

THEORETICAL STUDIES ON INDIRECT EXCHANGE INTERACTION
AND
CRYSTAL DISTORTION IN SOME MAGNETIC COMPOUNDS

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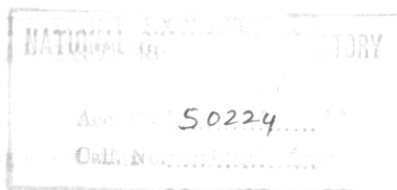
Theoretical Studies on Indirect Exchange Interaction

and

Crystal Distortion in some Magnetic Compounds

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Doctoral Dissertation in Physics

submitted to the

UNIVERSITY OF BRISTOL, ENGLAND.

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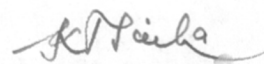
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P R E F A C E

The present dissertation is based on the work carried out by the author during his tenure as a post-doctoral research worker, from 1957 to 1959, in the H.H.Wills Physics Laboratory, University of Bristol (U.K.). As far as possible, references to subsequent publications in the relevant fields have been included.

The author is grateful to Professor M.H.L. Pryce, F.R.S., for valuable advice and interest in all phases of the work. He is indebted to his colleagues Drs. S. Koide and Y. Tanabe for discussions and assistance.


(K.P. Sinha)

S Y N O P S I S

The dissertation comprises of four chapters. Chapter 1 surveys the work on magnetic exchange interaction in magnetically ordered metals and compounds. Various mechanisms of exchange interactions, including those to be reported in the later chapters of the present work, are briefly discussed. A short resume of the crystal field theory and the electronic configurations of 3d metal ions in octahedral fields is given.

In chapter 2, the basic formulation of the indirect exchange mechanism for the spin coupling between paramagnetic ions, which are otherwise separated by intervening diamagnetic ions, in certain magnetic compounds is presented. This is done by following a new approach which takes into account the spatial correlations and the spin dependent polarization effects between the electrons of the intervening ions. This is described by formulating the appropriate semi-localized orbitals for each anion electron. An appropriate expression for the exchange interaction, which appears in the second order perturbation term, is derived using the spin operator formalism.

The conditions which lead to ferromagnetic and antiferromagnetic spin coupling between paramagnetic ions are then explored. It turns out that the coupling

is antiferromagnetic if the semilocalized orbitals of the anion show "angular correlation" effect and ferromagnetic if they suffer from "in-out" effect. The preference of one effect over the other depends on the relative symmetries and energies of the ground and excited orbitals involved. The problem is also analysed by the pure perturbational configuration interaction method. Quantitative calculations are carried out for "the three centre and four electron system" ($\dot{M}_1 - \ddot{X} - \dot{M}_2$) by the method of Slater determinantal functions. In this, the various eigenstates (which are linear combinations of Slater determinants) of the total spin operator (S^2) involving ground and excited states are formulated. The energy depressions of the zeroth order singlet (Antiferromagnetic) and triplet (ferromagnetic) states owing to interactions with the corresponding excited states are calculated. A rough numerical estimate for rock salt type systems (MnO, NiO etc.) is made and gives a reasonable agreement with the observed Ne'el Temperature.

In chapter 3, the spin polarization mechanism developed above is applied to the study of indirect exchange interaction in tetrahedral systems. For this purpose a "five centre and six electron system" ($(\dot{M})_4 \ddot{X}$), where the paramagnetic ions are at the corners of a regular tetrahedron and the anion at the centre, is chosen. The various quintet (ferromagnetic) and singlet (antiferromagnetic) states of the total spin are formulated

CHAPTER - I

GENERAL INTRODUCTION

In a quantum theoretical study of solids there is a growing realization of the importance of exchange and correlation phenomena in relation to certain spin dependant properties. That these effects together have a deeper bearing on the ferromagnetic and antiferromagnetic properties of magnetic substances needs further investigations. This is the motivation behind the work described in the first few chapters.

The basic concept of the quantum mechanical exchange interaction between two non-singlet like atoms was put forward by Heisenberg¹ invoking the Heitler-London theory² of the chemical bond. He demonstrated that the electrostatic interaction between the electrons when considered along with the principle of indistinguishability of like quantum particles and the exclusion principle gives rise to spin dependant terms in the energy of the system. This theory was further extended by Van Vleck³ using Dirac's approach of spin vectors.⁴ The nature of the coupling i.e. whether the spin alignment of the two atoms is ferromagnetic or antiferromagnetic is determined by the sign of the Heisenberg exchange integral,

$$J_H = \langle ab/V_{ab}/ba \rangle$$

$$= \iint \psi_a^*(1) \psi_b^*(2) \left(\frac{Ze^2}{R_{ab}} + \frac{e^2}{r_{12}} - \frac{Ze^2}{r_{1b}} - \frac{Ze^2}{r_{2a}} \right) \psi_b(1) \psi_a(2) d\tau_1 d\tau_2 ,$$

. (1.1)

where ψ_a and ψ_b are the localized atomic orbitals being respectively the solutions of

$$\left(\frac{p_1^2}{2m} - \frac{Ze^2}{r_{1a}} \right) \psi_a(1) = E_a \psi_a(1); \left(\frac{p_2^2}{2m} - \frac{Ze^2}{r_{2b}} \right) \psi_b(2) = E_b \psi_b(2)$$

. (1.2)

The constant nuclear repulsion term Ze^2/R_{ab} is ~~usually~~ taken out of (1.1) and treated as a parameter.

For orthogonal orbitals i.e. $S_{ab} = \langle a/b \rangle = \int \psi_a^* \psi_b d\tau = 0$, $J_H = \langle ab / \frac{e^2}{r_{12}} / ba \rangle$, which is always positive being the self energy of the overlap charge $e \psi_a^*(1) \psi_b(1)$. This would favour ferromagnetism (the triplet state). On the other hand for non-orthogonal orbitals

$$J_H = \langle ab / \frac{e^2}{r_{12}} / ba \rangle - 2S_{ab} \langle a/V/b \rangle \quad (1.3)$$

V being the attractive potential contained in (1.1). When the second term of equation (1.3) dominates, J_H is negative and antiferromagnetic coupling (i.e. the singlet state) is favoured.

This theory of direct exchange interaction between two paramagnetic atoms formed the basis of much theoretical work on ferro and anti-ferromagnetism.^{5,6,7}

Serious objections, however, were expressed on the quantitative aspects of the theory by Inglis⁸ and Slater⁹ owing to the suspected occurrence of divergence in the overlap and energy matrices when nonorthogonal orbitals are used and the number of electrons involved is infinitely large. Some recent rigorous examinations of the problem by Mizuno and Ezuyama,¹⁰ Arai¹¹ and Herring¹² have dispelled these doubts and have shown that the nonorthogonality catastrophe does not appear and the use of non-orthogonal orbitals can be reasonably solved.

This reassurance is indeed gratifying and in some of the later chapters the Hisenberg-Dirac approach will be employed. It is expedient for future reference to discuss a brief reformulation of the spin - Hamiltonian.^{4,11}

Let us consider a system consisting of N magnetic atoms each having one localized electron, the distinct orbital function of each being represented by

$\psi_1, \psi_2, \dots, \psi_N$. Within this orbital set, on including the spin functions, there are 2^N linearly independent states in that the spin variable σ_i can take either of the two possible values i.e. positive or negative. Denoting the spin functions by $\theta_m(\sigma_1, \sigma_2, \dots, \sigma_N)$, with $m = 1, 2, \dots, 2^N$, the antisymmetrized product wave

functions including both the orbital and spin parts can be written as

$$\Phi_m = \frac{1}{\sqrt{N!}} \sum_{P_t} (-1)^{P_t} P_t \psi_1(1) \psi_2(2) \dots \psi_N(N) \\ \times \Theta_m (\sigma_1, \sigma_2, \dots, \sigma_N), \dots (1.4)$$

where P_t is the permutation operator acting on both the orbital and the spin coordinates of the electrons.

Considering only the coulomb interaction between the electrons and the nuclei the Hamiltonian of the system is

$$H = \sum_i^N \left(\frac{p_i^2}{2m} - \sum_a \frac{e^2 Z_a}{r_{ai}} \right) + \sum_{i < j} \frac{e^2}{r_{ij}} = \sum_i^N H_i + \sum_{i < j} H_{ij} \dots (1.5)$$

The permutation $P_t = PP^\sigma$, where P applies on the orbital and P^σ on the spin coordinates. Thus the matrix element of the Hamiltonian connecting Φ_m and $\Phi_{m'}$ can be written as

$$\langle m/H/m' \rangle = \sum_P (-1)^P H_{p-1} \sum_\sigma \Theta_m P^\sigma \Theta_{m'}, \dots (1.6)$$

where $H_p = \langle P \psi_1(1) \psi_2(2) \dots \psi_N(N) / H / \psi_1(1) \psi_2(2) \dots \psi_N(N) \rangle$.

It follows from (1.6) that the evaluation of the energy matrix of the Hamiltonian is equivalent to the determination of the eigenvalues of the operator,

$$H_{\text{eff}} = \sum_P (-1)^P H_{P(-1)} P^\sigma \quad (1.7)$$

operating on the spin functions. Now Dirac⁴ has proved the identity that the permutation involving a pair of electrons can be expressed by the operator

$$P_{ij}^\sigma = \frac{1}{2} (1 + 4 \underline{S}_i \cdot \underline{S}_j) \quad (1.8)$$

where $\underline{S}_i$ and $\underline{S}_j$ are the one electron vector spin operators with components

$$S_{jx} = \frac{1}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad S_{jy} = \frac{1}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix},$$

$$S_{jz} = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

Since higher permutations can be broken down into products of pair permutations, i.e. $P_{ijk}^\sigma = P_{ij}^\sigma P_{jk}^\sigma$, $P_{M \geq 3}$ can be described by products of $\frac{1}{2} (1 + 4 \underline{S}_i \cdot \underline{S}_j)$. The effective Hamiltonian can thus be transformed to

$$H_{\text{eff}} = E - \frac{1}{2} \sum_{i < j} J_{ij} (1 + 4 \underline{S}_i \cdot \underline{S}_j) + \sum_{M \geq 3} \sum_{P_M} (-1)^P H_{P(-1)} O_M (\underline{S}_{i1}, \underline{S}_{i2} \dots \underline{S}_{iM}; P_M), \quad (1.9)$$

where the operator O_M is a function of spin operators

$\underline{S}_{i1}, \underline{S}_{i2}, \dots, \underline{S}_{iM}$, M denoting the number of electrons involved in the permutations. Under the assumption that the exchange integrals J_{ij} involving a permutation of single pair are much larger than H_p for $M \gg 3$, (1.9) reduces to the well known Heisenberg-Dirac Hamiltonian

$$H_{\text{eff}} \text{ (H-D)} = E_0 - \frac{1}{2} \sum_{i < j} J_{ij} (1 + 4 \underline{S}_i \cdot \underline{S}_j) \dots (1.10)$$

$$= E - 2 \sum_{i < j} J_{ij} (\underline{S}_i \cdot \underline{S}_j) .$$

It is useful to note that the operator $\underline{S}_1 \cdot \underline{S}_2$ has the eigen value $-\frac{3}{4}$ for the singlet state of a two electron system (i.e. $S = 0$) and $\frac{1}{4}$ for the triplet state (i.e. $S = 1$) (measuring the spins in units of $\hbar$).

The Hamiltonian (c.f. Equation (1.10)) found ready applications in systems having d and f electrons, which were assumed to be localized on the respective atoms. Aside from furnishing the basic microscopic mechanisms, this was adopted, within the framework of Weiss molecular field theory, by Heisenberg,¹ Van Vleck,^{5,7} and Ne'el⁶ in the study of the statistical behaviour of ferro and anti-ferromagnetic systems (See Danielian and Stevens^{7a} for a recent extension). For an arbitrary spin $\underline{S}_i$, the Hamiltonian for such purposes is

$$H = - 2 \sum_{l \neq m} J_{lm}(\underline{R}_{lm}) \underline{S}_l \cdot \underline{S}_m - \sum_l g \mu_B \underline{H} \cdot \underline{S}_l, \dots (1.11)$$

where l and m span the magnetic atoms of the system; the second term is the Zeeman term, $\underline{H}$ being the external field, g the spectroscopic splitting factor and μ_B the Bohr magneton. Since the macroscopic discussions are outside the plan of our study, we shall pass on to other aspects.

Before coming to the exchange interaction in compounds, another microscopic mechanism put forward for metals is relevant to our future work. When such crystals have conduction electrons (mainly due to s electrons), the role of exchange interaction between the localized magnetic electrons (say the d electrons) and the s electrons may become important. In this case the corresponding spin Hamiltonian can be written as

$$H_{sd} = - \frac{2}{N} \sum_{\underline{k}, \underline{k}'} J(\underline{k}, \underline{k}') \exp \left[i(\underline{k} - \underline{k}') \cdot \underline{R}_l \right] (\underline{S}_c \cdot \underline{S}_l), \dots (1.12)$$

where $\underline{S}_c$ is the spin operator for the conduction electron and $\underline{S}_l$ for the d electron, and

$$J(\underline{k}, \underline{k}') = \left\langle \psi_{\underline{k}'} \psi_l / \frac{e^2}{r_{12}} / \psi_{\underline{k}} \psi_l \right\rangle.$$

ψ_l is the localized d wave function and $\psi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{N}} \exp(i\underline{k} \cdot \underline{r}) U_{\underline{k}}(\underline{r})$ is the Bloch function for the

conduction electron. That the s-d exchange interaction can give rise to a coupling between two d atoms via the polarization of conduction electrons was first suggested by Zener.¹³ The detailed theoretical work was done by Kasuya¹⁴ and Yoshida.¹⁵ This coupling appears in the second order perturbation term after the conduction electron spin terms are eliminated. The effective interaction term is given by

$$H_{\text{eff}} = \sum_{l,m} I(R_{lm}) \underline{S}_l \cdot \underline{S}_m, \quad (1.13)$$

where

$$I(R_{lm}) = - \frac{9\pi}{2} \frac{N_s^2}{N^2} \frac{J_o^2}{\zeta} F(2k_o R_{lm})$$

$$F(x) = \frac{x \cos x}{x^4} - \frac{\sin x}{x^4}, \quad J_o = J(\underline{k}_1 \underline{k}_1)$$

i.e. the intra-atomic s-d exchange integral, N_s the total number of s electrons and ζ the Fermi energy; k_o is the propagation vector at the Fermi surface.

The sign of the interaction term depends on the function $F(2k_o R_{lm})$. Earlier, Ruderman and Kittel¹⁶ had discussed the indirect spin coupling between the spins of nuclei in a metal by precisely the same mechanism.

It is to be noted that the magnitude of this indirect exchange interaction decreases as the third power of the distance between the magnetic atoms. Furthermore, unlike the direct Heisenberg interaction term where nearest

neighbour interactions are of the greatest importance, the indirect coupling has a long range character. It appears therefore that the direct interaction may not be the dominant process in the ferro or antiferromagnetic ordering in metals. Furthermore, the indirect process is of particular significance in the magnetic ordering in dilute alloys and some rare earth metals.

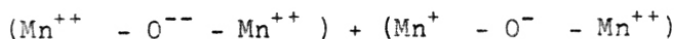
The situation in ordered magnetic compounds, where in addition to the paramagnetic ions, there are diamagnetic ions, becomes much more complicated. Most of the magnetic compounds of the transition elements (i.e. oxides, halides, sulphides, selenides etc.) show antiferromagnetic ordering. These cover ferromagnetic substances which are, in fact, non compensated antiferromagnets. (Nagamiya, Yoshida and Kubo;¹⁷ Anderson¹⁸). Furthermore, in the pure state they behave as insulators. Although there are some true ferromagnetic compounds which show metal like electrical conductivity, others (e.g. CrBr_3) are ferromagnetic insulators.¹⁹ The situation is difficult to reconcile with the band picture of solids and there is now general agreement with the Mott's²⁰ suggestion that the partially filled d shell electrons in these compounds are sufficiently localized at the respective magnetic ions.

The patterns of magnetic ordering as revealed by neutron diffraction studies (Shull et al.^{21,22}) indicate that the strongly coupled magnetic ions (next to nearest) are separated from each other by the intervening anion

($\uparrow \text{Mn}^{++} - \text{O}^{--} - \text{Mn}^{++} \downarrow$). Thus the large magnitude of the interaction cannot possibly be attributed to the direct exchange. This situation, therefore, suggests the importance of indirect exchange interactions involving various spin dependent excited configurations of the intermediate ions. This type of spin coupling, usually referred to as superexchange interaction, was first pointed out by Kramers.²³ Following him, several apparently distinct mechanisms have been suggested by several workers. These are usually confined to the study of the interactions in the basic interacting unit (three centres and four electrons). Yamashita and Kondo²⁴ have listed a number of these mechanisms. In what follows, the salient features of each are adumbrated.

Taking MnO as a typical example, let us consider two magnetic ions M_1^{2+} and M_2^{2+} separated by O^{--} ions. In the ground state, one assigns one d electron each to the magnetic ions and two paired electrons occupying the same p orbital of the anion. Some suggested mechanisms are :

- i) Kramers²³ - Anderson²⁵ model



The principal feature of this process can be described thus. One of the two anion electrons is transferred to one of the magnetic ions, say M_1 , occupying an s or a d orbital. The unpaired electron left behind in the anion has then exchange coupling with the electron

of the other magnetic ion M_2 . The perturbation chosen in this process is such that the orbital transition is spin independent with the result that the interaction appears in the third order of the perturbation theory, namely,

$$H_{tt'} = \sum_{uu'} \frac{\langle t/H^{tr}/u \rangle \langle u/H^{ex}/u' \rangle \langle u'/H^{tr}/t' \rangle}{(E_u - E_t) (E_{u'} - E_{t'})}, \dots (1.14)$$

where t and t' refer to the degenerate ground spin states and u and u' to the excited states. The perturbation as indicated is split into two parts $H^{tr} + H^{ex}$, where the former is spin independent and the latter is spin dependent. To this mechanism Anderson and Hasegawa²⁶ added another process in which the transferred electron to M_1 returns to the anion with the simultaneous jump of the other electron to M_2 . Neglecting overlap of the orbital functions the spin dependent Hamiltonian for both the processes can be expressed as

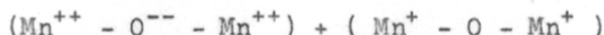
$$H_{eff}(KA+AH) = - \frac{4b^2}{(\Delta E)^2} (J_{pd} + J'_{pd}) (\underline{S}_{m_1} \cdot \underline{S}_{m_2}), \dots (1.15)$$

where

$$\begin{aligned} b &= \langle \psi_{d_1}(1)/H(1)/\psi_p(1) \rangle \\ J_{pd} &= \langle \psi_p \psi_{d_1}/H_{12}/\psi_d \psi_p \rangle \\ J'_{pd} &= \langle \psi_p \psi_{d_1}/H_{12}/\psi_{d_2} \psi_p \rangle ; \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \dots (1.16)$$

here J_{pd} refers to the Kramers-Anderson (K-A) mechanism and J'_{pd} to the Anderson-Hasegawa model. Actually the d and p orbitals are not orthogonal and hence qualitatively they inferred that J_{pd} and J'_{pd} will be negative. The important deductions for more than and less than half filled d shells of the magnetic ions are that according to the K-A mechanism the former situation will exhibit antiferromagnetic coupling and the latter ferromagnetic. On the contrary, the Anderson-Hasegawa mechanism leads to antiferromagnetic coupling in both the situations. There are many exceptions to these conclusions and hence it cannot be accepted as applicable. Another tentative conclusion was the 180° directionality in the interaction in that the interacting magnetic ions are on the opposite side of the dumbbell of the anion p orbital. This may seem to hold for a few systems but a general validity is doubtful when the role of other orbitals having different dispositions is considered. Furthermore, it is desirable to include the overlap of the wave functions in the calculations which was taken into account in the later work of Keffer and Oguchi²⁷ (see also Yamashita and Kondo²⁴). It is not possible to arrive at any decisive conclusion from their results in view of the choice of the orbital wave functions and the appearance of several parameters. Also, by a proper choice of the perturbations, the interaction should appear in a lower than the third order.

ii) The model suggested by Slater,²⁸ Pratt,²⁹ Goodenough^{30,95} and Nesbet:^{31,32}



The basic idea of this mechanism is that of the two paired electrons in the central ion p orbital one goes to the singly occupied orbital of the magnetic ion on the left side and simultaneously the other goes to the singly occupied magnetic ion orbital on the right side. This mechanism always leads to the antiferromagnetic super-exchange effect because one electron is transferred to the orbital having already a spin up electron and the other to the orbital having a spin down electron. The interaction appears in the second order of the perturbation theory and the stabilization of the antiferromagnetic states as given by Nesbet^{31,32} is expressed as:

$$D = \frac{\langle \psi_p^{(1)} \psi_p^{(2)} / \frac{e^2}{r_{12}} / \psi_{d_1}^{(1)} \psi_{d_2}^{(2)} \rangle^2}{\Delta E_N}, \quad (1.17)$$

where ΔE_N is the energy difference between $d_1^2 d_2^2$ and $(d_1 \alpha)^2 (d_2 \beta)^2$, α and β indicating the two spin states. Considerable doubt,²⁷ however, has been expressed concerning the quantitative estimates particularly the energy denominator and in view of the double ionization involved in the mechanism, this seems to be a feeble effect. The important feature to notice in the mechanism is that,

following Slater's suggestion, this appears to be the first serious attempt to consider the charge correlation effect of the two anion electrons.

iii) The delocalization model of Kondo³³ and Anderson³⁴ which stems from the band picture:



Kondo,³³ in his band picture calculation of superexchange interaction in NiO , was the first to obtain the appropriate expression, within this mechanism, of the energy difference between the parallel and antiparallel spin states. Later, Anderson³⁴ gave a sophisticated discussion of essentially the same delocalization term.

In the new reformulation of Anderson,³⁴ the electron transfer terms between the magnetic ions and the anions occurring in his old theory²⁵ are not explicitly taken into account. This is eliminated by assuming an exact solution of the one electron problem of the electrons of the magnetic ions in the presence of the diamagnetic lattice (ligand field effects⁴⁷). In other words, this solution, in principle, contains an antibonding admixture of the anion occupied orbital. Such electrons of the magnetic ions are assumed to be surrounded by spin independent electronic dielectric polarizations. Let us denote such electrons by d_1' , d_2' belonging to magnetic ions at sites M_1 and M_2 etc. in the ground state. Then it is assumed that by the virtual superposition of the ionized state in

which the electrons are transferred from one magnetic ion to another the system gains energy. This process is opposed by the coulomb repulsion of the two electrons on the same ion. The interaction terms appear in the second order perturbation and the coupling is antiferromagnetic when both the orbitals involved in the transfer are singly occupied. When the state to which transfer takes place is completely empty, the coupling, which is ferromagnetic, appears in the third order and involves both transfer and internal exchange integrals. Including both the situations the spin dependent energy terms are

$$H_{\text{eff}}(\text{delocalization}) = \sum_{m_1 \neq m_2} \left(\frac{2b_{12}^2}{U} - \sum_{\text{empty orbitals}} \frac{2b_{12}^2 J}{U^2} \right) \underline{s}_{m_1} \cdot \underline{s}_{m_2}, \quad (1.18)$$

where b_{12} is the transfer integral involving the two magnetic ions, J and U are the intra-atomic exchange integral (always positive) and the repulsive energy of the excited state respectively. The ferromagnetic term is weaker than the antiferromagnetic term by the factor $\frac{J}{U}$. Anderson³⁴ takes the reciprocal of this factor to be about 5 to 10. However, if the magnetic ions have several low lying empty orbital states, the antiferromagnetic term will be considerably weakened. The estimates of the parameters b_{12} and U made by Anderson are empirical in view

of the rough correlations of b_{12} with the ligand field theory parameter $10 Dq$ and liberal reductions made in the magnitude of U . The simplicity of the theory appears to be deceptive when one considers the starting assumption, namely, the availability of an exact solution of one electron problem in the presence of the diamagnetic lattice. It may, however, be mentioned that the attempt to bring in the role of ligand field theory is in the right direction. In this context it should be noted that Kamamori³⁵ first appreciated the importance of the symmetry of the singly occupied orbital functions of the magnetic ions subject to the crystalline field and the orbitals of the anions in relation to superexchange interactions (see also Wollan³⁶).

It will be seen in the discussion of the spin coupling owing to the spin polarization of the anion electrons that the symmetry of the excited orbital functions relative to the occupied orbitals is of central importance. This forms the subject matter of the few chapters of the present dissertation. This work was initiated by the author in an attempt to assess the combined role of correlation and exchange effects in the spin coupling of the magnetic compounds under discussion. Some parts of the work remain unpublished and the others have already appeared as single and joint publications. (Sinha,³⁷ Koide and Sinha;³⁸ Koide, Sinha and Tanabe;³⁹ Sinha and Koide;⁴⁰ Sinha.^{41,42}).

CHAPTER - II

IUPAC'S ROLE IN CHEMICAL NOTATION SYSTEMS

This mechanism, which is analogous to the Zener,¹³ Kasuya¹⁴ and Yoshida¹⁵ model of indirect exchange of magnetic ion spin coupling in metals, and the Ruderman, Kittel¹⁶ and Ramsey⁴³ - Bloembergen³³ model of spin coupling between nuclear spins, was pointed out for the first time by Sinha³⁷ and later along with co-workers^{38,39} in the study of the spin coupling in the magnetic compounds, being considered in the present work. It is interesting to note that this mechanism appeared automatically when the spin coupling was studied with due cognizance of spin and coulomb correlations between anion electrons without any attempt whatsoever of invoking the counterparts in metallic and nuclear problems. Anderson also gave a discussion of the analogous mechanism by a different method later.^{34,18}

In this context it is also relevant to note Slater's suggestion²⁸ that the potential energy of an up spin anion electron is different from that of the down spin anion electron in the identical orbital owing to interactions with the neighbouring magnetic ions. The resultant mechanism is effective only when the magnetic ions M_1 and M_2 have antiparallel spins. It will be seen in the next chapters that the spin polarization mechanism, in keeping with the coulomb correlation effects, can lead to either of the antiferromagnetic and ferromagnetic coupling depending on the symmetry and energies of the orbitals.

Since the energy levels, the nature and spatial

dispositions of the orbitals of the magnetic and the ligand ions in the crystal field are of importance in the study of exchange interaction, a brief discussion of this, by now, well known theory⁴⁵ will be in order (For details see e.g. Bleaney and Stevens⁴⁶ or Griffith⁴⁷). Here we follow the account given by Sinha and Tanabe.⁴⁸

Let us consider an atom or ion at the centre of an octahedron and also one ion each at the corners of the same. If the Hamiltonian of the free central ion is represented by H_0 , then the effect of the other six ions at the corners can be treated as a perturbation V at the central ion and which has a cubic symmetry. The Hamiltonian H_0 has the symmetry of the rotation group including inversion. Now the symmetry group O_h (to which the above octahedral arrangement of atoms belongs) is a subgroup of the rotation group and hence the symmetry of the total Hamiltonian,

$$H = H_0 + V$$

has the symmetry of the cubic group. As a result the degenerate energy levels of the central ion corresponding to the various irreducible representations D_l (dimension $2l+1$) of the rotation group will be split and the various split manifold will now belong to the various irreducible representations of the O_h group. This can be derived following group theoretical calculations and one gets the following classification

Irreducible Representations		
l	Rotation group	O_h group
0	D_0	A_{1g}
1	D_1	T_{1u}
2	D_2	$E_g + T_{2g}$
3	D_3	$A_{2u} + T_{1u} + T_{2u}$

and so on. The angular part of the orbital wave functions of the central ion which form the bases of these irreducible representations of the O_h group can be derived from the corresponding spherical harmonics. These are given below:

Irreducible Representations	Base functions
A_{1g}	$f_0(r), f_4(r) (x^4+y^4+z^4 - \frac{3}{5} r^4)$
A_{2g}	Cyclic $\sum_{xyz} x^4(y^2 - z^2)$
E_g	$(3z^2 - r^2), \sqrt{3}(x^2 - y^2)$
T_{1g}	$xy\sqrt{3}(x^2 - y^2), yz\sqrt{3}(y^2 - z^2), zx\sqrt{3}(z^2 - x^2)$
T_{2g}	$xy, yz, zx.$
A_{1u}	$xyz \sum_{cyclic} x^4(y^2 - z^2)$

Λ_{2u}	xyz
E_u	$xyz\sqrt{3}(x^2-y^2), \quad xyz(-3z^2+r^2)$
T_{1u}	$x, y, z.$
T_{2u}	$z\sqrt{3}(x^2-y^2), \quad x\sqrt{3}(y^2-z^2), \quad y\sqrt{3}(z^2-x^2)$

In the above Mulliken's⁴⁹ notation has been followed; the one dimensional non degenerate irreducible representations are denoted by Λ_1 and Λ_2 , the doubly degenerate (two dimensional) by E and the triply degenerate (three dimensional) by T_1 and T_2 . The subscripts 1 or 2 denote those which are symmetric or antisymmetric under one of the two fold rotations about an axis perpendicular to the principal axis and likewise g or u under the inversion transformation.

For present purposes, a discussion of the electronic configuration of iron group ions having incomplete 3 d shell is sufficient. In most of the compounds the positive magnetic ions are surrounded by an octahedron of negatively charged ligands (e.g. F^- , O^{--} , S^{--} , etc.).

In such systems the crystal field effects are much stronger than spin orbit perturbations (Pryce⁵⁰) and it is customary to classify the free ion states by first considering crystal field perturbations and then spin orbit effects (intermediate field scheme).⁴⁷

Conversely, the crystal field effects may be taken into account first, then the coulomb repulsion between electrons and finally spin orbit terms (strong field scheme).⁴⁷ Thus, for the purely electrostatic model, the d orbitals in the ^{cubic} ~~entire~~ field are split into doublet,

$d\gamma$: $d(2z^2 - x^2 - y^2)$, $d(x^2 - y^2)$ and the triplet

$d\epsilon$: $d(xy)$, $d(yz)$, $d(zx)$.

For an octahedron the $d\gamma$ orbitals lie higher than $d\epsilon$ (the reverse is the case for a tetrahedral arrangement of ligands) the energy difference being expressed as Δ or $10 Dq$. The angular dependence of the orbitals are such that the lobes of the two $d\gamma$ orbitals point towards the z axis and x and y axes respectively and $d\epsilon$ orbitals have their lobes pointing midway between the coordinate axes. When the mixing of these orbitals with the combination of ligand orbitals having appropriate symmetry (E_g or T_{2g}) is taken into account the resulting orbitals are denoted by e_g and t_{2g} . In the electrostatic (the point charge) model, the electronic configuration of the ions may be described as:

closed shell + $(d\epsilon)^n (d\gamma)^{n'}$,

$n+n' = N$, the number of d electrons. The lowest states of these ions are given below.⁵¹

	Free ion ground state	Intermediate field	Strong field	Ions
3d ¹	² D	² T _{2g} (d ¹)		Ti ³⁺
3d ²	³ F	³ T _{1g} (d ²)		V ³⁺ , Ti ²⁺
3d ³	⁴ F	⁴ A _{2g} (d ³)		Mn ⁴⁺ , Cr ³⁺ , V ²⁺
3d ⁴	⁵ D	⁵ E _g (d ³ dy)	³ T _{1g} (d ⁴)	Mn ³⁺ , Cr ²⁺
3d ⁵	⁶ S	⁶ A _{1g} (d ³ dy ²)	² T _{2g} (d ⁵)	Fe ³⁺ , Mn ²⁺
3d ⁶	⁵ D	⁵ T _{2g} (d ⁴ dy ²)	¹ A _{1g} (d ⁶)	Fe ²⁺
3d ⁷	⁴ D	⁴ T _{1g} (d ⁵ dy ²)	² E _g (d ⁶ dy)	Co ²⁺
3d ⁸	³ F	³ A _{2g} (d ⁶ dy ²)		Ni ²⁺
3d ⁹	² D	² T _{2g} (d ⁶ dy ³)		Cu ²⁺

Other components of the configuration in some ions
e.g. Ti²⁺, Co²⁺ are not given here.

The electronic configuration of some ions
involving orbital degeneracy (e.g. d⁴ or d⁹) give rise
to distortions in the surrounding arrangement of the
ions so as to remove the degeneracy; a study of this
problem including covalency effects will, however,
form the subject matter of the second part of the present
work (i.e. Chapter 4).

C H A P T E R - 2

SPIN POLARIZATION MECHANISMS OF INDIRECT EXCHANGE

Theoretical model and description of orbitals

In this chapter the basic formulation of the indirect exchange mechanism for the spin coupling between paramagnetic ions in certain compounds is presented on the basis of a new approach which takes into account the spatial correlation between the electrons of the intervening diamagnetic ions. The results will show that the spin coupling, within this mechanism, is intimately connected with correlation (configuration interaction) effects.

The correlation problem^{52,53} between electrons arises because of the mutual repulsive coulomb interaction e^2/r_{ij} which becomes very large as the distance r_{ij} tends to zero. The effect of this is to keep the electrons apart and in the description of the motion of many electrons one can talk of each electron being surrounded by a "coulomb hole".^{53,54} In the Hartree-Fock scheme,⁵³ where one uses a Slater determinant or in other words antisymmetrized product wave function of one electron orbitals, an appreciable part of the correlation effect is accounted for in that each electron of a given spin is surrounded by a "Fermi hole" with respect to other electrons having the

same (parallel) spin orientations. However, in the H.F. Scheme where some orbitals are occupied by two electrons with antiparallel spins (or more precisely, the two electrons are in the singlet state) so as to satisfy the exclusion principle, the correlation error remains. Thus the correlation energy is usually associated with such paired electrons.

The intervening diamagnetic ions (e.g. O^{--} with the ionic configuration $1s^2, 2s^2 2p^6$) with closed shell description involve doubly filled orbitals and the coulomb correlation effects for such ions are unaccounted for. One way out of this difficulty is to have different orbitals for different spins.^{52,55} Two situations can arise in this description. First, the "angular" correlation effect in which the two paired electrons tend to be on opposite side of the ion core. The second is the "in-out" effect with the orbital of one electron tending to be inside that of the other. In the formulation of the magnetic interaction problem, the influence of both these effects on the possible spin coupling of the adjacent paramagnetic ions will be investigated.

Neither the Heitler-London (HL) Scheme² nor the molecular orbital (MO) approach⁵⁶⁻⁶⁰ is very convenient to describe the correlation effect between antiparallel electrons quantitatively in that the probabilities of a large number of configurations have to be independently determined to give the minimum energy.

In the first section of this chapter an attempt is made to overcome these difficulties by using a method intermediate between the HL and the MO schemes. This is similar to the method proposed by Mueller and Eyring⁶¹ for the calculation of electronic states of molecules and extended by Löwdin to solids.⁵² This method of different orbital for different spins has many advantages in the description of electronic and magnetic properties of molecules and solids.

Let us consider the usual three centre problem, namely, $M_1^{2+} - X^{2-} - M_2^{2+}$, where the M's represent paramagnetic ions and X^{2-} the ligand ion. Such magnetically correlated collinear units occur in rock salt and perovskite type magnetic systems (e.g. NiO, MnO; LaFeO₃, CaMnO₃). Consider the case of NiO; in the ionic model each Ni²⁺ ion has the ($d\epsilon^6$, dy^2) configuration and is surrounded octahedrally by six oxygens. Each oxygen having the configuration ($1s^2$, $2s^2$ $2p^6$) is likewise surrounded by six Ni²⁺ ions. If the Ni-O-Ni axis is chosen to represent the z axis, it is easy to see that the important metal ion orbital for the present unit is $d(2z^2-x^2-y^2)$, denoted here by $d\sigma$. On the same basis the $2p_z$ (i.e. p_σ) orbital of the anion will have a larger overlap with the metal ion $d\sigma$ orbital. In order to include the covalency effects we start with bonding and antibonding orbitals. The bonding and antibonding orbitals for octahedral complexes involving transition ions have

been formulated by others (See Van Vleck,⁶² Owen⁶³ and Stevens⁶⁴). The appropriate orbitals for the present three centre unit are, however, chosen with respect to the symmetry plane intersecting the molecular axis normally at the centre. The orbitals are:

$$p = \frac{p_{\sigma} + \gamma (d\sigma_1 - d\sigma_2)}{\sqrt{1 + 2\gamma S_1 - 2\gamma S_2 + 2\gamma^2}} \quad \dots (2.1)$$

$$u_1 = \frac{d\sigma_1 - (\gamma + S_1) p_{\sigma}}{\sqrt{1 + \gamma^2 - S_1^2}} \quad \dots (2.2)$$

$$u_2 = \frac{d\sigma_2 + (\gamma - S_2) p_{\sigma}}{\sqrt{1 + \gamma^2 - S_2^2}} \quad \dots (2.3)$$

where γ is the covalency parameter, S_1 and S_2 are the overlap integrals; $S_1 = \langle d\sigma_1/p_{\sigma} \rangle$, $S_2 = \langle d\sigma_2/p_{\sigma} \rangle$, with $S_1 = -S_2$. It is seen that under reflection R in the symmetry plane $d\sigma_1 \xrightarrow{R} d\sigma_2$, $p_{\sigma} \xrightarrow{R} -p_{\sigma}$. Hence p is an odd function and $u_1 \xrightarrow{R} u_2$. Furthermore u_1 and u_2 are orthogonal to p (on neglecting third order terms in S and γ) and they are nearly so to each other as

$$\langle u_1/u_2 \rangle = \langle d\sigma_1/d\sigma_2 \rangle + S_1^2 - \gamma^2 \quad \dots (2.4)$$

where S_1^2 and γ^2 are comparable and hence cancel each and $\langle d\sigma_1/d\sigma_2 \rangle$ is negligible. The formulations (2.1) to (2.3) contain the appropriate admixture of metal ion and

ligand orbitals and therefore, as far as the occupied orbitals are concerned, the electron transfer effects are automatically included.

Apart from the appropriate ion core framework ($M_1^{3+} - X - M_2^{3+}$), four electrons are taken into interaction scheme, namely, two electrons in the p orbitals of the intervening ion and one representative electron each in two magnetic ions in the orbitals u_1 and u_2 , coupled strongly by intra-atomic spin dependent forces while moving in the field of respective ion cores (~~Hund's rule~~).

Next, the correlation effect of the two coupled electrons in the p orbital is considered. If the idea of doubly filled orbitals is abandoned and the appropriate semilocalized orbitals formulated,^{65,61} it would seem that the charge density of the two anion electrons is modified in such a way that they interact differently with the two metal ion electrons. The distortion of the p orbital function owing to the correlation effect under the influence of the adjacent paramagnetic ions can be described, to a large extent, by superposing appropriate available orbitals. The singly occupied orbitals such as u_1 and u_2 are not considered for this purpose in as much as they would lead to the usual superexchange interaction effects (Anderson,²⁵ Nesbet³¹). Thus only those atomic orbitals are considered which are empty.

It should be noted that in a crystal or in the unit under consideration such available orbitals cannot be attributed to any particular atom and should be better termed as the localized crystal orbitals. This description would be in keeping with the physical situation where, in the excited states, it is difficult to maintain the distinction between the electrons of the cation and those of the anion. For the symmetrical unit $M_1 - O - M_2$, two types of available excited orbitals should be considered namely, those having even and odd symmetry which are denoted respectively by ϕ_g and ϕ_u . Generalisations to ^{the} case where a series of excited orbitals of each symmetry is taken into account, will be given later (cf. equations (2.39) and (2.44)).

The following two sets of orbitals are considered:

$$\phi_1 = p \cos \theta + \phi_g \sin \theta \quad . . . (2.5a)$$

$$\phi_2 = -p \cos \theta + \phi_g \sin \theta \quad , \quad . . . (2.5b)$$

$$\text{with } \langle \phi_1 / \phi_2 \rangle = -\cos 2\theta \quad , \quad . . . (2.6)$$

and

$$p_1 = p \cos \delta + \phi_u \sin \delta \quad . . . (2.7a)$$

$$p_2 = p \cos \delta - \phi_u \sin \delta \quad , \quad . . . (2.7b)$$

$$\text{with } \langle p_1 / p_2 \rangle = \cos 2\delta \quad . . . (2.8)$$

Here the angles Θ and δ are called correlation angles.^{52,55} It should be noted that under reflection with respect to the symmetry plane defined above

$\phi_1 \xleftrightarrow{R} \phi_2$ and $Rp_1 = -p_1$ and $Rp_2 = -p_2$. The formulation is chosen in such a way that while ϕ_1 and ϕ_2 describe "angular correlation" effects, p_1 and p_2 describe "in-out" effects. While the two effects are kept in mind the two different orbitals are formally represented by ψ_1 and ψ_2 which may represent either sets (2.5) or (2.6) or any other complicated combination of orbitals such as

$$\psi_1 = \sum_i a_i \phi_i \quad \dots (2.9a)$$

$$\psi_2 = \sum_i b_i \phi_i \quad , \quad \dots (2.9b)$$

$$\text{with } \langle \psi_1 / \psi_2 \rangle = S_0 \quad , \quad \dots (2.10)$$

where a_i and b_i are variational parameters like Θ and δ to be determined by the minimization of energy and ϕ_i constitute an orthonormal set including p . It is to be noted that all the pairs of orbitals namely (ϕ_1, ϕ_2) , (p_1, p_2) or (ψ_1, ψ_2) are non-orthogonal.

Thus we start the formulation with four singly occupied orbitals, namely, $u_1 \psi_1 \psi_2 u_2$. In what follows, the derivation of the interaction terms will be given both using the Dirac's vector model^{4,5} and the method of determinantal functions. First the vector model method is followed.

2.1 Derivation of the interaction operator by the spin operator formalism^{37,41}

For a greater generality, the symmetry relations between $u_1, u_2, \gamma_1, \gamma_2$ are ignored. The result will be analysed with the symmetry restrictions after obtaining the general expression. The symbols $\underline{S}_{m_1}, \underline{S}_{m_2}, \underline{S}_{l_1}, \underline{S}_{l_2}$ denote the spin operators corresponding to the spins in u_1, u_2, γ_1 and γ_2 respectively. The occupation of each orbital by one electron only is shown in the following table

Index	m_1	l_1	l_2	m_2
Orbital	u_1	γ_1	γ_2	u_2
Spin operator	$\underline{S}_{m_1}$	$\underline{S}_{l_1}$	$\underline{S}_{l_2}$	$\underline{S}_{m_2}$

It is convenient to introduce the following vector sums of the spins:

$$\underline{S}_{m_1} + \underline{S}_{m_2} = \underline{S}_m; \quad \underline{S}_{l_1} + \underline{S}_{l_2} = \underline{S}_l; \quad \underline{S}_{m_1} + \underline{S}_l = \underline{S} \quad \dots (2.11)$$

Including the spin functions there will be sixteen independent antisymmetrized product functions. The eigenstates of the S^2 operator can be obtained by taking appropriate linear combinations from the above product functions. There would be one quintet, three triplets and two singlets. For the present purpose the quintet state is of no physical interest and hence is not considered.

In terms of the spin operators the three interacting triplets ${}^3\Psi_0$, ${}^3\Psi_1$, ${}^3\Psi_2$ and the two interacting singlets ${}^1\Psi_0$ and ${}^1\Psi_1$ are expressed as follows:

$$\begin{aligned}
 {}^3\Psi_0 &= \Psi(S_m=1, S_1=0, S=1) \\
 \text{or simply} &= \Psi(10, 1) \\
 \text{Similarly,} & \\
 {}^3\Psi_1 &= \Psi(01, 1) \\
 {}^3\Psi_2 &= \Psi(11, 1)
 \end{aligned}
 \tag{2.12a}$$

and

$$\begin{aligned}
 {}^1\Psi_0 &= \Psi(00, 0) \\
 {}^1\Psi_1 &= \Psi(11, 0)
 \end{aligned}
 \tag{2.12b}$$

Since Ψ_1 and Ψ_2 are not very different from each other (the coefficient of p is predominant compared to others) the states with $S_1=0$ would constitute the zeroth order ground state. These are ${}^3\Psi_0$ and ${}^1\Psi_0$ and are degenerate if one neglects the relatively small direct exchange interaction between u_1 and u_2 . The states with $S_1=1$ interact with the respective zeroth order ground states to bring about the energy depressions.

This appears in the second order term of the perturbation treatment. Now, the effect of the second order perturbation on the zeroth order ground states can be expressed by an effective Hamiltonian defined by

$$\langle S_m 0, S/H_{\text{eff}}/S'_m 0, S' \rangle = \sum \frac{\langle S_m 0, S/H_m/S''_m 1, S'' \rangle \langle S''_m 1, S''/H_m/S'_m 0, S' \rangle}{[E(0) - E(1)]}, \dots (2.13)$$

where $E(0)$ is the energy of the zeroth order ground triplet and singlet states and $E(1)$ is the mean energy of the excited states which correspond to $S_1=1$.

H_m denotes the spin dependent Hamiltonian which takes the following form in the present case (Dirac's vector model):⁴

$$\begin{aligned} H_m = & \left[C - J_{m_1 l_1} P_{m_1 l_1} - J_{m_1 l_2} P_{m_1 l_2} - J_{m_2 l_2} P_{m_2 l_2} - J_{m_2 l_1} P_{m_2 l_1} \right. \\ & - J_{l_1 l_2} P_{l_1 l_2} - 2K_{l_1 l_2}^{(m_1)} S_o P_{l_1 l_2} - 2K_{l_1 l_2}^{(m_2)} S_o P_{l_1 l_2} \\ & - 2h_{l_1 l_2} S_o P_{l_1 l_2} + J_{l_1 l_2}^{(m_1)} S_o P_{l_1 l_2} (P_{m_1 l_1} + P_{m_1 l_2}) \\ & \left. + J_{l_1 l_2}^{(m_2)} S_o P_{l_1 l_2} \times (P_{m_2 l_1} + P_{m_2 l_2}) \right] / (1-S_o^4)^{1/2} \\ & , \dots (2.14) \end{aligned}$$

where the various symbols stand for the following:

C = Constant terms

$$P_{ab} = 1/2 (1 + 4S_a \cdot S_b)$$

$$J_{ab} = \langle ab/ba \rangle, \quad J_{ab}^{(c)} = \langle ca/bc \rangle$$

$$K_{ab}^{(c)} = \langle ca/cb \rangle$$

$$h_{1,1} h_{2,2} = \langle \psi_{1/h} / \psi_2 \rangle$$

$$\langle ab/cd \rangle = \iint a^*(1)b^*(2) \frac{1}{r_{12}} c(1)d(2) d\tau_1 d\tau_2 \dots (2.15)$$

The total Hamiltonian (in atomic units $e = \hbar = m = 1$)
is expressed as

$$H = - \frac{1}{2} \sum_i \nabla_i^2 + \sum_i V(\underline{r}_i) + \sum_{i < j} \frac{1}{r_{ij}} \dots (2.16)$$

In the above, h represents the one electron part of the Hamiltonian i.e. $h_i = - \frac{1}{2} \nabla_i^2 + V(\underline{r}_i)$, $V(\underline{r}_i)$ being the total potential acting on the i^{th} electron due to the three nuclei and other electrons except the four under consideration. The term $\sum_{i < j} \frac{1}{r_{ij}}$ represents the usual coulomb repulsion between the four electrons.

The factor $(1 - S_0^4)^{-1/2}$ in (2.14) is related to the normalization of the wave functions and it is to be remembered that one must replace this by $(1 + S_0^2)^{-1}$ and $(1 - S_0^2)^{-1}$ in the calculation of the matrix elements

of H_m diagonal with respect to $S_{1,2}$ i.e.

$$\langle S_m 0, S/H_m/S'_m 0, S' \rangle \quad \text{and} \quad \langle S_m 1, S/H_m/S'_m 1, S' \rangle$$

respectively.

Let us introduce a projection operator O_p which annihilates all states with parallel spins in l_1 and l_2 . Then $O_s = 1 - O_p$ is also a projection operator and annihilates all the states with antiparallel spins in l_1 and l_2 . With the aid of these operators, we can write

$$\langle S_m 0, S/H_m/S''_m 1, S'' \rangle = \langle S_m S_{1,2} S / O_p H_m O_s / S''_m S''_{1,2}, S'' \rangle \dots (2.17)$$

It follows, therefore, that H_{eff} can be expressed as

$$H_{\text{eff}} = O_p H_m O_s H_m O_p / [E(0) - E(1)] \dots (2.18)$$

The explicit form of O_p is given by

$$\begin{aligned} O_p^2 = O_p &= \frac{1}{2} (1 - P_{1,2}) \\ &= \frac{1}{4} (1 - 4 \underline{S}_{1,1} \cdot \underline{S}_{1,2}) \dots (2.19) \end{aligned}$$

Likewise

$$O_s = \frac{1}{4} (3 + 4 \underline{S}_{1,1} \cdot \underline{S}_{1,2}) = O_s^2 \dots (2.20)$$

From these, the following important relations can be derived by making use of the well known properties of the

spin matrices.⁴ These are:

$$O_{p1_1} O_a = \frac{1}{4} (\underline{S}_{1_1} - \underline{S}_{1_2} - 2i [\underline{S}_{1_1} \times \underline{S}_{1_2}]) \quad \dots (2.21a)$$

$$O_{p1_2} O_a = \frac{1}{4} (\underline{S}_{1_2} - \underline{S}_{1_1} + 2i [\underline{S}_{1_1} \times \underline{S}_{1_2}]) \quad \dots (2.21b)$$

along with their hermitian conjugate relations. It follows from these that the relation

$$O_p (\underline{S}_{1_1} + \underline{S}_{1_2}) O_a = 0 \quad \dots (2.22)$$

and the equivalent conjugate relation hold. Further, if the following relations are used i.e.

$$O_p P_{1_1 1_2} O_a = O_p O_a = 0 \quad \dots (2.23)$$

(which can be easily proved by noting the relation

$$(\underline{S} \cdot \underline{a}) (\underline{S} \cdot \underline{b}) = \frac{1}{4} (\underline{a} \cdot \underline{b}) + \frac{1}{2} i \underline{S} \cdot [\underline{a} \times \underline{b}] ,$$

where $\underline{a}$ and $\underline{b}$ are any vectors)

and likewise

$$\left. \begin{aligned} O_p P_{1_1 1_2} (P_{m_1 1_1} + P_{m_1 1_2}) O_a &= O_p P_{1_1 1_2} \underline{S}_{m_1} \cdot (\underline{S}_{1_1} + \underline{S}_{1_2}) O_a \\ &= \underline{S}_{m_1} \cdot O_p (\underline{S}_{1_1} + \underline{S}_{1_2}) O_a = 0 \\ O_p P_{1_1 1_2} (P_{m_2 1_1} + P_{m_2 1_2}) O_a &= \underline{S}_{m_2} \cdot O_p \underline{S}_1 O_a = 0 \end{aligned} \right\} \dots (2.24)$$

all the terms of (2.14) excepting those on the first line can be eliminated. Thus one gets

$$\begin{aligned}
 O_p H_m O_a &= \frac{O_p (-J_{m_1 l_1} P_{m_1 l_1} - J_{m_1 l_2} P_{m_1 l_2} - J_{m_2 l_2} P_{m_2 l_2} - J_{m_2 l_1} P_{m_2 l_1})}{(1 - S_o^4)^{1/2}} \\
 &= \frac{O_p \left[-2(J_{m_1 l_1} - J_{m_1 l_2}) \frac{S_{m_1}}{S_{l_1}} - 2(J_{m_2 l_2} - J_{m_2 l_1}) \frac{S_{m_2}}{S_{l_2}} \right] O_a}{(1 - S_o^4)^{1/2}} \\
 &\dots\dots\dots (2.25)
 \end{aligned}$$

dropping the constant term in $P_{m_1 l_1}$ etc. and using (2.22) i.e. $O_{p-l_1} O_a = -O_{p-l_2} O_a$. For the sake of convenience let us define the following abbreviations:

$$J_\alpha = J_{m_1 l_1} - J_{m_1 l_2}; \quad J_\beta = J_{m_2 l_2} - J_{m_2 l_1} \quad \dots\dots (2.26)$$

The complete expression for the numerator of (2.18) is therefore

$$\begin{aligned}
 O_p H_m O_a H_m O_p &= \frac{O_p (-2J_\alpha \frac{S_{m_1}}{S_{l_1}} - 2J_\beta \frac{S_{m_2}}{S_{l_2}}) O_a (-2J_\alpha \frac{S_{m_1}}{S_{l_1}} - 2J_\beta \frac{S_{m_2}}{S_{l_2}}) O_p}{(1 - S_o^4)} \\
 &= (4J_\alpha^2 O_{p-m_1} \cdot \frac{S_{l_1}}{S_{a-m_1}} \cdot \frac{S_{l_1}}{S_{l_1}} O_p + 4J_\beta^2 O_{p-m_2} \cdot \frac{S_{l_2}}{S_{a-m_2}} \cdot \frac{S_{l_2}}{S_{l_2}} O_p \\
 &\quad + 4J_\alpha J_\beta O_{p-m_1} \cdot \frac{S_{l_1}}{S_{a-m_2}} \cdot \frac{S_{l_2}}{S_{l_2}} O_p + 4J_\beta J_\alpha O_{p-m_2} \cdot \frac{S_{l_2}}{S_{a-m_1}} \cdot \frac{S_{l_1}}{S_{l_1}} O_p) \\
 &\quad / (1 - S_o^4) \quad \dots\dots (2.27)
 \end{aligned}$$

For a further reduction of (2.27) it is expedient to note the following important relations involving spin operators.

$$\begin{aligned}
 \underline{S} \times \underline{S} &= i\underline{S} \\
 i\underline{S}_1 \cdot [\underline{S}_1 \times \underline{S}_2] &= -(\underline{S}_1 \cdot \underline{S}_2) = i[\underline{S}_1 \times \underline{S}_2] \cdot \underline{S}_2 \\
 i[\underline{S}_1 \times \underline{S}_2] \cdot \underline{S}_1 &= (\underline{S}_1 \cdot \underline{S}_2) = i\underline{S}_2 \cdot [\underline{S}_1 \times \underline{S}_2] \\
 \underline{S}_1 \times [\underline{S}_1 \times \underline{S}_2] &= i[\underline{S}_1 \times \underline{S}_2]/2 - \frac{\underline{S}_2}{2} \\
 \underline{S}_2 \times [\underline{S}_1 \times \underline{S}_2] &= \frac{i[\underline{S}_1 \times \underline{S}_2]}{2} + \frac{\underline{S}_1}{2} \\
 [\underline{S}_1 \times \underline{S}_2] \times \underline{S}_1 &= \frac{i[\underline{S}_1 \times \underline{S}_2]}{2} + \frac{\underline{S}_2}{2} \\
 [\underline{S}_1 \times \underline{S}_2] \times \underline{S}_2 &= \frac{i[\underline{S}_1 \times \underline{S}_2]}{2} - \frac{\underline{S}_1}{2} \\
 [\underline{S}_1 \times \underline{S}_2] \cdot [\underline{S}_1 \times \underline{S}_2] &= \frac{3}{8} - \frac{1}{2}\underline{S}_1 \cdot \underline{S}_2 = (\underline{S}_1^2 + \underline{S}_2^2 - 2\underline{S}_1 \cdot \underline{S}_2)/4 \\
 [\underline{S}_1 \times \underline{S}_2] \times [\underline{S}_1 \times \underline{S}_2] &= \frac{i}{4}(\underline{S}_1 + \underline{S}_2) \\
 (\underline{S} \cdot \underline{a})(\underline{S} \cdot \underline{b}) &= \frac{1}{3}(\underline{S} \cdot \underline{S})(\underline{a} \cdot \underline{b}) + \frac{1}{2}(\underline{S} \times \underline{S}) \cdot (\underline{a} \times \underline{b})
 \end{aligned} \tag{2.28}$$

Now

$$\begin{aligned}
 O_{p-1_1} \underline{S}_{1_1} O_a \underline{S}_{m_1} \underline{S}_{1_1} O_p &= (\underline{S}_{m_1} \cdot O_{p-1_1} \underline{S}_{1_1} O_a)(\underline{S}_{m_1} \cdot O_a \underline{S}_{1_1} O_p) \\
 &= \frac{1}{3}(\underline{S}_{m_1} \cdot \underline{S}_{m_1})(O_{p-1_1} \underline{S}_{1_1} O_a \cdot O_a \underline{S}_{1_1} O_p) + \frac{1}{2}[\underline{S}_{m_1} \times \underline{S}_{m_1}] \\
 &\quad [O_{p-1_1} \underline{S}_{1_1} O_a \times O_a \underline{S}_{1_1} O_p] \dots\dots\dots (2.29)
 \end{aligned}$$

CHAPTER - III

VARIOUS SYSTEMS OF CHEMICAL
NOTATION.

Using (2.21) and relations in (2.28) it can be shown that

$$[O_{p-1,1} O_a \times O_{a-1,1} O_p] = 0 = [O_{p-1,1} O_a \times O_{a-1,2} O_p]$$

and

$$(O_{p-1,1} O_a \cdot O_{a-1,1} O_p) = \frac{3}{4} O_p$$

Hence (2.29) reduces to

$$\frac{1}{4} S_{m_1}^2 O_p \quad \dots \quad (2.30)$$

Likewise ,

$$O_{p-m_2} \cdot S_{1_2} O_{a-m_2} \cdot S_{1_2} O_p = \frac{1}{4} S_{m_2}^2 O_p \quad \dots \quad (2.31)$$

and

$$\begin{aligned} (O_{p-m_1} \cdot S_{1_1} O_{a-m_2} \cdot S_{1_2} O_p) &= (O_{p-m_2} \cdot S_{1_2} O_a) (O_{a-m_1} \cdot S_{1_1} O_p) \\ &= -\frac{1}{4} (S_{m_1} \cdot S_{m_2}) O_p \quad \dots \quad (2.32) \end{aligned}$$

Finally using relations (2.27) through (2.32) H_{eff} [cf (2.18)] is given by

$$H_{eff} = \frac{\left(\frac{3}{4} J_\alpha^2 + \frac{3}{4} J_\beta^2 - 2 J_\alpha J_\beta S_{m_1} \cdot S_{m_2} \right)}{(1 - S_o^4) [E(0) - E(1)]} \quad \dots \quad (2.33)$$

where, as is well known, $S_{m_1} \cdot S_{m_2}$ will have the value $\frac{1}{4}$ for the triplet state and $-\frac{3}{4}$ for the singlet state. The above

expression furnishes the relevant operator for the spin coupling between the two paramagnetic ions, M_1 and M_2 , within the framework of the mechanism suggested here. In effect, it gives the energy depressions of the triplet or the singlet state owing to the second order perturbation of the zeroth order states involving spin dependant polarization of the anion electrons.

Various possibilities of the spin coupling depending on the signs of J_α and J_β can be easily seen from the equation (2.33). These are explained below.

The answer to the question as to whether the singlet or the triplet state lies lower is to be related to the numerator of (2.33). In order that the depression be more for the singlet than the triplet both J_α and J_β should be either positive or negative. For the triplet state to lie lowest one of these should be negative and the other positive. To study the point further let us examine the following relations.

$$\begin{aligned} J_\alpha &= J_{m_1 l_1} - J_{m_1 l_2} = \langle u_1 \chi_1 / \chi_1 u_1 \rangle - \langle u_1 \chi_2 / \chi_2 u_1 \rangle \\ J_\beta &= J_{m_2 l_2} - J_{m_2 l_1} = \langle u_2 \chi_2 / \chi_2 u_2 \rangle - \langle u_2 \chi_1 / \chi_1 u_2 \rangle \end{aligned} \quad (2.34)$$

All the exchange integrals involved in (2.34) are positive definite and hence the sign of J_α or J_β is determined by the differences in the magnitude of the corresponding exchange integrals. Thus the following

general conclusions regarding the spin coupling between the two magnetic ions can be deduced from (2.33) and (2.34).

When	Coupling
$J_{m_1 l_1} > J_{m_1 l_2}$ and $J_{m_2 l_2} > J_{m_2 l_1}$	Antiferromagnetic
$J_{m_1 l_1} < J_{m_1 l_2}$ and $J_{m_2 l_2} < J_{m_2 l_1}$	Antiferromagnetic
$J_{m_1 l_1} > J_{m_1 l_2}$ and $J_{m_2 l_2} < J_{m_2 l_1}$	Ferromagnetic
$J_{m_1 l_1} < J_{m_1 l_2}$ and $J_{m_2 l_2} > J_{m_2 l_1}$	Ferromagnetic

The magnitude of these exchange integrals would depend on the extent of overlap of the two orbital functions involved e.g. u_1 and ψ_1 in $J_{m_1 l_1}$. Thus the criterion of antiferromagnetic spin coupling, according to the present scheme, is that ψ_1 overlaps more with u_1 than with u_2 and ψ_2 overlaps more with u_2 than with u_1 or when the situation is converse. On the otherhand, for ferromagnetic coupling one of the ψ_1 and ψ_2 should overlap more with both u_1 and u_2 than the other.

One is therefore led to the conclusion that the correlation effects may occur in two ways, each giving rise to the corresponding spin coupling between the paramagnetic ions. The angular effect, in which the two electrons tend to be on opposite sides of the anion ion-core, leads to antiferromagnetic coupling of electrons in u_1 and

u_2 . The second, the 'in-out' effect in which the electrons pertaining to γ_1 and γ_2 tend to be inside the other, leads to ferromagnetic coupling.

The 'angular' and 'in-out' coulomb correlation effects were envisaged by Lennard-Jones and Pople in the study of the spatial correlation in Helium.⁶⁶ The present study, however, reveals the consequences of similar spin dependant correlation effects on the spin coupling between the adjacent paramagnetic ions.

Of these, which effect will predominate in a magnetic crystal would obviously depend on the electronic state of the paramagnetic ions and the spatial disposition and the orbital energies of the available excited orbitals on the three centres.

The derivation of the spin polarisation mechanism ensuing from (2.33) has a formal character. Specific results from it can be derived by analysing particular situations. Instead of the broad character of the different orbitals γ_1 and γ_2 , it is instructive to^{go} back to the set of orbitals (ϕ_1, ϕ_2) and (p_1, p_2), the former representing the effect of the superposition of an even orbital ϕ_g on p and the latter of an odd orbital~~s~~ (ϕ_u). Let us bring in the role of symmetry of the various orbitals for the three centre problem. If u_1 and u_2 on the two paramagnetic ions are the same type of orbital e.g. given by (2.2) and (2.3), then under the appropriate

reflections operator R, one gets

$$u_1 \xleftrightarrow{R} u_2$$

Also, as seen from (2.5a) and (2.5b) $\phi_1 \xleftrightarrow{R} \phi_2$.

On the other hand (p_1, p_2) (cf equations (2.7a)) and (2.7b)) behave differently i.e. $Rp_1 \longrightarrow -p_1$ and $Rp_2 \longrightarrow -p_2$. Consider the set $(u_1 \phi_1 \phi_2 u_2)$ first. In this case where

$$\left. \begin{aligned} J_\alpha(\phi_1\phi_2) &= \langle u_1\phi_1/\phi_1u_1 \rangle - \langle u_1\phi_2/\phi_2u_1 \rangle, \\ J_\beta(\phi_1\phi_2) &= \langle u_2\phi_2/\phi_2u_2 \rangle - \langle u_2\phi_1/\phi_1u_2 \rangle, \end{aligned} \right\} \quad (2.35)$$

$J_\alpha \xleftrightarrow{R} J_\beta$, and hence J_α is equal to J_β in sign and magnitude. Thus (2.33) reduces to

$$H_{\text{eff}}(\phi_1\phi_2) = J_\alpha^2(\phi_1\phi_2) \left(\frac{3}{2} - 2S_{m_1} \cdot S_{m_2} \right) / (1-S_g^4) [E(0)-E(1)] .$$

..... (2.36)

The above shows that the depression of the singlet is three times larger than the triplet. Thus ϕ_1 and ϕ_2 (which represent the angular correlation effect) always stabilize the antiferromagnetic state.

Next, consider the set $(u_1 p_1 p_2 u_2)$. This gives

$$\left. \begin{aligned} J_\alpha(p_1p_2) &= \langle u_1p_1/p_1u_1 \rangle - \langle u_1p_2/p_2u_1 \rangle, \\ J_\beta(p_1p_2) &= \langle u_2p_2/p_2u_2 \rangle - \langle u_2p_1/p_1u_2 \rangle, \end{aligned} \right\} \dots (2.37)$$

As seen from (2.7a) and (2.7b), p_1 and p_2 involve the mixing of orbitals having the same symmetry namely p and ϕ_u in the form $p_1 = p \cos \delta + \phi_u \sin \delta$ and $p_2 = p \cos \delta - \phi_u \sin \delta$. This describes the "in-out" situation, where the electron in p_2 will move inside that of the electron in p_1 (δ like θ is a small angle). Hence p_1 overlaps more with u_1 and u_2 than p_2 does and accordingly $J_\alpha = -J_\beta$. For this situation (2.33) reduces to

$$H_{\text{eff}}(p_1 p_2) = J_\alpha^2 (p_1 p_2) \left(\frac{3}{2} + 2S_{-m_1} \cdot S_{-m_2} \right) / (1 - S_u^4) [E(0) - E(1)] .$$

. (2.38)

This gives a depression of the triplet state and the singlet is unaffected. Thus, in this situation, the ferromagnetic coupling is favoured.

Since both the situations must be included in actual calculations the total interaction terms, involving the role of all possible even (g) and odd (u) excited orbital states, would be given by

$$H_{\text{eff}}(\text{total}) = \sum_g H_{\text{eff}}(\phi_1 \phi_2) + \sum_u H_{\text{eff}}(p_1 p_2) (2.39)$$

The above expression gives, in principle, the total effect owing to the spin polarization mechanism as described by superposition of configurations.

In order to make the formulation transparent, it would be advisable to express the relevant exchange

integrals in terms of the individual orbitals such as p, ϕ_g , ϕ_u etc. Then the expression (2.36) becomes

$$H_{\text{eff}}(\phi_1\phi_2) = \left(\frac{3}{2} - 2\underline{S}_{m_1} \cdot \underline{S}_{m_2} \right) \left\{ \frac{2|\langle u_1\phi_g/pu_1 \rangle|^2}{(E_0 - E_g)} + \frac{2C_{1\theta}C_{2\theta}|\langle u_1\phi_g/pu_1 \rangle|^2}{(E_0 - E_g)} \right\}, \quad \dots(2.40)$$

where

$$\begin{aligned} C_{1\theta} &= \cos^2\theta / (\cos^4\theta + \sin^4\theta)^{1/2} \\ \text{and} \\ C_{2\theta} &= \sin^2\theta / (\cos^4\theta + \sin^4\theta)^{1/2}. \end{aligned} \quad \dots(2.41)$$

A similar expression can be easily derived for $H_{\text{eff}}(p_1p_2)$, with the variational coefficients $C_{1\delta}$, $C_{2\delta}$ and the appropriate change of orbital from ϕ_g to ϕ_u and the factor $(\frac{3}{2} + 2\underline{S}_{m_1} \cdot \underline{S}_{m_2})$. Now the second term in the square bracket of (2.40) corresponds to the third order perturbation. This is shown as follows. Since the θ value as derived from the variational procedure is quite low (this is given elsewhere; see Koide and Sinha³⁸), the appropriate expression

$$\tan^2\theta - \cot^2\theta = \frac{2(A-C)}{B}$$

reduces to

$$\sin^2\theta = \frac{B}{2(C-A)} = \frac{\langle p\phi_g/\phi_gp \rangle}{\Delta E'} \quad \dots(2.42)$$

It should be noted, however, that the first term in the square bracket of (2.40) does not vanish even if $C_{20}=0$ i.e. when $\phi_1 = \phi_2$. Similar argument holds for p_1 and p_2 . Thus the second order interaction terms independent of θ and δ can be derived starting from the configuration with doubly occupied orbitals of the anion i.e. p^2 and considering spin dependent transitions to ϕ_g and ϕ_u etc. The effective Hamiltonian in this case will be defined as

$$\begin{aligned} & \langle S_m 0, S_g / H_{\text{eff}} / S_n 0, S'_g \rangle \\ &= \sum_{g,u} \langle S_m S(p^2=0), S / H_m / S_m S(\phi_{g,u} p=1), S'' \rangle \langle S_m S(\phi_{g,u} p=1), S'' \\ & \quad S'' / H_m / S'_m S(p^2=0), S' \rangle / [E(0) - E_{g,u}(1)] \dots (2.43) \end{aligned}$$

giving

$$H_{\text{eff}}(t) = - \left[\sum_g \frac{2J_g^2}{\Delta E_g} \left(\frac{3}{2} - 2S_{m1} \cdot S_{m2} \right) + \sum_u \frac{2J_u^2}{\Delta E_u} \left(\frac{3}{2} + 2S_{m1} \cdot S_{m2} \right) \right], \dots (2.44)$$

where $J_{g,u} = \langle u_1 \phi_{g,u} / p u_1 \rangle$ and ΔE_g and ΔE_u may be taken to be the excitation energies to ϕ_g and ϕ_u orbitals respectively i.e. $\Delta E_{g,u} = (E_{g,u} - E_0)$.

It is difficult to justify such a derivation within the framework of the Dirac's vector model in that the orbitals functions, in this approximations,¹¹ are assumed

to be the same for all the spin degenerate states. In the following section, therefore, a determinantal formulation, which gives essentially the same results as (2.44), will be given along with a quantitative calculation of the important terms.

2.2 The Method of Determinantal Wave Functions.

In the present section, the important results of the previous section will be derived following the method of Slater determinants. In essence, this consists of taking such linear combination of the Slater determinants, for the four electron system under consideration, that form eigenfunctions of the S^2 operator. The details of this part have already been published in a different form earlier (Koide, Sinha and Tanabe).³⁹ In the present description, however, only the contributions of the author will be emphasised. It is appropriate to point out the main difference. In the joint work, the orbital functions of the two anion electrons were described by a choice of orbitals which took simultaneously into account the role of both ϕ_g and ϕ_u orbitals or more explicitly

$$\chi_1 = C_o p + C_u \phi_u + C_g \phi_g \quad (2.45a)$$

$$\chi_2 = -C_o p - C_u \phi_u + C_g \phi_g \quad (2.45b)$$

where the coefficients are complex numbers, namely,

$C_o = |C_o| e^{i\theta_o}$, $C_u = |C_u| e^{i\theta_u}$ and $C_g = |C_g| e^{i\theta_g}$. As before, it was assumed that p and ϕ_u were orthogonalized to each other. Further $R\phi_1 \rightarrow \phi_2^*$ and $R\phi_2 \rightarrow \phi_1^*$. The idea was to describe such modified charge densities of the two anion electrons that if one points towards the first cation the other points towards the second.

Disregarding the resultant total spin of the system, the ferromagnetic and antiferromagnetic states may be represented by the following single determinantal functions

$$\text{Ferromagnetic} : [d_1 \psi_1 \bar{\psi}_2 d_2] \dots (2.46a)$$

$$\text{Antiferromagnetic} : [d_1 \psi_1 \bar{\psi}_2 \bar{d}_2] \dots (2.46b)$$

Here, and in the following, the bracket notation represents the usual Slater determinant multiplied by $(N!)^{-1/2}$ i.e. $(4!)^{-1/2}$ in (2.46). The orbitals without bar include up spin and with bar down spin functions of electrons in them. The difference in the energy expectation values of the ferromagnetic and antiferromagnetic states (cf (2.46a) and (2.46b)), neglecting the direct exchange, is then given by

$$E_f - E_{af} = J(d_1 \psi_1) - J(d_1 \bar{\psi}_2) \dots (2.47)$$

Since the overlap between d_1 and ψ_1 is expected to be greater than between d_1 and $\bar{\psi}_2$, $J(d_1 \psi_1)$ would be larger than $J(d_1 \bar{\psi}_2)$. This suggested that the antiferromagnetic state would be lower than the ferromagnetic one.

The results of calculations based on single determinantal functions (as also done by Yamashita and

Kondo²⁴⁾ are inadequate to describe the complete physical situation. In fact, the spin polarization mechanism cannot be derived by this. The situation is best described by taking the states with definite total spin into account. The formalism using (2.45a) and (2.45b), however, gets rather complicated.³⁹

In what follows, the formulation will be given by using a pure perturbation technique for the configuration interaction problem, involving ground orbital functions u_1, u_2, p and excited orbitals of the type ϕ_g and ϕ_u .

The wave function of the two anion electrons, under consideration, in the zeroth order ground state is expressed as

$$\left| {}^1\Psi_{\text{ev}}^{(M_S = 0)} \right\rangle_a = [p\bar{p}] = {}^1(p^2), \dots (2.48)$$

which is even under the symmetry operation R. The excited triplet states of the anion electrons where one electron makes transition to ϕ_g or ϕ_u are given by ${}^3(p\phi_g)$ i.e.

$$\left| {}^3\Psi_{\text{od}} \right\rangle_a : \begin{array}{l} [p\phi_g] \\ \frac{1}{\sqrt{2}} \{ [p\bar{\phi}_g] + [\bar{p}\phi_g] \} \\ [\bar{p}\bar{\phi}_g] \end{array} ; \begin{array}{l} M_S \\ 1 \\ 0 \\ -1 \end{array} \left. \vphantom{\begin{array}{l} [p\phi_g] \\ \frac{1}{\sqrt{2}} \{ [p\bar{\phi}_g] + [\bar{p}\phi_g] \} \\ [\bar{p}\bar{\phi}_g] \end{array}} \right\} \dots (2.49)$$

and $^3(p\phi_u)$

$$\left. \begin{array}{l} |^3\Psi_{\text{ev}}\rangle_a : [p\phi_u] \quad ; \quad 1 \\ \{ [p\bar{\phi}_u] + [\bar{p}\phi_u] \} / \sqrt{2} \quad ; \quad 0 \\ [\bar{p}\bar{\phi}_u] \quad ; \quad -1 \end{array} \right\} \dots (2.50)$$

The suffixes ev, od are the abbreviations for even and odd respectively and M_s represents the eigenvalue of the z component of the resultant spin operator. The suffix 'a' denotes the total anion function.

Likewise, there will be higher states such as the singlet states

$$\{ [p\bar{\phi}_{g,u}] - [\bar{p}\phi_{g,u}] \} / \sqrt{2} \quad \text{and} \quad [\phi_g\bar{\phi}_g], [\phi_u\bar{\phi}_u] \quad ,$$

however, these will not be of importance in the second order and are therefore not considered here.

The triplet and singlet wave functions of the two metal ion electrons in u_1 and u_2 are similarly expressed as

$$|^3\Psi_{\text{od}}^{(1)}\rangle_c = ^3(u_1u_2) = [u_1u_2] \quad \dots (2.51)$$

$$|^1\Psi_{\text{ev}}^{(0)}\rangle_c = ^1(u_1u_2) = \{ [u_1\bar{u}_2] - [\bar{u}_1u_2] \} / \sqrt{2} \quad \dots (2.52)$$

with suffix 'c' standing for the cation determinantal functions. Finally, the total product wave functions of the three centre, four electron system are expressed as:

Zeroth order ground states.

Triplet

$$|{}^3\Psi_0\rangle_{od} = {}^3\{ {}^3(u_1 u_2) {}^1(p^2) \} = [u_1 p \bar{p} u_2] \quad \dots (2.53)$$

Singlet

$$|{}^1\Psi_0\rangle_{ev} = {}^1\{ {}^1(u_1 u_2) {}^1(p^2) \} = \{ [u_1 p \bar{p} \bar{u}_2] - [\bar{u}_1 p \bar{p} u_2] \} / \sqrt{2} \quad \dots (2.54)$$

Excited states involving one electron transition to ϕ_g or ϕ_u from the anion orbital p :

Triplets

$$|{}^3\Psi_1^{g,u}(1)\rangle_{od,ev} = {}^3\{ {}^1(u_1 u_2) {}^3(p\phi_{g,u}) \} \\ = \{ [u_1 p \phi_{g,u} \bar{u}_2] - [\bar{u}_1 p \phi_{g,u} u_2] \} / \sqrt{2} \quad \dots (2.55)$$

$$|{}^3\Psi_2^{g,u}(1)\rangle_{ev,od} = {}^3\{ {}^3(u_1 u_2) {}^3(p\phi_{g,u}) \} \\ = \frac{1}{\sqrt{2}} |{}^3\Psi_{od}^{(0)}\rangle_c |{}^3\Psi_{od,ev}^{g,u}(1)\rangle_a - \frac{1}{\sqrt{2}} |{}^3\Psi_{od}^{(1)}\rangle_c |{}^3\Psi_{od,ev}^{g,u}(0)\rangle_a$$

$$= \left\{ [u_1 p \bar{\phi}_{g,u} \bar{u}_2] + [\bar{u}_1 p \bar{\phi}_{g,u} u_2] - [u_1 p \bar{\phi}_{g,u} u_2] - [\bar{u}_1 p \bar{\phi}_{g,u} \bar{u}_2] \right\} / 2$$

.....(2.56)

Singlets

$$\begin{aligned} & \left| \Psi_1^{g,u} \right\rangle_{\text{ev,od}}^{(0)} = \frac{1}{\sqrt{3}} \left\{ \left| \Psi_{\text{od}}^{(1)} \right\rangle_c \left| \Psi_{\text{od,ev}}^{g,u} \right\rangle_a^{(-1)} + \left| \Psi_{\text{od}}^{(-1)} \right\rangle_c \left| \Psi_{\text{od,ev}}^{(1)} \right\rangle_a \right. \\ & \quad \left. - \left| \Psi_{\text{od}}^{(0)} \right\rangle_c \left| \Psi_{\text{od,ev}}^{g,u} \right\rangle_a^{(0)} \right\} \\ & = \left\{ 2 [\bar{u}_1 p \bar{\phi}_{g,u} \bar{u}_2] + 2 [u_1 p \bar{\phi}_{g,u} u_2] - [\bar{u}_1 p \bar{\phi}_{g,u} u_2] - [u_1 p \bar{\phi}_{g,u} \bar{u}_2] \right. \\ & \quad \left. - [\bar{u}_1 p \bar{\phi}_{g,u} \bar{u}_2] - [u_1 p \bar{\phi}_{g,u} u_2] \right\} / \sqrt{12} \quad \text{.....(2.57)} \end{aligned}$$

The matrix elements of the Hamiltonian (cf equation (2.16)) within the manifold given above are derived below:

Diagonal elements:

Zeroth order ground states:

The diagonal matrix elements of the zeroth order ground states (3.53) and (3.54) can be described by the compact formula

$$\left\langle \Psi_o^{(2S+1)}(S_m) / H / \Psi_o^{(2S+1)}(S_m) \right\rangle = Q_o + (-1)^{S_m} J(u_1 u_2) \quad \text{.....(2.58)}$$

where

$$Q_0 = 2\epsilon(u_1) + 2\epsilon(p) + K(u_1 u_2) + 4K(u_1 p) + K(pp) - 2J(u_1 p) \quad \dots (2.59)$$

Excited states - These are also given by the compact formula

$$\begin{aligned} & \left\langle {}^{2S+1}\Psi_{(S_m S_1)} / H / {}^{2S+1}\Psi_{(S_m S_1)} \right\rangle \\ & = Q_{g,u} + (-1)^{S_m} J(u_1 u_2) \\ & - \left\{ 1 + \frac{S(S+1) - S_m(S_m+1) - S_1(S_1+1)}{2} \right\} [J(u_1 p) + J(u_1 \phi_{g,u})] , \\ & \dots (2.60) \end{aligned}$$

where

$$\begin{aligned} Q_{g,u} = & \left[2\epsilon(u_1) + \epsilon(p) + \epsilon(\phi_{g,u}) + K(u_1 u_2) + 2K(u_1 p) + 2K(u_1 \phi_{g,u}) \right. \\ & \left. + K(p \phi_{g,u}) - J(p \phi_{g,u}) \right] \quad \dots (2.61) \end{aligned}$$

In the above S_m and S_1 stand for the resultant spins of the two electrons in u_1 and u_2 and the two in p and $\phi_{g,u}$ respectively and the other symbols represent the following:

$$\begin{aligned} \epsilon(a) &= \left\langle a / -\frac{1}{2} \nabla^2 + V/a \right\rangle, \text{ the one electron term} \\ \text{and } K(ab) &= \left\langle ab/ab \right\rangle, \text{ the coulomb integral} \\ J(ab) &= \left\langle ab/ba \right\rangle, \text{ the exchange integral} \end{aligned} \quad \left. \vphantom{\begin{aligned} \epsilon(a) \\ K(ab) \\ J(ab) \end{aligned}} \right\} \dots (2.62)$$

In deriving the explicit forms of the matrix elements of the various states one has to make note of the respective values of S , S_m and S_1 as explained by the symbols in the wave functions, namely,

$$2S+1 \left\{ \begin{matrix} 2S_m+1 \\ (u_1 u_2) \end{matrix} \begin{matrix} 2S_1+1 \\ (p \phi_{g,u}) \end{matrix} \right\} .$$

Off-diagonal elements.

In calculating the off-diagonal elements connecting the triplet and singlet zeroth order ground states with the respective excited states, the parities of the wave functions have to be taken into account. As noted before the triplet ground state (3.53) has odd parity and the singlet (cf (3.54)) has even parity. It follows that $|\Psi_{10}^3\rangle_{od}$ will mix with excited states having odd parity and $|\Psi_{10}^1\rangle_{ev}$ with excited states having even parity. Since the energy depressions of the zeroth order ground states owing to mixing with suitable excited are of present interest, the off-diagonal elements between excited states will not be given here. To present the off-diagonal elements in a compact way it is convenient to describe the wave functions by the notations

$$|^{2S+1}\Psi_{(S_m S_{1o})}\rangle \quad \text{and} \quad |^{2S+1}\Psi_{(S_m S_{1e})}\rangle ,$$

where the suffixes o and e have been introduced to the corresponding resultant spins in the zeroth order ground

states and the excited states. Thus all the off-diagonal elements can be derived from

$$\begin{aligned} & \left\langle {}^{2S+1}\Psi_{(S_{m_o} S_{l_o})/H} / {}^{2S+1}\Psi_{(S_{m_e} S_{l_e})} \right\rangle \\ &= (-1)^S \frac{2}{S+1} \left[2 + (-1)^{S_{m_o}} \right] \left\{ \frac{\langle u_{1p}/\phi_{g,u} u_1 \rangle + (-1)^{S_{m_o} + S_{m_e}} \langle u_{2p}/\phi_{g,u} u_2 \rangle}{N_o N_e} \right\}, \\ & \dots\dots\dots(2.63) \end{aligned}$$

where N_o and N_e denote the normalization factors occurring in the denominators of the ground and excited wave functions respectively. For future reference, it would be desirable to have the explicit expressions of the various off-diagonal elements. These are:

$$\begin{aligned} \left\langle {}^3\Psi_{(10)/H} / {}^3\Psi_{(11)} \right\rangle &= -2 \langle u_{1p}/\phi_{u,u} u_1 \rangle \\ \left\langle {}^3\Psi_{(10)/H} / {}^3\Psi_{(01)} \right\rangle &= -\sqrt{2} \langle u_{1p}/\phi_{g,u} u_1 \rangle \\ \left\langle {}^1\Psi_{(00)/H} / {}^1\Psi_{(11)} \right\rangle &= \sqrt{6} \langle u_{1p}/\phi_{g,u} u_1 \rangle \end{aligned} \quad \left. \vphantom{\begin{aligned} \left\langle {}^3\Psi_{(10)/H} / {}^3\Psi_{(11)} \right\rangle \\ \left\langle {}^3\Psi_{(10)/H} / {}^3\Psi_{(01)} \right\rangle \\ \left\langle {}^1\Psi_{(00)/H} / {}^1\Psi_{(11)} \right\rangle \end{aligned}} \right\} \dots\dots(2.64)$$

The other matrix elements vanish because of parity consideration as seen from (2.63).

Study of Interaction by Perturbation Procedure.

It can be seen from (2.58) that the energies of the zeroth order ground triplet and singlet states are given

respectively as

$$^3E_0 = E_0 - J(u_1 u_2) \quad \text{and} \quad ^1E_0 = E_0 + J(u_1 u_2),$$

their mean being $E_0 = Q_0$. Likewise, for the energies (diagonal matrix elements cf (3.70)) of the various excited triplet and singlet states a mean can be taken, namely, $E_{g,u} = Q_{g,u}$, neglecting the relatively small exchange integrals compared to coulomb and one electron terms contained in $Q_{g,u}$. Now, the depressions of the zeroth order singlet or triplet states, other than that due to the direct exchange $J(u_1 u_2)$, as a result of second order perturbation interaction with the corresponding excited states, can be expressed as:

$$\delta(^{2S+1}E) = \sum_{\substack{\text{Excited} \\ \text{states}}} \frac{\langle S_1(p^2)=0/H/S_1(p\phi_{g,u})=1 \rangle \langle S_1(p\phi_{g,u})=1/H/S_1(p^2)=0 \rangle}{[E_0 - E_{g,u}]} \quad \dots\dots\dots(2.65)$$

The energy depressions of the triplet and singlet states are thus easily derived with the help of (2.65) and (2.64) etc. The results, for a formally complete set of excited orbitals with even and odd parity, are

$$\delta(^3E) = - \sum_g \frac{2 |\langle u_1 p / \phi_{g u_1} \rangle|^2}{\Delta E_g} - \sum_u \frac{4 |\langle u_1 p / \phi_{u u_1} \rangle|^2}{\Delta E_u} \quad \dots(2.66)$$

and

$$\delta(^1E) = - \frac{6 |\langle u_1 p / \phi_{g u_1} \rangle|^2}{\Delta E_g} \quad \dots(2.67)$$

These results also follow from the relation (2.44) obtained by Dirac's vector model, namely,

$$H_{\text{eff}} = - \left[\sum_g \frac{2J_g^2}{\Delta E_g} \left(\frac{3}{2} - 2\mathbf{S}_{m_1} \cdot \mathbf{S}_{m_2} \right) + \sum_u \frac{2J_u^2}{\Delta E_u} \left(\frac{3}{2} + 2\mathbf{S}_{m_1} \cdot \mathbf{S}_{m_2} \right) \right], \quad (2.44)$$

with $J_{g,u} = \langle u_1 p | \phi_{g,u} u_1 \rangle$. Here ΔE_g and ΔE_u represent $(E_{g,u} - E_0)$ i.e. the energy difference between the corresponding excited states and the ground state. The equivalence of the results (3.66) and (3.67) with that of (2.44) furnishes the justification of the results based on the Dirac's vector model. Identifying ΔE_g and ΔE_u with the excitation energy to ϕ_g and ϕ_u orbitals, the energy difference between the ferromagnetic (triplet) and antiferromagnetic (singlet) states can be expressed as

$$\begin{aligned} 2J_{\text{eff}} &= E_f - E_{\text{af}} \\ &= \sum_g \frac{4J_g^2}{E_g} - \sum_u \frac{4J_u^2}{E_u} - 2J(u_1 u_2) \dots \end{aligned} \quad (2.68)$$

In certain cases, it may be desirable to consider electron excitations from the anion orbital which has even parity with respect to the symmetry operation R. A parallel derivation can be easily given for this. Thus the most general result is expressed as

2.3 Quantitative Estimates

In order to carry out estimates of the results obtained in the previous section, it is of great importance to understand the nature and the relative energies of the various excited orbitals available to the anion electrons. There are two possibilities in this description. First, which is called the excitation model here, the low lying available orbitals are the appropriate excited orbitals of the central ion itself. Then (in the charge transfer model) there may be orbitals arising out of a linear combination of the empty cation orbitals. It must be noted that there is no clear distinction between these two. For studying the exchange coupling, all these orbitals or their suitable linear combinations should be taken into account. In what follows, estimates will be made for the antiferromagnetic systems of the type MO such as NiO and MnO.

For such systems, the role of the occupied p orbital which overlaps with the adjoining magnetic atoms M_1 and M_2 is of importance. Regarding the excited orbitals, consider first the excited orbitals centred at the anion. Since an adequate knowledge is not available even for the lowest $2p$ orbitals,³⁹ it is very difficult to have a precise idea about the excited orbital of the O^{2-} ion in the crystal. At best a qualitative discussion may be attempted and the relative importance of $3s$, $3p$ and $3d$ orbitals on an O^{2-} ion in a crystal considered. The

influence of the environment is represented by an electric field acting on the ion in question. As is well known, octahedrally situated six adjacent cations (e.g. in NiO, which is of rocksalt structure, the six Ni^{2+} ions are surrounding the O^{2-} ion and vice versa) give rise to the crystal field with cubic symmetry which does not affect 3s and 3p but would lower $3d\gamma$ orbitals. One may liken the excited oxygen electron moving in the field of O^- , forming a sort of hydrogen like orbitals. A rough estimate shows that the $3d\gamma$ orbitals in this system (one electron in the field of O^-) are lowered relative to 3s and 3p by an amount of the order of $10^5 \text{ cm}^{-1} = \frac{1}{2} \text{ a.u.}$ Therefore, it seems that $3d\gamma$ is lower than 3p and would form a virtual bound state. Furthermore, of the two $3d\gamma$ orbitals, namely, $d(2z^2 - x^2 - y^2)$ and $d(x^2 - y^2)$, only $3d\gamma_1$ (i.e. $d(2z^2 - x^2 - y^2)$) which points towards the anion, is of importance for the three centre linear model under consideration.

The above considerations show that for the excited anion orbitals (the excitation model), the contributions of the second term in (2.68), namely, $4J_u^2 / \Delta E_u$ is relatively negligible compared to the first, which is of the type $4J_g^2 / \Delta E_g$, where ϕ_g in $J_g = \langle u_1 p / \phi_g u_1 \rangle$ stands for $3d\gamma_1$ on O^{2-} . This would favour antiferromagnetic coupling.

Let us now consider the charge transfer model involving the spin dependant transfer of the anion

electron to empty excited orbitals of the cations. On each M^{2+} ion (e.g. Ni^{2+} or Mn^{2+}) the set of low lying available orbitals that may be considered are 4s, 4p and, to a certain extent, 4d; the others will involve very high energy denominators. A better approach for the present purpose would be to take χ_1 and χ_2 as one of the hybridized 4s 4p³ 4d² orbitals around the respective cations having the appropriate directionality (i.e. pointing towards the central ion). Thus the two linear combinations of these orbitals having the appropriate symmetry and orthogonality properties are

$$\phi_g^c = (\chi_1 + \chi_2) / \sqrt{2} \quad \dots (2.70)$$

$$\phi_u^c = (\chi_1 - \chi_2 - 2S_e p) / \sqrt{2(1-2S_e^2)}, \quad (2.71)$$

where

$$S_e = \langle \chi_1 / p \rangle.$$

It is to be noted here that the orbital energies of ϕ_g^c and ϕ_u^c will normally be different. This difference arises owing to the fact that the energy of the odd function ($\chi_1 - \chi_2$) is expected to be pushed up because of the mixing with the p orbital of the anion which has the same symmetry. Even if one assumed that the orbital energies are not very different, the exchange integrals $\langle u_1 p / \phi_g^c u_1 \rangle$ and $\langle u_1 p / \phi_u^c u_1 \rangle$ will differ from each other because of the factor S_e appearing in (2.71).

One must therefore bear in mind that the non-orthogonality of the orbitals p and $(\chi_1 - \chi_2)/\sqrt{2}$ cannot be neglected.

A rough estimate in terms of (2.70) and (2.71) is now given. The energy difference between the triplet and the singlet states is now expressed as

$$2J_{\text{eff}} = {}^3E - {}^1E$$

$$= 4 \left\{ |\langle u_1 p / \phi_g^u u_1 \rangle|^2 - |\langle u_1 p / \phi_u^c u_1 \rangle|^2 \right\} / (E_m - E_o) ,$$

.....(2.72)

where E_m represents the mean orbital energy of ϕ_g^c and ϕ_u^c .

In the absence of any precise theoretical or experimental idea of the covalency parameter (cf. equations (2.1) to (2.3)) in the system under consideration, calculations were carried out using atomic orbitals, namely with $u_1 = d\sigma_1$, $u_2 = d\sigma_2$, $p = p_\sigma$.³⁹ With this redefinition, the integrals in (2.72) are expressed as:

$$\left. \begin{aligned} \langle u_1 p / \phi_g^c u_1 \rangle &\approx \langle u_1 p / \chi_1 u_1 \rangle / \sqrt{2} \\ \langle u_1 p / \phi_u^c u_1 \rangle &\approx \left\{ \langle u_1 p / \chi_1 u_1 \rangle - 2S_e \langle u_1 p / p u_1 \rangle \right\} / \sqrt{2(1-2S_e^2)} \end{aligned} \right\} (2.73)$$

Since the calculation of the two centre integrals is very complicated, Mulliken's⁶⁷ and the uniformly charged sphere⁶⁸

approximations were used in their evaluation. Thus

$$J(u_1 p) = \langle u_1 p / p u_1 \rangle \approx \frac{1}{2} S_1^2 \{ K(pp) + 2K(u_1 p) + K(u_1 u_1) \}$$

$$\langle u_1 p / \chi_1 u_1 \rangle \approx \frac{1}{2} S_1 \{ \langle u_1 u_1 / u_1 \chi_1 \rangle + \langle u_1 p / \chi_1 p \rangle \},$$

where S_1 , as noted before, is the overlap between $d\sigma_1$ and p_σ .

The values of the relevant integrals for the unit $Mn - O - Mn$ determined are sent out in the following table:

Table No.1: Values of various integrals in atomic units.

Integrals	Numerical value in a.u.	Approximations used
$K(pp)$	0.753	Slater function ⁶⁹ for 2p orbital in O^{2-}
$K(u_1 u_1)$	0.78	Scaled Slater function for 3d orbital of Mn^{2+}
$K(u_1 p)$	0.267	Uniform sphere app ⁿ (u.s.a.)
$J(u_1 p)$	0.013	u.s.a. + Mulliken's app ⁿ
$\langle u_1 u_1 / \chi_1 u_1 \rangle$	0.0720	u.s.a. + orbital function
$\langle u_1 p / \chi_1 p \rangle$	0.0302	u.s.a. + orbital function
$\langle u_1 p / \chi_1 u_1 \rangle$	0.0082	u.s.a. + Mulliken's app ⁿ
S_1	0.16	Jaffe and Dosk Table ⁷⁰
S_e	0.3	Slater function + Mulliken et al method ⁷¹

The values of the integrals seem reasonable when one compares them with some recent calculations e.g. $K(d p)$ for Ni-F system is 0.286 (Sugane and Shulman)⁷² and compares favourably with $K(u, p)$ above. Further the hybrid coulomb integral $\langle u_1 u_1 / \chi_1 u_1 \rangle$ is an order of magnitude smaller than $K(u_1 u_1)$, as it should be because of the orthogonality of χ_1 and u_1 .

Using the above values it turns out that

$$|\langle u_1 p / \phi_u^c u_1 \rangle|^2 \approx \frac{|\langle u_1 p / \phi_g^c u_1 \rangle|^2}{100}$$

Hence, the second term in (2.72) is negligible compared to the first.

An estimate of the denominator ($E_m - E_0$) can be made from the ionization potential⁷³ of Mn(II) and electron affinity data⁷⁴ of $O^- \rightarrow O^{2-}$. This is estimated to be of the order of 1 a.u. Thus the difference between the triplet and singlet energies i.e. ${}^3E - {}^1E = 1.2 \times 10^{-4}$ a.u.

Now according to the molecular field model^{75, 5, 76} the strength of the exchange interaction between two sublattices can be defined as:⁷⁷

$$kT_s = \frac{1}{2} K(T_n + \Theta) = \frac{1}{3} zS(S+1) \Delta E \quad (2.74)$$

where T_n , Θ and S are the Ne'el temperature,⁷⁷ Curie-Weiss constant⁷⁷ and the spin quantum number of the ion respectively. ΔE is the energy difference between the ferromagnetic and antiferromagnetic state, and z is the number of magnetic ions correlated to a given magnetic

ion. Thus with $z = 6$ and using $\Delta E = 1.2 \times 10^{-4}$ a.u., the value of T_s is given by

$$T_s = (T_n + \Theta)/2 = 650^\circ\text{K}.$$

The observed mean value is about 370°K . Although, the above estimate gives the right order of magnitude, this is higher than what is expected. The value would be reduced on making the covalency corrections involved in the orbital functions u_1 and p given by (2.1) and (2.2) etc. This procedure would also take care of the corrections for the Mc Weeny orthogonality effect.⁷⁸

2.4 Concluding Remarks.

The analyses presented in the foregoing sections indicate that the indirect exchange interaction given by the spin polarization mechanism does lead to spin coupling between paramagnetic ions in certain compounds. A rigorous quantitative calculation, based on this approach, is extremely complicated owing to the fact that a large number of excited configurations have to be included. That the lowest available excited states will have the dominant role is to be expected. At present, however, it is very difficult to get a reliable knowledge about the excited states.

The excited orbitals were chosen on two models, namely, (i) the excitation model and (ii) the charge transfer model. In the specific orbitals considered, it is difficult to ascertain, for example, as to which of the

even orbitals $3d\gamma_1$ on O^{2-} and $(\chi_1 + \chi_2) / \sqrt{2}$ is the lowest. In point of fact, the effect of both should be taken into account. It may be remarked that the choice of orbitals ϕ_g^c and ϕ_u^c is such that it incorporates the role of both types of correlation effects discussed in Section 1, in the formulation. Furthermore, these linear combinations of the empty cation orbitals provide the appropriate directionality as well as the additional covalency effects involved in the spin polarization effect. It may be noted, that the recent measurements of the covalent spin density distributions in MnF_2 (Nathan et al⁷⁹) indicate that the part of the ligand ions closest to the 3d unpaired electrons carries the same sign as the magnetic ion. This result would seem to provide a direct experimental evidence in support of the spin polarization mechanism.

Although, the formulations in sections 2.2 and 2.3 followed a pure perturbation approach, the spin dependant polarization of the anion electrons which is responsible for the energy difference (2.68) or (2.69) is not quite independent of the general correlation effects discussed in 2.1.

The calculation given in 2.3 is much more relevant for Nickel compounds (e.g. NiO , NiF_2 etc) where the singly occupied magnetic orbitals involved are of the $d\gamma$ type. For Mn^{2+} or Fe^{3+} systems, the calculations ought to be extended to the 90° indirect exchange effects i.e. invoking $d(xy)$, p_π and excited orbitals. That the

right angled exchange interaction between the nearest neighbour paramagnetic ions via the intervening ions may be quite appreciable has been recently pointed out by several workers.⁸⁰⁻⁸³

As emphasized in the introduction, the mechanism presented here is analogous to the Ruderman-Kittel mechanism of the hyperfine interaction in metals and Zener-Kasuya-Yoshida mechanism for the magnetic properties in metals and alloys. The role of the intervening ion corresponds to that of the conduction electrons in metals. Although, the indirect spin polarization mechanism seems to be universally applicable for all systems (i.e. nuclear and atomic spin coupling in metals and compounds), it is not the intention of the present work to decide in its favour. There are other mechanisms as discussed in the introduction and the truth may be a compromise of all these in order of importance. In the absence of reliable quantitative calculations one has to await some decisive experimental results arising from studies involving paramagnetic resonance^{80,84}, hyperfine coupling by nuclear resonance,⁸² and neutron scattering techniques.^{79,85}

In the next section an extension of the present approach to other systems is considered.

C H A P T E R - 3

STUDY OF INDIRECT EXCHANGE INTERACTION IN TETRAHEDRAL SYSTEMS

In this chapter, the ideas of the spin polarization mechanism are extended to the study of spin coupling in magnetic compounds having ZnS and CaF_2 type structures.*

3.1 Introduction

In the zinc blende (ZnS) type magnetic systems,⁸⁶ the paramagnetic ions are surrounded tetrahedrally by four anions and each anion is likewise surrounded by four paramagnetic ions. In CaF_2 type systems,⁸⁶ each Ca^{2+} ion is surrounded tetrahedrally by four paramagnetic ions and each paramagnetic ion by eight anions. Typical examples are β -MnS and TiH_2 respectively.

For such structures, the elementary unit chosen is M_4X , where the intermediate ion (X) is placed at the centre of the tetrahedron and the paramagnetic ions (M) at the four corners.

* Part of this work in a different form using the method of semilocalized orbitals has been published (Sinha and Koide).⁴⁰ In the present chapter, however, a perturbation procedure is given and contains, by and large, the author's work.

In TiH_2 , which is antiferromagnetic, two 3d electrons of the Ti^{2+} ions singly occupy the two $d\gamma$ orbitals, namely, $d(2z^2-x^2-y^2)$ and $d(x^2-y^2)$, and in the anion H^- there are two coupled electrons in the s orbital; the unit is $(\text{Ti}_4^{2+}\text{H}^-)$.

The magnetic structure of β -MnS (Zinc blende type) has been given by Corliss, Elliott and Hastings on the basis of their neutron diffraction studies.⁸⁷ The results indicate an antiferromagnetic ordering.

In this case the elementary unit is $(\text{Mn}^{2+})_4\text{S}^{2-}$. The electronic configuration of S^{2-} is Ne shell plus $(3s)^2(3p)^6$. It is the latter two 3s and six 3p electrons which are supposed to take part in the indirect exchange interaction leading to the spin coupling of the four paramagnetic ions Mn^{2+} . A complete treatment would require the study of the interaction of all these eight electrons with those of the electrons of the paramagnetic ions, namely, the five 3d electrons of each ion. This task is formidable. In the following, therefore, an attempt will be made to show qualitatively what results one can get according to the spin polarization mechanism for the unit M_4X . Hence for simplicity, one representative 3d electron from each paramagnetic ion will be considered and two electrons from the central ion in an s-like orbital. This will be appropriate for the unit $(\text{Ti}_4^{2+}\text{H}^-)$ also. This description will suffice for a formal development of the essential features of the

previous theory when extended to a 'six electron and five centre' problem. The central idea is to study the stabilization of the antiferromagnetic or ferromagnetic state of the system (M_4X) by the polarization of the intervening ion owing to the spatial and spin correlation between its electrons. The inclusion of the effect of 3p orbitals of S^{2-} can be carried out by following the procedure outlined below.

As before, the eigenstates of the total spin (S^2) of the system are considered. The spin dependent energy appears because of the interaction of the various excited states with the respective zeroth order states.

Formulation of the wave functions.

3.2 The wave functions of the central ion electrons

The cations at the corners of the tetrahedron are numbered 1, 2, 3 and 4 with the anion at the centre. In the system β -MnS a large degree of covalency is expected and hence a charge transfer model would be more appropriate for the description of the excited states. Thus the excited orbitals are taken as the linear combinations of those empty cation orbitals which point towards the central ion and have σ type symmetry with respect to the bond axis. The respective orbitals are denoted by $\phi_1, \phi_2, \phi_3, \phi_4$. The possible combinations are $(\phi_1 + \phi_2 + \phi_3 + \phi_4)$, $(\phi_1 + \phi_2 - \phi_3 - \phi_4)$, $(-\phi_1 + \phi_2 - \phi_3 + \phi_4)$ and $(-\phi_1 + \phi_2 + \phi_3 - \phi_4)$. The transformation properties of these

under the symmetry properties of the point group T_d must be noted and should be orthogonalized with respect to the ground anion orbitals (e.g. s orbital of the central ion).

Table No.2 : The Character Table for T_d (After Griffith)⁴⁷

Irreducible Representation	The character $\chi_i(R)$ for the symmetry transformation.				
	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	-1	1
T_2	3	0	-1	1	-1

These are classified as (cf. the character table for T_d group given in Table 2).

$$A_1 : a = \frac{(\phi_1 + \phi_2 + \phi_3 - 4\lambda_s s)}{2\sqrt{(1 - 4\lambda_s^2)}} \dots \dots (3.1)$$

$$T_1 : t_x = \frac{(\phi_1 + \phi_2 - \phi_3 - \phi_4)}{2} \dots \dots (3.2)$$

$$t_y = \frac{(-\phi_1 + \phi_2 - \phi_3 + \phi_4)}{2} \quad \dots \dots (3.3)$$

$$t_z = \frac{(-\phi_1 + \phi_2 + \phi_3 - \phi_4)}{2} \quad , \dots \dots (3.4)$$

where

$$\lambda_s = \langle s / \phi_i \rangle$$

All the orbitals from (3.1) to (3.4) are orthogonal to s; t_x , t_y , and t_z from symmetry considerations and 'a' is appropriately orthogonalized. If $3p_x$, $3p_y$ and $3p_z$ were to be considered then the t orbitals should be orthogonalized with respect to anion p orbitals. The orbital energy of 'a' will be different from that of the degenerate orbitals t. Also, an important difference arises because of the overlap mixing (i.e. the presence of the term $4\lambda_s$). In terms of the orbitals, s, a, and t, the singlet and the triplet states of the two anion electrons can be written as:

Zeroth order ground singlet

$$^1A_1 \quad ; \quad |^1\chi\rangle = [s\bar{s}] \quad , \dots (3.6)$$

where $[\dots]$ denotes the determinantal function.

Excited triplets:

$$^3T_1 \quad : \quad |^3\alpha\rangle = [t_x s] \quad \dots \dots (3.7)$$

$$|{}^3\beta\rangle = [t_y s] \quad \dots (3.8)$$

$$|{}^3\gamma\rangle = [t_z s] \quad \dots (3.9)$$

$${}^3A_1 : |{}^3\Sigma\rangle = [ss] \quad \dots (3.10)$$

The symbols A_1 , A_2 , T_1 , T_2 , E etc. denote the irreducible representations of the tetrahedral group (cf. Table 2).

In addition to the wave functions noted, there will be excited singlets involving one or two electron transitions to the excited orbitals. These involve still higher energy states compared to those already given and hence are not considered.

3.3 The wave functions of the cation electrons

The singly occupied orbital functions of the paramagnetic ions are denoted by u_1 , u_2 , u_3 and u_4 . It is assumed that ~~the~~ under the symmetry operations of the T_d group, these four transform into each other without change of sign. This implies that each orbital u has either σ -type axial symmetry with respect to its bond with the central ion or its angular dependence is such that the above condition is fulfilled. To be more precise u has the angular dependence of $d(2z^2 - x^2 - y^2)$ where x , y , z are the axes defined with respect to the cube axes. Alternatively, it behaves like $d = d(2z^2$

$d\sigma = d(z'^2 - x'^2 - y'^2)$ where the new axis z' coincides with the direction of the bond in question. The above is assumed for convenience in calculations.

Including the spin functions, the linear combinations of the Slater determinants give the states 1E , 3T_2 and 5A_2 which belong to different irreducible representations of the tetrahedral group. Of course these, 1E may be regarded as representing the antiferromagnetic state and 5A_2 the ferromagnetic state. The explicit forms are expressed as:

$$^1E : |\phi_I\rangle = \{ [\bar{u}_1\bar{u}_2u_3u_4] + [\bar{u}_1u_2\bar{u}_3u_4] + [u_1\bar{u}_2u_3\bar{u}_4] + [u_1u_2\bar{u}_3\bar{u}_4] - 2[\bar{u}_1u_2u_3\bar{u}_4] - 2[u_1\bar{u}_2\bar{u}_3u_4] \} / \sqrt{12}, \dots\dots\dots(3.11)$$

$$|\phi_{II}\rangle = \{ [\bar{u}_1\bar{u}_2u_3u_4] - [\bar{u}_1u_2\bar{u}_3u_4] - [u_1\bar{u}_2u_3\bar{u}_4] + [u_1u_2\bar{u}_3\bar{u}_4] \} / 2 \dots\dots\dots(3.12)$$

$$^3T_2 : |^3X(M_S=0)\rangle = \{ [u_1u_2\bar{u}_3\bar{u}_4] - [\bar{u}_1\bar{u}_2u_3u_4] \} / \sqrt{2} \dots(3.13)$$

$$|^3Y(0)\rangle = \{ [\bar{u}_1u_2\bar{u}_3u_4] - [u_1\bar{u}_2u_3\bar{u}_4] \} / \sqrt{2} \dots(3.14)$$

$$|^3Z(0)\rangle = \{ [\bar{u}_1u_2u_3\bar{u}_4] - [u_1\bar{u}_2\bar{u}_3u_4] \} / \sqrt{2} \dots(3.15)$$

etc.

$$^5A_2 : |^5\Lambda_2^{(2)}\rangle = [u_1u_2u_3u_4] \text{ etc. } \dots(3.16)$$

CHAPTER - IV

DEVELOPMENT OF CHEMICAL
NOTATION SYSTEMS FOR
MECHANIZATION

The states with different M_s values can be easily obtained by making use of the raising and lowering spin operators, namely, $(S_x + iS_y)$ and $(S_x - iS_y)$.

3.4 The wave functions of the total system.

In order to formulate the wave functions of the total system, such products of the anion and cation electron wave functions (§ 3.2 and § 3.3) are taken that form the base functions of the irreducible representations of the T_d group. The symmetry of the cation electron and anion electron functions as shown below will indicate the nature of the product functions.

Cation system	Anion system
1E	1A_1 (ground state)
3T_2	3T_1 (excited state)
5A_2	3A_1 (excited state)

The zeroth order ground states will be the products of the anion 1A_1 ground state and the cation states 1E_1 , 3T_2 and 5A_2 . Since 1A_1 belongs to the one dimensional totally symmetric irreducible representation, its products with 1E_1 , 3T_2 and 5A_2 will constitute the base functions of the irreducible representations of the T_d group. Thus the antiferromagnetic zeroth order state is taken to be the product of 1A_1 and 1E_1 , namely, equations (3.6) and (3.11) and (3.12). Likewise, the ferromagnetic zeroth order state is the product of (3.6) and (3.16) and has the

symmetry Λ_2 . In addition to these, there will be triplet states also; however, they are not considered here in as much as their energies lie intermediate between the ferromagnetic and antiferromagnetic states (for details see Sinha and Koide).⁴⁰ The explicit expressions of the various states are:

Ground state

Antiferromagnetic

$$\begin{aligned}
 |^1E_I\rangle &= |^1\chi \cdot ^1\phi_I\rangle \\
 &= \left\{ [\bar{u}_1\bar{u}_2u_3u_4s\bar{s}] + [\bar{u}_1u_2\bar{u}_3u_4s\bar{s}] + [u_1\bar{u}_2u_3\bar{u}_4s\bar{s}] \right. \\
 &\quad \left. + [u_1u_2\bar{u}_3\bar{u}_4s\bar{s}] - 2[\bar{u}_1u_2u_3\bar{u}_4s\bar{s}] - 2[u_1\bar{u}_2\bar{u}_3u_4s\bar{s}] \right\} \\
 &\quad / \sqrt{12} \quad \dots (3.17)
 \end{aligned}$$

$$\begin{aligned}
 |^1E_{II}\rangle &= |^1\chi \cdot ^1\phi_{II}\rangle \\
 &= \left\{ [\bar{u}_1\bar{u}_2u_3u_4s\bar{s}] - [\bar{u}_1u_2\bar{u}_3u_4s\bar{s}] - [u_1\bar{u}_2u_3\bar{u}_4s\bar{s}] \right. \\
 &\quad \left. + [u_1u_2\bar{u}_3\bar{u}_4s\bar{s}] \right\} / 2 \quad \dots (3.18)
 \end{aligned}$$

Ferromagnetic

$$\begin{aligned}
 |^5\Lambda_2\rangle &= |^1\chi \cdot ^5\Lambda_2\rangle \\
 &= [u_1u_2u_3u_4s\bar{s}] \quad \dots (3.19)
 \end{aligned}$$

The various excited states are the products of anion states 3T_1 and 3A_1 and the cation states 1E_1 , 3T_2 , 5A_2 . The reducible products are decomposed to the various irreducible ones. Of these only those states are taken which form the base functions of the irreducible representations and have the ^{same} symmetry as the corresponding zeroth order states. These are:

Excited States

Singlets

$$\begin{aligned}
 |^1E_1\rangle &= \frac{1}{\sqrt{2}} |^3\alpha \cdot ^3X\rangle - \frac{1}{\sqrt{2}} |^3\beta \cdot ^3Y\rangle = \frac{1}{\sqrt{6}} \{ |^3\alpha_{(M_S=1)} \cdot ^3X(1)\rangle \\
 &\quad - |^3\alpha(0) \cdot ^3X(0)\rangle + |^3\alpha(1) \cdot ^3X(-1)\rangle - |^3\beta(-1) \cdot ^3Y(1)\rangle \\
 &\quad + |^3\beta(0) \cdot ^3Y(0)\rangle - |^3\beta(1) \cdot ^3Y(-1)\rangle \} \\
 &= \frac{1}{\sqrt{24}} \{ ([u_1 u_2 \bar{u}_3 u_4 \bar{t}_x \bar{s}] + [u_1 u_2 u_3 \bar{u}_4 \bar{t}_x \bar{s}] - [\bar{u}_1 u_2 u_3 u_4 \bar{t}_x \bar{s}] \\
 &\quad - [u_1 \bar{u}_2 u_3 u_4 \bar{t}_x \bar{s}] - [u_1 u_2 \bar{u}_3 \bar{u}_4 \bar{t}_x \bar{s}] - [u_1 u_2 \bar{u}_3 \bar{u}_4 \bar{t}_x \bar{s}] \\
 &\quad + [\bar{u}_1 \bar{u}_2 u_3 u_4 \bar{t}_x \bar{s}] + [\bar{u}_1 \bar{u}_2 u_3 u_4 \bar{t}_x \bar{s}] + [\bar{u}_1 u_2 \bar{u}_3 \bar{u}_4 \bar{t}_x \bar{s}] \\
 &\quad + [u_1 \bar{u}_2 \bar{u}_3 \bar{u}_4 \bar{t}_x \bar{s}] - [\bar{u}_1 \bar{u}_2 \bar{u}_3 u_4 \bar{t}_x \bar{s}] - [\bar{u}_1 \bar{u}_2 u_3 \bar{u}_4 \bar{t}_x \bar{s}]) \\
 &\quad - ([\bar{u}_1 u_2 u_3 u_4 \bar{t}_y \bar{s}] + [u_1 u_2 \bar{u}_3 u_4 \bar{t}_y \bar{s}] - [u_1 \bar{u}_2 u_3 u_4 \bar{t}_y \bar{s}] \\
 &\quad - [u_1 \bar{u}_2 u_3 \bar{u}_4 \bar{t}_y \bar{s}] - [\bar{u}_1 u_2 \bar{u}_3 u_4 \bar{t}_y \bar{s}] - [\bar{u}_1 u_2 \bar{u}_3 u_4 \bar{t}_y \bar{s}]) \}
 \end{aligned}$$

$$\begin{aligned}
 & + [u_1 \bar{u}_2 u_3 \bar{u}_4 t_y s] + [u_1 \bar{u}_2 u_3 \bar{u}_4 t_y s] + [\bar{u}_1 \bar{u}_2 \bar{u}_3 u_4 t_y s] \\
 & + [\bar{u}_1 u_2 \bar{u}_3 \bar{u}_4 t_y s] - [\bar{u}_1 \bar{u}_2 u_3 \bar{u}_4 t_y s] - [u_1 \bar{u}_2 \bar{u}_3 \bar{u}_4 t_y s] \Big) \Big\} \\
 & \dots\dots\dots(3.20)
 \end{aligned}$$

$$\begin{aligned}
 |^1E_{II}\rangle &= \frac{1}{\sqrt{6}} |^3\alpha \cdot ^3X\rangle + \frac{1}{\sqrt{6}} |^3\beta \cdot ^3Y\rangle - \frac{2}{\sqrt{6}} |^3\gamma \cdot ^3Z\rangle \\
 &= \frac{1}{\sqrt{18}} \Big\{ |^3\alpha(-1) ^3X(1)\rangle - |^3\alpha(0) ^3X(0)\rangle + |^3\alpha(1) ^3X(-1)\rangle \\
 &+ |^3\beta(-1) ^3Y(1)\rangle - |^3\beta(0) ^3Y(0)\rangle + |^3\beta(1) ^3Y(-1)\rangle \\
 &- 2|^3\gamma(-1) ^3Z(1)\rangle + 2|^3\gamma(0) ^3Z(0)\rangle - 2|^3\gamma(1) ^3Z(-1)\rangle \Big\} \\
 &\dots\dots\dots(3.21)
 \end{aligned}$$

Its determinantal form including the spin part can be easily written following the pattern given in (3.20); however, the explicit form is rather lengthy and hence is not given here.

Likewise, the excited ferromagnetic states are given as: Quintet

$$\begin{aligned}
 |^5A_2(2)\rangle &= \frac{1}{\sqrt{3}} \Big\{ |^3\alpha(1) \cdot ^3X(1)\rangle + |^3\beta(1) \cdot ^3Y(1)\rangle + |^3\gamma(1) \cdot ^3Z(1)\rangle \Big\} \\
 &= \frac{1}{\sqrt{12}} \Big\{ [u_1 u_2 \bar{u}_3 u_4 t_x s] + [u_1 u_2 u_3 \bar{u}_4 t_x s] - [\bar{u}_1 u_2 u_3 u_4 t_x s] \Big\}
 \end{aligned}$$

$$\begin{aligned}
 & - [u_1 \bar{u}_2 u_3 u_4 t_x s] + [\bar{u}_1 u_2 u_3 u_4 t_y s] + [u_1 u_2 \bar{u}_3 u_4 t_y s] \\
 & - [u_1 \bar{u}_2 u_3 u_4 t_y s] - [u_1 u_2 u_3 \bar{u}_4 t_y s] + [\bar{u}_1 u_2 u_3 u_4 t_z s] \\
 & + [u_1 u_2 u_3 \bar{u}_4 t_z s] - [u_1 \bar{u}_2 u_3 u_4 t_z s] - [u_1 u_2 \bar{u}_3 u_4 t_z s] \} . \\
 & \dots\dots\dots (3.22)
 \end{aligned}$$

$$\begin{aligned}
 |^5A_2''(2)\rangle &= {}^5 |^3\Sigma \cdot {}^5\Lambda_2\rangle \\
 &= \frac{1}{\sqrt{3}} |^3\Sigma(1) \cdot {}^5\Lambda_2(1)\rangle - \frac{2}{\sqrt{6}} |^3\Sigma(0) \cdot {}^5\Lambda_2(2)\rangle \\
 &= \frac{1}{\sqrt{12}} \{ [u_1 u_2 u_3 \bar{u}_4 a s] + [u_1 u_2 \bar{u}_3 u_4 a s] + [u_1 \bar{u}_2 u_3 u_4 a s] \\
 & \quad + [\bar{u}_1 u_2 u_3 u_4 a s] - 2[u_1 u_2 u_3 u_4 \bar{a} s] - 2[u_1 u_2 u_3 u_4 a \bar{s}] \} , \\
 & \dots\dots\dots (3.23)
 \end{aligned}$$

3.5 Evaluation of the energy matrix

The Hamiltonian in atomic units ($e = \hbar = m = 1$) is

$$- \frac{1}{2} \sum_i \nabla_i^2 + \sum_i V(\underline{r}_i) + \sum_{i < j} \frac{1}{r_{ij}} \dots\dots (3.24)$$

where $V(\underline{r}_i)$ is the potential acting on the i^{th} electron owing to the five nuclei and all other electrons except the six under consideration. The energy matrix of the Hamiltonian within the manifold described in § 3.4 is given below.

Diagonal elements:

Neglecting the direct exchange integrals

$J(u_i u_j)$ these are:

Zeroth order ground states

$$\begin{aligned} \langle {}^1E/H {}^1E \rangle &= \langle {}^5A_2/H/{}^5A_2 \rangle \\ &= Q_s = \left[\sum_i \epsilon(u_i) + 2\epsilon(s) + \frac{1}{2} \sum_{i \neq j} K(u_i u_j) + 8K(u_i s) + K(ss) \right. \\ &\quad \left. - 4J(u_i s) \right] \dots\dots\dots(3.25) \end{aligned}$$

This shows that the ferromagnetic and antiferromagnetic zeroth order states are degenerate when the weak direct exchange integrals between the paramagnetic ions are neglected. The various notations occurring in (3.25) and in the following have already been explained in the previous chapter.

Excited States

$$\langle {}^1E'/H {}^1E' \rangle = Q_t + 2 \langle u_3 t_x / t_y u_3 \rangle \dots\dots(3.26)$$

$$\begin{aligned} \langle {}^5A_2'/H/{}^5A_2' \rangle &= Q_t - 3J(u_1 t_x) - 3J(u_1 s) + 2 \langle u_1 t_y / t_z u_1 \rangle \\ &\dots\dots(3.27) \end{aligned}$$

$$\langle {}^5A_2''/H/{}^5A_2'' \rangle = Q_a \dots\dots(3.28)$$

where

$$Q_m = \left[\sum_i \epsilon(u_i) + \epsilon(m) + \epsilon(s) + \frac{1}{2} \sum_{i \neq j} K(u_i u_j) + 4K(u_1 m) + 4K(u_1 s) + K(ms) - J(ms) \right] ,$$

with m denoting any of the excited orbitals t or s . It is to be noted that the dominant terms in the diagonal elements are always the Q 's and the relatively small exchange or off-diagonal exchange integrals can be neglected.

The off-diagonal elements are as follows:

$$\langle {}^1E_H / {}^1E' \rangle = \sqrt{24} \langle u_1 s / t_x u_1 \rangle = M_{af} , \quad (3.29)$$

$$\langle {}^5A_2 / {}^5A_2' \rangle = \sqrt{12} \langle u_1 s / t_x u_1 \rangle = M_f , \quad (3.30)$$

$$\langle {}^5A_2 / {}^5A_2'' \rangle = \sqrt{12} \langle u_1 s / a u_1 \rangle = M_f' , \quad (3.31)$$

where t_x stands for the orbital (3.2) and 'a' is given by (3.1). The above results are shown in the compact form below:

	1E_I	${}^1E_{II}$	${}^1E'_I$	${}^1E'_{II}$
1E_I	E_{af}	0	M_{af}	0
${}^1E_{II}$	0	E_{af}	0	M_{af}
${}^1E'_I$	M_{af}	0	$E_{af} + \Delta E_t$	0
${}^1E'_{II}$	0	M_{af}	0	$E_{af} + \Delta E_t$

(3.32)

	$5A_2$	$5A'_2$	$5A''_2$	
$5A_2$	E_f	M_f	M'_f	
$5A'_2$	M_f	$E_f + \Delta E_t$	X	
$5A''_2$	M'_f	X	$E_f + \Delta E_a$	 (3.33)

The energy depressions of the zeroth order antiferromagnetic and ferromagnetic states owing to interaction with the corresponding excited states are obtained by the second order perturbation procedure discussed in the previous chapter. The results are given below:

$$\delta(^1E) = -24 |\langle u_1 s / t_x u_1 \rangle|^2 / \Delta E_t \quad \dots (3.34)$$

$$\delta(5A_2) = - \frac{12 |\langle u_1 s / t_x u_1 \rangle|^2}{\Delta E_t} - \frac{12 |\langle u_1 s / a u_1 \rangle|^2}{\Delta E_a} \dots (3.35)$$

As in the previous case, ΔE_t may be taken to represent the excitation energy to orbital t and ΔE_a to the orbital 'a'. Thus the energy difference between the ferromagnetic (quintet) and the antiferromagnetic (singlet) states becomes

$$\begin{aligned} E'_f - E'_{af} &= \delta(5A_2) - \delta(^1E) \\ &= \frac{12}{\Delta E_t} |\langle u_1 s / t_x u_1 \rangle|^2 - \frac{12}{\Delta E_a} |\langle u_1 s / a u_1 \rangle|^2 \quad \dots (3.36) \end{aligned}$$

This result is exactly parallel to that obtained for the three centre and four electron symmetrical problem. The result can be easily generalized to the case when several orbitals in ground as well as excited states are considered. The question as to which of the ferromagnetic and the antiferromagnetic states lies deepest depends on the magnitude of the denominators (i.e. the orbital energies) and the hybrid exchange integrals such as $\langle u_1 s / t_x u_1 \rangle$ and $\langle u_1 s / a u_1 \rangle$.

The method of spin operators developed in chapter 2 can be extended to the present problem involving four paramagnetic ions and one intervening ion. The essential parallelism to remember is the role of two coupled anion electrons in the zeroth order ground state, which makes a transition to the triplet state in the intermediate excited state. The interaction operator describing the depressions of the various zeroth order states can be written as

$$\delta \left({}^{2S+1} \Gamma \right) = - \frac{2J_{ts}}{\Delta E_t} \left[\left(\sum_{i=1}^4 S_{m_i}^2 \right) \chi_t(E) - 2 \sum_{j>i=1}^4 S_{m_i} \cdot S_{m_j} \right] - \frac{2J_{as}}{\Delta E_a} \left[\left(\sum_{i=1}^4 S_{m_i}^2 \right) \chi_a(E) + 2 \sum_{j>i=1}^4 S_{m_i} \cdot S_{m_j} \right], \dots (3.37)$$

where

$$J_{ts} = \langle u_1 s / t_x u_1 \rangle, \quad J_{as} = \langle u_1 s / a u_1 \rangle,$$

and $\chi_t(E)$ and $\chi_a(E)$ represent the dimensions of the irreducible representations to which the orbitals t and 'a' belong. Further, if the relation (Van Vleck⁸⁸)

$$2 \sum_{j>i} S_i \cdot S_j = \left(\sum_i S_i \right)^2 - \sum_i S_i^2 = S(S+1) - \frac{3}{4} n \quad (3.38)$$

is used, the above can be simplified to

$$\begin{aligned} \delta \left({}^{2S+1}\Gamma \right) = & - \frac{2J_{ts}^2}{\Delta E_t} \left[\frac{3}{4} n \chi_t(E) - \left\{ S(S+1) - \frac{3}{4} n \right\} \right] \\ & - \frac{2J_{as}^2}{\Delta E_a} \left[\frac{3}{4} n \chi_a(E) + \left\{ S(S+1) - \frac{3}{4} n \right\} \right]. \quad (3.39) \end{aligned}$$

Here n represents the number of singly occupied orbitals u_1, u_2, u_3, u_4 i.e. $n = 4$ and S is the total resultant spin of the four electrons in them. $\chi_t(E) = 3$ for the orbitals t and $\chi_a(E) = 1$. Expressions (3.34) and (3.35) easily follow from (3.39) on making the appropriate substitutions. It should be noted that (3.39) gives correctly the depression of the ground triplet state considered by Sinha and Koide.⁴⁰ The result, when written in terms of the present formalism, is

$$\delta \left({}^3T_2 \right) = - \frac{20 |\langle u_1 s / t_x u_1 \rangle|^2}{\Delta E_t} - \frac{4 |\langle u_1 s / a u_1 \rangle|^2}{\Delta E_a}, \quad (3.40)$$

which indicates that the total state $|{}^3T_2\rangle_{gr}$ will lie

intermediate between the ferromagnetic $|^5\Lambda_2\rangle_{gr}$ and the antiferromagnetic $|^1E\rangle_{gr}$ states. This conclusion is borne out by the fact, as seen from the estimates of chapter 2, that the quantities such as $|\langle u_1s/t_x u_1 \rangle|^2/\Delta E_t$ and $|\langle u_1s/su_1 \rangle|^2/\Delta E_g$ differ considerably in magnitude. In what follows, some rough numerical estimates of these quantities are given.

3.6 Numerical estimate for β -MnS

For this purpose, the overlap between u's and ϕ 's having different suffixes are neglected. Accordingly,

$$\left. \begin{aligned} \langle u_1s / t_x u_1 \rangle &\approx \frac{1}{2} \langle u_1s / \phi_1 u_1 \rangle \\ \langle u_1s / su_1 \rangle &\approx \frac{\langle u_1s / \phi_1 u_1 \rangle - 4\lambda_s \langle u_1s / su_1 \rangle}{2 \sqrt{(1 - 4\lambda_s^2)}} \end{aligned} \right\} \quad (3.41)$$

Further, making use of Mulliken's approximation,⁶⁷ the exchange and hybrid exchange integrals take the forms given below:

$$\left. \begin{aligned} J(u_1s) = \langle u_1s / su_1 \rangle &\approx \frac{1}{2} S_1^2 \{ K(u_1u_1) + 2K(u_1s) + K(ss) \} \\ \langle u_1s / \phi_1 u_1 \rangle &\approx \frac{1}{2} S_1 \{ \langle u_1u_1 / \phi_1 u_1 \rangle + \langle u_1s / \phi_1 s \rangle \} \\ S_1 &= \langle u_1 / s \rangle \end{aligned} \right\} \quad (3.42)$$

The relatively simple one centre integrals are evaluated by using the following forms of the orbital functions u_1 , s , and ϕ_1 .

$$s \propto r^2 [\exp - (4.75/3) r] , \quad \dots(3.43)$$

and

$$u_1 \propto r^2 [\exp - (8.4/3) r] Y_{20}(\theta' \phi') , \quad \dots(3.44)$$

where z' refers to the bond direction joining u_1 and s . For the empty orbital ϕ_1 , the role of $4s$ and $4p$ on Mn^{2+} is considered by taking one of the sp^3 hybridized orbitals of the cation which points towards the central anion. This is given by

$$\phi_1 = \frac{1}{2} |4s\rangle + \frac{\sqrt{3}}{2} |4p_{z'}\rangle \quad \dots(3.45a)$$

with the radial part

$$f(r) \propto r^3 e^{-(3/2)r} \quad \dots(3.45b)$$

which is assumed to be common to $4s$ and $4p$ functions.

In deriving the exponents of (3.44) and (3.45b) the appropriate exponents of the Slater type functions are multiplied by a factor 1.5 so as to conform better with a Hartree-Fock function (as done in Koide, Sinha and Tanabe).³⁹

The overlap integrals for the observed interatomic distance between the cation and anion in β -MnS (4.6 a.u.) were evaluated by the methods suggested by Mulliken et al⁷¹

and Jaffe and Doak.⁷⁰ The values $\lambda_s = 0.30$ and $S_1 = 0.20$ were used in the appropriate places in equations (3.41) and (3.42). For evaluating other integrals the uniform sphere approximation, as mentioned in Chapter 2, was used. The values of the relevant integrals are set out in the following table.

Table No.3: Values of various integrals in a.u.

Integrals	Numerical values	Approximation used.
$K(u_1 u_1)$	0.780	Orbital function (3.44)
$K(ss)$	0.409	Orbital function (3.43)
$K(u_1 s)$	0.264	u.s.a.
$J(u_1 s)$	0.014	Mullikens approximation
$\langle u_1 u_1 / \phi_1 u_1 \rangle$	0.070	Mullikens approximation + KST ³⁹ calculations.
$\langle u_1 s / \phi_1 s \rangle$	0.030	" "
$\langle u_1 s / t_x u_1 \rangle$	0.005	" "
$\langle u_1 s / a u_1 \rangle$	-0.001	" "

Although, the orbital energy of the orbitals 't' will probably lie lower than 's' owing to the mixing of the latter with s, both these will be approximated by $\epsilon(t) = \epsilon(s) = \epsilon(\phi_1)$. This may seem reasonable here in that the mixing of the t orbitals with the p orbitals of the anion have not so far been considered.

It may be noted that this mixing will not alter the value of the integral $\langle u_1 s / t_x u_1 \rangle$ in as much as this will involve the appearance of extra terms such as $4 \lambda_t \langle u_1 s / p u_1 \rangle$, where $\langle u_1 s / p u_1 \rangle$ will be negligible as compared to $\langle u_1 s / s u_1 \rangle$ in (3.41).

As before, the approximation $\Delta E_t = \Delta E_s = \Delta E_m$ is used and ΔE_m is identified with $\epsilon(\phi_1)_{\epsilon(s)}$. This is determined from the appropriate ionization energy⁷³ and the electron affinity⁷⁴ data for the manganese and sulphur ions respectively. Thus ΔE_m turns out to be about 20 eV. However, to be on the safe side, the value 1 a.u. (i.e. 27.2 eV) will be used. The rough values in the table indicate that $\langle u_1 s / t_x u_1 \rangle$ is about five times larger than $\langle u_1 s / s u_1 \rangle$. This means that

$$\frac{|\langle u_1 s / t_x u_1 \rangle|^2}{\Delta E_m} \approx \frac{25 |\langle u_1 s / s u_1 \rangle|^2}{\Delta E_m}$$

and the first term in (3.36) will dominate, favouring the antiferromagnetic state. However, taking both terms into account the energy difference $\epsilon(^5A_2) - \epsilon(^4E) = 3 \times 10^{-4}$ a.u., which in the temperature unit is about 80°K.

Since it is difficult to connect the present model with the simple statistical theories of magnetic ordering, no attempt is made to relate the energy difference with the Ne'el temperature. Only a rough idea of the Ne'el temperature can be had from the above figure. It may be

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noted that β -MnS (Zinc blende type) is antiferromagnetic with its Ne'el temperature lying between 75 - 150°K.⁸⁷

The agreement should not, however, be taken seriously as no account has been taken of the spin polarization effects of the 3p like orbitals of the central ion and the numerical estimates given above are rather crude. The model chosen for the formulation of the mechanism and subsequent calculations are illustrative and show that the spin polarization mechanism for the systems ~~under systems~~ under consideration would lead to a greater stability of the antiferromagnetic state than the ferromagnetic state.

3.7 Concluding Remarks.

As remarked earlier, the foregoing calculations apply equally well for systems such as TiH_2 where the anion has only the occupied s orbital. It may seem more reasonable to define the occupied cation orbital e.g. $d\gamma_1 = d(2z^2 - x^2 - y^2)$ with respect to the cube axes. If this is done so, then $u_1 = d\gamma_1$ is orthogonal to s (a point also noted by Kanamori)³⁵ and the question of antibonding admixture with s would not arise. For the excited orbitals, one of the sp^3 hybridized orbitals on the cation pointing towards the anion may still be chosen. For Ti^{2+} , however, the d_e orbitals have also to be considered. When dealing with

orthogonal orbitals Mulliken's approximations cannot be used and complicated two centre integrals ought to be evaluated by other methods. Since no pretence is made here for a quantitative completeness in the calculations, we shall turn towards other points.

The above formulation has been confined to a symmetrical and isotropic situation. If the complete tetrahedral symmetry is not there, the two singlet states

$|^1E_I\rangle$ and $|^1E_{II}\rangle$ may have different degrees of stabilization owing to the present mechanism. If the latter is stabilized, then the paramagnetic atoms in (001) layer will have parallel coupling and are coupled antiparallel with the adjacent layers. This type of antiferromagnetic ordering has been observed in TbD_2 and HoD_2 (Calcium fluoride type structure) by Cox et al.⁸⁹ It may be noted that the spin polarization is expected to be the dominant process for the rare earth compounds. The calculations of the present chapter can be suitably extended to the above systems provided the symmetry of the f electrons is taken into account.

In addition to the isotropic exchange interaction (type A $\underline{S}_i \cdot \underline{S}_j$) such as the spin polarization and other mechanisms, anisotropic superexchange interactions⁹⁰ ($\underline{D}_{ij} \cdot \underline{S}_i \times \underline{S}_j$) may also be permissible for β -MnS type systems. Keffer⁹¹ and Pearson⁹² have carried out this type of calculations.

CHAPTER - 4

ON THE TETRAGONAL DISTORTION OF OCTAHEDRAL SYSTEMS IN E_g ELECTRONIC STATE

In this chapter the tetragonal distortion of octahedral (ML_6 , where M stands for a transition metal ion and L denotes the ligand) systems having two fold orbital degeneracy is analysed on the basis of a model which takes into account both the covalency and the essential features of the Jahn-Teller effect.

4.1 Introduction

The tetragonal distortion from cubic symmetry occurring in certain transition metal compounds, e.g. Mn_3O_4 , has been treated on the basis of spatial ordering of distorted elementary octahedra (Sinha et al,⁹³ Wojtowicz⁹⁴). The tetragonally distorted spinels, e.g. Mn_3O_4 and $CuFe_2O_4$, contain the transition metal ions Cu(II) or Mn(III) at the octahedral sites. Thus the origin of distortion has been related to the behaviour of such ions when placed in the octahedral environment of the ligands (e.g. O^{2-}). Some authors (Goodenough and Loeb⁹⁵) have attributed the origin to the ability of such ions (having d^4 or d^9 outer electronic configuration) to form dsp^2 empty hybrid orbitals which take

part in the covalent coplaner square bonds with the overlapping orbitals of the four anions, the other two remaining electrovalently bonded. This theory, however, does not seem to be of general validity and there are situations which are difficult to rationalize on this basis.⁹⁶ The approach which invokes crystal field theory and Jahn-Teller⁹⁷ distortions of the environment seems to be more successful in correlating the magnetic, optical, and structural properties of such systems (Dunitz and Orgel,⁹⁶ Griffith⁴⁷). The theory of Dunitz and Orgel,⁹⁶ although qualitatively successful, relied entirely on the electrostatic model. Thus, there remains considerable scope for the generalization of this promising method by combining the molecular orbital approach with the crystal field theory (Van Vleck,⁶² Owen,⁶³ Sinha⁹⁸).

In the following treatment, however, the bulk crystal is not considered and only the nature of distortion in isolated octahedral complexes (ML_6) will be investigated. Pioneering work on the Jahn-Teller distortion of octahedral complexes has already been done on the basis of the electrostatic model by Van Vleck⁹⁹ and Öpik and Pryce.¹⁰⁰ Liehr and Ballhausen¹⁰¹ have attempted an extension of the above treatments by including additional second order terms of the nuclear displacements to the electronic energy of the complex.

The procedure amounts to introducing a new phenomenological constant, the sign of which is arbitrarily fixed to have agreement with the observed result. Furthermore, the calculations are confined within the premises of the electrostatic model and no account is taken of the covalency between the central ion and the ligands. On the other hand, Öpik and Pryce¹⁰⁰ had included the anharmonic terms of the quasi-elastic potential energy and pointed out that the third order terms in the normal displacements were of crucial importance in pinning the nature of distortion (See also Kanamori¹⁰² for a discussion of the two theories).

Since covalency does exist in such systems to a greater or lesser extent (Stevens,⁶⁴ Owen^{63,103}), it is desirable to consider a model in which an account of this effect is included. In what follows, we give a formal analysis of the energy states of octahedral systems in E_g electronic states following a molecular orbital approach which takes into account the essential features of the Jahn-Teller effect. The role of the first and second order terms in this scheme, which now include covalency effects, and the Öpik-Pryce anharmonic terms will be assessed in relation to the nature of tetragonal distortion i.e. elongation or contraction along one of the axes of the octahedron.

4.2 Theoretical Model

For this purpose, we consider an elementary octahedron with six ligands (e.g. O^{2-}), one at each corner, and a transition metal ion having $3d^4$ or $3d^9$ (Mn^{3+} or Cu^{2+}) outer electronic configuration at the centre. The positions and the displacements of ligands will be described in terms of normal coordinates which transform according to the irreducible representations of the relevant symmetry group (O_h for the undistorted octahedron). The definitions and notations used here are the same as those of Öpik and Pryce¹⁰⁰ and Van Vleck.⁹⁹ The two ligand ions on the $\pm x$ axis are respectively numbered 1 and 4, the two on the $\pm y$ axis 2 and 5 and the two on the $\pm z$ axis 3 and 6. Out of the fifteen normal coordinates representing vibration, we shall enumerate only those coordinates which are of physical interest for the present problem. These are:

$$\left. \begin{aligned} Q_1(A_{1g}) &= (X_1 - X_4 + Y_2 - Y_5 + Z_3 - Z_6) / \sqrt{6}, \\ Q_2(E_g) &= (X_1 - X_4 - Y_2 + Y_5) / 2, \\ Q_3(E_g) &= [2(Z_3 - Z_6) - (X_1 - X_4 + Y_2 - Y_5)] / \sqrt{12}, \end{aligned} \right\} (4.1)$$

The other vibrational normal coordinates corresponding to the irreducible representations T_{1u} , T_{2g} , T_{2u} etc. are not considered. In other words, for convenience in calculations, they are assumed to be zero. In equation

(4.1) X_i , Y_i and Z_i represent the x, y, z components, respectively, of the displacement of the i^{th} ligand.

It will be useful to express the displacements of the ligands, whose regular octahedral positions are defined by $(\pm R_0, 0, 0)$, $(0, \pm R_0, 0)$ and $(0, 0, \pm R_0)$, in terms of the normal coordinates given by (4.1). Thus

$$\left. \begin{aligned} X_1 &= -X_4 = Q_1/\sqrt{6} + Q_2/2 - Q_3/\sqrt{12} \\ Y_2 &= -Y_5 = Q_1/\sqrt{6} - Q_2/2 - Q_3/\sqrt{12} \\ Z_3 &= -Z_6 = Q_1/\sqrt{6} + Q_3/\sqrt{3} \end{aligned} \right\} \quad (4.2)$$

For the construction of the molecular orbitals of the system ML_6 according to the LCAO, MO (Linear combination of atomic orbitals, molecular orbital) method, the various atomic orbitals are classified as the core and the valence orbitals. Thus the orbitals on the metal ions important for mixing with those of the ligand ones are nd, (N+1)s, and (n+1)p. Likewise, the ligand orbitals which have an appreciable overlap with the appropriate metal ion orbitals will be involved in the bonding and antibonding orbitals of the total system.

To fix ideas, let us consider, as an example, one Mn^{3+} ion at the centre and six O^{2-} ions, one each at the corner. Then the total number of electrons to be accommodated in various orbitals are $22(Mn) + 6 \times 10(O^{2-}) = 82$. Of these, 18 (in $1s^2 2s^2 2p^6 3s^2 3p^6$) can be regarded with

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sufficient accuracy as completely located on the Mn^{3+} centre and likewise $6x_4$ are located on oxygens (in the configuration $1s^2 2s^2$). The remaining electrons ($4 + 36 = 40$) would occupy orbitals which can approximately be regarded as built up from the combinations of 2p atomic orbitals on oxygens and 3d, 4s, and 4p atomic orbitals on Mn^{3+} .

Before proceeding further, it should be noted that the bonding molecular orbitals involving the σ (i.e. $2p_{\sigma}$) orbitals of the oxygen will be of lower energy than those involving the π (i.e. $2p_{\pi}$) orbitals because the σ orbital function overlaps more on to the Mn and makes use of its strong attractive field than the π orbitals. Here σ and π refer respectively to those orbitals which have even and odd symmetry under rotation by 180° about the axis joining the metal and the ligand ions.

Then in the increasing order of energy the molecular orbitals and the electrons are assumed to be accounted for as follows:

1. Bonding combinations involving σ orbitals.

a) A_{1g} : One orbital (a_{1g}), being the combination of 4s on Mn and

$$\left[\sigma_1(x_1) - \sigma_4(x_4) + \sigma_2(y_2) - \sigma_5(y_5) + \sigma_3(z_3) - \sigma_6(z_6) \right] / \sqrt{6}$$

: two electrons.

b) E_g : appropriate combinations of the cation $3d\gamma$

orbitals with corresponding anion combinations. Two orbitals (e_g) : four electrons.

c) T_{1u} : appropriate combinations of the cation $4p$ (p_x, p_y, p_z) with anion combinations

$$[\sigma_1(x_1) + \sigma_4(x_4)]/\sqrt{2}, [\sigma_2(y_2) + \sigma_5(y_5)]/\sqrt{2}, [\sigma_3(z_3) + \sigma_6(z_6)]/\sqrt{2} .$$

Three orbitals : six electrons.

2. Bonding combination of π orbitals

The degree of mixing is smaller than σ because of smaller overlap

a) T_{2g} : Weakly bonding combination of $3d\epsilon$ on Mn with

$$[\pi_1(y_1) - \pi_4(y_4) + \pi_2(x_2) - \pi_5(x_5)] / 2 ,$$

$$[\pi_1(z_1) - \pi_4(z_4) + \pi_3(x_3) - \pi_6(x_6)] / 2 ,$$

$$[\pi_2(z_2) - \pi_5(z_5) + \pi_3(y_3) - \pi_6(y_6)] / 2 .$$

Three orbitals : six electrons.

b) T_{1u} : weakly bonding combinations of $4p$ on Mn with

$$[\pi_2(x_2) + \pi_5(x_5) + \pi_3(x_3) + \pi_6(x_6)] / 2 ,$$

$$[\pi_1(y_1) + \pi_4(y_4) + \pi_3(y_3) + \pi_6(y_6)] / 2 ,$$

$$[\pi_1(z_1) + \pi_4(z_4) + \pi_2(z_2) + \pi_5(z_5)] / 2 .$$

Three orbitals : six electrons.

c) T_{1g} : Non bonding orbitals (t_{1g})

$$\left[\pi_2(z_2) - \pi_5(z_5) - \pi_3(y_3) + \pi_6(y_6) \right] / 2 ,$$

$$\left[\pi_4(z_4) - \pi_1(z_1) + \pi_3(x_3) - \pi_6(x_6) \right] / 2 ,$$

$$\left[\pi_1(y_1) - \pi_4(y_4) - \pi_2(x_2) + \pi_5(x_5) \right] / 2 .$$

Three orbitals : six electrons.

d) T_{2u} : Non bonding orbitals (t_{2u})

$$\left[\pi_2(x_2) + \pi_5(x_5) - \pi_3(x_3) - \pi_6(x_6) \right] / 2 ,$$

$$\left[\pi_1(y_1) + \pi_4(y_4) - \pi_3(y_3) - \pi_6(y_6) \right] / 2 ,$$

$$\left[\pi_1(z_1) + \pi_4(z_4) - \pi_2(z_2) - \pi_5(z_5) \right] / 2 .$$

Three orbitals : six electrons.

3. T_{2g} : Weakly antibonding combinations of 3d ϵ on Mn and the appropriate combinations of anion π orbitals (t_{2g}^*) which are orthogonal to (2a) above.

Three orbitals : three electrons.

So far, we have accounted for the 39 electrons. The remaining electrons would go to

4. E_g : The strong antibonding combination (e_g^*) of d_{γ} orbitals with the σ combinations,

$$[2\sigma_3(z_3) - 2\sigma_6(z_6) - \sigma_1(x_1) + \sigma_4(x_4) - \sigma_2(y_2) + \sigma_5(y_5)] / \sqrt{12},$$

$$[\sigma_1(x_1) - \sigma_4(x_4) - \sigma_2(y_2) + \sigma_5(y_5)] / 2$$

and orthogonal to (1b). It is with the last set of degenerate orbitals that we shall be most concerned in the study of distortion. The antibonding combinations with 4s and 4p orbitals of the metal ion will give highly excited orbitals and will be empty. These will not be considered, in view of their higher orbital energies. For $\text{Cu}^{2+}(\text{O}^{2-})_6$, there will be six electrons in t_{2g}^* and three in e_g^* , the others being occupied equivalently as above.

With the above example, we now consider the explicit formulation of the problem. The explicit forms of the valence orbitals under consideration are then taken as follows:

For the central metal ion:

$$\phi_a = R(r) Y_{20}(\theta, \phi), \quad (4.3a)$$

$$\phi_b = R(r) \{ Y_2^2(\theta, \phi) + Y_2^{-2}(\theta, \phi) \} / \sqrt{2}, \quad (4.3b)$$

where $R(r)$ is the radial part of the orbital function and Y 's are the spherical harmonics representing the angular dependence. The appropriate combinations of the ligand orbitals are re-written as

$$\chi_a(Q_i, s) = (2[z] - [x] - [y]) / \sqrt{12}, \quad (4.4a)$$

$$\chi_b(Q_1's) = ([x] - [y]) / \sqrt{2} \quad (4.4b)$$

where $[x] = \sigma_1(x_1) - \sigma_4(x_4)$ etc.

It would be useful to note the transformation properties of the above orbitals and normal coordinates involved under symmetries of various point groups showing descending order of symmetry.

		O_h	D_{4h}	D_{2h}
Q_3	$\phi_a \chi_a$	$3z^2 - r^2$	Λ_{1g}	Λ_{1g}
Q_2	$\phi_b \chi_b$	$x^2 - y^2$	B_{1g}	A_{1g}

With the above choice of the model, we now proceed to develop a formalism suitable for the study of the tetragonal distortion of the octahedral system having an electron in E_g electronic state (for the metal ion with d^4 or d^9 outer electronic configuration).

4.3 Formulation and solution of Energy Matrix.

The Hamiltonian for the one electron problem (in atomic units) is

$$H = - \frac{1}{2} \sum_j \nabla_j^2 + V(\underline{r}_j, \underline{R}_n) \quad \dots \quad (4.5)$$

where the first term is the kinetic energy operator of the electrons and the second represents the total potential

energy of the electrons and nuclei. The potential V can be further decomposed as

$$V_0(\underline{r}) + \sum_{i=1}^6 V_i(|\underline{r} - \underline{R}_i|), \quad (4.5)$$

where $V_0(\underline{r})$ is the potential on the electron owing to the central ion and V_i due to the i^{th} ligand ion core. Each has spherical symmetry about its own position; however, the total potential V in the undistorted configuration of the octahedron will have cubic symmetry.

Consider the four by four secular matrix of the Hamiltonian with respect to the orbitals ϕ_a , χ_a , ϕ_b and χ_b . Since we are interested in the tetragonal distortion only, we decompose the above matrix further by assuming $Q_2=0$, in the first instance. Then the following two, two by two matrices are constructed and are to be diagonalized separately.

$$\begin{array}{c} \begin{array}{cc} & \begin{array}{cc} \phi_a & \chi_a \end{array} \\ \begin{array}{c} \phi_a \\ \chi_a \end{array} & \begin{array}{cc} A_a - E & C_a - S_a E \\ & B_a - E \end{array} \end{array}, \quad (4.6a) \end{array}$$

$$\begin{array}{c} \begin{array}{cc} & \begin{array}{cc} \phi_b & \chi_b \end{array} \\ \begin{array}{c} \phi_b \\ \chi_b \end{array} & \begin{array}{cc} A_b - E & C_b - S_b E \\ & B_b - E \end{array} \end{array}, \quad (4.6b) \end{array}$$

where $A_a = \langle \phi_a / H / \phi_a \rangle$, $B_a = \langle \chi_a / H / \chi_a \rangle$,

$$C_a = \langle \phi_a / H / \chi_a \rangle, \quad S_a = \langle \phi_a / \chi_a \rangle \quad \text{etc.}$$

The effect of Q_2 in the first and second order terms in the development of the energy matrix will be included later.

Within this approximation, we define the antibonding molecular orbitals γ_a and γ_b as follows:

$$\gamma_a(Q_1 Q_2 Q_3) = \gamma_a(Q_1 0 Q_3) + \dots \quad (4.7a)$$

$$\gamma_b(Q_1 Q_2 Q_3) = \gamma_b(Q_1 0 Q_3) + \dots \quad (4.7b)$$

Similarly, the Hamiltonian is taken as

$$H(Q_1 Q_2 Q_3) = H(Q_1 0 Q_3) + \dots,$$

Now, we have to consider the solutions of the two by two secular equation,

$$\begin{vmatrix} \langle \gamma_a / H / \gamma_a \rangle - E & \langle \gamma_a / H / \gamma_b \rangle - E \langle \gamma_a / \gamma_b \rangle \\ \langle \gamma_a / H / \gamma_b \rangle - E \langle \gamma_a / \gamma_b \rangle & \langle \gamma_b / H / \gamma_b \rangle - E \end{vmatrix} = 0 \quad (4.8)$$

The two solutions within the approximation $Q_2=0$ can be defined as $E_a(Q_1 0 Q_3)$ and $E_b(Q_1 0 Q_3)$. These must be equal to

$$E_a(Q_1 0 Q_3) = \langle \psi_a(Q_1 0 Q_3) / H(Q_1 0 Q_3) / \psi_a(Q_1 0 Q_3) \rangle, \quad (4.9a)$$

and

$$E_b(Q_1 0 Q_3) = \langle \psi_b(Q_1 0 Q_3) / H(Q_1 0 Q_3) / \psi_b(Q_1 0 Q_3) \rangle. \quad (4.9b)$$

In order to find the explicit forms of the solutions, we consider the following forms of antibonding and bonding orbitals which diagonalize the matrices (4.6a) and (4.6b)

$$\psi_a(Q_1 0 Q_3) = \{ (\cos \alpha_a) \phi_a - \cos(\sigma_a + \alpha_a) \chi_a \} / \sin \sigma_a \quad (4.10a)$$

.....(antibonding),

$$\chi'_a(Q_1 0 Q_3) = \{ \sin(\sigma_a + \alpha_a) \chi_a - (\sin \alpha_a) \phi_a \} / \sin \sigma_a \quad (4.10b)$$

.....(bonding).

Similarly ,

$$\psi_b(Q_1 0 Q_3) = \{ (\cos \alpha_b) \phi_b - \cos(\sigma_b + \alpha_b) \chi_b \} / \sin \sigma_b \quad (4.11a)$$

.....(antibonding),

$$\chi'_b(Q_1 0 Q_3) = \{ \sin(\sigma_b + \alpha_b) \chi_b - (\sin \alpha_b) \phi_b \} / \sin \sigma_b \quad (4.11b)$$

.....(bonding) ,

$$\text{where } \cos \sigma_a = S_a = \langle \phi_a / \chi_a \rangle \text{ and } \cos \sigma_b = S_b = \langle \phi_b / \chi_b \rangle. \quad (4.12)$$

The coefficients involved in (4.10) and (4.11) can be determined from the relations given below; the relations are given in a general form without the suffixes a and b.

We have,

$$\tan 2(\sigma + \alpha) = \frac{2(C-AS)\sin\sigma}{A-B+2S(C-AS)}, \dots (4.13)$$

or

$$\tan 2\alpha = \frac{2(C-BS)\sin\sigma}{A-B-2S(C-BS)}, \dots (4.14)$$

or

$$\frac{C-BS}{\sin 2\alpha} + \frac{(C-AS)}{\sin (2\alpha + \sigma)} = 0 \dots (4.15)$$

It is to be noted that the above three relations are not independent. Any one of them will serve the purpose. The diagonalization procedure for (4.6a) or (4.6b) finally gives for the antibonding orbitals,

$$\langle \psi_H / \psi \rangle = \left\{ A+B-2CS + \sqrt{(A-B)^2 + 4(C-AS)(C-BS)} \right\} / 2\sin^2\sigma. \dots (4.16)$$

It would be useful to write (4.16) in a form which separates the terms arising due to covalency from those which follow from the electrostatic model. Making use of relations (4.12) and (4.13) etc. we get

$$E(Q_1 Q_3) = \langle \psi_H / \psi \rangle = A - \left\{ (C-AS) \cot(\alpha + \sigma) / \sin\sigma \right\}, (4.17)$$

where the term in the curly bracket represents the covalent part.

In order to derive suitable expressions for the derivatives $\partial E / \partial Q_i$ and $\partial^2 E / \partial Q_i \partial Q_j$ etc., involved in the expression of the energy matrix with respect to normal coordinates, we introduce the following notations.

$$\psi = p\phi - q\chi, \quad (4.18)$$

where $p = \cos\alpha / \sin\sigma$; $q = \cos(\sigma+\alpha) / \sin\sigma$, with relations

$$\begin{aligned} p - qS &= \sin(\sigma+\alpha) \\ pS - q &= \sin\alpha \\ \text{and the normalization condition} \\ p^2 + q^2 - 2pqS &= 1 \end{aligned} \quad (4.19)$$

Thus (4.17) can be written as

$$E = A - (C - AS) / (p - qS) \quad (4.17')$$

We consider the case where all the algebraic entities E , A , B , C , S , q and p are functions of the normal coordinates.

Let $()_{Q_i}$ and $()_{Q_i Q_j}$ stand for $\partial() / \partial Q_i$ and

$\partial^2() / \partial Q_i \partial Q_j$ respectively. Then after some complicated algebra involving relations given in (4.19) and (4.17') and their derivatives, we get the following relations

$$E_{Q_i} = A_{Q_i} - 2 \left\{ (C - AS)_{Q_i} + (A - E)S_{Q_i} \right\} pq - (A - B)_{Q_i} q^2, \quad (4.20)$$

and

$$\begin{aligned}
 E_{Q_1 Q_j} = & A_{Q_1 Q_j} - 2 \left\{ (C-AS)_{Q_1 Q_j} + (\Lambda-E) S_{Q_1 Q_j} + (\Lambda-E)_{Q_1} S_{Q_j} \right. \\
 & \left. + (\Lambda-E)_{Q_j} S_{Q_1} \right\} pq - (\Lambda-B)_{Q_1 Q_j} q^2 \\
 - \frac{2}{\Lambda - E} & \left\{ (\Lambda-E)_{Q_1} (p-qS) - \left[(C-AS)_{Q_1} + (\Lambda-E) S_{Q_1} \right] q \right\} \times \\
 & \left\{ (\Lambda-E)_{Q_j} (p-qS) - \left[(C-AS)_{Q_j} + (\Lambda-E) S_{Q_j} \right] q \right\}. \quad (4.21)
 \end{aligned}$$

With these relations in hand, we consider the "Taylor Series" development of E_a and E_b (cf equations (4.9) and (4.17)) with respect to Q_1 and Q_3 . We get

$$\begin{aligned}
 E_a(Q_1, Q_3) = & E_a(0,0) + (\partial E_a / \partial Q_1) Q_1 + \left(\frac{\partial E_a}{\partial Q_3} \right) Q_3 \\
 & + \frac{1}{2} \left(\frac{\partial^2 E_a}{\partial Q_1^2} \right) Q_1^2 + \frac{1}{2} \left(\frac{\partial^2 E_a}{\partial Q_3^2} \right) Q_3^2 + \left(\frac{\partial^2 E_a}{\partial Q_1 \partial Q_3} \right) Q_1 Q_3 + \dots \quad (4.22)
 \end{aligned}$$

with a similar expression for $E_b(Q_1, Q_3)$. Further we have the following relations between the derivatives involved in the expressions:

$$\left. \begin{aligned}
 \frac{\partial E_a}{\partial Q_1} &= \frac{\partial E_b}{\partial Q_1} ; & \frac{\partial^2 E_a}{\partial Q_1^2} &= \frac{\partial^2 E_b}{\partial Q_1^2} \\
 \frac{\partial E_a}{\partial Q_3} &= - \frac{\partial E_b}{\partial Q_3} ; & \frac{\partial^2 E_a}{\partial Q_3^2} &\neq \frac{\partial^2 E_b}{\partial Q_3^2}
 \end{aligned} \right\} \quad (4.23)$$

and

$$\frac{\partial^2 E_a}{\partial Q_1 \partial Q_3} = - \frac{\partial^2 E_b}{\partial Q_1 \partial Q_3}$$

Using these relations, we get a convenient development of the energy matrix (cf. equation (4.8)) with respect to Q_1 . We obtain

$$\begin{pmatrix} W + \alpha Q_3 + \frac{1}{2} \beta (Q_3^2 - Q_2^2) & \alpha Q_2 - \beta Q_2 Q_3 \\ \alpha Q_2 - \beta Q_2 Q_3 & W - \alpha Q_3 - \frac{1}{2} \beta (Q_3^2 - Q_2^2) \end{pmatrix}, \quad (4.24)$$

where the various symbols stand for the following:

$$W = E_a(000) + \left(\frac{\partial E_a}{\partial Q_1} \right) Q_1 + \frac{1}{2} \left(\frac{\partial^2 E_a}{\partial Q_1^2} \right) Q_1^2 + \frac{1}{4} \left(\frac{\partial^2 E_a}{\partial Q_3^2} + \frac{\partial^2 E_b}{\partial Q_3^2} \right) (Q_3^2 + Q_2^2) \dots \dots \dots (4.25)$$

$$\alpha = \frac{\partial E_a}{\partial Q_3} + \left(\frac{\partial^2 E_a}{\partial Q_1 \partial Q_3} \right) Q_1 \dots \dots \dots (4.26)$$

$$\frac{1}{2} \beta = \frac{1}{4} \left(\frac{\partial^2 E_a}{\partial Q_3^2} - \frac{\partial^2 E_b}{\partial Q_3^2} \right) \dots \dots \dots (4.27)$$

To solve (4.24), we define polar coordinates ρ and θ in the space of Q_2 and Q_3 :¹⁰⁰

$$Q_3 = \rho \cos \theta \quad ; \quad Q_2 = \rho \sin \theta \quad (4.28)$$

At this stage, we take into account the third order term of the quasi-elastic potential energy associated with Q_2 and Q_3 as suggested by Öpik and Pryce,¹⁰⁰ namely, $\Lambda_3 (Q_3^3 - 3Q_3 Q_2^2)$, Λ_3 being the coefficient defined by

them. Adding this term to (24) and making use of p and θ we get

$$E = W \pm p(\alpha^2 + \beta^2 p^2 + \alpha\beta p \cos 3\theta)^{\frac{1}{2}} + \Lambda_3 p^3 \cos 3\theta \quad \dots (4.29)$$

When $Q_2 = 0$, then for $\theta=0$, $\theta=\pi$

$$E = W \pm \epsilon p(\alpha + \epsilon \frac{1}{2} \beta p) + (\epsilon \Lambda_3 p^3) \quad \dots (4.30)$$

where $\epsilon = 1$ for $\theta = 0$

$\epsilon = -1$ for $\theta = \pi$.

Under these conditions the explicit forms of E_a and E_b can be written as:

$$E_a(Q_1, Q_3) = K + \alpha Q_3 + \gamma_a Q_3^2 + \Lambda_3 Q_3^3 \quad , \quad (4.31a)$$

$$E_b(Q_1, Q_3) = K - \alpha Q_3 + \gamma_b Q_3^2 + \Lambda_3 Q_3^3 \quad , \quad (4.31b)$$

where

$$\left. \begin{aligned} K &= E_a(0,0) + \left(\frac{\partial E_a}{\partial Q_1} \right) Q_1 + \frac{1}{2} \left(\frac{\partial^2 E_a}{\partial Q_1^2} \right) Q_1^2 , \\ \gamma_a &= \frac{1}{2} \frac{\partial^2 E_a}{\partial Q_3^2} \quad \text{and} \quad \gamma_b = \frac{1}{2} \frac{\partial^2 E_b}{\partial Q_3^2} . \end{aligned} \right\} \quad (4.32)$$

The extremization of E_a and E_b gives

$$E_a : Q_3 = \frac{-\gamma_a \pm \sqrt{\gamma_a^2 - 3\alpha\Lambda_3}}{3\Lambda_3} \quad (4.33a)$$

$$E_b : Q_3 = \frac{-\gamma_b \pm \sqrt{\gamma_b^2 + 3\alpha\Lambda_3}}{3\Lambda_3} \quad . \quad (4.33b)$$

For a minimum, however, we should respectively have

$$3\Lambda_3 Q_3 + \gamma_a > 0 \quad , \quad . \quad (4.34a)$$

and

$$3\Lambda_3 Q_3 + \gamma_b > 0 \quad . \quad . \quad (4.34b)$$

To be consistent with (3.34), we can choose only the plus sign before the radicals in (4.33). Thus,

for

$$E_a^{\min} ; Q_{3(\min)}^a = \frac{-\gamma_a + \sqrt{\gamma_a^2 - 3\alpha\Lambda_3}}{3\Lambda_3} \quad , \quad (4.35a)$$

and

for

$$E_b^{\min} ; Q_{3(\min)}^b = \frac{-\gamma_b + \sqrt{\gamma_b^2 + 3\alpha\Lambda_3}}{3\Lambda_3} \quad , \quad (4.35b)$$

provided the quantities under the radicals are positive.

If one uses the approximations that $\gamma_a^2 \gg 3\alpha\Lambda_3$ and $\gamma_b^2 \gg 3\alpha\Lambda_3$ (similar to that used by Liehr and Ballhausen; although our parameters α and γ are different from theirs), then¹⁰⁸

$$Q_{3(\min)}^a = -\frac{\alpha}{2\gamma_a} \quad \text{and} \quad Q_{3(\min)}^b = \frac{\alpha}{2\gamma_b} \quad , \quad (4.36)$$

and

$$E_s^{\min} - E_b^{\min} = \frac{\alpha^2 (\gamma_a - \gamma_b)}{4 \gamma_a \gamma_b} = \frac{\alpha^2 \beta}{2 \gamma_a \gamma_b}, \quad (4.37)$$

with $\beta = \frac{1}{2} (\gamma_a - \gamma_b)$. The above results (cf 4.36) and (4.37)) may be interpreted as a generalization of the results of Liehr and Ballhausen with the additional terms arising out of covalency effects. However, the approximation of neglecting the third order terms does not seem justifiable and we shall go back to the earlier relations i.e. (4.31) and (4.35).

4.4 Discussion

Let us assume that the term K in (4.31) will give rise to equal displacements of the centre of gravity of the energy levels of E_s and E_b (this is implied by (4.23)). If we displace the scale of energies accordingly, only the three terms dependent on Q_3 are left in (4.31). Now, Öpik and Pryce found that the sign of A_3 is negative. For α , we have

$$\alpha = \frac{\partial E_s}{\partial Q_3} + \left(\frac{\partial^2 E_s}{\partial Q_1 \partial Q_3} \right) Q_1$$

The explicit form, as determined with the help of (4.20) and (4.21), turns out to be unwieldy, particularly the second term. A rough estimate on the basis of the electrostatic model shows that the second term is much smaller than the first. In the following, therefore, we shall neglect the effect of the second term even for the present model. Then,

$$\alpha \approx \frac{\partial E_a}{\partial Q_3} = \frac{p^2 \partial \Lambda^a}{\partial Q_3} + \frac{q^2 \partial B^a}{\partial Q_3} - 2pq \frac{\partial C^a}{\partial Q_3} + 2pq E_0^a \frac{\partial S^a}{\partial Q_3} \dots (4.38)$$

Within this approximation, for a moderate degree of covalency (i.e. p is not very much different from unit) it is likely that the first term in (4.38) dominates. Thus we assume that α is positive. This however is not strictly true and the final answer would depend on the calculation of all the terms involved. γ_a and γ_b are quite complicated and may, for the present, be treated as parameters of the theory. It seems, however, that for the stability of the system both γ_a and γ_b should be positive.

The following qualitative conclusions may be derived from (4.31) and (4.35) depending on the various values of the parameters chosen.

Fixing, $\alpha > 0$, $\Lambda_3 < 0$ and $\gamma_b^2 > 3\alpha |\Lambda_3|$ (always), we have:

i) for $\gamma_a > 0$, $\gamma_b > 0$,

$$Q_3^a (\min) = \frac{-\gamma_a + \sqrt{\gamma_a^2 + 3\alpha |\Lambda_3|}}{-3 |\Lambda_3|} < 0,$$

and

$$Q_3^b (\min) = \frac{-\gamma_b + \sqrt{\gamma_b^2 - 3\alpha |\Lambda_3|}}{-3 |\Lambda_3|} > 0.$$

Furthermore, if $\gamma_a \gg \gamma_b$, then $|Q_3^b(\min)| > |Q_3^a(\min)|$ and $E_b^{\min}$ is likely to lie deeper than $E_a^{\min}$ at the minimum position. This would favour an elongation of the octahedron along the z - axis. The above seems to be true provided $3\alpha/\Lambda_3$ is not very much smaller than γ_b^2 . Even for

$$\gamma_a < \gamma_b \text{ but } |3\alpha\Lambda_3| < \gamma_b^2 \leq 2|3\alpha\Lambda_3|,$$

$|Q_3^b(\min)| > |Q_3^a(\min)|$. $E_b^{\min}$ may still be less than $E_a^{\min}$. On the other hand, for $\gamma_a < \gamma_b$ and

$$\gamma_b^2 > 2|3\alpha\Lambda_3|,$$

$|Q_3^b(\min)| < |Q_3^a(\min)|$. It is difficult to say as to which of $E_a^{\min}$ and $E_b^{\min}$ will lie deeper; however, probably $E_a^{\min} < E_b^{\min}$ and contraction of the octahedron along the c - axis is likely to occur,

ii) for $\gamma_a < 0$, $\gamma_b > 0$,

$$Q_3^a(\min) < 0,$$

and

$$Q_3^b(\min) > 0.$$

iii) for $\gamma_a > 0$, $\gamma_b < 0$,

$$Q_3^a(\min) < 0,$$

and

$$Q_3^b(\min) < 0.$$

iv) for $\gamma_a < 0$, $\gamma_b < 0$

$$Q_3^a(\min) < 0,$$

and

$$Q_3^b(\min) < 0.$$

The cases ii) to iv) are not discussed further in as much as they do not seem physically feasible. Finally, it should be noted that if $\alpha < 0$, the other conditions remaining as enumerated above, then conclusions inverse to those contained in i) to iv) follow

The above are some very broad conclusions. The nature of distortion in each case could be ascertained only after determining as to which of the E_a and E_b lies deeper at the respective minimum values. In the absence of quantitative calculations of the parameters involved this is not attempted here. It may, however, be remarked that the case (i) seems to be physically likely and the elongation will be generally possible. Nevertheless, a contraction of the c -axis (or more precisely $Q_3(\min) < 0$ and $E_a^m < E_b^m$) cannot be ruled out.

4.5 Concluding Remarks.

In the foregoing sections we have given a formal analysis of the tetragonal distortion in octahedral complexes involving magnetic ions having d^4 or d^9 type outer electronic configurations. The conclusions broadly suggest that both situations are theoretically possible i.e. either elongation or contraction along one of the axes.

The advantage of the present model is the inclusion of the additional terms owing to covalency effects. These may influence the sign of the parameters involved in a different way compared to those obtained before. The covalency analysis is, however, restricted to the case where $\theta = 0$ or π i.e. the non zero values of Q_2 (pertaining to other equivalent minima) are not covered as done by others in the electrostatic model.^{100,101}

Quantitative calculations have been postponed for future work. This will involve the calculation of the matrix elements such as A,B,C, explicitly in terms of integrals involving atomic orbitals. It would then be possible to correlate the parameters calculated with observed results.

We now discuss a few compounds where the above treatment will be applicable and which may have varying degree of covalency. We have already mentioned the cases of spinels such as $Mn(Mn_2)O_4$, $Zn(Mn_2)O_4$, $Cd(Mn_2)O_4$, $Fe(CuFe)O_4$ where the ions within the bracket occupy octahedral positions.⁹³ The distortion is related to the presence of Mn (III) or Cu(II) ions. We expect an appreciable degree of covalency. The $c/a > 1$. Next, let us examine the series of compounds CuF_2 , $CuCl_2$, $CuBr_2$ where c/a ratios (for the distorted octahedron) are 1.17, 1.30 and 1.32 respectively.¹⁰⁴ The covalency in such systems is expected to increase as we go from F to Br because of the corresponding decrease in the electronegativity difference

between Cu(II) and the halide ion in question. The electronegativity of F, Cl, and Br are 4, 3 and 2.8 respectively. It would thus seem that the increase in covalency favours elongation of the c-axis. One would therefore expect that in systems where the covalency effect is very small, a distortion, where the tetragonal axis contracts, takes place. An example of this is probably furnished by K_2CuF_4 where $Q_3 < 0$ (four F^- ions are ^{at} 2.08 Å from Cu^{2+} and two at 1.95 Å, with $c/a = 0.94$).¹⁰⁵ Perhaps the presence of K^+ ions renders the system more ionic in character.

It appears that in systems having a fair degree of covalency the condition i) of section 4.4 with E_b lying deeper than E_a obtains favouring $Q_3 > 0$. In ionic crystals the situation seems to be the reverse.

The distortion of the octahedra in MnF_3 and CrF_2 is such that there are three different bond lengths.^{106,107} The theoretical approach for such systems is essentially the same as given above except that we must take into account the effect of both Q_3 and Q_2 (D_{2h} symmetry case).

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MEMORANDUM

The author initiated the work on "Spin Polarization Mechanism of Indirect Exchange" in magnetic compounds and was later on assisted by Drs. S. Koide and Y. Tanabe. Chapter 2 covers only those parts of the investigations which contain, by and large, the contributions of the author.

Chapter 3, dealing with the indirect exchange interaction in tetrahedral systems, describes the author's version and some extensions over the joint work with Dr. Koide.

The Chapter 4 deals with the work "On the tetragonal distortion of Octahedral Systems in E_g Electronic State". Following the approach suggested by Professor M.H.L.Pryce, the work was carried out by the author. He had frequent discussions with Dr. Y. Tanabe in the course of calculations.

The opinions, other than the quoted results, expressed in the general introduction (Chapter 1) are entirely of the author.


(K.P.Sinha).