

Molecular Model of the Heisenberg Exchange Interaction*†

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The electronic wave function of N_2 has been calculated for a series of internuclear distances, in the simplest LCAO approximation, including the principal effects of configuration interaction. As the internuclear distance increases there is a well-defined sequence of regions in which the ground state is most closely approximated by configurations in which successively more orbitals are represented as localized functions (definitely associated with one of the two atoms) rather than as the odd or even linear combinations of these appropriate to the full molecular symmetry. This corresponds to a continuous change in the nature of the unrestricted Hartree-Fock valence orbitals from molecular to atomic character as the atoms are separated. In the intermediate range of internuclear separation, it is a better approximation to treat some of the valence orbitals as modified atomic orbitals, coupled

by an antiferromagnetic Heisenberg exchange interaction, than as molecular orbitals. Various contributions to the Heisenberg "exchange integral," of the kinds considered for the transition metals, are evaluated and compared. It is found that the ordinary direct exchange (which leads to ferromagnetic coupling) is small compared with the sum of the various antiferromagnetic effects, none of which can be described within the traditional Hartree-Fock approximation, which for solids becomes the energy band theory. A method is proposed by which the magnetic interaction in solids could be evaluated quantitatively, by modifying the usual energy band calculations in the same way that the usual molecular orbital theory is modified in the present work. Similar refinements to the band theory of the transition metals have recently been proposed by Goodenough on empirical grounds.

I. INTRODUCTION

AT a very early stage in the development of quantum mechanics, the Heitler-London calculation of the binding energy of the H_2 molecule¹ established the basis for the quantum theory of the chemical bond, and provided in the subsequent work of Heisenberg² a qualitative explanation of the phenomenon of ferromagnetism. Despite the fact that the particular formalism used by Heitler and London cannot be very easily applied to molecules more complicated than H_2 , the idea of chemical binding through an exchange interaction has proved to be a very fruitful concept. It underlies the valence bond theory of chemistry and most of the subsequent development of the theory of magnetic materials.

Despite the value of the Heitler-London theory as an intuitive scheme, there are important theoretical and practical objections to attempts to apply it to systems more complicated than H_2 .³ It is possible to develop the theory of chemical binding, using the molecular orbital theory, without ever introducing the non-orthogonal spatial orbitals that are the most awkward feature of the Heitler-London theory. As has been shown in recent papers,⁴ this is also possible in the theory of the Heisenberg exchange interaction.

The purpose of the present paper is to work out, for the N_2 molecule, a detailed calculation of the mechanism

of covalent binding. At large internuclear distances, the simplest approximation to the lowest state of this molecule is given by the Heisenberg formalism, describing an antiparallel coupling of the spins of orbitals associated with the two different atoms. At small internuclear distances the lowest state is more adequately described by the usual ground state configuration of molecular orbital theory.

The method used is a straightforward application of a general method for many-electron systems⁵ (Hartree-Fock calculation followed by use of perturbation theory to estimate configuration interaction effects), facilitated by restricting the spatial orbitals to a single orthonormal set, by being more careful than is usual in the molecular orbital theory to choose the configuration of lowest energy at large internuclear distances, and by using the projection operator formalism to pick out many-electron wave functions that have well-defined total spin.

The calculations, although within the context of the molecular orbital theory, lead in a natural way to the concept of exchange coupling between localized electrons at large internuclear distances, an idea that is the principal contribution of the Heitler-London theory to the theory of magnetic interactions. It has already been shown in the case of H_2 , as discussed by Slater,⁶ that such an exchange coupling is describable within the molecular orbital theory if the correct configuration is used at large internuclear distances (so that orbitals of different spin are not constrained to be identical). Slater points out that this effect is inherent in the Hartree-Fock theory, and is needed to describe the phenomenon of antiferromagnetism.

Here this argument is extended to a more complicated case, the N_2 molecule, which provides at large inter-

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† A preliminary account of this work has been given at the Neutron Diffraction Conference, Gatlinburg, Tennessee, April, 1960 (unpublished).

¹ W. Heitler and F. London, *Z. Physik* **44**, 455 (1927).

² W. Heisenberg, *Z. Physik* **49**, 619 (1928).

³ J. C. Slater, *Revs. Modern Phys.* **25**, 199 (1953).

⁴ R. K. Nesbet, *Ann. of Phys.* **4**, 87 (1958); *Phys. Rev.* **119**, 658 (1960).

⁵ R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955); *Revs. Modern Phys.* **33**, 28 (1961).

⁶ J. C. Slater, *Phys. Rev.* **82**, 538 (1951).

nuclear distances a model of the Heisenberg exchange interaction coupling the spins of weakly interacting valence orbitals. The formalism developed in earlier papers⁴ is used to calculate the effective exchange integral that characterizes this interaction.

One conclusion from the present work is that energy band calculations, if done by the usual methods, would not be capable of describing correctly the exchange coupling in magnetic materials, as has been recognized by Mott⁷ and by Slater.⁶ Application of the method of the present paper to the band theory of solids is discussed in Secs. VI and VII.

The molecular calculations carried out will not be reported in detail in the present paper, except for those results relevant to discussion of the $^1\Sigma_g^+$ ground state and the higher multiplets associated with it at large internuclear distances through the Heisenberg exchange interaction. A calculation of the same form as that carried out by Scherr⁸ at the equilibrium internuclear distance was done at each of the internuclear distances for which results are given here. Each calculation required evaluation of all possible integrals of the operators in the many-electron Hamiltonian for the smallest set of basis orbitals capable of describing the separated atoms, calculation of the Hartree-Fock orbitals for the usual ground state configuration approximated as linear combinations of this basis set, and transformation of all integrals to the basis of these orthonormal self-consistent orbitals. The exponents used for the basis orbitals were those obtained by Roothaan⁹ by variational calculations on the ground state of the nitrogen atom; they differ slightly from the Slater exponents used by Scherr. The calculations can be considerably improved by including more orbitals in the basis set, but this will not affect the qualitative results of the present work, such as the relative magnitude of various contributions to the effective Heisenberg exchange integral.

II. DESCRIPTION OF THE GROUND STATE

The method used in the present calculations is a compromise between the traditional molecular orbital theory, which would be based upon the ground-state configuration $\sigma_g^2\pi_u^4$ for the valence orbitals of N_2 at all internuclear distances, and the unrestricted Hartree-Fock method,⁵ based on a configuration constructed from nonorthogonal spatial orbitals as in the Heitler-London theory. In the first case, because the chosen configuration necessarily goes to ionic states of quite high energy in the limit of separated atoms, it is not possible to use perturbation theory to establish any simple relation between this configuration and the actual ground state wave function. In the second case, at intermediate internuclear distances the spatial

orbitals of one spin are neither identical with nor orthogonal to the spatial orbitals of the other spin, and the formulas for matrix elements of the many-electron Hamiltonian become very complicated if overlap integrals are included properly. In neither case can the part of the correlation energy that depends on total spin be separated out of the over-all calculation in an intuitively satisfying manner.

However, by looking a bit more carefully into the question of choosing a trial configuration, it is possible to avoid the difficulties of either extreme case, while retaining their advantages, i.e., to be able to apply second-order perturbation theory and still to use a single orthonormal basis of spatial orbitals. A reasonable starting point would be to find the Slater determinant constructed from orthonormal spatial orbitals that is closest to the unrestricted Hartree-Fock function. It is obvious from considering the nature of the wave function that describes two separated atoms in their ground states^{6,10} that the valence orbitals must be described by orthogonalized atomic orbitals in this limit, rather than by symmetry orbitals (σ_g or π_u) with respect to the full transformation group of the molecule. The requirement that the occupied orbitals have definite inversion symmetry is not compatible with the structure of the unrestricted Slater determinant of lowest energy for internuclear distances greater than a certain value; the same is true for the Slater determinant of lowest energy that can be constructed from a single set of orthonormal spatial orbitals.

The problem is to find, at each internuclear distance, the Slater determinant of restricted form (orthonormal spatial orbitals) of lowest energy when the requirement of inversion symmetry is relaxed. The occupied orbitals will be either symmetry orbitals for the molecule, or, in the sense of Lennard-Jones,¹¹ equivalent orbitals that may be thought of as symmetrically orthogonalized atomic orbitals. A fundamental property of a Slater determinant is that it is invariant up to a phase factor under any unitary transformation of the occupied orbitals.¹¹ This implies that there is no difference between Slater determinants constructed from orthonormal orbitals σ and σ' , equivalent but localized about the two different atoms, so long as both are occupied with the same spin, and the determinants constructed from the corresponding even and odd molecular symmetry orbitals σ_g and σ_u , again if both are occupied with the same spin. In the present paper, the localized equivalent orbitals are taken to be

$$\begin{aligned}\sigma &= (\sigma_g + \sigma_u)/\sqrt{2}, \\ \sigma' &= (\sigma_g - \sigma_u)/\sqrt{2},\end{aligned}$$

¹⁰ C. A. Coulson and I. Fischer, *Phil. Mag.* **40**, 386 (1949); J. C. Slater, *J. Chem. Phys.* **19**, 220 (1951); R. K. Nesbet, *Mass. Inst. Technol. Quart. Progr. Rept., Solid State and Molecular Theory Group*, January 15, 1955, pp. 18-22 (unpublished).

¹¹ J. E. Lennard-Jones, *Proc. Roy. Soc. (London)* **A198**, 1, 14 (1949); G. G. Hall and J. E. Lennard-Jones, *ibid.* **A202**, 155 (1950); J. E. Lennard-Jones and J. A. Pople, *ibid.* **A202**, 166 (1950).

⁷ N. F. Mott, *Proc. Phys. Soc. (London)* **A62**, 416 (1949).

⁸ C. W. Scherr, *J. Chem. Phys.* **23**, 569 (1955).

⁹ C. C. J. Roothaan, *Tech. Rept., Laboratory of Molecular Structure and Spectra*, University of Chicago, 1955, pp. 24-47 (unpublished).

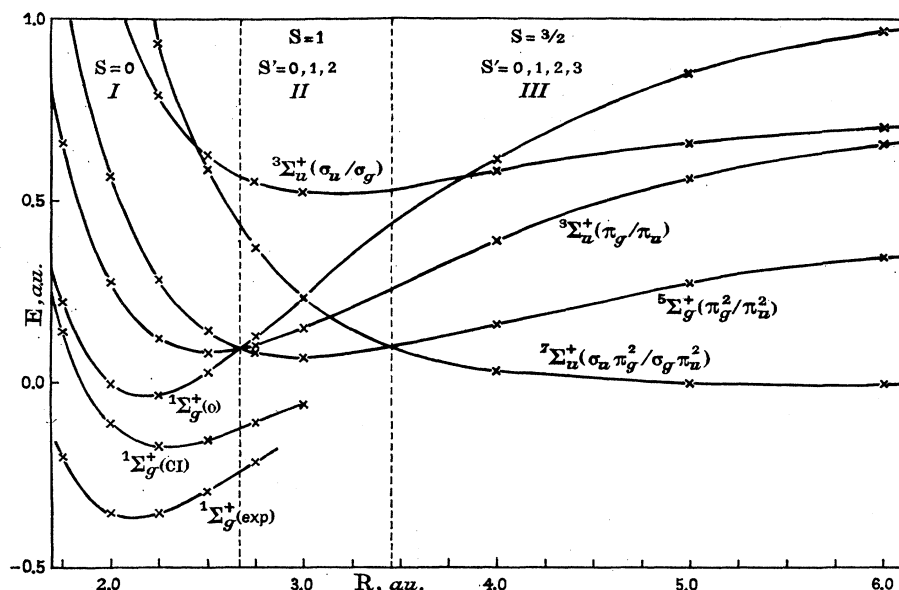


FIG. 1. Energies of projected determinants obtained from Φ_0 , the approximate ground-state wave function of molecular orbital theory, with configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 \pi_u^4$, by replacing bonding orbitals by antibonding orbitals as indicated. Energies are calculated relative to the $4S$ states of the separated atoms, calculated with the same basis orbitals. The experimental curve is taken from Vanderslice, Mason and Lippincott [J. T. Vanderslice, E. A. Mason and E. R. Lippincott, J. Chem. Phys. **30**, 129 (1959)], shifted to give a dissociation energy of 9.8 ev, the value recommended by Gaydon [A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall Ltd, London, 1953), 2nd ed.]. The units are Hartree atomic units, such that 1 a.u.(energy) = 27.21 ev and 1 a.u.(distance) = 0.5292 Å.

with corresponding formulas for the π orbitals. Thus, for the two molecular inner shells in N_2 ,

$$\det(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2) \equiv \det(1\sigma^2 1\sigma'^2 2\sigma^2 2\sigma'^2). \quad (1)$$

As the atoms separate, $1\sigma \rightarrow 1s$ and $2\sigma \rightarrow 2s$. Hence the inner shells can equally well be described as orbitals of molecular or atomic type at all internuclear distances.

This is not true for the valence orbitals in general, which will either be described by doubly occupied molecular orbitals, or by singly occupied orbitals identified with the separate atoms. In the latter case, the dependence of energy upon the relative orientation of the spin of orbitals on the two atoms leads to the spin coupling usually described by the Heisenberg exchange operator.⁴ If configuration interaction effects are left out of account, Hund's rule will apply to the molecule as a whole, and the single determinant of lowest energy will be that in which all singly occupied orbitals have the same spin. This particular single determinant is a pure spin state. In the case of two identical atoms, corresponding orbitals from both atoms will be occupied with the same spin in this determinant. As in Eq. (1),

$$\det(\sigma\alpha\sigma'\alpha) \equiv \det(\sigma_g\alpha\sigma_u\alpha), \quad (2)$$

and similarly for the π orbitals.

By Eq. 2, the determinant of lowest energy belongs to a special sort of configuration in terms of the usual molecular orbitals—one in which a bonding valence orbital of one spin (such as $\sigma_g\beta$) occupied in the usual molecular orbital ground state configuration is replaced

by an antibonding orbital of the opposite spin ($\sigma_u\alpha$ in this case). The energy of such a determinant can be calculated easily from tables of integrals for the molecular orbitals. Energies of various Slater determinants of this type are plotted in Fig. 1, for several internuclear distances.

It should be emphasized that only the state of highest multiplicity in each case can be compared with the traditional molecular orbital ground state function Φ_0 . The states of lower multiplicity must be described in terms of atomic, not molecular, orbitals. In particular, the singlet derived from the pure triplet of Eq. (2) is not

$$[\det(\sigma_g\alpha\sigma_u\beta) + \det(\sigma_u\alpha\sigma_g\beta)]/\sqrt{2} \quad (3)$$

but

$$[\det(\sigma\alpha\sigma'\beta) + \det(\sigma'\alpha\sigma\beta)]/\sqrt{2}. \quad (4)$$

These two singlet functions have very different energies, and the second is not orthogonal to the molecular orbital singlet $\det(\sigma_g\alpha\sigma_g\beta)$. In fact, the singlet considered here is a linear combination of functions from several configurations in the usual molecular orbital theory. For example,

$$[\det(\sigma\alpha\sigma'\beta) + \det(\sigma'\alpha\sigma\beta)]/\sqrt{2} \\ = \det[(\sigma_g\alpha\sigma_g\alpha) - \det(\sigma_u\beta\sigma_u\beta)]/\sqrt{2}. \quad (5)$$

The single determinant $\det(\sigma\alpha\pi\alpha\pi'\alpha\sigma'\beta\pi'\beta\pi'\beta)$ is a linear combination of 64 different determinants constructed from molecular symmetry orbitals. Although the energy of the projected singlet can be worked out very easily in terms of the atomic orbitals, this would be a difficult

configuration interaction problem if it were approached by use of molecular symmetry orbitals. The corresponding problem in a paramagnetic solid would be intractable, if treated in terms of configurations constructed from Bloch waves (molecular symmetry orbitals for a solid).

As can be seen from Fig. 1, the restricted Hartree-Fock function of lowest energy has a different structure in three different regions. In region I, at small internuclear distances, the traditional molecular orbital function is lowest in energy; in this region all valence orbitals are bonding molecular orbitals, and no free spin is associated with the individual atoms. In region II, at intermediate internuclear distances, the $2p\pi$ orbitals are atomic in nature, and the $2p\sigma$ orbitals are molecular; spin $S=1$ is associated with each atom, coupled to total spin $S'=0, 1$ or 2 for the molecule. In region III, at large internuclear distances, both $2p\pi$ and $2p\sigma$ orbitals are atomic; spin $\frac{3}{2}$ is associated with each atom (corresponding to the $4S$ ground states of the separated atoms), coupled to total spin $0, 1, 2$, or 3 for the molecule.

In both regions II and III there are configuration interaction effects that depend on the total molecular spin S' . In so far as these are linear in S' ($S'+1$) they contribute, together with the ordinary exchange effect due to antisymmetry (always ferromagnetic in sign), to an effective Heisenberg exchange coupling. The various contributions to the net "exchange integral" are considered in the following sections.

III. LINEAR CONTRIBUTIONS TO THE EFFECTIVE EXCHANGE INTEGRAL

The method to be used here has been described in earlier papers.⁴ The essential point is that a Slater determinant with singly occupied orbitals contains components belonging to several different values of the total S' . These components are constructed by use of the appropriate projection operator. The expression *principal Slater determinant* will be used to denote the determinant of lowest energy in each of the regions discussed in Sec. II for which all spatial orbitals are orthonormal and for which $M_S=0$. In this determinant singly occupied orbitals of atomic form will have opposite spin on the two different atoms. The mean value of the energy and various spin-dependent configuration interaction effects are evaluated as functions of S' by considering the normalized functions proportional to the S' projections of the principal Slater determinant and of other determinants that interact with it. Matrix elements of the many-electron Hamiltonian for two such normalized projected determinants are evaluated from the following formula¹²:

$$(\Psi_\mu, H\Psi_\nu) = [(\Phi_\mu, H\{\Phi_\nu + \sum x_{\nu i} \Phi_{\nu i}\}) \times \langle \{\Phi_\mu + \sum x_{\mu j} \Phi_{\mu j}\}, H\Phi_\nu \rangle]^{1/2}, \quad (6)$$

¹² R. K. Nesbet, Ann. Phys. 3, 397 (1958).

where Ψ_μ and Ψ_ν are normalized functions proportional to the S' projections of Slater determinants Φ_μ and Φ_ν , respectively. If the orbitals are chosen from an orthonormal set, matrix elements of H vanish between Slater determinants differing by more than two orbitals. Because of this, the only coefficients $x_{\nu i}$ (matrix elements of the projection operator) that are required are those for which $\Phi_{\nu i}$ differs from Φ_ν by the exchange of the spins of a single pair of spatial orbitals. In the case under consideration, when each determinant has total $M_S=0$, these coefficients have been evaluated by Löwdin¹³ to be

$$x(n, S') = [n - S'(S'+1)]/n^2, \quad (7)$$

where n is the number of singly occupied orbitals of either spin ($\pm\frac{1}{2}\hbar$) and S' is the total spin, in units of \hbar .

The projected determinants describe a state with total spin S' of two coupled n -electron subsystems, in each of which the spin is well defined and equal to its maximum value $S=\frac{1}{2}n$. If the n orbitals of the same spin are orbitals belonging to one atom, and the orbitals of opposite spin belong to the other atom, then the corresponding projected determinants describe the spin coupling between these two atoms, each constrained to be in its state of maximum internal spin.

When the effect of configuration interaction is sufficiently small that the eigenvalues of total energy can be approximated by second-order perturbation theory (treating the nondiagonal part of the configuration interaction matrix as a perturbation) then the largest spin dependent contributions to the total energy are found to be linear in $x(n, S')$, hence linear in $S'(S'+1)$.⁴ In these circumstances the energy can be described by an effective Hamiltonian, of the form introduced by Heisenberg²:

$$H_{\text{eff}} = E_{\text{av}} - 2JS_i \cdot S_j. \quad (8)$$

This follows for $E(S')$ linear in $S'(S'+1)$, since then

$$E(S') = E_{\text{av}} - J[S'(S'+1) - 2S(S+1)], \quad (9)$$

where $S=\frac{1}{2}n$ for equivalent atoms. The present paper will consider contributions to the effective Heisenberg exchange integral J in the form:

$$4S^2J = n^2J = C - D - E - F - G. \quad (10)$$

The separate contributions to the effective exchange integral have been calculated for several internuclear distances for the configurations appropriate to regions II and III, and are listed in Table I. The terms F and G , which arise from polarization of the diamagnetic core by the unbalanced spin of the valence electrons, are found to be essentially nonlinear, and will be discussed in Sec. IV. The three terms C , D , and E are linear in $S'(S'+1)$ and have been considered in previous papers. The derivations are summarized here.

To simplify the discussion, it is convenient to intro-

¹³ P. O. Löwdin, Phys. Rev. 97, 1509 (1955).

TABLE I. Contributions to the effective exchange integral. Hartree atomic units (a.u.).

R	C	D	E	G ₁	G ₂	S'=0 S'=1, 2 4S ² J (a.u.)	(ev)
2.5 ^a	0.00620	0.00035	0.18601	0.00852	0.00036	-0.18904	-5.14
2.75	0.00409	0.00023	0.09985	0.00754	0.00128	-0.10480	-2.85
3.0	0.00259	0.00010	0.05412	0.00665	0.00280	-0.06108	-1.66
4.0 ^a	0.00030	0.00001	0.00430	0.00216	0.01447	-0.02064	-0.56

R	C	D	E	F ₁	F ₂	S'=0, 1, 2, 3 4S ² J (a.u.)	(ev)
3.0 ^a	0.07945	0.00012	0.34651	0.04357	0.01965	-0.33040	-8.99
4.0	0.01867	-0.00015	0.04104	0.00838	0.01113	-0.04173	-1.14
5.0	0.00361	-0.00003	0.00500	0.00165	0.00262	-0.00563	-0.15
6.0	0.00072	0.00000	0.00050	0.00035	0.00088	-0.00101	-0.03

^a Calculation extended into adjoining region, where perturbation formula is not expected to be valid.

duce an abbreviated notation for Slater determinants as follows:

$$\det(ba_1\alpha a_2\alpha b\beta a_1'\beta a_2'\beta) \equiv (ba_1a_2, ba_1'a_2'). \quad (11)$$

a_1, a_2, \dots will denote atomic orbitals of one atom; a_1', a_2', \dots equivalent atomic orbitals of the other; and b, c, \dots various molecular orbitals. Whenever possible the doubly occupied orbitals of the inner shells will be omitted from the notation, when they do not affect the matrix elements under consideration. Also only one valence orbital of atomic form such as a will be indicated specifically, although it is to be understood that when several such orbitals are present there will be contributions to matrix elements from each of these, and appropriate sums are to be taken. All spatial orbitals are normalized and mutually orthogonal.

The principal Slater determinant in each region will be of the form

$$\Phi_A = (bc \dots a_1a_2 \dots, bc \dots a_1'a_2' \dots). \quad (12)$$

Here the index A stands for "antiferromagnetic" since the structure of this determinant appears at first sight to be associated with coupling the free spin on one atom in a sense opposed to that on the other. However, the normalized projections of Φ_A , denoted by ${}^{2S'+1}\Psi_A$ (or simply Ψ_A when the meaning is clear), describe ferromagnetic as well as antiferromagnetic coupling, since the total spin S' ranges from zero to $2S=n$, for n singly-occupied orbitals on each atom.

The term C of Eq. (10) arises from the ordinary exchange integrals that result from the antisymmetry of the many-electron wave function. For arbitrary S' , from Eq. (6),

$$(\Psi_A, H\Psi_A) = \text{const} - x(n, S') \sum_i \sum_j [a_i a_j' | a_j' a_i]; \quad (13)$$

hence,

$$C = \sum_i \sum_j [a_i a_j' | a_j' a_i]. \quad (14)$$

Since the individual exchange integrals are non-negative, C is always ferromagnetic in effect. Here the bracket symbol is a two-electron integral of the Coulomb

interaction, in the notation,

$$[ab|cd] \equiv \int d\tau_1 \int d\tau_2 a^*(1)b(1)(1/r_{12})c^*(2)d(2). \quad (15)$$

The term D of Eq. (10) is a correlation effect due to interaction between Φ_A and determinants in which two core orbitals are replaced by two of the unoccupied atomic valence orbitals. If b is a doubly occupied core orbital, then the general form of the correlation effect is obtained by considering the interaction between a projected determinant:

$$\Psi_A \sim (ab, ba') + x(n, S') \{ (a'b, ba) + \dots \} + \dots, \quad (16)$$

and another projected determinant of the form

$$\Psi_D \sim (aa', aa') + \dots. \quad (17)$$

The difference between the diagonal matrix elements $(\Psi_D, H\Psi_D)$ and $(\Psi_A, H\Psi_A)$ can be approximated by

$$\begin{aligned} \Delta_D &= (\Phi_D, H\Phi_D) - (\Phi_A, H\Phi_A) \\ &= (a'\alpha, \mathcal{H}_A a'\alpha) + (a\beta, \mathcal{H}_A a\beta) - 2(b, \mathcal{H}_A b) \\ &\quad + [aa|a'a'] + [bb|bb] - 4[aa|bb] + 2[ab|ba], \end{aligned} \quad (18)$$

where \mathcal{H}_A is the effective one-electron Hamiltonian determined by the Slater determinant Φ_A .⁵ Here the fact that $[aa|bb] = [a'a'|bb]$ has been used; this follows from the molecular form of orbital b (either odd or even with respect to inversion of the molecule in the midpoint of its axis). Also, because of the structure of Φ_A , matrix elements $(a'\alpha, \mathcal{H}_A a'\alpha)$ and $(a\beta, \mathcal{H}_A a\beta)$ are equal.

The spin-dependent part of the correlation effect arises from the numerator of the second-order perturbation theory formula:

$$\Delta E(S') = -(\Psi_D, H\Psi_A)^2 / \Delta_D. \quad (19)$$

From Eq. (6) the matrix element in the numerator is

$$(\Psi_D, H\Psi_A) = \{1 + x(n, S')\}^3 [a'b|ab]. \quad (20)$$

Hence, substituting in Eq. (19), and picking out the coefficient of $S'(S'+1)/n^2$, we obtain

$$D = \sum_j [a_j' b | a_j b]^2 / \Delta_{Dj}. \quad (21)$$

Mixed terms, involving integrals such as $[a_j' b | a_k b]$, do not occur unless two atomic valence orbitals have the same axial angular momentum; in the case of N_2 the orbitals are σ , π , and π^* so there are no mixed terms if one chooses $(\pi_A)'$ to be π_B^* .

The derivation given above holds whenever there is a unique doubly occupied orbital that can be identified with the orbital b . This is the case only for the doubly occupied valence orbital σ_g in region II in the present calculations. If there are two doubly occupied orbitals of similar energy, as in the case of doubly occupied core orbitals of the two atoms, then the cross term involving the excitation of each into a different unoccupied atomic orbital must also be taken into account. Here this arises in the case of orbitals $2\sigma_g$ and $2\sigma_u$, both doubly occupied

in Φ_A . These orbitals will be denoted by b and c in the derivation. Consider the projected determinants of total spin S' :

$$\begin{aligned}\Psi_A &\sim (abc, bca') + x(n, S')\{(a'bc, bca) + \dots\} + \dots, \\ \Psi_{D1} &\sim (aba', aca') + x(n, S')\{(aca', aba') + \dots\} + \dots, \\ \Psi_{D2} &\sim (aca', aba') + x(n, S')\{(aba', aca') + \dots\} + \dots.\end{aligned}\quad (22)$$

By Eq. (6), $(\Psi_{D2}, \Psi_{D1}) = x(n, S') \neq 0$, so the perturbation theory must be based on the orthonormal odd and even linear combinations of Ψ_{D2} and Ψ_{D1} . Also, by Eq. (6),

$$\begin{aligned}(\Psi_{D1}, H\Psi_A) &= [a'c|ab] + x(n, S')[ac|a'b], \\ (\Psi_{D2}, H\Psi_A) &= [ac|a'b] + x(n, S')[a'c|ab].\end{aligned}\quad (23)$$

Hence for the orthonormal linear combinations, we have

$$\left(\frac{\Psi_{D1} + \Psi_{D2}}{[2 + 2x(n, S')]^{\frac{1}{2}}}, H\Psi_A\right) = \left[\frac{1+x}{2}\right] \times ([a'c|ab] + [ac|a'b]), \quad (24)$$

and

$$\left(\frac{\Psi_{D1} - \Psi_{D2}}{[2 - 2x(n, S')]^{\frac{1}{2}}}, H\Psi_A\right) = \left[\frac{1-x}{2}\right] \times ([a'c|ab] - [ac|a'b]). \quad (25)$$

As before, the difference in energy mean values is approximately that of the two determinants Φ_{D1} and Φ_A . This energy difference will be denoted by Δ . It can be taken to be identical for Ψ_{D1} and Ψ_{D2} . Then

$$\begin{aligned}\Delta E(S') &= -\frac{1+x}{2\Delta}([a'c|ab] + [ac|a'b])^2 - \frac{1-x}{2\Delta} \\ &\quad \times ([a'c|ab] - [ac|a'b])^2 \\ &= \text{const} - \frac{2}{\Delta}x(n, S')[a'c|ab][ac|a'b],\end{aligned}\quad (26)$$

Hence, picking out the coefficient of $S'(S'+1)/n^2$ as before, we have

$$D = \sum_j 2[a_j'c|a_jb][a_jc|a_j'b]/\Delta_j. \quad (27)$$

When c is odd and b is even, then

$$[a'c|ab] = -[ac|a'b]. \quad (28)$$

If both orbitals arise from the same atomic shell they can be denoted b_u and b_g , respectively, and

$$D = -\sum_j 2[a_j'b_u|a_jb_g]^2/\Delta_j. \quad (29)$$

An effect of this kind arises from the orbitals $2\sigma_u$ and $2\sigma_g$, asymptotically $2s_u$ and $2s_g$. Although this effect is nearly cancelled by the corresponding positive terms arising from virtual excitation of $2\sigma_u^2$ and $2\sigma_g^2$, the net effect of term D is ferromagnetic at large internuclear distances.

TABLE II. One-electron energies (principal Slater determinant) in atomic units.

R=	Region I			
	1.75	2.0	2.25	2.5
$2\sigma_g$	-1.65477	-1.51541	-1.38845	-1.28112
$2\sigma_u$	-0.73477	-0.74937	-0.76728	-0.78633
σ_g	-0.61372	-0.57677	-0.54341	-0.51123
σ_u	1.51603	1.13484	0.85479	0.65111
π_u	-0.73774	-0.63044	-0.54256	-0.47106
π_g	0.32213	0.25615	0.20304	0.16032
R=	Region II			
	2.75	3.0		
$2\sigma_g$	-1.17429	-1.10636		
$2\sigma_u$	-0.79592	-0.81576		
σ_g	-0.45944	-0.43133		
σ_u	0.50213	0.39328		
$\pi\alpha$	-0.53086	-0.52041		
$\pi\beta$	0.26613	0.27266		
R=	Region III			
	4.0	5.0	6.0	
$2\sigma_g$	-0.93413	-0.90514	-0.89612	
$2\sigma_u$	-0.84722	-0.87849	-0.88841	
$\sigma\alpha$	-0.47913	-0.49990	-0.50291	
$\sigma\beta$	0.33585	0.32755	0.32728	
$\pi\alpha$	-0.49921	-0.50274	-0.50326	
$\pi\beta$	0.32880	0.32782	0.32781	

The largest of all the terms considered here can be attributed to the delocalization effect discussed recently by Anderson.¹⁴ This term, denoted by E in Eq. (10), represents exchange polarization of an occupied atomic valence orbital as a result of interaction between Φ_A and determinants in which orbital a is replaced by the unoccupied orbital a' on the other atom. This effect represents the tendency for an electron to drift from one atom to the other. Because of the exclusion principle, since one localized orbital is occupied on each atom this drift can only occur when the electrons have opposite spin. Hence the perturbation energy depends on the orientation of the atomic spins with respect to each other.

To evaluate the term E , consider the interaction between the S' projection of the principal determinant:

$$\Psi_A \sim (a, a') + x(n, S')\{(a', a) + \dots\} + \dots, \quad (30)$$

and another projected determinant of the form

$$\Psi_E \sim (a', a') + \dots. \quad (31)$$

The perturbation energy is doubled because of an identical interaction between Ψ_A and the projection of (a, a) . The difference between the diagonal matrix elements for the normalized projected functions will again be approximated by

$$\begin{aligned}\Delta &= (\Phi_E, H\Phi_E) - (\Phi_A, H\Phi_A) \\ &= (a'\alpha, \mathcal{H}a'\alpha) - (a\alpha, \mathcal{H}a\alpha) - [aa|a'a'] + [aa'|a'a].\end{aligned}\quad (32)$$

¹⁴ P. W. Anderson, Phys. Rev. **115**, 2 (1959).

Again the dependence of the perturbation energy on spin comes from the nondiagonal matrix element, using Eq. (6),

$$(\Psi_B, H\Psi_A) = [1 + x(n, S')]^{\frac{1}{2}} (a'\alpha, \mathcal{H}_A a\alpha). \quad (33)$$

As before, \mathcal{H}_A is the effective one-electron Hamiltonian defined by the principal Slater determinant Φ_A . Matrix elements can be evaluated directly from the definition of \mathcal{H}_A ,⁵ using tables of the two-electron integrals and matrix elements of \mathcal{H}_0 , the one-electron Hamiltonian for the ground state configuration of ordinary molecular orbital theory. Diagonal matrix elements of \mathcal{H}_A are listed in Table II and nondiagonal elements in Table III. It should be noted that \mathcal{H}_A is defined differently in regions II and III, because the principal Slater determinants have different configurations in the different regions.

By second-order perturbation theory, adding the effects of the projections of (a', a') and (a, a) ,

$$\Delta E(S') = - (2/\Delta) (1+x) (a', \mathcal{H}_A a)^2. \quad (34)$$

Hence, picking out the coefficient of $S'(S'+1)/n^2$:

$$E = \sum_j 2(a'_j, \mathcal{H}_A a_j)^2 / \Delta_j. \quad (35)$$

It can be seen from Table III that the nondiagonal matrix elements of \mathcal{H}_A decrease exponentially with increasing internuclear distance. Because of this behavior it has been suggested⁴ that in the case of the antiferromagnetic oxides such as MnO the principal contribution to $(a', \mathcal{H}_A a)$ comes not from the exchange potential due to the metal ions themselves (analogous to the present calculations) but from the exchange potential due to the outer orbitals of the intervening oxygen ion. Since the matrix elements of this exchange potential are identical with the matrix elements due to the intervening ion that occur in the numerator of the correlation effect D , Eq. (21), the terms D and E should be of comparable magnitude in the antiferromagnetic oxides, although D is negligible compared to E in the present case of two atoms interacting directly with each other.

IV. NONLINEAR TERMS

The effects considered in the previous section are linear in $S'(S'+1)$, to the second order of perturbation theory applied to the matrix of the many-electron Hamiltonian. The unbalanced spin in the principal

Slater determinant Φ_A , fundamental to the present analysis, leads to other spin dependent effects of a more complicated nature. These arise from the induced spin polarization of the doubly occupied orbitals of the atomic cores or of any closed shell system interacting with the atoms under consideration. These polarization effects will be shown to be nonlinear in $S'(S'+1)$, hence not compatible with the empirically postulated Heisenberg exchange interaction, but to be small compared with the linear terms in the present case.

In a recent paper, Keffer and Oguchi¹⁵ have suggested that the principal superexchange effect in the antiferromagnetic oxides is due to induced polarization of a doubly occupied core orbital by admixture of an unoccupied atomic valence orbital. Their analysis used nonorthogonal orbitals, and would mix together several of the terms considered as separate effects in the present work. The effect that corresponds to that of Keffer and Oguchi, when analyzed in terms of orthogonal orbitals, arises from configuration interaction between the principal projected determinant:

$$\Psi_A \sim (ab, ba') + x(n, S') \{ (a'b, ba) + \dots \} + \dots, \quad (36)$$

and other projected determinants of the form

$$\Psi_F \sim (ab, aa') + x(n, S') \{ (aa', ab) + \dots \} + \dots. \quad (37)$$

The perturbation energy will be doubled by an identical interaction with the projection of (aa', ba') . The difference between the diagonal matrix element is approximated by

$$\Delta = (\Phi_F, H\Phi_F) - (\Phi_A, H\Phi_A), \quad (38)$$

calculated as in Eq. (32). The nondiagonal matrix element between the projected determinants is, from Eq. (6),

$$(\Psi_F, H\Psi_A) = (a\beta, \mathcal{H}_A b\beta) - x(n, S') \sum_j [aa'_j | a'_j b]. \quad (39)$$

Hence, adding the two identical terms, by second-order perturbation theory,

$$\Delta E(S') = - \frac{2}{\Delta} \{ (a\beta, \mathcal{H}_A b\beta) - x(n, S') \sum_j [aa'_j | a'_j b] \}^2, \quad (40)$$

obviously quadratic in $S'(S'+1)$. In order to compare this with the true linear terms, a linear formula will be used which agrees with $\Delta E(S')$ for the two extreme values $S'=0$ and $S'=n$. This gives

$$\Delta E(S'=0, n) = (\Delta'E)_F - [1 + x(n, S')] F, \quad (41)$$

where

$$(\Delta'E)_F = \Delta E(n) = - \frac{2}{\Delta} \{ (a\beta, \mathcal{H}_A b\beta) + \sum_j [aa'_j | a'_j b] \}^2, \quad (42)$$

¹⁵ F. Keffer and T. Oguchi, Phys. Rev. **115**, 1428 (1959).

TABLE III. Nondiagonal matrix elements of \mathcal{H}_A in atomic units.

R	Region II			
	2.5	2.75	3.0	4.0
$(\pi', \mathcal{H}_A \pi)$	-0.14433	-0.10865	-0.08131	-0.02433
R	Region III			
	3.0	4.0	5.0	6.0
$(\sigma', \mathcal{H}_A \sigma)$	-0.23751	-0.09958	-0.03803	-0.01261
$(\pi', \mathcal{H}_A \pi)$	-0.07800	-0.02355	-0.00646	-0.00163

and

$$F = -\frac{4}{\Delta} \left\{ (a\beta, \mathcal{H}_A b\beta) + \frac{n-1}{2n} \sum_j [aa_j' | a_j' b] \right\} \times \left\{ \sum_j [aa_j' | a_j' b] \right\}. \quad (43)$$

Contributions to $\Delta'E$ and F were evaluated for both $2\sigma_u$ and $2\sigma_g$ as the core orbital b . Nonvanishing matrix elements arise only from valence orbital σ as orbital a .

Part of the term F ought properly to be included in the term E in the present calculations, since the orbitals do not satisfy the Hartree-Fock equations appropriate to Φ_A , but instead were obtained by solving the equations appropriate to Φ_0 , the usual molecular orbital ground state configuration. To pick out that part of F that can definitely be attributed to core polarization, it is convenient to consider the form of the Hartree-Fock equations appropriate to a determinant Φ_P , the analog of Φ_A in which all singly occupied orbitals have parallel spins (let this be $+\frac{1}{2}\hbar$). Then if orbital b is an eigenfunction of the one-electron operator appropriate to spin $-\frac{1}{2}\hbar$, the analog of Brillouin's theorem⁵ is

$$(a\beta, \mathcal{H}_P b\beta) = (a\beta, \mathcal{H}_A b\beta) + \sum_j [aa_j' | a_j' b] = 0. \quad (44)$$

If Eq. (44) were satisfied, the term F of Eq. (43) would be reduced to

$$F_1 = -\frac{2}{\Delta} \frac{n+1}{n} \left\{ \sum_j [aa_j' | a_j' b] \right\}^2. \quad (45)$$

This term gives the part of F that can be attributed to core polarization independently of the approximations made in this particular calculation. The remainder,

$$F_2 = F - F_1, \quad (46)$$

should properly be included as part of the delocalization effect E , since it arises from admixture of orbital $a\beta$ with the part of orbital $a'\beta$ that is mixed with the core orbital b as a result of an arbitrary approximation made to facilitate the present calculations. These terms are tabulated separately in Table I. Term F does not occur in region II because of conservation of axial angular momentum: the core orbitals (all σ) cannot mix with the localized valence orbitals (all π).

Another core polarization effect, due to induced polarization of a doubly occupied core orbital by admixture of an unoccupied orbital other than the valence orbitals, has recently been proposed by Kondo¹⁶ as the most important term in the superexchange interaction in MnO. This effect has been estimated by the present author to be small compared with D or E even in the case of the oxides,⁴ when evaluated in a basis of orthogonal Hartree-Fock orbitals. It is of interest to evaluate the analogous term for the present case of two directly interacting atoms, even though the magnitude of the term calculated here cannot be compared with the

corresponding term arising from polarization of an ion intervening between the two interacting atoms. It will be shown that this effect is not linear in $S'(S'+1)$, and hence cannot properly be included in the usual Heisenberg formalism.

Consider the interaction between a projected determinant

$$\Psi_A \sim (ab, ba') + x(n, S') \{ (a'b, ba) + \dots \} + \dots, \quad (47)$$

and other projected determinants of the form

$$\begin{aligned} \Psi_{G1} &\sim (ac, ba') + x(n+1, S') \\ &\quad \times \{ (ab, ca') + (aa', bc) + (bc, aa') + \dots \} + \dots, \\ \Psi_{G2} &\sim (ab, ca') + (n+1, S') \\ &\quad \times \{ (ac, ba') + (aa', cb) + (cb, aa') + \dots \} + \dots. \end{aligned} \quad (48)$$

These last two functions are not orthogonal. By Eq. (6),

$$(\Psi_{G2}, \Psi_{G1}) = x(n+1, S'). \quad (49)$$

As before, the denominator in the perturbation formula for the energy is approximated by

$$\Delta = (\Phi_{G1}, H\Phi_{G1}) - (\Phi_A, H\Phi_A). \quad (50)$$

The nondiagonal matrix elements, by Eq. (6), are

$$(\Psi_{G1}, H\Psi_A) = [1 + x(n+1, S')]^{\frac{1}{2}} (ca, \mathcal{H}_A b\alpha), \quad (51)$$

$$(\Psi_{G2}, H\Psi_A) = [1 + x(n+1, S')]^{\frac{1}{2}} (c\beta, \mathcal{H}_A b\beta).$$

Because of the structure of the determinant Φ_A , the effective one-electron Hamiltonian \mathcal{H}_A contains exchange potential terms of opposite spin for the localized orbitals on the two different atoms. It follows that the two matrix elements of Eq. (51) are equal if the product bc is even under inversion of the molecular coordinate system in the midpoint of the internuclear axis, and that they are equal in magnitude but have opposite signs when bc is odd. In either case, one linear combination of Ψ_{G1} and Ψ_{G2} will not interact with Ψ_A , and the matrix element for the normalized linear combination orthogonal to this is

$$\begin{aligned} \left(\frac{\Psi_{G1} \pm \Psi_{G2}}{[2 \pm 2x(n+1, S')]^{\frac{1}{2}}}, H\Psi_A \right) &= \left[\frac{2+2x}{1 \pm x} \right]^{\frac{1}{2}} \\ &\quad \times (ca, \mathcal{H}_A b\alpha), \quad \begin{cases} +bc \text{ even} \\ -bc \text{ odd.} \end{cases} \end{aligned} \quad (52)$$

Since this matrix element is independent of x (hence of S') when bc is even, only bc odd contributes to spin coupling. Hence,

$$\Delta E(S') = -\frac{2}{\Delta} \frac{1+x}{1-x} (ca, \mathcal{H}_A b\alpha)^2, \quad (53)$$

for bc odd only. This is obviously not linear in $S'(S'+1)$. However, for comparison with other contributions to spin coupling, this can be approximated as before

¹⁶ J. Kondo, Progr. Theoret. Phys. (Kyoto) 22, 41 (1959).

[Eq. (41)] by a linear formula valid for $S'=0$ and $S'=n$ only. This leads to

$$(\Delta'E)_G = -(2/n\Delta)(c\alpha, \mathcal{C}_A b\alpha)^2, \quad (54)$$

and

$$G = (2/\Delta)(c\alpha, \mathcal{C}_A b\alpha)^2. \quad (55)$$

The term arising from polarization of the doubly occupied bonding orbital $2\sigma_g$ by admixture of the unoccupied orbital σ_u is analogous to the effect considered by Kondo.¹⁶ This is listed as G_1 in Table I. However, the interaction between the occupied bonding valence orbital σ_g and the corresponding antibonding orbital σ_u cannot be described as a core polarization effect, since it is part of the tendency for valence orbitals to change from molecular to atomic form as the atoms are separated. This has been calculated separately and is listed as G_2 in Table I. Terms G do not occur in region III in the present calculations since there are no completely unoccupied orbitals in this region for the minimal basis set used here, which cannot represent configurations of the separated atoms with orbitals beyond the L shell.

V. DISCUSSION OF RESULTS

The various contributions to the effective exchange integral are summarized for regions II and III in Table I. The most striking result is that in all cases the net effect is antiferromagnetic, and the largest individual contribution in general is due to term E , the delocalization effect. This term (together with some contribution from terms F and G) is essentially the same as the effect considered by Anderson¹⁴ to represent incipient covalent bonding between the atomic valence orbitals. As the internuclear distance is decreased, this effect becomes too large to be described by second-order perturbation theory in terms of atomic orbitals, the spin-dependent energy becomes nonlinear in $S'(S'+1)$, and it is necessary to describe the valence electrons by doubly occupied bonding molecular orbitals. The boundary between regions III and II marks the transition from atomic to molecular form of the $2p\sigma$ valence orbitals, while the boundary between regions II and I marks the transition from atomic to molecular form of the $2p\pi$ valence orbitals. In both cases an antiferromagnetic Heisenberg spin-coupling effect at large internuclear distances becomes a covalent bond at small distances, and the effective atomic spin is reduced.

The ordinary exchange term C is the only ferromagnetic effect of any significance, and it is smaller (particularly at the smaller internuclear distances) than the terms that describe incipient covalent bonding. If there were a diamagnetic atom or ion between the two nitrogen atoms, the correlation term D might be expected to be much larger than in the present case, for it would then correspond to the superexchange coupling in antiferromagnetic crystals such as MnO. In the present case, with no intervening atom, this term is negligible.

The terms F and G arise from interaction between

the principal Slater determinant and determinants differing from it by a single orbital. These terms describe a spin-dependent polarization effect, since the sum of two such determinants can be expressed as a single Slater determinant with one orbital modified from the principal configuration.

Term F is absent in region II, while term G consists of one part, G_1 , that arises from polarization of the core of doubly occupied orbitals, and another part G_2 from polarization of the doubly occupied valence orbital σ_g . Only the term G_1 can be considered to describe spin polarization of the core, analogous to the effect considered by Kondo¹⁶ in the case of the antiferromagnetic crystal MnO. In the present calculations, G_1 is a quite small fraction of the total effect, but decreases less rapidly with increasing internuclear distance.

The term G_2 , which *increases* with increasing internuclear distance in region II, arises from the polarization of the bonding molecular orbital σ_g by admixture of the corresponding antibonding orbital σ_u . The effect of this admixture is to convert σ_g into the atomic orbital σ or σ' as the atoms are separated. There is a contribution that does not depend on total spin to the energy given in Table IV from this effect as well as from the corresponding double substitution (σ_u^2 replacing σ_g^2). These effects become sufficiently large at $R=4.0$ atomic units (a.u.) that second-order perturbation theory is no longer a reasonable approximation, as might be expected from the fact that the principal configuration at $R=4.0$ a.u. is that of region III, with atomic orbitals σ, σ' occupied in preference to the bonding molecular orbital σ_g .

Term G is absent in region III, while term F consists of one part F_1 that arises from core polarization, analogous to the effect considered by Keffer and Oguchi,¹⁵ and another part F_2 that should be included as part of the delocalization term E . In the present calculations, F_1 is small compared with the total exchange effect. It should be noted that F and G are not linear in $\mathbf{S}_A \cdot \mathbf{S}_B$, and cannot properly be included in the Heisenberg formalism.

The energy of the lowest $^1\Sigma_g^+$ state is calculated by second-order perturbation theory in all three regions, using in each case the singlet projection of the appropriate principal Slater determinant as zeroth order approximation, and including only those configurations in which the inner shell orbitals remain occupied except for the small spin-dependent polarization effects discussed above.

This brings in the spin-dependent effects in exactly the form that they are used to calculate $4S^2J$, with the addition of terms that are independent of spin. For comparison with the second-order perturbation results, the configuration interaction matrix for the eight projected $^1\Sigma_g^+$ functions of greatest weight at small internuclear distances has been calculated exactly and diagonalized for $R \leq 3.0$ a.u. These results are given in Table IV. The principal Slater determinant in each

TABLE IV. Energy of $^1\Sigma_g^+$ ground state, in atomic units (a.u.).

R	Second-order perturbation theory			Lowest eigenvalue of eight-term configuration interaction matrix		Experiment ^b (ev)
	Region I	Region II	Region III	(a.u.)	(ev)	
1.75	0.12454			0.14791	4.025	-5.4
2.0	-0.15005			-0.10583	-2.880	-9.5
2.25	-0.25066			-0.16989	-4.623	-9.4
2.5	-0.29153	-0.14846 ^a		-0.15088	-4.105	-7.9
2.75	-0.32933 ^a	-0.09040		-0.10257	-2.791	-5.7
3.0		-0.05320	-0.20757 ^a	-0.05082	-1.383	
4.0		-0.00668 ^a	-0.02098			
5.0			-0.00293			
6.0			-0.00027			

^a Calculation extended into adjoining region.^b J. T. Vanderslice, E. A. Mason and E. R. Lippincott, J. Chem. Phys. 30, 129 (1959).

region has been used as zeroth-order approximation for a second-order perturbation calculation at one point in each neighboring region. These values are marked by superscript a in Table IV.

It can be seen that the perturbation result is quite close to the correct energy in region II, and appears to be reasonable in the outer region. However, in region I, the perturbation theory greatly overestimates the binding energy. This is due to the large number of low-lying configurations that interact strongly with each other and with the molecular orbital ground-state configuration. In fact, apparently it is preferable to treat the π orbitals as atomic orbitals rather than as molecular orbitals even at $R=2.5$ a.u., which is within region I.

The one-electron energies appropriate to the principal Slater determinant in each region are listed in Table II. These are the diagonal matrix elements of the effective one-electron Hamiltonian defined by this determinant.⁵ These one-electron energies are equal to the energy gained by removing to infinity an electron from one of the occupied orbitals, or, alternatively, to the energy required to bring from infinity an electron to fill one of the unoccupied orbitals. Contrary to a widely held but fallacious idea, these statements follow from simple identities, and have no physical content. However, if the orbitals are canonical Hartree-Fock orbitals, (i.e., eigenfunctions of the effective one-electron Hamiltonian), then by Koopmans' theorem¹⁷ these one-electron energies are first-order approximations to the ionization potentials and electron affinities of the system. These energies correspond to the mean energies of energy bands in a crystal.

In region II, atomic orbitals $\pi\alpha$ and $\pi'\beta$ are both occupied and have equal energy (negative), while orbitals $\pi\beta$ and $\pi'\alpha$ are both unoccupied, and have equal energy (positive). Thus the orbital energy depends both on spin and location for an atomic orbital, as a result of the structure of the principal Slater determinant, which assigns a definite orientation to the unbalanced spin on each atom. The energies of the doubly occupied orbitals of molecular form do not depend on spin. The large splitting between $\pi\alpha$ and $\pi\beta$ is an "exchange"

effect due to the Coulomb interaction of charge density $(\pi)^2$ with itself. In region III, similar statements hold for occupied orbitals $\sigma\alpha$ and $\sigma'\beta$, and for unoccupied orbitals $\sigma\beta$ and $\sigma'\alpha$. The splitting between $\sigma\alpha$ and $\pi\alpha$ is a "crystalline field" effect due to the nonspherical environment (the other atom); it vanishes for large internuclear separation.

VI. BAND STRUCTURE OF THE TRANSITION METALS

Recently a detailed model of the band structure of the transition metals has been proposed by Goodenough.¹⁸ In attempting to correlate a very large amount of experimental data on the transition metals and their alloys, Goodenough was led to make several assumptions that represent a departure from more traditional ideas of the band theory of metals. Perhaps the most interesting result of the present discussion of N_2 is that it demonstrates, for a system that is simple enough to make calculations possible, the desirability of modifying the traditional molecular orbital theory in a manner closely analogous to the postulates proposed by Goodenough for the band theory of metals. Calculations on diatomic molecules containing transition metal atoms could be carried out in exactly the same way as these for nitrogen; the generalization to energy band calculations for metals will be discussed in the following section.

The idea of making a distinction between localized and collective electrons is not in itself a novelty since this is inherent in the idea of the special nature of the transition metals and rare earths. However, as was emphasized by Mott,⁷ it is necessary to distinguish between the concept of localized orbitals with oriented spins in nonconducting crystals and the apparently incompatible concept of Bloch waves describing metallic electrons, and to recognize that both concepts are needed in describing the transition metals. It has also been recognized by Slater⁶ that the band theory must be modified to allow the description of a magnetic sublattice structure in the case of antiferromagnetic crystals, in the sense that the occupied Bloch orbitals of each spin can be made up of atomic orbitals from one sublattice only. These ideas of Mott and Slater can be reconciled if one adopts the point of view that the Wannier functions made up from the separate bands discussed by Slater should be identified with the localized orbitals of Mott.⁴ This is based on the theory of localized equivalent orbitals in molecular structure developed by Lennard-Jones and his collaborators,¹¹ using the theorem that a single Slater determinant (the Hartree-Fock approximation to the electronic wave function of a molecule or crystal) is not changed by an arbitrary unitary transformation of the occupied orbitals, for example, by the transformation from Bloch waves for filled bands to the corresponding Wannier functions.

¹⁷ T. Koopmans, *Physica* 1, 104 (1933).¹⁸ J. B. Goodenough, *Phys. Rev.* 120, 67 (1960).

It is clear from earlier work¹⁰ and from the present calculations on N_2 that it is not qualitatively correct to base a description of weakly interacting valence electrons on the idea of doubly occupied bonding molecular orbitals. However, the alternative description in terms of localized orbitals with spins coupled by the Heisenberg exchange interaction can be carried through quantitatively by the methods used here. In agreement with the description postulated by Goodenough, valence orbitals should be considered as localized atomic orbitals for large internuclear distances, but as bonding or antibonding molecular orbitals for small internuclear distances. Since the boundary between these inner and outer regions is different for each different subshell of atomic valence orbitals, e.g., $2p\sigma$ and $2p\pi$ in N_2 , it is reasonable to expect, as Goodenough has assumed, that the d_e and d_i orbitals can be similarly distinguished in a cubically symmetrical environment. Since the internuclear distance is determined primarily by the s and p valence orbitals in the transition metals or rare earths, it is to be expected that even at the equilibrium separation of two such atoms some of the d or f orbitals can still be so weakly coupled that they must be described as localized atomic orbitals. In N_2 , of course, the p orbitals are themselves the principal bonding orbitals, so the Heisenberg spin coupling effect only appears if the nuclei are constrained to be further apart than the equilibrium distance.

In the present calculations the antiferromagnetic coupling effects for neighboring atoms are found to be considerably larger than the ferromagnetic effects. This is due primarily to the delocalization effect emphasized by Anderson,¹⁴ which will always occur in the case of less than half-filled shells of valence orbitals, and is characterized as incipient covalent bonding. It might be expected that this will be a general result, as assumed by Goodenough for the transition metals. Furthermore, this effect diminishes exponentially with increasing distance, in agreement with Goodenough's assumption that nearest neighbor interactions will be significantly larger than next-nearest neighbor interactions. However, this will depend somewhat on the angular distribution of the atomic valence orbitals.

It is reasonable to assume that localized valence orbitals can be coupled ferromagnetically when one or more antibonding valence orbitals are also occupied (the more-than-half-filled case of Goodenough), since the localized orbitals are coupled to the antibonding orbitals by *atomic* exchange integrals, generally larger than any of the coupling terms between different atoms. The fact that the ground state of the O_2 molecule is paramagnetic is not in itself evidence for this postulate, since there are no localized valence orbitals at the equilibrium internuclear separation. However, the oxygen molecule illustrates the tendency for degenerate orbitals to be occupied with parallel spin (Hund's rule), which would induce ferromagnetic coupling between any localized orbitals also present. In the case of the

"antibonding band" in Goodenough's model, the degeneracy of the antibonding orbitals is removed because of the band structure. It is difficult to see why this situation should be different from the usual case of Pauli paramagnetism, except for the presence of localized orbitals. But the ferromagnetic coupling between localized orbitals on two atoms, induced by their interaction in the sense of Pauli paramagnetism with a partially filled valence band, could be greater than the net antiferromagnetic coupling due to their direct interaction. The band structure postulated by Goodenough for the bcc metals is particularly favorable for this, since the narrow d_e band is assumed to be almost entirely above the bonding d_i band, but to overlap the antibonding d_i band somewhat. In these circumstances the metals would be Pauli paramagnetic for less than three occupied d orbitals per atom, antiferromagnetic for between three and five d orbitals, and possibly ferromagnetic for five or more d orbitals, depending on the magnitude of the induced coupling via the partially filled antibonding band. Perhaps Goodenough's special assumptions about the band structure in bcc Fe could be replaced by the hypothesis that this induced coupling is sufficiently large to outweigh the direct antiferromagnetic coupling between atomic d_e orbitals on nearest neighbor atoms. In this form, this assumption is compatible with the rest of Goodenough's discussion, in particular with the rather delicate balance of forces shown by the rich variety of crystal structures of Mn and Fe.

VII. CALCULATION OF ELECTRONIC ENERGIES IN SOLIDS

It should be noted that a calculation by the usual band theory, neglecting configuration interaction, even if made self-consistent in the sense of the Hartree-Fock equations, cannot describe the antiferromagnetic effects considered here. This would give a completely false result for the effective Heisenberg exchange integral in the case of less than half-filled valence orbitals. This situation would not be improved by even a very elaborate configuration interaction calculation carried out with Bloch orbitals, unless an infinite number of configurations were chosen. It would certainly not be possible to use ordinary perturbation theory.

If band theory were modified in the sense suggested by Slater,⁶ to allow orbitals of opposite spin to belong to separate orthonormal sets, not mutually orthogonal, the antiferromagnetic effect discussed by Anderson¹⁴ could at least be described qualitatively, but a quantitative calculation would have to surmount the formidable barrier of an infinite set of non-zero overlap integrals.

However, the method used in the present paper can be extended to the quantitative calculation of the effective Heisenberg exchange integral in solids without any change in the formalism. It would be necessary first to solve the Hartree-Fock equations in their tra-

ditional form for a configuration in which all singly occupied orbitals have parallel spin. This of course would require iterated energy band calculations, with inclusion of exchange, by the self-consistent field method, but it is probably not unreasonable to hope for such results in the foreseeable future. Then the occupied orbitals (calculated as Bloch waves) should be transformed to the equivalent set of Wannier functions,¹⁹ localized as much as possible on single atoms in the crystal. The singly occupied Wannier functions on each atom should be occupied with parallel spin. The various contributions to the Heisenberg exchange integral can then be evaluated by the formulas given in the present paper. These formulas depend for their validity only on the orthogonality of the spatial orbitals, which is maintained by the unitary transformation from Bloch waves to Wannier functions. For metals this procedure would in some cases have to be modified to account for partially filled bands by introducing an appropriate sublattice structure, as described in an earlier paper.⁴

ACKNOWLEDGMENTS

The calculations reported in this paper were carried out on the IBM 704 computer, using a package of computer programs for molecular calculations programmed by the author. The program for matrix self-consistent

¹⁹ G. H. Wannier, *Phys. Rev.* **52**, 91 (1937).

field calculations by the method of Roothaan [C. C. J. Roothaan, *Revs. Modern Phys.* **23**, 69 (1951)] as modified by the author [R. K. Nesbet, *Mass. Inst. Technol. Quart. Prog. Rept., Solid State and Molecular Theory Group*, October 15, 1955, pp. 4-8 (unpublished)] and the program for data retrieval were coded at the National Bureau of Standards by A. Beam, P. Walsh, and J. D. Waggoner, under the supervision of Dr. E. Haynesworth. The programs for evaluation of two-center integrals were coded by the author [R. K. Nesbet, *Revs. Modern Phys.* **32**, 272 (1960)] using methods developed by P. Merryman. This work was supported by RIAS.

The programs used were tested by the usual internal checks, and also in detail against the earlier calculations on N₂ by Scherr (reference 8). Errors of a numerical nature are expected to affect the results quoted here at most in the fourth figure after the decimal point.

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Nonexistence of a 9.0-Mev Level in C¹²†

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An energy level in C¹² at 9.0 Mev has been reported as a result of (*p*,*γ*,*γ*) triple coincidence measurements on the B¹⁰(He³,*p*)C¹² reaction at *E*_{He³}=2.2 Mev. This reaction has been reinvestigated in a similar experimental arrangement by using alternately Pilot-B, CsI and NaI scintillators for detection of the protons. Only the Pilot-B, which had been used in the previous work, exhibits the proton group corresponding to a "9.0-Mev level" in C¹². The triple coincidence effect in this case is actually due to the intense ~17-Mev protons in the B¹⁰(He³,*p*)C¹² reaction leading to the 4.43-Mev first excited state of C¹² which upon entering the scintillator can inelastically scatter from carbon and produce secondary gamma radiation of 4.43 Mev. The net energy deposited in the scintillator has the appearance of a proton group to a 9.0-Mev level in C¹² in triple coincidence with two 4.43-Mev gamma rays. The magnitude of the effect is calculated from published cross sections for inelastic scattering and it agrees with the apparent population intensity of the nonexistent "9.0-Mev level."

A CONSIDERATION of possible gamma-ray background effects when using plastic scintillators for the detection of energetic protons has led us to a re-investigation of the B¹⁰(He³,*p*)C¹² reaction. (*p*,*γ*,*γ*)

triple coincidence measurements¹ had suggested the existence of a weakly populated energy level in C¹² at 9.0 Mev. In these experiments the protons were detected in a Pilot-B scintillator close to the target which accepted protons emitted in the angular range 0°-60° and the gamma rays were detected in two large NaI

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¹ D. E. Alburger and R. E. Pixley, *Phys. Rev.* **119**, 1970 (1960).