

Antiferromagnetic Superexchange Effect

R. K. NESBET

Department of Physics, Boston University, Boston, Massachusetts

(Received December 21, 1959)

The delocalization effect recently proposed by Anderson as the principal contribution to the antiferromagnetic coupling of magnetic ions is analyzed by methods used in an earlier paper to derive the Heisenberg exchange operator formalism for both ferromagnetic and antiferromagnetic coupling. It is shown that Anderson's effect can be included, together with the superexchange correlation effect treated previously, as contributions to the Heisenberg exchange integral for ions of arbitrary spin. In the case of the antiferromagnetic oxides MnO, FeO, CoO, and NiO these two effects are found to be of comparable size, although the correlation effect is larger and determines the qualitative behavior of the Néel temperatures, which increase with decreasing spin through this sequence of transition metal ions. Agreement with the experimental Néel temperatures is significantly improved by including both effects.

INTRODUCTION

IN an earlier paper,¹ it was shown that the Heisenberg exchange operator formalism should be a valid description of the interaction of two paramagnetic ions in a crystal, either ferromagnetic or ferri- or antiferromagnetic, under assumptions considerably less restrictive than in previous derivations. In addition to the ordinary exchange integral, which contributes to ferromagnetic coupling, it was shown that a pure correlation effect, requiring the interaction of singly-occupied orbitals on the coupled magnetic ions with another doubly-occupied orbital, contributes to antiferromagnetic coupling. These were taken to be the dominant contributions to the two types of magnetic coupling. This antiferromagnetic effect should be especially large when a diamagnetic ion intervenes between the two coupled paramagnetic ions, as in the structure of the oxides MnO, FeO, CoO, and NiO. It was shown for these oxides that the behavior of the antiferromagnetic transition temperatures (Néel temperatures), which increase sharply with decreasing spin, could be accounted for by this effect.

An effect of a different nature has been proposed as the principal contribution to antiferromagnetic coupling in a recent paper by Anderson.² The effect emphasized by Anderson can be described within the context of the Hartree-Fock approximation, unlike the correlation effect mentioned above, which arises from the interaction of configurations that differ by two occupied orbitals. Anderson's effect amounts to the partial drift of an electron from one paramagnetic ion to another when, because the spins are oppositely oriented, a similar vacant orbital is available. This delocalization effect clearly can occur only for the antiferromagnetic state of ions, and hence contributes to antiferromagnetic coupling. A somewhat more abstract description of this effect is that two orbitals of opposite spin in the unrestricted Hartree-Fock approximation are not required to have orthogonal spatial factors. The spatial factors of orbitals of the same spin can always be taken to be

orthogonal, since any determinantal many-particle wave function with nonorthogonal occupied orbitals is equal to one with orthonormal orbitals, multiplied by a numerical factor. Hence a constraint is removed when two orbitals are given opposite spin, and the antiferromagnetic state of two coupled ions is stabilized by this effect.

It was assumed in the previous derivation of the Heisenberg formalism¹ that the effect proposed by Anderson can be neglected whenever the Heisenberg formalism is valid. This assumption has been found to be invalid. The present paper is concerned with an analysis of this effect, which is shown to be describable within the Heisenberg formalism, and to contribute a quantity of the same order of magnitude as the correlation effect considered earlier to the "exchange integral" in the case of the antiferromagnetic oxides MnO, etc. Although the correlation effect is the larger term, and alone shows an increase with decreasing spin, agreement with the experimental Néel temperatures is significantly improved by including the delocalization effect of Anderson.

ANALYSIS OF ANDERSON'S DELOCALIZATION EFFECT

Because of the well-known difficulties in many-particle calculations when sets of orbitals are used which are not orthonormal, it is convenient to analyze the delocalization effect by the method of superposition of configurations, using only one orthonormal set of orbitals for all states.

If it is assumed that the orthonormal set of spatial orbitals are obtained from a Hartree-Fock calculation on the ferromagnetically coupled system of two paramagnetic ions, then the Hartree-Fock equations and self-consistent orbitals for the corresponding antiferromagnetically coupled system would be somewhat different, because of the absence of exchange integrals between orbitals of opposite spin. If the same spatial orbitals are used in the two cases, configuration interaction effects occur which compensate for the constraint on the orbitals that this introduces in the antiferro-

¹ R. K. Nesbet, *Ann. Phys.* **4**, 87 (1958).

² P. W. Anderson, *Phys. Rev.* **115**, 2 (1959).

magnetic case. As shown in an earlier paper,³ these effects are described by the superposition of determinantal wave functions that differ by only one orbital.

Only the symmetrical case of identical paramagnetic ions will be considered. In the ferromagnetic state all singly-occupied orbitals have parallel spin, which will be taken to be positive. The Hartree-Fock equations for positive spin orbitals can be solved exactly, and spatial factors of orbitals of negative spin chosen to be identical with those of positive spin that correspond to doubly-occupied orbitals. This last restriction introduces configuration interaction effects which in general can be expected to be small, and represent the exchange polarization of the diamagnetic system by the unbalanced spin of the singly-occupied orbitals.

The singly-occupied orbitals can be taken to be eigenfunctions of an effective one-particle spatial operator \mathcal{H}_F , which contains negative exchange potential contributions from each singly-occupied orbital. In the case of two identical ions in a symmetrical environment these eigenfunctions will have definite parity, and will be distributed either symmetrically or antisymmetrically about the two ions. If only two ions are concerned, there would be two eigenfunctions a_g (even) and a_u (odd) for each independent singly-occupied orbital a localized on one ion. If the mirror-image of a on the other ion is a' , and a and a' are taken to be orthonormal, they are related to a_g and a_u by a unitary transformation. The localized orbitals are equivalent orbitals in the sense of Lennard-Jones⁴ and will have identical energies. If the eigenfunctions a_g and a_u have energies ϵ_g and ϵ_u , respectively, then

$$(a, \mathcal{H}_F a') = \frac{1}{2}(\epsilon_g - \epsilon_u). \quad (1)$$

Similarly there will be a matrix element of \mathcal{H}_F proportional to the width of the appropriate ferromagnetic state energy band between any two corresponding orbitals (Wannier functions) localized on different ions in a crystal. Clearly \mathcal{H}_F can be diagonalized over the set of orbitals localized on any single ion, so only matrix elements between different ions have to be considered.

If orbital a and others localized on the same ion are occupied with positive spin, and orbital a' and others on a second ion are occupied with negative spin, matrix elements of the form of Eq. (1) plus some additional exchange integrals lead to the delocalization effect of Anderson. These matrix elements describe the tendency of an occupied orbital a' to mix with unoccupied orbital a of the same spin, and vice versa.

The precise matrix elements involved are those between the Slater determinant Φ_0 , in which orbitals on the two different ions are occupied with opposite spin, and another Slater determinant Φ_E in which orbital $a'\beta$ has been replaced by $a\beta$, so that orbital a is doubly occupied. Exactly the same effect occurs between Φ_0

and the Slater determinant $\Phi_{E'}$, in which orbital a' is doubly occupied.

The matrix element between Φ_0 and Φ_E can be expressed in terms of an effective one-electron operator \mathcal{H}_0 , the Hartree-Fock operator for Φ_0 . This differs from \mathcal{H}_F in that when \mathcal{H}_0 is applied to orbitals of positive spin, only exchange potential terms from the occupied orbitals of positive spin occur; when applied to orbitals of negative spin, only exchange potential terms from occupied orbitals of negative spin occur. The matrix element to be evaluated is³

$$\begin{aligned} (\Phi_E, H\Phi_0) &= (a\beta, \mathcal{H}_0 a'\beta) \\ &= (a, \mathcal{H}_F a') + \sum_j [aa_j | a'a_j], \end{aligned} \quad (2)$$

where the index j runs over all singly-occupied orbitals of positive spin in Φ_0 . The bracket symbol $[a_i a_j | a_k a_l]$ is Mulliken notation for the electrostatic interaction between charge distribution $a_i a_j$ and charge distribution $a_k a_l$. Since all orbitals are orthonormal, the exchange integrals in Eq. (2) may in general be expected to be very small, and by Eq. (1), $(\Phi_E, H\Phi_0)$ is approximately proportional to the difference of energies of the odd and even two-center orbitals, or to the energy band width in the ferromagnetic state of a crystal.

The remainder of the analysis of the delocalization effect follows exactly the derivation of the Heisenberg exchange formula given previously.¹ Matrix elements H_{E0} of the many-electron Hamiltonian between the projected determinants (eigenfunctions of total spin) obtained from Φ_0 and Φ_E are calculated, as are the energy mean values H_{EE} and H_{00} of the projected determinants.

If there are $n=2S$ singly-occupied orbitals on each ion with spin S (which remains a good quantum number for all of the projected states of total spin S' of the coupled ions), then the dominant terms in $H_{EE} - H_{00}$ are independent of spin, and for given S' ,

$$H_{E0} = \left[\frac{n(n+1) - S'(S'+1)}{n^2} \right]^{\frac{1}{2}} (\Phi_E, H\Phi_0). \quad (3)$$

Hence by second-order perturbation theory

$$\begin{aligned} \Delta E(S') &= - \frac{H_{E0}^2}{H_{EE} - H_{00}} \\ &= \text{const} + \frac{S'(S'+1)}{n^2} \frac{(\Phi_E, H\Phi_0)^2}{H_{EE} - H_{00}}. \end{aligned} \quad (4)$$

For identical ions, the matrix elements $(\Phi_E, H\Phi_0)$ and $(\Phi_{E'}, H\Phi_0)$ are both equal to $(a, \mathcal{H}_0 a')$, which is the same for both spins. Since H_{EE} and $H_{E'E'}$ are also equal, this doubles the energy effect. When all singly-occupied orbitals a_k are taken into account, the "exchange integral" becomes

$$J = \frac{1}{4S^2} \{C - D - E\}, \quad (5)$$

³ R. K. Nesbet, Proc. Roy. Soc. (London) **A230**, 312 (1955).

⁴ J. E. Lennard-Jones, Proc. Roy. Soc. (London) **A198**, 14 (1949).

where the terms C and D are the ordinary exchange and correlation superexchange terms, respectively, considered before,¹ and the term

$$E = \sum_k \frac{2(a_k | \mathcal{H}_0 | a'_k)^2}{H_{EE} - H_{00}} \quad (6)$$

is due to the delocalization effect of Anderson.² Since Φ_0 is assumed to represent the ground state of the system, the denominator in Eq. (6) must be positive for consistency, and the coupling effect is always antiferromagnetic.

NÉEL TEMPERATURES OF THE ANTIFERROMAGNETIC OXIDES

In the oxides MnO, \dots , NiO each two paramagnetic ions that are antiferromagnetically coupled are separated by an $O^{=}$ ion, with the three ions lying in a straight line.⁵ The magnetic ions are sufficiently far apart, separated by a large negative ion, that it should be a reasonable approximation to neglect all matrix elements which involve products of orbitals aa' , or of their derivatives, where a and a' are localized orbitals on different paramagnetic ions.

Under this approximation, the matrix element of Eq. (2) reduces to a sum of terms which arise from the exchange potential contributions of the doubly-occupied orbitals of the system. This is exactly the form of the matrix element that occurs in the numerator of the expression for the correlation term D of Eq. (5), derived previously. Hence exactly the same general remarks apply, and by an appropriate choice of basis, to pick out a single intervening orbital b for which the superexchange effect is greatest, the contribution E of Eq. (6) becomes

$$E \cong \sum_k \frac{2[ba_k | ba'_k]^2}{H_{EE} - H_{00}}. \quad (7)$$

The total $D+E$ is then proportional to $1/\Delta E + 2/\Delta E'$ where ΔE , the denominator in the correlation term D , is estimated by Eq. (34) of reference 1,⁶ and an approxi-

mate value of $\Delta E'$ can be calculated from the formula

$$\begin{aligned} \Delta E' = & (\text{energy of } X^+ - \text{energy of } X^{++}) \\ & + (\text{energy of } X^{+++} - \text{energy of } X^{++}) \\ & + (\text{Coulomb energy difference between point} \\ & \text{charge arrays } +3, -2, +1 \text{ and } +2, -2, \\ & +2 \text{ at the observed lattice spacing}). \end{aligned} \quad (8)$$

The required difference in energies of ions are taken for configurations $(3d)^n$ from spectroscopic data on the free paramagnetic ions.⁷ Since $[ba | ba']$ is not known only the ratios between the four exchange integrals J can be calculated.

Results are given in Table I. When compared with the calculation using $1/\Delta E$ alone,¹ the present results are considerably closer to agreement with experiment. It should be noted that the most striking feature of the Néel temperatures, the rapid increase with decreasing spin, is entirely dependent on the correlation term $1/\Delta E$, since $2/\Delta E'$ is approximately the same for all four ions.

The integral $[ba | ba']$ can be approximated by the electrostatic interaction between two parallel electric dipoles separated by the ionic diameter of $O^{=}$. Since this varies only as the inverse cube of distance, and since in a crystal the ionic diameter of $O^{=}$ is roughly independent of its environment, it is reasonable to treat $[ba | ba']$ as independent of the paramagnetic ion, as has been done here. The value of $[ba | ba']$ required to fit the transition temperature of MnO is approximately 0.1 ev.

DISCUSSION

The case of the antiferromagnetic oxides considered here is especially simple, because the complete separation of the coupled ions by an intervening diamagnetic ion can be expected to have the effect of making the numerators of the terms D and E identical.

A much more complicated situation might be expected in the corresponding fluorides MnF_2 , etc., since the F^- ions are not located directly on the lines between coupled paramagnetic ions. The fact that two coupled ions are to a certain extent in direct contact with each other will increase the ordinary exchange term C , and will introduce more structure into the numerator of the delocalization term E . The denominator of the correlation term

neighbors. This gives a change in electrostatic energy, including the Madelung energy, of only 39 ev, less than the value used in calculating ΔE . In view of this, the net effect of the change in electrostatic energy for a transition involving neighboring ions should probably be considered as an empirical quantity. The agreement with the Néel temperatures found here would be destroyed by any large change of this quantity (10 ev or more). This suggests that the values of ΔE used here are reasonable estimates despite the fact that they depend on the cancellation of various large electrostatic effects depending on the electronic charge distribution. These effects are very small in the case of $\Delta E'$, since the transition involves only non-neighboring ions, and the Madelung term vanishes by symmetry.

⁷ C. E. Moore, *Atomic Energy Levels*, National Bureau of Standards Circular No. 457 (U. S. Department of Commerce, Washington, D. C., 1952), Vol. II.

⁵ C. G. Shull, W. A. Strauser, and E. O. Wollan, *Phys. Rev.* **83**, 333 (1951).

⁶ Note added in proof.—The denominator ΔE for the correlation effect, calculated in the previous paper,¹ contains a large term representing the change in electrostatic energy. This term is very sensitive to the details of the electronic charge distribution when it arises from transfer of charge between contiguous ions, and is subject to a large correction arising from the change in Madelung energy. Neglecting both of these effects, the electrostatic term for MnO was calculated to be 42.2 ev. On the point charge model, the Madelung correction is approximately 24 ev. However, the point charge model greatly overestimates the polarity of the charge distribution, as is known from the dipole moments of polar molecules. In the transition from the p_σ orbital on $O^{=}$ to the d_σ orbital on Mn^{++} , to the extent that the corresponding orthogonalized orbitals interpenetrate, the charge transfer is just the opposite to that indicated by the point charge model. For example, if as much as half of the charge associated with the $O^{=}p_\sigma$ orbital is in the same region of the MnO bonds as are the corresponding lobes of the d_σ orbitals, the net effect of the transition considered is to transfer half of an electronic charge from $O^{=}$ to each of its two Mn^{++}

TABLE I. Néel temperatures of the antiferromagnetic oxides.

Crystal	Spin	$1/\Delta E$	$2/\Delta E'$	Total	$kT_N/4S^2J^a$	T_N : calc.	observed ^b
MnO	$\frac{5}{2}$	0.1287 ev^{-1}	0.1198 ev^{-1}	0.2485 ev^{-1}	1.128	(116)°K	116°K
FeO	2	0.2020	0.1768	0.3788	1.202	188	186
CoO	$\frac{3}{2}$	0.3096	0.1546	0.4642	1.323	254	292
NiO	1	0.5917	0.1492	0.7409	1.552	476	523

^a From results for the antiferromagnetic simple cubic lattice by P. W. Kasteleijn and J. Van Kranendonk, *Physica* **22**, 367 (1956).

^b M. Foëx, *Compt. rend. acad. sci. (Paris)* **227**, 193 (1948).

D will include the large energy difference $E(F^+) - E(F^-)$ and in addition will be increased because the orbital b which interacts most strongly with orbitals on both paramagnetic ions must probably be thought of as a hybrid constructed from $2s$ as well as $2p$ orbitals of F^- . Hence the term D should be very small for the fluorides. This can account qualitatively for the relatively low transition temperatures of the fluorides.⁸ A more detailed analysis would have to take into account the distance dependence of the ordinary exchange integrals and the special exchange integrals occurring in Eq. (2), as well as the width of the d -orbital energy band, which enters through Eq. (1).

In a recent paper,⁹ Keffer and Oguchi have considered a contribution to the antiferromagnetic "exchange integral" which differs qualitatively from both of the effects considered here [terms D and E of Eq. (5)]. The effect considered by Keffer and Oguchi arises from the exchange polarization of a diamagnetic ion intervening between two paramagnetic ions. Their formalism is based on nonorthogonal orbitals.

The general method of the present paper can be used to analyze this effect in terms of orthonormal self-consistent orbitals. If the orbitals are chosen to be eigenfunctions of the Hartree-Fock effective Hamiltonian for orbitals of negative spin, in the Slater determinant in which all singly occupied orbitals have positive spin, it follows immediately from Brillouin's theorem⁸ that this determinant has no configuration interaction matrix elements with determinants of the configurations considered by Keffer and Oguchi. However, since the effective Hamiltonian for the Slater determinant that corresponds to antiferromagnetic coupling differs from that for ferromagnetic coupling, there will be matrix elements for states of lower spin, and the antiferromagnetic state will be stabilized relative to the ferromagnetic state.

The energy is given by a formula similar to Eq. (4). The numerator in this formula, in the case considered by Keffer and Oguchi, will contain only the exchange integrals which represent the difference between the effective Hamiltonians for the ferromagnetic and antiferromagnetic states. These integrals involve charge distributions which are products of orthogonal orbitals localized on different ions, in particular on the two paramagnetic ions. The denominator in the energy

formula in this case is more difficult to estimate than those previously considered, since it requires an estimate of the first ionization potential of O^- in the environment of an oxide crystal. The estimate used in the present work¹ for the double ionization energy was obtained originally from data for O^- in such crystals. The energy is measured relative to neutral oxygen, which should be much less sensitive to environment than are negative ions. Data on the free O^- ion is not immediately applicable here because of the large effect to be expected from the environment for a negative ion. If all effects are included it might be estimated that the energy denominator is roughly half or one-quarter of the quantity ΔE considered here, and proportional to it. The numerator consists only of integrals of the kind that have been considered to be negligible in the argument of the present paper. However, the denominator may be sufficiently small that there would be an appreciable contribution from this effect. It combines with the term D of Eq. (5) to give the observed increase of T_N through the sequence of oxides. It might be expected that the effect considered by Keffer and Oguchi would be of more importance in the case of the fluorides, because the integrals in the numerator would be larger.

It is found in molecular calculations that integrals of the kind neglected here, in going from Eq. (6) to the approximation given by Eq. (7), are decreased by very large factors by transforming from nonorthogonal to orthogonal localized orbitals. A detailed discussion of this point has been given by McWeeny,¹⁰ who gives several numerical examples. McWeeny finds this factor of diminution to be ten or twenty. Since even for non-orthogonal orbitals these integrals decrease exponentially with distance, the integrals involving the overlap product aa' of orthogonal orbitals localized on two non-contiguous paramagnetic ions can consistently be neglected, as is done here. This includes the kinetic energy integrals, which can be expressed as integrals of the products of derivatives of such orbitals.

In view of recent work by Coles, Orton, and Owen¹¹ on Mn impurities in MgO, which indicates that the nearest-neighbor and next-nearest-neighbor interactions between paramagnetic ions are of comparable magnitude, it is important to point out that the Néel temperatures of the oxides should depend only on the

⁸ J. W. Stout and H. E. Adams, *J. Am. Chem. Soc.* **64**, 1535 (1942); J. W. Stout and E. Catalano, *Phys. Rev.* **92**, 1575 (1953).

⁹ F. Keffer and T. Oguchi, *Phys. Rev.* **115**, 1428 (1959).

¹⁰ R. McWeeny, *Proc. Roy. Soc. (London)* **A227**, 288 (1955).

¹¹ B. A. Coles, J. W. Orton, and J. Owen, *Phys. Rev. Letters* **4**, 116 (1960).

next-nearest-neighbor interaction that is considered here. This follows from a theorem proved by Anderson¹² in connection with the Weiss molecular field model. This theorem states that the Néel temperature is a direct measure of the amount of energy due to the magnetic alignment in the long range ordered structure stable at low temperatures. Since in the oxides considered here this ordered structure is such that the nearest-neighbor interactions cancel each other out, only the next-neighbor interaction should contribute to the Néel temperature. According to Anderson's calculation, the large ratio between θ , the Curie-Weiss constant, and T_N can be attributed to the relatively strong nearest-neighbor interactions, which become important when the long range order breaks down, at temperatures above T_N .

Recently, various contributions to the exchange integral in MnO have been estimated by Kondo,¹³ through fairly detailed calculations based on expansion in powers of the overlap integrals between nonorthogonal nearest neighbor atomic orbitals. He finds that the largest effect is due to exchange polarization of the oxygen ion, not by replacing oxygen orbitals by the unoccupied d orbitals on Mn, as in the case of Keffer and Oguchi,⁹ but by unoccupied orbitals localized at the oxygen ion. Such orbitals would necessarily have quite large energies, greater than the ionization potential of oxygen, since they are considerably more localized than the orbitals of the spectroscopic series of oxygen. When Brillouin's theorem is taken into account, the numerators in the perturbation formula reduce to two-center exchange integrals, involving two different orthogonal orbitals on oxygen. These should be of the order of magnitude of the numerator of the correlation term D of Eq. (5), while the denominator is necessarily very much larger. Hence this effect might be estimated to be quite small compared with D and E of Eq. (5), and perhaps smaller even for the oxides than the principal effect considered by Keffer and Oguchi. Kondo's result may in part be attributed to the general difficulty of estimating small effects by approximate methods, when they appear in the formalism as differences of larger quantities of opposite sign. The use of Brillouin's theorem in the present work allows the small effects under consideration to be estimated directly, since they are represented as corrections to a quantity that is necessarily zero in the Hartree-Fock approximation.

Of course, it is not possible to compare results of the various approaches considered here term by term, since wave functions expressed in terms of nonorthogonal orbitals may in fact contain large components of what would be described as different configurations when using orthogonal orbitals. As is shown by the comments

here, there is some advantage to the consistent use of orthogonal orbitals for purposes of cataloging qualitatively different effects in configuration interaction.

The inherent limitations on the quantitative accuracy of the approximations made in this paper should be emphasized. The purpose of this work is to develop a semiempirical theory of the Heisenberg exchange operator, not to make accurate quantitative calculations. The principal requirement is that of internal consistency. The example of the antiferromagnetic oxides allows a consistency test of the theoretical approach that involves a minimum of empirical data. According to the theoretical results, the ratios of Néel temperatures of the oxides should depend primarily on the energy differences estimated here by the simplest possible approximation. The numerical agreement with these ratios is probably better than might have been anticipated. However, the basic argument in this work is that intraatomic energies are large compared with interatomic energies in molecules and crystals, and hence that significant distortions of the atomic orbitals except in their outer regions are costly in energy, and unlikely to occur. From this point of view, the ionization potentials of neutral atoms or positive ions cannot be greatly affected by their environment, except for the gross change of potential energy taken into account by the model of point charges. Of course this kind of approximation can only be used when the structure of a molecule or crystal is such that Hartree-Fock orbitals can be localized at a single atom (i.e., ionic molecules or crystals). Otherwise the appropriate model would have to be based on molecular units large enough for single orbitals to be localized in them. This point is discussed in the previous paper¹ in connection with the problem of applicability of the present ideas to metals. Given a valid ionic model, in the above sense, the changes in structure of a localized orbital in a crystal from the corresponding free atom orbital should be small enough to justify the approximations used here and to estimate the energy denominators within a few electron volts.

In situations such as that of the fluorides, where several effects of comparable magnitude probably have to be considered, the present approach could be used in connection with quantitative estimates of the numerators occurring in the perturbation formula, and with more detailed estimates of the denominators. For this purpose, to sort out the various different contributions to the effective exchange integral, it would be desirable to have data from reliable *ab initio* calculations on systems of two or three atoms.

ACKNOWLEDGMENT

The author is indebted to Dr. P. W. Anderson for very helpful correspondence on this subject.

¹² P. W. Anderson, Phys. Rev. **79**, 705 (1950).

¹³ J. Kondo, Progr. Theoret. Phys. (Kyoto) **22**, 41 (1959).