

## Theory of Superexchange\*

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The Dirac-Van Vleck-Serber spin-operator expansion, first applied by Anderson to the Kramers superexchange problem, is extended, simplified, and systematized in order to handle all overlap contributions arising from a number of interacting configurations. The linear cation-anion-cation (e.g.,  $Mn^{++}-O^{--}-Mn^{++}$ ) four-electron problem is worked out in detail, taking account of all contributions from configurations (*A*) ionic, (*B*) electron transferred to right, (*C*) electron transferred to left. Group symmetry requirements are invoked; and these, together with a simple approximation equivalent to perturbation theory, are shown to reduce the complicated matrix formulation to a single linear equation. The solution contains terms previously obtained by Anderson, by Anderson and Hasegawa, and by Yamashita, and a number of important extra terms. All superexchange terms are fourth

order or higher in the overlap  $S$ . A rough numerical evaluation with modified Slater wave functions appropriate to MnO-type crystals yields an effective superexchange integral of the required size. Brief consideration is given to configurations in which two electrons are transferred, in particular (*D*) simultaneous transfer of electrons to right and to left (Slater mechanism). Unless the energy required to form this configuration is surprisingly small, its contribution is probably not so important, although the problem needs to be investigated in detail. Some consideration is also given to the linear cation-anion-anion-cation (e.g.,  $Mn^{++}-Br^{-}-Br^{-}-Mn^{++}$ ) problem; the formal solution for the ionic configuration is worked out; and it is shown that superexchange terms first appear in the order  $S^4T^2$ , where  $S$  is the anion-cation overlap and  $T$  is the anion-anion overlap.

### I. INTRODUCTION

IN this paper we demonstrate a relatively simple procedure for handling the formal portion of the theory of superexchange. We confine ourselves to the problem of three nuclei and four electrons (such as Mn-O-Mn). The extension of the method to an anion surrounded octahedrally by six paramagnetic cations will be discussed in a subsequent paper.

We consider three configurations and their interactions:

- A. The ionic configuration.
- B. The configuration in which an electron is transferred from the anion to the cation on the right.
- C. The configuration in which an electron is transferred from the anion to the cation on the left.

We use electronic orbitals appropriate to the free ions, but we take account of overlap between anion and cation orbitals. In the absence of this overlap, there can be no superexchange effects of any kind. Thus the overlap is fundamental to the theory, and one must be careful to include all terms arising from it. Our results contain superexchange effects which may be traced to

- (1) overlap in the ionic configuration (Yamashita mechanism<sup>1</sup>);
- (2) transfer of an electron to right or to left (Anderson mechanism<sup>2</sup>—also treated by Van Vleck<sup>3</sup>);
- (3) interaction between configurations *B* and *C* (Anderson-Hasegawa mechanism<sup>4</sup>);

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<sup>1</sup> J. Yamashita and J. Kondo, *Phys. Rev.* **109**, 730 (1958).

<sup>2</sup> P. W. Anderson, *Phys. Rev.* **79**, 350 (1950).

<sup>3</sup> J. H. Van Vleck, *J. phys. radium* **12**, 262 (1951).

<sup>4</sup> Nagamiya, Yosida, and Kubo, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.

(4) additional overlap terms within and between the configurations, and not previously considered.

Thus we confine ourselves to the ground state and to states in which a single electron has been transferred. One may also distinguish the following configurations:

*D*. The configuration in which one electron is transferred from the anion to the cation on the left, and at the same time another electron is transferred from the anion to the cation on the right. This has been considered by Slater,<sup>5</sup> Pratt,<sup>6</sup> Goodenough and Loeb,<sup>7</sup> and Nesbet.<sup>8</sup> It should be unimportant in halides, but it may be of significance in oxides and sulfides. In the latter, however, the large crystalline Coulomb fields will cause the energy of the configuration *D* to lie well above the energy of configurations *B* and *C*. We believe, in particular, that Nesbet has underestimated the energy of *D*. However, *D* may still be important. Pratt<sup>6</sup> has shown that if orthogonal orbitals are used, and regardless of the nature of these orbitals, configuration *D* must be included; otherwise the ferromagnetic state is lowest. This important work first drew attention to the very serious nature of the orthogonalization problem in antiferromagnetism.

*E*. The configuration in which one electron is transferred from the anion to the cation on the left, and at the same time an electron is transferred from the cation on the right to the vacated anion orbital. This has been considered by Yamashita and Kondo.<sup>1</sup> Its energy is fairly high due to the large ionization potential of the cation; on the other hand, it is favored by the crystalline Coulomb fields, i.e., it actually lowers the Madelung energy.

*F*. Same as *E*, except all transfers to the right.

<sup>5</sup> J. C. Slater, Quarterly Progress Reports, Massachusetts Institute of Technology, July 15 and October 15, 1953 (unpublished).

<sup>6</sup> G. W. Pratt, *Phys. Rev.* **97**, 926 (1955).

<sup>7</sup> J. B. Goodenough and A. L. Loeb, *Phys. Rev.* **98**, 391 (1955).

<sup>8</sup> R. K. Nesbet, *Ann. Phys. (N. Y.)* **4**, 87 (1958).

G. Configurations in which one of the anion electrons is excited to a higher orbital. These have been considered by Slater<sup>5</sup>; Pratt<sup>6</sup> has shown that they are probably unimportant.

A general discussion of the various proposed configurations has been given by Yamashita and Kondo.<sup>1</sup> It should be noted, however, that whereas we shall use configuration interaction of a number of Slater determinants, Yamashita and Kondo confine their analysis, for the most part, to a single Slater determinant composed of molecular orbitals.

Although the contributions of configurations  $D$  through  $F$  should not be ignored, we believe that our analysis of configurations  $A$ ,  $B$ , and  $C$  presents the salient features of configuration interaction, and in particular demonstrates the power of our method. The extension to the other configurations, and to more dimensions, will be considered in a subsequent paper.

Our method is an extension of the Dirac-Van Vleck<sup>9</sup> vector model in the manner introduced by Serber<sup>10</sup> for handling configuration interaction and nonorthogonality effects. However, we do not explicitly employ the permutation matrices, or their spurs, as does Serber. Since we are interested only in the dependence of the energy upon spin directions, the spin-permutation operators are retained throughout the calculation, and at the end are simply replaced by the equivalent product of spin operators. Somewhat this sort of scheme was used by Anderson,<sup>2</sup> but not to the fullest extent and simplicity, and also not to include nonorthogonality of the orbitals. Furthermore, we introduce the essential simplification—making the three-dimensional problem tractable—of properly combining the excited configurations so as to satisfy group-symmetry requirements.

## II. THE IONIC CONFIGURATION

To illustrate the method we first work out the effects of overlap in the ionic configuration. To fix ideas, let this configuration be  $\text{Mn}^{++}\text{-O}^{--}\text{-Mn}^{++}$ . Let the basis function of this configuration be, in Serber's notation,

$$\psi^A = (\alpha_1 | r_1)(\alpha_2 | r_2)(\alpha_3 | r_3)(\alpha_4 | r_4). \quad (1)$$

We will call this function  $\alpha$  for short, and we will designate the corresponding functions with orbitals permuted by  $P\alpha$ . It is to be noted that the  $\alpha_i$  are the space orbitals only.

Let  $\alpha_1 = \alpha_2$  be the orbitals for a pair of  $\text{O}^{--}$  electrons, which may be either  $2s$  or  $2p_x$ . Let  $\alpha_3$  be the left-side  $\text{Mn}^{++}$   $3d$  orbital with maximum directed towards the oxygen (i.e., of the form  $Y_2^0$  with respect to the Mn-O-Mn, or  $x$ , axis), and let  $\alpha_4$  be the corresponding  $3d$  function of the right-side  $\text{Mn}^{++}$ . The overlap integrals

will be given by

$$\begin{aligned} (\alpha_1 | \alpha_4) &= S, \\ (\alpha_1 | \alpha_3) &= \pm S. \end{aligned} \quad (2)$$

Here, and in the future, the top of the  $\pm$  sign is to be used if  $\alpha_1 = 2s$  function, the bottom if  $\alpha_1 = 2p_x$  function.

Serber's method starts with the Dirac expansion<sup>11</sup> for the Hamiltonian:

$$H^{AA} = \sum_P H_P^{AA} P, \quad (3)$$

where

$$H_P^{AA} = (P\alpha | H | \alpha). \quad (4)$$

Here  $H^{AA}$  and  $P$  are ordinarily to be considered as matrices, the latter being the so-called "regular representation" of the permutation group operating on the space orbitals. Dirac shows that for basis functions of the form (1) one may replace the matrices  $P$  by the spin-permutation matrices  $P^\sigma$  as follows:

$$P \rightarrow (-)^P P^\sigma, \quad (5)$$

where  $(-)^P$  is  $-$  or  $+$  for odd or even number of equivalent two-function permutations. Furthermore, Dirac shows that one may think of the  $P^\sigma$  as no longer matrices, but as operators, and in particular the two-function permutations may be replaced by

$$P_{ij}^\sigma = \frac{1}{2} + 2\mathbf{S}_i \cdot \mathbf{S}_j, \quad (6)$$

where  $\mathbf{S}_i$  and  $\mathbf{S}_j$  are the one-electron vector spin operators. Higher permutations may be replaced by products of  $P_{ij}^\sigma$ ; for example,  $P_{ijk}^\sigma = P_{ij}^\sigma P_{jk}^\sigma$ .

If, now, the orbitals are nonorthogonal, Eq. (3) is to be replaced by

$$(H - W)^{AA} = \sum_P (H - W)_P^{AA} P, \quad (7)$$

where

$$W_P^{AA} = (P\alpha | W | \alpha) = W(P\alpha | \alpha). \quad (8)$$

Here  $W$  is the unknown energy appearing in the secular equation.

One more important point needs to be considered before Eq. (7) may be applied to our problem, namely, the effect of identical orbitals, such as  $\alpha_1 = \alpha_2$ . As Serber points out, in this case  $P_{12}\alpha = \alpha$ , or  $P_{12}$  can only have the eigenvalue  $+1$ . To take proper account of this, Serber divides the entire group of  $n!$  permutations into one set of  $n!/2$  "independent" permutations, and a second set of  $n!/2$  permutations which can be obtained by multiplying each of the first set on the left by  $P_{12}$ . We label the first set by  $\mathbf{P}$ , the second set by  $P_{12}\mathbf{P}$ . For example, in the case of three orbitals,  $\mathbf{P}$  contains  $P_I, P_{13}, P_{23}$ ; and  $P_{12}\mathbf{P}$  contains  $P_{12}, P_{132}, P_{123}$ . (Here  $P_I$  is the identity permutation.) In the case of our four orbitals,  $\mathbf{P}$  contains  $P_I, P_{13}, P_{14}, P_{23}, P_{24}, P_{34}, P_{134}, P_{143}, P_{234}, P_{243}, P_{13,24}, P_{14,23}$ ; and  $P_{12}\mathbf{P}$  contains  $P_{12}, P_{132}, P_{142}, P_{123}, P_{124}, P_{12,34}, P_{1342}, P_{1432}, P_{1234}, P_{1243}, P_{1324}, P_{1423}$ .

If one wishes to handle Eq. (7) as a matrix equation,

<sup>9</sup> J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

<sup>10</sup> R. Serber, Phys. Rev. **45**, 461 (1934); J. Chem. Phys. **2**, 697 (1934).

<sup>11</sup> P. A. M. Dirac, *The Principles of Quantum Mechanics* (Clarendon Press, Oxford, 1947), third edition, p. 218.

one must be extremely careful, as Serber points out, to eliminate from the matrix those rows and columns corresponding to the impossible eigenvalue  $-1$  for  $P_{12}$ . Anderson has shown that, if one wishes to handle (7) as an operator equation, the impossible eigenvalues may be eliminated by use of projection operators. We discuss this in the Appendix. However, one need not use the projection-operator formalism providing one is careful to evaluate all operators in accordance with the restricting condition,  $P_{12}=1$ . With this condition, the set  $P_{12}\mathbf{P}$  simply repeats all the  $\mathbf{P}$  terms in (7), and we have

$$(H-W)^{AA} = 2 \sum_{\mathbf{P}} (-)^{\mathbf{P}} (H-W)_{\mathbf{P}}^{AA} \mathbf{P}^{\sigma}. \quad (9)$$

As Serber has shown, this expression is incorrectly normalized. In going from nonequivalent to equivalent orbitals the wave function (1) should be divided by  $\sqrt{2}$ , and hence the right side of (9) should be divided by 2. It makes no difference, however, since we are going to formally solve for  $W$ , in terms of the operators (6), by setting the right side of (9) equal to zero. Thus our problem is reduced to simply finding the solution  $W$  to the linear equation

$$\sum_{\mathbf{P}} (-)^{\mathbf{P}} (H-W)_{\mathbf{P}}^{AA} \mathbf{P}^{\sigma} = 0, \quad (10)$$

under the restriction  $P_{12}^{\sigma} = -1$ .

To a high approximation we may neglect any overlap or matrix elements between the cation functions  $\alpha_3$  and  $\alpha_4$ . The anion-cation overlaps are given by Eq. (2). Thus Eq. (10) becomes

$$\begin{aligned} (H_I^{AA} - W) - (H_{13}^{AA} - WS^2)(P_{13}^{\sigma} + P_{23}^{\sigma}) \\ - (H_{14}^{AA} - WS^2)(P_{14}^{\sigma} + P_{24}^{\sigma}) \\ + (H_{13,24}^{AA} - WS^4)(P_{13,24}^{\sigma} + P_{14,23}^{\sigma}) = 0. \end{aligned} \quad (11)$$

In this equation  $H_{ij}$  is shorthand for  $H_{F_{ij}}$ .

Under the restriction  $P_{12}^{\sigma} = -1$ , we obtain from (6)

$$P_{13}^{\sigma} + P_{23}^{\sigma} = P_{14}^{\sigma} + P_{24}^{\sigma} = 1. \quad (12)$$

From this we also obtain

$$\begin{aligned} P_{13,24}^{\sigma} + P_{14,23}^{\sigma} &= (P_{13}^{\sigma} + P_{23}^{\sigma})(P_{14}^{\sigma} + P_{24}^{\sigma}) \\ &\quad - P_{13}^{\sigma} P_{14}^{\sigma} - P_{23}^{\sigma} P_{24}^{\sigma} \\ &= 1 - P_{14}^{\sigma} P_{34}^{\sigma} - P_{24}^{\sigma} P_{34}^{\sigma} \\ &= 1 - P_{34}^{\sigma}. \end{aligned} \quad (13)$$

With the use of (12) and (13) one readily reduces (11) to

$$W = \frac{H_I^{AA} - (H_{13}^{AA} + H_{14}^{AA}) + H_{13,24}^{AA}(1 - P_{34}^{\sigma})}{1 - 2S^2 + S^4(1 - P_{34}^{\sigma})}. \quad (14)$$

To order  $S^4$  the spin-dependent part of this energy is

$$\Delta W = -2\mathbf{S}_3 \cdot \mathbf{S}_4 (H_{13,24}^{AA} - S^4 H_I^{AA}). \quad (15)$$

Here  $H_{13}^{AA}$  and  $H_{14}^{AA}$  have been dropped as being of order  $S^2$  compared to  $H_I^{AA}$ . We consider the order of a quantity involving two overlapping functions to be

given by

$$(P\alpha|H|\alpha) = \text{order of } (\alpha|H|\alpha)(P\alpha|\alpha). \quad (16)$$

The Hamiltonian to be used in Eq. (4) is

$$H = \sum_i H_i + \sum_{i \neq j} G_{ij}, \quad (17)$$

where

$$H_i = H_{0i} + V_i, \quad (18)$$

$$H_{0i} = (p_i^2/2m) - e^2(Z_g/r_{ig}), \quad (19)$$

$$V_i = -e^2 \sum'_{g \neq g_i} (Z_g/r_{ig}), \quad (20)$$

$$G_{ij} = e^2/2r_{ij}. \quad (21)$$

Here  $Z_g$  is the atomic number of the nucleus at the point  $g$ ,  $r_{ig}$  is the distance between the electron  $i$  and the point  $g$ , and  $r_{ij}$  is the distance between electrons  $i$  and  $j$ . The Hamiltonian has been split in the form (18) since

$$(\alpha_j|H_{0i}|\alpha_i) = (\alpha_j|\alpha_i)E_{0i}, \quad (22)$$

and hence the  $H_0$  terms in  $S^4 H_I^{AA}$  will just equal those in  $H_{13,24}^{AA}$ .

$$\begin{aligned} H_I^{AA} &= 2(\alpha_1|H_1|\alpha_1) + 2(\alpha_3|H_3|\alpha_3) + 8(\alpha_1\alpha_3|G|\alpha_1\alpha_3) \\ &\quad + 2(\alpha_3\alpha_4|G|\alpha_3\alpha_4) + 2(\alpha_1\alpha_2|G|\alpha_1\alpha_2); \end{aligned} \quad (23)$$

$$\begin{aligned} H_{13,24}^{AA} &= S^3[2(\alpha_2|H_4|\alpha_4) + 2(\alpha_4|H_2|\alpha_2)] \\ &\quad + S^2[4(\alpha_3\alpha_1|G|\alpha_1\alpha_3) \pm 8(\alpha_1\alpha_2|G|\alpha_3\alpha_4)]. \end{aligned} \quad (24)$$

Here, as in (2), the  $+$  sign is to be used for  $2s$  anion functions, the  $-$  for  $2p$  functions.

When (23) and (24) are inserted into (15) the terms in  $H_0$  cancel, and we obtain the result given by Eq. (15) of Yamashita and Kondo<sup>1</sup> (YK), except for two small errors in the latter. Their term  $(BB|G|BB)$ , which is equivalent to our  $(\alpha_1\alpha_2|G|\alpha_1\alpha_2)$ , should be positive, rather than negative; and their term  $(AB|G|BB)$  should not be present. It is important to note that YK calculate the difference in energy between a ferromagnetic  $\uparrow\uparrow$  state and an antiferromagnetic  $\uparrow\downarrow$  state, rather than between a triplet  $\uparrow\uparrow$  and a singlet  $\uparrow\downarrow - \downarrow\uparrow$ . Thus for our result to correspond to theirs we must take  $\mathbf{S}_3 \cdot \mathbf{S}_4 = +\frac{1}{4}$  for ferromagnet,  $-\frac{1}{4}$  for antiferromagnet.

It is also possible to get an exact solution to the problem, analogous to Eq. (16) of YK, by inserting the eigenvalues of  $\mathbf{S}_3 \cdot \mathbf{S}_4$  directly into our Eq. (14).

The method used by YK is an expansion in orthogonal Löwdin functions. This is extremely tedious, involving long algebraic expressions. We have checked the YK result by their method, and have obtained our answer, but not without first making a number of algebraic errors of our own.

In contrast, the operator expansion, although it requires careful study of the machinery, produces a result with a bare minimum of algebra. Furthermore, it has the considerable advantage of a compact notation, as witness the simple form of Eq. (15).

The overwhelming advantage of the operator expansion becomes apparent when more complicated

problems are tackled. For example, we consider the problem of superexchange along the row cation-anion-anion-cation. We number the wave functions from left to right  $\alpha_5, \alpha_1=\alpha_2, \alpha_3=\alpha_4, \alpha_6$ . Let the anion-cation overlaps, as before, be designated by  $S$ ; the anion-anion overlap by  $T$ . Then an elementary extension of the arguments leading to Eq. (15) yields

$$\Delta W = -2\mathbf{S}_5 \cdot \mathbf{S}_6 (H_{51,23,46}^{AA} - S^4 T^2 H_I^{AA}). \quad (25)$$

If the anions are identical,  $T^2$  may be fairly large, and this form of superexchange may be appreciable. This could be an important effect in structures such as  $\text{MnBr}_2$  which have double layers of anions between cation layers. Although the ordering pattern of  $\text{MnBr}_2$  is quite complicated, there is a definite antiferromagnetic coupling along nearly linear Mn-Br-Br-Mn bond linkages.<sup>12</sup> Of course, Eq. (25) contains only the terms from the ionic configuration; but, as will be seen in the next section, the other configurations contribute terms of the same order of magnitude.

Superexchange across two anions may also be important in  $\beta$ -cubic and  $\beta$ -hexagonal MnS which have ordering of the third kind.<sup>13</sup> Here the near-neighbor cations connect through a single anion, and this is probably the predominant exchange effect. But the fact that next-neighbor cations also try to order antiferromagnetically indicates that the more complicated kind of exchange represented by Eq. (25) is probably also present.

By a simple extension, we see that superexchange across three identical anions will be proportional to  $S^4 T^4$ , etc.

We next demonstrate the simplicity of the operator expansion when applied to configuration interaction.

### III. CONFIGURATION INTERACTION

The three configurations  $A, B$ , and  $C$ , defined in Sec. I, will now be considered. The orbitals will be labeled according to the following scheme:

	Cation (a)	Anion (b)	Cation (c)	
$\psi^A$ :	$\alpha_3$	$\alpha_1=\alpha_2$	$\alpha_4$	(26)
$\psi^B$ :	$\beta_3$	$\beta_4$	$\beta_1=\beta_2$	
$\psi^C$ :	$\gamma_1=\gamma_2$	$\gamma_3$	$\gamma_4$	

Actually, all the orbitals in any column are identical. They are labeled differently in order to facilitate the permutation problem, as shall be seen.

We note that our calculation is restricted to the case of identical cation orbitals in the excited configurations. Thus it may be applied to  $\text{MnO}$ , but not to an antiferromagnet in which the  $3d$  shell is less than half-filled, so that the cation electrons can be in different orbitals. However, our general method can be extended without

too much trouble to this case, as will be shown in a subsequent paper.

With the labelling as in (26),  $P_{12}$  will permute identical orbitals in all three configurations. Thus the entire secular equation will contain only the permutations  $\mathbf{P}$  and will be of the form

$$\begin{vmatrix} (H-W)^{AA} & (H-W)^{AB} & (H-W)^{AC} \\ (H-W)^{BA} & (H-W)^{BB} & (H-W)^{BC} \\ (H-W)^{CA} & (H-W)^{CB} & (H-W)^{CC} \end{vmatrix} = 0. \quad (27)$$

Here the correctly normalized matrix element  $(H-W)^{AA}$  is given by the left-hand side of (11). Let  $H_P^{BA} = (P\beta|H|\alpha)$ , etc. Then the other matrix elements of (27) are

$$\begin{aligned} (H-W)^{BA} &= (H_I^{BA} - WS^3) \\ &\quad - (H_{14}^{BA} - WS)(P_{14}^\sigma + P_{24}^\sigma) \\ &\quad + (H_{134}^{BA} - WS^3)(P_{134}^\sigma + P_{234}^\sigma); \end{aligned} \quad (28)$$

$$(H-W)^{CA} = \pm (H-W)^{BA}; \quad (29)$$

$$\begin{aligned} (H-W)^{BB} &= (H-W)^{CC} = (H_I^{BB} - W) \\ &\quad - (H_{14}^{BB} - WS^2)(P_{14}^\sigma + P_{24}^\sigma) \\ &\quad - (H_{34}^{BB} - WS^2)P_{34}^\sigma; \end{aligned} \quad (30)$$

$$(H-W)^{CB} = (H_{13,24}^{CB} \mp WS^2)(P_{13,24}^\sigma + P_{14,23}^\sigma). \quad (31)$$

Here, as in Sec. II, the upper sign is to be used with  $2s$  anion orbitals, the lower with  $2p$ ; also it is understood that all operators are to be evaluated subject to the restriction  $P_{12}^\sigma = -1$ . The matrix (27) is Hermitian, so all the elements are given by the above equations. These equations may be simplified by use of (12), (13), and the relation

$$(P_{134}^\sigma + P_{234}^\sigma) = (P_{13}^\sigma + P_{23}^\sigma)P_{34}^\sigma = P_{34}^\sigma. \quad (32)$$

Let us introduce a notation to show explicitly the order and the sign of the matrix elements:

$$h_I^{BA} = H_I^{BA} / (P_I\beta|\alpha) = H_I^{BA} / S^3, \quad (33)$$

$$h_{13,24}^{CB} = H_{13,24}^{CB} / (P_{13,24}\gamma|\beta) = \pm H_{13,24}^{CB} / S^2,$$

etc. [see Eq. (16)]. The order of all  $h$  will be  $S^0$ . Let us further introduce

$$w_I^{BA} = h_I^{BA} - W, \quad (34)$$

etc. Then the matrix elements may be written

$$\begin{aligned} (H-W)^{AA} &= (H_I^{AA} - W) - S^2(w_{13}^{AA} + w_{14}^{AA}) \\ &\quad + S^4 w_{13,24}^{AA} (1 - P_{34}^\sigma); \end{aligned} \quad (35)$$

$$(H-W)^{BA} = S^3 w_I^{BA} - S w_{14}^{BA} + S^3 w_{134}^{BA} P_{34}^\sigma; \quad (36)$$

$$\begin{aligned} (H-W)^{BB} &= (H-W)^{CC} = w_I^{BB} \\ &\quad - S^2(w_{14}^{BB} + w_{34}^{BB} P_{34}^\sigma); \end{aligned} \quad (37)$$

$$(H-W)^{CB} = \pm S^2 w_{13,24}^{CB} (1 - P_{34}^\sigma). \quad (38)$$

The  $A$  configuration is gerade (even), as can be seen from general considerations or from an examination of (35). This can combine only with the even combination

<sup>12</sup> Wollan, Koehler, and Wilkinson, Phys. Rev. **110**, 638 (1958).

<sup>13</sup> Corliss, Elliott, and Hastings, Phys. Rev. **104**, 924 (1956).

of excited configurations,

$$\psi^G = 2^{-1/2}(\psi^B \pm \psi^C). \quad (39)$$

This means that the matrix (27) factors into a  $1 \times 1$  ungerade (odd) part and the  $2 \times 2$  matrix of interest

$$\begin{vmatrix} (H-W)^{AA} & (H-W)^{AG} \\ (H-W)^{GA} & (H-W)^{GG} \end{vmatrix} = 0. \quad (40)$$

The matrix elements are given by (35) and by

$$(H-W)^{GA} = (2^{1/2})(H-W)^{BA}; \quad (41)$$

$$(H-W)^{GG} = w_I^{BB} - S^2(w_{14}^{BB} + w_{34}^{BB} P_{34}^G) + S^2 w_{13,24}^{CB} (1 - P_{34}^G). \quad (42)$$

We note that the matrix elements appear formally the same, when written in this notation, for both  $(2s)^2$  and  $(2p)^2$  anion orbitals.

The exact solution of (40) involves nothing more than a quadratic equation in  $W$ , but the algebra is rather messy. Since we are interested only in the perturbed energy of the ionic configuration, and only in those terms involving  $\mathbf{S}_3 \cdot \mathbf{S}_4$ , we may make use of a simple approximation, equivalent to perturbation theory. We replace the unknown  $W$  everywhere but in the term  $H_I^{AA} - W$  by its zeroth-order approximation  $H_I^{AA}$ . This amounts to a change of

$$w_I^{BA} \rightarrow q_I^{BA} \equiv h_I^{BA} - H_I^{AA}, \quad (43)$$

etc.<sup>14</sup> We then have a simple linear equation in  $W$ , the solution of which is a term not involving  $\mathbf{S}_3 \cdot \mathbf{S}_4$  plus

$$\begin{aligned} \Delta W = & -2S^4 \mathbf{S}_3 \cdot \mathbf{S}_4 \{ q_{13,24}^{AA} \\ & + 2[(q_{14}^{BA})^2 (q_{34}^{BB} + q_{13,24}^{CB}) / (q_I^{BB})^2] \\ & - 4(q_{14}^{BA} q_{134}^{BA} / q_I^{BB}) \}. \quad (44) \end{aligned}$$

This is our result. We repeat here the notation:

$$q_I^{\alpha\beta} \equiv [H_I^{\alpha\beta} / (P\alpha|\beta)] - H_I^{AA}. \quad (45)$$

The first term in (44) is the effect of overlap in the ionic configuration, and is the same as (15). The term in square brackets is a generalization of the sum of the Anderson and the Anderson-Hasegawa mechanisms, as we shall see in detail in the next section. The last term in (44) is completely new.

As previously noted by Yamashita and Kondo,<sup>1</sup> all configurations first contribute to superexchange in the order  $S^4$ .

#### IV. MATRIX EXPRESSIONS

In this section we exhibit the detailed form of the matrices entering into Eq. (44). We write all matrix elements in terms of the orbitals  $a$ ,  $b$ , and  $c$ , as given by the scheme of (26), and we use the simplest notation possible. To illustrate this notation, the matrix elements

<sup>14</sup> This procedure can be shown to be correct, to order  $S^4$  in  $\mathbf{S}_3 \cdot \mathbf{S}_4$ , by the more general method of expanding  $W$  in a power series in  $S$  everywhere in (40) and equating like powers of  $S^2$ ,  $S^4$ , and  $S^4 \mathbf{S}_3 \cdot \mathbf{S}_4$ .

given in (23) and (24) are rewritten as follows:

$$\begin{aligned} H_I^{AA} = & 2H_{bb}^b + 2H_{cc}^c + 8G_{bc, bc} \\ & + 2G_{ac, ac} + 2G_{bb, bb}; \quad (46) \end{aligned}$$

$$\begin{aligned} H_{13,24}^{AA} = & S^3(2H_{bc}^c + 2H_{cb}^b) \\ & + S^2(4G_{ab, ba} \pm 8G_{bb, ac}). \quad (47) \end{aligned}$$

The other matrix elements are:

$$\begin{aligned} H_{14}^{BA} = & H_{cb}^b + 2G_{bc, bb} + 2G_{ac, ab} + 2G_{cc, cb} \\ & + S(H_{bb}^b + 2H_{aa}^a + 4G_{ab, ab} + 2G_{ac, bc}); \quad (48) \end{aligned}$$

$$\begin{aligned} H_{134}^{BA} = & S(2G_{ab, ba} \pm 4G_{ac, bb}) \\ & + S^2(H_{cb}^b \pm H_{ab}^b \pm H_{ba}^a + 2G_{cc, bc} \pm 4G_{ac, bc}) \\ & + S^3 H_{cc}^c; \quad (49) \end{aligned}$$

$$\begin{aligned} H_{34}^{BB} = & 2G_{ba, ab} \pm S(8G_{bc, ac} + H_{ba}^a + H_{ab}^b) \\ & + S^2(2H_{cc}^c + 2G_{cc, cc}); \quad (50) \end{aligned}$$

$$\begin{aligned} H_{13,24}^{CB} = & 2G_{ba, cb} + S(H_{ab}^b + H_{ba}^a + 4G_{aa, ab} + 4G_{ac, bc}) \\ & \pm S^2(2H_{cc}^c + 2G_{ac, ac}); \quad (51) \end{aligned}$$

$$H_I^{BB} = H_{bb}^b + 3H_{cc}^c + 2G_{cc, cc} + 4G_{ac, ac} + 6G_{bc, bc}. \quad (52)$$

In these equations the  $+$  signs are to be taken when considering  $(2s)^2$  anion orbitals, the  $-$  signs when considering  $(2p)^2$ . From (22) it can be seen that the  $H_0$  terms will cancel in all the  $q_I^{\alpha\beta}$  appearing in (44) except  $q_I^{BB}$ . This latter will contain, in addition to terms in  $V$  and  $G$ , a term

$$H_{0, aa}^a - H_{0, bb}^b = \epsilon, \quad (53)$$

where  $\epsilon$  is the transfer energy.

From an examination of the matrix elements it can be seen that, if we neglected terms containing  $S$  explicitly, the ionic contribution (47) would disappear. Furthermore,  $H_{14}^{BA}$  would become Anderson's transfer integral  $b$ , except that we have added terms in  $G$ ;  $H_{34}^{BB}$  would become Anderson's exchange integral  $J'$ ; and  $H_{13,24}^{CB}$  would become the Anderson-Hasegawa exchange integral  $J''$ . Equation (44) would reduce to the familiar form<sup>4</sup>:

$$\Delta W \rightarrow -2\mathbf{S}_3 \cdot \mathbf{S}_4 [2b^2(J' + J'') / (\Delta E)^2], \quad (54)$$

where  $\Delta E$  is the energy difference between excited and ground configurations. The extra factor of 2 on the Anderson term comes from adding the contributions of our two configurations  $B$  and  $C$ .

#### V. NUMERICAL CONSIDERATIONS

A rough numerical evaluation of Eq. (44), appropriate to the MnO problem, will now be attempted. Probably most of the superexchange comes from the oxygen  $2p$  orbitals. We express these very approximately as the Slater functions:

$$b(r, \theta) = (\delta^5/\pi) r e^{-\delta r} P_1(\cos\theta); \quad (55)$$

and we use for the manganese orbitals

$$a(r) = (\delta^5/3\pi) r e^{-\delta r}, \quad (56)$$

with origins a distance  $\pm R$  from the oxygen. We take  $R$ , for convenience, as 4 atomic units; this is very nearly the observed separation. The value of  $\delta$  is given below.

The functions (55) and (56) are, of course, extremely crude. They are, however, relatively simple to handle, and molecular integrals using these functions have been well tabulated.<sup>15</sup> The chief difficulty is that the Slater functions drop off with distance much more slowly than the more accurate Hartree functions, and therefore will give an overestimate of all of our integrals. We may remedy this defect, however, by picking  $\delta$  so as to give a reasonable value of the overlap integral  $S$ . For ease in handling the tables, we choose

$$\delta = 9/4, \quad (57)$$

which gives

$$S = 0.04649. \quad (58)$$

This is reasonable. A determination of the overlap in  $\text{MnF}_2$ , with use of Hartree functions, yields<sup>16</sup>  $S = 0.060$ ; and it is probable that the overlap in  $\text{MnO}$  is close to this value.

In evaluating the  $V$  integrals, we have used an effective nuclear charge of  $+2$  on all ions. This amounts to treating the metal ions as  $\text{He}^+$ -like, and the anions as neutral  $\text{He}$ -like. The three-center integrals have been approximated as best we could, assuming the overlap small.

The values are

$$\begin{aligned} q_{13,24}^{AA} &= -1.50; & q_{14}^{BA} &= -0.660; \\ q_{34}^{BB} &= -0.708; & q_{13,24}^{CB} &= -1.16; \\ q_{134}^{BA} &= -1.35; & q_I^{BB} &= 0.0089 + \epsilon. \end{aligned} \quad (59)$$

Here  $\epsilon$  is given by (53).

We now evaluate Eq. (44) as a sum of three terms:

- (I) the ionic term involving  $q_{13,24}^{AA}$ ;
- (II) the term in square brackets, which is a generalization of the Anderson and the Anderson-Hasegawa terms;
- (III) the remainder involving  $q_{134}^{BA}$ .

Thus we write Eq. (44) in the form

$$W = -2S^4 \mathbf{S}_3 \cdot \mathbf{S}_4 (\text{I} + \text{II} + \text{III}) = -2\mathbf{S}_3 \cdot \mathbf{S}_4 J. \quad (60)$$

In Table I we give the values of I, II, III, and  $J$  for three different values of  $\epsilon$ . Elsewhere<sup>16</sup> we have estimated  $\epsilon$  for  $\text{MnF}_2$  to lie between 10 and 15 ev.

Since the Néel point should be of the order of the number of linear couplings (in this case 3) times  $J$ , it is seen that the values are very good. It should be noted that all three terms contribute to an antiferromagnetic coupling and that terms II and III are most important. In term II, according to (59), the generalized Anderson-

TABLE I. Evaluation of the terms in Eq. (60) for different values of the transfer energy. All values, except where noted, are in atomic units.

$\epsilon$	I	II	III	$J$
0.184 (5 ev)	-1.50	-21.7	-13.0	$1.69 \times 10^{-4}$ (53°K)
0.368 (10 ev)	-1.50	-7.77	-7.79	$0.80 \times 10^{-4}$ (25°K)
0.735 (20 ev)	-1.50	-2.38	-4.33	$0.38 \times 10^{-4}$ (12°K)

Hasegawa exchange  $q_{13,24}^{CB}$  is larger than the generalized Anderson exchange  $q_{34}^{BB}$ .

We have made the evaluation using only the oxygen  $(2p)^2$  orbitals. To this should be added the contribution from the  $(2s)^2$  orbitals. The latter orbitals will have an overlap integral which is only slightly smaller and a transfer energy  $\epsilon$  which is very much larger than the former, at least if  $\text{MnO}$  is similar to  $\text{MnF}_2$ , for which careful calculations have been made.<sup>16</sup> This means that the contributions to the three terms from the  $(2s)^2$  orbitals, as compared to that from the  $(2p)^2$  orbitals, will probably be as follows: about the same or slightly smaller from term I, very much smaller from term II, much smaller from term III. The total contribution from the  $(2s)^2$  orbitals may be of the order of one-fourth that from the  $(2p)^2$ .

In a subsequent paper we will consider in detail the contributions from the other configurations mentioned in Sec. I. As an example of what happens, we now discuss briefly the contribution from the interaction between configurations  $A$  and  $D$ . By second-order perturbation, the exchange-like term will be

$$\Delta W = 2S^4 \mathbf{S}_3 \cdot \mathbf{S}_4 (M)^2 / q_I^{DD}, \quad (61)$$

where  $M$  is a matrix element connecting the configurations. By an elementary consideration it is seen that  $M$  is identical to  $q_{13,24}^{CB}$ , the Anderson-Hasegawa term. [For orthogonal orbitals, from (51), this reduces to  $2G_{ba,cb}$ , which is the integral considered by Nesbet.<sup>8</sup>] The contribution of (61) to  $J$  will thus be given by

$$\begin{aligned} J^{AD} &\approx (1.16)^2 (0.0465)^4 / q_I^{DD} \\ &\approx (0.063 \times 10^{-4}) / q_I^{DD} \text{ a.u.} \end{aligned} \quad (62)$$

This will only be of importance compared to the terms in Table I if the double-electron transfer energy  $\epsilon_2$ , which is the principal part of  $q_I^{DD}$ , is less than  $\sim 0.37$  a.u., or 10 ev. Because of the very large crystalline electrostatic energy involved in this transfer, we doubt that  $\epsilon_2$  can be this small. It should be pointed out that our orbitals are different from the orthogonal set used by Nesbet,<sup>8</sup> and no direct comparison of Eq. (61) should be made with his results. By an orthogonalization process one automatically mixes into the  $AD$  matrix elements some of the overlap terms contained in our matrix (40); and because of this Nesbet's  $AD$  terms might well be more important than ours. Nesbet does not consider configuration interaction due to transfer of a single electron ( $B$  and  $C$  configurations) because the effects

<sup>15</sup> Kotani, Amemiya, Ishiguro, and Kimura, *Table of Molecular Integrals* (Maruzen Company, Ltd., Tokyo, 1955).

<sup>16</sup> Keffer, Oguchi, O'Sullivan, and Yamashita, *Phys. Rev.* (to be published).

“vanish to second order in perturbation theory.” We believe, however, that the important criterion is not the order of perturbation theory, but the order of the overlap. It is true that our  $B$  and  $C$  contributions arise only in third-order perturbations, but they come in as  $S^4$  and are therefore of the same order of magnitude as (61). Indeed, they are probably larger if our estimate of  $\epsilon_2$  is correct.

To the contribution (61) must, of course, be added the terms coming from the interaction of  $D$  with  $B$  and  $C$ . These contributions, together with those from the other configurations mentioned in Sec. I, must be considered in any complete theory.

### APPENDIX

In this Appendix we demonstrate various numbering schemes for handling the configuration interaction. For simplicity we consider only the ground state  $\psi^A$  and the single excited configuration  $\psi^B$ , and we neglect overlap of wave functions except insofar as it is involved in transfer and exchange integrals. We will discuss three methods of numbering the orbitals.

*First Method.*—This is the same as used in the text, that is:

$$\begin{array}{ccc} & a & b & c \\ \psi^A: & \alpha_3 & \alpha_1 = \alpha_2 & \alpha_4 \\ \psi^B: & \beta_3 & \beta_4 & \beta_1 = \beta_2 \end{array}.$$

The secular matrix is

$$\begin{vmatrix} (H_I^{AA} - W) & (H_{14}^{AB}P_{14} + H_{24}^{AB}P_{24}) \\ (H_{14}^{BA}P_{14} + H_{24}^{BA}P_{24}) & (H_I^{BB} + H_{34}^{BB}P_{34} - W) \end{vmatrix}. \quad (\text{A.1})$$

We define the transfer integral  $b$ , the exchange integral  $J'$ , and the energy difference between the ground and excited states  $\Delta E$  as follows:

$$\begin{aligned} b &= \int \varphi_b(1)H(1)\varphi_c(1)d\tau; \\ J' &= \int \varphi_a(3)\varphi_b(4)H(3,4)\varphi_b(3)\varphi_a(4)d\tau_3d\tau_4; \end{aligned} \quad (\text{A.2})$$

$$\Delta E = H_I^{BB} - H_I^{AA}.$$

Since  $H_{14}^{AB} = H_{24}^{AB} = b$ , and we can use (12) of the text, we find by the method of the text that the superexchange is given by

$$\Delta W = -2J'(b/\Delta E)^2 \mathbf{S}_3 \cdot \mathbf{S}_4. \quad (\text{A.3})$$

This is the Anderson term for a single excited configuration.

*Second Method.*—The numbering scheme is the same

as the first method, except

$$\psi^B: \quad \beta_4 \quad \beta_3 \quad \beta_1 = \beta_2.$$

The secular matrix now becomes

$$\begin{vmatrix} (H_I^{AA} - W) & (H_{134}^{AB}P_{134} + H_{234}^{AB}P_{234}) \\ (H_{143}^{BA}P_{143} + H_{243}^{BA}P_{243}) & (H_I^{BB} + H_{34}^{BB}P_{34} - W) \end{vmatrix}. \quad (\text{A.4})$$

We note that  $H_{143}^{BA} = H_{243}^{BA} = b$ , and we may use Eq. (32) since we still have  $P_{12} = 1$  everywhere in the matrix. We obtain

$$\Delta W = (bP_{34}^\sigma)(-2J'\mathbf{S}_3 \cdot \mathbf{S}_4)(bP_{34}^\sigma)/(\Delta E)^2. \quad (\text{A.5})$$

This readily reduces to (A.3).

*Third Method.*—The numbering scheme is the same as the first method, except

$$\psi^B: \quad \beta_3 \quad \beta_1 \quad \beta_2 = \beta_4.$$

This is the method of Anderson. We note that  $P_{12} = 1$  in the ground configuration, whereas  $P_{24} = 1$  in the excited configuration. We may impose these restrictions by introducing the projection operators

$$O_{ij} = \frac{1}{2}(1 + P_{ij}). \quad (\text{A.6})$$

These operators have the eigenvalues 1 and 0 according to whether  $P_{ij}$  has the eigenvalues 1 or  $-1$ ; that is, the operators project out only the symmetric space functions, as is appropriate for identical orbitals. The secular matrix is

$$\begin{vmatrix} O_{12}(H_I^{AA} - W)O_{12} & O_{12}(H_I^{AB} + H_{24}^{AB}P_{24})O_{24} \\ O_{24}(H_I^{BA} + H_{12}^{BA}P_{12})O_{12} & O_{24}(H_I^{BB} + H_{13}^{BB}P_{13} - W)O_{24} \end{vmatrix}. \quad (\text{A.7})$$

We now use  $H_I^{BA} = H_{12}^{BA} = H_I^{AB} = H_{24}^{AB} = b$  and we obtain

$$\begin{aligned} \Delta W &= O_{12}(1 + P_{24})O_{24}O_{24}(-2J'\mathbf{S}_1 \cdot \mathbf{S}_2) \\ &\quad \times O_{24}O_{24}(1 + P_{12})O_{12}(b/\Delta E)^2. \end{aligned} \quad (\text{A.8})$$

This also reduces to the result (A.3). However, the method is more involved than that used in the text. We note that Anderson, in his paper<sup>2</sup> and in his lecture at the University of Tokyo (1953), took the nondiagonal element of (A.7) as  $b$  instead of  $b(1 + P_{12}) = b(1 + P_{24}) = 2b$  (when properly projected). Thus his numerical factor is different from ours.

The projection-operator method *must* be used, of course, if the cation orbitals  $c$  are not identical, as may be the case if the  $3d$  shell is less than half-full. The simple method of the text is adequate, however, for Mn, Fe, Co, and Ni salts.