

Heisenberg Exchange Interaction of Two Mn Atoms

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A complete *ab initio* approximate Hartree-Fock calculation has been carried out on the Mn_2 molecule at three internuclear distances, $R=4.5, 5.0,$ and $5.5 a_0$. The theory of the Heisenberg exchange interaction, applied in an earlier paper to the nitrogen molecule at large R , is used to identify the Hartree-Fock configuration of lowest energy and to evaluate the effective exchange integral J . The Hartree-Fock energy has a minimum value with respect to separated atoms in a ${}^2\Sigma_g^+$ state. The exchange integral is small but negative, so a ${}^1\Sigma_g^+$ state of complex structure lies below this. The energy of this ${}^1\Sigma_g^+$ state has a minimum value of -0.79 eV, with respect to separated atoms, at $R=2.88 \text{ \AA}$, neglecting the part of the net molecular correlation energy that is independent of spin. These two states are members of a closely spaced set with total spin $S'=0, 1, 2, 3, 4$ coming from the coupling of spins $S=2$ on each atom. The last occupied σ orbital is of molecular form (bonding molecular orbital, doubly occupied) while the last π and δ orbitals are localized and singly occupied. The existence of localized spin-coupled orbitals at equilibrium R is very unusual for diatomic molecules, and this is the distinctive property of magnetic materials expected in the present theory.

I. INTRODUCTION

IN a recent series of papers,^{1,2} the theory of exchange interactions between atoms or ions has been developed from first principles by an argument that meets a number of serious objections to earlier derivations. The resulting theory is applicable to isolated molecules or to atoms or ions in a crystal. For insulating crystals, the theory leads in special cases to the well-known Heisenberg exchange interaction, given by the effective Hamiltonian

$$-\sum_{ab} J_{ab} \mathbf{S}_a \cdot \mathbf{S}_b, \quad (1)$$

where indices a and b denote atoms or ions, not individual electrons. In general, the interaction is a more complicated function of the ionic spins than is indicated by Eq. (1), but the dominant part of the interaction is expected to be of the Heisenberg form.² In the case of metals, the theory must be augmented by consideration of indirect exchange due to polarization of a conduction band by localized moments,³ and of spontaneous polarization of a conduction band in the sense of the older band theory of ferromagnetism.⁴ Both of these effects are generally treated by band theoretical methods. When localized spins are present in a metal, the appropriate method to use is a synthesis of the present method with band theory for the conduction band, but this has not yet been formulated adequately.

The present theory is a many-electron theory throughout. The matrix of the many-electron Hamiltonian is analyzed to pick out the spin dependence of individual matrix elements, and then the spin-dependent contributions to the second-order perturbation energy are evaluated. The perturbation theory is based on an

energy expansion, not on an overlap expansion, so the quantities required to be small are ratios of energies. The theory is formulated in terms of localized transforms (analogous to Wannier functions) of the canonical Hartree-Fock orbitals⁵ for the system under consideration (Bloch waves for a crystal). In this formulation, the energy ratios required to be small are the same as similar ratios that occur in the theory of isolated atoms and molecules. Hence, the growing body of evidence supporting the accuracy of the Hartree-Fock approximation for simple systems is support for the validity of the present formalism. The explicit form of Eq. (1) is a consequence of the second-order perturbation theory, and empirical evidence supporting Eq. (1) is also an indication of the validity of this approximation. If second-order perturbation theory, referring of course to energy ratios in the present context, is found to be inadequate in any specific application, one can go immediately to the use of higher order theory, for example by using the Bethe-Goldstone equations to improve the treatment of correlation effects between pairs of electrons. If this is necessary, the exchange interaction no longer has the simple linear form of Eq. (1). Since the present theory is concerned with interatomic correlation effects, which are at worst of the magnitude of dispersion forces, the second-order perturbation theory is used here to treat rather weak interactions, and should be expected to give useful results.

In order to compare states of different total spin of the system under consideration, advantage is taken of the fact that only one- and two-particle excitations from an assumed Hartree-Fock configuration occur in second-order perturbation theory. Spin-dependent one-particle excitations occur because exchange terms in the Hartree-Fock equations depend on spin.⁶ Thus, at most, two atoms at a time are affected by individual

¹ R. K. Nesbet, *Ann. Phys. (N. Y.)* **4**, 87 (1958); *Phys. Rev.* **119**, 658 (1960).

² R. K. Nesbet, *Phys. Rev.* **122**, 1497 (1961).

³ C. Zener, *Phys. Rev.* **81**, 440 (1951); **83**, 299 (1951); T. Kasuya, *Progr. Theoret. Phys. (Kyoto)* **16**, 45 (1956); K. Yosida, *Phys. Rev.* **106**, 893 (1957).

⁴ Earlier references are reviewed by F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), pp. 426-432; A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1954), 2nd ed., pp. 182-186.

⁵ R. K. Nesbet, *Rev. Mod. Phys.* **33**, 28 (1961).

⁶ J. C. Slater, *Phys. Rev.* **82**, 538 (1951); R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955).

terms in the perturbed energy, so detailed analysis can be restricted to two atoms at a time. By use of projection operators, the explicit dependence of energy matrix elements on the total spin of a pair of atoms is given by very simple formulas.⁷ In the Hartree-Fock approximation in its usual (restricted⁵) form, localized orbitals are either doubly occupied or singly occupied with all spins parallel, in agreement with Hund's rules for the ground state of an atom. The spin S is a good quantum number for each atom or ion in this approximation. The scalar product $\mathbf{S}_a \cdot \mathbf{S}_b$ for two such atoms is an explicit function of the total spin S' of the atom pair. Since the perturbation energy of each atom pair is obtained in the present theory as a function of S' , it is immediately expressible as a function of $\mathbf{S}_a \cdot \mathbf{S}_b$. Equation (1) is clearly a very special case of such a function. Thus, when the Heisenberg exchange interaction is found to be a consequence of the present theory, this is not a trivial result. Some nonlinear terms have been found, particularly for interactions attributed to spin-dependent polarization of closed shells by the unbalanced spins of coupled open-shell atoms.²

It should be emphasized that the atomic spin S is also determined by the present theory and is not assumed *a priori*. This parameter simply counts the number of singly occupied localized orbitals on a given atom or ion. This number will change with the strength of the interatomic interaction, since localized singly occupied orbitals are replaced by doubly occupied molecular orbitals as atoms are brought together. These structural changes have been examined in detail in calculations by the present method on two interacting nitrogen atoms at various internuclear distances.² At the observed molecular equilibrium distance there is no localized spin and the molecule is characterized as nonmagnetic. However, at large internuclear separation, there are two localized orbitals on each nitrogen atom, and the interaction is described by an antiferromagnetic exchange interaction. At still larger internuclear separation there are three localized orbitals on each atom, going to the limit of free atoms in their $4S$ ground states. An important aspect of this situation is that the change from localized singly occupied orbitals to delocalized doubly occupied orbitals occurs at internuclear distances that are significantly different for orbitals of different symmetry. As a result of this fact, it is not at all unlikely that at a given internuclear separation the valence orbitals which interact most strongly must be described as covalently bonded, with no magnetic properties, while other valence orbitals that interact less strongly are described in terms of localized spins, interacting through an exchange interaction. In cubic transition metals the d_e and d_t orbitals may thus have quite different qualitative properties,⁸ and an observed

localized moment is not necessarily a direct measure of the number of occupied d orbitals.

In the present theory there is a clear distinction between magnetic and nonmagnetic materials. Nonconducting magnetic materials will have singly occupied localized orbitals in the Hartree-Fock approximation at the nuclear equilibrium configuration. Nonmagnetic materials will have doubly occupied orbitals only. By this criterion, the N_2 molecule considered previously is nonmagnetic. In the present paper, similar analysis will be applied to the Mn_2 molecule, and it will be shown that this is a magnetic material, characterized by an antiferromagnetic exchange interaction. In a sense this is the first *a priori* demonstration that the transition metals have magnetic properties that distinguish them from normal nonmagnetic elements.

The present status of the theory of exchange interactions in nonmetals has been reviewed in considerable detail in a recent article by Anderson.⁹ Unfortunately, the present general formalism was not discussed, although the particular application of this formalism to the superexchange interaction in the oxides of the MnO series¹ was criticized by Anderson on the ground that unreasonable values of empirical parameters were used. It should be pointed out that there is no essential difference between the present formalism and that described in detail by Anderson, when applied to systems with a single localized orbital on each atom or ion. The chief formal difference is that the present theory, by the use of projection operators, is able to consider the explicit dependence of perturbation energies on the spin quantum numbers. It is not clear how Anderson's formalism would be applied to the example of two interacting nitrogen atoms, each with spin $\frac{3}{2}$. The relationship to Hartree-Fock theory and to the problem of establishing a criterion to distinguish between magnetic and nonmagnetic material is also more explicit in the present theory. Actually the present formalism is sufficiently closely related to the theory of molecular structure, where explicit quantitative calculations are possible, that experience gained in molecular theory can be helpful in suggesting sound approximations to the values of matrix elements that occur as parameters in perturbation formulas. Some comments on the choice of these parameters for the MnO series and on Anderson's criticism⁹ of the choice made by the present author¹ will be given in a separate paper.

The relationship between the Heisenberg exchange interaction and the Heitler-London method has recently been discussed by Herring,¹⁰ who shows that despite the failure of the usual Heitler-London formalism in the extreme limit of widely separated atoms, a theory with similar formal structure can be devised that is correct in this limit and that leads to the Heisenberg interaction.

⁷ P.-O. Löwdin, Phys. Rev. **97**, 1509 (1955); R. K. Nesbet, Ann. Phys. (N. Y.) **3**, 397 (1958); J. Math. Phys. **2**, 701 (1961).

⁸ J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience Publishers, Inc., New York, 1963).

⁹ P. W. Anderson in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 14, pp. 99-214.

¹⁰ C. Herring, Rev. Mod. Phys. **34**, 631 (1962).

However, the weakness of the Heitler-London method is most serious at the internuclear distances characteristic of near-neighbor atoms in crystals. A recent calculation by Freeman and Watson on two interacting cobalt atoms¹¹ used the Heitler-London formalism. In a later paper, using the present formalism,¹² it was shown that in the case of the nuclear point charge model considered in some of the original calculations¹¹ the Heitler-London formalism underestimated the antiferromagnetic exchange integral by a factor of from three to ten for the largest exchange integrals. This striking discrepancy is due to the fact that a two-electron system described by two linearly independent basis orbitals has, in general, three independent singlet states but only one triplet state. The exchange integral is determined by the difference between the energy of this unique triplet state and the energy of the lowest stationary linear combination of the singlet states. Any method such as that of Heitler and London which picks out an arbitrary singlet state to compare with the triplet is likely to be in error. The error will systematically underestimate an antiferromagnetic exchange integral or overestimate a ferromagnetic exchange integral, since the singlet energy is artificially constrained while the triplet energy is independent of any arbitrary choice of representation. To avoid this difficulty, the so-called ionic configurations must be included, as they are in the present formalism. In addition to the advantage of including ionic configurations, the present theory also provides an explicit treatment of spin dependence when there are several unpaired spins on each atom, without getting into the overlap problem inherent in the Heitler-London theory. Again, the example of N₂ at large internuclear separation can be used to compare the practicability of the two methods.

The work by Freeman and Watson¹¹ is probably the most ambitious attempt so far to obtain an *a priori* computed value for the Heisenberg exchange integral between two directly interacting transition metal atoms. Staying within the framework of the Heitler-London formalism, characterized by the specific choice of the singlet wave function discussed above, they included terms in the variational formulas for the singlet-triplet energy difference that had been omitted in previous work. Their calculations with point charge potentials are complete for the assumed model, with fixed orbitals taken from atomic calculations. They also report calculations in which the one-electron potential fields of the inner shell Hartree-Fock orbitals replace the crude point charge model. Correction terms that are quadratic in the overlap integrals between the singly occupied *d* orbitals on one atom and inner shell orbitals on the other are included. This is, except for the overlap approximation, a valid many-particle calculation. Since fixed single outer orbitals and closed inner shells are

assumed, the energy formulas are the same as those of Heitler and London. The calculation is equivalent to a Heitler-London calculation with two electrons occupying fixed *d* orbitals orthogonalized to the inner shells.

The work reported here is an extension of this in several respects. The formalism includes the ionic configurations that are omitted in the Heitler-London theory. The outer orbitals are not assumed to be known from the beginning, but are determined by a variational calculation for the full 50-electron Mn₂ molecule. The resulting orbitals are orthonormal, so there is no overlap approximation. All inner shell orbitals have been included explicitly. The very large number of two-electron integrals are evaluated with the same computer programs used for the N₂ calculations² and other details are identical with that work. Similar accuracy is expected, but there is no comparable work for comparison, and the quantitative accuracy of the effective exchange integral reported here is difficult to estimate. However, the main purpose of this work is essentially qualitative, to illustrate the application of the present theory to a specific case of interacting transition element atoms.

II. DESCRIPTION OF CALCULATIONS

The localized spin is determined in the present method by consideration of the structure of the Slater determinant of lowest energy at any given internuclear distance. Since this is not known in advance, an approximate Hartree-Fock calculation is carried out for a particular configuration, and the energies of others are computed with respect to it by well-known formulas.¹³ In work of higher quantitative accuracy than the present, the Hartree-Fock calculation should be repeated for the particular configuration found to have lowest energy. This was not done in the present case, which follows the earlier work on N₂² by computing all molecular orbitals by a matrix Hartree-Fock calculation¹⁴ on the lowest closed-shell configuration, a pure ¹Σ_g⁺ state for the molecule. This configuration for Mn₂ is

$$1\sigma_g^2 \dots 7\sigma_g^2 1\sigma_u^2 \dots 6\sigma_u^2 1\pi_u^4 \dots 3\pi_u^4 1\pi_g^4 2\pi_g^4 1\delta_g^4. \quad (2)$$

TABLE I. Basis orbitals for production runs.

Orbital	Type	Exponent
1	1sσ	24.4097
2	2sσ	8.8730
3	3sσ	4.3464
4	4sσ	1.505
5	2pσ	10.5386
6	3pσ	4.0435
7	4pσ	1.505
8	3dσ	3.544
9	2pπ	10.5386
10	3pπ	4.0435
11	3dπ	3.544
12	3dδ	3.544

¹¹ A. J. Freeman and R. E. Watson, Phys. Rev. **124**, 1439 (1961).

¹² A. J. Freeman, R. K. Nesbet, and R. E. Watson, Phys. Rev. **125**, 1978 (1962).

¹³ See Ref. 6.

¹⁴ R. K. Nesbet, Rev. Mod. Phys. **35**, 552 (1963).

TABLE II. Molecular valence orbitals. Coefficients $x_{i\alpha}$ of even and odd molecular symmetry orbitals constructed from atomic basis orbitals listed in Table I.

(a) $R=4.5a_0$								
ϕ_i	x_{i1}	x_{i2}	x_{i3}	x_{i4}	x_{i5}	x_{i6}	x_{i7}	x_{i8}
$6\sigma_g$	-0.03073	0.10658	-0.30725	0.72381	0.05043	-0.17262	0.29244	0.08516
$7\sigma_g$	0.00665	-0.03029	0.04040	-0.53453	0.08548	-0.28898	0.83501	0.25323
$8\sigma_g$	0.00007	0.00216	0.01074	0.06783	-0.02562	0.08642	-0.27380	0.96134
$6\sigma_u$	-0.02464	0.09717	-0.20373	1.20902	-0.02914	0.10185	-0.16118	-0.13231
$7\sigma_u$	0.00138	0.01705	0.09449	1.08678	0.05943	-0.17766	1.46976	-0.66720
$8\sigma_u$	-0.00569	0.04798	0.04849	1.53642	0.06173	-0.18409	1.65413	0.74772
ϕ_i	x_{i9}	x_{i10}	x_{i11}		ϕ_i	x_{i12}		
$3\pi_u$	0.00542	-0.01713	0.99910		$1\delta_g$	0.99994		
$3\pi_g$	0.00205	-0.00657	1.00007		$1\delta_u$	1.00008		
(b) $R=5.0a_0$								
ϕ_i	x_{i1}	x_{i2}	x_{i3}	x_{i4}	x_{i5}	x_{i6}	x_{i7}	x_{i8}
$6\sigma_g$	-0.02816	0.09961	-0.27405	0.74911	0.04257	-0.14545	0.28517	0.06326
$7\sigma_g$	0.00862	-0.03560	0.06591	-0.52390	0.07842	-0.26539	0.82469	0.24379
$8\sigma_g$	-0.00156	0.00718	-0.00835	0.07427	-0.02716	0.08781	-0.24935	0.96746
$6\sigma_u$	-0.02588	0.09944	-0.22387	1.14544	-0.02403	0.08364	-0.17432	-0.14235
$7\sigma_u$	-0.00234	0.02056	0.02159	0.76077	0.06979	-0.21956	1.28922	-0.65514
$8\sigma_u$	-0.01056	0.05226	-0.04782	1.05499	0.06122	-0.19641	1.29911	0.74833
ϕ_i	x_{i9}	x_{i10}	x_{i11}		ϕ_i	x_{i12}		
$3\pi_u$	0.00460	-0.01465	0.99972		$1\delta_g$	0.99999		
$3\pi_g$	0.00218	-0.00708	1.00023		$1\delta_u$	1.00002		
(c) $R=5.5a_0$								
ϕ_i	x_{i1}	x_{i2}	x_{i3}	x_{i4}	x_{i5}	x_{i6}	x_{i7}	x_{i8}
$6\sigma_g$	-0.02640	0.09498	-0.25187	0.79603	0.03410	-0.11545	0.25225	0.02207
$7\sigma_g$	0.00898	-0.03585	0.07325	-0.48141	0.08158	-0.27379	0.85334	0.14366
$8\sigma_g$	-0.00184	0.00727	-0.01339	0.04470	-0.00491	0.01856	-0.14826	0.98846
$6\sigma_u$	-0.02652	0.10042	-0.23547	1.10158	-0.02462	0.08369	-0.19593	-0.09948
$7\sigma_u$	-0.00549	0.02714	-0.02697	0.61872	0.06774	-0.22141	1.19320	-0.61916
$8\sigma_u$	-0.01067	0.04576	-0.07395	0.71143	0.06784	-0.22011	1.02587	0.78003
ϕ_i	x_{i9}	x_{i10}	x_{i11}		ϕ_i	x_{i12}		
$3\pi_u$	0.00203	-0.00638	0.99991		$1\delta_g$	1.00000		
$3\pi_g$	0.00013	-0.00041	1.00005		$1\delta_u$	1.00000		

The atomic basis orbitals are normalized functions in the form of products of exponentials, powers of r , and spherical harmonics. Parameters defining these orbitals are listed in Table I. The symbols (σ, π, δ) in common molecular notation denote values (0,1,2) of the axial angular momentum quantum number m . Coordinates for each atom are chosen so that the Z axes point toward each other.

The orbital exponents, except for the valence orbitals, are those obtained by Clementi and Raimondi¹⁵ by a variational calculation of the 6S ground state of Mn. Improved values of the $4s$ and $3d$ exponents, appropriate to the Mn_2 molecule, were obtained by a preliminary series of molecular calculations. It was found that $4p\sigma$ basis orbitals had a significant effect on the structure of the molecular states, so these orbitals were included with exponents determined by molecular calculations. The energy of the separated atoms, which establishes the zero of energy in Table III, below, was corrected for

¹⁵ E. Clementi and D. L. Raimondi, J. Chem. Phys. **38**, 2686 (1963).

the admixture of basis $4p\sigma$ orbitals with the $2p$ and $3p$ inner shells.

Since Mn_2 has a center of inversion symmetry, the normalized atomic basis orbitals are combined to give unnormalized even (g) and odd (u) molecular basis orbitals, as indicated by

$$\begin{aligned}\sigma_{g,u} &= (\sigma \pm \sigma')/2^{1/2}, \\ \pi_{u,g} &= (\pi \pm \pi')/2^{1/2}, \\ \delta_{g,u} &= (\delta \pm \delta')/2^{1/2}.\end{aligned}\quad (3)$$

Here the unprimed symbol refers to one atom, the primed symbol to the other. The matrix Hartree-Fock calculation obtains occupied and unoccupied molecular orbitals for the configuration of Eq. (2) as linear combinations of the unnormalized symmetry orbitals of Eq. (3). Coefficients computed for the molecular orbitals of interest here are listed in Table II(a), (b), (c).

It is well known that a Slater determinant is invariant (except possibly for multiplication by a complex phase factor) under unitary transformation of its occupied

TABLE III. Energy of configurations obtained by replacing occupied bonding molecular orbitals in the standard closed-shell configuration Φ_0 by unoccupied antibonding orbitals of opposite spin. Energies are relative to separated atoms.

Configuration	R		
	$4.5a_0$	$5.0a_0$	$5.5a_0$
$^1\Sigma_g^+(0)$	54.088 eV	49.851 eV	49.307 eV
$^3\Sigma_u^+(7\sigma_u/7\sigma_g)$	56.539	53.243	52.337
$^5\Sigma_g^+(3\pi_g^2/3\pi_u^2)$	32.899	27.663	26.506
$^5\Sigma_g^+(1\delta_u^2/1\delta_g^2)$	32.671	27.836	26.821
$^9\Sigma_g^+(3\pi_g^2 1\delta_u^2/3\pi_u^2 1\delta_g^2)$	6.692	0.864	-0.758
$^{11}\Sigma_u^+(7\sigma_u 3\pi_g^2 1\delta_u^2/7\sigma_g 3\pi_u^2 1\delta_g^2)$	7.646	2.832	1.050

orbitals. If a bonding molecular orbital, such as σ_g , and the corresponding antibonding orbital σ_u are both occupied with the same spin, they can be transformed by the inverse of Eq. (3) to localized orthonormal orbitals associated with the individual atoms. This does not change a Slater determinant in which both orbitals are occupied. Such transformations can obviously be carried out for the doubly occupied inner shell orbitals, which can thus be associated with the atoms. But this is not possible for the doubly occupied bonding molecular orbitals $7\sigma_g$, $3\pi_u$, and $1\delta_g$ in the Slater determinant Φ_0 described by Eq. (2). These orbitals are characteristic of covalent bonding. When a molecule dissociates these orbitals must be replaced by orbitals that describe the separated atoms. This can be examined, while retaining the molecular orbital framework, by considering configurations in which occupied bonding molecular orbitals are replaced by the corresponding antibonding orbitals with opposite spin, as in $(\sigma_u\alpha/\sigma_g\beta)$. This gives configurations in which bonding and antibonding orbitals are singly occupied, all with the same spin, equivalent by the argument given above to singly occupied atomic orbitals coupled to the maximum total spin on each atom. Since interatomic interactions are very much smaller than intra-atomic interactions, a state of this kind, with a number of singly occupied atomic orbitals of parallel spin, must be a member of a group of states which maintain these atomic spin quantum numbers, but which couple the atomic spins to all possible values of total spin S' for the atom pair. The explicit dependence on S' of the total energy is obtained to the second order of perturbation theory by using projection operator techniques to

evaluate spin-dependent matrix elements of the many-electron Hamiltonian.⁷

Energies of various states obtained from Φ_0 by replacing occupied bonding orbitals by unoccupied antibonding orbitals are listed in Table III. Throughout the range of internuclear distances R considered here the lowest state is $^9\Sigma_g^+$, for which all the bonding π and δ molecular valence orbitals are replaced by singly occupied atomic orbitals. From the general argument given above, this state is associated with a group of states characterized by atomic spins $S=2$ coupled to total spin $0 \leq S' \leq 4$. The σ valence orbitals in this range of R are of molecular form. Since the separated atoms have spin $S=\frac{5}{2}$, there will be some larger value of R where $^{11}\Sigma_u^+$ crosses below $^9\Sigma_g^+$, giving an outer region characterized by atomic spins $S=\frac{5}{2}$ coupled to $0 \leq S' \leq 5$.

The splitting between the group of states with $0 \leq S' \leq 4$ in the region of R under consideration is given by an effective Heisenberg exchange integral J , treating Eq. (1) as an effective Hamiltonian. In the present theory this takes the form

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

where the terms on the right-hand side have been analyzed in detail elsewhere.^{1,2} In the present calculations the terms C , E , and G are found to be most important. Computed values, together with $4S^2J$, are listed in Table IV. In general the spread of energy between the highest and lowest state of a group described by Eq. (1) is $-2S(2S+1)J$. This quantity must be of the same magnitude as the thermal transition energy kT_N , and in fact it has been shown that $kT_N/4S^2J$ is close to unity in antiferromagnetic crystals.¹⁶ Thus, $|4S^2J|$ gives a qualitative estimate of the Néel temperature in a nonmetallic lattice of directly interacting Mn atoms. In comparing J with previous calculations it must be remembered that $4S^2$ is 16 here.

Without repeating details given previously,^{1,2} the parameters C , E , and G can be attributed to specific kinds of interaction. The term C is the ordinary direct exchange between orthogonal orbitals, a sum of Coulomb self-energies of charge densities described by products of orthonormal orbitals from the two different atoms. The term E is the delocalization effect originally discussed by Anderson.¹⁷ This term describes the spin-dependent partial delocalization of an occupied atomic

TABLE IV. Contributions to the effective exchange integral.

R	C	E	G	$4S^2J$		
				(au)	(eV)	(°K)
$4.5a_0$	0.0000502 au	0.0001131 au	0.0021939 au	-0.0022568	-0.06141	712.6
5.0	0.0000268	0.0000114	0.0012968	-0.0012814	-0.03487	404.6
5.5	0.0000170	0.0000012	0.0001912	-0.0001754	-0.00477	55.4

¹⁶ P. W. Kasteleijn and J. Van Kranendonk, *Physica* **22**, 367 (1956).

¹⁷ P. W. Anderson, *Phys. Rev.* **115**, 2 (1959).

orbital a on one atom due to the tendency of an electron to drift into a similar unoccupied orbital a' on the other atom. Physically, this term represents incipient covalent bonding, since a complete transfer between a and a' corresponds to a doubly occupied bond orbital. The term G arises from the spin-dependent polarization of a doubly occupied orbital. This is a small effect for inner shell orbitals, but in the present case there is a doubly occupied molecular valence orbital which interacts rather strongly with the localized atomic valence orbitals. The polarization considered here is a partial mixing of the antibonding valence orbital $7\sigma_u$ with the doubly occupied bonding orbital $7\sigma_g$. Physically, this term represents just the converse effect to that of term E , since a complete transfer between $7\sigma_g$ and $7\sigma_u$ corresponds to a change of configuration to one with localized atomic orbitals 7σ , $7\sigma'$. In general, it should be expected that both E and G will be important whenever, as in the present case, some valence orbitals are localized while others are not. Detailed analysis of this effect shows that the dependence on $\mathbf{S}_a \cdot \mathbf{S}_b$ is more complicated than the usual linear Heisenberg formula, Eq. (1).² As in the earlier paper, this total spin dependence is simplified here by fitting the linear formula to the two extreme values $S'=0, 4$, to define the approximate parameter G for use in the Heisenberg formula.

Since J is negative, the lowest state of the group considered here has $S'=0$ and is a $^1\Sigma_g^+$ state. The whole group of states are displaced downward equally by configuration interaction effects, not considered here, that do not depend on S' . Including only that part of this additional correlation energy associated with term G^2 , the ground state is found by quadratic interpolation to have a minimum energy of -0.79 eV at

$$R_e = 5.44a_0 = 2.88 \text{ \AA}.$$

The value of $4S^2J$ computed by interpolating to the computed R_e is -0.0082 eV, equivalent to 95.2°K .

III. RESULTS AND DISCUSSION

The principal result of the present work is to demonstrate that the diatomic Mn molecule can be characterized as a magnetic material in the sense of the present theory. This means that at the equilibrium internuclear distance in this molecule the electronic wave function must be described in terms of localized, singly occupied atomic valence orbitals, coupled by a spin-dependent exchange interaction to give a closely spaced group of molecular states of different total spin. A nonmagnetic material would be described in terms of doubly occupied bonding molecular orbitals at nuclear equilibrium.

The computed equilibrium internuclear distance is found to be 2.88 \AA , which is in qualitative agreement with an empirical estimate of 2.658 \AA made by Clementi.¹⁸ The Mn_2 molecule has not been observed directly, so no experimental data are available for comparison. The dissociation energy computed in the present work is 0.79 eV. This will be increased by a correction for the net correlation energy contribution to binding energy,¹⁹ and will probably increase, judging from experience with smaller molecules,²⁰ when the calculations are improved by including more basis orbitals. Thus, the present results imply that Mn_2 is bound with respect to dissociation into ground-state atoms.

One particular result of the present calculations must be modified when comparison is made between the Mn_2 molecule and two Mn atoms interacting in a crystal. In a cubic crystalline environment, $4s$ and $4p$ orbitals are of different symmetry from the $3d$ orbitals, and mixing of the kind found in the present work cannot occur on a single atom. Nevertheless, $3d$ orbitals on one atom can combine with appropriate combinations of $4s$ or $4p$ orbitals on neighboring atoms, and the admixture of orbitals of this kind might be significant.

¹⁸ E. Clementi, Ann. Chim. **50**, 548 (1960).

¹⁹ E. Clementi, J. Chem. Phys. **38**, 2780 (1963).

²⁰ R. K. Nesbet, J. Chem. Phys. **36**, 1518 (1962).