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The Heisenberg Exchange Integral in a Non-Orthogonal Basis for Antiferromagnetic and Ferromagnetic Systems

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The Dirac–Van Vleck–Serber permutation degeneracy method is used to demonstrate that the Heisenberg spin exchange Hamiltonian, $\mathscr{H}_{\mathrm{ex}} = -2J_{12}\mathscr{s}_1 \cdot \mathscr{s}_2$, is a good approximate Hamiltonian for the theoretical interpretation of antiferromagnetic and ferromagnetic systems. The approach does not neglect double or higher-order permutations and covers the general case of a single N-electron configuration as well as that of configuration interaction. An analogy between antiferromagnetic and hydrogen-molecule-like systems is established, and a formula for the estimation of the Heisenberg exchange integral is derived.

Key words: Heisenberg exchange integral – Heisenberg exchange Hamiltonian

1. Introduction

The antiferromagnetic and ferromagnetic coupling between the spins of unpaired electrons on proximate centres is a subject on which there is a plethora of experimental data. Not surprisingly, therefore, there has been a similar abundance of theoretical papers on this subject. Apart from situations in which the problem corresponds to putative bond formation (as in the hydrogen molecule) the phenomenon has proved a difficult one for which to obtain an entirely satisfactory theoretical picture. Typical is the problem of two transition metal ions separated by a, formally, closed shell anion, the system being either linear or bent with an angle of ninety degrees. Fundamental here is the work of Anderson [1, 2], of Kanamori [3], of Goodenough [4, 5], and of Keffer and Oguchi [6]. The relationships between the approximations made by these various workers has been clarified more recently by the work of Huang and Orbach [7–9]. Even if the details are frequently somewhat obscure the general picture that emerges is clear. The energy separation between the high spin and low spin states that is associated with the phenomenon called antiferromagnetism is a small one. Relatively small contributions to this separation may therefore be important. This means that even apparently innocuous approximations must be regarded with suspicion. Thus, the neglect of cation-cation overlap in situations such as those described above is a weakness in the Anderson model. Although it is clear that Configuration Interaction (CI) (between states based on localized orbital configurations) is of paramount importance, the extent to which such interaction has been included is somewhat limited. The major part of the work to date has been as much algebraic as numerical, a feature which has limited CI to that involving valence-shell basis functions. It may well be that the inclusion of more excited states, such as may be used to include the effects of polarization, would show that they make significant contributions to the small energy gap under study. However, the difficulty of extensive inclusion of excited states (including continuum states) is well known. In this uncertain theoretical situation the experimentalist has resorted to the use of spin Hamiltonians and addressed himself to the measurement of the parameters involved. The theoretical uncertainty is then reflected in the uncertain relationship to be expected between the values of the spin Hamiltonian parameters measured in different systems. The use of such spin Hamiltonians finds justification in the work of McWeeny and Yonezawa [10], who considered a rather general many-electron system. However, in their work they neglected double and high-order electron permutations. In the present paper we demonstrate that with inclusion of these terms the spin-Hamiltonian approach remains valid and, incidentally, give an improved general formulation of the "exchange integral" of the spin Hamiltonian. Before embarking upon this part of our work, it is convenient first to briefly review the Heisenberg exchange integral for hydrogen-molecule-like systems.

2. The Hydrogen-Molecule Approach

2.1. Introduction

In discussions of the mechanism of antiferromagnetic coupling between transition metal ions the hydrogen molecule occupies a unique role. This is because the energies of the lowest lying spin singlet and triplet states may be simply evaluated and the factors determining their separation readily enumerated. The belief that, *mutatis mutandis*, similar factors will be involved in more complicated states has been an important guiding factor in the theoretical treatment of such systems (the analogy with dimeric copper(II) systems is particularly clear). However, the validity of the assumption of the direct applicability of the hydrogen-molecule treatment to such systems has not been examined in detail. This is because in these extensions the single Valence Bond (VB) theory has to be extensively modified firstly because of the common presence of intervening anions and secondly because of the inclusion of excited electronic configurations involving charge transfer.

In this section we summarize the pseudo-hydrogen-molecule approach to the problem of exchange interactions in antiferromagnetic and ferromagnetic systems; within this scheme a spin-Hamiltonian formulation of the case of non-orthogonal basis functions will be developed, and a comparison made with the well known orthogonal case.

2.2. *The Energy of the Hydrogen Molecule* (*Valence-Bond Treatment*)

The simple VB treatment[1] of the hydrogen molecule [12, 13] gives the energy of the lowest spin singlet and the lowest spin triplet as

$$^{1/3}E = 2E_{\mathrm{H}} + \frac{Q \pm J}{1 \pm S^2}. \tag{1}$$

Here, $2E_{\mathrm{H}}$ is the energy of two non-interacting hydrogen atoms and S, Q and J are the overlap, Coulomb and exchange integrals respectively defined by[2]

$$\begin{aligned} S &= \langle 1s_a(1) \mid 1s_b(2) \rangle, \\ Q &= -\left\langle 1s_a(1) \left| \frac{1}{r_{b1}} \right| 1s_a(1) \right\rangle - \left\langle 1s_b(2) \left| \frac{1}{r_{a2}} \right| 1s_b(2) \right\rangle \\ &\quad + \left\langle 1s_a(1) 1s_b(2) \left| \frac{1}{r_{12}} \right| 1s_a(1) 1s_b(2) \right\rangle + \frac{1}{r_{ab}}, \end{aligned} \tag{2}$$

$$\begin{aligned} J &= -S \left\langle 1s_a(1) \left| \frac{1}{r_{b1}} \right| 1s_b(1) \right\rangle - S \left\langle 1s_b(2) \left| \frac{1}{r_{a2}} \right| 1s_a(2) \right\rangle \\ &\quad + \left\langle 1s_a(1) 1s_b(2) \left| \frac{1}{r_{12}} \right| 1s_a(2) 1s_b(1) \right\rangle + \frac{S^2}{r_{ab}}. \end{aligned} \tag{3}$$

It must be emphasized that the Q and J as used in the VB theory are different from the Coulomb and exchange integrals of the MO theory where Coulomb and exchange integrals are usually defined as the third terms in (2) and (3) respectively. From (1) the energy separation is

$$^1E - {}^3E = \frac{2(J - QS^2)}{1 - S^4}. \tag{4}$$

In what follows it will be more convenient to consider instead of the energy separation (4) half of this quantity; we have then

$$J_{12} \equiv \frac{^1E - {}^3E}{2} = \frac{J - QS^2}{1 - S^4}. \tag{5}$$

It is important to distinguish between the cases of orthogonal and non-orthogonal orbitals. In the former $S = 0$, and from (5) and (3) the half-energy separation becomes

$$J_{12} = J = \left\langle 1s_a(1) 1s_b(2) \left| \frac{1}{r_{12}} \right| 1s_a(2) 1s_b(1) \right\rangle \tag{6}$$

that is, the exchange integral of MO usage. This is always positive – see, for instance, the books by Slater [15] and Pilar [16]. Hence one is led to the clear prediction that

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[1] Dance has shown [11] that the Heitler-London wave functions are more suitable than the LCAO wavefunctions for the study of the exchange interaction.

[2] For further details see, for instance, the book by Murrell *et al.* [14].

the triplet state has then the lower energy. It is, therefore, non-orthogonality which can make the spin singlet state lower in energy than the spin triplet; this, of course, is the case with the hydrogen molecule where it is found that the exchange integral (3) is negative, hence from (1) the singlet state is lower in energy than the triplet.

2.3. *Spin-Hamiltonian Formulation*

Because the function $s(s+1)-1$ has values of -1 for the singlet and $+1$ for the triplet, and is algebraically equal to $\frac{1}{2}+2s_1 \cdot s_2$ (Dirac's identity [17]), it is possible to exploit the fact that the singlet and triplet states are eigenfunctions of s^2 with eigenvalue $s(s+1)$ in order to give a general spin-operator expression for (1). This has far-reaching consequences, in that it permits the use of the spin variables as a basis for the calculation. The spin variables are relatively easy to handle since in their use there are only two linearly independent functions of spin for each electron rather than the three required to describe the orbital motion. One further advantage of working in "spin-only" space is that the interaction energies arise directly as a linear combination of the coefficients of spin variables, while in the usual "spinless" formalism one has to calculate energy differences. This, apart from simplifying the algebra (one has to calculate one quantity instead of two), becomes very important when one takes into consideration the fact that the quantities involved are very small and it is probably more accurate to calculate them directly [18].

2.3.1. Orthogonal Orbitals

In this case, one can immediately write the spin Hamiltonian

$$\mathscr{H}_s = Q - J(\tfrac{1}{2} + 2s_1 \cdot s_2) \tag{7}$$

which is such that the expression

$$E = \langle \Theta | \mathscr{H}_s | \Theta \rangle$$

gives $E = Q + J$ when Θ is a spin singlet eigenfunction, and $E = Q - J$ when Θ is a spin triplet eigenfunction.

The spin-dependent part of $\mathscr{H}_s$ is the well known Heisenberg Exchange Hamiltonian [19]

$$\mathscr{H}_{ex} = -2J s_1 \cdot s_2 \tag{8}$$

so that the coefficient of $s_1 \cdot s_2$ gives directly the interaction energy ${}^1E - {}^3E = 2J$.

Although the above development suggests that exchange effects are formally equivalent to a vector coupling of electron spins (the Dirac Vector Model [20]), it must be remembered that, apart from small magnetic effects, there is no physical coupling between the spins [21, 22].

2.3.2. Non-Orthogonal Orbitals

From (1) the interaction part of the energy of the singlet and triplet state is

$$ {}^{1/3}E_{\text{int}} = \frac{Q \pm J}{1 \pm S^2}, \tag{9} $$

and this can be written, after a binomial expansion of the denominator to order S^4, as

$$ {}^{1/3}E_{\text{int}} = (1 \mp S^2 + S^4)(Q \pm J). \tag{10} $$

Putting again the operator $\frac{1}{2} + 2\mathscr{s}_1 \cdot \mathscr{s}_2$ in place of the $\mp$ signs in the above equation, we have the spin-Hamiltonian

$$ \mathscr{H}_s = E_0 - 2J_1 \mathscr{s}_1 \cdot \mathscr{s}_2 - 4J_2(\mathscr{s}_1 \cdot \mathscr{s}_2)^2 \tag{11} $$

where

$$ E_0 = \left(1 + \frac{S^2}{2} + S^4\right)\left(Q - \frac{J}{2}\right), \tag{12} $$

$$ J_1 = J(1 + S^2 + S^4) - QS^2, \tag{13} $$

$$ J_2 = JS^2. \tag{14} $$

The half-energy separation is found from (9)

$$ \frac{{}^1E - {}^3E}{2} \equiv J_{12} = \frac{J - QS^2}{1 - S^4} \simeq J(1 + S^4) - QS^2. \tag{15} $$

Comparing (15) with (13) and (14), we see that

$$ J_{12} = J_1 - J_2. \tag{16} $$

That is, strictly speaking, we have lost the simple result of the orthogonal case [cf. Eq. (6)]. However, it is a good approximation to neglect in (13) and (15) the powers of S as compared to unity, and by doing so we obtain

$$ \mathscr{H}_{\text{ex}} = -2J_1 \mathscr{s}_1 \cdot \mathscr{s}_2 \tag{17} $$

and

$$ J_{12} = J_1 = J - QS^2. \tag{18} $$

That is, in this case J_1 is not exactly the "true" exchange integral, J, of Heisenberg. Similarly, J_{12} can take now both positive and negative values.

2.4. Comparison with Löwdin's Spin Hamiltonian

Löwdin [23] has derived a spin Hamiltonian of the form

$$ \mathscr{H}_s = E'_0 - 2J_{12} \mathscr{s}_1 \cdot \mathscr{s}_2 \tag{19} $$

for a two electron system by defining the "exchange integral", J_{12}, as the half-energy separation between the spin singlet and triplet states, and then considering the relation

$$E=\tfrac{1}{2}({}^1E+{}^3E)-\tfrac{1}{2}\kappa({}^1E-{}^3E). \tag{20}$$

In this, $\kappa=-1$ gives $E={}^1E$ and $\kappa=+1$ gives $E={}^3E$. This led him to substitute the operator $\tfrac{1}{2}+2\mathscr{s}_1\cdot\mathscr{s}_2$ for the symbol κ in (20), thus obtaining the spin Hamiltonian (19) with

$$E'_0=\tfrac{1}{4}({}^1E+3{}^3E). \tag{21}$$

He concluded that (19) "is an exact form of the vector-model formula, independent of any assumptions about correlation, non-orthogonality, polar states, relativistic effects, etc.". It follows that an equivalence should exist between (11) and (19) and this we now demonstrate.

From (21) and (10) we find (to order S^4)

$$E'_0=\tfrac{1}{4}({}^1E+3{}^3E)=\left(1+\frac{S^2}{2}+S^4\right)\left(Q-\frac{J}{2}\right)-\tfrac{3}{4}JS^2,$$

so that, from (12) and (14), we have

$$E'_0=E_0-\tfrac{3}{4}J_2.$$

Now, from (11), we have

$$\begin{aligned}\mathscr{H}_s&=E_0-2J_1\mathscr{s}_1\cdot\mathscr{s}_2-J_2(\tfrac{1}{2}+2\mathscr{s}_1\cdot\mathscr{s}_2)^2+\frac{J_2}{4}+2J_2\mathscr{s}_1\cdot\mathscr{s}_2\\&=E_0-\tfrac{3}{4}J_2-2(J_1-J_2)\mathscr{s}_1\cdot\mathscr{s}_2\\&=E'_0-2J_{12}\mathscr{s}_1\cdot\mathscr{s}_2\end{aligned}$$

the final result being Eq. (19), with J_{12} interpreted as equal to J_1-J_2 (cf. Eq. (16)). However, if one is to calculate an interaction energy directly, i.e. without first calculating the individual energies of the two states, then one has to use (11), so that Eq. (19) has no computational advantages.

3. *N*-Electron Antiferromagnetic and Ferromagnetic Systems

3.1. *Spin Hamiltonians for Orthogonal Orbital Bases*

For an N-electron system the normalized wave function is

$$\Phi=\frac{1}{\sqrt{N!}}\mathscr{A}[\Omega(\mathbf{r}_1,\ldots,\mathbf{r}_N)\Theta(s_1,\ldots,s_N)],$$

where Ω is the orbital part (usually a Hartree product), Θ is the spin part, $\mathscr{A}$ is the antisymmetrizer so that the energy is given by solving

$$\sum_{\mathscr{P}}{}'(-1)^p\langle\Omega|\mathscr{H}-E|\mathscr{P}^{r}\Omega\rangle\langle\Theta\mid\mathscr{P}^{s}\Theta\rangle=0 \tag{22}$$

where $\mathscr{P}^{r}$ and $\mathscr{P}^{\sigma}$ are permutation operators acting on orbital and spin functions respectively, and the summation is carried over the $N!/2^{r_I}$ permutations which differ by more than an interchange of identical orbitals in the configuration R_I (N is the number of electrons and r_I is the number of filled orbitals)[3].

For orthogonal orbitals, the only non-vanishing contributions to (22) arise from permutations involving single interchanges, so that

$$E=\langle\Omega|\mathscr{H}|\Omega\rangle-\sum_{i,j}\langle\Omega|\mathscr{H}|\mathscr{P}^{r}_{ij}\Omega\rangle\langle\Theta\mid\mathscr{P}^{\sigma}_{ij}\Theta\rangle. \tag{23}$$

On replacing $\mathscr{P}^{\sigma}_{ij}$ by $\frac{1}{2}+2\mathfrak{s}_i\cdot\mathfrak{s}_j$ we obtain the spin Hamiltonian

$$\mathscr{H}_s=Q-\sum_{i,j}J_{ij}(\tfrac{1}{2}+2\mathfrak{s}_i\cdot\mathfrak{s}_j)$$

of which the spin-dependent part gives the exchange Hamiltonian

$$\mathscr{H}_{\text{ex}}=-2\sum_{i,j}J_{ij}\mathfrak{s}_i\cdot\mathfrak{s}_j=-2\sum_{i=1}^{n_{\text{A}}}\sum_{j=1}^{n_{\text{B}}}J_{ij}\mathfrak{s}_i\cdot\mathfrak{s}_j \tag{24}$$

where the labels i and j refer to atoms of different types, A and B.

Van Vleck [25] has shown that when the unclosed shells of each atom are in a state such that the orbital part of the angular momentum has been quenched, the exchange Hamiltonian (24) can further be written

$$\mathscr{H}_{\text{ex}}=-\frac{2}{n_{\text{A}}n_{\text{B}}}\mathscr{S}_{\text{A}}\cdot\mathscr{S}_{\text{B}}\sum_{i=1}^{n_{\text{A}}}\sum_{j=1}^{n_{\text{B}}}J_{ij}=-2J_{\text{AB}}\mathscr{S}_{\text{A}}\cdot\mathscr{S}_{\text{B}}, \tag{25}$$

where $\mathscr{S}_{\text{A}}=\sum_i\mathfrak{s}_i$, $\mathscr{S}_{\text{B}}=\sum_j\mathfrak{s}_j$, n_{A} and n_{B} are, respectively, the number of unpaired spins for atoms A and B, and J_{AB} is the exchange integral between the total spins of the two atoms on the assumption that the exchange integral is independent of the electron state. When, however, there is an orbital contribution to the angular momentum, Eq. (25) is not applicable as there is then more than one state of maximum multiplicity.

3.2. *Spin Hamiltonians for Non-Orthogonal Orbital Bases*

Spin Hamiltonians such as given above have been widely used in the interpretation of data in antiferromagnetic systems, systems in which, almost invariably, the orthogonal orbital assumption is invalid. This practice has provoked strong criticism, particularly by Slater [26]. The immediate question which arises is that of whether it is possible, theoretically, to justify the use of spin Hamiltonians in these situations and, if so, what interpretation is to be placed on the J values so obtained.

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[3] In a superexchange interaction between two transition metal ions the cation's singly occupied d orbitals interact via the filled p orbitals of one (or more) intervening anions. Following Serber [24], in the case of filled orbitals the set of $N!$ permutation operators is partitioned into 2^{r_I} subsets each having $N!/2^{r_I}$ elements. Serber showed that one has then to consider only one of these subsets, the so-called "independent set".

In the present work, the following notations will be used

$$\begin{aligned} \langle \Omega|\mathscr{H}|\mathscr{P}^{r}\Omega\rangle &\equiv H_p, \\ \langle \Omega \mid \mathscr{P}^{r}\Omega\rangle &\equiv T_p, \\ \langle \Theta \mid \mathscr{P}^{s}\Theta\rangle &\equiv P^s. \end{aligned} \tag{26}$$

The H_p's are sums of one-electron and two-electron integrals multiplied by products of overlap integrals. The T_p's are, generally, products of overlap integrals.

Equation (22) for the energy can now be written

$$\sum_{\mathscr{P}}{}' (-1)^p \langle \Omega|\mathscr{H}-E|\mathscr{P}^{r}\Omega\rangle\langle \Theta \mid \mathscr{P}^{s}\Theta\rangle = \sum_{\mathrm{P}}{}' (-1)^{\mathrm{p}}(H_p - ET_p)\mathrm{P}^{\mathrm{s}} = 0 \tag{27}$$

from which we find

$$E = \frac{H_I + \sum\limits_{P' \neq I}{}' (-1)^p H_{P'} P^{s'}}{1 + \sum\limits_{P' \neq I}{}' (-1)^p T_{P'} P^{s'}} \tag{28}$$

or, after a binomial expansion of the denominator,

$$\begin{aligned} E = &\left[1 - \sum_{P' \neq I}{}' (-1)^p T_{P'} P^{s'} + \left(\sum_{P' \neq I}{}' (-1)^p T_{P'} P^{s'}\right)^2 - \cdots\right] \\ &\times\left[H_I + \sum_{P' \neq I}{}' (-1)^p H_{P'} P^{s'}\right]. \end{aligned} \tag{29}$$

We note that the squared and higher-order terms involve, respectively, squares and higher powers, as well as cross products of overlap integrals, and, therefore, we neglect these terms, (29) becoming

$$E = \left[1 - \sum_{P' \neq I}{}' (-1)^p T_{P'} P^{s'}\right]\left[H_I + \sum_{P' \neq I}{}' (-1)^p H_{P'} P^{s'}\right]. \tag{30}$$

Now, any permutation operator which involves more than one interchange can always be written in terms of single-interchange permutation operators. Thus,

$$\begin{aligned} \mathscr{P}_{kij} &= \mathscr{P}_{ki}\mathscr{P}_{ij} \\ \mathscr{P}_{kl,\,ij} &= \tfrac{1}{2}(1 + \mathscr{P}_{ij}) \end{aligned} \tag{31}$$

the latter relation resulting on placing the restriction $\mathscr{P}^{s}_{kl} = -1$, i.e. the electrons k and l belong to the same orbital. This suggests that we can partition the set of permutation operators into two subsets, one including those operators, $\mathscr{P}^{\mathrm{i}}$, which act on both the electrons, (i, j), involved in the magnetic interaction, the other including the remaining operators, $\mathscr{P}^{\mathrm{ni}}$, (ni standing for non-interacting).

As an example, let us consider the case of a four-electron system with (3, 4) being the pair of interacting electrons; then,

$$\{\mathscr{P}^{\mathrm{i}}\}=\{\mathscr{P}_{34},\mathscr{P}_{134},\mathscr{P}_{234},\mathscr{P}_{143},\mathscr{P}_{243},\mathscr{P}_{13,24},\mathscr{P}_{14,23}\}$$

$$\{\mathscr{P}^{\mathrm{ni}}\}=\{\mathscr{P}_{\mathrm{I}},\mathscr{P}_{13},\mathscr{P}_{23},\mathscr{P}_{14},\mathscr{P}_{24}\},$$

that is, we have partitioned the "independent" set of permutation operators $\{\mathscr{P}^{\mathrm{ind}}\}$ into $\{\mathscr{P}^{\mathrm{i}}\}$ and $\{\mathscr{P}^{\mathrm{ni}}\}$, so that $\{\mathscr{P}^{\mathrm{ind}}\}=\{\mathscr{P}^{\mathrm{i}}\}\cup\{\mathscr{P}^{\mathrm{ni}}\}$.

Considering only one pair, (i,j), of interacting electrons, we now write (30) as follows

$$E=\left[1-\sum_{p\mathrm{ni}\neq I,p\mathrm{i}}{}'(-1)^p T_{p\mathrm{ni}}P^{s,\mathrm{ni}}-\sum_{p\mathrm{i}}{}'(-1)^p T_{p\mathrm{i}}P^{s,\mathrm{i}}\right]$$
$$\times\left[H_I+\sum_{p\mathrm{ni}}{}'(-1)^p H_{p\mathrm{ni}}P^{s,\mathrm{ni}}+\sum_{p\mathrm{i}}{}'(-1)^p H_{p\mathrm{i}}P^{s,\mathrm{i}}\right].$$

Since the two states, the singlet and the triplet, differ only in the spins of the interacting electrons, it is apparent that the energy difference will result only from the terms containing the $P^{s,i}$'s. Now, $P^s_{ij}=-1$ for the singlet and $+1$ for the triplet. Hence it follows that

$$\frac{{}^1E-{}^3E}{2}=\sum_{p\mathrm{i}}{}'(-1)^p T_{p\mathrm{i}}\tilde{P}^{s,\mathrm{i}}\left[H_I+\sum_{p\mathrm{ni}}{}'(-1)^p H_{p\mathrm{ni}}P^{s,\mathrm{ni}}\right]$$
$$-\sum_{p\mathrm{i}}{}'(-1)^p H_{p\mathrm{i}}\tilde{P}^{s,\mathrm{i}}\left[1-\sum_{p\mathrm{ni}}{}'(-1)^p T_{p\mathrm{ni}}P^{s,\mathrm{ni}}\right], \tag{32}$$

where the $\tilde{P}^{s,i}$'s are the matrix elements of the coefficients of the $\mathscr{P}^{\mathscr{s},i}$'s in the expansion of the latter operators in terms of $\mathscr{P}^{\mathscr{s}}_{ij}$. For instance, from Eq. (31) we obtain

$$\tilde{P}^s_{kij}=\mathrm{P}^s_{ki}$$

$$\tilde{P}^s_{ij}=1 \quad \text{and} \quad \tilde{P}^s_{kl,ij}=\tfrac{1}{2}.$$

We now turn to the spin-Hamiltonian formulation of the problem, following the procedure that we have used in Sect. 2.3. After the expansion of the permutation operators in terms of $\mathscr{P}^{\mathscr{s}}_{ij}$, we leave $\mathscr{P}^{\mathscr{s}}_{ij}$ unspecified and express it by means of the Dirac's identity. This process gives a spin Hamiltonian of the form

$$\mathscr{H}_S=E_0-2J_1\mathscr{s}_i\cdot\mathscr{s}_j-4J_2(\mathscr{s}_i\cdot\mathscr{s}_j)^2, \tag{33}$$

where

$$E_0=\left[1-\sum_{p\mathrm{ni}}{}'(-1)^p T_{p\mathrm{ni}}P^{s,\mathrm{ni}}-\frac{1}{2}\sum_{p\mathrm{i}}{}'(-1)^p T_{p\mathrm{i}}\tilde{P}^{s,\mathrm{i}}\right]$$
$$\times\left[H_I+\sum_{p\mathrm{ni}}{}'(-1)^p H_{p\mathrm{ni}}P^{s,\mathrm{ni}}+\frac{1}{2}\sum_{p\mathrm{i}}{}'(-1)^p H_{p\mathrm{i}}\tilde{P}^{s,\mathrm{i}}\right], \tag{34}$$

$$J_1 = \sum_{p\mathrm{i}}{}' (-1)^p T_{p\mathrm{i}} \tilde{P}^{s,\mathrm{i}} \left[H_I + \sum_{p\mathrm{ni}}{}' (-1)^p H_{p\mathrm{ni}} P^{s,\mathrm{ni}} \right]$$

$$- \sum_{p\mathrm{i}}{}' (-1)^p H_{p\mathrm{i}} \tilde{P}^{s,\mathrm{i}} \left[1 - \sum_{p\mathrm{ni}}{}' (-1)^p T_{p\mathrm{ni}} P^{s,\mathrm{ni}} - \sum_{p\mathrm{i}}{}' (-1)^p T_{p\mathrm{i}} \tilde{P}^{s,\mathrm{i}} \right], \tag{35}$$

$$J_2 = \sum_{p\mathrm{i}}{}' (-1)^p H_{p\mathrm{i}} \tilde{P}^{s,\mathrm{i}} \sum_{p\mathrm{i}}{}' (-1)^p T_{p\mathrm{i}} \tilde{P}^{s,\mathrm{i}}. \tag{36}$$

Comparing (32), (35), and (36), we see that

$$\frac{{}^1E - {}^3E}{2} = J_1 - J_2 \tag{37}$$

analogous to the result obtained previously in our treatment of the hydrogen molecule.

Neglecting in (32), (34), (35) and (36)

a) all those terms which occur together with but which are small compared to unity, and
b) all those terms which occur together with but which are small compared to H_I,

we obtain[4]

$$\frac{{}^1E - {}^3E}{2} = J_1 = -\sum_{p\mathrm{i}}{}' (-1)^p (H_{p\mathrm{i}} - H_I T_{p\mathrm{i}}) \tilde{P}^{s,\mathrm{i}} \tag{38}$$

$$E_0 = H_I. \tag{39}$$

At this point we note that one can arrive immediately at Eq. (38) by replacing E in all terms in (27) except in the term $H_I - E$ by its zero-order approximation H_I. This process has been followed by Keffer and Oguchi [6], and by Huang and Orbach [7–9], in their treatment of particular systems, and is described as equivalent to perturbation theory. This substitution simplifies our discussion of configuration interaction.

3.3. Configuration Interaction

The analogy between the hydrogen molecule and the single magnetic configuration, manifest in the application of the Heitler-London method to the latter problem, also prompts a refinement in the analysis. Just as the method over-emphasizes the left-right correlation in H_2, a defect which can be ameliorated by the mixing of ionic states into the ground state [27], so a similar situation may hold in the present case. It is to be noted, however, that it has recently been argued that this is not so [28]. Certainly, it is clear that the method, with or without ionic refinement, is generally

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[4] Notice that these are analogous to the approximations used in the proof of the validity of the Heisenberg Spin Hamiltonian in the case of the hydrogen molecule. This is another indication of the analogy between the hydrogen molecule and antiferromagnetic systems

inappropriate at very large internuclear distances. This particular problem has been studied by Herring who, however, neglected higher-order permutations [29, 30].

3.3.1. The Interaction between Two Configurations

The matrix element connecting configuration R_I with configuration R_J is given by Serber's formula [24]

$$(\mathscr{H}-E)^{R_I R_J}=\sqrt{2}^{r_I-r_J}\sum_{\hat{P}}{}'(-1)^p\langle\Omega_{R_I}|\mathscr{H}-E|\mathscr{P}^s\Omega_{R_J}\rangle\langle\Theta_{R_I}|\mathscr{P}^s\Theta_{R_J}\rangle, \tag{40}$$

where r_I equals the number of pairs of filled orbitals in configuration $R_I(r_I\geqslant r_J)$, and the summation is carried over the $N!/2^{r_I}$ permutations which differ by more than an interchange of identical orbitals in R_I (N is the number of electrons).

Using the notations of (26), Eq. (40) assumes the form

$$(\mathscr{H}-E)^{R_I R_J}=\sqrt{2}^{r_I-r_j}\left[\sum_P{}'(-1)^p H_P^{IJ}P^s-E\sum_P{}'(-1)^p T_P^{IJ}P^s\right]. \tag{41}$$

Replacing E in all terms in (41) by its zero-order approximation H_I^{11}, where configuration R_1 is the ground state configuration, we find the following expression for $(\mathscr{H}-E)^{R_I R_J}$

$$(\mathscr{H}-E)^{R_I R_J}=\sqrt{2}^{r_I-r_J}(E_0^{IJ}-2J_1^{IJ}\mathscr{s}_i\cdot\mathscr{s}_j) \tag{42}$$

with

$$E_0^{IJ}\equiv H_I^{IJ}-H_I^{11}T_I^{IJ}+\sum_{P^{\text{ni}}\neq I,P^{\text{i}}}{}'(-1)^p(H_{P^{\text{ni}}}^{IJ}-H_I^{11}T_{P^{\text{ni}}}^{IJ})P^{s,\text{ni}}$$

$$+\frac{1}{2}\sum_{P^{\text{i}}\neq I,P^{\text{ni}}}{}'(-1)^p(H_{P^{\text{i}}}^{IJ}-H_I^{11}T_{P^{\text{i}}}^{IJ})\tilde{P}^{s,\text{i}}, \tag{43}$$

$$J_1^{IJ}=-\sum_{P^{\text{i}}}{}'(-1)^p(H_{P^{\text{i}}}^{IJ}-H_I^{11}T_{P^{\text{i}}}^{IJ})\tilde{P}^{s,\text{i}}. \tag{44}$$

Thus, we have the same formula for the half-interaction energy as (38). However, the spin-independent energy E_0^{IJ} differs from the one-configuration case because $T_I^{II}=1$, but $T_I^{IJ}\neq 1$ $(I\neq J)$[5].

3.3.2. The General Configuration Interaction Problem

In order to solve the general CI problem, one has to solve the following secular equation

$$\sum_{\mathscr{P}^{L_J}}(-1)^p\mathscr{P}^{L_J}(\mathscr{H}-E)^{1L_1}(\mathscr{H}-E)^{2L_2}\cdots(\mathscr{H}-E)^{KL_K}=0 \tag{45}$$

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[5] Notice, that the binomial expansion of the denominator in (28) – which is now $T_I^{IJ}+\sum'_{P'\neq I}(-1)^p T_{P'}^{IJ}P^{s'}$ – is not now straightforward, but depends on the particular problem under study.

where K is the number of configurations under consideration and the permutation operator $\mathscr{P}^{L_J}$ forms $K!$ different permutations of the column indices $L_1, L_2, \ldots, L_k$ with the row indices being in natural order. The matrix element connecting configuration R_I with the configuration R_J $(IJ \neq 11)$ is approximately given by (42). For $(\mathscr{H}-E)^{R_1R_1}$ we use the expression [cf. (38) and (39)]

$$(\mathscr{H}-E)^{R_1R_1} = H_I^{11} - 2J_1^{11}\mathscr{s}_i \cdot \mathscr{s}_j - E. \tag{46}$$

Using (42) and (46) in (45), we find the following spin Hamiltonian

$$\mathscr{H}_S = H_I^{11} - 2J_1^{11}\mathscr{s}_i \cdot \mathscr{s}_j + \frac{\sum\limits_{L_1 \neq 1} (-1)^p \mathscr{P}_1^{L_J} \varepsilon (E_0^{1L_1} - 2J_1^{1L_1}\mathscr{s}_i \cdot \mathscr{s}_j) \cdots (E_0^{KL_K} - 2J_1^{KL_K}\mathscr{s}_i \cdot \mathscr{s}_j)}{\sum\limits_{L_J \neq 1} (-1)^p \mathscr{P}_2^{L_J} \eta (E_0^{2L_2} - 2J_1^{2L_2}\mathscr{s}_i \cdot \mathscr{s}_j) \cdots (E_0^{KL_K} - 2J_1^{KL_K}\mathscr{s}_i \cdot \mathscr{s}_j)} \tag{47}$$

where

$$\varepsilon \equiv \sqrt{2}^{\sum_{\varepsilon'=1}^{K} |r_{\varepsilon'} - r_{L_{\varepsilon'}}|}, \qquad \eta \equiv \sqrt{2}^{\sum_{\eta'=2}^{K} |r_{\eta'} - r_{L_{\eta'}}|} \tag{48}$$

We expand the terms in (47) as follows

$$\begin{aligned}(E_0^{1L_1} &- 2J_1^{1L_1}\mathscr{s}_i \cdot \mathscr{s}_j) \cdots (E_0^{KL_K} - 2J_1^{KL_K}\mathscr{s}_i \cdot \mathscr{s}_j) \\ &= E_0^{1L_1} \cdots E_0^{KL_K} - 2[J_1^{1L_1}E_0^{2L_2}E_0^{3L_3} \cdots E_0^{KL_K} + J_1^{2L_2}E_0^{1L_1}E_0^{3L_3} \cdots E_0^{KL_K} \\ &\quad + \cdots + J_1^{KL_K}E_0^{1L_1}E_0^{2L_2} \cdots E^{(K-1)L_{(K-1)}}]\mathscr{s}_i \cdot \mathscr{s}_j \\ &\quad - 4[-J_1^{1L_1}J^{2L_2}E_0^{3L_2}E_0^{4L_4} \cdots E_0^{KL_K} - J_1^{1L_1}J_1^{3L_3}E_0^{2L_2}E_0^{4L_4} \cdots E_0^{KL_K} \\ &\quad - \cdots - J_1^{(K-1)L_{(K-1)}}J_1^{KL_K}E_0^{1L_1}E_0^{2L_2} \cdots E_0^{(K-2)L_{(K-2)}}](\mathscr{s}_i \cdot \mathscr{s}_j)^2.\end{aligned} \tag{49}$$

The coefficient of $\mathscr{s}_i \cdot \mathscr{s}_j$ involves only terms of the form J_1^{IJ}, while the coefficient of $(\mathscr{s}_i \cdot \mathscr{s}_j)^2$ involves terms of the form $J_1^{IJ}J_1^{MN}$[6]. The square (and the higher powers) of J_1 produces a final coefficient of $(\mathscr{s}_i \cdot \mathscr{s}_j)^2$ which is smaller[7] than J_1. We, therefore, conclude that we need not further consider the square (and higher powers) of the dot product $\mathscr{s}_i \cdot \mathscr{s}_j$. This reduces the situation to that of the familiar Heisenberg Exchange Hamiltonian,

$$\mathscr{H}_{\mathrm{ex}} = -2J_1\mathscr{s}_i \cdot \mathscr{s}_j. \tag{50}$$

From (49) we have

$$\begin{aligned}(E_0^{1L_1} &- 2J_1^{1L_1}\mathscr{s}_i \cdot \mathscr{s}_j) \cdots (E_0^{KL_K} - 2J_1^{KL_K}\mathscr{s}_i \cdot \mathscr{s}_j) \\ &= E_0^{1L_1} \cdots E_0^{KL_K}[1 - 2(q_1^{1L_1} + q_1^{2L_2} \cdots + q_1^{KL_K})\mathscr{s}_i \cdot \mathscr{s}_j],\end{aligned} \tag{51}$$

---

[6] Had we included the terms $-4J_2^{IJ}(\mathscr{s}_i \cdot \mathscr{s}_j)^2$, the coefficient of $(\mathscr{s}_i \cdot \mathscr{s}_j)^2$ would have also involved terms of the form J_2^{IJ}. J_2 is, however, much smaller than J_1 [cf. (35) and (36)].

[7] This arises because the multipliers of J_1 contain, in general, products of overlap integrals.

where

$$q_1^{IL_I} \equiv \frac{J_1^{IL_I}}{E_0^{IL_I}}. \tag{52}$$

The denominator in (47) can be expanded similarly

$$\begin{aligned}
&\sum_{L_J \neq 1} (-1)^p \mathscr{P}_2^{L_J} \eta (E_0^{2L_2} - 2J_1^{2L_2} \mathscr{s}_i \cdot \mathscr{s}_j) \cdots (E_0^{KL_K} - 2J_1^{KL_K} \mathscr{s}_i \cdot \mathscr{s}_j) \\
&\quad = E_0^{22} \cdots E_0^{KL_K} \Bigg\{ 1 - 2(q_1^{22} + \cdots + q_1^{KK}) \mathscr{s}_i \cdot \mathscr{s}_j \\
&\qquad + \sum_{L_J \neq 1, \mathscr{P}_3 \neq I} (-1)^p \mathscr{P}_3^{L_J} \eta \frac{E_0^{2L_2} \cdots E_0^{KL_K}}{E_0^{22} \cdots E_0^{KK}} [1 - 2(q_1^{2L_2} + \cdots + q_1^{KL_K}) \mathscr{s}_i \cdot \mathscr{s}_j] \Bigg\}.
\end{aligned} \tag{53}$$

Noting that the integral H_I^{II} is, in general, much greater than the integral H_I^{IJ} $(I \neq J)$, (this is because the latter contains as factors overlap integrals), we can expand the denominator in (47) [in the form given by (53)] according to the binomial theorem.

We obtain

$$\begin{aligned}
\mathscr{H}_S = H_I^{11} - 2J_1^{11} \mathscr{s}_1 \cdot \mathscr{s}_j + \Bigg\{ & 1 + 2(q_1^{22} + \cdots + q_1^{KK}) \mathscr{s}_1 \cdot \mathscr{s}_j \\
& - \sum_{L_J \neq 1, \mathscr{P}_3 \neq I} (-1)^p \mathscr{P}_3^{L_J} \eta \frac{E_0^{2L_2} \cdots E_0^{KL_K}}{E_0^{22} \cdots E_0^{KK}} [1 - 2(q_1^{2L_2} + \cdots + q_1^{KL_K}) \mathscr{s}_i \cdot \mathscr{s}_j] \Bigg\} \\
& \times \sum_{L_1 \neq 1} (-1)^p \mathscr{P}_1^{L_J} \varepsilon \frac{E_0^{1L_1} \cdots E_0^{KL_K}}{E_0^{22} \cdots E_0^{KK}} [1 - 2(q_1^{1L_1} + \cdots + q_1^{KL_K}) \mathscr{s}_i \cdot \mathscr{s}_J].
\end{aligned} \tag{54}$$

The coefficient, J_{ij}, of $-2\mathscr{s}_i \cdot \mathscr{s}_j$ in (54) is

$$\begin{aligned}
J_{ij} = J_1^{11} + & \left[1 - \sum_{L_J \neq 1, \mathscr{P}_3 \neq I} (-1)^p \mathscr{P}_3^{L_J} \eta \frac{E_0^{2L_2} \cdots E_0^{KL_K}}{E_0^{22} \cdots E_0^{KK}} \right] \\
& \times \left[\sum_{L_1 \neq 1} (-1)^p \mathscr{P}_1^{L_J} \varepsilon \frac{E_0^{1L_1} \cdots E_0^{KL_K}}{E_0^{22} \cdots E_0^{KK}} (q_1^{1L_1} + \cdots + q_1^{KL_K}) \right] \\
& - \left[\sum_{L_J \neq 1} (-1)^p \mathscr{P}_2^{L_J} \eta \frac{E_0^{2L_2} \cdots E_0^{KL_K}}{E_0^{22} \cdots E_0^{KK}} (q_1^{2L_2} + \cdots + q_1^{KL_K}) \right] \\
& \times \left[\sum_{L_1 \neq 1} (-1)^p \mathscr{P}_1^{L_J} \varepsilon \frac{E_0^{1L_1} \cdots E_0^{KL_K}}{E_0^{22} \cdots E_0^{KK}} \right].
\end{aligned} \tag{55}$$

Equation (55) is a general formula for the calculation of the exchange integral for a single exchange pathway with inclusion of CI but in the absence of spin-orbit coupling. Although (55) looks cumbersome, in practice, at least as far as simple systems are concerned, it is not so complex. We shall report elsewhere on the results obtained from its use.

4. Conclusion

We have shown that the Heisenberg spin exchange Hamiltonian (50) is a good approximate Hamiltonian for the estimation of the exchange interactions in antiferromagnetic and ferromagnetic systems irrespective of the particular model (single configuration, configuration interaction) used in the approach. We have also examined the relationship between several approaches to the energy separation between the lowest singlet and triplet of the hydrogen molecule as well as the connection between the hydrogen-molecule approach and the general N-electron magnetic configuration. Finally, we have derived a new formula for the estimation of the "exchange integral" in the general magnetic configuration.

We conclude this paper with a review of the approximations upon which we have established the validity of (50). Had we not made any approximations, we would have found that the correct spin exchange Hamiltonian would have been

$$\mathscr{H}_s = E_0 - 2J_1 \mathscr{s}_1 \cdot \mathscr{s}_2 - 4J_2(\mathscr{s}_i \cdot \mathscr{s}_2)^2 - 8J_3(\mathscr{s}_i \cdot \mathscr{s}_j)^3 \cdots \tag{56}$$

spin-orbit effects being neglected. With (56) the energy is given by $E = \langle \Theta | \mathscr{H}_s | \Theta \rangle$. Now, it is readily found that

$$\langle \Theta | \mathscr{s}_i \cdot \mathscr{s}_j | \Theta \rangle \begin{cases} = -\tfrac{3}{4} \text{ (singlet)} \\ = \tfrac{1}{4} \text{ (triplet)} \end{cases}$$

$$\langle \Theta | (\mathscr{s}_i \cdot \mathscr{s}_j)^2 | \Theta \rangle \begin{cases} = \tfrac{9}{16} \text{ (singlet)} \\ = \tfrac{1}{16} \text{ (triplet)} \end{cases}$$

$$\langle \Theta | (\mathscr{s}_i \cdot \mathscr{s}_j)^3 | \Theta \rangle \begin{cases} = -\tfrac{27}{64} \text{ (singlet)} \\ = \tfrac{1}{64} \text{ (triplet)} \end{cases}$$

etc. Thus we calculate the energies of the singlet and the triplet states as follows

$$^1E = E_0 + \tfrac{3}{2}J_1 - \tfrac{9}{4}J_2 + \tfrac{27}{8}J_3 \pm \cdots$$

$$^3E = E_0 - \tfrac{1}{2}J_1 - \tfrac{1}{4}J_2 - \tfrac{1}{8}J_3 \pm \cdots$$

so that

$$\frac{^1E - {}^3E}{2} = J_1 - J_2 + \tfrac{7}{4}J_3 \pm \cdots. \tag{57}$$

Our objective, therefore, has been to examine whether the terms beyond J_1 are numerically important. The discussion following Eq. (29) indicated that terms beyond J_2 could be neglected. We had, however, to carry the discussion further, before [Eq. (49) *et seq.*] we obtained conditions which enabled J_2 to be discarded. However, it must be recognized that specific cases may exist where the neglect of J_2 is not justified [31, 32].

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