

Two-Electron Heisenberg Exchange Interaction between Neighboring Atoms

A. J. FREEMAN

Materials Research Laboratory, Ordnance Materials Research Office, Watertown, Massachusetts

AND

R. K. NESBET

Department of Physics, Boston University, Boston, Massachusetts

AND

R. E. WATSON*†

Avco, RAD, Wilmington, Massachusetts

(Received November 1, 1961)

The method of Nesbet is applied to the model investigated by Freeman and Watson to describe the Heisenberg exchange interaction between neighboring transition metal atoms. Pairs of atomic Hartree-Fock d orbitals obtained from calculations on Co^{++} and Co are used; the nuclei and the remaining electrons are represented by two point charges at the nearest neighbor internuclear separation of Co atoms in the metal. Nuclear charges, Z , of one and ten are used to examine the effect of changing the assumed potential. The effective Heisenberg exchange parameter is large and negative for all values of the parameters used here. The present results agree in sign with the earlier results of Freeman and Watson, who used the Heitler-London method without the

ionic configuration, but differ by an order of magnitude for $Z=1$, and are somewhat closer for $Z=10$. The discrepancy is probably due to this omission, since the present formalism takes all configurations into account for a system described by two basis orbitals. Since the observed exchange parameter for metallic cobalt is positive (ferromagnetic), and since previous investigations suggest that additional effects (due to including the remaining electrons of the ions) will not substantially alter the computed value, it appears that the ferromagnetic coupling must be explained by some mechanism other than the two-atom Heisenberg exchange interaction between localized d orbitals.

I. INTRODUCTION

THE theory of the Heisenberg exchange interaction and the mechanism of spin coupling between two paramagnetic ions has recently been re-examined. A new theoretical derivation that meets several serious objections to earlier work has been developed in a series of papers by Nesbet.^{1,2} A recent investigation by Freeman and Watson,³ using the older Heitler-London formalism, with modifications of earlier work by Stuart and Marshall,⁴ has shown that the Heisenberg exchange parameter (J) in this formalism is strongly dependent on the form of atomic orbitals used and on assumptions made about the potential field acting on the electrons. It was also shown that the terms neglected by Stuart and Marshall are large enough to change the sign of the calculated exchange integral. In the case of two Co atoms separated by their equilibrium distance in metallic cobalt, the calculated two-electron exchange integral,⁵ was found to be negative, indicating a net antiferromagnetic coupling, and of the order of magnitude of the experimental (ferromagnetic) value. The atomic Hartree-Fock orbitals obtained by Watson⁶ for both Co and Co^{++} were used.

The present paper will report the results of a calculation by Nesbet's method, using the integrals obtained by Freeman and Watson in their application of the Heitler-London method. Calculations were carried out for the two-electron model used by Freeman and Watson, with basis orbitals considered in pairs of the same symmetry (σ , π or δ). The potential field is that of two positive point charges Ze , separated by the internuclear distance 4.75 atomic units (a.u.). Results are given for $Z=1$, which in some ways is the most reasonable value for a two-electron model, and also for $Z=10$ (which is close to the Z value⁷ for which the Co $3d$ orbitals act as if they are eigenfunctions of the one-center, point-charge Hamiltonian in the Heitler-London formalism), to give an idea of the dependence of calculated quantities on the assumed value of Z .

The actual potential in a metal is the self-consistent potential including exchange, taking all electrons into account. Since the d orbitals in Co are part of nearly filled shells, the potential seen by an orbital due to the inner shells of its own atom will be only incompletely screened, and the large value of Z might be a reasonable choice. However, the potential due to the other atom will be nearly completely screened. The exchange potential terms cannot easily be taken into account without carrying out a complete calculation, as has been done recently for the N_2 molecule, which is described by a Heisenberg interaction at large internuclear distances.² The calculations by Freeman and Watson introduced the electrostatic field of the other electrons as an effective potential and in addition they considered the effect of the nonorthogonality of these electrons (to second order in overlap integrals). A treatment similar

* Part of the work of this author was supported by the Ordnance Materials Research Office, Watertown, Massachusetts.

† Present address: Theoretical Physics Division, AERE, Harwell, Berkshire, England.

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

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

³ A. J. Freeman and R. E. Watson, *Phys. Rev.* **124**, 1439 (1961).

⁴ R. Stuart and W. Marshall, *Phys. Rev.* **120**, 353 (1960).

⁵ The work reported as reference 3 covers both the case of exchange between two electrons (one on each of two atoms) and between two holes (one hole, in an otherwise closed $3d$ shell, on each of two atoms).

⁶ R. E. Watson, Solid State and Molecular Theory Group, Massachusetts Institute of Technology Technical Report No. 12, 1959 (unpublished).

⁷ See the Z 's and $J(Z)$'s in Table III of reference 3 and the associated text for an indication of this.

TABLE I. One-electron integrals for nonorthogonal basis orbitals in atomic units, such that 1 a.u. (energy)=27.21 eV and 1 a.u. (distance)=0.5292 Å. The internuclear distance is 4.75 a.u.

		$\langle A B\rangle$	$\langle A -\frac{1}{2}\nabla^2 A\rangle$	$\langle A -\frac{1}{2}\nabla^2 B\rangle$	$\langle A 1/r_A A\rangle$	$\langle A 1/r_B A\rangle$	$\langle A 1/r_A B\rangle$
Co ⁺⁺ :	$\sigma\sigma$	0.02128	8.3470	0.00503	1.3264	0.1471	0.00972
	$\pi\pi$	0.01132	8.3470	-0.00063	1.3264	0.2121	0.00453
	$\delta\delta$	0.00169	8.3470	-0.00044	1.3264	0.2078	0.00061
Co:	$\sigma\sigma$	0.04640	6.7779	0.0307	1.1647	0.1649	0.02250
	$\pi\pi$	0.05563	6.7779	0.0191	1.1647	0.2151	0.02078
	$\delta\delta$	0.01672	6.7779	0.0028	1.1647	0.2064	0.00523

to the N₂ calculation (i.e., orthogonalized orbitals, configuration mixing and all electrons accounted for) is not yet practicable for the transition metals. Hence the simpler two-electron point charge model is used here. In the Heitler-London treatment,³ this approximation appreciably affected the computed J 's and thus the present results are expected to be of qualitative value only.

II. DESCRIPTION OF THE CALCULATIONS

The customary procedure for estimating J is to expand the energy formulas of the Heitler-London method (with configuration interaction sometimes included) in powers of the overlap integral $\langle A|B\rangle$, and then to retain the spin-dependent terms of order $\langle A|B\rangle^2$. (A and B are used to denote the nuclear center an electron is centered on.) In the method of Nesbet¹ the spin coupling formalism is worked out to the second order of perturbation theory, where the exact non-diagonal elements of the electronic Hamiltonian are treated as a perturbation in a basis of many-electron states of definite total spin. An essential feature of this method is the requirement that the basis orbitals used are orthonormal, and related by a unitary transformation to the occupied Hartree-Fock orbitals for the system. Thus the overlap integral no longer appears as an explicit expansion parameter. The formalism can be applied to a model system, as in the present work, on the assumption that orthogonalized orbitals obtained from whatever basis orbitals which are used are a reasonable approximation to the localized self-consistent orbitals of the theory. Since matrix elements of the Hartree-Fock effective Hamiltonian also occur in the theory, these must also be reasonably approximated by the assumed model. These assumptions are implicit in earlier work.

The pairs of nonorthogonal basis orbitals, A and B , of the same symmetry but on different atoms, can be orthonormalized (they are normalized to unity) by the following transformation:

$$\begin{aligned} a &= PA - QB, \\ b &= PB - QA, \end{aligned} \quad (1)$$

where

$$\begin{aligned} P+Q &= 1/[1 - \langle A|B\rangle]^{\frac{1}{2}}, \\ P-Q &= 1/[1 + \langle A|B\rangle]^{\frac{1}{2}}. \end{aligned} \quad (2)$$

The orbitals a , b are equivalent under interchange of

the two atoms, and are orthonormal. The matrix elements of various operators in the electronic Hamiltonian, for the 3d orbitals obtained by Watson⁶ for Co and Co⁺⁺, are listed in Tables I and II.

The two most important contributions to the effective Heisenberg exchange integral J for two directly interacting atoms are the ordinary direct exchange term,

$$C = \langle ab|ba\rangle$$

$$\equiv \int \int \varphi_a^*(\mathbf{r}_1) \varphi_b(\mathbf{r}_1) r_{12}^{-1} \varphi_b^*(\mathbf{r}_2) \varphi_a(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (3)$$

always positive (ferromagnetic) for orthogonal orbitals a , b , and the delocalization effect, considered by Anderson⁸ to be the dominant superexchange effect, that is qualitatively described as due to incipient covalent bonding. In the present investigation this corresponds to mixing in those singlet configurations constructed with both electrons on the same nucleus. In the present formalism this term is²

$$E = 2\mathcal{C}_{ab}^2/\Delta, \quad (4)$$

defined so that the positive sign corresponds to antiferromagnetic coupling. Here

$$\Delta \equiv \langle aa|aa\rangle - \langle aa|bb\rangle, \quad (5)$$

and

$$\mathcal{C}_{ab} \equiv \langle a|-\frac{1}{2}\nabla^2 - Z/r_A - Z/r_B|b\rangle + \langle aa|ab\rangle. \quad (6)$$

E is the only superexchange term that enters the two-electron approximation. Additional superexchange terms, such as those appearing in the N₂ investigation, appear when one goes to a many-electron description. The N₂ results suggest that C and E dominate, deter-

TABLE II. Two-electron integrals for nonorthogonal basis orbitals in atomic units. The symbol $\langle ij|kl\rangle$ denotes

$$\int \int \phi_i^*(1) \phi_j(1) (1/r_{12}) \phi_k^*(2) \phi_l(2) d\mathbf{r}_1 d\mathbf{r}_2.$$

		$\langle AA AA\rangle$	$\langle AA BB\rangle$	$\langle AB BA\rangle$	$\langle AA BA\rangle$
Co ⁺⁺ :	$\sigma\sigma$	0.991714	0.15042	0.000430	0.010309
	$\pi\pi$	0.953088	0.21344	0.000067	0.004490
	$\delta\delta$	0.970396	0.20486	0.000001	0.000594
Co:	$\sigma\sigma$	0.823017	0.17007	0.003140	0.020267
	$\pi\pi$	0.792868	0.216179	0.001440	0.024717
	$\delta\delta$	0.806572	0.20174	0.000085	0.005079

⁸ P. W. Anderson, Phys. Rev. **115**, 2 (1959).

TABLE III. Integrals for orthonormal basis orbitals and other calculated quantities, all in atomic units. Here $\Delta = (aa|aa) - (aa|bb)$, $C = (ab|ba)$, $\mathcal{H}_{ab} = (a|-\frac{1}{2}\nabla^2 - Z/r_A - Z/r_B|b) + (aa|ab)$, $\text{Crit} = -2\mathcal{H}_{ab} - \frac{1}{2}\Delta - 2C$, and $E = 2\mathcal{H}_{ab}^2/\Delta$. If $\text{Crit} < 0$, $4S^2J = C - E$; otherwise J is not defined.

		Δ	C	\mathcal{H}_{ab}	Crit	$Z=1$		$Z=10$	
						E	$4S^2J$	E	$4S^2J$
Co ⁺⁺ :	$\sigma\sigma$	0.84169	0.00025	-0.17456+0.01193Z	<0	0.06283	-0.06257	<0	0.00727
	$\pi\pi$	0.73974	0.00004	-0.09723+0.00836Z	<0	0.02136	-0.02132	<0	0.00050
	$\delta\delta$	0.76555	0.00000	-0.01495+0.00137Z	<0	0.00048	-0.00048	<0	0.00000
Co:	$\sigma\sigma$	0.65442	0.00234	-0.28721+0.01671Z	>0			<0	0.04401
	$\pi\pi$	0.57785	0.00025	-0.36247+0.03537Z	>0			<0	0.00030
	$\delta\delta$	0.60501	0.00006	-0.11397+0.01248Z	<0	0.03402	-0.03396	<0	0.00038

mining at least the qualitative behavior of J and this assumption is retained here as well. The various calculated quantities that occur in the above equations are listed in Table III. For atomic spin S , the effective exchange integral J is given by

$$4S^2J = C - E. \quad (7)$$

The formulas used are derived in the papers cited above.^{1,2}

The discussion in these papers shows that the Heisenberg exchange formalism should not be valid when the quantity denoted by Crit is positive. Crit, which has the form

$$\text{Crit} \equiv -2\mathcal{H}_{ab} - \frac{1}{2}\Delta - 2C, \quad (8)$$

is the energy difference between the triplet state constructed from the two independent determinants with one orbital centered on A and one on B [$\det(a,b)$] and the molecular orbital ground state configuration in which a bonding molecular orbital is doubly occupied. The singlet associated with $\det(a,b)$ is the lowest singlet only if this energy difference is negative; otherwise the orbitals in question should be considered to be covalently coupled, and there is no free spin due to them associated with the individual atoms. Hence this criterion decides between covalent bonding and spin coupling by the Heisenberg mechanism, and these are shown to require different descriptions of the electronic states of lowest energy. This point is discussed at length elsewhere,² with the nitrogen molecule as an example.

III. DISCUSSION

The exchange integrals J (equal to $4S^2J$ for spin $S=\frac{1}{2}$ on each atom) calculated for $Z=1$ and 10 are compared with the two-electron Heitler-London results³ (i.e., not the many-electron results) in Table IV. The Heitler-London results for $Z=10$ were calculated for comparison with the present calculations and differ from the corresponding calculations in reference 3, where somewhat smaller values of Z were determined to affect the cancellation of certain correction terms. Note that the earlier values of J were all negative. The present method includes the ionic configuration, and the dominant term E in the calculated exchange integral

is due to it. Because the orbitals used in the Heitler-London method are not orthogonal, this configuration is present to some extent, but the corresponding ionic configuration is not included explicitly. Since it is the interaction of this configuration that describes incipient covalent bonding, the qualitative source of the negative exchange integral in the present method, it must be concluded that the discrepancies indicated in Table IV are largely due to the use of a pure "covalent" structural formula in the Heitler-London calculation. In the region where the criterion for the applicability of the Heisenberg formalism is satisfied, the present method should, subject to limitations in the model, be quantitatively superior.

It is important to be aware of some of the shortcomings of the model. The "core" electrons on the two ions have been neglected whereas their inclusion was found to affect the Heitler-London results significantly by reducing the magnitude of J . In the present method the presence of "core" electrons introduces new superexchange terms and we have relied on the N_2 calculation to indicate that these terms are relatively unimportant. It should be noted that these "core" electrons include other $3d$ electrons. For that matter one should also account for the presence of $4s$ electrons.³ Also, this is a two-atom treatment from which we are trying to derive information pertinent to a solid. If one assumes that such matters are unimportant one concludes that the Heisenberg exchange interaction between localized orbitals does not seem to account for ferromagnetism. Hence one conclusion from these calculations is that they provide further evidence in

TABLE IV. Comparison with Heitler-London calculation for $J(Z)$ in a.u.

		$J(1)$ H-L ^a	$J(1)$ Present	$J(10)$ H-L ^b	$J(10)$ Present
Co ⁺⁺ :	$\sigma\sigma$	-0.00648	-0.06257	-0.00191	-0.00701
	$\pi\pi$	-0.00192	-0.02132	-0.00022	-0.00046
	$\delta\delta$	-0.00004	-0.00048	0.00000	0.00000
Co:	$\sigma\sigma$	-0.0220	covalent	-0.00806	-0.04167
	$\pi\pi$	-0.0351	covalent	0.00010	-0.00005
	$\delta\delta$	-0.0033	-0.03396	0.00050	-0.00032

^a A. J. Freeman and R. E. Watson, reference 3.

^b Calculated for comparison with the present work.

support of ideas such as those of Zener,⁹ expressed more recently in a somewhat different form by Goodenough,¹⁰ that ferromagnetic interactions in the transition metals cannot be attributed to direct coupling of localized orbitals. The fact that some of the Co orbitals (σ and π), for $Z=1$, are indicated to be covalently coupled is consistent with the suggestion by Goodenough that

the ferromagnetic interaction might arise from indirect coupling of localized orbitals through quasi-degenerate orbitals of a metallic or antibonding d band, since any occupied d orbital beyond five per atom would have to be either an antibonding covalently coupled orbital or else an energetically unfavorable localized dd orbital with spin antiparallel to the net spin on its atom. A partially filled antibonding band is required for the ferromagnetic coupling mechanism discussed by Goodenough.

⁹ C. Zener, Phys. Rev. **81**, 440 (1951); **83**, 299 (1951).

¹⁰ J. B. Goodenough, Phys. Rev. **120**, 67 (1960).

Repulsive Interaction between Two Ground-State Helium Atoms*†

P. E. PHILLIPSON‡

Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago, Illinois

(Received October 12, 1961)

The repulsion energy between two ground-state helium atoms ($^1\Sigma_g^+$ state of He_2) has been investigated in the single-configuration MO (molecular orbital) approximation and then further refined to include the effects of electron correlation by the inclusion of superposition of configurations. In the former case, the wave function is expressed as a single antisymmetrized spin-orbital product (ASOP) of the form $|\sigma_g 1s(1)\alpha(1)\sigma_g 1s(2)\beta(2)\sigma_u 1s'(3)\alpha(3)\sigma_u 1s'(4)\beta(4)|$, where the MO's $\sigma_g 1s$ and $\sigma_u 1s'$ are approximated as the sum and difference of Slater-type orbitals (STO's) $1s$ and $1s'$, respectively, and the energy minimized with respect to the orbital exponents. In addition to the repulsion energy at small internuclear distances the slight polarization of the $\sigma_u 1s'$ MO effected by the ζ variation, permitted the single ASOP wave function to give indications of the van der Waals energy minimum at large distances. The superposition of configurations treatment employed a linear combina-

tion of configurations constructed out of a $1s, 1s', 2p\sigma, 2p\pi$ STO basis set, and at five internuclear distances R between 0.5 and 2.0 Å, the STO orbital exponents were varied to minimize the energy. Various wave functions including from 10 to 64 electron configurations were tried, which were so chosen that the wave functions would go properly as $R \rightarrow 0$ into the 1S ground-state function of beryllium and as $R \rightarrow \infty$ go into a product of two 1S helium atom functions. The computed repulsion energies in the region $0.5 \text{ Å} \leq R \leq 1.0 \text{ Å}$ are 2.8 to 1.2 times higher than values deduced from experimental scattering data obtained several years ago, and since the difference between the lowest computed (64-configuration) energy and the estimated exact energy is much smaller than this, a reinvestigation of the scattering analysis is emphasized.

I. INTRODUCTION

THE exchange or repulsive interaction potential between two 1S ground-state helium atoms has been investigated by several people over the past ten years using approximate electronic wave functions of varying degrees of accuracy. The earlier calculations by Slater¹ and Rosen² were of the valence-bond type in which the interaction between the two atoms was treated as a perturbation, so that the molecular wave function was constructed from approximate wave functions of the individual helium atoms.

In subsequent investigations³⁻⁸ the molecular orbital

approach was followed, in which the two helium atoms are regarded as a He_2 molecule in which each of the four electrons is assigned to a one-electron orbital wave function, or molecular orbital (MO), which extends over the whole molecule. The MO calculations assumed that two electrons are assigned to a bonding $1\sigma_g$ MO with opposite spins α and β and two electrons are assigned to an antibonding MO $1\sigma_u$, likewise with opposed spins. The molecular wave function is then expressed as a single antisymmetrized spin-orbital product (ASOP) or Slater determinant:

$$\Psi_{\text{MO}} = (4!)^{-\frac{1}{2}} |1\sigma_g(1)\alpha(1)1\sigma_g(2)\beta(2)1\sigma_u(3)\alpha(3)1\sigma_u(4)\beta(4)|. \quad (1)$$

The several reported MO calculations differ formally first in the specified form of the MO's, and secondly in the treatment of the variational parameters. A sum-

* This work was assisted by the Office of Naval Research and by a grant from the National Science Foundation.

† Submitted in partial fulfillment for the degree of Doctor of Philosophy, Department of Physics, University of Chicago.

‡ Shell Oil Fellow, 1958-1959. Present address: Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan.

¹ J. C. Slater, Phys. Rev. **32**, 349 (1928).

² P. Rosen, J. Chem. Phys. **18**, 1182 (1950).

³ V. Griffing and J. F. Wehner, J. Chem. Phys. **23**, 1024 (1955); referred to hereafter as G-W.

⁴ M. Sakamoto and E. Ishiguro, Progr. Theoret. Phys. (Kyoto) **15**, 37 (1956).

⁵ S. Huzinaga, (a) Progr. Theoret. Phys. (Kyoto) **18**, 140 (1957); (b) *ibid.* **20**, 15 (1958).

⁶ T. Hasino and S. Huzinaga, Progr. Theoret. Phys. (Kyoto) **20**, 631 (1958).

⁷ N. Moore, J. Chem. Phys. **33**, 471 (1960).

⁸ B. J. Ransil, J. Chem. Phys. **34**, 2109 (1961).