ {}^4A_2\ (e_a e_b)\ {}^3E$	$e_a t_a$	—	—	7/10	1/20*	—	—	1/20	9/20
$t_a^3\ {}^4A_2\ (e_a t_1)\ {}^3T_2 — t_a^2\ {}^3T_1\ (e_a^2 t_1)\ {}^4T_2$	$t_a e_a$	21/20*	3/40*	—	—	3/40	27/40*	—	—
$t_a^2\ {}^3T_1\ (e_a^2 t_1)\ {}^4T_2 — t_a^3\ {}^4A_2\ (e_a t_1)\ {}^3T_2$	$e_a b_a$	1/20*	1/40*	—	—	1/40	9/40	—	—

*The sign of the square root of the numbers with asterisk is negative

Table 3.5. Reduced matrix elements $|\langle \chi_3 Sh \Vert \sum_i \zeta_i\, \underline{\ell}^i \cdot \underline{s}^i \Vert \chi'_3 S'h' \rangle|^2$

χ_3	χ'_3	$\langle 1/2\ c \Vert \zeta\ \underline{\ell}\cdot\underline{s} \Vert 1/2\ d\rangle$ = cd	Sh - S'h'							
			${}^6T_1-{}^6T_2$	${}^6T_1-{}^4T_2$	${}^6T_1-{}^6E$	${}^6T_1-{}^4E$	${}^4T_1-{}^6T_2$	${}^4T_1-{}^4T_2$	${}^4T_1-{}^6E$	${}^4T_1-{}^4E$
$(t_a^3\ {}^4A_2e_a)\ {}^5E\ (t_b^0t_1)\ {}^2T_2$	$(t_a^3\ {}^4A_2e_a)\ {}^5E\ (t_bt_1^0)\ {}^2T_1$	t_bt_1	7/20*	2/5	—	—	2/5*	1/10	—	—
$(t_a^3\ {}^4A_2e_a)\ {}^5E\ (t_be_b^0)\ {}^2T_2$	$(t_a^3\ {}^4A_2e_a)\ {}^5E\ (t_b^0e_b)\ {}^2E$	t_be_b	—	—	7/10*	4/5	—	—	4/5*	2/10
$(t_a^2\ {}^3T_1e_a^2\ {}^3A_2)\ {}^5T_2\ (t_be_b^0)\ {}^2T_2$	$(t_a^3\ {}^4A_2e_a)\ {}^5T_2\ (t_b^0e_b)\ {}^2E$	t_be_b	21/20	6/5*	—	—	6/5	3/10*	—	—
$(t_a^2\ {}^3T_1e_a^2\ {}^3A_2)\ {}^5T_2\ (t_bt_1^0)\ {}^2T_2$	$(t_a^3\ {}^4A_2e_a)\ {}^5T_2\ (t_b^0t_1)\ {}^2T_1$	t_bt_1	7/20*	2/5	7/10*	4/5	2/5*	3/20	4/5*	2/10
$(t_a^2\ {}^3T_1e_a^2\ {}^3A_2)\ {}^5T_2\ (e_bt_b^0)\ {}^2E$	$(t_a^3\ {}^4A_2e_a)\ {}^5T_2\ (e_b^0t_b)\ {}^2T_2$	e_bt_b	7/20*	2/5	14/15	16/15*	2/5*	3/10	16/15	4/15*
$(t_a^2\ {}^3T_1e_a^2\ {}^3A_2)\ {}^5T_2\ (e_bt_1^0)\ {}^2T_1$	$(t_a^3\ {}^4A_2e_a)\ {}^5T_2\ (e_b^0t_1)\ {}^2T_1$	e_bt_1	21/20	6/5*	—	—	6/5	3/10*	—	—
$(t_a^3\ {}^4A_2e_a\ {}^2E)\ {}^5E\ (t_1t_b^0)\ {}^2T_1$	$(t_a^3\ {}^4A_2e_a)\ {}^5E\ (t_1^0t_b)\ {}^2T_2$	t_1t_b	7/20	2/5*	—	—	2/5	1/10*	—	—
$(t_a^3\ {}^4A_2e_a\ {}^2E)\ {}^5E\ (t_1e_b)\ {}^2T_1$	$(t_a^3\ {}^4A_2e_a)\ {}^5E\ (t_1^0e_b)\ {}^2E$	t_1e_b	—	—	7/10*	4/5	—	—	4/5*	2/10
$(t_a^2\ {}^3T_1e_a^2\ {}^3A_2)\ {}^5T_2\ (t_1t_b^0)\ {}^2T_1$	$(t_a^3\ {}^4A_2e_a)\ {}^5T_2\ (t_1^0t_b)\ {}^2T_2$	t_1t_b	7/20*	2/5	7/30*	4/15	2/5*	3/20	4/15*	2/30
$(t_a^2\ {}^3T_1e_a^2\ {}^3A_2)\ {}^5T_2\ (t_1e_b^0)\ {}^2T_1$	$(t_a^3\ {}^4A_2e_a)\ {}^5T_2\ (t_1^0e_b)\ {}^2E$	t_1e_b	7/20	2/5*	—	—	2/5	1/10*	—	—

*The sign of the square root of the numbers with asterisk is negative

5. COUPLING COEFFICIENTS OF SPIN ORBIT INTERACTION $K_{JJ'}\begin{pmatrix}SS'T_1\\ h'\ ht\end{pmatrix}$

Here, we want to obtain the coupling coefficients $K_{JJ'}$, which were defined in (3.13). These coefficients couple the matrix elements of spin orbit interaction, from a pair of states identified by their irreducible representations $|J\ t>$ and $|J't>$ in the cubic double group, to the reduced matrix elements $\langle \chi\ S\ h||\sum_i \zeta_i\ \underline{\ell}^i\cdot\underline{s}^i||\chi'S'h'\rangle$ between the states $|\chi\ S\ h>$, and $|\chi'S'h'>$ from which the states $|J\ t>$ and $|J't>$ are constructed.

Following (3.12 - 3.13), we have

$$\langle \chi\ S\ h\ J\ t\ \tau|\sum_i \zeta_i\ \underline{\ell}^i\cdot\underline{s}^i|\chi'S'h'J't\ \tau\rangle = \langle \chi\ S\ h||\sum_i \zeta_i\ \underline{\ell}^i\cdot\underline{s}^i||\chi'S'h'\rangle\ K_{JJ'}\begin{pmatrix}SS'T_1\\ h'\ ht\end{pmatrix}$$

where (Griffith, p.82):

$$K_{JJ'}\begin{pmatrix}SS'\ T_1\\ K\ h\ t\end{pmatrix} = \Omega_{JJ'}\begin{pmatrix}SS'\ T_1\\ h'\ h\ t\end{pmatrix}$$

$$= \sum_{\substack{rMM'\\ \theta\theta}} (-1)^{S-M'+1}[-1]^{h+\theta}\ \bar{V}\begin{pmatrix}SS'\ 1\\ -MM'r\end{pmatrix}V\begin{pmatrix}hh'\ T_1\\ -\theta\theta'-r\end{pmatrix}$$

$$(x)\ \langle S\ h\ J\ t\ \tau|S\ h\ M\ \theta\rangle\langle S'h'M'\theta'|S'h'J't\ \tau\rangle \qquad (3.15)$$

The symbol, $\bar{V}\begin{pmatrix}a&b&c\\ \alpha&\beta&\gamma\end{pmatrix}$ in (3.15) is related* to 3-j symbols by $(-1)^{a+b+c}$, and $V\begin{pmatrix}a&b&c\\ \alpha&\beta&\gamma\end{pmatrix}$ is related to V by $(-1)^{2(b-c)}$. The symbols, $<S\ h\ J\ t\ \tau|S\ h\ M\ \theta>$ are coefficients of coupling S and h to obtain t of the cubic double group with occurrence number or angular momentum J. The latter coefficients are given by Griffith (Ref. 16, pp. 400-408) for spin quartets, $^5T_2$ and ^5E only. Therefore, the coefficients

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*U. Fano and G. Racah, "Irreducible Tensorial Sets," Academic Press, New York, (1959) p. 50

$\langle S\ h\ M\ \theta | S\ h\ J\ t\ \tau\rangle$ of Sh = ^6E, $^6T_1$ and $^6T_2$, which are not found in the literature, are obtained and given in Tables 3.6 to 3.8.

Having obtained the coefficients, $\langle S\ h\ M\ \theta | S\ h\ J\ t\ \tau\rangle$, we now are able to calculate the coupling coefficients, $K_{JJ'}\begin{Bmatrix} SS'T_1 \\ hh'\ t \end{Bmatrix}$, for h = A_1 and h' = E. T_1 and T_2. These are given in Tables 3.9 to 3.12.

After substituting for reduced matrix elements and the coupling coefficients in matrix elements, $\left\langle \chi\ S\ h\ J\ t\ \tau \middle\| \sum_i \zeta_i\ \underline{\ell}^i \cdot \underline{s}^i \middle| \chi' S' h' J' t\ \tau \right\rangle$, in (3.13), we find this quantity as a function of single electron reduced matrix elements such as

$$t_b t_b,\ t_a t_a, \ldots .t_1 t_1,\ e_a t_b,$$

given in Tables 3.3 through 3.5. These matrix elements will be determined in the next section.

Table 3.6. Transformation of ^6E into the IR's of double valued group T'_d: $|\langle ShM\theta | ShJt\tau\rangle|^2$

			Jt τ	E'		E''		1U'				2U'			
S	M	h	θ	α'	β'	α''	β''	κ	λ	μ	ν	κ	λ	μ	ν
5/2	5/2	E	u			5/12*					5/12				1/6*
	3/2						1/12*	1/12*				5/6*			
	1/2			1/2					1/2*						
	-1/2				1/2					1/2					
	-3/2					1/12*					1/12				5/6
	-5/2						5/12*	5/12*				1/6			
5/2	5/2	E	v	5/12					5/12				1/6		
	3/2				1/12					1/12*				5/6	
	1/2					1/2					1/2				
	-1/2						1/2	1/2*							
	-3/2			1/12					1/12				5/6*		
	-5/2				5/12					5/12*				1/6*	

*The sign of the square root of coefficients with asterisk is negative

Table 3.7. Transformation coefficients of $^6T_1$ into the IR's of double valued group T'_d; $|\langle 5/2T_1M\theta|5/2T_1Jt\theta\rangle|^2$

$^6T_1$	J	3/2				5/2						7/2							
	t	U'				E''		U'				E'		E''		U'			
M	θ τ	κ	λ	μ	ν	α''	β''	κ	λ	μ	ν	α'	β'	α''	β''	κ	λ	μ	ν
5/2	1												5/12*					7/12	
	0					5/42					25/42			3/14					1/14
	-1	2/3					5/21*	1/21*							1/84	1/28			
3/2	1					1/21*					5/21			15/28					5/28
	0	4/15*					3/14*	3/70*							5/42	5/14			
	-1		2/5						16/35			1/12					5/84*		
1/2	1	1/15					8/21	8/105							5/42	5/14			
	0		2/5*						1/35			1/3					-5/21		
	-1			1/5						18/35*			1/6*					5/42*	
-1/2	1		1/5						18/35*			1/6					5/42*		
	0			2/5*						1/35			1/3*					5/21*	
	-1				1/15	8/21*					8/105			5/42*					5/14
-3/2	1			2/5						16/35		1/12*						5/84*	
	0				4/15*	3/14					3/70*			5/42*					5/14
	-1						5/21*								15/28*	5/28			
-5/2	1				2/3	5/21					1/21*			1/84*					1/28
	0						5/42*		25/42						3/14*	1/14			
	-1										5/12						7/12		

*The sign of the square root of number with asterisk is negative

Table 3.8. Transformation coefficients of $^6T_2$ into the IR's of double valued group T'_d $|\langle 5/2T_2M\theta|5/2T_2Jt\tau\rangle|^2$

$^6T_2$	J	3/2				5/2						7/2							
	t	U'				E'		U'				E''		E'		U'			
M	τ / θ	κ	λ	μ	ν	α'	β'	κ	λ	μ	ν	α''	β''	α'	β'	κ	λ	μ	ν
5/2	1												5/12			7/12*			
	0					5/42			25/42					3/14			1/14		
	-1			2/3			5/21*			1/21*					1/84			1/28	
3/2	1					1/21*			5/21*					15/28			5/28		
	0			4/15*			3/14*			3/70*					5/42			5/14	
	-1				2/5*						16/35*	1/12							5/84
1/2	1			1/15			8/21			8/105					5/42			5/14	
	0				2/5						1/35*	1/3							5/21
	-1	1/5*						18/35					1/6*			5/42			
-1/2	1				1/5*						18/35	1/6							5/42
	0	2/5						1/35*					1/3*			5/21			
	-1		1/15			8/21*			8/105					5/42*			5/14		
-3/2	1	2/5*						16/35*					1/12*			5/84			
	0		4/15*			3/14			3/70*					5/42*			5/14		
	-1						1/21			5/21*					15/28*			5/28	
-5/2	1		2/3			5/21			1/21*					1/84*			1/28		
	0						5/42*			25/42					3/14*			1/14	
	-1											5/12							7/12*

*The sign of the square root of the numbers with asterisk is negative

Table 3.9. Coupling coefficients $K_{JJ'}$ for h = A_1

J	J'	S	S	t	$K_{J'J}(SST_1,A_1T_1t)$
5/2	5/2	5/2	5/2	U'	$(1/18)^{1/2}$
				E''	$(1/18)^{1/2}$

Table 3.10. Coupling coefficients $K_{JJ'}$ for h = T_1

J	J'	S	S	t	$K_{J'J}(SST_1,T_1T_1t)$
5/2	5/2	5/2	5/2	U'	$(1/15)\ (5/7)^{1/2}$
				E''	$(1/15)\ (5/7)^{1/2}$
			3/2	U'	$-(7/45)\ (5/7)^{1/2}$
				E''	$-(5/45)\ (5/7)^{1/2}$
		3/2	3/2	U'	$-(1/2)\ (1/10)^{1/2}$
				E'	$-(1/2)\ (1/10)$

Table 3.11. Coupling coefficients $K_{JJ'}$ for h = E

J	J'	S	S	t	$K_{J'J}(SST_1,T_1Et)$	J	J'	S	S	t	$K_{J'J}(SST_1,T_1T_2t)$
5/2	1	5/2	5/2	U'	$(16/105)$	5/2	1	3/2	5/2	U'	$-(2/15)$
	2	5/2	5/2	U'	$-(2/105)\ (10)^{1/2}$		2	3/2	5/2	U'	$(1/60)\ (10)^{1/2}$
		5/2	5/2	E''	$-(4/105)\ (5)^{1/2}$	5/2	2	3/2	5/2	E''	$(1/30)\ (5)^{1/2}$
			3/2	U'	$(1/10)\ (3/7)^{1/2}$		2	3/2	3/2	U'	$-(1/10)(3/2)^{1/2}$
		5/2	3/2	E''	$(1/2)\ (3/35)^{1/2}$			3/2	3/2	E''	$-(1/2)(3/10)^{1/2}$

Table 3.12. Coupling coefficients $K_{JJ'}$ for h = T_2

J	T'	S	S	t	$K_{J'J}(SST_1,T_1T_2t)$	J	J'	S	S	t	$K_{J'J}(SST_1,T_1T_2t)$
5/2	3/2	5/2	5/2	U'	$-(8/35)\ (1/30)^{1/2}$	5/2	7/2	5/2	3/2	E''	$(1/2)\ (1/105)^{1/2}$
	5/2	5/2	5/2	U'	$-(35/35)\ (1/105)^{1/2}$	5/2	3/2	3/2	5/2	U'	$(1/5)\ (1/30)^{1/2}$
	7/2	5/2	5/2	U'	$(8/21)\ (1/35)^{1/2}$	5/2	5/2	3/2	5/2	U'	$(3/10)\ (3/35)^{1/2}$
						5/2	7/2	3/2	5/2	U'	$-(1/3)\ (1/35)^{1/2}$
		5/2	5/2	E''	$(8/21)\ (1/5)^{1/2}$	5/2	7/2	3/2	5/2	E''	$-(1/3)\ (1/5)^{1/2}$
5/2	3/2	5/2	3/2	U'	$-(4/5)\ (1/105)^{1/2}$	5/2	3/2	3/2	3/2	U'	$(4/5)\ (1/30)^{1/2}$
							5/2	3/2	3/2	U'	$(3/10)\ (3/10)^{1/2}$
5/2	5/2	5/2	3/2	U'	$-(9/10)\ (1/105)^{1/2}$		7/2	3/2	3/2	E''	$-(1/2)\ (1/30)^{1/2}$

6. SINGLE ORBITAL REDUCED MATRIX ELEMENTS $\langle 1/2\ a || \zeta\ \underline{\ell}\cdot\underline{s} || 1/2\ b \rangle$

The matrix elements of $\sum_i \zeta_i\ \underline{\ell}^i\cdot\underline{s}^i$ from a pair of states with electronic configurations χ and χ', (3.8), are related, among other factors, to these configurations. This dependence on the electronic configuration of the orbitals giving rise to the above states, is manifested by the presence of single orbital reduced matrix elements of the type, $t_a t_a = \langle 1/2\ t_a || \zeta\ \underline{\ell}\cdot\underline{s} || 1/2\ t_a \rangle$ and $t_a e_b = \langle 1/2\ t_a || \zeta\ \underline{\ell}\cdot\underline{s} || 1/2\ e_b \rangle$ which appear in Tables 3.3 through 3.5. To find $t_a t_a$...., we should express them in terms of atomic symmetry orbitals.

Since the determination of the energies of the molecular orbitals t_a, e_a of Fig. 3.1 is beyond the scope of the present work, no numerical values of the coefficients of linear combinations of atomic symmetry orbitals, $d(e, t_2)$ and $p_\pi(t_1, e, t_2)$, (Fig. 3.1), are available. Therefore, we choose a set of arbitrary coefficients, α, β, κ, λ, μ and ν, to express the molecular orbitals, t_a, e_a, t_1, e_b and t_b, as follows:

$$t_a = \kappa|d\ t_2\rangle - \lambda|\pi\ t_2\rangle - \mu|\sigma\ t_2\rangle - \nu|s\ t_2\rangle$$

$$e_a = \alpha|\ d\ e\rangle - \beta|\pi\ e\rangle$$

$$t_1 = |\pi\ t_1\rangle$$

$$t_b = \lambda'|d\ t_2\rangle + \kappa'|\pi\ t_2\rangle + \mu'|\sigma\ t_2\rangle + \nu'|s\ t_2\rangle$$

$$e_b = \beta|d\ e\rangle + \alpha|\pi\ e\rangle \qquad (3.16)$$

where all coefficients, α, β,.... ν', are real and positive.

Moreover,

$$\alpha^2 + \beta^2 = \kappa^2 + \lambda^2 + \mu^2 + \nu^2 = \kappa'^2 + \lambda'^2 + \mu'^2 + \nu'^2 = 1 \quad (3.17)$$

Substituting for $t_a, \ldots . t_b$, we find the single orbital reduced matrix elements as given in Table 3.13:

Table 3.13. Single orbital reduced matrix elements

No.	a, b	$\langle 1/2a \Vert \zeta \underline{\ell}\cdot\underline{s} \Vert 1/2b \rangle$	No.	a, b	$\langle 1/2a \Vert \zeta \underline{\ell}\cdot\underline{s} \Vert 1/2b \rangle$
1	$e_a t_1$	$\sqrt{3}\ \beta\ \zeta_p$	7	$t_1 t_a$	$1/2\ \sqrt{3}\ \lambda\ \zeta_p$
2	$e_a t_a$	$-3\sqrt{2}\ \alpha\ \kappa\ \zeta_d - 3\ \beta\ \lambda\ \zeta_p$	8	$t_1 t_b$	$-1/2\ \sqrt{3}\ \kappa\ \zeta_p$
3	$e_a t_b$	$-3\sqrt{2}\ \alpha\ \lambda\ \zeta_d + 3\ \beta\ \kappa\ \zeta_p$	9	$t_a t_b$	$-3\sqrt{2}\ \kappa\ \lambda\ \zeta_d - 3/2\ \lambda\ \kappa\ \zeta_p$
4	$e_b t_1$	$-\sqrt{3}\ \alpha\ \zeta_p$	10	$t_1 t_1$	$3/2\ \zeta_p$
5	$e_b t_a$	$-3\sqrt{2}\ \beta\ \kappa\ \zeta_d + 3\ \alpha\ \lambda\ \zeta_p$	11	$t_a t_a$	$3\ \kappa^2\ \zeta_d + 3/2\ \kappa^2\ \zeta_p$
6	$e_b t_b$	$-3\sqrt{2}\ \beta\ \lambda\ \zeta_d - 3\ \alpha\ \kappa\ \zeta_p$	12	$t_b t_b$	$3\ \lambda^2\ \zeta_d + 3/2\ \kappa^2\ \zeta_p$

With the spin orbit matrix elements known, we can now proceed to formulate 3a in the following section.

CHAPTER IV

CUBIC FIELD SPLITTING 3a

In this section, we wish to obtain the contribution of spin orbit interaction to cubic field splitting 3a, with the intention of carrying the calculations through the lowest order of perturbation required for the ground state, $^6A_1$, to split. Our task, therefore, is to establish the lowest perturbation order first, and then, carry on the numerical computations to obtain an estimate of 3a (under certain assumptions regarding the coefficients) for some special cases.

1. DETERMINATION OF THE LOWEST ORDER OF PERTURBATION BY $H_p = \sum_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i$ THAT CAN SPLIT $^6A_1$

The first step in determining the lowest order perturbation required for the splitting of $^6A_1$, is to find those coupling coefficients, $K_{JJ'}\begin{pmatrix} SS'T_1 \\ h'\ ht \end{pmatrix}$, which have different values for t = U' and t = E'' levels of $^6A_1$. Because the energy associated with level $|^6A_1\ J = 5/2\ t = U'>$ must differ from that energy associated with the level, $|^6A_1,\ J = 5/2\ t = E''>$, in order for the matrix element of $\sum \zeta_i\ \underline{\ell}^i \cdot s^i$ to contribute toward splitting 3a. As shown in Appendix D, we have

$$K_{JJ'}\begin{pmatrix} SS'T_1 \\ hA_1\ t \end{pmatrix} = \sqrt{\frac{1}{(\hbar)}\ \frac{1}{(25 + 1)}}\ \delta_{SJ}\delta_{S'J'}\delta_{h'T_1} \tag{4.1}$$

and

$$K_{JJ'}\begin{pmatrix} SS'T_1 \\ T_1T_1t \end{pmatrix} = (-1)^{J+S}\ \delta_{JJ'}\ \overline{W}\begin{pmatrix} 1\,1,\,1 \\ S\,S'\,J \end{pmatrix} \tag{4.2}$$

It is immediately evident from (4.1)-(4.2), that the matrix elements between $|{}^6A_1\rangle$ and $|{}^6T_1\rangle$ and those between $|{}^6T_1\rangle$ and $|{}^6T'_1\rangle$ contribute the same amount to both levels t = U' and t = E'', and their contribution to 3a vanishes.

The chains of the products of the matrix elements:*

$$\left\langle {}^6A_1 - {}^6T_1 \right\rangle \left\langle {}^6T_1 - {}^6A_1 \right\rangle \qquad (4.3)$$

and

$$\left\langle {}^6A_1 - {}^6T_1 \right\rangle \cdot \left\langle {}^6T_1 - {}^6T'_1 \right\rangle \cdot \left\langle {}^6T'_1 - {}^6A_1 \right\rangle \qquad (4.4)$$

are the only nonvanishing products which give rise to terms for the evaluation of the second and third order energy contribution to levels with IR t = U' and t = E'' of the ground state. These energy contributions are the same, and consequently, both second and third order contributions to 3a, by spin-orbit interaction, vanish. Moreover, contributions from higher than third order perturbation with excited states having T_1 symmetry vanish too. The next perturbation order to consider is fourth order.

Considering Tables 3.11 and 3.12, it is evident that for the excited states with T_2 and E symmetries, the coupling coefficients, $K_{JJ'}\begin{pmatrix} SS'T_1 \\ h' \; ht \end{pmatrix}$, differ for t = U and t = E''. Therefore, a splitting will occur.

This indicates that the fourth order perturbation is the lowest one which contributes to the splitting.

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*$\left\langle {}^6A_1 - {}^6T_1 \right\rangle \equiv \left\langle {}^6A_1 \; Jt\tau \middle| \sum_i \zeta_i \; \underline{\ell}' \cdot \underline{s}' \middle| {}^6T_1 \; J't'\tau \right\rangle$

2. CONTRIBUTION TO THE CUBIC FIELD SPLITTING 3a FROM FOURTH ORDER PERTURBATION OF $^6A_1$ BY $\sum_i \zeta_i \underline{\ell}^i\cdot\underline{s}^i$

Here, we formulate the 3a by considering the following relationships (3.1):

$$3a = E(U') - E(E'') \cong E^{(4)}(U') - E^{(4)}(E'') \qquad (4.5)$$

where $E^{(4)}(U')$ and $E^{(4)}(E'')$ are the fourth order contribution from spin orbit interaction to the levels U' and E'' of the ground state $^6A_1$ of the S-state ion. The expression for $E^{(4)}(U') - E^{(4)}(E'')$ is:

$$E^{(4)}(U') - E^{(4)}(E'') = -\sum_{\substack{jk\ell\\ mnp}} (E_j E_k E_\ell)^{-1} \Big\{ R_{oj} R_{jk} R_{k\ell} R_{\ell o}$$

$$(x) \Big[\Big\{ K_{om}(oj) K_{mn}(jk) K_{np}(k\ell) K_{po}(\ell o) \Big\}_{U'} - \Big\{ K_{om}(oj)\, K_{mn}(jk) K_{np}(k\ell) K_{po}(\ell o) \Big\}_{E''} \Big] \Big\}$$

where

$$R_{jk} = \left\langle \chi_j S_j h_j \,||\, H_p \,||\, \chi_k S_k h_k \right\rangle$$

and

$$K_{mn}(jk) = K_{J_m J_n} \begin{pmatrix} S_j S_k T_1 \\ h_k h_j \;\; t \end{pmatrix} \qquad (4.5a)$$

The parameters χ_j, ..., χ_ℓ in (4.5a) represent the molecular electronic configuration and $|\chi_j S_j h_j\rangle$ characterize the orbital part of configuration χ_j.

Substituting for the various parameters involved, the expression for 3a will be of the form:

$$3a^{(4)} = \sum_{i=o}^{4} C_i\, \zeta_d^{4-i}\, \zeta_p^{\,i} \tag{4.6}$$

where C_i are complicated functions of the coefficients; α, β, κ .... given in (3.16) and the promotion energies E_i, E_j and E_k of the excited states appearing in (4.6). The precise numerical values of α, β and κ could be obtained from solving eigenvalue equations from which the energies; $E_i \ldots E_j$ and E_k could be found too. As mentioned earlier, the determination of $E_i \ldots E_k$ is beyond the scope of the present work and as a result of this, we can use only a set of arbitrarily chosen numbers for both the coefficients and the energies involved. For the following set of coefficients:[*]

$$\alpha^2 = 1 - \beta^2 = 0.7,$$

$$\kappa^2 = 0.8 - \lambda^2 = 0.6,$$

$$\mu^2 + \nu^2 = 0.2,$$

and

$$\kappa \sim \kappa', \ \lambda \sim \lambda';$$

we find the coefficients C_i of (4.6) as given in Table 4.1.

Table 4.1

The Coefficients C_i $(-2/5625\ E_6^{\,3})^{-1}$

C_0	C_1	C_2	C_3	C_4
87.17	-138.99	-164.94	14.63	35.75

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[*] (See 3.16)

Substituting for C_i in (4.6), one finds 3a as a function of the ratio ζ_p/ζ_d. The result in units of $10^{-1}\ \zeta_d^{\ 4}/E_6^{\ 3}$ are given in Table 4.2.

Table 4.2

Calculated Values of 3a for Spin Sextets

ζ_p/ζ_d	3a ($10^{-1}\ \zeta_d^{\ 4}/E_6^{\ 3}$)	ζ_p/ζ_d	3a ($10^{-1}\ \zeta_d^{\ 4}/E_6^{\ 3}$)
0.5	0.07	6	-152.30
1	0.59	8	-507.40
1.5	0.993	10	-126.30
2	0.573	12	-2645
3	-5.30	16	-8443
4	-24.90	20	-20562

A discussion of these results will be given in the next section.

CHAPTER V

DISCUSSION

We want to give a brief discussion of various models used to calculate 3a, first, and then apply the result of these models to the 3a of Fe^{3+} in the compounds ZnS, ZnSe, and ZnTe.

As was mentioned in Chapter I, Watanabe[5] was the first to calculate 3a on the basis of the point charge model. His work was followed by Powell[6] and by Low and Rosengarten.[7,8] Azarbayejani, Kikuchi and Watanabe[15] substituted the point charge model with the molecular orbital model and obtained the contributions to ground state splitting arising from charge transfer between σ-bonding and σ-nonbonding orbitals of the complex consisting of a central S-state ion and its four tetrahedrally coordinated neighbors. In the present work, the contribution to 3a arising from charge transfer between the π-orbitals of the same complex has been found. To make an assessment of these various contributions to 3a and their relative importance, we are considering all of the above-mentioned calculations, in turn, as follows.

1. CONTRIBUTION TO 3a FROM WATANABE'S CALCULATION

The cubic field splitting obtained by Watanabe is given in (15) of Ref. 5. The expression for 3a is as follows:

$$(3a)_W = 3\,(Dq)^2\,[2.015 + 15.9\,M_0 - 149.5\,M_2 - 5.937\,(M_0 - 8M_2)^2$$

$$- 0.388\,(M_0 - 8M_2)^2\,(Dq)^2\,10^{-6}] \times 10^{-10}\ \text{cm}^{-1} \qquad (5.1)$$

where 10 Dq* is the cubic field strength of the host compound around the S-state ion and is about 3000 to 4000 cm^{-1} for Mn^{2+} and 5000 to 6000 cm^{-1} for Fe^{3+}

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*See the first footnote on the following page.

in II-VI compounds of T_d symmetry. The coefficients M_0 and M_2 are (see Ref. 6, Part a) 0.204 and 0.0159 cm^{-1}, respectively. Substituting for M_0 and M_2, one obtains:

$$\begin{aligned}(3a)_w &= 3\ (Dq)^2\ [2.015 + 15.94 \times 0.204 - 149.5\ (0.0159) - 5.037\ (0.024 \\ &\quad - 0.127)^2 - 0.0388\ (0.077)^2\ (Dq)^2 \times 10^{-6}] \times 10^{-10}\ cm^{-1} \\ &= 3\ (Dq)^2\ [2.015 + 0.87 - 0.029 - 2.25 \times 10^{-9}\ (Dq)^2] \times 10^{-10}\ cm^{-1}\end{aligned}$$

or

$$(3a)_w = 8.57 \times 10^{-10}\ (Dq)^2 - 76.5 \times 10^{-20}\ (Dq)^4\ cm^{-1} \qquad (5.2)$$

2. CONTRIBUTION TO 3a FROM POWELL'S CALCULATIONS

The ground state splitting given by Powell et al (Ref. 6, part b) can be expressed as:

$$(3a)_P = K_P\ \zeta_d^4\ (Dq)^n\ ;\ 3.5 < n < 6\ ;\ Dq > 10^3\ cm^{-1} \qquad (5.3)$$

The equation (5.3) was obtained by limiting their calculation to MgO:Mn where MgO is an octahedral II-VI compound for which Dq is large ($Dq > 10^{-3}\ cm^{-1}$). For the II-VI compounds of T_d symmetry, Powell et al (Ref. 6a) give some numerical values of 3a as a function of (Dq) as given in Table 5.1.

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[*] Ref. 16, Table 11.3 p. 310 gives 10 Dq $[Mn\ (H_2O)_6]^{2+}$ and $[Fe\ (H_2O)_6]^{3+}$ as 8300 and 14700, respectively. Pappalardo and Dietz (Phys. Rev 123 1188 (1961) have concluded Dq (CdS):Ni) = -0.85 x 4/9 Dq$[Ni\ (H_2O)_6]$. Thus, in an analogous way, 10 Dq $[CdS:Mn^{2+}] \cong -3100$.

Table 5.1. Calculated$^+$ 3a in Mn^{2+} in units of 10^{-4} cm^{-1}

Dq (cm^{-1})	0	-200	-400	-600	-800	-1000
$(3a)_P$ with doublets	0	3.56	11.0	23.8	45.1	81.4
$(3a)_P$ without doublets	0	0.115	0.338	0.668	1.09	1.59
$(3a)_W$ Eq. (5.2)	0	0.35	1.4	3.15	5.6	8.75

$^+$These values are obtained for the spin-orbit constant, = 400 cm^{-1} and spin-spin interaction constants, M_0 and M_2 as 0.284 cm^{-1} and 0.0159 cm^{-1}, respectively.

The first row of Table 5.1 gives 3a arising from all spin multiplets within the $3d^5$ manifold, whereas the second row is obtained without taking the spin doublets of the $3d^5$ manifold into account. Watanabe's calculations are based on spin quartets alone and are given in the third row of Table 5.1. The numerical values of the first row of Table 5.1 give the total contributions from excited states generated within the $3d^5$ manifold. Now, we consider the calculation by Low and Rosengarten.

3. CONTRIBUTION TO 3a FROM LOW AND ROSENGARTEN CALCULATIONS

The cubic field splitting given by Low and Rosengarten, $(3a)_{LR}$, was obtained from the same spin quartets and doublets of $(3d)^5$ manifold considered by Powell et al. However, the techniques used by the former authors differ from those of the latter. Low et al diagonalized the energy matrices of E', E'' and U' levels which contain five parameters; B, C, Dq, ζ_d and α.* Powell el at, on the other hand, diagonalized the

---

*B, C are Racah coefficients, Dq is the cubic crystal field strength, α is Tree's correction factor and M_0 and M_2 are spin-spin interaction parameters.

energy matrices of A_1, A_2, E, T_1 and T_2 levels as functions of six parameters B, C, Dq, ζ_d, M_0 and M_2, first. Then, they obtained the energies of levels E" and U' from the energy values of the above levels, $A_1 \ldots T_2$ by sixth order perturbation.

The numerical values obtained by Low et al are given in Table 5.2.

Considering Table 5.2, it is evident that $(3a)_{LR}$ and $(3a)_P$ are of the same order of magnitude, whereas $(3a)_W$ (Table 5.1), calculated by Watanabe, is much less than these two. This is expected because both $(3a)_{LR}$ and $(3a)_P$ have been found by taking into account all spin multiplets of $(3d)^5$ configuration, whereas $(3a)_W$ is obtained from spin quartets of $(3d)^5$ only. As for $(3a)_{LR}$ and $(3a)_P$, the latter gives 3a as a function of Dq and ζ_d. Therefore, it is more suitable for the calculation

Table 5.2.* Comparison of $(3a)_{LR}$ with $(3a)_P$ and $(3a)_{Exp}$.

	Mn^{2+}			Fe^{3+}		
	MnF_2	$MnCl_2$	$Mn(H_2O)_6$	MgO:Fe	$Be_3Al_2(SiO_3)_6$:Fe	$Fe(H_2O)_6$
$(3a)_{LR}$ 10^{-4} cm^{-1}		10			160	
Dq(cm^{-1}) ζd(cm^{-1})		750 320			1350 420	
$(3a)_P$ $(10^{-4} cm^{-1})^+$		11			325	
$(3a)_{Exp.}$ $(10^{-4} cm^{-1})$	12	6	20-30	615	450	350

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[*] $(3a)_{LR}$ is the 3a calculated by Low and Rosengarten, $(3a)_P$ is the 3a calculated by Powell and $(3a)_{Exp}$ is the experimentally determined value of 3a.

[+] $(3a)_P$ are obtained from the relationship; $(3a)_{P_1} = K_P \zeta_d^4 (Dq)^4$ and from the numerical values of $(3a)_P$ at Dq = 1000 cm^{-1} and ζ_d = 376 cm^{-1}.

of the 3a of a certain ion in compounds of different Dq. Thus, we choose $(3a)_P$ as the contribution to 3a from the excited states within the $(3d)^5$ configuration and, discuss the charge transfer contribution in the next section.

4. CONTRIBUTION TO 3a FROM σ-BONDING CHARGE TRANSFER STATES

The contribution to 3a from the σ-bonding charge transfer states was obtained previously.[15] Here, it will be reviewed briefly in order to make a comparison between this and the contribution of the π-bonding transfer states given in the next section.

The irreducible representations of the metal d orbital and ligand σ-orbitals in II-VI compounds of T_d symmetry are:*

$$h\,(d) = h\,(\ell = 2) = e + t_2 \tag{5.4}$$

and

$$h\,(\sigma) = a_1 + t_2 \tag{5.5}$$

Considering (5.4)-(5.5), it is evident that the molecular orbitals consist of a d orbital of e symmetry, a σ-orbital of a_1 symmetry and a pair of orbitals comprised of metal d-orbital and ligand σ-orbital of t_2 symmetry. In the last two orbitals, the orbital with the higher energy is the antibonding, denoted by $t_2{}^a$, whereas the one with the lower energy is called bonding and is denoted by $t_2{}^b$. Thus, the molecular orbitals of interest to us, are (a_1 is ignored):

$$|e\rangle = |de\rangle\ ,\ |t_2{}^a\rangle = \alpha_T|dt_2\rangle - \beta_T|\sigma t_2\rangle$$

and

$$|t_2{}^b\rangle = \beta_T|dt_2\rangle + \alpha_T|\sigma t_2\rangle \tag{5.6}$$

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*Ballhausen, "Introduction to Ligand Field Theory," McGaw-Hill Book Company, New York (1962), p. 53 [Eq. (3.34)], p. 171.

The energy diagram for such bonding is given in Fig. 5.1.

The electronic configuration characteristic of the ground state, $^6A_1$, of a tetrahedral complex of $3d^5$ ^6S ion and its bonding-nonbonding and bonding-antibonding states are given in Fig. 5.2. The $^6T_1{}^n$ and $^6T_2{}^n$ in Fig. 5.2(b) result from an electron transfer from the $t_2{}^b$ orbital to e^n, whereas the levels; $^6E^a$, $^6T_1{}^a$ and $^6T_2{}^a$ result from the above process taking place between the $t_2{}^b$ and $t_2{}^a$ orbitals as shown in Fig. 5.2(c).

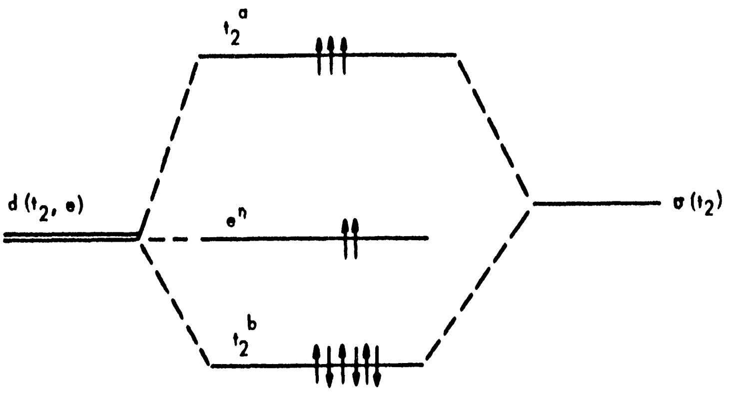
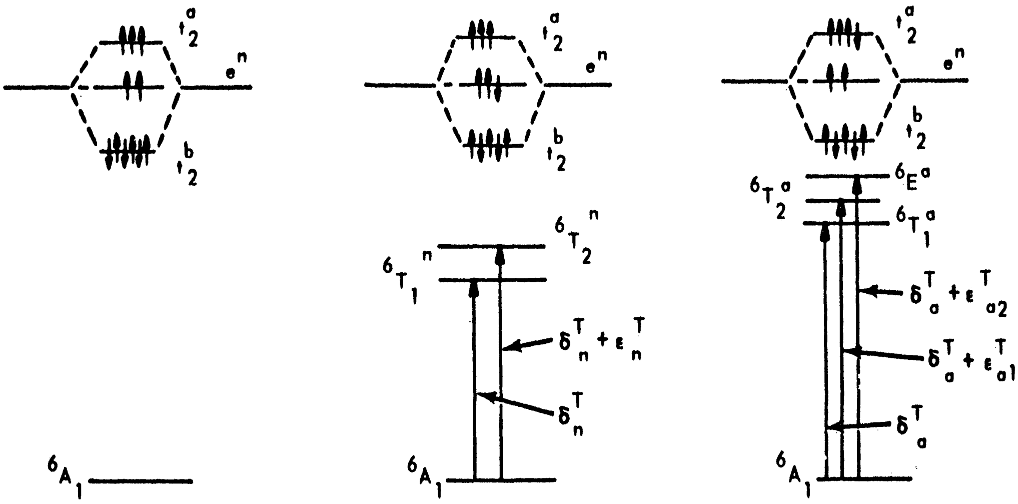


Fig. 5.1. σ-bonding molecular orbitals in II-VI compounds of T_d symmetry.



(a) (b) (c)

Fig. 5.2. (a) Ground state of complex $[\Sigma\Lambda_4]^{-n'}$, (b) $t_2{}^b$-e^n charge transfer states and their schematic energy levels, and (c) $t_2{}^b$-$t_2{}^a$ charge transfer states and their schematic energy levels.

The contribution of these σ-bonding levels to 3a depends on their stability for a given S-state ion in a given compound. In the case of compounds where levels $^6E^a$, $^6T_1{}^a$ and $^6T_2{}^a$ may not be localized because of the small energy band gap of compound, only $^6T_1{}^n$ and $^6T_2{}^n$ can be taken into account. For the general case where anitbonding levels are also localized, the simultaneous effort of both antibonding and bonding levels on 3a must be considered. The contribution, 3a(σ), to the cubic field splitting 3a, from the above σ-bonding orbitals can be expressed as:*

$$3a(\sigma) = E^{(4)}\ (U') - E^{(4)}\ (E'') \tag{5.7}$$

We first obtain the 3a(σ) for $^6T_1{}^n$ and $^6T_2{}^n$ alone. Then, we include the states $^6E^a$, $^6T_1{}^a$ and $^6T_2{}^a$.

4.1 Bonding-Nonbonding Charge Transfer

The contribution to 3a(σ) from $^6T_1{}^n$ and $^6T_2{}^n$ will be identified by 3a(σ;b-n). This can be obtained both from (4.11) or from the different techniques described in Appendix F. The result is:[15]

$$3a(\sigma;b\text{-}n) = 0.1728\ \beta_T{}^6\ \zeta_d{}^4\ (1 - \varepsilon_n T/\delta_n T)\ (\delta_n T)^{-3} \tag{5.8}$$

where $\beta_T{}^2 = 1 - \alpha_T{}^2$ is the covalency of the d-orbitals of the S-state ion in the desired complex. ζ_d is the single electron spin orbit parameter and is the same as λ in Ref. 15. $\delta_n{}^T$ and $\varepsilon_n{}^T$ are as shown in Fig. 5.1.

4.2 Bonding-Nonbonding and Bonding-Antibonding Charge Transfer

Using the same techniques as those employed for the bonding-nonbonding process, one finds the contributions to 3a(σ) arising from

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*For definition of U' and E'' see Table 3.1

${}^6T_1{}^n$, ${}^6T_2{}^n$, ${}^6E^a$, ${}^6T_1{}^a$, and ${}^6T_2{}^a$ as shown in Appendix F. The result is a function of the coefficients of atomic orbitals α_T and β_T ($\alpha_T{}^2 = 1 - \beta_T{}^2$) in the molecular orbitals used, and the energies; $\delta_n{}^T$, $\varepsilon_n{}^T$, $\delta_a{}^T$, $\varepsilon^T{}_{a1}$ and $\varepsilon^T{}_{a2}$ as shown in Fig. 5.1. For a particular case where

$$\varepsilon^T{}_n = \varepsilon^T{}_{a1} = \varepsilon^T{}_{a2} = 0 \qquad (5.9)$$

and with the assumption that[*]

$$\delta_a{}^T = r\, \delta_n{}^T \qquad (5.10)$$

one finds that:

$$3a(\sigma) = (108:625)\ (\delta_n{}^T)^{-3}\ (x)$$

$$(x) \left[\beta_T{}^4 - 2\,(1 - \beta_T{}^4)\ r^{-1} + (1 - \beta_T{}^2)(3 - 5\,\beta_T{}^2)\ r^{-2}\right] \beta_T{}^2\ \zeta_d{}^4 \qquad (5.11)$$

The parameter r and its power denote the presence of ${}^6T_1{}^a$, ${}^6T_2{}^a$ or ${}^6E^a$ in the matrix elements from which $3a(\sigma)$ is obtained. Thus, the first term in the bracket in (5.11) represents contributions arising exclusively from ${}^6T_1{}^n$ and ${}^6T_2{}^n$, whereas the last two terms give the contribution arising from the presence of both ${}^6T_1{}^n$ and ${}^6T_2{}^n$, and ${}^6E^a$, ${}^6T_1{}^a$ and ${}^6T_2{}^a$. An examination of (5.11) reveals that only for $r \to 0$ or $\delta_a{}^T \to \infty$ one obtains $3a(\sigma) > 0$. Numerical values of $3a(\sigma)$ as functions of both $\beta_T{}^2 = 1 - \alpha_T{}^2$ and r can be found from the following relationships:

$$3a(\sigma,\ \beta_T{}^2 = 0.2) = \left[(18/625)\ (\delta_n{}^T)^{-3}\right] \left[0.048 - 2.3r^{-1} + 1.92\ r^{-2}\right] \zeta_d{}^4 \qquad (5.12)$$

---

[*] r is a real number chosen as the ratio of the two energies $\delta_a{}^T$ and $\delta_n{}^T$.

$$3a(\sigma,\ \beta_T{}^2 = 0.3) = \left[(18/625)\ (\delta_n{}^T)^{-3}\right]\left[0.162 - 3.3\ r^{-1} + 1.89\ r^{-2}\right]\zeta_d{}^4 \tag{5.13}$$

$$3a(\sigma,\ \beta_T{}^2 = 0.4) = \left[(18/625)\ (\delta_n{}^T)^{-3}\right]\left[0.384 - 4.03\ r^{-1} + 1.44\ r^{-2}\right]\zeta_d{}^4 \tag{5.14}$$

The numerical values obtained from (5.12)-(5.14) are given in Table 5.3.

An examination of Table 5.3 indicates that a positive contribution to 3a(σ) takes place only in very covalent compounds ($\beta_T{}^2 = 0.4$) and for $\delta_a{}^T : \delta_n{}^T = 12$. The latter condition is unrealistic because for $\delta_n{}^T$ in the order of 1-2 e.v., $\delta_a{}^T$ must be 12-24 e.v. which makes E^a, $T_1{}^a$ and $T_2{}^a$ levels unstable. Thus, one can conclude that:

(1) 3a(σ) is positive if only bonding-nonbonding states are localized $\left(\delta_a{}^T/\delta_n{}^T \to \infty\right)$.

(2) 3a(σ) is negative when both bonding-nonbonding and bonding-antibonding states are localized, and $r = \delta_a{}^T : \delta_n{}^T$ is 1-10.

(3) 3a(σ) depends only on ζ_d as shown in (5.12)-(5.13).

Since 3a(π) depends on both ζ_d and ζ_p,* it is desirable to elaborate further on the absence of ζ_p in 3a(σ). The fact that 3a(σ) does not depend on ζ_p is intuitively clear since σ orbitals arise from atomic s and p_z orbitals, and since the matrix elements of spin orbit

Table 5.3. Numerical values of 3a(σ) in $(18/625)\ (\delta_n{}^T)^{-3}\ \zeta_d{}^4$

r $\beta_T{}^2$	1.2	1.6	2	5	10	12	14	16	18	20
0.2	-0.54	-0.6	-0.60	-0.34	-0.17	-0.134	-0.106	-0.088	-0.072	-0.062
0.3	-1.25	-1.14	-0.94	-0.42	-0.15	-0.100	-0.064	-0.037	-0.015	0.002
0.4	-1.85	-1.55	-1.26	-0.37	-0.03	0.058	0.103	0.138	0.165	0.187

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*See Section 5.

interaction between such pairs of atomic orbtials, automatically vanish. To put this in a more rigorous language, we will consider the part of the matrix elements of $H_p = \sum_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i$ between a pair of states of antibonding orbitals $t_a = \alpha_T|dt_2\rangle - \beta_T|\sigma t_2\rangle$. The matrix elements arising exclusively from the ligand σ orbitals have the general form of:[+]

$$M_{aa}\ (\sigma,\ m\xi,\ m'\eta') = \langle 1/2\ m\ \sigma t_2\ \xi|\zeta\ \underline{\ell}\cdot\underline{s}|1/2\ m'\ \sigma t_2\ \eta'\rangle \qquad (5.15)$$

where (Ref. 23, p. 108):

$$|\sigma t_2\ \xi\rangle = |\sigma t_2\ yz\rangle = (1/2)(\sigma_1 + \sigma_3 - \sigma_2 - \sigma_4) \qquad (5.16)$$

$$|\sigma t_2\ \eta\rangle = |\sigma t_2\ zx\rangle = (1/2)(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4) \qquad (5.17)$$

and

$$\sigma_k = a_s(k) + b\ p_z(k),\ a^2 + b^2 = 1,\ k = 1,..,\ 4 \qquad (5.18)$$

Substituting in (5.15), we find that:

$$M_{aa}\ (\sigma,\ m\xi,\ m'\eta') = (1/4)[R_1 - R_2 - R_3 + R_4]$$

where

$$R_k = a^2\ \langle 1/2\ m\ s(k)|\zeta\ \underline{\ell}\cdot\underline{s}|1/2\ m'\ s(k)\rangle + b^2\ \langle 1/2\ m\ p_z(k)|\zeta\ \underline{\ell}\cdot\underline{s}|1/2\ m'\ p_z(k)\rangle$$

resulting in

$$M_{aa}\ (\sigma,\ m\xi,\ m'\eta) = (1/4)[R - R - R + R] = 0$$

[+] ξ and η are the components of T_2 irreducible representation behaving as yz and zx.

Thus, the off-diagonal elements, M_{aa} (σ, mξ, m'η'), vanish. For diagonal elements, we have*

$$M_{aa}\ (\sigma,\ m\xi,\ m\xi) = (1/4)[R_1 + R_2 + R_3 + R_4]$$

where

$$R = b^2 \left\langle 1/2\ m\ p_z \middle| \zeta\ \underline{\ell}\cdot\underline{s} \middle| 1/2\ m'\ p_z \right\rangle = (1/2)b^2\ \zeta_p \left\langle p_z \middle| \ell_z \middle| p_z \right\rangle \delta_{mm'}$$

$$= (1/2)b^2\ \zeta_p \left\langle p \middle|\middle| \ell \middle|\middle| p \right\rangle \bar{V} \begin{pmatrix} 111 \\ 000 \end{pmatrix} \delta_{mm'} \equiv 0 \qquad (5.19)$$

Thus, we conclude that: (1) charge transfer from bonding to nonbonding σ-orbitals gives a positive contribution to 3a, (2) simultaneous bonding-nonbonding and bonding-antibonding charge transfer give a negative contribution to 3a for $\delta_a^T : \delta_n^T$ varying from 1 to 10, and (3) these contributions do not depend on ζ_p, the ligand spin orbit interaction.

5. CONTRIBUTION TO 3a FROM π-BONDING CHARGE TRANSFER STATES

The last contribution to consider is that of the π-orbitals. This was included in the calculations of 3a in the previous chapter. From (4.17) we have:

$$3a^{(4)} = 3a^{(4)}(\sigma,\pi) = \sum_{i=o}^{4} C_i\ \zeta_d^{\ 4-i}\ \zeta_p^{\ i} \qquad (5.20)$$

The above result was obtained by substituting the promotion energies, for charge transfer among various orbitals t_b, e_b, t_1, e_a and t_a of Fig. 3.1 by an average energy. To refine the above result further we consider the case of $t_1 \rightarrow e_a$ electron transfer first and then discuss the

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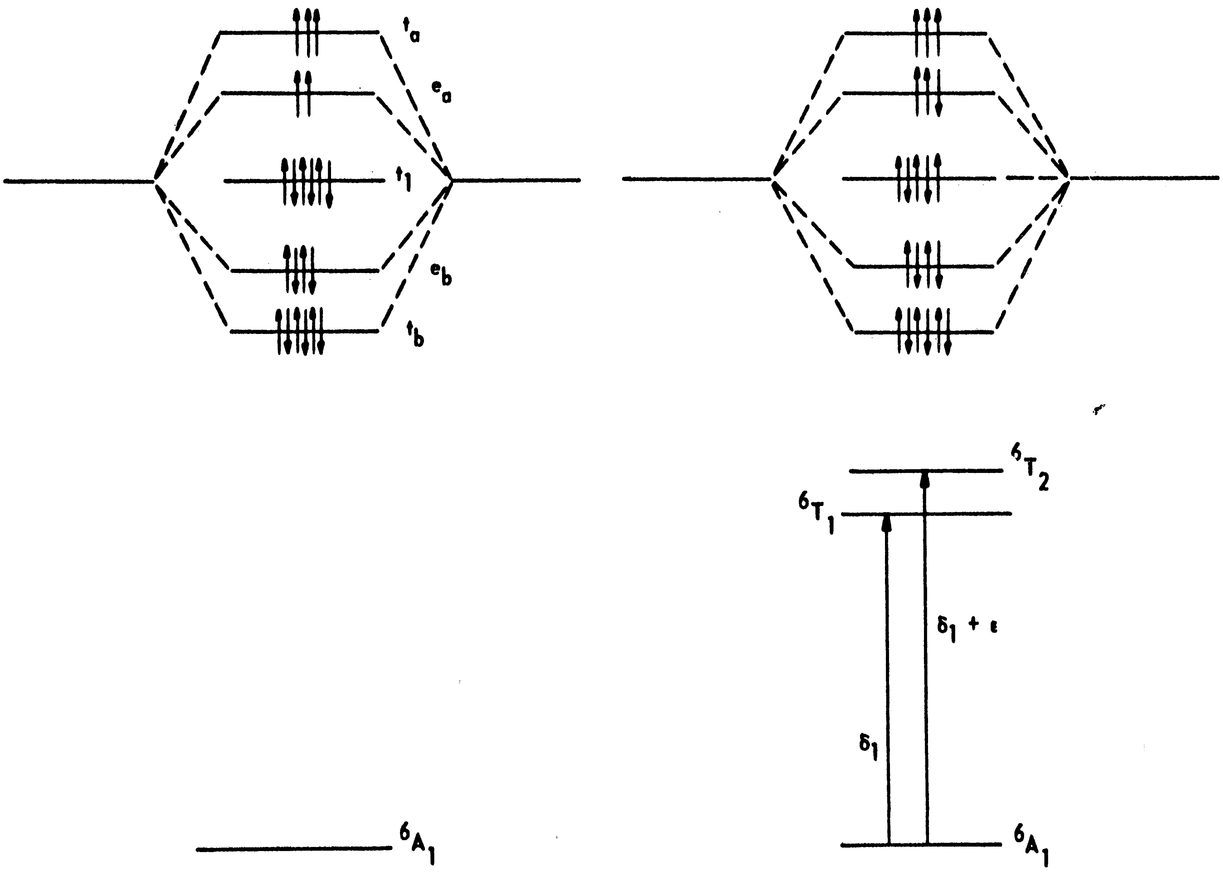
*$\bar{V} \begin{pmatrix} 111 \\ 000 \end{pmatrix}$ in (5.19) is vector coupling coefficient of two vectors.

general case where all six transfers $t_b \rightarrow e_a$, $e_b \rightarrow e_a$, $t_1 \rightarrow e_a$, $t_b \rightarrow t_a$, $e_b \rightarrow t_a$ and $t_1 \rightarrow t_a$ are taken into account.

5.1 Determination of 3a (σ,π, $t_1 \rightarrow e_a$)

The effect of $t_1 \rightarrow e_a$ charge transfer states on 3a (σ,π) will be discussed in this section. The symmetry and electronic configurations of the π-bonding molecular orbitals of $t_1 \rightarrow e_a$ charge transfer are shown in Fig. 5.3.



(a)

(b)

Fig. 5.3. Molecular orbital and energy levels of (a) the ground level $^6A_1$ and (b) the $t_1 \rightarrow e_a$ electron transfer levels $^6T_1$ and $^6T_2$

3a $(\sigma,\pi,\ t_1 \rightarrow e_a)$ can be obtained from the following relation.

$$3a\ (\sigma,\pi,\ t_1 \rightarrow e_a) = -\left[\delta_1^{\,2}\ (\delta_1 + \varepsilon)\right]^{-1} (18)^{-1}$$

$$(x)\left\{\left\langle {}^6A_1||H_p||{}^6T_1\right\rangle\left\langle {}^6T_1||H_p||{}^6T_2\right\rangle\left\langle {}^6T_2||H_p||{}^6T_1\right\rangle\left\langle {}^6T_1||H_p||{}^6A_1\right\rangle\right.$$

$$(x)\left[\sum_J K_{5/2\ J}\left|5/2\ 5/2\ T_1,\ T_2\ T_1\ U'\right| K_{J\ 5/2}\left|5/2\ 5/2\ T_1,\ T_1\ T_2\ U'\right|\right.$$

$$\left.\left. - \sum_{J'} K_{5/2\ J'}\left|5/2\ 5/2\ T_1,\ T_2\ T_1\ E''\right| K_{J'\ 5/2}\left|5/2\ 5/2\ T_1,\ T_1\ T_2\ E''\right|\right]\right\}$$

Substituting for reduced matrix elements from Tables 3.3 - 3.4, and for $K_{JJ'}$ from Tables 3.9 - 3.12 one finds,

$$3a\ (\pi,\ t_1 \rightarrow e_a) = -\left[\delta_1^{\,2}\ (\delta_1 + \varepsilon)\right]^{-1}$$

$$(x)\left[(-)\sqrt{7/5}\ (-)\sqrt{21/20}\ (+)\sqrt{21/20}\ (-)\sqrt{7/5}\ (-)\ (1/18)(128/9800)\right]$$

$$(e_at_1)(t_1e_a)(t_1t_1)(t_1t_1)$$

Substituing for e_at_1 and t_1t_1 from Table 3.13 we find

$$3a\ (\sigma,\pi;\ t_1 \rightarrow e_a) = -\ (9/1250)\ \left[\delta_1^{\,2}\ (\delta_1 + \varepsilon)\right]^{-1} \beta^2\ \zeta_p^{\,4} \qquad (5.21)$$

5.2 Determination of 3a $(\sigma,\pi;\ t_b \rightarrow e_a)$

The contribution from $t_b \rightarrow e_a$ charge transfer can be obtained in a similar fashion. The energy diagram is as shown in Fig. 5.4.

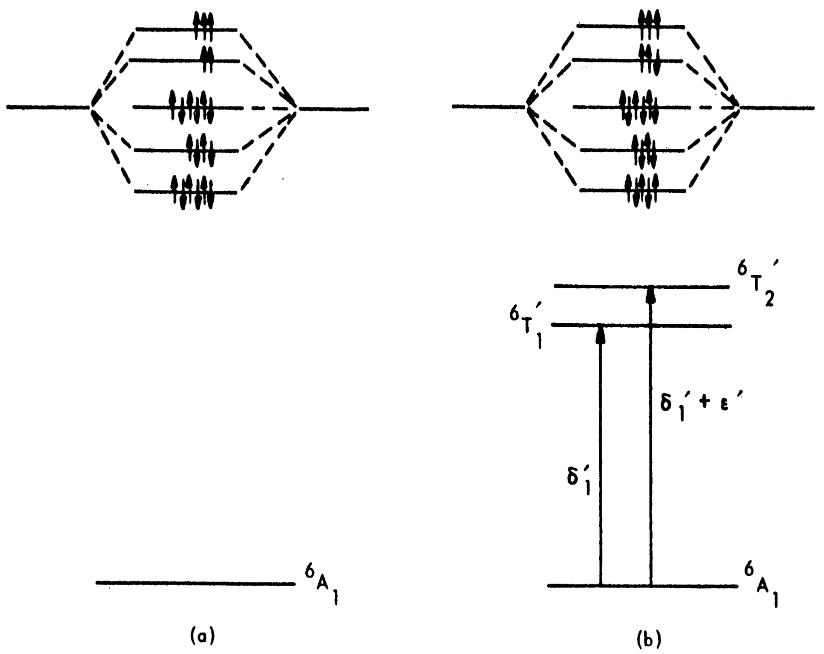


Fig. 5.4. Molecular orbital and energy levels of (a) ground level $^6A_1$ and (b) the $t_b \rightarrow e_a$ electron transfer levels $^6T_1'$ and $^6T_2'$

The effect of $^6T_1'$ and $^6T_2'$ on 3a can be written as *

$$3a(\pi,\ t_b \rightarrow e_a) = - [\delta_1'^2\ (\delta_1' + \varepsilon')]^{-1}$$

$$(x) \left\{ (-)\sqrt{7/5}\ (+)\sqrt{21/20}\ (-)\sqrt{21/20}\ (+)\sqrt{7/5}\ [(-)(1/18)(128/9800)] \right.$$

$$\left. (e_a t_b)^2 (t_b t_b)^2 \right\} \qquad (5.22)$$

Table 3.13 gives

$$e_a t_b = - 3\sqrt{2}\ \alpha\lambda\zeta_d + \sqrt{3}\ \beta\kappa\zeta_p \qquad (5.23)$$

---

* The fact that 3a (π, $t_b \rightarrow$ ea) $\equiv$ 3a(σ,π;$t_b \rightarrow e_a$) and also 3a(π) $\equiv$ 3a(σ,π) is evident from the choice of $\kappa^2 + \lambda^2 = 0.8 < 1$ in (5.26). The reason is that the only role played by σ orbitals is to reduce the coefficient of κ and λ of dt_2 and πt_2 orbitals in molecular orbitals of t_2 symmetry.

$$t_b t_b = 3\lambda^2 \ \zeta_d + 3/2\ \kappa^2 \zeta_p \tag{5.24}$$

Substituting for $e_a t_b$ and $t_b t_b$ in (5.22) one finds

$$3a(\sigma,\pi;t_b \rightarrow e_a) = (18/625)[\delta_1'^2(\delta_1' + \varepsilon')]^{-1}$$

$$(x)\Big\{6\ \alpha^2\lambda^6\zeta_d{}^4 + (6\ \alpha^2\kappa^2\lambda^4 - 2\sqrt{6}\ \alpha\beta\kappa\lambda^5)\zeta_d{}^3\zeta_p$$

$$+(3/2\alpha^2\lambda^2\kappa^4 + \beta^2\kappa^2\lambda^4)\ \zeta_d{}^2\ \zeta_p{}^2 + (\beta^2\kappa^4\lambda^2 - (3/2)^{1/2}\alpha\beta\kappa^5\lambda)$$

$$(x)\ \zeta_d\zeta_p{}^3 + (4)^{-1}\ \beta^2\kappa^6\zeta_p{}^4\Big\} \tag{5.25}$$

The numerical value of $3a(\pi,\ t_b \rightarrow e_a)$ can be obtained from following coefficients

$$\alpha^2 = 1-\beta^2 = 0.7$$

$$\kappa^2 = 0.8 - \lambda^2 = 0.6 \tag{5.26}$$

and it is found as

$$3a(\sigma,\pi;t_b \rightarrow e_a) =$$

$$\Big[(18/625)(\delta_1'^2)\Big|\delta_1' + \varepsilon_1')\Big|\Big]^{-1}\Big[.034\ \zeta_d{}^4 + .0674\zeta_d{}^3\zeta_p$$

$$+\ .0827\ \zeta_d{}^2\zeta_p{}^2 - \ .0487\ \zeta_d\zeta_p{}^3 + \ .0251\zeta_p{}^4\Big] \tag{5.27}$$

5.3 Determination of Total $3a(\sigma,\pi)$

The $3a(\sigma,\pi)$ representing the effect of all charge transfer states of transfers $t_b \to e_a$, $e_b \to e_a$, $t_1 \to e_a$, and $t_b \to t_a$, $e_b \to t_a$ and $t_1 \to t_a$, can be expressed as (4.6):

$$3a(\sigma,\pi) = 3a^{(4)} = \sum_{i=o}^{4} C_i \, \zeta_d^{\,4-i} \zeta_p^{\,i} \tag{5.28}$$

where C_i are functions of $\alpha,\beta,\kappa,\lambda$ and the charge transfer energies such as δ_1 and δ_1' in (5.21) and (5.27).

The numerical values of the coefficients C_i are calculated for $\alpha^2,\beta^2,\kappa^2,\lambda^2$ as in (5.26) and for

$$\delta_1 = \delta_1 + \varepsilon \sim \delta_1' = E_6$$

The results, given in Table 4.1, and 4.2 indicate that

$$3a^{(4)}>0$$

$$\zeta_p/\zeta_d \leq 2 \tag{5.29}$$

and

$$3a^{(4)} <0$$

$$\zeta_p/\zeta_d \geq 3 \tag{5.30}$$

For ligands 0^{--} and S^{--} and S-state ions Mn^{2+} or Fe^{3+} the $\zeta_p/\zeta_d \leq 2$ holds and consequently

$$3a(\pi,0^{--}),\quad 3a(\pi,S^{--}) > 0 \tag{5.31}$$

whereas for Se^{--} and Te^{--} the condition $\zeta_p/\zeta_d \geq 3$ applies and one concludes that

$$3a(\pi,\ Se^{--}),\ 3a(\pi,\ Te^{--}) < 0 \qquad (5.32)$$

Comparing sections 4 and 5 one concludes that (1) in both σ- and π-bonding schemes $t_2 \rightarrow e$ charge transfer gives a positive contribution to 3a, (2) $t_2^b \rightarrow e$ charge transfer seems to be the most probable in σ-bonding scheme whereas the $t_1 \rightarrow e$ transfer seems to be the most probable in π-bonding scheme and gives a negative contribution to $3a(\pi)$ and (3) the $3a(\sigma)$, for an average charge transfer energy*$E_6(\sigma)$ is negative whereas $3a(\pi)$, under similar condition is positive if $\zeta_p/\zeta_d \leq 2$.

Now we proceed to the next section for comparison of $(3a)_w$, $(3a)_p$, $3a(\sigma)$ and $3a(\pi)$.†

6. COMPARISON

The five separate calculations given in Sections 1 through 5 can be compared now. To simplify this comparison we ignore the effects of spin-spin interaction on 3a which appear as small corrections in calculations of Watanabe and those of Powell. This enables us to describe their results as functions of ζ_d^4 and $(Dq)^n$. The result is

$$(3a)_W = K_w\ \zeta_d^4 (Dq)^2$$

$$(3a)_P = K_P\ \zeta_d^4 (Dq)^n \qquad 3.5 < n < 6$$

$$3a(\sigma) = K_\sigma\ \zeta_d^4$$

$$3a(\sigma,\pi) = \sum_{i=0}^{4} C_i\ \zeta_d^{4-i}\ \zeta_p^{i} \qquad (5.33)$$

---

*Let δ_a^T: $\delta_n^T = r = 1$ in (5.11)

†$3a(\pi) \equiv 3a(\sigma,\pi)$

where $(3a)_W$ and $(3a)_P$ are contributions to 3a from calculations by Watanabe[5] and by Powell[6], respectively, and $3a(\sigma)$ and $3a(\sigma,\pi)$ in (5.33) are contributions from charge transfer excited states. Since $(3a)_P$ results from spin doublets and quartets of $3d^5$ manifold, whereas $(3a)_W$ results from spin quartets alone, one immediately concludes that $(3a)_W$ is included in $(3a)_P$:

$$(3a)_W \subset (3a)_P \tag{5.34}$$

In a similar fashion*

$$3a(\sigma) \subset 3a(\sigma,\pi) \tag{5.35}$$

Therefore, the total contribution from spin multiplets within $3d^5$ manifold and charge transfer states is

$$(3a)_P + 3a(\sigma,\pi) \tag{5.36}$$

The experimentally measured 3a can be affected by spin quartets and doublets which arise as a result of charge transfer. In this case, 3a can be written as

$$3a = (3a)_P + 3a(\sigma,\pi) + (3a)_r \tag{5.37}$$

where $(3a)_r$ represents the rest of terms ignored in the evaluation of $3a(\sigma,\pi)$.

7. COMPARISON WITH MEASURED 3a OF Fe^{3+} IN ZnS, ZnSe AND ZnTe

We want to compare the measured 3a of Fe^{3+} in Zns, ZnSe and ZnTe with 3a in (5.37) on the assumption that $(3a)_r = 0$.

The measured 3a of Fe^{3+} for above compounds are given in Table 2-2 and are repeated here in Table 5-4.

---

*$3a(\sigma,\pi) = 3a(\pi)$ [See the footnote to Eq. (5.26)]

TABLE 5.4

Measured[†] 3a of Fe^{3+} in 10^{-4} cm^{-1}

ZnS	ZnSe	ZnTe
384	144.9	-7800

[†] Reference 27

To find the contribution $(3a)_P$ to the measured 3a values in Table 5-4 we assume: (i) that the measured 3a of Fe^{3+} in ZnS arises completely from $(3a)_P$, (ii) the power n in $(Dq)^n$ of the expression*

$$(3a)_P = K_P \zeta_d^{\,4} (Dq)^n$$

is equal to 4 and (iii) (Dq) is proportional to inverse fifth power of interionic distance R. With these assumptions, the ratios of $(3a)_P$ of Fe^{3+} in ZnS, ZnSe and ZnTe can be obtained as follows:

$$(3a)_P(\text{ZnS}) : (3a)_P(\text{ZnSe}) : (3a)_P(\text{ZnTe}) = 10.1{:}5.3{:}1. \qquad (5.38)$$

The $(3a)_P$ obtained from (5.38) are given in Table 5.5.

---

*K_P, in $(3a)_P = K_P \zeta_d^{4} (Dq)^n$, depends on several parameters such as Racah coefficients B and C. For simplicity, however, both this and ζ_d are assumed to remain constant in three compounds ZnS, ZnSe and ZnTe.

TABLE 5.5

Estimated $(3a)_p$ for Fe^{3+} in 10^{-4} cm^{-1}

ZnS	ZnSe	ZnTe
384	204	38

The contribution $3a(\sigma,\pi)$ can be obtained for the appropriate values of ζ_p/ζ_d. The ζ_d* for Fe is 0.049 e.v. and ζ_p† for S, Se and Te are 0.06, 0.35 and 0.9 e.v., respectively. Thus, the ζ_p/ζ_d ratios are 1.09, 6.4 and 16.4 for Fe^{3+} in the three compounds ZnS, ZnSe and ZnTe respectively. The $3a(\sigma,\pi^{§})$ at these ratios of ζ_p/ζ_d and for $\zeta_d = 0.049$ e.v. and $E_6 = 4$ e.v. is obtained from Table 4.2 as given in Table 5-6.

The sum of $(3a)_p$ and $3a(\sigma,\pi)$ is given in Table 5-7.

---

*Ref. 16, p. 431, (ζ_d of Fe^0 is chosen instead of ζ_d of Fe^{3+} because the effective charge of Fe in ZnSe and ZnTe is expected to be close to zero).

†J. Dimmock et al "Band Structure of PbS, PbSe and PbTe," Phys. Rev. 135, A824(1964).

§

$$3a^{(4)} = \sum_{i=0}^{4} C_i \zeta_d^{4-i} \zeta_p^{i}$$

Table 5.6. Calculated $3a(\sigma,\pi)$ of Fe^{3+}

	ZnS	ZnSe	ZnTe
ζ_p/ζ_d	1.09	6.4	16.4
$3a(\sigma,\pi)$ $(10^{-4}cm^{-1})$	0.564	-141.0	-6620

Table 5.7. Measured and calculated values of 3a of Fe^{3+}

	ZnS	ZnSe	ZnTe
$(3a)_p+3a(\sigma,\pi)$ (in $10^{-4}cm^{-1}$)	384.56	63	-6582
$(3a)_{Exp.}$ $(10^{-4}cm^{-1})$	384	144.9	-7800†

A comparison of the calculated and measured 3a indicates that a ligand to metal charge transfer process is capable of accounting for the variation of 3a of the Fe^{3+} in the series of ZnS, ZnSe and ZnTe compounds. A detailed examination of the coefficient C_4 of ζ_p^4 in the expression of $3a^{(4)}$ in (4.6)* indicates that the sign of this coefficient is insensitive to coefficients of the linear combination of atomic orbitals α,β,κ and λ in the molecular orbitals, whereas the coefficients of $\zeta_d^4 \ldots \zeta_d\zeta_p^3$ are the sum of almost equal number of positive and negative terms. With small variations in such terms the sign and magnitude of these coefficients will change.

Therefore, the spin sextet and ligand to metal charge transfer approximations are valid for metals of higher formal valency and ligands for which $\zeta_p/\zeta_d \sim 10$. ZnTe:Fe^{3+} meets both of these requirements. Hence, the agreement found should not be surprising.

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*See the footnote § on the preceding page

†See Ref. 27

In addition to Fe^{3+} discussed above Cr^{+} and Mn^{2+}, the other two S-state ions of $3d^5$ configuration, deserve a brief discussion. In case of these two ions, in addition to the ligand to metal charge transfer process, employed for Fe^{3+}, another charge transfer should be taken into account. This latter charge transfer permits the transfer of an electron from the antibonding orbitals* t_a and e_a to the higher lying antibonding orbitals localized in the vicinity of the next nearest neighbor metal ions such as Mn→Zn charge transfer in ZnTe:Mn. For brevity, this is called the outgoing charge transfer whereas the former one is called the incoming charge transfer. The matrix elements arising from such processes can be obtained from general expressions given in Chapter III with slight modifications. The evaluation of charge transfer energies, however, would involve the next nearest ions Zn and Cd in (Zn, Cd) (S, Se, Te) compounds and more caution is needed for a correct assessment of such energies. The extension of present theory to these two ions has to be deferred to a later time when more accurate charge transfer energies are available.

8. COMPARISON OF $3(\sigma,\pi)$ OF T_d AND O_h CASES

Considering Table 5-6 one finds that both the absolute value and the sign of 3a is determined by the presence of ζ_p in the expression of $3a(\sigma,\pi) = \sum_{i=0}^{4} C_i \zeta_d^{4-i} \zeta_p^{i}$. A question arises on the nature of the role of ζ_p in $3a(\sigma,\pi)$ of Fe^{3+} in compounds of O_h symmetry.

Before considering the above question it is worthwhile to give a brief remark on the 3a in T_d case. Recalling (5.37) the total expression of the 3a is

$$3a = (3a)_p + 3a(\sigma,\pi) + (3a)_r \tag{5.39}$$

---

*The orbitals t_a and e_a are the half filled orbitals which are localized near the S-state ion and in ionic case form the components of the d orbitals of the S-state ions.

where $(3a)_P$ is given in Table 5.1 and $3a(\sigma,\Pi)$ and $(3a)_r$ can be expressed as

$$3a(\sigma,\Pi) = -\left(\sum_{klm} E_k E_l E_m\right)^{-1} \left\{ [M_{0k}^{ss} M_{kl}^{ss} M_{lm}^{ss} M_{m0}^{ss}]_{U'} - [M_{0k}^{ss} M_{kl}^{ss} M_{lm}^{ss} M_{m0}^{ss}]_{E''} \right\} \tag{5.40}$$

and

$$\begin{aligned} 3a_r = -\Bigg\{ & \sum_{klm'} \left(E_k E_l E_{m'}\right)^{-1} \left[\left(M_{0k}^{ss} M_{kl}^{ss} M_{lm'}^{sq} M_{m'0}^{qs}\right)_{U'} - \left(M_{0k}^{ss} M_{kl}^{ss} M_{lm'}^{sq} M_{m'0}^{qs}\right)_{E''} \right] \\ & + \sum_{kl'm'} \left(E_k E_{l'} E_{m'}\right)^{-1} \left[\left(M_{0k}^{ss} M_{kl'}^{sq} M_{l'm'}^{qq} M_{m'0}^{qs}\right)_{U'} - \left(M_{0k}^{ss} M_{kl'}^{sq} M_{l'm'}^{qq} M_{m'0}^{qs}\right)_{E''} \right] \\ & + \sum_{k'l'm'} \left(E_{k'} E_{l'} E_{m'}\right)^{-1} \left[\left(M_{0k'}^{sq} M_{k'l'}^{qq} M_{l'm'}^{qq} M_{m'0}^{qs}\right)_{U'} - \left(M_{0k'}^{sq} M_{k'l'}^{qq} M_{l'm'}^{qq} M_{m'0}^{qs}\right)_{E''} \right] \\ & + \sum_{k'l''m'} \left(E_{k'} E_{l''} E_{m'}\right)^{-1} \left[\left(M_{0k'}^{sq} M_{k'l''}^{qd} M_{l''m'}^{dq} M_{m'0}^{qs}\right)_{U'} - \left(M_{0k'}^{sq} M_{k'l''}^{qd} M_{l''m'}^{dq} M_{m'0}^{qs}\right)_{E''} \right] \Bigg\} \end{aligned} \tag{5.41}$$

The M_{0k}^{ss}, M_{kl}^{sq}, ---- $M_{l'm'}^{dq}$ in (5.41) are the matrix element of $H_p = \sum_i \zeta_i \underline{l}^i \cdot \underline{s}^i$ and the superscripts s, q and d refer to the spin sextet, quartet and doublet, respectively and E_n, $E_{n'}$ and $E_{n''}$ (n = k, l, m) refer to energies of these states.

An important distinction between II-VI compounds of O_h and T_d symmetries lies in the fact that the band gap energies in the former case varies from* 4-8 e.v. whereas in the latter case it varies from 0.02-3.7 e.v. Therefore it is probable that the energies of quartets, $E_{n'}$, and doublets, $E_{n''}$, are below 8 e.v. and as a result of this the spin quartets or doublets can be localized around the complexes of O_h symmetry. Thus an a priori omission of $(3a)_r$ does not seem to be a reliable approximation for the O_h case. Another obstacle, in the O_h case is lack of experimental information on 3a of Fe^{3+} in such compounds as SrSe or SrTe where ζ_p becomes significant. Therefore it is impossible to assess the contribution to $3a(\sigma,\pi)$ in the ocathedral case. In the case of Fe^{3+} in the tetrahedral compounds, such as CdTe or ZnTe where the energy band gaps are, respectively, 1.5 and 2.1 e.v., it is possible to assume that none of the charge transfer spin quartets are localized. As a result of this the $(3a)_r$ may be ignored and only $3a(\sigma,\pi)$ taken into account. In case of ZnTe:Mn^{2+} where $(3a)_{exp.} > 0$ one may conjecture that the charge transfer spin quartets also contribute to $3a(\sigma,\pi)$ as well as spin sextets of outgoing charge transfer process referred to in section 7.

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*See R. Bube, "Photoconductivity of Solids" John Wiley and Sons, Incorporated, New York, (1960) p. 233

CHAPTER VI

SUMMARY AND CONCLUSIONS

1. SUMMARY

A calculation of cubic field splitting of S-state ions in II-VI compounds was planned. To achieve this, the following steps were taken:

(1) Molecular orbital techniques were employed to construct the excited states of complexes $(\Sigma\Lambda_4)^{-n'}$ with Σ as the S-state ion and Λ as O, S, Se or Te.

(2) A ligand to metal electron transfer process was taken into account and the excited states arising from such phenomenon were constructed with σ and π ligand orbitals.

(3) The cubic field splitting 3a was expressed as the lowest order splitting of the spinor levels U' and E'' (Mulliken's notation) of the ground state as a result of perturbation by excited states through the spin orbit Hamiltonian,

$$H_p = \sum_i \zeta_i \, \underline{\ell}^i \cdot \underline{s}^i$$

(4) Utilizing group theory arguments, it was established that (a), the lowest order perturbation, was four and (b), at this order of perturbation the contribution to 3a arises exclusively from the two groups of three excited states having symmetries of T_1, E, T_1 or T_1, T_2, T_1 respectively.

(5) Utilizing reduced matrix techniques the matrix elements of H_p between any pair of states

$$|ik\rangle = |\chi_i \; S_i \; h_i \; J_k \; t \; \tau\rangle$$

and

$$|j\ell\rangle = |\chi_j \; S_j \; h_j \; J_\ell \; t \; \tau\rangle$$

was obtained in terms of the reduced matrix elements R_{ij} and the coupling coefficients $K_{k\ell}$ as follows:

$$\left\langle \chi_i\ S_i\ h_i\ J_k\ t\ \tau\ |H_p|\ \chi_j\ S_j\ h_j\ t\ \tau \right\rangle = \left\langle \chi_i\ S_i\ h_i || H_p || \chi_j\ S_j\ h_j\ \ K_{k\ell} \right\rangle$$

$$= R_{ij}\ K_{k\ell}$$

where

$$R_{ij} = \left\langle \chi_i\ S_i\ h_i || H_p || \chi_j\ S_j\ h_j \right\rangle$$

and

$$K_{k\ell} = K_{J_k J_\ell}\ (S_i\ S_j\ T_1,\ h_j\ h_i\ t)$$

and $|J\ t\tau >$ is the component of the irreducible representation of angular momentum J in the cubic point group as defined by Griffith[16] (p. 395).*

(6) 3a was obtained as a sum of the products of the four matrix elements:

$$\left\langle \chi_o\ {}^6A_1\ 5/2\ t\tau | H_p | \chi_i\ S_i\ T_1\ J_\ell\ t\tau \right\rangle$$

$$\left\langle \chi_i\ S_i\ T_1\ J_\ell\ t\tau | H_p | \chi_j\ S_j\ h_j\ J_m\ t\tau \right\rangle \qquad h_j = E \text{ or } T_2$$

$$\left\langle \chi_j\ S_j\ h_j\ J_m\ t\tau | H_p | \chi_k\ S_k\ T_1\ J_n\ t\tau \right\rangle$$

and

$$\left\langle \chi_k\ S_k\ T_1\ J_n\ t\tau | H_p | \chi_o\ {}^6A_1\ 5/2\ t\tau \right\rangle$$

---

*For example $\left|5/2\ U'\nu\right\rangle = \sqrt{1/6}\ [\sqrt{5}\ \left|5/2\ 5/2\right\rangle + \left|5/2\ 3/2\right\rangle]$

with χ_i .... χ_k representing various electronic configurations giving rise to S_i T_1 .... S_k T_1.

(7) The numerical values of the 3a of Fe^{3+} in Zn(S, Se, Te) compounds was obtained with restrictions of

$$S_i = S_j = S_k = 5/2$$

$$E_i = E_j = E_k = E_6$$

and ζ_d and ζ_p as the spin orbit constants of metal and ligand orbitals. For appropriate values of ζ for Fe, S, Se and Te, and with 32,000 cm^{-1} for E_6 it was found that the calculated 3a accounts satisfactorily for the difference between measured values and the ionic contributions to the 3a of Fe^{3+} in the compounds ZnS, ZnSe and ZnTe.

2. CONCLUSIONS

Most of the conclusions drawn from this study concern the effect of charge transfer states on the cubic field splitting 3a of S-state ions in II-VI compounds with tetrahedral symmetry. These conclusions are classified as follows:

(1) The cubic field splitting 3a of S-state ions in covalent II-VI compounds of tetrahedral symmetry depends strongly on the excited states arising from charge transfer from ligand π orbitals to metal d-orbitals.

(2) The effect of these π orbitals is relatively insensitive to the choice of promotion energies and coefficients of linear combinations of atomic orbitals.

(3) To refine present theory, it is necessary to establish (a), the energy levels beyond which excited states are no longer localized, (b), the perturbation order beyond which the contribution to the initial splitting 3a is negligible, and (c), a search for a few parameters characteristic of charge transfer state energies.

(4) To verify the predictions of this theory with experiments, it is desirable to (a) determine the sign of the 3a of Cr^{+}, Mn^{2+} and Fe^{3+} wherever it is in doubt, (b) prepare single crystals of (Mg, Ca, Sr) (Se, Te) which have ocathedral symmetry and to measure the 3a of S-state ions, particularly Fe^{3+} in such compounds.

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APPENDIX A

DEFINITION OF SYMBOLS

The frequently occurring symbols, in both the Latin and Greek alphabet, are defined in Table A1 of this Appendix. The former group of symbols is given first and then the latter one.

TABLE A-1
DEFINITION OF SYMBOLS

$^6A_1$	Term designation of a state of space irreducible representation, A_1, and spin $S = 5/2$.
3a	The cubic crystalline field splitting of a 6S level.
C_i	Numerical coefficients of the expression for the charge transfer contribution.
$\mathcal{D}_i$	Square root of the product of dimensions of space and spin representations h_i and S_i of a state $\|S_ih_i\rangle$. Thus, for a state $\|S_ih_i\rangle = \|5/2\ T_i\rangle$ one has $\mathcal{D}_i = [(2S_i + 1)(h_i)]^{1/2} = [(6)(3)]^{1/2} = [18]^{1/2}$.
E''	An irreducible representation of cubic double group as defined in Table 3-1.
e_a	Antibonding molecular orbital of symmetry E (Table 3.1).
e_b	Bonding molecular orbital of symmetry E (Table 3.1).
E(U')	The lowest energy value of levels of symmetry U' (Table 3.1)
E(e'')	The lowest energy value of levels of symmetry E'' (Table 3.1)
E_{jk}	The energy difference of states 1j and 1k: $E_{jk} = E_k - E_j$.
E_j	The energy of state 1j from that of ground state: $E_j = E_j - E_o$.
H_p	Perturbation Hamiltonian: $H_p = \Sigma_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i = \sum_{\kappa} su(\kappa)$
h	An irreducible representation of single valued cubic group.

	An identifying number of the irreducible representation resulting from the coupling of spin S and the irreducible representation h of a state $\|Sh\rangle$ such as $U'_J = U'_{3/2}$ of the state $\|5/2\ T_1\rangle$, and $U'_J = U'_2$ of the state $\|5/2\ E\rangle$. In the case of h = T_1, T_2 the index J behaves as total angular momentum associated with Russel Saunders level $\|SL\rangle = \|SL = 1\rangle$ whereas for h = A_2, E it is a designating number.
$K_{JJ}'(SS'T_1,h'ht)$	Spin-orbit matrix element coupling coefficient between states $\|ShJt\tau\rangle$ and $\|S'h'J't\tau\rangle$.
M	Magnetic quantum number associated with spin S.
MO	Molecular orbital.
IR	Irreducible representation.
$\underline{S}$	Total spin associated with a total level or its sublevels.
$\underline{s}$	Single electron spin operator.
t	An irreducible representation in the cubic double group of the coupling, the spin S, and space irreducible representation h of a given state $\|Sh\rangle$ such as U' of $\|5/2\ T_1\rangle$.
t_a	Antibonding orbital of symmetry T_2 (Table 3.1)
t_b	Bonding orbital of symmetry T_2 (Table 3.1)
t_1	Non-bonding molecular orbital of symmetry T_1.
U'	An irreducible representation of cubic double group (Table 3.1)
$V(abc,\alpha\beta\gamma)$	Coupling coefficient of the components α and β of the irreducible representations a and b into the γ component of the irreducible representation c such as V $(ET_1T_2\theta x\xi) = 1/2$. The components Θ, x, ξ of the

	representations E, T_1, T_2 ... and their symmetry properties are defined in Table A.16 of Ref. 16.
$\bar{V}$ (abc,$\phi\beta\gamma$)	Coupling of ϕ and β components of spins a and b into γ components of spin c such as $\bar{V}$ (5/2 5/2 1, 1/2 -1/2 0) = $(1/210)^{1/2}$. Tables of $\bar{V}$ are given by Rotenberg <u>et</u> <u>al</u>. (Ref. 26 footnote of p. 86).
W(abc,def)	An invariant product of four coefficients V(abk,$\phi\beta\gamma$) ...defined as W(abc,def) = $\Sigma\alpha\beta\gamma\delta\epsilon\phi$ V(abc,$\alpha\beta\gamma$). V(aef,$\alpha\epsilon\phi$) $\cdot$ V(bfd,$\beta\phi\delta$) $\cdot$ V(cde,$\gamma\delta\epsilon$). The tables of coefficients W (abc,def) are given by Griffith (Ref. 26 p. 114)
$\bar{W}$(abc,def)	An invariant product of four coefficients $\bar{V}$(abc,$\alpha\beta\gamma$) ...defined as $\bar{W}$(abc,def) = $\Sigma\alpha\beta\gamma\delta\epsilon\phi$ (x) $(-1)^{a-\alpha+b-\beta+c-\gamma+d-\delta+e-\epsilon+f-\phi}$ $\bar{V}$(abc,$\alpha\beta\gamma$) (x) $\cdot$ $\bar{V}$(aef,$\alpha\epsilon\phi$) $\cdot$ $\bar{V}$(bfd,$\beta\phi\delta$) $\cdot$ $\bar{V}$(cde,$\gamma\delta\epsilon$). Values of $\bar{W}$ are the same as the 6-J symbols corresponding to a, b, ... ,f and the latter are given by Rotenberg <u>et</u> <u>al</u>. (Ref. 26 footnote of p. 86).
$\mathcal{W}(N_iN_jN_o,N_kN_lN_m)$	Product of a W and $\bar{W}$ coefficient as $\mathcal{W}(N_iN_jN_o,N_kN_lN_m)$ = $\bar{W}$ $(S_iS_j1,S_kS_lS_m)$ (x) W $(h_ih_jT_1,h_kh_lh_m)$.
X(abc,def,ghk)	An invariant sum of the products of six coefficients V(abc,$\alpha\beta\gamma$), ... V(cfk,$\gamma\phi\kappa$) expressed as X (abc,def,ghk) = $\Sigma\alpha\beta\gamma\delta\epsilon\phi\eta\theta\kappa$ V(abc,$\alpha\beta\gamma$). (x) V(def,$\delta\epsilon\phi$) $\cdot$ V(ghk,$\eta\theta\kappa$) $\cdot$ V(adg,$\alpha\delta\eta$) $\cdot$ V(beh,$\beta\epsilon\theta$) (x) V(cfk,$\gamma\phi\kappa$). These X coefficients are defined by Griffith (Ref. 26).

$\bar{X}(abc,def,ghk)$	This is similar to $X(abc,def,ghk)$ defined above except instead of $V(abc,\alpha\beta\gamma)$, one takes $\bar{V}(abc,\alpha\beta\gamma)$. Thus $\bar{X}(abc,def,ghk) = \Sigma_{\alpha\beta\gamma\delta\varepsilon\phi\eta\theta\kappa}\ \bar{V}(abc,\alpha\beta\gamma)$. (x) $V(def,\delta\epsilon\phi) \cdot \bar{V}(ghk,\eta\theta\kappa)\ \ldots\ldots\ \bar{V}(cfk,\gamma\varepsilon\kappa)$. The coefficients X are given by Howell (Ref. 26 footnote p. 86)
$\mathcal{X}(N_iN_jN_k,N_i'N_j'N_k',N_aN_bN_o)$	Product of coefficients $\bar{X}$ and X related to $N_iN_jN_k$, $N_i'N_j'N_k'$, $N_aN_bN_o$ as follows: $\mathcal{X}(N_iN_jN_k,N_i'N_j'N_k',N_aN_bN_o) = \bar{X}(S_iS_jS_k,S_i'S_j'S_k',S_aS_b1) \cdot X(h_ih_jh_k,h_i'h_j'h_k',h_ah_bT_1)$.
Λ	The ligands surrounding the metal ion of II-VI compounds such as S^{--}, Se^{--} and Te^{--}.
Σ	The S-state ion substituting the metal ion of a II-VI compound such as Mn^{2+} in Zn site of ZnS single crystals.
$(\Sigma\Lambda_4)^{-n'}$	A complex formed of an S-state ion and its four nearest neighbors, with a formal negative charge of n'. For $\Sigma = Cr^+$, Mn^{2+} or Fe^{3+} the number n' is, 7, 6 or 5 respectively.
ζ_i	Single electron spin orbit inter-action of an electron in the ith orbitals.
ζ_d	ζ_d of a d orbital of the S-state ion.
ζ_p	ζ_p of a p orbital of the ligands S, Se or Te.
τ	Component of t denoting an irreducible representation of the cubic double group. The properties of these components are given by Griffith (Ref. 16).
χ'	Electron configuration of five orbitals t_a, e_a, t_1, e_b and t_b as defined in (3.8a).
χ	Hole configuration of the five orbitals t_a, e_a, t_1, e_b and t_b as defined in (3.8b).

$\|\chi Shjt\tau\rangle$	τ component of Jth irreducible representation t arising from coupling of spin S and space irreducible representation h of the state $\|Sh\rangle$ belonging to the χ configuration.
$\langle\chi Sh\|\|H_p\|\|\chi'S'h'\rangle$	Reduced matrix element of H_p between states $\|\chi Sh\rangle$ and $\|\chi'S'h'\rangle$.

APPENDIX B

SPIN ORBIT COUPLING IN MO SCHEME

This Appendix gives the appropriate form of the spin orbit interaction Hamiltonian H_{SO} in the molecular orbital (MO) scheme. The expression of H_{SO} for an n electron system is*

$$H_{SO} = \frac{\beta e}{mc} \left[\Sigma_\alpha Z_\alpha r_{i\alpha}^{-3} (\underline{r}^i \times \underline{p}^i) \cdot \underline{s}^i - \sum_{i \neq j} r_{ij}^{-3} (\underline{r}^{ij} \times \underline{p}^i) \cdot (\underline{s}^i + 2\underline{s}^j) \right] \quad \text{(B1)}$$

where α refers to all nuclei; $r_{i\alpha}$ is the distance between electron i and nucleus α, Z_α is the charge of nucleus α; i and j refer to all electrons in the complex and the remaining parameter have their usual meanings. The first sum in (B1) gives the spin orbit interaction of each electron in the Coulomb field of all the nuclei in the complex whereas the second sum describes the interaction of each electron in the field of the other electrons and also the coupling of each spin with the orbital magnetic moment of the other electrons (spin-other-orbit interaction). The H_{SO} can be rewritten as:

$$H_{SO} = \Sigma_{i\alpha} H_{i\alpha} - \Sigma_{i \neq j} H_{ij} \quad \text{(B2)}$$

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*H. A. Bethe and E. E. Salpeter, Quantum Mechanics of One and Two Electron Atoms (Springer - Verlag, Berlin, 1957), p. 181.

where

$$H_i = (\beta e/mc)\ Z_\alpha\ r_{i\alpha}^{-3}\ (\underline{r}^i \times \underline{p}^i) \cdot \underline{s}^i = \xi_\alpha\ (r_{i\alpha})\ \underline{\ell}^{i\alpha} \cdot \underline{s}^i \qquad \text{(B3)}$$

and

$$H_{ij} = \beta e (mc)^{-1}\ r_{ij}^{-3}\ (\underline{r}^{ij} \times \underline{p}^i) \cdot (\underline{s}^i + 2\underline{s}^j) \qquad \text{(B4)}$$

Misetich and Buch+ have shown that for the molecular orbital wavefunctions ψ_o and ψ_n related to symmetry wavefunctions ϕ_o and ϕ_n of a given term of the free central ion of the complex, one has

$$\left\langle \psi_o \middle| H_{SO} \middle| \psi_n \right\rangle = \left\langle \psi_o \middle| \Sigma_i{}'\ \xi_c\ (r_{ic})\ \underline{\ell}^{ic} \cdot \underline{s}^i + \Sigma'_{i,L}\ \xi_L\ (r_{iL})\ \underline{\ell}^i \cdot \underline{s}^i \middle| \psi_n \right\rangle \qquad \text{(B5)}$$

The parameters $\xi_c\ (r_{ic})$ and $\xi_L\ (r_{cL})$ in (B5) give the spin orbit constants ζ_c and ζ_L after being integrated over r_{ic} and r_{iL} respectively except for the fact that their numerical values depend on the coefficients of linear combination of atomic orbitals used.

In the general case where the MO wavefunctions ψ_o and ψ_n cannot be related directly to free ion such as the charge transfer states in a complex $[\Sigma\ \Lambda_4]^{-n'}$, the spin orbit interaction can be considered in a slightly different way. Considering (B1) - (B4) and denoting the single electron spin orbit interaction by $H_{SO}(i)$, one has:

$$H_{SO}(i) = \Sigma_\alpha\ H_{i\alpha} - \sum_{j\ (\neq i)} H_{ij} = \Sigma_\alpha\ \xi_\alpha\ (r_{i\alpha})\ \underline{\ell}^{i\alpha} \cdot \underline{s}^i - \sum_{j (\neq i)} H_{ij}$$

$$= \xi_c\ (r_{ic})\ \underline{\ell}^{ic} \cdot \underline{s}^i + \Sigma_L\ \xi_L\ (r_{iL})\ \underline{\ell}^{iL} \cdot \underline{s}^i - \sum_{j\ (\neq i)} H_{ij} \qquad \text{(B6)}$$

+A. A. Misetich and T. Buch, "Gyromagnetic Factors and Spin-Orbit Coupling in Ligand Field Theory," J. Chem. Phys. <u>41</u>, 2524 (1964).

where the parameters c and L denote central and ligand ions respectively.

The matrix element of $H_{SO}(i)$ between the ground state ψ_o and an excited state of the system ψ_n is

$$\left\langle \psi_o \middle| H_{SO}(i) \middle| \psi_n \right\rangle = \left\langle i \middle| H_{ic} + \Sigma_L H_{iL} \middle| i' \right\rangle - \sum_{j\,(\neq i)} \left\langle ij \middle| H_{ij} \middle| i'j \right\rangle \tag{B7}$$

The single orbital wavefunctions i and j can be described as

$$\left| i \right\rangle = \kappa_i \left| i_c \right\rangle - \lambda_i \left| i_L \right\rangle \tag{B8}$$

$$\left| j \right\rangle = \kappa_j \left| j_c \right\rangle - \lambda_j \left| j_L \right\rangle \tag{B9}$$

where

$$\kappa_i^{\,2} + \lambda_i^{\,2} = 1 \tag{B10}$$

Substituting in (B7) one finds:

$$\begin{aligned}\left\langle \psi_o \middle| H_{SO}(i) \middle| \psi_n \right\rangle &= \kappa_i \kappa'_i \left\langle i_c \middle| H_{ic} \middle| i'_c \right\rangle + \lambda_i \lambda'_i \left\langle i_L \middle| \Sigma_L H_{Li} \middle| i'_L \right\rangle \\ &\quad - \Sigma_j \kappa_i \kappa'_i \left\langle i_c j_c \middle| \kappa_j^{\,2} H_{ij} \middle| i'_c j_c \right\rangle \\ &\quad - \Sigma_j \lambda_i \lambda'_i \left\langle i_L j_L \middle| \lambda_j^{\,2} H_{ij} \middle| i_L j_L \right\rangle \\ &= \kappa_i \kappa'_i \left\langle i_c \middle| H_{ic} - \Sigma'_j \left\langle j_c \middle| \kappa_j^{\,2} H_{ij} \middle| j_c \right\rangle \middle| i'_c \right\rangle \\ &\quad + \lambda_i \lambda'_i \left\langle i_L \middle| \Sigma_L H_{iL} - \Sigma'_j \left\langle j_L \middle| \lambda_j^{\,2} H_{ij} \middle| j_L \right\rangle \middle| i'_L \right\rangle \end{aligned} \tag{B11}$$

If both i_c and i'_c have the same radial wavefunctions then the radial integration of the first sum gives the spin orbit constant of the central ion for the orbital i_c being corrected for a change in the electron density in orbitals j, measured by κ_j^2. Since in this work, the molecular orbitals i_c are constructed from d orbitals of the central ion, they have the same radial part. Thus the first term in (B11) can be expressed as*

$$\kappa_i \kappa'_i \left\langle i_c \middle| H_{ic} - \sum_{j\,(\neq i)}{}' \left\langle j_c \middle| \kappa_j^2 \; H_{ij} \middle| j_c \right\rangle \cdot \middle| i'_c \right\rangle$$

$$= \kappa_i \kappa'_i \left\langle i_c \middle| \zeta_c \; \underline{\ell}^{ic} \cdot \underline{s}^i \middle| i'_c \right\rangle' \tag{B12}$$

Similarly the radial parts of i_L and i'_L in the second term of (B11) are the same. Thus

$$\lambda_i \lambda'_i \left\langle i_L \middle| \Sigma_L \; H_{iL} - \sum_j \left\langle j_L \middle| \lambda_j^2 \; H_{ij} \middle| j_L \right\rangle \middle| i'_L \right\rangle$$

$$= \lambda_i \lambda'_i \left\langle i_L \middle| \Sigma_L \; \zeta_L \; \underline{\ell}^{iL} \cdot \underline{s}^i \middle| i'_L \right\rangle \tag{B13}$$

Now we define a spin-orbit interaction operator $\zeta_i \; \underline{\ell}^i \cdot \underline{s}^i$ such that

$$\zeta_i \; \underline{\ell}^i \cdot \underline{s}^i \left| i_c \right\rangle = \zeta_d \; \underline{\ell}^{di} \cdot \underline{s}^i \left| i_c \right\rangle \tag{B14}$$

and

$$\zeta_i \; \underline{\ell}^i \cdot \underline{s}^i \left| i_L \right\rangle = \zeta_p \; \underline{\ell}^{pi} \cdot \underline{s}^i \left| i_L \right\rangle \tag{B15}$$

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*The prime sign on $\left\langle i_c \middle| \zeta_c \; \underline{\ell}^{ic} \cdot \underline{s}^i \middle| i'_c \right\rangle$ in (B12) indicates it has been integrated over r_{ic}

The parameters d and p in (B14) - (B15) indicate that i_c and i_L are constructed from d and p atomic orbitals respectively. Substituting in (B11) one finds

$$\begin{aligned}\left\langle\psi_d\middle|H_{SO}(i)\middle|\psi_n\right\rangle &= \kappa_i\kappa'_i\left\langle i_c\middle|\zeta_i\,\underline{\ell}^i\cdot\underline{s}^i\middle|i'_c\right\rangle \\ &+ \lambda_i\lambda'_i\left\langle i_L\middle|\zeta_i\,\underline{\ell}^i\cdot\underline{s}^i\middle|i'_L\right\rangle \\ &\cong \left\langle\left(\kappa_i\left\langle i_c\right| - \lambda_i\left\langle i_L\right|\right)\middle|\zeta_i\,\underline{\ell}^i\cdot\underline{s}^i\middle|\right. \\ &\qquad \left.\left(\kappa'_i\left|i'_c\right\rangle - \lambda'_i\left|i'_c\right\rangle\right)\right\rangle \\ &\cong \left\langle i\middle|\zeta_i\,\underline{\ell}^i\cdot\underline{s}^i\middle|i'\right\rangle \\ &= \left\langle\psi_o\middle|\zeta_i\,\underline{\ell}^i\cdot\underline{s}^i\middle|\psi_n\right\rangle\end{aligned} \tag{B16}$$

Since

$$H_{SO} = \Sigma_i\, H_{SO}(i) \tag{B17}$$

then

$$\left\langle\psi_o\middle|H_{SO}\middle|\psi_n\right\rangle = \left\langle\psi_o\middle|\sum_i \zeta_i\,\underline{\ell}^i\cdot\underline{s}^i\middle|\psi_n\right\rangle$$

resulting in

$$H_{SO} = \Sigma_i\,\zeta_i\,\underline{\ell}^i\cdot\underline{s}^i = \sum_i \mathrm{su}(i) \tag{B18}$$

where

$$\underline{u}(i) = \zeta_i \, \underline{\ell}^i \qquad \text{(B19)}$$

and

$$su(i) = \zeta_i \, \underline{\ell}^i \cdot \underline{s}^i \qquad \text{(B20)}$$

In (B16) - (B20) $\zeta_i \, \underline{\ell}^i$ behaves as operators defined in (B14) and (B15). The above definition of spin orbit Hamiltonian for the charge transfer states of a complex $(\Sigma\ \Lambda_4)^{-n'}$ is certainly an approximate definition which will not be adequate for the precise evaluation of the matrix elements of H_{SO} but is sufficient compared to other approximations made in construction of the molecular orbitals $|i\rangle$ and excited wavefunctions $|\psi_n\rangle$.

APPENDIX C

SPIN ORBIT MATRIX ELEMENTS FROM THREE AND FOUR ORBITAL WAVEFUNCTIONS

The purpose of this Appendix is to give the spin orbit matrix elements between charge transfer states consisting of three or four types of distinct orbitals each having at least one electron such as those in Table 3-1. The spin orbit matrix elements between pair of states consisting of only two orbitals have been calculated by Tanabe and Kamimura* and by Griffith.+ The ligand to metal charge transfer process, in cubic complexes of S-state ions, results at least in three open shells of electrons two of these around metal and the third around the ligand. Thus the desired states consist of at least three orbitals. As a result of this the formulae by above authors should be modified and extended to be applicable for these wavefunctions.

We proceed by giving a brief description of charge transfer wavefunctions first and then discuss the matrix elements of $H_p = \Sigma_i \zeta_i \underline{s}^i \cdot \underline{\ell}^i$ between them.

1. CHARGE TRANSFER WAVEFUNCTIONS

A description of the orbital part of the ligand to metal charge transfer wavefunctions, in complex $[\Sigma\Lambda_4]^{-n}$, will be given here. Their radial part is omitted for simplicity; it must, however, be taken into account in a more refined analysis of this subject.

Considering Table 3.1, one finds the electronic configurations p,q,..t and the representations t_a, e_a, t_1, e_b and t_b of the orbitals in a charge transfer state. Denoting the spin and magnetic quantum number of the participating orbitals by S_iM_i and their space irreducible representation$^{(IR)}$ by $h_i\theta_i$ one can describe a charge transfer state of spin SM and irreducible representation hθ as follows.

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*Y. Tanabe and H. Kamimura "On the Absorption Spectra of Complex Ions IV. The Effect of the Spin-Orbit Interaction and the Field of Lower Symmetry on d-Electrons in Cubic Field" J. Phys. Soc. Japan 13, 394 (1958)

+J.S. Griffith (Ref.26)

$$|\chi_i ShM\theta\rangle = \left[t_a^{\,p}\ S_1h_1M_1\theta_1,\ e_a^{\,q}\ S_2h_2M_2\theta_2, \ldots t_b^{\,t}\ S_5h_5M_5\theta_5; ShM\theta\rangle\right] \quad \text{(C1)}$$

For example one of the states arising from the first row of Table 3.2 is

$$|\chi_i 5/2\ T_1\ 5/2Z\rangle = |t_a^{\,2}\ 1T_1\ 1x,\ e_a^{\,2}\ 1A_2 1a_2,\ t_1^{\,1}\ 1/2T_1\ 1/2y$$

$$e_b^{\,0}0A_1 0a_1,\ t_b^{\,0}\ 0A_1\ 0a_1;\ 5/2\ T_1\ 5/2Z\rangle$$

$$= |t_a^{\,2}3T_1\ 1x,\ e_a^{\,2}\ 3A_2 1a_2,\ t_1^{\,1}2T_1\ 1/2y$$

$$e_b^{\,0}1A_1a_1;{}^6T_1\ 5/2Z\rangle \quad \text{(C2)}$$

where χ_i in (C2), as before, denotes the manner by which the five orbitals t_a, e_a, ..., t_b have coupled to give ${}^6T_1$ in (C2).

2. MATRIX ELEMENTS OF $H_p = \Sigma_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i$

The matrix elements of H_p between pairs of charge transfer states $|\chi_j ShM\theta\rangle$ and $|\chi_k S'h'M'\theta'\rangle$ will be obtained in this section. To simplify the notation the above matrix element will be denoted by $M_{jk}(ShM\theta\text{-}S'h'M'\theta')$:

$$M_{jk}\ (ShM\theta\text{-}S'h'M'\theta') = \langle \chi_j ShM\theta | H_p | \chi_k S'h'M'\theta'\rangle$$

$$= R_{jk}(Sh\text{-}S'h')\ Q(ShM\theta\text{-}S'h'M'\theta') \quad \text{(C3)}$$

where

$$R_{jk}(Sh\text{-}S'h') = \langle \chi_j Sh || H_p || \chi_k S'h'\rangle \quad \text{(C4)}$$

is called the reduced matrix element and $Q(ShM\theta\text{-}S'h'M'\theta')$ is the coefficient of the coupling of $|ShM\theta\rangle$ and $|S'h'M'\theta'\rangle$ through spin orbit interaction and it is independent of j and k as will be seen later. Now we consider $R_{jk}(Sh\text{-}S'h')$ and leave $Q(ShMO\text{-}S'h'MO')$ for Appendix D.

3. REDUCED MATRIX ELEMENTS $R_{jk}(Sh\text{-}S'h')$

R_{jk} depends on χ_j and χ_k. The χ_j and χ_k, in turn, depend on the configuration p, q, ..., t of orbitals t_a, e_a ..., t_b as shown in (C1). Therefore the reduced matrix elements R_{jk} between a pair of states $|j\rangle$ and $|k\rangle$ can be characterized by the configurational numbers p_j, q_j, ... t_j and p_k, q_k, ... t_k in these two states. Considering this fact in mind and observing Table 3.2, one immediately finds that there are three classes of reduced matrix elements as follows:

$$\text{(i)} \quad p_j = p_k,\ q_j = q_k,\ u_j = u_k \quad u = r,s,t \tag{C5}$$

$$\text{(ii)} \quad p_j = p_k \pm 1,\ q_j = q_k \mp 1,\ u_j = u_k \quad u = r,s,t \tag{C6}$$

$$\text{(iii)} \quad p_j = p_k,\ q_j = q_k;\ u_j \neq u_k \quad u = r,s,t \tag{C7}$$

The numbers p,q, ... t in (C5) - (C7) are given in rows of the hole configuration column in Table 3.2. In case (i) both states $|j\rangle$ and $|k\rangle$ have three open orbitals with the same configuration such as $|\chi_j\, {}^6T_1\rangle$ and $|\chi_k\, {}^6T_2\rangle$ of the first row in Table 3.2. R_{jk} in this case may be called homo-configuration three orbital reduced matrix element. In case (ii) the orbitals involved are the same but their configuration differ and therefore the R_{jk} of this case is called hetero-configuration three orbital reduced matrix element. In case (iii) only one of the five orbitals t_a, e_a, t_1, e_b and t_b remains closed in both states $|j\rangle$ and $|k\rangle$ such as t_b in ${}^6T_1$ of row 2 and ${}^6T_2$ of row 3 in Table 3.2. The R_{jk} of this case will be called hetero-configuration four orbital reduced matrix elements. These three cases will be considered in the following sections.

4. HOMOCONFIGURATION THREE ORBITAL REDUCED MATRIX ELEMENTS

Here we consider the case of R_{jk} between states $|j\rangle$ and $|k\rangle$ with both $|j\rangle$ and $|k\rangle$ containing three open orbitals of the same symmetry and configuration.

The R_{jk} in this case can be expressed as

$$R_{jk}(Sh,\ S'h') = \left\langle \chi_j Sh || H_p || \chi_k S'h' \right\rangle \tag{C8}$$

where

$$|\chi_j Sh\rangle = \left| \left[a^p S_1 h_1 (b^q S_2 h_2 c^r S_3 h_3) S_4 h_4 \right]_j ; Sh \right\rangle \tag{C9}$$

$$|\chi_k S'h'\rangle = \left| \left[a^p S_1' h_1' (b^q S_2' h_2' c^r S_3' h_3') S_4' h_4' \right]_k ; S'h' \right\rangle \tag{C10}$$

The orbitals a, b and c, in (C8) - (C10), represent three of the five orbitals t_a, e_a .., t_b of Table 3.2 and the subscripts j and k denote the coupling of such orbitals.

Since the perturbation Hamiltonian $H_p^{*} = \sum_i \zeta_i \cdot \underline{\ell}^i \cdot \underline{s}^i = \sum_i \underline{s} \cdot \underline{u}\ (i)$ is in terms of single electron operators we must express the total wavefunction in terms of the single electron orbital which constitute such a wavefunction. To obtain this we rewrite (C8) as follows:[+]

$$R_{jk}(Sh\text{-}S'h') = \Big\langle a^p S_1 h_1 (b^q S_2 h_2\ c^r S_3 h_3) S_4 h_4,\ Sh \Big|\Big| \sum_{i=1}^{p} \underline{s}^i \cdot \underline{u}^i + \sum_{i=p+1}^{p+q} \underline{s} \cdot \underline{u}(i)$$

$$+ \sum_{i=p+q+1}^{p+q+r} \underline{s} \cdot \underline{u}(i) \Big|\Big| a^p S_1' h_1' (b^q S_2' h_2' c^r S_3' h_3') S_4' h_4',S'\ h' \Big\rangle$$

$$= R_{jk}[p(qr)p, Sh\text{-}S'h'] + R_{jk}[p(qr)q, Sh\text{-}S'h'] + R_{jk}[p(qr)r, Sh\text{-}S'h'] \tag{C11}$$

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[*] To simplify notation $\underline{\zeta_i \ell}^i$ is substituted by $\underline{u}^i$

[+] To simplify notation the brackets $[....]_j$ and $[....]_k$ are omitted from $|\chi_j Sh$ and $|\chi_k S'h'$ in (C11).

the first sum operates on electrons in a^p, the second on b^q and the third on c^r and

$$R_{jk}[p(qr)p,Sh\text{-}S'h'] = \left\langle a^pS_1h_1\ (b^qS_2h_2c^rS_3h_3)S_4h_4;\ Sh \right\|\sum_{i=1}^{p}$$

$$\underline{s}\cdot\underline{u}(i)(1\cdot1)(1\cdot1)\Big\|\quad (x)\quad \Big\|a^pS_1'\ h_1'\ (b^qS_2'h_2',\ c^rS_3'h_3')S_4'h_4',\ S'h'\Big\rangle \tag{C12}$$

$$R_{jk}[p(qr)q,Sh\text{-}S'h'] = \Big\langle \Big[a^pS_1h_1(b^qS_2h_2c^rS_3h_3)S_4h_4, Sh\Big\|$$

$$(1\cdot1)x\left(\sum_{k=1}^{p}\underline{s}\cdot\underline{u}(k)x(1\cdot1)\right)\ \Big\|\Big[a^pS_1'h_1'(b^qS_2'h_2'c^rS_3'h_3')S_4'h_4', S'h'\Big\rangle \tag{C13}$$

$$R_{jk}[p(qr)r,Sh\text{-}S'h'] = \Big\langle a^pS_1h_1, (b^qS_2h_2, c^rS_3h_3)S_4h_4, Sh\Big\|$$

$$(1\cdot1)x(1\cdot1)x\sum_{k=1}^{r}\underline{s}\cdot\underline{u}(k)\ \Big\|a^pS_1'h_1'(b^qS_2'h_2', c^rS_3'h_3')S_4'h_4', S'h'\Big\rangle \tag{C14}$$

The symbols 1·1 represent double tensor operators of zero rank which operate on their respective part in (C12) - (C14). The first symbol 1 of 1·1 acts as a spin operator with $S = M_s = 0$ and the second symbol ·1 of 1·1 acts as the irreducible representation A_1 of the cubic group. R_{jk}, in (C12) - (C14), should be determined by the techniques of double tensor operators on coupled systems.

This subject is discussed by Griffith[26] and will be given here as follows.

Let a system n of electrons to be composed of two separate and independent parts ℓ and m. Then

$$|\ell mn\nu\rangle = \sum_{\lambda\mu}\langle \ell\lambda m\mu|\ell mn\nu\rangle\ |\ell\lambda\rangle|m\mu\rangle \tag{C15}$$

gives the $|n\nu\rangle$ state in terms of products of $|\ell\lambda\rangle$ and $|m\mu\rangle$. Now the reduced matrix elements of a single electron operator* D^d_δ operating on the $|\ell\lambda\rangle$ part can be described in terms of $|n\nu\rangle$ states as follows†

$$\langle \ell m\ n\ \nu || D^d || \ell' m' n' \nu' \rangle = (-1)^{\ell+n+n'+d} \sqrt{(n)(n)'}\ \langle \ell || D^d || \ell' \rangle\ W \begin{pmatrix} \ell' \ell d \\ nn'm \end{pmatrix}$$

$$(x)\ \delta_{mm'} \tag{C16}$$

Similarly an operator E^e operating on $|m\mu\rangle$ states has the reduced matrix elements

$$\langle \ell mn || E^e || \ell' m' n' \rangle = (-1)^{\ell+m'+n+e} \sqrt{(n)(n')}\ \langle m || E^e || m' \rangle W \begin{Bmatrix} m'me \\ nn' \end{Bmatrix}\ \ell \tag{C17}$$

where (n) and (n)' are dimensions of these two irreducible representations and W coefficients behave as six j symbols. For spin orbit interaction both orbital and spin wavefunctions of each electrons should be taken into account. Considering, m, ..., n' as space representations of the states and operators involved one will add S_1, $S_2 \ldots S'$ for spin part. Thus (C16) can be rewritten as

$$\left\langle S_1 \ell S_2 m S n || D^{pd} || S_1' \ell' S_2 m' S' n' \right\rangle = (-1)^{S_1+S'+p+\ell+m'+n'+d}$$

$$(x) \left[(2S+1)\ (2S'+1)\ (n)(n') \right]^{1/2} \left\langle S_1 \ell || D^{pd} || S_1' \ell' \right\rangle \bar{W} \begin{pmatrix} S_1 S_1' p \\ S\ S' S_2 \end{pmatrix} W \begin{pmatrix} \ell \ell' d \\ nn'm \end{pmatrix}$$

$$(x)\ \delta_{S_2 S_2'}\ \ \delta_{mm'} \tag{C18}$$

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*$D^d{}_\delta$ is the component of operator behaving as component of the irreducible representation d.

†Ref. 26, p. 47

and
$$\left\langle S_1\ell\ S_2 mSn \middle|\middle| E^{pe} \middle|\middle| S_1'\ell' S_2 m' S' n' \right\rangle = (-1)^{S_1+S_2+S+q+h_1+h_2+h+e}$$

$$(x)\ \left[(2S+1)(2S+1)(n)'n')\right]^{1/2} \left\langle S_2 m \middle|\middle| E^{qe} \middle|\middle| S_2' m' \right\rangle\ \bar{W}\begin{pmatrix} S_2 S_2 q \\ S\ S' S_1 \end{pmatrix} W \begin{pmatrix} m & m & e \\ n & n' & \ell \end{pmatrix}$$

$$(x)\ \delta_{S_1 S_1'} \quad \delta_{\ell\ell'} \qquad \text{(C19)}$$

Following (C17) the reduced matrix elements in (C12) - (C14) can be decomposed as follows:

$$R_{jk}(Sh-S'h',p) = (-1)^{S_1+S_4+S+1+h_1+h_4'+h+T_1}$$

$$(x)\ \left[(2S+1)(2S'+1)(h)(h')\right]^{1/2} \left\langle a^p S_1 h_1 \middle|\middle| \sum_{i=1}^{p} (\underline{s}(i)\ \cdot\ \underline{u}(i))^{1T_1} \middle|\middle| a^p S_1' h'_1 \right\rangle$$

$$\bar{W}\begin{pmatrix} S_1' S_1 & 1 \\ S\ \ S' & S_4 \end{pmatrix} W \begin{pmatrix} h'_1 h_1 T_1 \\ h\ \ h' & h_4 \end{pmatrix} \delta_{S_4 S'_4} \quad \delta_{h_4 h'_4} \qquad \text{(C20)}$$

The $R_{jk}[p(qr)q,Sh-S'h']$ and $R_{jk}[p(qr)r,Sh-S'h']$ must be obtained in two stages. First the part of the system represented by S_4h_4 should be decoupled from the part represented by S_1h_1 and then the parts S_2h_2 and S_3h_3 in S_4h_4 should be treated as in (C20). Denoting part represented by S_4h_4 as $R_{jk}(q,r)$ and considering (C16) - (C20) one finds

$$R_{jk}(q,r) = (-1)^{S_1+S_4+S+1+h_1+h'_4+h+T_1}\ (x)\ \left[(2S+1)(2S'+1)(h)(h')\right]^{1/2}$$

$$\left\langle (b^q S_2 h_2,\ c^r S_3 h_3) S_4 h_4 \middle|\middle| \sum_{\kappa=1} \underline{s}(\kappa)\cdot\underline{u}(\kappa) \middle|\middle| (b^q S_2' h_2'\ c^r S_3'\ h_3') S_4' h_4' \right\rangle$$

$$(x)\ \ \bar{W}\begin{pmatrix} S_4' S_4 & 1 \\ S\ S' & S_1 \end{pmatrix} W \begin{pmatrix} h_4' h_4 T_1 \\ h\ h' & h_1 \end{pmatrix} \delta_{S_1 S_1'} \quad \delta_{h_1 h_1'}$$

(C21)

The term*

$$T = \left\langle b^q S_2 h_2 c^r S_3 h_3) S_4 h_4 \right|\left| \sum_{\kappa=1}^{q} \underline{s}\cdot\underline{u}(\kappa) + \sum_{\kappa=1}^{r} su(\kappa) \right.$$

$$\left.\left|\right| (b^q S_2' h_2' c^r S_3' h_3') S_4' h_4' \right\rangle \tag{C22}$$

in (C21), should be factorized in the same manner described in (C19) - (C20).

$$T = (-1)^{S_2+S_3+h_2+h_3'} \left[(2S_4+1)(2S'_4+1)(h_4)(h_4')\right]^{1/2}$$

$$(x)\left[(-1)^{S_4'+h_4'} \delta_{S_3S_3'} \delta_{h_3h_3'} \bar{W}\begin{pmatrix} S_2'S_2 \ 1 \\ S_4S_4'S_3 \end{pmatrix} W\begin{pmatrix} h_2'h_2T_1 \\ h_4h_4'h_3 \end{pmatrix}\right.$$

$$(x)\left\langle b^q S_2 h_2 \right|\left| \sum_{\kappa=1}^{q} su(\kappa) \right|\left| b^q S_2' h_2' \right\rangle$$

$$+(-1)^{S_4+h_4} \delta_{S_2S_2'} \delta_{h_2h_2'} \bar{W}\begin{pmatrix} S_3'S_31 \\ S_4S_4'S_2 \end{pmatrix} \bar{W}\begin{pmatrix} h_3'h_3T_1 \\ h_4h_4'h_2 \end{pmatrix}$$

$$\left.(x)\left\langle c^r S_3 h_3 \right|\left| \sum_{\kappa=1}^{r} su(\kappa) \right|\left| c^r S_3' h_3' \right\rangle\right] \tag{C24}$$

Substituting in (C21) one finds $R_{jk}(Sh\text{-}S'h',q)$ and $R_{jk}(Sh\text{-}S'h',qr)$ of (C13) and (C14) as the coefficients of $\left\langle b^q S_2 h_2 \right|\left| \sum_{\kappa} su(\kappa) \right|\left| b^q S_2' h_2' \right\rangle$ and $\left\langle c^r S_3 h_3 \right|\left| \sum_{\kappa} su(\kappa) \right|\left| c^r S_3 h_3' \right\rangle$ respectively. Thus,

$$R_{jk}[p(qr)q,Sh\text{-}S'h'] = \delta_{S_1S_1'}$$

$$\delta_{h_1h_1'}(-1)^{S_1+S_4+S+h_1+h_4'+h+S_2+S_3+h_2+h_3+S_4+h_4}$$

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*Hereafter $\underline{s}(\kappa) \cdot \underline{u}(\kappa) \equiv su(\kappa)$

$$(x)\ \delta_{S_3S'_3}\ \delta_{h_3h'_3}\ \left[(2S=1)(2S'+1)(h')(2S_4+1)(h_4)(h'_4)(h)\right]^{1/2}$$

$$(x)\ \bar{W}\begin{pmatrix} S_4S'_41 \\ SS'S_1 \end{pmatrix}\ \bar{W}\begin{pmatrix} S'_2S_21 \\ S_4S'_4S_3 \end{pmatrix}\ W\begin{pmatrix} h'_4h_4T_1 \\ h\ h\ h_1 \end{pmatrix}\ W\begin{pmatrix} h'_2h_2T_1 \\ h_4h'_4h_3 \end{pmatrix}$$

$$(x)\left\langle b^qS_2h_2 \middle|\middle| \sum_{\kappa} su(\kappa) \middle|\middle| b^qS'_2h'_2 \right\rangle \qquad (C25)$$

and

$$R_{jk}[p(qr)r,Sh\text{-}S'h'] = \delta_{S_1S'_1}\ \delta_{h_1h'_1}\ (-1)^{S_1+S_4+h_1+h_4+h+S_2+S_3+h_2+h_3}$$

$$(x)(-1)^{S_4+h_4}\ \delta_{S_2S'_2}\ \delta_{h_2h'_2}\ \left[(2S+1)(2S'+1)(h)(h')(2S_4+1)(2S_4+1)(h_4)(h'_4)\right]^{1/2}$$

$$\bar{W}\begin{pmatrix} S'_4S_41 \\ S\ S'\ S_1 \end{pmatrix}\ \bar{W}\begin{pmatrix} S'_3S_31 \\ S_4S'_4S_3 \end{pmatrix}\ W\begin{pmatrix} h'_4h_4T_1 \\ h\ h'h_1 \end{pmatrix}\ W\begin{pmatrix} h'_3h_3T_1 \\ h_4h'_4h_2 \end{pmatrix}$$

$$\left\langle c^rS_3h_3 \middle|\middle| \sum_{\kappa} su(\kappa) \middle|\middle| c^rS'_3h'_3 \right\rangle \qquad (C26)$$

Substituting in (C11) we have

$$R_{jk}(Sh\text{-}S'h') = \left\langle \left[a^pS_1h_1(b^qS_2h_2c^rS_3h_3)S_4h_4\right]_j, Sh \ \middle|\middle| \sum_{\kappa=1}^{p+q+r} su(\kappa)\right.$$

$$\left. \middle|\middle| \left[a^pS_1h_1(b^qS_2h_2c^rS_3h_3)S_4h_4\right]_k S'h' \right\rangle$$

$$= R_{jk}[p(qr)p,Sh\text{-}S'h'] + R_{jk}[p(qr)q,Sh\text{-}S'h'] \qquad (C27)$$

$$+ R_{jk}[p(qr)r,Sh\text{-}S'h']$$

The R_{jk} in (C27) are given in (C20) and (C25) - (C26). They are given here in simpler form as follows:

$$R_{jk}[p(qr)p,Sh\text{-}S'h']\ (-1)^{S_1+S_4+S+h_1+h_4'+h'}\ \mathcal{D}\mathcal{D}'\left\langle a^p S_1 h_1 \right|\left| \sum_{\kappa} su(\kappa) \right|\left| a^p S_1' h_1' \right\rangle\ \mathcal{W}\begin{pmatrix} N_1' N_1 N_o \\ N\ N\ N_4 \end{pmatrix}\ \delta_{N_4 N_4'} \tag{C28}$$

$$R_{jk}[p(qr)q,Sh\text{-}S'h'] = (-1)^{S_1+S_4+S+h_1+h_4+h+S_2+S_3+h_2+h_3'+S_4'+h_4'}$$

$$(x)\ \mathcal{D}\mathcal{D}'\mathcal{D}_4\mathcal{D}_4 \cdot \mathcal{W}\begin{pmatrix} N_2' N_2 N_o \\ N_4 N_4' N_3 \end{pmatrix}\ \mathcal{W}\begin{pmatrix} N_4'\ N_4 No \\ N\ N'\ N_1 \end{pmatrix}$$

$$(x)\ \left\langle b^q S_2 h_2 \right|\left| \sum_{\kappa=1}^{q} su(\kappa) \right|\left| b^q S_2' h_2' \right\rangle\ \delta_{N_1 N'_1}\ \delta_{N_3 N_3} \tag{C29}$$

and

$$R_{jk}[p(qr)r,Sh\text{-}S'h'] = (-1)^{S_1+S_4+S+h_1+h_4'+h+S_2+S_3+h_2+h_3'+S_4+h_4}$$

$$(x)\ \mathcal{D}\mathcal{D}'\ \mathcal{D}_4\mathcal{D}_4\ \mathcal{W}\begin{pmatrix} N_3'\ N_3 N_o \\ N_4\ N_4 N_2 \end{pmatrix}\ \mathcal{W}\begin{pmatrix} N_4' N_4 N_c \\ N\ N' N_1 \end{pmatrix}$$

$$(x)\ \left\langle c^r S_3 h_3 \right|\left| \sum_{\kappa=1}^{r} su(\kappa) \right|\left| c^r S_3' h_3' \right\rangle\ \delta_{N_1 N_1'}\ \delta_{N_2 N_2'} \tag{C30}$$

where

$$\mathcal{D}_i = \left[(2S_i + 1)\ (h_i)\right]^{1/2}$$

$$\mathcal{W}\begin{pmatrix} N_i N_j N_o \\ N_k N_\ell N_m \end{pmatrix} = \bar{W}\begin{pmatrix} S_i S_j 1 \\ S_k S_\ell S_m \end{pmatrix} W\begin{pmatrix} h_i h_j T_1 \\ h_k h\ h_m \end{pmatrix}$$

$$\delta_{N_i N_j} = \delta_{S_i S_j}\ \delta_{h_i h_j} \tag{C31}$$

The coefficient $\bar{W}$ in (C31) is defined as[*]

$$\bar{W}\begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix} = \sum_{\alpha\beta\gamma\delta\epsilon\phi} (-1)^{a-\alpha+b-\beta+c-\gamma+d-\delta+e-\epsilon+f-\phi}$$

$$(x)\ \bar{V}\begin{pmatrix} a & b & c \\ -\alpha & -\beta & -\gamma \end{pmatrix} \bar{V}\begin{pmatrix} a & e & f \\ \alpha & \epsilon & -\phi \end{pmatrix} \bar{V}\begin{pmatrix} d & b & f \\ -\delta & \beta & \phi \end{pmatrix} \bar{V}\begin{pmatrix} d & e & c \\ \delta & -\epsilon & \gamma \end{pmatrix}$$

and

$$\bar{V}\begin{pmatrix} J_1 J_2 J_3 \\ m_1 m_2 -m_3 \end{pmatrix} = \frac{(-1)^{2J_2+J_3-m_3}}{\sqrt{2J_3+1}} \quad (J_1J_2J_3m_3|J_1m_1J_2m_2) \tag{C33}$$

$\bar{V}$ and $\bar{W}$ are used for spin coupling coefficiencts whereas for coupling of space irreducible representations the simpler V and W are used where (Ref. 26, p. 10 and p. 33)

$$V(abc,\alpha\beta\gamma) = \sqrt{c}\ \langle ab\alpha\beta|abc\gamma\rangle \tag{C34}$$

and

$$W(abcdef) = \Sigma\alpha\beta\gamma\delta\epsilon\phi\ V(abc,\alpha\beta\gamma)$$

$$(x)\ V(aef,\alpha\epsilon\phi)\ V(bfd,\beta\phi\delta)\ \ V(cde,\gamma\delta\epsilon) \tag{C35}$$

The numerical values of $\bar{W}$ are taken from Rotenberg's tables of 6J symbols[**] and W are obtained from Griffith's tables.[†] The dimensions of h_i entering D_i of (C31) are the same as their character under identity class in the character table. The $(-1)^{h+i} = \pm 1$ as defined by Griffith[†] (p. 15). Both of these numerical parameter are given in Table C.1.

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[*] V. Fano and G. Racah "Irreducible Tensorial Sets" Academic Press, New York 1959, pp. 50-54

[**] M. Rotenberg, R. Bivins, N. Metropolis and J.K. Wooten, "The 3-j and 6-j symbols." The Technology Press, Massachusetts Institute of Technology (1959).

[†] Ref. 26, p. 114

TABLE C-1

The Values of (h) and $(-1)^h$

h	A_1	A_2	E	T_1	T_2
$(-1)^h$	1	-1	1	-1	1
(h)	1	1	2	3	3

The last unknown in R_{jk} (p,p),...R_{jk} (r,r) in (C28) - (C30) is the single orbital reduced matrix elements of the type

$$\rho(pp) = \left\langle a^p Sh \right|\left| \sum_{\kappa=1}^{p} su(\kappa) \right|\left| a^p S'h' \right\rangle$$

$$= p \left\langle a^p Sh \right|\left| su(p) \right|\left| a^p S'h' \right\rangle \qquad \text{(C36)}$$

To obtain $\rho(pp)$ we express it in terms of its matrix elements between pairs of $|a^p ShM\theta\rangle$ and $|a^p S'h'M'\theta'\rangle$.

$$\left\langle a^p Sh \right|\left| \left[\sum_{\kappa=1} su(\kappa) \right]^{1\;T_1} \right|\left| a^p S'h' \right\rangle (-1)^{S-M}\, \bar{V} \begin{pmatrix} SS'1 \\ MM'-i \end{pmatrix} \bar{V} \begin{pmatrix} hh'T_1 \\ \theta\theta' i \end{pmatrix}$$

$$= \left\langle a^p ShM\theta \right| \left[\sum_{\kappa=1} su(\kappa) \right]^{1\;T_1}_{-ii} \left| a^p S'h'M'\theta' \right\rangle$$

Multiplying both sides by $(-1)^{S-M}\,\bar{V}\,(S,S'1,\,-MM'-i)$ and $V(hh'T_1\;\theta\theta'i)$ and summing over the six parameter $-M,\ldots i$ one finds

$$\rho(pp) = p \sum_{\substack{MM'i\\ \theta\theta'}} \left\langle a^p ShM\theta \right| [su(p)]^{1\;T_1}_{-ii} \left| a^p S'h'M'\theta' \right\rangle \,(x)$$

$$(x)\;(-1)^{S-M}\,\bar{V}\,(SS'1,\,-MM'-i)\cdot V(hh'T_1,\theta\theta'i) \qquad \text{(C37)}$$

In terms of the coefficients of fractional parentage (cfp) we have*

$$\left| a^p ShM\theta \right\rangle = \sum_{\substack{S_1M_1m\\ h_1\theta_1\alpha}} \left\langle a^{p-1}S_1h_1,a \right| \left. \right\} a^p Sh\rangle \left\langle S_1\tfrac{1}{2}M_1m \right| S_1\tfrac{1}{2}SM\rangle$$

$$(x)\;\left\langle h_1a\theta_1\alpha \right| h_1ah\theta\rangle \left| a^{p-1}S_1h_1M_1\theta_1\right\rangle\cdot\left| am\alpha\right\rangle \qquad \text{(C38)}$$

Substituting for $\left|a^pShM\theta\right\rangle$ and $\left|a^pS'h'M'\theta'\right\rangle$ in (C37) one finds

$$\rho(p,p) = p \sum_{\substack{S_1M_1mMM'iS'M'm'\\ h_1\theta_1\alpha\theta\theta'ih_1\theta_1\alpha'}} \begin{array}{l} \left\langle a^pSh\;\right| a,a^{p-1}S_1h_1\rangle \left\langle S_1\tfrac{1}{2}SM \right| S_1\tfrac{1}{2}M_1m\rangle (x) \\ \left\langle h_1ah\theta \right| h_1a\theta_1\alpha\rangle\cdot\left\langle a^{p-1}S_1h_1M_1\theta\right|\cdot\left\langle am\alpha\right| \end{array}$$

$$\left| [su(p)]^{1\;T_1}_{-ii} \right| am'\alpha'\rangle\cdot\left|a^{p-1}S_1'h_1'M_1'\theta_1'\right\rangle$$

$$(x)\;\left\langle h_1'a\theta_1'\alpha' \right| h_1'ah'\theta'\rangle \left\langle S_1'\tfrac{1}{2}M_1'm \right| S_1'\tfrac{1}{2}S'M'\rangle \left\langle a^{p-1}S_1'h_1',a \right| \left. \right\} a^pS'h'\rangle$$

$$(x)\;(-1)^{S_1-M_1}\,\bar{V}\,(SS'1,-MM'-i)\cdot V\,(hh'T_1,\theta\theta'i) \qquad \text{(C39)}$$

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*Ref. 26, p. 62

The matrix element in (C39) can be abbreviated as follows:

$$\left\langle a^{p-1}S_1h_1M_1\theta_1 \right| \cdot \left\langle am\alpha \,|su(p)|\, am'\alpha' \right\rangle \cdot \left| a^{p-1}S_1'h_1'M_1'\theta \right\rangle$$

$$= \left\langle am\ \alpha|su|am'\alpha' \right\rangle \cdot \delta_{S_1S_1'}\ \delta_{h_1h_1'}\ \delta_{M_1M_1'}\ \delta_{\theta_1\theta_1'}$$

$$= \left\langle 1/2a||su||1/2a \right\rangle (-1)^{1/2-m}\ \bar{V}(1/2\ 1/2\ 1,\ mm'-i)\ V\ (aa'T_1,\alpha\alpha' i)$$

$$\delta_{S_1S_1'} \cdot \delta_{M_1M'} \cdot \delta_{h_1h_1'} \cdot \delta_{\theta_1\theta_1'} \qquad \text{(C40)}$$

The remaining coupling coefficients in (C39) may also be expressed in terms of $\bar{V}$ and V. Thus

$$\left\langle S_1 1/2SM|S_1 1/2M_1m \right\rangle = (2S+1)^{1/2}\ (-1)^{1+S-M}\ \bar{V}(S_1 1/2S,M_1m-M) \qquad \text{(C41)}$$

$$\left\langle h_1ah\theta|h_1a\theta_1\alpha \right\rangle = (h)^{1/2}\ \ V(h_1a\ h,\theta_1\alpha\theta) \qquad \text{(C42)}$$

Substituting in (C39) and considering the effect of $\delta_{S_1S_1'}$, ... $\delta_{\theta_1\theta_1'}$ in (C40) one finds

$$\rho(p,p) = p \sum_{\substack{S_1M\ mM'm'im' \\ h_1\theta_1\theta\ \theta'}} (-1)^{S-M+1+S-M+1/2-m} \mathscr{D}\mathscr{D}'\ (-1)^{+1+S'-M'}$$

$$(x)\left\langle a^pSh \left\{ |a,a^{p-1}S_1h_1 \right\rangle \cdot \left\langle a^{p-1}S_1h_1,a| \right\} a^pS'h' \right\rangle$$

$$(x)\ \bar{V}(S_1 1/2 S,\ M_1 m-M)\bar{V}(1/2\ 1/2\ 1,-mm'-i)\bar{V}(S_1' 1/2 S',M_1' m'-M')\bar{V}(SS_1' 1-MM'-i)$$

$$(x)\ V(h_1 ah,\theta_1 \alpha\theta)\ V(aaT_1,\alpha\alpha' i)\ V(h_1' ah',\ \theta_1' \alpha'\theta')\ V(hh'T_1,\theta\theta' i)$$

$$(x)\ \left\langle 1/2a \| su \| 1/2a \right\rangle \tag{C43}$$

The coefficients $\bar{V}$ and V may be rearranged according to the rules*

$$\bar{V}\begin{pmatrix} abc \\ \alpha\beta\zeta \end{pmatrix} = \bar{V}\begin{pmatrix} cab \\ \zeta\alpha\beta \end{pmatrix} = (-1)^{a+b+c}\,\bar{V}\begin{pmatrix} bac \\ \beta\alpha\zeta \end{pmatrix} = (-1)^{a+b+c}\bar{V}\begin{pmatrix} abc \\ -\alpha-\beta-\zeta \end{pmatrix} \tag{C44}$$

and

$$V\begin{pmatrix} abc \\ \alpha\beta\zeta \end{pmatrix} = (-1)^{a+b+c}\ V\begin{pmatrix} bac \\ \beta\alpha\zeta \end{pmatrix}. \tag{C45}$$

Carrying through symmetry operations of (C44) and (C45), on coefficients $\bar{V}$ and V in (C43), one finds

$$\bar{V}(S_1 1/2S,\ M_1 m-M)\ldots = (-1)^{2(S_1+S')}\bar{V}\begin{pmatrix} 1/2\ \ 1/2\ \ 1 \\ -m\ \ m-i \end{pmatrix}\bar{V}\begin{pmatrix} 1/2S'S_1 \\ m'M'M \end{pmatrix}\ \bar{V}\begin{pmatrix} 1/2S_1S' \\ m-M_1M_1' \end{pmatrix}$$

$$\bar{V}\begin{pmatrix} 1\ SS' \\ i-MM' \end{pmatrix}$$

and

$$\sum_{m_1 mMm' im'} \bar{V}(S_1 1/2SM\ m-M)\cdot\bar{V}\ \ldots = \sum_{M_1 mMm' iM'} (-1)^{-S_1+S+S'+(m-m-i-M-M'-M_1)}$$

$$(x)\ (-1)^{+2+S-S'+S_1-(m-m+i-M-M'-M_1)}$$

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*Ref. 26 p. 77 and p. 15

$$(x)\ \bar{V}\begin{pmatrix} 1/2 & 1/2 & 1 \\ & -m' & m-i \end{pmatrix} \bar{V}\begin{pmatrix} 1/2 & S' & S_1 \\ m' & -M' & M_1 \end{pmatrix} \bar{V}\begin{pmatrix} 1/2 & S_1 & S' \\ -m & -M_1 & M \end{pmatrix} \bar{V}\begin{pmatrix} 1 & S & S' \\ i & -M & M' \end{pmatrix} \tag{C46}$$

The first three powers of (-1) result into

$$(-1)^{+S'-M'+1/2-m-S-S'-S_1+\ (m'-m+i-M-M'-M_1)}$$

$$= (-1)^{S'-M'+1/2-m+S-S'-S_1-M-M'-M_1} = (-1)^{1/2-2M+S-S_1}$$

$$= (-1)^{-(1/2+S+S_1)\ +1} = (-1)^{1/2+S+S_1+1} \tag{C47}$$

Similarly the four V coefficients can be rearranged as follows

$$V\begin{pmatrix} h_1 & a & h \\ \theta_1 & \alpha & \theta \end{pmatrix} V(\ldots)\ \ldots = (-1)^{T_1+h_1+h'+a}\ V\begin{pmatrix} a & a & T_1 \\ \alpha' & \alpha & i \end{pmatrix}\ V\begin{pmatrix} a & h' & h \\ \alpha' & \theta' & \theta \end{pmatrix}$$

$$V\begin{pmatrix} a & h_1 & h \\ \alpha & \theta_1 & \theta \end{pmatrix}\ V\begin{pmatrix} T_1 & h & h' \\ i & \theta & \theta' \end{pmatrix} \tag{C48}$$

Substituting in (C43) we find

$$\rho(p,p) = p \sum_{S_1 h_1} (-1)^{S+S_1+1/2+h_1+h'} \left\langle a^p Sh \left\{ |a, a^{p-1} S_1 h_1 \right\rangle \left\langle a^{p-1} S_1 h_1 a| \right\} \right.$$

$$\left. a^p S'h' \right\rangle \left\langle 1/2a || su || 1/2a \right\rangle\ (x)$$

$$(x) \sum_{M m M_1 M' i m'} (-1)^{1/2+1/2+1+S+S+S'+S_1-(m'-m+i-M-M'-M_1)}$$

$$(x)\ \bar{V}\begin{pmatrix} 1/2 & 1/2 & 1 \\ -m' & m & -i \end{pmatrix} \bar{V}\begin{pmatrix} 1/2 & S' & S \\ m' & -M' & M_1 \end{pmatrix} \bar{V}\begin{pmatrix} 1/2 & S_1 & S' \\ -m & -M_1 & M' \end{pmatrix} \bar{V}\begin{pmatrix} 1 & S & S' \\ i & -M' & M \end{pmatrix}$$

$$(x) \sum_{\theta'\alpha\theta\theta'\alpha'} V\begin{pmatrix} a & a & T_1 \\ \alpha' & \alpha & i \end{pmatrix} V\begin{pmatrix} a & h' & h_1 \\ \alpha' & \theta' & \theta_1 \end{pmatrix} V\begin{pmatrix} a & h_1 & h' \\ \alpha & \theta' & \theta' \end{pmatrix} V\begin{pmatrix} T_1 & h & h' \\ i & \theta & \theta' \end{pmatrix} \qquad (C49)$$

The second and third sums are identical to (C32) and (C35) respectively. Thus they can be substituted by their appropriate $\bar{W}$ and W coefficients. The final result is*

$$\rho(p,p) = G^p_a\ (Sh-S'h') \left\langle 1/2a \| su \| 1/2a \right\rangle \qquad (C50)$$

where

$$G^p_a(Sh-S'h') = \sum_{S_1 h_1} (-1)^{S+S_1+1/2+h'+h_1+a} \left\langle a^p S h \left\{ | a, a^{p-1} S_1 h_1 \right\rangle \left\langle a^{p-1} S_1' h_1', a \right\} \right.$$

$$\left. | a^p S' h' \right\rangle$$

$$(x)\ p \left[(2S+1)\ (2S'+1)\ (h)\ (h')\right]^{1/2}$$

$$(x)\ \bar{W}\ (1/2\ 1/2\ 1,\ S\ S'\ S_1)\cdot W\ (a\ a\ T_1,\ hh'h_1) \qquad (C51)$$

---

* p, q and r must be less than half shell numbers. If not they should be substitutde by p' = 2(a)-p, q'=2(b)-q and r'=2(c)-r where (a), (b) and (c) are dimensions of a, b and c respectively.

Substituting in (C28) - (C30) we have*

$$R_{jk}[p(qr)p,Sh\text{-}S'h'] = (-1)^{Sp}\mathcal{D}\mathcal{D}'\mathcal{W}(N_1'N_1N_o,\ N\,N'N_4)$$

$$(x)\ G^p_a\ (S_1h_1\text{-}S'h')\ \langle 1/2\ a\|su\|1/2a\rangle\ \delta_{N_4N_4'}\ , \tag{C52}$$

$$R_{jk}[p(qr)q,Sh\text{-}S'h'] = (-1)^{Sq}\ \mathcal{D}\mathcal{D}'\mathcal{D}_4\mathcal{D}_4'\mathcal{W}(N_2'N_2N_o,N_4N_4'N_3)$$

$$\mathcal{W}(N_4'\ N_4\ N_o,\ N\,N'N_1)$$

$$(x)\ G^q_b\ (S_2h_2\text{-}S_2'h_2')\ \langle 1/2\ b\|su\|1/2b\rangle\delta_{N_1N_1'}\ \delta_{N_3N_3'} \tag{C53}$$

and

$$R_{jk}[p(qr)r,Sh\text{-}S'h'] = (-1)^{Sr}\ \mathcal{D}\mathcal{D}'\mathcal{D}_4\mathcal{D}_4'\mathcal{W}(N_3'N_3N_o,N_4N_4'N_2)$$

$$(x)\ \mathcal{W}(N_4N_4'N_o,\ NN'N_1)$$

$$G^r_c(S_3h_3\text{-}S_3'h_3')\ \langle 1/2c\|su\|1/2c\rangle\ \delta_{N_1N_1'}\ \delta_{N_2N_2'} \tag{C54}$$

5. HETERO CONFIGURATION THREE ORBITAL REDUCED MATRIX ELEMENTS $R_{jk'}(pqr\ Sh,\ pq'r'S'h')$

Here, we consider the reduced matrix elements $R_{jk'}$ between states $|j\rangle$ and $|k'\rangle$ with both having three open orbitals of the same symmetry but different configurations.

---

*Sp, Sq and Sr are the sum of powers of (-1) in $\rho(pp)$, $\rho(qq)$ and $\rho(rr)$ respectively.

The $R_{jk'}$ in this case, can be expressed as

$$R_{jk'}(Sh,S'h') = \left\langle \chi_j Sh \middle\| H_p \middle\| \chi_{k'} S'h' \right\rangle \qquad \text{(C55)}$$

where

$$|\chi_j Sh\rangle = \left|\left[a^p S_1 h_1 (b^{q-1} S_2 h_2 c^r S_3 h_3) S_4 h_4\right]_j ; Sh \right\rangle \qquad \text{(C56)}$$

$$|\chi_{k'} S'h'\rangle = \left|\left[a^p S'_1 h'_1 (b^q S'_2 h'_2 c^{r-1} S'_3 h'_3) S'_4 h'_4\right]_{k'}, S'h' \right\rangle \qquad \text{(C57)}$$

The orbitals a, b and c, in (C56) - (C57) represent three of the five orbitals t_a, e_a, ..., t_b of Table 3-2.

Subscripts j and k' denote the electronic configuration and coupling scheme of the three orbitals a, b and c. The determination of $R_{jk'}$ follows that of the R_{jk} defined in (C12) - (C14). Considering these equations, $R_{jk'}$ can be written as follows:

$$R_{jk'}(Sh\text{-}S'h') = \left\langle a^p S_1 h_1 (b^{q-1} S_2 h_2 c^r S_3 h_3) S_4 h_4 ; Sh \right\|$$

$$(x) \sum_{\kappa=1}^{p+q+r} su(\kappa) \left\| a^p S'_1 h'_1 (b^q S'_2 h'_2 c^{r-1} S'_3 h'_3) S'_4 h'_4 ;\ S'h' \right\rangle$$

$$= R_{jk}(Sh\text{-}S'h',p) + R_{jk'}(Sh\text{-}S'h',qr) \qquad \text{(C58)}$$

where

$$R_{jk}(Sh\text{-}S'h',p) = \left\langle a^p S_1 h_1 (b^{q-1} S_2 h_2 c^r S_3 h_3) S_4 h_4 , Sh \right\| \sum_{\kappa=1}^{p} su(\kappa) \|$$

$$(x) \left\| a^p S'_1 h'_1 (b^q S'_2 h'_2 c^{r-1} S'_3 h'_3) S'_4 h'_4 ;\ S'h' \right\rangle \qquad \text{(C59)}$$

and

$$R_{jk'}(Sh-S'h',qr) = \langle a^pS_1h_1(b^{q-1}S_2h_2c^rS_3h_3)S_4h_4,Sh|| \sum_{\kappa=p+1}^{p+q+r} su(\kappa)||$$

$$(x) \ || a^pS'h'(bqS_2'h_2'c^{r-1}S_3'h_3')S_4'h_4';S'h' \rangle \qquad (C60)$$

The $R_{jk}(Sh-S'h',p)$ of (C59) is given in (C20), whereas $R_{jk'}$ of (C60) is a new type of reduced matrix element to be examined in the following. Considering (C21) and (C31) one finds that

$$R_{jk'}(Sh-S'h',qr) = (-1)(S_1+S_4+ h_1+h_4'+h) \ (x) \ \mathcal{D}\mathcal{D}'$$

$$(x) \ \langle (b^{q-1}S_2h_2,c^rS_3h_3)S_4h_4|| \sum_{\kappa=1}^{q+r} su(\kappa)||(b^rS_2'h_2'c^{r-1}S_3'h_3')S_4'h_4' \rangle$$

$$(x) \ \mathcal{W}(N_4'N_4N, NN'N_1) \ \delta_{N_1N_1'} \qquad (C61)$$

where as in (C31)

$$\mathcal{D}_i = \left[(2S_i+1) \quad (h_i)\right]^{1/2} \qquad (C62)$$

and

$$\mathcal{W}(N_iN_jN_o,N_kN_\ell N_m) = \bar{W} \ (S_iS_j1, \ S_kS_\ell S_m) \ (x)$$

$$(x) \ W \ (h_ih_jT_1, \ h_kh_\ell h_m) \equiv \bar{W} \begin{bmatrix} S_iS_j1 \\ S_kS_\ell S_m \end{bmatrix} W \begin{bmatrix} h_ih_jT_1 \\ h_kh_\ell h_m \end{bmatrix} \qquad (C63)$$

The dimensions (h_i) of h_i in (C62) are 1, 1, 2, 3 or 3 for $h_i = A_1, A_2$, E, T_1 or T_2 irreducible representations of the cubic group, $\bar{W}$ and W are related to the 6j symbols as defined in (C32) - (C35). The last term to be determined in (C61) is:

$$R_{jk'}\left[q-1,\ r;\ q,\ r-1\right] = \left\langle (b^{q-1} S_2 h_2,\ c^r S_3 h_3) S_4 h_4 \right\| \sum_{\kappa=1}^{q+r} su(\kappa) \left\|\right.$$

$$(x) \quad \left\| (b^q S_2' h_2' c^{r-1} S_3' h_3') S_4' h_4' \right\rangle \qquad \text{(C64)}$$

Before considering $R_{jk'}(q-1,r,q,r-1)$, a preliminary investigation of the permutational part of the simplification of the bra $\langle Z'|$ of $b^{q-1}c^r$ and the ket $|Z\rangle$ of $b^q c^{r-1}$ is helpful. For any single electron operator, $F = \Sigma_k f\ (k)$, the matrix element between $\langle Z'| = \langle (b^{q-1}c^r|$ and $|Z\rangle = |b^q c^{r-1}\rangle$ may be described as follows:

$$|Z\rangle = \left[q!(r-1)!\ (q+r-1)!\right]^{-1/2} \sum_{\mu} (-1)^{\mu} P_{\mu} |b^q\ \alpha\rangle \cdot |c^{r-1} \beta'\rangle$$

$$\langle Z'| = \left[(q-1)!\ r!\ (q+r-1)!\right]^{-1/2} \sum_{\nu} (-1)^{\nu} P_{\nu} \langle b^{q-1}\ \alpha'| \langle c^r \beta|$$

Then,

$$\langle Z'|F|Z\rangle = \left[q!(r-1)!(q+r-1)!\right]^{-1/2} \langle Z'| \sum_{\mu} (-1)^{\mu} P_{\mu} F |b^q \alpha\ \ c^{r-1} \beta'\rangle$$

$$= \sum_{\mu,\nu}^{q+r-1} (-1)^{\mu+\nu} P_{\nu} \langle b^{q-1} \alpha'| \cdot \langle c^r \beta | P_{\mu} F | b^q \alpha\rangle\ c^{r-1} \beta'\rangle$$

$$(x)\ [q!\ (q-1)!r!\ (r-1)!\ (q+r-1)!\ (q+r-1)!]^{-1/2} \qquad \text{(C65)}$$

where $\langle b^{q-1}\alpha' | \cdot \langle c^r \beta|$ is a simple product. The next step is to express the $|b^q\alpha\rangle$ and $|c^r\beta\rangle$ as function of their coefficients of fractional parentages:

$$|b^q\alpha\rangle = \sum_{\alpha''} \langle b^{q-1}\alpha'',b|\} b^q\alpha\rangle \cdot |b^{q-1}\alpha'' \cdot b, \alpha\rangle \tag{C66}$$

$$|c^r\beta\rangle = \sum_{\beta''} \langle c^r\beta \{|c,c^{r-1}\beta''\rangle \cdot |c,c^{r-1}\beta'', \beta\rangle \tag{C67}$$

where α,β,α' and β' in (C66) - (C67) denote the characterizing symbols of $|b^q\rangle,\ldots\ldots|c^r\rangle$, such as $S_2'h_2'$ in (C61) for $|b^q\rangle$. Substituting in (C65), we find:

$$\begin{aligned}\langle Z'|F|Z\rangle = \left[q!(r-1)!(q+r-1)!\right]^{-1} \sum_{\alpha'',\beta''} \sum_{\mu,\nu} (-1)^{\mu+\nu} P_\nu \\ (x) \langle c^r\beta \{|c,c^{r-1}\beta''\rangle \cdot \langle c.c^{r-1}\beta'',\beta| \cdot \langle b^{q-1}\alpha'|P_\mu F|b^{q-1}\alpha'' \cdot b,\alpha\rangle \\ (x)\ |c^{r-1}\beta'\rangle \langle b^{q-1}\alpha'', b|\} b^q\alpha\rangle (q/r)^{1/2}\end{aligned} \tag{C68}$$

Considering that

$$F = \sum_{\kappa=1}^{q+r-1} f(k)$$

one has

$$\sum_\mu P_\mu F = (q+r-1)!\ F$$

Substituting in (C68) one has

$$\langle Z'|F|Z\rangle = \left[q!\ (r-1)!\right]^{-1} \sum_{\nu} (-1)^{2\nu} P_{\nu} \sum_{\alpha''\beta''} \langle c^{r}\beta \{|c, c^{r-1}\beta''\rangle$$

$$(x) \langle c,\ c^{r-1}\beta'', \beta| \cdot \langle b^{q-1}\alpha'\ |F|\ b^{q-1}\alpha'' \cdot b, \alpha\rangle\ |c^{r-1}\beta'\rangle$$

$$(x) \langle b^{q-1}\alpha'',\ b|\} b^{q}\alpha\rangle\ (q/r)^{1/2}$$

$$= \sum_{\alpha'',\beta''} \left[q!(r-1)!\right]^{-1} \sum_{\nu} P_{\nu} \langle c^{r}\beta\{|c, c^{r-1}\beta''\rangle\langle b^{q-1}\alpha'', b|\} b^{q}\alpha\rangle$$

$$\langle c, c^{r-1}\beta'', \beta| \cdot \langle b^{q-1}\alpha'|F(q)|b^{q-1}\alpha'' \cdot b,\ \alpha\rangle|c^{r-1}\beta'\rangle\ (q/r)^{1/2}$$

$$= \sum_{\alpha'',\beta''} \left[q!(r-1)!\right]^{-1} \langle c^{r}\beta\ \{|c, c^{r-1}\beta''\rangle\ \langle a^{q-1}\alpha'', b\ |\} b^{q}\alpha\rangle$$

$$(x) \langle c|f|b\rangle (r-1)!\ \delta_{\beta'\beta''}(q-1)!\delta_{\alpha'\alpha''} \cdot (q/r)^{1/2} \cdot (qr)$$

$$= (qr)^{1/2} \langle c^{r}\beta\{|c, c^{r-1}\beta'\rangle\ \langle b^{q-1}\alpha',\ b|\}\, b^{q}\alpha\rangle\ \langle c|f|b\rangle$$

Thus

$$\langle\ b^{q-1}\alpha',\ c^{r}\beta| \sum_{\kappa}^{q+r-1} f(\kappa)|b^{q}\alpha,\ c^{r-1}\beta'\rangle$$

$$= (qr)^{1/2} \langle b^{q-1}\alpha',\ b|\} b^{q}\alpha\rangle\langle c^{r}\beta\ \{|c, c^{r-1}\beta'\rangle \cdot\langle c|f|b\rangle \qquad \text{(C69)}$$

We now apply (C69) to obtain

$$\sqcup = \left\langle (b^{q-1} S_2 h_2, c^r S_3 h_3)\ S_4 h_4 \right|\left| \sum_{\kappa=1}^{q+r} su(\kappa) \right|\right|$$

$$(x)\ \left|\left| (b^q S_2' h_2',\ c^{r-1} S_3' h_3')\ S_4' h_4' \right\rangle \tag{C70}$$

$$= \sum_{iM_4 M_4' \theta_4 \theta_4'} (-1)^{S_4 - M_4} \left\langle b^{q-1} S_2 h_2 c^r S_3 h_3 ; S_4 h_4 M\theta \right| \sum_k su(k) \left| b^q S_2' h_2' \right. \tag{C71}$$

$$(x)\ c^{r-1} S_3' h_3',\ S_4' h_4' M' \theta' \Big\rangle\ \bar{V}\ (S_4 S_4'\ 1, -M\ M' i)\ V\ (h_4 h_4' T,\ \theta\theta' - i).$$

Here

$$\left\langle b^{q-1} S_2 h_2 c^r S_3 h_3 ; S_4 h_4 M_4 \theta_4 \right| = \sum_{\substack{M_2 \theta_2 M_3 M_3'\ m \\ \theta_2 \theta_2 \theta_3'\ \mu}} \left\langle S_2 S_3 M_2 M_3 \middle| S_2 S_3 S_4 M \right\rangle$$

$$(x) \left\langle h_2 h_3 \theta_2 \theta_3\ \middle|\ h_2 h_3 h_4 \theta_4 \right\rangle \left\langle b^{q-1} S_2 h_2 M_2 \theta_2 \right| \left\langle c^r S_3 h_3 \right\{ \left| c, c^{r-1} \right.$$

$$\left. S_3' h_3' M_3' \theta_3' \right\rangle \left\langle 1/2 S_3' m M_3'\ \middle|\ 1/2 S_3' S_3 M_3 \right\rangle \left\langle c h_3' \mu \theta_3'\ \middle| c h_3' h_3 \theta_3 \right\rangle$$

$$\left\langle c^{r-1} S_3' h_3' M_3' \theta_3' \right| \left\langle c\ mu \right| \tag{C72}$$

Also,

$$\left| b^q S_2' h_2' c^{r-1} S_3' h_3' S_4' h_4' M_4' \theta_4' \right\rangle = \sum_{\substack{M_2' M_2' M_3 m' \\ \theta_2 \theta_2 \theta_3' \mu'}} \left\langle S_2' S_3' M_2' M_3' \middle|\ S_2 S_3 S_4 M_4 \right\rangle$$

$$(x) \left\langle h_2' h_3' \theta_2' \theta_3' \mid h_2' h_3' h_4' \theta_4' \right\rangle \left\langle b^{q-1} S_2 h_2 ,\ b\ m' \mu' \right| \left.\right\} b^q S_2' h_2' \right\rangle$$

$$\left\langle S_2 1/2 M_2 m' \middle| S_2 1/2 S_2' M_2' \right\rangle \left\langle h_2 b \theta_2 \mu' \mid h_2 b h_2' \theta_2' \right\rangle \left| bm'u' \right\rangle \left| c^{r-1} S_3' h_3' M_3' \theta_3 \right\rangle$$

$$(x) \left| b^{q-1} S_2' h_2' M_2' \theta_2' \right\rangle$$

Substituting in (C71), one finds:

$$L = \sum_{\substack{i M_4 M_4' \\ \theta_4 \theta_4'}} \ \sum_{\substack{M_2 M_3 M_3' m \\ \theta_2 \theta_3 \theta_3' \mu}} \ \sum_{\substack{M_2' M_2 M_3' m' \\ \theta_2' \theta_2 \theta_3' \mu}} (-1)^{h_4 - \theta_4} (-1)^{S_4 - M_4}$$

$$(qr)^{1/2}\ \bar{V}(S_4 S_4' 1, -M_4 M_4' - i)$$

$$(x) \left\langle S_2 S_3 M_2 M_3 \middle| S_2 S_3 S_4 M_4 \right\rangle \left\langle 1/2\ S_3' m\ M_3' \middle|\ 1/2 S_3' S_3 M_3 \right\rangle$$

$$(x) \left\langle S_2' S_3' M_2' M_3' \middle| S_2 S_3 S_4 M_4 \right\rangle \left\langle S_2 1/2 M_2 m' \middle| S_2 1/2 S_2' M_2' \right\rangle$$

$$(x)\quad V(h_4' h_4 T_1,\ \theta_4 \theta_4'\ i)$$

$$(x) \left\langle h_2' h_3 \theta_2 \theta_3 \middle| h_2 h_3 h_4 \theta_4 \right\rangle \left\langle c h_3' \mu \theta_3 \middle| c h_3' h_3 \theta_3 \right\rangle$$

$$(x) \left\langle h_2' h_3' \theta_2 \theta_3 \middle| h_2' h_3' h_4' \theta_4' \right\rangle \left\langle h_2 b \theta_2 \mu' \middle| h_2 b h_2 \theta_2' \right\rangle$$

$$(x) \left\langle c^{r-1} S_3 h_3 \left\{ \left| c,\ c^{r-1} S_3' h_3' \right\rangle \left\langle b^{q-J} S_2 h_2 , b \right| \right\} b^q S_2' h_2' \right\rangle$$

$$(x)\left\langle b^{q-1} S_2 h_2 M_2 \theta_2 \right| \left\langle c^{r-1} S_3' h_3' M_3' \theta_3' \right| \left\langle c m \mu \right| su \Big|$$

$$(x)\ \left| b m' \mu' \right\rangle \left| c^{r-1} S_3' h_3' M_3' \theta_3' \right\rangle \left| b^{q-1} S_2 h_2 M_2 \theta_2 \right\rangle \qquad (C74)$$

The individual coefficients appearing in (C74) can be simplified further as follows:

$$\left\langle c m \mu \right| su \left| b\ m' \mu' \right\rangle = (-1)^{1/2-m}\ \bar{V}\ (1/2\ 1/2\ 1,\ -m\ m'-i)\ \left[-1\right]^{c-\mu}$$

$$(x)\ V\ (c\ b\ T_1,\ -\mu\ \mu' i) \left\langle 1/2\ c \right\| su \left\| 1/2\ b \right\rangle$$

$$\left\langle S_i S_j M_i M_j \middle| S_i S_j S_k M_k \right\rangle = (2S_k+1)^{1/2} (-1)^{2S_j + S_k - M_k}$$

$$(x)\ \bar{V}\ (S_i S_j S_k,\ M_i M_j - M_k)$$

and

$$\left\langle h_i h_j \theta_i \theta_j \middle| h_i h_j h_k \theta_k \right\rangle = (h_k)^{1/2}\ V(h_i h_j h_k,\ \theta_i \theta_j \theta_k)$$

Substituting for coefficients in (C74), we find

$$\sqcup = \sum_{\substack{i M_4 M_2 M_3 M M' M_2' M_3' m' \\ \theta_4 \theta_2 \theta_3 \mu\ \theta' \theta_2' \theta_3' \mu'}} (-1)^{S_2 - S_2' + S_3' - S_3 + h_1 + h_2 + h_2}$$

$$(qr)^{1/2}\ \mathcal{D}_4 \mathcal{D}_4' \mathcal{D}_2' \mathcal{D}_3 \left\langle c^r S_3 h_3 \left\{ \middle| c,\ c^{r-1} S_3' h_3 \right\rangle \left\langle b^{q-1} S_2 h_2 b \middle| \right\} b^q S_2'\ h_2' \right\rangle$$

$$(x)\ \bar{V}\ (S_4 S_4' 1, -M_4 M_4 - i)\ \bar{V}(S_2 S_3 S_4; M_2 M_3 - M_4)\ \bar{V}\ (1/2 S_3' S_3, -m - M_3' + M_3)$$

$$(x)\ \bar{V}\ (S_2' S_3' S_4', -M_2 - M_3 + M_4')\ \bar{V}\ (S_2 1/2 S_2', M_2 m - M_2')\ \bar{V}\ (1/2\ 1/2\ 1, -m\ m' - i)$$

$$(x)\ V\ (h_4 h_4' T_1, \theta_4 \theta_4 i)\ V\ (h_2 h_3 h_4)\ V\ (c\ h_3' h_3, \mu \theta_3' \theta_3)$$

$$(x)\ V\ (h_2' h_3' h_4', \theta_2' \theta_3' \theta_4')\ V\ (h_2 b\ h_2', \theta_2 \mu\ \theta_2')\ V\ (c\ b\ T_1, \mu\ \mu\ i) \tag{C75}$$

$$= (-1)^{S_2 - S_2 + S_3 - S_3 + h_2 + h_2 + h_3} (qr)^{1/2} \mathcal{D}_2 \mathcal{D}_3 \mathcal{D}_4 \mathcal{D}_4'$$

$$(x) \left\langle b^{q-1} S_2 h_2, b \right| \Big\} b^q\ S_2' h_2' \Big\rangle \Big\langle c^r S_3 h_3 \Big\{ \Big| c, c^{r-1} S_3' h_3' \Big\rangle$$

$$\left\langle 1/2\ c \| su \| 1/2\ b \right\rangle$$

$$(x) \sum_{\substack{i M_4 M_2 M_3 m \\ M_4' M_2' M_3' m'}} \bar{V}\ (S_2 S_3 S_4, M_2 M_3 - M)\ \bar{V}\ (S_3 S_3'\ 1/2, M_3 - M_3' - m)$$

$$(x)\ \bar{V}\ (S_2' S_3' S_4', -M_2' - M_3' M')\ \bar{V}\ (S_4 S_4' i, -M_4 M_4' - i)$$

$$(x)\ \bar{V}\ (S_2 S_2'\ 1/2, -M_2 M_2' m')\ \bar{V}\ (1/2\ 1/2\ 1, m' - m - i)$$

$$(x) \sum_{\substack{\mu\ \theta_2\theta_3\theta_4 i \\ \mu'\theta'_2\theta'_3\theta'_4}} V(h_2h_3h_4, \theta_2\theta_3\theta_4)\ V(h_3h'_3c, \theta'_3\theta'_3\mu)\ V(h'_2h'_3h'_4, \theta'_2\theta'_3\theta'_4)$$

$$(x)\ V(h_4h'_4T_1, \theta_4\theta'_4 i)\ V(h_2h'_2b, \theta_2\theta_2\mu)\ V(cbT_1, \mu\mu' i) \tag{C76}$$

The sums in (C76) are the same as the 9-j symbol* and defined as:

$$X\left[abc,\ def,\ ghk\right] = \Sigma\alpha\beta\gamma\delta\varepsilon\phi\eta\theta\kappa\ \ V(abc, \alpha\beta\gamma)\cdot V(def, \delta\varepsilon\phi)$$

$$(x)\ (ghk, \eta\theta\kappa)\cdot V(adg, \alpha\delta\eta)\cdot V(geh, \eta\varepsilon\theta)\cdot V(cfk, \gamma\phi\kappa) \tag{C77}$$

Substituting for the sums in (C76) and recalling from (C64) and (C70) that, $R_{jk'}(q-1,r;\ q,\ r-1) \equiv L$, one has

$$R_{jk'}(q-1,r;q,r-1) = (-1)^{S_2-S'_2+S'_3-S_3+h_2+h'_2+h_3+h'_3}(qr)^{1/2}$$

$$\left\langle\ b^{q-1}S_2h_2, b\right|\Big\}\ b^q S'_2h'_2\ \Big\rangle\Big\langle c^r S'_3h'_3\Big\{\left|c, c^{r-1}S_3h_3\ \right\rangle$$

$$(x)\ \mathcal{D}_2\mathcal{D}_3\mathcal{D}_4\mathcal{D}'_4\ \ \chi\left[N_2N_3N_4,\ N'_2N'_3N'_4, N_bN_cN_o\right]$$

$$(x)\ \left\langle 1/2c\|su\|1/2b\right\rangle\cdot \tag{C78}$$

where

$$\chi[N_iN_jN_k, N_\ell N_mN_n, N_bN_cN_o] = \bar{X}\left[S_iS_jS_k,\ S_\ell S_mS_n,\ 1/2\ 1/2\ 1\right]$$

$$(x)\ X\left[h_ih_jh_k,\ h_\ell h_mh_n,\ b\ c\ T_1\right]\cdot \tag{C79}$$

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*They are also called X coefficients (See Ref. 26) and the remaining coefficients have their usual meanings. Substituting in (C61) and taking into account (C58) - (C60), one finds

$$\left\langle a^p S_1h_1 \; (b^{q-1}S_2h_2, \; c^r S_3h_3) \; S_4h_4, \; Sh \right\| \textstyle\sum_\kappa su(\kappa)$$

$$(x) \; \left\| a^p S'_1h'_1 \; (b^q S'_2h'_2, \; c^{r-1}S'_3h'_3) \; S'_4h'_4 ; S'h' \right\rangle$$

$$= R_{jk'} \; (Sh - S'h') = R_{jk}(Sh - S'h', \; p-p)$$

$$+ R_{jk'}\left[p, (q-1, r, Sh) - (q, r-1, \; S'h')\right]$$

$$= (-1)^{S_1+S_4+S+h_1+Sh'_4+h} \mathscr{D}\mathscr{D}' \; \mathscr{W}(N'_4N_4N_o, \; NN'N_1)$$

$$(x) \; G^p_a \; (S_1h_1 - S'_1h'_1) \left\langle 1/2a \| su \| 1/2a' \right\rangle \delta_{N_4N'_4}$$

$$+ (-1)^{S_1+S_4+S+h_1+h_4+h} \quad \mathscr{D}\mathscr{D}' \; \mathscr{W}(N'_4N_4N_o, \; NN'N_1)\delta_{N_1N'_1}$$

$$(x) \; (-1)^{S_2-S_2+S_3-S_3+h_2+h_2+h_3+h_3} \quad (qr)^{1/2}$$

$$(x)\left\langle b^{q-1}S_2h_2, \; b \right| \Big\} b^q S'_2h'_2 \Big\rangle \cdot \Big\langle \; c^r S'_3h'_3 \Big\{ \Big| c, c^{r-1}S_3h_3 \Big\rangle$$

$$(x) \quad \mathscr{D}'_2\mathscr{D}_3\mathscr{D}_4\mathscr{D}'_4 \quad \mathscr{X}\left[N_2N_3N_4, \; N'_2N'_3N'_4, \; N_bN_cN_o\right]$$

$$(x) \left\langle 1/2c \| su \| 1/2 \; b \right\rangle . \qquad \text{(C80)}$$

The complex conjugate of etero-configuration; three orbital reduced matrix elements can be obtained from (C80) by appropriate symmetry transformation on W and X coefficients in this equation. The result is:

$$R_{k'j}(S'h'-Sh) = \Big\langle a^p S_1'h_1'(b^q S_2'h_2'\ c^{r-1} S_3'h_3')\ S_4'h_4';S'h' \Big|\Big| \sum_{\kappa} su(\kappa) \Big|\Big|$$

$$(x)\ \Big|\Big| a^p S_1h_1(b^{q-1} S_2h_2 c^r S_3h_3)\ S_4h_4,\ Sh \Big\rangle$$

$$= R_{k'j}(p,S'h'-Sh) + R_{k'j}\Big[p,\ (q,r-1,S'h')-(q-1,r,Sh)\Big] \qquad \text{(C81)}$$

where

$$R_{k'j}(p,S'h'-Sh)=(-1)^{S_1'+S_4'+S+h_1'+h_4+h}\ \mathscr{D}\,\mathscr{D}'\ \mathscr{W}(N_1N_1'1,N'NN_4)$$

$$(x)\ G_a^p\ (S_1'h_1'-S_1h_1)\ \Big\langle 1/2a \Big|\Big| su \Big|\Big| 1/2a \Big\rangle\ \delta_{N_4'N_4} \qquad \text{(C82)}$$

and

$$R_{k'j}\Big[p,\ (q,r-1,S'h') - (q-1,r,Sh)\Big] = (-1)^{S_1'+S_4'+S'+h_1'+h_4+h'}$$

$$\mathscr{D}\cdot\mathscr{D}'\cdot\mathscr{W}(N_4N_4'N_o,\ N'NN_1')\ (qr)^{1/2}$$

$$(x)\Big\langle b^q S_2'h_2' \Big\{ \Big| b,b^{q-1} S_2h_2 \Big\rangle \cdot \Big\langle c,c^{r-1} S_3h_3 \Big| \Big\} c^r S_3h_3 \Big\rangle \Big\langle 1/2b \Big|\Big| su \Big|\Big| 1/2c \Big\rangle$$

$$(x)\,\mathscr{D}_2\mathscr{D}_3'\mathscr{D}_4\,\mathscr{D}_4'\cdot\ \mathscr{X}\Big[N_2'N_3'N_4',\ N_2N_3N_4,\ N_bN_cN_o\Big]\ \delta_{N_1'N_1} \qquad \text{(C83)}$$

Recalling (C56) - (C57), one finds that in both χ_j and χ_k the a^p parts of the system appears first and then b^q, b^{q-1} and c^{r-1}, c^r parts. Moreover, part b^q and c^{r-1} are always coupled together, first, and then their results are coupled to a^p. The desired matrix elements are not, however, arranged in this fashion and appropriate recouplings and couplings are needed to bring the three participating parts of the system in the above form. This has been done by using the following formula:

$$\left\langle \left[S_1h_1S_2h_2\right]S_\varepsilon h_\varepsilon,\ S_3h_3;\ Sh \right|\left| \sum_\kappa \mathrm{su}(\kappa) \right|\left| \left[S_1'h_1'S_2'h_2'\right] S_\varepsilon'h_\varepsilon', S_3'h_3', S'h' \right\rangle$$

$$= \sum_{S_\phi S_\phi' h_\phi h_\phi'} (-1)^{S_1+S_2+S_3+S+S_1'+S_2'+S_3'+S'+h_1+h_2+h_3+h_1'+h_2'+h_3'+h+h'}$$

$$(\mathrm{x})\ \mathcal{D}_\varepsilon \mathcal{D}_\varepsilon' \mathcal{D}_\phi \mathcal{D}_\phi' \cdot \mathcal{W}(N_1N_2N_\varepsilon,\ N_3NN_\phi) \cdot \mathcal{W}(N_1'N_2'N_\varepsilon'N_3'N'N_\phi')$$

$$(\mathrm{x}) \left\langle S_1h_1(S_2h_2S_3h_3)\ S_\phi h_\phi,\ Sh \right|\left| \sum_\kappa \mathrm{su}(\kappa) \right|\left| S_1'h_1'(S_2'h_2'S_3'h_3'), S_\phi'h_\phi', S'h' \right\rangle \tag{C84}$$

For the spin sextets, the sum reduces to one term because there is only one $S_\phi h_\phi$ and one $S_\phi' h_\phi'$ which results in the same Sh and S'h'. The values of $R_{jk'}$ are given in Table 3-4. Now, we consider the problem of four orbital reduced matrix elements.

6. HETERO-CONFIGURATION FOUR ORBITAL REDUCED MATRIX ELEMENTS

$R_{jk''}$(pqrs-1Sh,pqr-1s S'h')

Here, we consider the reduced matrix elements $R_{jk''}$ between states

$|j\rangle$ and $|k''\rangle$ both having four orbitals of the same symmetry. Two of these have the same configuration p and q in both $|j\rangle$ and $|k''\rangle$, whereas the remaining two have configurations r and s-1 in $|j\rangle$ and r-1 and s in $|k''\rangle$. Therefore,

$$R_{jk''}\,[(pqr\ s-1)\ Sh-\ (pqr-1s)\ S'h']$$

$$=\left\langle \chi_j(pqr,s-1)Sh\,\middle\|\,\sum_k su(k)\,\middle\|\,\chi_{k''}(pqr-1,s)S'h'\right\rangle \tag{C85}$$

where

$$|\chi_j(pqr,s-1)Sh\rangle = |(a^pS_1h_1b^qS_2h_2)S_3h_3(c^rS_4h_4d^{s-1}S_5h_5)S_6h_6;Sh\rangle \tag{C86}$$

and

$$|\chi_{k''}(pqr-1s)\ S'h'\rangle = |(a^pS_1'h_1'b^qS_2'h_2')S_3'h_3'(c^{r-1}S_4'h_4'sS_5h_5)S_6h_6;Sh\rangle \tag{C87}$$

All states can be arranged according to $|\chi_j(pqrs-1)Sh\rangle$ and $\chi_{k''}(pqr-1,s)S'h'\rangle$ by transformation similar to (C84). Hence the remaining calculations will be limited to the determination of $R_{jk''}[(pqrs-1)Sh-(pqr-1s)S'h']$.

Using (C16) - (C17), one decomposes $R_{jk''}\left[(pqr,s-1)\ h-(pqr-1s)Sh'\right]$ in terms of $R_{jk}(pq)$ and $R_{jk'}(r,s)$. $R_{jk}(p,q)$ and $R_{jk'}(rs)$ are, respectively, similar to the $R_{jk}(qr)$ given in (C21) and the $R_{jk'}(qr)$ given in (C61), except for the subscripts of various spin operators S_i and irreducible representations h_i. Taking this into account, one can immediately write down the $R_{jk''}$ as follows:

$$R_{jk''}\left[(pqrs-1)\ h-(pqr-1s)S'h'\right] = R_{jk''}(pqrs,Sh-S'h')$$

$$= \Big\langle (a^p S_1 h_1 b^q S_2 h_2) S_3 h_3 (c^r S_4 h_4 d^{s-1} S_5 h_5) S_6 h_6 ; Sh \Big|\Big| \sum_{\kappa} su(\kappa) \Big|\Big|$$

$$(x) \Big|\Big| (a^p S'_1 h'_1 b^q S'_2 h'_2) S'_3 h'_3 (c^{r-1} S'_4 h'_4 d^s S'_5 h'_5) S'_6 h'_6 ; S'h' \Big\rangle$$

$$= (-1)^{S_1+S_2+S_3+S_6+S'_3+S'+h_1+h'_2+h_3+h'_3+h'_6+h'} \cdot \mathcal{D}\mathcal{D}'\mathcal{D}_3\mathcal{D}_3'$$

$$(x) \mathcal{W}(N'_1 N_1 N_o, N_3 N_3 N_2) \quad \mathcal{W}(N'_3 N_3 N_o, NN'N_6)$$

$$(x) \; G^p_a(S_1 h_1 - S'_1 h'_1) \Big\langle 1/2a \Big|\Big| su \Big|\Big| 1/2a \Big\rangle \delta_{N_2 N'_2} \quad \delta_{N_6 N'_6}$$

$$+ (-1)^{S_1+S_2+2S_3+S_6+S'+h'_1+h'_2+h'_6+h'} \mathcal{D}\mathcal{D}'\mathcal{D}_3\mathcal{D}'_3$$

$$(x) \; \mathcal{W} N'_2 N_2 N_o, N_3 N'_3 N_1) \cdot \mathcal{W} N'_3 N_3 N_o, NN'N_6)$$

$$(x) \; G^q_b(S_2 h_2 - S'_2 h'_2) \Big\langle 1/2b \Big|\Big| su \Big|\Big| 1/2b \Big\rangle \cdot \; \delta_{N_1 N'_1} \quad \delta_{N_6 N'_6}$$

$$+ (-1)^{S_3+S_6+S+h_3+h'_6+h} \quad (rs)^{1/2} \, \mathcal{D}\mathcal{D}'\mathcal{D}'_4\mathcal{D}_5\mathcal{D}_6\mathcal{D}'_6$$

$$(x) \Big\langle c, c^{r-1} S'_4 h'_4 \Big| \Big\} c^r S_4 h_4 \Big\rangle \cdot \Big\langle d^s S'_5 h'_5 \Big\{ \Big| d, d^{s-1} S_5 h_5 \Big\rangle$$

$$(x)\mathscr{W}(N\ N\ N\ ,NN'N\ )\ \ \mathscr{X}(N_4N_5N_6,N'_4N'_5N'_6,N_cN_dN_o)$$

$$(x)\ \langle 1/2c||su||1/2d\rangle\ \delta_{N_3N'_3} \qquad \text{(C88)}$$

The matrix elements $R_{jk''}$ are given in Table 3.5.

APPENDIX D

COUPLING COEFFICIENTS OF SPIN ORBIT MATRIX ELEMENTS TO THEIR REDUCED MATRIX ELEMENTS

The purpose of this Appendix is to discuss the relationships between the matrix elements of spin orbit interaction between a pair or state and its corresponding reduced matrix element between the same states.

The states which are suitable for calculation of spin orbit interaction are those behaving as the irreducible representations t of the spinor group. The spin orbit matrix elements arising from $|\chi_j Shjt\tau\rangle$ and $|\chi_k S'h'J't'\tau'\rangle$ of the two states $|\chi_j Sh\rangle$ and $|\chi_k S'h'\rangle$ can be expressed as* (3.13)

$$\left\langle \chi_j ShJt\tau \middle| \Sigma_\kappa \; su(\kappa) \middle| \chi_k S'h'J't'\tau' \right\rangle$$

$$= \left\langle \chi_j Sh \middle\| \Sigma_\kappa \; su(\kappa) \middle\| \chi_k S'h' \right\rangle \cdot K_{JJ'} \; (SS'T_1, \; h'ht) \; \delta_{tt'} \; \delta_{\tau\tau'} \qquad \text{(D1)}$$

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[*] Considering (5.22) and (2.20) of Ref. 26 one has

$$\left\langle \chi ShJt\tau \middle| \Sigma_{i\alpha\beta} \left[\left(\zeta_i \ell^i \right)_\alpha {}^{T_1} \; (s^i)_\beta \; T_1 \right]_\gamma {}^{A_1} \middle| \chi' S'h'J't'\tau' \right\rangle$$

$$= \left\langle \chi ShJt\tau \middle\| \Sigma_{i\alpha\beta} \left[\left(\zeta_i \ell^i \right)_\alpha {}^{T_1} \; (s^i)_\beta \; T_1 \right]_\gamma {}^{A_1} \middle\| \chi' S'h'J't'\tau' \right\rangle$$

$$(x) \; V(tt' \; A_1, \; \tau\tau' \; \gamma)$$

$$= \left\langle \chi ShJt \middle\| \Sigma_{i\alpha\beta} \left[\left(\zeta_i \ell^i \right)_\alpha {}^{T_1} \; (s^i)_\beta \; {}^{T_1} \right] {}^{A_1} \middle\| \chi' S'h'J't' \right\rangle$$

$$[(t)]^{-1/2} \; \delta_{tt'} \; \delta_{\tau\tau'}$$

The $\langle \chi_J Sh || \Sigma_\kappa su(\kappa) || \chi_k S'h' \rangle$ was discussed in Appendix C. Here we focus our attention on $K_{JJ'}$. This coefficient may be also called the spin orbit matrix coupling coefficient or simply S-O matrix coupling coefficient. Moreover, it is written in several different forms as occasion demands. These are:

$$K_{JJ'} \equiv K_{JJ'}\ (SS'T_1,\ h'ht) \equiv K_{JJ'} \begin{vmatrix} SS'T_1 \\ h'\ ht \end{vmatrix} \qquad \text{(D2)}$$

The coefficient $K_{JJ'}$ is obtained from the formula (Ref. 26, p. 82)

$$K_{JJ'}\ (SS'T_1,\ h'ht) = \sum_{rMM'\theta\theta} (-1)^{S-M'+1}\ [-1]^{h+\theta}$$

$$(x)\ \bar{V}\ (SS'1,\ -MM'r)\ V\ (hh'T_1,\ -\theta\theta'-r)$$

$$(x)\ \langle ShJt\tau | ShM\theta \rangle \cdot \langle S'h'M'\theta' | S'h'J't\tau \rangle \qquad \text{(D3)}$$

The numerical values of $K_{JJ'}$ are given in Tables (3.9) - (3.12). The cases where $h = A_1$ and $h = h' = T_1$ are of particular importance for evaluation of spin orbit matrix elements between ground state $^6A_1$ of $(3d)^5\ ^6S$ ions in crystals and charge transfer states and will be examined in more detail as follows.

1. DETERMINATION OF $K_{JJ'}$ $(SS'T_1,\ h'ht)$ for $h = A_1$

Here, we consider the coupling coefficient which relates the matrix elements of the spin orbit interaction between the ground state $^6A_1$ and charge transfer excited states to its corresponding reduced matrix elements.

We represent the above charge transfer excited state by $|\chi' S' h' J' t\tau\rangle$ where, as before, χ', S' and h' are, respectively, the electronic configuration, spin, and irreducible representation of the cubic group of this state and J', t and τ are pseudo-angular momentum, irreducible representation of the state in spinor group and its component, respectively. Instead of the ground state $^6A_1$, 5/2, the state $|S\ A_1\ J\ \tau\rangle$ will be used and the result will be applied to the particular case of $|^6A_1, 5/2\ \tau\rangle$.

Considering (D3), we have

$$K_{JJ'}\ (SS'T_1,\ h'A_1t) = \sum_{rMM'\theta\theta'} (-1)^{S-M'+1}\ [-1]^{h+\theta}\ V\begin{pmatrix} SS'1 \\ -MM'r \end{pmatrix}$$

$$(x)\ V\begin{pmatrix} A_1 h' T_1 \\ i\ \theta\text{-}r \end{pmatrix} \langle S\ A_1 Jt|SAMi\rangle \cdot \langle S'h'M'\theta'|S'h'Jt\tau\rangle$$

Considering Griffith[17], p. 117, gives:

$$V\begin{pmatrix} A_1 h' T_1 \\ i\ \theta\text{-}r \end{pmatrix} = \frac{1}{\sqrt{(T_1)}}\ \delta_{T_1 h'} \cdot \delta_{r,\theta'}$$

also[17](p. 77)

$$\bar{V}\begin{pmatrix} SS'1 \\ -MM'r \end{pmatrix} = (-1)^{2S'+S-M} \sqrt{\frac{1}{(2S+1)}}\ \langle 1S'rM'|1S'SM\rangle$$

Thus

$$K_{JJ'}\,(SS'T_1,\ h'A_1t) = (-1)^{S-M'+1}\ [-1]^{A+i}$$

$$\sqrt{\frac{1}{(T_1)}\cdot\frac{1}{(2S+1)}}\cdot\sum_{\substack{rMM'\\ \theta\theta'}}\delta_{T_1h'_1}\cdot\delta_{\theta' r}$$

$$(x)\ \left\langle 1S'rM'\,|\,1S'SM\right\rangle\cdot\left\langle S\ A_1Jt\tau\,|\,SAM\theta\right\rangle\left\langle S'h'M'\theta'\,|\,S'h'J't\tau\right\rangle$$

$$= \sqrt{\frac{1}{(T_1)}\,\frac{1}{(2S+1)}}\ (-1)^{S+1}\sum_{MM'r}(-1)^{-M'}\left\langle 1S'rM'\,|\,1S'SM\right\rangle$$

$$(x)\ \left\langle S\ A_1Jt\tau\,|\,S\ A_1M\theta\right\rangle\left\langle S'T_1M'r\,|\,S'h'J't'\tau\right\rangle$$

$$= \sqrt{\frac{1}{(T_1)}\,\frac{1}{(2S+1)}}\ (-1)^{S+1}\sum_{M}\left\langle SAJt\tau\,|\,S\ A_1M\theta\right\rangle\sum_{M''M'r}(-1)^{-M'}$$

$$(x)\ \left\langle 1S'rM'\,|\,1S'SM\right\rangle\left\langle 1S'rM'\,|\,1S'J'M''\right\rangle\left\langle J'M''\,|\,J't\tau\right\rangle$$

$$= \sqrt{\frac{1}{(T_1)}\,\frac{1}{(2S+1)}}\ (-1)^{S+1}\sum_{MM''}\left\langle SAJt\tau\,|\,S\ A_1M\theta\right\rangle\left\langle JM''\,|\,J't\tau\right\rangle\sum_{M'r}(-1)^{-M'}$$

$$(x)\ \left\langle 1SrM'\,|\,1S'SM\right\rangle\left\langle 1S'rM'\,|\,1S'J'M''\right\rangle$$

$$= \sqrt{\frac{1}{(T_1)}\cdot\frac{1}{(2S+1)}}\sum_{MM''}\left\langle S\ A_1Jt\tau\,|\,S\ A_1M\theta\right\rangle\left\langle J'M''\,|\,J't\tau\right\rangle\delta_{MM''}\delta_{SJ'}\delta_{h'T_1}$$

$$= \sqrt{\frac{1}{(T_1)}\cdot\frac{1}{(2S+1)}}\sum_{M}\left\langle SA_1Jt\,|\,SA_1M\theta\right\rangle\left\langle SM\,|\,St\tau\right\rangle\delta_{SJ'}\cdot\sqrt{\frac{1}{(T_1)}\,\frac{1}{(2S+1)}}\ \delta_{SJ}\delta_{h'T_1}$$

Therefore

$$K_{JJ'}\begin{pmatrix} SS'T_1 \\ h'A_1t \end{pmatrix} = \sqrt{\frac{1}{3(2S+1)}}\ \delta_{SJ}\ \delta_{SJ'}\ \delta_{h'T_1} \tag{D4}$$

Several important conclusions may be drawn from (D4):

(i) The spin orbit interactions couples the ground states only to excited states $|\chi\ {}^6T_1\ 5/2t\tau\rangle$ and $|\chi\ {}^4T_{1i}\ 5/2t\tau\rangle$

(ii) The matrix element is independent of t and, as a result of this, no splitting will occur from a second order perturbation.

(iii) The matrix elements are independent of S' and thus, the energy shift resulting from ${}^4T_{1i}$ and ${}^6T_{1i}$ depends only on their reduced matrix elements.

The next important coupling coefficient to determine is between $|\chi_i Sh\rangle$ and $|\chi'_i S'h'\rangle$ where h, h' have T_1, symmetry.

2. DETERMINATION OF $K_{JJ'}$ $(SS'T_1,\ h'ht)$ for $h = h' = T_1$

The coupling coefficients relating a matrix element of the spin orbit interaction between a pair of charge transfer excited states whose irreducible representation in the cubic point group is T_1 will be analyzed in this section. The importance of considering this coefficient is apparent from (D4):

$$K_{JJ'}\ (SS'T_1,\ h\ A_1t) = \sqrt{1/3\ (2S+1)}\ \delta_{SJ}\cdot\delta_{SJ'}\ \ \delta_{h'T_1},$$

which indicates that the ground state ${}^6A_1$ couples to charge transfer excited states of T_1 symmetry alone and is not split by that. Consequently, a splitting by spin orbit interaction of the ground state ${}^6A_1$ of the complex $[\Sigma\ \Lambda_4]^{-n'}$ may occur through higher than second order perturbation and through the intermediary states, two of which, at least, must have symmetry T_1. Therefore, determination of $K_{JJ'}$, related to such states of T_1 symmetry deserves particular attention and we begin by studying $K_{JJ'}$ $(SS'T_1, T_1T_1t)$ as follows (D3):

$$K_{JJ'}\begin{pmatrix} SS'T_1 \\ T_1T_1t \end{pmatrix} = \sum_{rMM'\theta\theta'} (-1)^{S-M'+1} [-1]^{T_1+\theta} \bar{V}\begin{pmatrix} SS'1 \\ -MM'r \end{pmatrix} V\begin{pmatrix} T_1T_1t \\ -\theta\theta'-r \end{pmatrix}$$

$$(x) \left\langle ST_1Jt\tau | ST_1M\theta \right\rangle \cdot \left\langle S'T_1M'\theta' | S'T_1J't\tau \right\rangle$$

where

$$\bar{V}\begin{pmatrix} SS'1 \\ -MM'r \end{pmatrix} = \sqrt{\frac{1}{2S+1}} \left\langle S'1M'r | SM \right\rangle; \quad V\begin{pmatrix} T_1T_1T_1 \\ -\theta\theta'r \end{pmatrix} = V\begin{pmatrix} 111 \\ \theta\theta'r \end{pmatrix}$$

$$\left\langle ShJt | ShM\theta \right\rangle = \sum_{M''} \left\langle ShJt\tau | JM'' \right\rangle \left\langle JM'' | S1M\theta \right\rangle$$

$$\left\langle S'h'M'\theta' | S'h'J't\tau \right\rangle = \sum_{M'''} \left\langle S'h'M'\theta' | S'J'M''' \right\rangle \left\langle J'M''' | S'1J't\tau \right\rangle$$

Thus

$$K_{JJ'}\begin{pmatrix} SS'T_1 \\ T_1T_1t \end{pmatrix} = \sum_{MM''M'''} \cdot \sum_{rM'\theta\theta} \bar{V}\begin{pmatrix} SS'1 \\ -MM'r \end{pmatrix} \bar{V}\begin{pmatrix} 111 \\ -\theta\theta r \end{pmatrix} \sqrt{(2J+1)(2J'+1)}$$

$$(x) \; \bar{V}\begin{pmatrix} S'1J' \\ M'\theta'M''' \end{pmatrix} \bar{V}\begin{pmatrix} S1J \\ M-\theta M'' \end{pmatrix}$$

$$(x) \left\langle S1Jt\tau | JM'' \right\rangle \left\langle J'M''' | 1S'J't\tau \right\rangle$$

$$= \sum_{M'M'''} \sum_{\substack{MM''r \\ \theta\theta'}} \bar{V}\begin{pmatrix} SS'1 \\ -MM'\theta \end{pmatrix} \bar{V}\begin{pmatrix} 111 \\ -\theta\theta' r \end{pmatrix} \bar{V}\begin{pmatrix} S'1J' \\ M'\theta'M''' \end{pmatrix} \bar{V}\begin{pmatrix} S1J \\ M-\theta M'' \end{pmatrix}$$

$$(x)\ \sqrt{(2J'+1)(2J+1)}\ \langle S1Jt\tau | JM''\rangle\langle J'M''' | S'1J't\tau\rangle$$

$$= \sum_{M''M'''} \left(\frac{1}{2J+1}\right) \delta_{JJ'}\ \delta_{M''M'''}\ \bar{W}\begin{pmatrix} 111 \\ SS'J \end{pmatrix}\ \sqrt{(2J'+1)(2J+1)}$$

$$(x)\ \langle S_1 Jt\tau | JM''\rangle\langle J'M'' | J't\tau\rangle$$

$$= \sum_{M''} \bar{W}\begin{pmatrix} 111 \\ SS'J \end{pmatrix}\ \langle Jt\tau | JM''\rangle\langle JM'' | Jt\tau\rangle\ \delta_{JJ'} = \bar{W}\begin{pmatrix} 111 \\ SS'J \end{pmatrix}\ \delta_{JJ'}$$

APPENDIX E

FOURTH ORDER PERTURBATION

This Appendix gives the formulae necessary for the evaluation of the fourth order correction to the energy of the degnerate state $^6A_1$ of the complex* $[\Sigma\ \Lambda_4]^{-n'}$. In Chapter IV it was shown that the fourth order is the lowest order of spin-orbit perturbation of $^6A_1$ by charge transfer states which can lift the degeneracy of $^6A_1$ and contribute to the cubic field splitting 3a. Therefore, to determine 3a one must employ fourth order perturbation formulae.

These formulae can be obtained from the general expressions of nth order perturbation given by Corson+

$$E_n^{(s)}\ H^r = \Sigma_{jk} \left\langle H^{r,s}|V|H^{j,k}\right\rangle \left\langle H^{j,k}|K^{r,s};\ n-1\right\rangle$$

$$- \sum_{\nu=2}^{n-2} E_\nu^{(s)}\ H^r \left\langle H^{r,s}|K^{r,s};\ n-\nu\right\rangle \quad j \neq r \qquad \text{(E1)}$$

where $|H^{r,s}\rangle$, $|H^{j,k}\rangle$ are respectively the ground and excited states being involved in evaluation of $E_n^{(s)}\ H^r$, the superscripts s and k in $|H^{r,s}\rangle$ and $|H^{j,k}\rangle$ designate the sth and kth degenerate states belonging to the energy levels H^r and H^j,

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*See Appendix A

+E. M. Corson "Perturbation Methods in Quantum Mechanics of n-Electron," Hofner, New York (1951) p. 75

$$\left\langle H^{j,k} \middle| K^{r,s};\, n \right\rangle = -\sum_{\ell,m} \frac{\left\langle H^{j,k} \middle| V \middle| H^{\ell m} \right\rangle \left\langle H^{\ell m} \middle| K^{r,s};\, n-1 \right\rangle}{H^j - H^r}$$

$$+ \sum_{\nu=1}^{n-1} \frac{E_\nu^{(s)}\, H^r \left\langle H^{j,k} \middle| K^{r,s};\, n-\nu \right\rangle}{H^j - H^r} \qquad j \neq r \tag{E2}$$

and

$$\left\langle H^{j,k} \middle| K^{r,s}, 1 \right\rangle = (H^r - H^j)^{-1} \left\langle H^{j,k} \middle| V \middle| H^{r,s} \right\rangle . \tag{E3}$$

Substituting in (E1) - (E2) one obtains the desired $E_n^{(s)}$. The $^6A_1$ ground state of the complex $[\Sigma\ \Lambda_4]^{-n'}$, behaves as angular momentum J = 5/2. The irreducible representations of J = 5/2 in the cubic double group are E'' and U'. Thus

$$E_n^{(s)}\ {}^6A_1 = E^{(n)}(s);\ s = U' \text{ or } E'' \tag{E4}$$

For determination of the cubic field splitting, 3a, up to fourth order perturbation, a much simpler formulation is enough as will be seen below. 3a is the difference of the energy corrections $E^{(4)}$ (U') and $E^{(4)}$ (E''),

$$3a = E^{(4)}\ (U') - E^{(4)}\ (E''), \tag{E5}$$

and fourth order perturbation is the lowest one giving rise to such splitting. Thus all terms containing $E_\nu^{(s)}\ H^r = E^{(\nu)}(s)$ will vanish and the only contributing terms to (E5) are obtainable from the general formula

$$E^{(4)}(s) - E^{(4)}(s') = E_4^{(s)}\, H^r - E_4^{(s')} H^r$$

$$= \sum_{jk} \Big[\Big\langle H^{r,s} | V | H^{j,k} \Big\rangle \Big\langle H^{j,k} | K^{r,s}, 3 \Big\rangle$$

$$- \Big\langle H^{r,s} | V | H^{j,k} \Big\rangle \Big\langle H^{j,k} | K^{r,s}\ , 3 \Big\rangle \Big] \tag{E6}$$

where

$$\Big\langle H^{j,k} | K^{r,s}, 3 \Big\rangle = - \sum_{\ell,m} \frac{\langle H^{j,k} | V | H^{\ell,m} \rangle \langle H^{\ell,m} | K^{r,s}, 2 \rangle}{H^j - H^r}$$

$$+ \sum_{\nu=1}^{n-1} \frac{E_\nu^{(s)}\, H^r \Big\langle H^{j,k} | K^{r,s};\ 3-\nu \Big\rangle}{H^j - H^r} \tag{E7}$$

and

$$\Big\langle H^{\ell,m} | K^{r,s}, 2 \Big\rangle = - \Sigma_{p,q} \frac{\langle H^{\ell,m} | V | H^{p,q} \rangle \langle H^{p,q} | V | H^{r,s} \rangle}{(H^p - H^r)(H^r - H^\ell)}$$

$$+ E_i^{(s)} \frac{H^r \langle H^{p,q} | K^{r,s}, 1 \rangle}{H^j - H^r} \tag{E8}$$

Substituting in (E6) and eliminating terms having $E^{(s)}$ one immediately finds that:

$$\begin{aligned}
3a = - \sum_{jk;\ell m,pq} \Big\{ & \left\langle H^{r,U'} | V | H^{j,k} \right\rangle \left\langle H^{j,k} | V | H^{\ell m} \right\rangle \left\langle H^{\ell m} | V | H^{pq} \right\rangle \\
& (x) \left\langle H^{pq} | V | H^{r,U'} \right\rangle \left[(H^{j} - H^{r})(H^{\ell} - H^{r})(H^{p} - H^{r}) \right]^{-1} \\
& - \left\langle H^{r,E''} | V | H^{j,k} \right\rangle \left\langle H^{j,k} | V | H^{\ell m} \right\rangle \left\langle H^{\ell m} | V | H^{pq} \right\rangle \\
& (x) \left\langle H^{pq} | V | H^{r,E''} \right\rangle \left[(H^{j} - H^{r})(H - H^{r})(H^{p} - H^{r}) \right]^{-1} \Big\}
\end{aligned} \qquad \text{(E9)}$$

or more simply

$$\begin{aligned}
3a = - \sum_{j\ell p,kmq} (E_j E_\ell E_p)^{-1} \Big\{ & V(rU',jk)\ V(jk,\ell m)\ V(\ell m,pq)\ V(pq,rU') \\
& - V\ (rE'',jk)\ V(jk,\ell m)\ V(\ell m,pq)\ V(pq,rE'') \Big\}
\end{aligned} \qquad \text{(E10)}$$

where

$$V(rU',jk) = \left\langle H^{rU'} | V | H^{j,k} \right\rangle$$

and

$$E_i = H^i - H^r; \quad i = j,\ell,p \qquad \text{(E11)}$$

Since spin orbit interaction is diagonal in U' and E'' we can substitute for k m and q in (E10)

$$J_k U', \; J_m U', \; \ldots\ldots \; J_q E'' \qquad \text{(E12)}$$

APPENDIX F

SPIN-ORBIT MATRIX ELEMENTS BETWEEN $|\chi\ ShM\theta\rangle$ AND $|\chi' S' h' M' \theta'\rangle$ FOR $S \equiv S'$

In this Appendix we consider a different method of finding spin-orbit matrix elements which is applicable to pair of states of the same spin value, $S = S'$. This technique is particularly useful for the evaluation of the contribution to the cubic field splitting 3a from the spin sextuplets of charge transfer states. Since $S = 5/2$ for all states it can be considered as a constant and integration to be carried out over the orbital part of spin-orbit Hamiltonian only. Thus, instead of bases of the spinor group, $|Jt\tau\rangle$, we choose the bases $|h\theta\rangle$ of the single valued cubic group for the evaluation of the matrix elements.

Following (9.26) of Ref. 16 and considering the fact that for $S = 5/2$, there is only one state $|h\theta\rangle$ for any of the charge transfer states given in Table 3.2 one can describe the spin-orbit matrix elements in the $|ShM\theta\rangle$ scheme as follows:

$$\left\langle \chi\ ShM\theta \right| \sum_i \zeta_i \underline{\ell}^i \cdot \underline{s}^i \left| \chi' Sh' M' \theta' \right\rangle$$

$$= \sum_i \left\langle \chi\ ShM\theta \right| \zeta_i \underline{\ell}^i \left| \chi' Sh' M\theta' \right\rangle \cdot \left\langle \chi\ Sh' M\theta' \right| \underline{s}^i \left| \chi' Sh' M' \theta' \right\rangle \tag{F1}$$

The vector $\underline{s}^i$ in (F1) can be replaced as follows*

$$S(S+1) \left\langle \chi\ Sh' M\theta' \right| \underline{s}^i \left| \chi' Sh' M' \theta' \right\rangle$$

$$= \left\langle \chi\ Sh' M\theta' \right| \underline{S} \left| \chi' Sh' M' \theta' \right\rangle \left\langle \chi' Sh' M' \theta' \right| \underline{s}^i \cdot \underline{S} \left| \chi' Sh' M' \theta' \right\rangle \tag{F2}$$

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*E.U. Condon and G.H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press (1959) p. 61

where

$$\underline{s}^i \cdot \underline{S} = \underline{s}^i \cdot \underline{s}^i + \underline{s}^i \cdot \underline{S}'$$

$$= (1/2)(3/2) + (1/2)\ [S(S + 1) - (1/2)(3/2) - (S - 1/2)(S + 1/2)]$$

$$= (1/2)(S + 1). \qquad \text{(F3)}$$

Substituting in (F1) and (F2) one finds

$$\left\langle \chi\ Sh'M\theta' \middle| \underline{s}^i \middle| \chi' Sh'M'\theta' \right\rangle = \frac{(1/2)\ (S + 1)}{S(S + 1)} \left\langle \chi\ Sh'M\theta' \middle| \underline{S} \middle| \chi' Sh'M'\theta' \right\rangle$$

$$= \left\langle \chi\ Sh'M\theta' \middle| (2S)^{-1} \underline{S} \middle| Sh'M'\theta' \right\rangle \qquad \text{(F4)}$$

and

$$\left\langle \chi\ ShM\theta \middle| \sum_i \zeta_i \underline{\ell}^i \underline{s}^i \middle| \chi\ Sh'M'\theta' \right\rangle$$

$$= (2S)^{-1} \left\langle \chi\ ShM\theta \middle| \underline{S} \middle| \chi' ShM'\theta \right\rangle \cdot \sum_i \left\langle \chi\ ShM'\theta \middle| \zeta_i \underline{\ell}^i \middle| Sh'M'\theta' \right\rangle \qquad \text{(F5)}$$

To obtain the cubic field splitting from these matrix elements one carries a fourth order perturbation calculation on one of the components of $\underline{S}$ such as S_x and selects those states $|\mu\theta\rangle$ which would result to a non-vanishing term $bS_x{}^4$. Comparing this term with the spin Hamiltonian given in (2.1) one immediately finds that the contribution from the spin sextuplets of the charge transfer states to 3a is

$$[3a\ (\sigma, \Pi)]_s = 18 \sum_j b_j \qquad \text{(F6)}$$

where j covers all fourth order perturbation channels giving rise to terms of $b_jS_x^{\,4}$. Our initial results[15] were obtained by this very simple technique. The disadvantage of this method is its limitation to a fixed manifold of spin S and, consequently, it is not applicable to spin quadruplets and doublets of the complex $[\Sigma\ \Lambda_4]^{-n'}$ which has a ground state spin S = 5/2. Moreover, in this technique an apriori knowledge of the spin-Hamiltonian is necessary which is in contrast to the method described in the text.

APPENDIX G

COVALENCY DEPENDENCE OF THE CHARGE TRANSFER CONTRIBUTION TO THE CUBIC FIELD SPLITTING 3a (σ,Π)

In this Appendix, we examine the dependence of the cubic field splitting, $3a(\sigma,\Pi)$ on the covalency of the molecular orbitals involved.

Recalling (4.6) one has

$$3a(\sigma,\pi) = 3a^{(4)} = \sum_{i=0}^{4} C_i \, \zeta_d^{\,4-i} \, \zeta_p^{\,i} \tag{G1}$$

Here, ζ_d is the spin orbit interaction constant of the d orbitals of the S-state ion (e.g. Mn^{2+}), ζ_p is the spin orbit interaction constant of the p orbitals of the surrounding ligands [e.g. S in ZnS:Mn] and C_i are functions of the coefficients of linear combinations of atomic d and p orbitals.

Now, a question arises on the nature of the coefficients C_i in the limit of ionic approximation where the coefficients of ligand orbitals vanish.

To investigate this we examine $3a(\sigma,\pi;t_1 \rightarrow e_a)$ of (5.21) and $3a(\sigma,\pi;t_b \rightarrow e_a)$ of (5.25). The first one is

$$3a(\sigma,\pi;t_1 \rightarrow e_a) = -\,(9/1250)[\delta_1^{\,2}(\delta_1 + \varepsilon_1)]^{-1} \, \beta^2 \, \zeta_p^{\,4} \tag{G2}$$

Comparing (G2) with (G1) one finds for $3a(\sigma,\pi;t_1 \rightarrow e_a)$

$$C_0 = C_1 \quad C_2 \quad C_3 = 0$$

and

$$C_4 = -(9/1250)[\delta_1^2 (\delta_1 + \varepsilon_1)]^{-1} \beta^2 \qquad \text{(G3)}$$

where δ_1 and $\delta_1 + \varepsilon_1$ are energies required for a ligand to metal electron transfer as shown in Fig. 5.3 and β^2 is the covalency of the de orbitals of the S-state ion as described in (3.16). For an S-state ion in a II-IV compound with higher ionicity δ_1 increases whereas β^2 decreases. Thus at the ionic limit where $\beta^2 \to 0$ one has

$$\lim_{\beta^2 \to 0} C_4 \to 0 \qquad \text{(G4)}$$

and consequently

$$\lim_{\beta^2 \to 0} 3a(\sigma,\pi;t_1 \to e_a) \to 0 \qquad \text{(G5)}$$

Now we examine $3a(\sigma,\pi;t_b \to e_a)$. The coefficients C_i of this term are given in (5.25) as follows:

$$C_0 = \left[(18/625)[\delta_1'^2(\delta_1' + \varepsilon_1')]^{-1}\, 6\, \alpha^2\right]\lambda^6$$

$$C_1 = \left[(18/625)[\delta_1'^2(\delta_1' + \varepsilon_1')]^{-1}(6\, \alpha^2\, \kappa^2 - 2\sqrt{6}\, \alpha\, \beta\, \kappa\, \lambda)\right] \lambda^4$$

$$C_2 = \left[(18/625)[\delta_1'^2(\delta_1' + \varepsilon_1')]^{-1}(3\, \alpha^2\, \kappa^4/2 + \beta^2\, \kappa^2\, \lambda^2)\right]\lambda^2$$

$$C_3 = \left[(18/625)[\delta_1'^2(\delta_1' + \varepsilon_1')]^{-1}[\beta\, \kappa^4\lambda - (\sqrt{6}/2)\, \alpha\, \kappa^5]\right]\beta\lambda$$

and

$$C_4 = \left[(18/625)[\delta_1{}'^2(\delta_1{}' + \varepsilon_1{}')]^{-1}(4)^{-1}\,\kappa^6\right]\beta^2$$

At the ionic limit both β and λ approach to zero whereas $\delta_1{}'$ and $\delta_1{}' + \varepsilon_1{}'$ increase. Thus

$$\lim_{\beta,\,\lambda \to 0} C_{1i} \to 0; \qquad i = 0, 1, \ldots, 4 \qquad \text{(G6)}$$

and consequently

$$\lim_{\beta,\lambda \to 0} 3a(\sigma,\pi;t_b \to e_a) \to 0 \qquad \text{(G7)}$$

The vanishing of $3a(\sigma,\pi,t_a \to e_a)$ and $3a(\sigma,\pi,t_b \to e_a)$ follows from the fact that in each term contributing to $3a(\sigma,\pi)$ of (G1) there is at least one spin orbit matrix element of the type $t_a t_1$, $t_a e_b$, and $t_a t_b$ where

$$ab = \left\langle 1/2\ a \| \zeta\ \underline{\ell}\cdot\underline{s} \| 1/2\ b \right\rangle; \quad a, b = e_a, t_a, t_1, t_b, e_b\ .$$

The reduced matrix elements ab are given in Table 3.13. It is evident from this Table that all such reduced matrix elements contain β and or λ. Both of these vanish at ionic approximation and consequently all contributions to $3a(\sigma,\pi)$ of (G1) vanish at the ionic limit as expected.

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