THE ROLE OF EMPTY ORBITALS IN SUPEREXCHANGE INTERACTION

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ABSTRACT. In the wake of our spin polarization mechanism developed for the indirect exchange interaction in some magnetic systems, certain additional superexchange effects involving empty orbitals are explored. Analysis of the usual 'three-centre and four-electron' system reveals that the delocliazation of two electrons, one each from the two magnetic ions, to the lowest available empty orbital for the unit, always stabilizes the singlet state. This type of perturbation thus leads to antiferromagnetic superexchange effect.

An estimate of the relevant interaction term shows that the effect is quite appreciable and strengthens the former mechanism, which also operates through the agency of such empty orbitals. The importance of these two mechanisms, in relation to those emanating from singly occupied orbitals for fundamentally antiferro-magnetic compounds is stressed.

INTRODUCTION

An indirect exchange interaction mechanism involving empty localized crystal orbitals was recently proposed by us (Koide, Sinha and Tanabe, 1959; hereafter referred to as I) which contributes significantly towards the spin coupling in magnetic compounds where the paramagnetic ions are otherwise separated by the intervening diamagnetic ions. According to this mechanism, the spin coupling between the paramagnetic ions is achieved via those perturbations which entail a spin dependent transition of one of the intervening ion electrons to the lowest available empty orbitals for the appropriate unit in the crystal. This treatment developed originally for magnetic compounds having rock salt or perovskite type structure (I), has been extended to those having zinc blende (Sinha and Koide, 1960) and spinel (Sinha, 1961) type structures.

In the present paper, certain additional superexchange effects invoking the interplay of the empty orbitals are envisaged. In this scheme the main interaction term arises due to two electron transitions to the lowest excited orbital, one each from the two paramagnetic ions. It may, however, be remarked that we do not here consider the superexchange effects which involve transitions to singly occupied orbitals. Such mechanisms have been discussed by others (Anderson, 1950, 1959; Keffer and Oguchi, 1959; Nesbet, 1958 and 1960), The moti-

vation behind our present series of papers is to assess the various types of exchange interactions arising through the role of empty excited orbitals hitherto not considered for the magnetic systems of interest.

FORMULATION OF THE INTERACTION MECHANISM

As in 1, we consider a system of two magnetic ions with an intervening nonmagnetic ion situated collinearly. This is the usual three centre problem represented by $M^{2+}-X^{2-}-M^{2+}$. Since the superexchange effect arising out of the spatial and spin correlation between the electrons of the intervening ion has been studied in detail in the previous paper (I), we shall consider two electrons of the central ion in the singlet state and occupying the same orbital ϕ_0 (i.e $\psi p \tau$), in the present analysis. The d orbital wave functions of the two electrons one from each magnetic ions are denoted by u_1 and u_2 respectively. These will be used to describe the zeroth order ground states of the four electron system in the appropriate ion-core frame work ($d^{n+1}-X-M^{3+}$). In the present formalism, only the excited states involving transitions of the cation electrons to empty excited orbitals are considered. For the symmetrical unit under consideration, the appropriate lowest orbital has even symmetry and is accordingly represented by ϕ_g (1). Including the spin functions with the above spatial orbitals, we can construct the following states which are the eigenfunctions of the S^2 operator for the four electron system :

Ground states :

Triplet :

$$| ^3\psi_0 > = {}^3\{^3(u_1 u_2)^1(\phi^2_0)\} = |u_1\phi_0\bar\phi_0 u_2| \qquad \dots (1)$$

Singlet :

$$| ^1\psi_0 > = {}^1\{^1(u_1 u_2)^1(\phi_0{}^2)\} = \{|u_1\phi_0\bar\phi_0\bar u_2| - |\bar u_1\phi_0\bar\phi_0 u_2|\}/\sqrt{2} \qquad \dots (2)$$

Excited states : (Involving single electron transition to ϕ_g)

Triplets :

$$| ^3\psi_1 > = {}^3\{^3(u_1\phi_g)^1(\phi_0{}^2)\} = |u_1\phi_0\bar\phi_0\phi_g| \qquad \dots (3)$$

$$| ^3\psi_2 > = {}^3\{^3(\phi_g u_2)^1(\phi_0{}^2)\} = |\phi_g\phi_0\bar\phi_0{}_2 u_2|| \qquad \dots (4)$$

Singlets :

$$| ^1\psi_1 > = {}^1\{^1(u_1\phi_g)^1(\phi_0{}^2)\} = \{|u_1\phi_0\bar\phi_0\bar\phi_g| - |\bar u_1\phi_0\bar\phi_0\phi_g|\}/\sqrt{2} \qquad \dots (5)$$

$$| ^1\psi_2 > = {}^1\{^1(\phi_g u_2)^1(\phi_0{}^2)\} = \{|\phi_g\phi_0\bar\phi_0\bar u_2| - |\bar\phi_g\phi_0\bar\phi_0 u_2|\}/\sqrt{2} \qquad \dots (6)$$

Excited state involving two electron transitions to ϕ_g:

Singlet :

$$| ^1\psi_3 > = {}^1\{^1(\phi_g{}^2)^1(\phi_0{}^2)\} = |\phi_g\phi_0\bar\phi_0\bar\phi_g| \qquad \dots (7)$$

(As before, the square bracket notation denotes the Slater determinants multiplied by the appropriate normalizing factor; we indicate the down spin function by putting a bar over the orbital and up spin function without a bar)

The Hamiltonian (in atomic units) is taken as (I)

$$H = \sum_i H_i + \sum_{i<j} \frac{1}{r_{ij}} \qquad \ldots \quad (8)$$

where H_i is the one electron operator which contains, in addition to the kinetic energy operator, the potential acting on the ith electron due to the three nuclei and other electrons except the four under consideration. There is no point in writing the explicit froms of all the matrix elements of the Hamiltonian within the manifold described above. We consider those which are elevant to the present discussion. The orbitals ϕ_g and ϕ_0 are orthogonal from symmetry consideration; however, to simplify the calculations the non-orthogonality of others will be neglected. The effect of this for u_1, u_2 and ϕ_g can be included, if the choice of ϕ_g warrants it.

In the absence of the feeble direct exchange interaction between the magnetic ions, the diagonal matrix elements of the triplet and singlet ground states are degenerate,

$$<^3\psi_0\,|\,H\,|\,^3\psi_0> \ = \ <^1\psi_0\,|\,H\,|\,^1\psi_0> \ = \ E_0 \qquad (9)$$

The excited state of interest to us in the present scheme is

$$<^1\psi_3\,|\,H\,|\,^1\psi_3> \ = E_m \qquad (10)$$

Actually, we shall need the explicit form of the difference of Eqs. (10) and (9)) i.e.,

$$\Delta E = E_m - E_0$$

$$\approx \{[2\epsilon(\phi_g) - \epsilon(u_1) - \epsilon(u_2)] + [4K(\phi_g\phi_0) - 2K(u_1\phi_0) - 2K(u_2\phi_0)]$$

$$+ [J(u_1\phi_0) + J(u_2\phi_0) - 2J(\phi_g\phi_0)] + [K(\phi_g\phi_g) - K(u_1u_2)]\} \qquad (11)$$

where $\epsilon(a)$, $K(ab)$ and $J(ab)$ denote the one electron, coulomb and exchange integrals respectively. A study of the diagonal terms $<^3\psi_1\,|\,H\,|\,^3\psi_1>$, $<^1\psi_1\,|\,H\,|\,^1\psi_1>$ etc. and the off diagonal terms $<^3\psi_0\,|\,H\,|\,^3\psi_1>$ and $<^1\psi_0\,|\,H\,|\,^1\psi_1>$ reveals that interactions involving single cation electron transition for both singlet and triplet states have common dominant terms. Such terms would not, therefore, lead to any appreciable singlet triplet splitting up to second order of perturbation theory. Hence, we do not give any detailed considerations for interaction involving single electron transition.

The important of diagonal element is thus :

$$<{}^1\psi_0 \,|\, H \,|\, {}^1\psi_3> \;=\; \sqrt{2} <u_1\phi_g \,|\, g_{12} \,|\, u_2\phi_g> \qquad \dots (12)$$

where $\quad <ab \,|\, g_{12} \,|\, cd> \;=\; \int a^*(\mathbf{r}_1)b(\mathbf{r}_1)1/r_{12}\, c^*(\mathbf{r}_2)d(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2.$

This would give rise to a lowering of the singlet ground state only, the depression according to second order perturbation being given by :

$$\delta E \;=\; |\, <{}^1\psi_0 \,|\, H \,|\, {}^1\psi_3> \,|^2 / (E_m'-E_0)$$
$$=\; 2 |\, <u_1\phi_g \,|\, g_{12} \,|\, u_2\phi_g> \,|^2 / (E_m-E_0) \qquad \dots (13)$$

For further clarification of the results obtained, we shall consider the derivation of the exchange interaction term by the Dirac spin operator method as modified by Serber (1934). The ground state orbitals for the four electron systems are $(u_1 u_2)$ and $(\phi_0{}^2)$; for the excited states we have $(\phi_g{}^2)$ and $(\phi_0{}^2)$. In both the ground and excited states the two electrons occupying ϕ_0 are in singlet states with S value zero. Let the spin operators associated with the two electrons of the magnetic ions be $\overrightarrow{S_1}$ and $\overrightarrow{S_2}$ respectively. Then for the ground state the vectors sum is denoted by $\overrightarrow{S_1}+\overrightarrow{S_2} = \overrightarrow{S}$. In the excited configuration these two occupy the same orbital ϕ_g and hence they must be in the singlet state. Accordingly, the effect of the second order perturbation on the zeroth order ground state can be expressed by an effective Hamiltonian defined by :

$$<S \,|\, H_{eff} \,|\, S'> \;=\; \Sigma <S \,|\, H_m \,|\, 0> <0 \,|\, H_m \,|\, S'>/\Delta E \qquad \dots (14)$$

where ΔE is the energy difference between the ground triplet or singlet states and the excited states which corresponds to $\overrightarrow{S_1}+\overrightarrow{S_2} = 0$. H_m is the spin dependent Hamiltonian which is of the following form in the present case

$$H_m \;=\; \text{constant term} \;-\sqrt{2}\; {}^gJ_{12}P_{12} \qquad \dots (15)$$

with ${}^gJ_{12}$ standing for $<u_1\phi_g \,|\, g_{12} \,|\, u_2\phi_g>$ and P_{12} is the Dirac identity $P_{12} = (1/2)(1+4\overrightarrow{S_1}\cdot\overrightarrow{S_2})$. The factor $\sqrt{2}$ in Eq. (15) is used as the necessary correction in going from non equivalent $(u_1 u_2)$ to equivalent $(\phi_g\phi_g)$ orbitals. In fact, it has been shown by Anderson (1950) that the transition matrix element must be multiplied by $\sqrt{2}$ for each pair of identical orbitals in either configuration which do not also appear in the other configuration. We introduce a projection operator which annihilates all states with parallel spin for 1 and 2 i.e. $O_p = (1/4)(1-4\overrightarrow{S_1}\cdot\overrightarrow{S_2}) = O_p{}^2$.

Thus we can write :

$$<S \,|\, H_m \,|\, 0> \;=\; <S \,|\, H_m O_p \,|\, S''>$$

It follows then,

$$H_{eff} = (H_m O_p H_m)/\Delta E = (2^g J^2{}_{12})[P_{12}O_p P_{12}]/\Delta E \qquad \ldots (16)$$

Using the properties of spin operators, it is a trival matter to prove that $P_{12}O_p P_{12}$ $= O_p - (1/4)(1 - 4\vec{S_1} \cdot \vec{S_2})$. Eq. (16), therefore, reduces to

$$H_{eff} = (2^g J_{12}{}^2)[(1/4)(1 - 4\vec{S_1} \cdot \vec{S_2})]/\Delta E \qquad \ldots (17)$$

It can be easily seen that the effect of this operator for the triplet state (where $\vec{S_1} \cdot \vec{S_2} = 1/4$) is identically zero. However, it reduces the energy of the singlet state $(\vec{S_1} \cdot \vec{S_2} = -3/4)$ by

$$\delta E = (2^g J_{12}{}^2)/\Delta E \qquad \ldots (18)$$

which is the same expression as Eq (13). Thus the superexchange effect due to the present scheme always favours the antiferro-magnetic coupling of the spin of magnetic ions.

DISCUSSION AND ESTIMATES

In this section, the relationship of the scheme envisaged here with the previous mechanism (I) will be discussed. We shall also consider certain semi-quantitative features based on an identification of the orbital ϕ_g.

For a straightforward comparison, it is better to write the previous result for the orbitals considered in this paper i.e. u_1, u_2, ϕ_0, ϕ_g. (In I, we had treated the two anion electrons by the method of semi-localized orbitals). Thus for the symmetrical case $u_1 \longleftrightarrow u_2$, the second order perturbation term, which involves a spin dependent transition of one of the anion electrons to ϕ_g, gives the effective interaction terms as

$$H^a{}_{eff} = (2^{u_1} J^2{}_{g_0})(\tfrac{1}{2} - 2\vec{S_1} \cdot \vec{S_2})/\Delta E' \qquad (19)$$

where $^{u_1}J_{g_0} = \langle u_1\phi_g | g_{12} | u_1\phi_0 \rangle$ and $\Delta E'$ is the energy denominator involved in this case (I). According to this, the stabilization of the singlet state is thrice as much as that of the triplet. The total lowering of the singlet state relative to the triplet state owing to both the effects is then given by

$$\frac{2 | \langle u_1\phi_g | g_{12} | u_2\phi_g \rangle |^2}{\Delta E} + \frac{4 | \langle u_1\phi_g | g_{12} | u_1\phi_0 \rangle |^2}{\Delta E'} \qquad \ldots (20)$$

A reasonable estimate of Eq. (18) i.e., the first term of Eq. (20), would of course, depend on the choice of ϕ_g which is in conformity with the physical situation existing in magnetic crystals. In I, we have given a quantitative estimate for MnO; it is easier for comparison if we choose the same system for the present purpose.

However, the choice of a $3d_{\gamma_{a}}$ on the oxide ion centre would not be appropriate for ϕ_g in that it would involve an excessive accumulation of charge at the intervening ion. Furthermore, its nonorthogonality with u_1 and u_2 may not be negligible. The greatest difficulty lies in having an unambiguous knowledge about the energy of this orbital. While the role of this type of empty orbital may be of significance in the spin-polarization mechanism involving anion electrons (I), it seems more appropriate for the present purpose to consider orbitals constituted out of a linear combination of available cation orbitals. As in I, we take the σ-type hybridised orbitals from each cation namely χ_1 and χ_2. In the present mechanism, the importance of the ground state anion odd orbital ϕ_0 enters in virtue of its mixing with the odd combination $\chi_1 - \chi_2$ and pushing its energy further up. Here again, the appropriate lowest orbital available to us is the even orbital.

$$\phi_g{}^e = (\chi_1 + \chi_2)/\sqrt{2} \tag{21}$$

Fourtunately, the estimate in the previous paper is also based on the above orbital. In the following, we make a rough estimate with the same choice of ϕ_g. Neglecting the overlap of functions, when their suffixes are diferent, and using real function, we have

$$u_1(1)\phi_g(1)\,|\,g_{12}\,|\,u_2(2)\phi_g(2) \approx \tfrac{1}{2} \, u_1(1)\chi_1(1)\,|\,g_{12}\,|\,u_2(2)\chi_2(2) \tag{22}$$

Following the method described in the Appendix of I, we replace the factors $u_1\chi_1$ and $u_2\chi_2$ by two uniformly charged spheres of radius 1 a.u. each with density $(\rho_u\rho_\chi)^{\frac{1}{2}}$ situated at the appropriate distances deduced from the observed inter atomic distance. This method of calculation yields $u_1\phi_g\,|\,g_{12}\,|\,u_2\phi_g \approx$ 0.006 a.u. Although this approximation is likely to underestimate the integral, it furnishes a rough guidance. We shall, however place reliance in the value 0.01 a.u. i.e. around 0.25 eV with confidence. This is of the same order of magnitude as the integral $<u_1\phi_g{}^e\,|\,g_{12}\,|\,u_1\phi_0>$ occurring in the numerator of the second term of Eq. (20).

The relevent energy denominator ΔE, expressed in terms of $\phi_g{}^e = (\chi_1 + \chi_2)/\sqrt{2}$ to orders of coulomb integral, is

$$\Delta E \approx \{[\epsilon(\chi_1) - \epsilon(u_1)] + [\epsilon(\chi_2) - \epsilon(u_2) + [\tfrac{1}{2}K(\chi_1\chi_1) + \tfrac{1}{2}K(\chi_1\chi_2) - K|u_1u_2)]$$
$$+ 2[K(\chi_1\phi_0) - K(u_1\phi_0)] + 2[K(\chi_2\phi_0) - K(u_2\phi_0)]\} \tag{23}$$

Making use of the integrals evaluated in the previous papers (I; and Sinha and Koide, 1960), the following order of magnitude assessment is possible.

$$[\tfrac{1}{2}K(\chi_1\chi_1) + \tfrac{1}{2}K(\chi_1\chi_2) - K(u_1u_2)] \approx 0.2 \text{ a.u.}$$
$$[K(\chi_1\phi_0) - K(u_1\phi_0)] \approx 0.1 \text{ a.u. etc.}$$

The main difficulty remains about the assessment of one electron terms such as $[\epsilon(\chi_1) - \epsilon(u_1)]$. If, however, it is taken that the $3d$ shell for the magnetic atoms in

crystals is extended upto $4s$ and $4p$ orbitals when hybrid orbitals are formed (Goodenough 1955), then the difference between $\epsilon(\chi_1)$ and $\epsilon(u_1)$ etc. will be extremely small. On the basis of this, one would arrive at a lower limit of ΔE at about 0.5 to 0.6 a.u. (i.e. around 15 eV). In case it is underestimated, we shall take an upper limit, by including the energy difference between the configurations $d^4S(^6D)$ and $d^5(^6S)$. From the calculations of Tanabe and Sugano (1954), for $3d$ electrons in complexes, this is ascertained to be about 12 eV. i.e. around 0.5 a.u. We shall therefore choose a range for ΔE from 0.5 a.u. to 2 a.u.

The denominator $\Delta E'$ for the spin-polarisation effect i.e. second term of Eq. (20) was estimated to be of the order of 1 a.u. (See I). It is thus concluded that the term due to the present mechanism i.e. $2\,|<u_1\phi_g g_{12}\,|\,u_2\phi_g>\,|^2/\Delta E$ is at best (with $\Delta E \approx 0.5$ a.u.) of the same order of magnitude and at worst (with $\Delta E \approx 2.0$ a.u.) 25% of the term due to the previous mechanism $4 < u_1\phi_g\,|\,g_{12}\,|\,u_1\phi_0>\,|^2/\Delta E'$. In either limit, it leads to an appreciable contribution towards antiferromagnetic superexchange interaction. In fact, both the mechanisms, the previous (I) and the present, favour anti-ferro-magnetic coupling reinforcing each other effectively. The role of the empty orbital such as ϕ_g involves juxtaposition of the interactions effect owing to the delocalization of the two magnetic ion electrons and their spread in this orbital, as well as the correlation effects wherein an anion electron makes a spin dependent transition to ϕ_g. One can describe the physical situation further by stating that the interactions are such that the cation electrons have some probability in the vicinity of the anion and the anion electrons at the cation centres through the empty orbitals.

The importance of superexchange effects involving singly occupied orbitals such as u_1 and u_2 is, of course, also admitted. The contributions due to the correlation effects arising out of the transitions of the two anion electrons to u_1 and u_2 (Nesbet 1958, 1960) and the delocalisation effect involving virtual migration of an electron from one magnetic ion to another (Anderson, 1959), seems to be, at best, of the same order of magnitude as the terms in Eq. (20).

Since all mechnisms are acting in the same direction, the actual transition temperatures observed in such antiferro-magnetic systems are related to the sum of these interactions i.e. arising through singly occupied as well as empty orbitals. An attempt to derive the integrals so as to fit with the transition temperature as done by some authors amounts to overemphasising their mechanism.

We, therefore, conclude with the remark that the role of empty orbitals is of considerable importance in superexchange interaction effects and proper cognisance ought to be taken for these while studying the spin coupling in such magnetic systems.

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