precision intensity scale and very high, known resolving power), we find that the strong emission line involving the valence band electrons probably does not in general give much information about the normal unperturbed valence band itself. This conclusion, contrary to the most fundamental postulate in x-ray spectroscopy of the solid state, is more or less tentative. If this conclusion is wrong, we seem obliged to believe that the valence band in KCl is only 0.33 ev wide at the half-maximum of the density-of-states curve. Resolution of the question awaits a more precise theoretical treatment than has yet been made.

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Antiferromagnetism*

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The nature of the spin coupling in MnO is discussed, the details of the discussion being based on a very simplified three-center system. The coupling between magnetic ions whose charge densities interact with an intervening nonmagnetic ion but not directly with each other is described as the result of the polarization of the nonmagnetic ion. The configuration interaction representation of this polarization is treated by non-orthogonal orbitals, orthogonal orbitals, and by a method due to Kramers. These three approaches are applied to a numerical example. It is concluded that a reliable description of the simple three-center problem is more complicated than generally believed due to the importance of highly excited states of the system which have been neglected in previous treatments of the problem.

INTRODUCTION

THE problem of the spin coupling of paramagnetic atoms or ions whose outer charge densities overlap an intervening nonmagnetic atom or ion, but do not directly overlap each other, is of considerable interest in understanding antiferromagnetism. Such a situation is met in MnO, an antiferromagnetic oxide of simple cubic structure. The magnetic ordering has been determined by neutron diffraction.[1] The (111) planes consist alternately of Mn^{++} ions and $O^{=}$ ions. The spins of the Mn^{++} ions on a given plane are coupled ferromagnetically but the coupling between neighboring planes of Mn^{++} ions is antiferromagnetic as shown in Fig. 1. The distance between Mn^{++} ions on adjacent planes appears to be so large that no important direct overlap, hence interaction, exists. The antiferromagnetic spin coupling between planes seems to arise in part through an interaction involving the $O^{=}$ ions. A detailed analysis of the actual situation in the crystal would be very difficult. It seems reasonable, however, that an examination of an $Mn^{++}-O^{=}-Mn^{++}$ unit lying on a straight line connecting three planes, as shown by the dotted lines in Fig. 1, may explain the role of the oxygen ions in the spin coupling of the Mn^{++} ions. The energies of various spin orientations of the system must be found and compared. As the energy differences involved will be small, a meaningful result can be obtained only by a fairly complete configuration interaction investigation. Even the $Mn^{++}-O^{=}-Mn^{++}$ problem is a very hard model to treat, and to further simplify the situation we will consider a three-center system containing four electrons. Here we have two magnetic ions A and A' separated by a nonmagnetic atom B as illustrated in Fig. 2. This situation was first investigated by Kramers[2] and more recently by Anderson.[3] It is the purpose of this paper to re-examine the problem in detail and to point out some of the requirements for an adequate description of the spin coupling.

THREE-CENTER SYSTEM

The ground configuration of our three-center system will be taken to be that in which there is one electron in a localized orbital u_A or $u_{A'}$ about the magnetic ions A and A', respectively, and two electrons with opposite spin occupying a single orbital u_B localized about the nonmagnetic center B. We speak of A and A' as being magnetic centers since they have a net spin associated with them in their lowest state. B is called a nonmagnetic center as it has a closed shell structure for its ground state. Clearly the energy of the ground configuration of the system will be independent of the spin orientation of the electrons about A and A' if the localized orbitals about these centers do not directly overlap since an undistorted closed shell ion does not care how the spins of its neighbors are situated. In order to get an energy separation for the states of different spin we must break up the structure of the intervening nonmagnetic ion. We wish, therefore, to find the answers to the following questions: First, when we have included the necessary configurations to describe this

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[1] Shull, Strauser, and Wollan, Phys. Rev. **83**, 333 (1951).

[2] H. A. Kramers, Physica **1**, 182 (1934).

[3] P. W. Anderson, Phys. Rev. **79**, 350 (1950).

system, will the spins of the electrons about A and A' tend to set themselves parallel or antiparallel? Secondly, what are the excited configurations which must be considered to answer the first question?

The presence of the Mn^{++} ions in MnO will distort the charge distribution of the $\mathrm{O}^{=}$ ions. A consequence of this polarization will be a spin coupling of the Mn^{++} ions surrounding the oxygen. Hence we could approach this problem by trying to find the best method of expressing the distortion of the $\mathrm{O}^{=}$ ion and then the spin coupling would fall out automatically. In order to translate these ideas to the three-center problem, we must consider excited states in which electrons about the nonmagnetic center B are either excited into higher-lying orbitals about that center or are transferred from the B center to the adjacent magnetic centers. Following Anderson's[3] treatment of the three-center problem, we will restrict ourselves to excited states where electrons have been transferred to the magnetic centers; these can be called the superexchange configurations. The problem will be discussed in terms of nonorthogonal orbitals, orthogonal orbitals, and by a method due to Kramers for the purpose of bringing out some of the limitations of each approach.

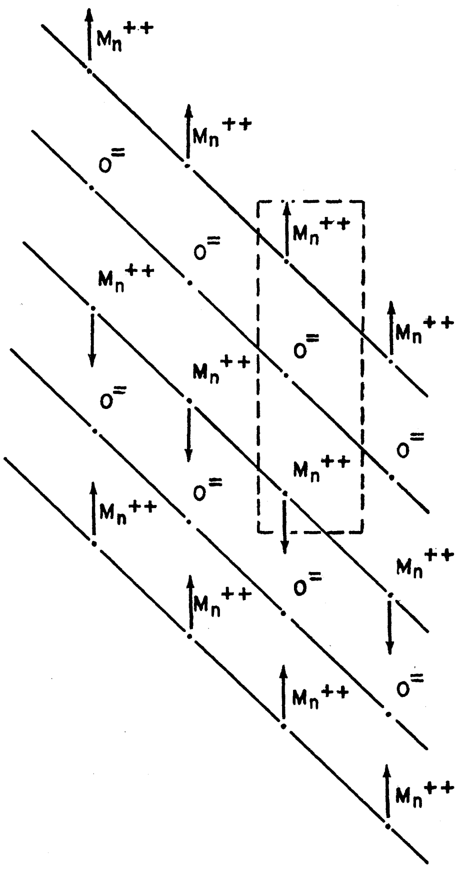

FIG. 1. Coupling of spins for MnO structure.

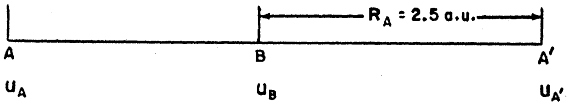

FIG. 2. Arrangement for the three-center system containing four electrons. A and A' are magnetic ions separated by a nonmagnetic atom B.

NONORTHOGONAL ORBITALS

The configuration interaction which describes the coupling of the magnetic ions in the three-center problem is quite straightforward when carried out in terms of nonorthogonal orbitals. The excited configurations in which an electron has been removed from the nonmagnetic center B and placed on A or A' leaves an unpaired spin in u_B and on one of the A centers leading to a spin coupling due to the direct overlap of these charge densities. The localized, nonorthogonal orbitals will be denoted by u_A, u_B, $u_{A'}$ and are assumed to have the following overlap matrix:

$$\begin{array}{c|ccc} & u_A & u_B & u_{A'} \\ \hline u_A & 1 & d & 0 \\ u_B & d & 1 & d \\ u_{A'} & 0 & d & 1 \end{array} \tag{1}$$

where d is the overlap integral between u_B and u_A or $u_{A'}$. The various electron assignments for the three configurations are shown in Table I. When singlet and triplet states are set up for each configuration, reflection symmetry being taken account of, we get a 2×2 secular equation for each multiplicity. The interaction of these states results in an energy separation between the lowest singlet and triplet. The method of nonorthogonal orbitals is examined more closely in the following numerical example.

ORTHOGONAL ORBITALS

The orthogonal orbitals will be taken to be

$$\begin{aligned} v_A &= u_A, \\ v_{A'} &= u_{A'}, \\ v_B &= \{u_B - d(u_A + u_{A'})\}/(1-2d^2)^{\frac{1}{2}}. \end{aligned} \tag{2}$$

In terms of orthogonal orbitals our ground configuration is that in which an electron occupies v_A, one in $v_{A'}$, and two in v_B. The excited configurations are those in which an electron is transferred from v_B to v_A or $v_{A'}$. These configurations are indicated in Table II as well as an additional excited state where both electrons are removed from the B center and put on the A centers. We now encounter a very interesting and an important feature of the orthogonal orbital approach. *It can be shown, regardless of the nature of the orthogonal orbitals, that there is only one possible result that can be obtained if we do not include the last configuration of Table II. This*

TABLE I. Electron assignments for three configurations of nonorthogonal orbitals.

u_A	u_B	$u_{A'}$
1	2	1
2	1	1
1	1	2

is that the lowest singlet cannot possibly lie below the lowest triplet. To show this, we set up the Hamiltonian matrix for the triplet states plus a difference matrix D:

$$H_{S=0}=H_{S=1}+D. \tag{3}$$

The singlet states are

$$\psi_0=\frac{A}{\sqrt{2}(4!)^{\frac{1}{2}}}\{v_A(\alpha)v_B(\alpha)v_B(\beta)v_{A'}(\beta) \\ -v_A(\beta)v_B(\alpha)v_B(\beta)v_{A'}(\alpha)\}, \tag{4}$$

and

$$\psi_1=\frac{A}{2(4!)^{\frac{1}{2}}}\{v_A(\alpha)v_A(\beta)v_B(\alpha)v_{A'}(\beta) \\ -v_A(\alpha)v_A(\beta)v_B(\beta)v_{A'}(\alpha) \\ +v_A(\alpha)v_B(\beta)v_{A'}(\alpha)v_{A'}(\beta) \\ -v_A(\beta)v_B(\alpha)v_{A'}(\alpha)v_{A'}(\beta)\}, \tag{5}$$

where A is the antisymmetrizing operator and the singlets are even under reflection in a plane perpendicular to the internuclear axis through the nonmagnetic center B. For the sake of simplicity, it will be assumed that under this symmetry operation v_A goes into $v_{A'}$ in the entire discussion of the three-center problem. The triplet states made up of the first three configurations of Table II are

$$\chi_0=\frac{A}{(4!)^{\frac{1}{2}}}\{v_A(\alpha)v_B(\alpha)v_B(\beta)v_{A'}(\alpha)\}, \tag{6}$$

$$\chi_1=\frac{A}{(4!)^{\frac{1}{2}}\sqrt{2}}\{v_A(\alpha)v_A(\beta)v_B(\alpha)v_{A'}(\alpha) \\ +v_A(\alpha)v_B(\alpha)v_{A'}(\alpha)v_{A'}(\beta)\}, \tag{7}$$

and these states are odd under reflection. By straightforward methods it can be shown that the form of the difference matrix D is

$$D=\begin{vmatrix} 0 & 0 \\ 0 & D_{22} \end{vmatrix}, \tag{8}$$

where D_{22} is

$$D_{22}=2\{v_A(1)v_B(2)|H_{12}|v_B(1)v_{A'}(2)\} \\ +2\{v_A(1)v_B(2)|H_{12}|v_B(1)v_A(2)\}. \tag{9}$$

TABLE II. Electron assignments for three configurations of orthogonal orbitals.

v_A	v_B	$v_{A'}$
1	2	1
2	1	1
1	1	2
2	0	2

It is easily established that D_{22} is positive definite using familiar inequalities and the fact that exchange integrals are positive definite. If Φ_0 is the eigenvector corresponding to the lowest-lying energy E_0 of $H_{S=0}$, then from (3):

$$(\Phi_0|H_{S=0}|\Phi_0)=(\Phi_0|H_{S=1}|\Phi_0)+(\Phi_0|D|\Phi_0), \tag{10}$$

or

$$E_0=\mathcal{E}_{01}+D_{00}.$$

But $\mathcal{E}_{01}$ is surely $\geq E_1$, the lowest-lying triplet energy; hence,

$$E_0\geq E_1+D_{00}. \tag{11}$$

Knowing that D has no negative eigenvalues, we have $D_{00}\geq 0$; consequently,

$$E_0\geq E_1. \tag{12}$$

Therefore, the lowest singlet cannot lie below the lowest triplet if we do not include in our configuration interaction the last configuration of Table II. By omitting this higher excited state all the physical meaning is lost. The vital character of the highly excited states was first pointed out by Slater,[4] in his analysis of the hydrogen molecule. In this case one finds that if we do not mix in ionic states when using orthogonal orbitals, the singlet state analogous to the Heitler-London ground state does not even show binding. One is forced to the conclusion that when using orthogonal orbitals, we will almost certainly arrive at meaningless results unless adequate configuration interaction is carried out. In the three-center problem it is the highest-lying state which completely determines how the spins prefer to be aligned, parallel or antiparallel.

KRAMERS' METHOD

Kramers[2] developed a unique method of handling configuration interaction problems and first applied it to the interaction between magnetic atoms in a paramagnetic crystal. It has been the basis for several discussions of superexchange interaction and, in particular, for Anderson's treatment of the three-center problem. The idea of this method will be indicated briefly here, the reader being referred to Kramers' excellent paper for further details.

Suppose we have a system consisting of $2n$ A-type centers and n B-type nonmagnetic centers. Let the localized orbital associated with the ith A center be v_{Ai} and that associated with the jth B center be v_{Bj}. We consider here a $4n$-electron problem and assume the orbitals $v_{A,B}$ to be orthonormal. The ground configuration is defined to be that in which each v_{Bk} is doubly occupied and each v_{Aj} singly occupied. With no loss of generality we can limit ourselves to only those states

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[4] J. C. Slater, J. Chem. Phys. 19, 220 (1951).

with total $m_s=0$. The ith state corresponding to the ground configuration is distinguished by the spin assignment made to the one-electron orbitals and is represented by the antisymmetrized product:

$$\varphi_i=A\{v_{A1}\alpha v_{B1}\alpha v_{B1}\beta v_{A2}\beta\cdots\}. \tag{13}$$

There will be $(2n)!/(n!)^2$ states φ_i corresponding to the ground configuration. The excited state η_α corresponds to a configuration in which one or more electrons have been transferred from the nonmagnetic atoms B to the magnetic atoms A and η_α will be represented by an antisymmetrized product of the $v_{A,\,B}$'s with a particular spin assignment. The lowest eigenstate of the system will be of the form:

$$\Psi=\sum_i A_i\varphi_i+\sum_\alpha B_\alpha\eta_\alpha. \tag{14}$$

The coefficients A and B satisfy the set of equations:

$$\sum_i A_i(\varphi_k{}^*H\varphi_i)+\sum_\alpha B_\alpha(\varphi_k{}^*H\eta_\alpha)=A_kE, \tag{15}$$

$$\sum_i A_i(\eta_\delta{}^*H\varphi_i)+\sum_\alpha B_\alpha(\eta_\delta H\eta_\alpha)=B_\delta E. \tag{16}$$

It is possible to eliminate the coefficients B_α from (15) by expressing them in terms of the A_m's in the form

$$B_\alpha=\sum_m C_{\alpha m}A_m. \tag{17}$$

We then get the equation

$$\sum_m A_m[\{(\varphi_k{}^*H\varphi_m)+\sum_\alpha C_{\alpha m}(\varphi_k{}^*H\eta_\alpha)\}-E\delta_{km}]=0. \tag{18}$$

The matrix

$$U_{km}=(\varphi_k{}^*H\varphi_m)+\sum_\alpha C_{\alpha m}(\varphi_k{}^*H\eta_\alpha)$$

is defined as the effective Hamiltonian, allowing us to express our problem as

$$\sum_m\{U_{km}-E\delta_{km}\}A_m=0. \tag{19}$$

Löwdin[5] has given a very clear treatment of this general procedure and shows that

$$U_{km}=H_{km}+\sum_\alpha\frac{H_{k\alpha}H_{\alpha m}}{E-H_{\alpha\alpha}}+\sum_{\alpha\neq\beta}\frac{H_{k\alpha}H_{\alpha\beta}H_{\beta m}}{(E-H_{\alpha\alpha})(E-H_{\beta\beta})}+\cdots. \tag{20}$$

We have now reduced our original configuration interaction problem to a secular equation whose order is only the number of states φ_i rather than this number plus that of all of the excited states. Even though the effective energy operator U contains the unknown energy E in it, very often approximations can be made which will minimize this difficulty. The excited states η_α are treated as a perturbation of the states φ_i, the perturbing Hamiltonian being

$$\sum_\alpha\frac{H_{m\alpha}H_{\alpha k}}{E-H_{\alpha\alpha}}+\sum_{\alpha\neq\beta}\frac{H_{m\alpha}H_{\alpha\beta}H_{\beta k}}{(E-H_{\alpha\alpha})(E-H_{\beta\beta})}+\cdots. \tag{21}$$

One of the essential features of this approach is that the secular equation is kept to a minimum order and in many respects our insight into the problem is enhanced.

The spin coupling between the nonoverlapping magnetic atoms first appears in the third-order term in U_{mn}. This is simply another statement of the fact that it is the higher-order terms which completely determine the nature of the energy dependence on the spin. The importance of the third-order terms has been well known for a long time, but they appear to have been incorrectly treated. If U_{mn} for $m\neq n$ is negative, then Hund's rule will apply and we have a ferromagnetic coupling. If U_{mn} for $m\neq m$ is positive, then the center of gravity of the singlet energies lies lowest and the average energy of the states of a given multiplicity increases with the multiplicity. For a system containing a large number of electrons these average energies will be very closely spaced. We can never get an antiferromagnetic-coupling out of this procedure in the sense that, if the system is divided into two sublattices, all the spins on one sublattice point in one direction and all those on the other sublattice point in the opposite direction. Such a state is not an eigenfunction of S^2 and, unless the Hamiltonian contains an interaction which destroys S^2 as a good quantum number, all we can properly talk about are magnetic or nonmagnetic states. The three-center problem, however, is a special case as it is possible to speak of parallel or antiparallel orientations with a spin-independent Hamiltonian. Our approach to antiferromagnetism is thus one of first finding the stationary states of the system with S^2 regarded as a good quantum number, and then to use these states to treat the spin-dependent interactions by perturbation theory. In the case of antiferromagnetism, presumably the solution to the spin-independent problem will be that in which U_{mn} is positive so that the spins prefer not to line up as in a ferromagnetic. We would expect that the various nonmagnetic states would be very closely spaced in energy so that a rather small spin-dependent interaction could cause a relatively large splitting. Therefore, a knowledge of the role of the nonmagnetic ions and the spin-independent solution is of fundamental importance although polarization effects as treated here cannot produce the actual antiferromagnetic spin-ordering.

Let us apply the Kramers approach to the three-center problem. The two unperturbed ground states are

$$\varphi_1=(4!)^{-\frac{1}{2}}A\{v_A(\alpha)v_B(\alpha)v_B(\beta)v_{A'}(\beta)\}, \tag{22}$$

$$\varphi_2=(4!)^{-\frac{1}{2}}A\{v_A(\beta)v_B(\alpha)v_B(\beta)v_{A'}(\alpha)\}. \tag{23}$$

The excited states are

$$\eta_1=(4!)^{-\frac{1}{2}}A\{v_A(\alpha)v_A(\beta)v_B(\alpha)v_{A'}(\beta)\}, \tag{24}$$

$$\eta_2=(4!)^{-\frac{1}{2}}A\{v_A(\alpha)v_A(\beta)v_B(\beta)v_{A'}(\alpha)\}, \tag{25}$$

$$\eta_3=(4!)^{-\frac{1}{2}}A\{v_A(\alpha)v_B(\beta)v_{A'}(\alpha)v_{A'}(\beta)\}, \tag{26}$$

$$\eta_4=(4!)^{-\frac{1}{2}}A\{v_A(\beta)v_B(\alpha)v_{A'}(\alpha)v_{A'}(\beta)\}, \tag{27}$$

$$\eta_5=(4!)^{-\frac{1}{2}}A\{v_A(\alpha)v_A(\beta)v_{A'}(\alpha)v_{A'}(\beta)\}. \tag{28}$$

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[5] P. O. Löwdin, J. Chem. Phys. 19, 1396 (1951).

The zero of energy is taken as $U_{11}=U_{22}=0$, or $(\varphi_1^*|H|\varphi_1)=(\varphi_2^*|H|\varphi_2)=0$. U_{12} is given as

$$U_{12}=(\varphi_1^*|H_{\text{eff}}|\varphi_2)=-\frac{2d^2(J+g)}{(E-E_1)^2}-\frac{4hdg}{(E-E_1)(E-E_2)}, \quad (29)$$

where

$$d=(v_A|H_1|v_B)+(v_Av_B|H_{12}|v_Av_A)+(v_Bv_B|H_{12}|v_Bv_A)+(v_Av_{A'}|H_{12}|v_Av_{A'}), \quad (30)$$

$$J=(v_Bv_A|H_{12}|v_Av_B), \quad (31)$$

$$g=(v_Bv_A|H_{12}|v_{A'}v_B), \quad (32)$$

$$h=(v_A|H|v_B)+2(v_Av_B|H_{12}|v_Av_{A'})+(v_Bv_A|H_{12}|v_Av_A). \quad (33)$$

Here E_1 and E_2 in (29) are the energies required to transfer one and two electrons, respectively, to a magnetic center from the nonmagnetic ion B.

If U_{12} is less than zero, then the triplet lies below the singlet. The first term of U_{12}, which involves only the excited states n_1 through n_4, is negative definite. This is in accord with the fact that the exclusion of the doubly excited state n_5 precludes the singlet lying below the triplet. The second term of U_{12} must, therefore, be large enough to reverse the sign of the matrix element if a third-order theory is to be adequate to show a nonmagnetic coupling. This condition leads to the inequality:

$$|h|>\left|d\left(\frac{J+g}{2g}\right)\left(\frac{E-E_2}{E-E_1}\right)\right|. \quad (34)$$

Anderson's[3] treatment of the three-center, four-electron problem is an application of Kramers' method. Excitations of two different types are considered, that in which an electron is taken from the nonmagnetic center and put in an occupied orbital on one of the magnetic ions, and that in which the transferred electron goes into an unoccupied orbital about one of the magnetic ions. These two types of excitation were considered separately. In the first case, where the excited electron goes into an occupied orbital, it has been proved above that we must include the excited configuration in which both electrons are removed from the nonmagnetic ion. Since Anderson has not included this doubly excited state, his results for this type of excitation cannot properly describe the nature of the spin coupling.

In the case where the excited electron goes into an unoccupied orbital about a magnetic ion, the proof of the necessity of doubly excited configurations no longer holds. The two ground states are as in (22) and (23). Let the excited electron go into an orbital v_C or $v_{C'}$ about one or the other magnetic ion. A typical excited state would be

$$(4!)^{-\frac{1}{2}}A\,(v_A\alpha v_C\alpha v_B\beta v_{A'}\beta).$$

There will be twelve such excited states all with four electrons in four different orthogonal orbitals and each state with total $M_s=0$. If we were to diagonalize the spin and the symmetry operation, we would find two singlets, three triplets, and one quintet each of which can be either even or odd under reflection. If we apply Kramers' method to this problem and restrict ourselves to a third-order theory, it turns out that there is a good deal of cancellation and only four of the twelve excited states enter. Apparently the third-order theory will not give a very complete description of the effect of these excited states in the configuration interaction unless the series expression for the effective Hamiltonian (20) is very rapidly convergent.

NUMERICAL EXAMPLE

The use of nonorthogonal orbitals, orthogonal orbitals, and Kramers' method has been discussed. It is of interest to illustrate the remarks made concerning these various approaches by a numerical example. In the case of nonorthogonal orbitals it is possible to give a satisfactory description of the spin coupling by using only those configurations listed in Table I. Let us examine the three-center problem by this method. To this end we take the following model. The magnetic ions A and A' will be He$^+$-like ions and the nonmagnetic ion B of Fig. 2 will be a neutral He-like atom. Let the AB distance be 2.5 a.u. (1 a.u.$\equiv\hbar^2/me^2$) and all the orbitals be s-like Gaussians with a half-width factor of unity. The separation of centers has been chosen such that $u_A(x)u_{A'}(x)$ will be taken as zero for all x. The only overlap integral appearing is $d_{AB}=d_{A'B}$, and for this case it is

$$d_{AB}=0.0439.$$

The nonorthogonal orbitals are

$$\begin{aligned}u_A&=(2/\pi)^{\frac{3}{4}}\exp[-(r+R_A)^2],\\ u_B&=(2/\pi)^{\frac{3}{4}}\exp(-r^2),\\ u_{A'}&=(2/\pi)^{\frac{3}{4}}\exp[-(r-R_A)^2].\end{aligned} \quad (35)$$

The ground configuration has a singlet and a triplet associated with it, as do the two excited configurations in which an electron is transferred from u_B to u_A or $u_{A'}$. The ground singlet is

$$\psi_0=\frac{A}{(4!)^{\frac{1}{2}}}\left\{\frac{u_A(\alpha)u_B(\alpha)u_B(\beta)u_{A'}(\beta)-u_A(\beta)u_B(\alpha)u_B(\beta)u_{A'}(\alpha)}{(2-4d^2+4d^4)^{\frac{1}{2}}}\right\}. \quad (36)$$

The ground triplet is

$$\chi_0=\frac{A}{(4!)^{\frac{1}{2}}}\left\{\frac{u_A(\alpha)u_B(\alpha)u_B(\beta)u_{A'}(\alpha)}{(1-2d^2)^{\frac{1}{2}}}\right\}. \quad (37)$$

The singlet corresponding to the excited state of the same inversion symmetry as ψ_0 is

$$\psi_1=\frac{A}{(4!)^{\frac{1}{2}}[4(1+2d^2)]^{\frac{1}{2}}}\{u_A(\alpha)u_B(\beta)u_{A'}(\alpha)u_{A'}(\beta)-u_A(\beta)u_B(\alpha)u_{A'}(\alpha)u_{A'}(\beta)+u_A(\alpha)u_A(\beta)u_B(\alpha)u_{A'}(\beta)-u_A(\alpha)u_A(\beta)u_B(\beta)u_{A'}(\alpha)\}. \quad (38)$$

The triplet corresponding to the excited state of the same inversion symmetry as χ_0 is

$$\chi_1=\frac{A}{(4!)^{\frac{1}{2}}[2(1-2d^2)]^{\frac{1}{2}}}\{u_A(\alpha)u_A(\beta)u_B(\alpha)u_{A'}(\alpha)+u_A(\alpha)u_B(\alpha)u_{A'}(\alpha)u_{A'}(\beta)\}. \quad (39)$$

The results of the configuration interaction are given in Table III. The overlap integral between the ground and excited singlets was the same as that between the ground and excited triplets

$$(\psi_0,\psi_1)=(\chi_0,\chi_1)=-0.062.$$

The lowest roots of the two secular equations were

$$E_{S=0}=-0.139,$$
$$E_{S=1}=-0.129.$$

Clearly in this example the superexchange interaction does lead to a description of the system in which the spins of the electrons about the magnetic atoms A and A' prefer to set themselves antiparallel. The calculation has been carried out with no overlap integrals or three-center integrals neglected.

Since the point of interest here is the energy difference between two spin orientations in a weakly coupled system, some of the approximation methods often used with nonorthogonal orbitals may not be valid. For example one often neglects the square or higher powers of the overlap integral and also three-center integrals. Such an approximation is thought to be reliable in those situations where the overlap integrals are small as is true in this problem. If this is done here, the energy separation turns out to be

$$E_{S=0}-E_{S=1}=-0.014,$$

as compared to the accurate value of -0.010. Although we are led to the same qualitative result, the percentage difference in the answers is rather large. Another approximation is to treat the nonorthogonal orbitals as though they were orthogonal and to find the matrix elements of the Hamiltonian on that basis. However, in order to account for the fact that the orbitals are not actually orthogonal, whenever an exchange integral appears in the formalism, it is set equal to a Heisenberg exchange integral J'. The energy difference between the two spin orientations will be a function of J'. When one follows this procedure and uses the exchange integral J' which is

$$J'=\{u_A(x_1)u_B(x_2)|H_1+H_2+H_{12}|u_B(x_1)u_A(x_2)\}=-0.0243,$$

the energy difference is

$$E_{S=0}-E_{S=1}=-0.016.$$

TABLE III. Results of the configuration interaction.

Singlets	Triplets
$H_{00}=0.000$	$H_{00}=\ 0.000$
$H_{01}=1.182$	$H_{01}=-1.181$
$H_{11}=0.163$	$H_{11}=\ 0.197$

In all of the numerical work a sufficient number of digits was retained so that the results could be expressed with three significant figures. In this problem where the overlap integral is quite small, which means that our orbitals are very nearly orthogonal, an error of approximately 50 percent in the final energy separation is incurred by the effective exchange integral treatment.

The use of nonorthogonal orbitals introduces many complications in an actual calculation, as is well known. Furthermore, the results of these calculations appear to be rather sensitive to any approximations made which would simplify the nonorthogonality problem. Therefore, it seems that an approach based on orthogonal orbitals is more suitable. If we take the results obtained from the calculation by using the nonorthogonal u's and expand them in terms of the orthogonal v's, we find that all of the configurations listed in Table II are necessary. The result of such an expansion is to determine the coefficients with which the orthogonal configurations enter. However, if we were to do the problem entirely over starting with the v's and find the lowest singlet and triplet states, we would find a singlet with an energy at least as low as that found in terms of the nonorthogonal orbitals and that the lowest triplet energy would be unaffected for this case. Therefore, the energy separation of the two spin orientations would be at least as great as that found by the calculation using nonorthogonal orbitals.

Let us now apply the method of Kramers to this system. We have to evaluate U_{12} as given in (29). To determine whether the third-order approximation is adequate, the behavior of the inequality (34) must be examined. For this numerical example the values turn out to be

$$\left|d\left(\frac{J+g}{2g}\right)\left(\frac{E-E_2}{E-E_1}\right)\right|=0.356\left(\frac{E-E_2}{E-E_1}\right), \quad (40)$$

and

$$|h|=0.1717. \quad (41)$$

The inequality (34) is not satisfied and, therefore, for this problem the third-order theory is not sufficient to describe the true state of affairs. The convergence properties of Kramers' method are not well known and they may turn out to be a serious limitation to the usefulness of this approach.

CONCLUSION

Two problems have been discussed here. First, the role of the oxygen ion in MnO in determining the spin coupling of the surrounding Mn^{++} ions. The polarization of the $O^{=}$ ion by the Mn^{++} ions breaks up the closed shell structure of the $O^{=}$ ion and an energy dependence on the spin orientation of the Mn^{++} ions appears. This idea, originally due to Kramers, has been examined by considering a drastically simplified three-center model by configuration interaction where the excited states are those in which electrons are transferred from the nonmagnetic ion to the adjacent magnetic ions. A numerical example has been worked out giving the singlet or nonmagnetic state as of lowest energy.

The second problem considered has been the examination of various methods of carrying out the configuration interaction. The approaches of nonorthogonal orbitals, orthogonal orbitals, and Kramers have all been applied to the three-center problem. The use of nonorthogonal orbitals as opposed to orthogonal orbitals has the advantage that generally fewer configurations have to be considered and the choice of these configurations has a more direct physical motivation. However, in dealing with nonorthogonal orbitals the very serious problems created by nonorthogonality make the use of these orbitals impractical. In the type of problem discussed in this paper involving the energy separation of states in a weakly coupled system, the usual approximations made using nonorthogonal orbitals can introduce large errors.

It has been emphasized that when using orthogonal orbitals, it will almost always be essential to use configurations which would appear entirely unnecessary when thought of in terms of nonorthogonal orbitals. Thus one suffers the disadvantage of larger order secular equations but enjoys the enormous simplifications introduced by orthogonality. The advantages of selecting configurations using nonorthogonal orbitals can be combined with the advantages of orthogonal orbitals in a rather obvious way. Suppose our nonorthogonal orbitals are $u_1, u_2, \cdots u_n$. Let the orthogonal orbitals be $v_1, v_2, \cdots v_N$ with $N \geq n$. Usually the v's are related to the u's so that u_k corresponds most closely to v_k. Or, if we write

$$u_k = \sum_j (u_k, v_j) v_j,$$

then (u_k, v_k) is nearly unity and the other coefficients are nearly zero. Let us assume the v's have been chosen in this way and that the number N of orthogonal orbitals is chosen such that (u_i, v_{N+1}) is negligible for all i. If we have an m electron problem, $m \leq n$, then a state corresponding to a given configuration will be a linear combination of $m \times m$ determinants. Each determinant

$$A(u_i u_j \cdots u_t)$$

can be expressed in terms of the v's as

$$A\{\sum_q \sum_r \cdots \sum_s (u_i, v_q)(u_j, v_r) \cdots (u_t, v_s) v_q v_r \cdots v_s\}.$$

The leading term in the summation is for $q=i$, $r=j$, $\cdots s=t$, the other terms becoming smaller the greater the deviation from these values of q, r, $\cdots s$. Knowing how the factors (u_g, v_h) fall off for $g \neq h$ one can estimate the number of terms in the summation which must be carried. Each term retained corresponds to a different configuration in terms of the v's. Therefore, by examining all of the configurations written in terms of the nonorthogonal orbitals in this manner one can arrive at the number and type of orthogonal configurations necessary.

Kramers' method is a simplification of configuration interaction using orthogonal orbitals where the order of the secular equation is reduced by using an effective Hamiltonian. It has generally been assumed that the third order theory is adequate to describe spin coupling of nonoverlapping paramagnetic ions. Since the third-order term,

$$\sum_{\alpha \neq \beta} \frac{H_{m\alpha} H_{\alpha\beta} H_{\beta n}}{(E - H_{\alpha\alpha})(E - H_{\beta\beta})},$$

can at best take into account configurations differing by two orbitals from the ground configuration, and because the third-order term will usually not completely account for the effect of configurations differing from the ground configuration by only one orbital, one can conclude that higher-order terms will be necessary in most problems.

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