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Effective Exchange Integral*

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The magnetic properties of a linear chain of monovalent atoms are investigated from the point of view of perturbation theory. The many-electron wave functions for the system are expanded as linear combinations of determinantal functions which are eigenfunctions of S^2 and S_z. These determinantal functions are constructed from orthonormal one-electron orbitals of the Wannier type so that the nearest neighbor exchange integral is positive definite and approaches zero at large lattice spacings. The secular equation is set up using the method of the Dirac vector model. By means of the Kramers perturbation technique, the interaction of ionic states with those arising from the ground configuration is represented by means of an effective Hamiltonian operator with its associated matrix. The results of this treatment are analogous to those obtained by Paul in that an analytic expression is found for an effective nearest neighbor exchange integral J'. This quantity is represented as the difference between the positive definite exchange integral and additional terms from ionic states. The present treatment defines in a fairly precise manner the type configurations which contribute to this effective exchange integral and the limits for which this parameterization is valid. The results of this analysis are compared with those obtained from recent calculations on a system of six hydrogen atoms.

I. INTRODUCTION

In this paper, we consider the magnetic properties of a linear chain of N monovalent atoms with periodic boundary conditions. The single outer electron associated with each atom is assumed to be in an s state. While this treatment can be generalized quite readily to a general system of monovalent atoms containing closed inner shells, we shall, for simplicity, limit our attention to a hydrogenic system in which there is a single electron associated with each atom.

The many-electron wave functions for this system are expanded as linear combinations of determinantal functions which are eigenfunctions of the square of the total spin angular momentum operator (S^2) and its z component (S_z). The one-electron orbitals which make up these determinantal functions are assumed to be orthonormal, atomic-like Wannier functions[1] so that the nearest neighbor exchange integral is positive definite and the various energy levels reduce to atomic states at infinite separation.

We approach this problem using a form of perturbation theory due to Kramers.[2] In this approach, the effect of ionic states on those arising from the ground configuration is represented by means of an effective Hamiltonian operator with its associated matrix. The results of this treatment are similar to those obtained by Paul[3] in that an analytic expression is obtained for an effective nearest neighbor exchange integral J'. This parameter is represented as a sum of the positive-definite exchange integral J_1 plus additional negative terms resulting from the effects of ionic configurations. The sign of J' is determined by the relative magnitudes of the two contributions.

The results of recent calculations on a chain of six hydrogen atoms indicate that J' is negative for that particular system.[4] Furthermore, these calculations reveal that at large lattice spacings, the eigenvalue spectrum of the Heisenberg exchange operator,

$$H=-2J'\sum_i (\mathbf{s}_i\cdot\mathbf{s}_{i+1}-\tfrac{1}{4}), \tag{1}$$

provides an accurate description of the low-lying energy levels obtained from the more accurate configuration interaction calculations. The values of J' obtained by fitting the eigenvalues of Eq. (1) to the results of the configuration interaction calculations compare favorably with those obtained by evaluating the analytic expression for J' derived in the present discussion.

Equally important is the fact that the present treatment specifies in a precise manner the approximations which are essential to the derivation of an expression for the effective exchange integral J'. This permits one to evaluate the limits for which Eq. (1) provides an accurate description of the magnetic interaction in a non-ferromagnetic system such as the present one. For example, it is shown that Eq. (1) depends not on the fact that the second nearest neighbor exchange integral is negligibly small compared to the nearest neighbor integral, but rather that the parameter J_2' (which represents the sum of a second nearest neighbor exchange integral plus additional terms due to ionic states) is negligible in comparison to J'.

II. METHOD

The method employed here involves a form of perturbation theory which was first introduced by Kramers.[2] This perturbation technique is useful in physical situations where a finite energy gap exists between a relatively small number of low-lying states which are of primary interest and a multitude of excited states which interact with these low-lying states. This condition is satisfied at large internuclear separations in the problem presently under consideration. The low-lying states represent those arising from the ground configura-

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[1] G. Wannier, Phys. Rev. **52**, 191 (1937).

[2] H. A. Kramers, Physica **1**, 182 (1934).

[3] D. I. Paul, Phys. Rev. **118**, 92 (1960).

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tion where there is a single electron associated with each atomic site. The excited states include those ionized states which have up to $N/2$ pairs of doubly filled orbitals. The lowest excited states correspond to a single doubly filled orbital, and the energy gap in this case corresponds approximately to the energy required to take an electron from a neutral atom and transfer it to a neighboring atom. This is approximately equal to the difference between the ionization energy and the electron affinity for the atoms in question. The energy separation between the states arising from the ground configuration is small compared to this gap, since it is proportional to the nearest neighbor exchange integral which is zero at infinity and therefore is quite small at large separations.

The procedure is best illustrated using Löwdin's matrix representation of the Kramers technique.[5] It is assumed that the matrix of the Hamiltonian operator has been set up using determinantal functions formed from orthonormal one-electron orbitals. The secular equation has the following form:

$$\begin{pmatrix} \mathbf{H}_{00} & \mathbf{H}_{01} \\ (\mathbf{H}_{01})^{+} & \mathbf{H}_{11} \end{pmatrix} \begin{pmatrix} \mathbf{C}_0 \\ \mathbf{C}_1 \end{pmatrix} = E \begin{pmatrix} \mathbf{C}_0 \\ \mathbf{C}_1 \end{pmatrix}. \tag{2}$$

The ground and excited configurations have been represented by the subscripts 0 and 1, respectively, in this equation. The dimension of the ground configuration portion depends on the number of electrons and the multiplicity, and is determined by means of the usual branching diagram analysis. The eigenvector $\mathbf{C}$, representing the combining coefficients for the determinantal functions, has been subdivided into two portions $\mathbf{C}_0$ and $\mathbf{C}_1$ which correspond to the ground and ionic functions, respectively.

If the matrix multiplication of Eq. (2) is carried out in block form, the following relations are obtained:

$$\mathbf{H}_{00}\mathbf{C}_0 + \mathbf{H}_{01}\mathbf{C}_1 = E\mathbf{C}_0, \tag{3a}$$

$$\mathbf{H}_{01}^{\dagger}\mathbf{C}_0 + \mathbf{H}_{11}\mathbf{C}_1 = E\mathbf{C}_1. \tag{3b}$$

If Eq. (3b) is rewritten,

$$(E\mathbf{1} - \mathbf{H}_{11})\mathbf{C}_1 = \mathbf{H}_{01}^{\dagger}\mathbf{C}_0. \tag{4}$$

By assuming that the matrix $(E\mathbf{1} - \mathbf{H}_{11})$ has an inverse which is denoted by $(E\mathbf{1} - \mathbf{H}_{11})^{-1}$, it follows that

$$\mathbf{C}_1 = (E\mathbf{1} - \mathbf{H}_{11})^{-1}\mathbf{H}_{01}^{\dagger}\mathbf{C}_0, \tag{5}$$

which can be substituted into Eq. (3a) to yield the relation

$$[\mathbf{H}_{00} + \mathbf{H}_{01}(E\mathbf{1} - \mathbf{H}_{11})^{-1}\mathbf{H}_{01}^{\dagger}]\mathbf{C}_0 = E\mathbf{C}_0. \tag{6}$$

The first term in the brackets represents the matrix connecting only the ground configuration determinantal functions. The second term describes the interaction of these ground configuration functions with ionic states. According to Löwdin, the matrix $(E\mathbf{1} - \mathbf{H}_{11})^{-1}$ can be expanded by dividing $\mathbf{H}_{11}$ into its diagonal and nondiagonal parts, representing these by $\mathbf{H}_{11}{}^{d}$ and $\mathbf{H}_{11}{}^{n}$, respectively. Then, denoting the matrix contained within the square brackets of Eq. (6) by $\mathbf{H}_{00}'$, Löwdin shows that

$$\begin{aligned} \mathbf{H}_{00}' = \mathbf{H}_{00} &+ \mathbf{H}_{01}\frac{1}{E\mathbf{1} - \mathbf{H}_{11}{}^{d}}\mathbf{H}_{01}^{\dagger} \\ &+ \mathbf{H}_{01}\frac{1}{E\mathbf{1} - \mathbf{H}_{11}{}^{d}}\mathbf{H}_{11}{}^{n}\frac{1}{E\mathbf{1} - \mathbf{H}_{11}{}^{d}}\mathbf{H}_{01}^{\dagger} + \cdots, \end{aligned} \tag{7}$$

where $1/(E\mathbf{1} - \mathbf{H}_{11}{}^{d})$ represents the inverse of the diagonal matrix $(E\mathbf{1} - \mathbf{H}_{11}{}^{d})$. The secular equation of Eq. (6) is complicated by the fact that the Hamiltonian portion contains the energy eigenvalue E explicitly. As a result, this equation must be solved by means of an iteration scheme unless the difference between the unperturbed and perturbed energies is negligible. In this case, it is possible to compute $\mathbf{H}_{00}'$ using the unperturbed energy as an approximation to E in Eq. (7).

III. THE SECULAR EQUATION

We use the method of the Dirac vector model to set up the secular equation for the system. Since this method involves determinantal functions which are eigenfunctions of S^2 and S_z, it is quite straightforward to show that there are no matrix elements of the Hamiltonian and identity operators connecting states of different S or M_s. Thus, the secular equation is factored into several noncombining portions, each of which can be solved separately. The basis functions for the secular equation have the form

$$\begin{aligned} \psi_i{}^{\nu m}(N,S,M_s) = (2)^{-\nu/2}(N!)^{-\frac{1}{2}} &\textstyle\sum_P (-1)^P P^s P^\sigma \\ &\times \Phi^{\nu m}(1,2,\cdots N)\theta_i(N,S,M_s), \end{aligned} \tag{8}$$

where $(2)^{-\nu/2}(N!)^{-\frac{1}{2}}$ is a normalization constant and $\sum_P (-1)^P P^s P^\sigma$ is the antisymmetrizing operator, P^s and P^σ representing permutation operators for electronic spatial and spin coordinates, respectively. $\Phi^{\nu m}$ is a product of N orthonormal, atomic-like, one-electron functions $w_{m_i}(\mathbf{r}_i)$ containing ν pairs of doubly filled orbitals

$$\begin{aligned} \Phi^{\nu m} = w_{m_1}(\mathbf{r}_1)w_{m_2}(\mathbf{r}_2) \\ \cdots w_{m_{2\nu-1}}(\mathbf{r}_{2\nu-1})w_{m_{2\nu}}(\mathbf{r}_{2\nu})\cdots w_{m_N}(\mathbf{r}_N). \end{aligned} \tag{9}$$

The superscript m enumerates the different configurations containing ν doubly filled orbitals. The integral subscripts m_i indicate the atomic sites about which the various orbitals are localized. For ν doubly filled orbitals, the m_i corresponding to a given configuration are chosen such that

$$\begin{aligned} m_1 = m_2 \neq m_3 = m_4 \neq \cdots \neq m_{2\nu-1} \\ = m_{2\nu} \neq m_{2\nu+1} \neq \cdots \neq m_N. \end{aligned} \tag{10}$$

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[5] P. O. Löwdin, J. Chem. Phys. **19**, 1396 (1951).

For ν paired orbitals, the total number of possible configurations N_ν is given by

$$N_\nu = N(N-1)(N-2)\cdots(N-2\nu+1)/(\nu!\nu!), \quad (11)$$

so that m takes on N_ν values.

The function $\theta_i(N,S,M_s)$ in Eq. (8) represent the N electron spin product functions which diagonalize S^2 and S_z and form the basis for an irreducible representation for the group of spin coordinate permutations. From this last property,

$$P^\sigma\theta_j(N,S,M_s) = \sum_i \Gamma_s'(P)_{ij}\theta_i(N,S,M_s). \quad (12)$$

When considering ν doubly filled orbitals, it is necessary that the corresponding spin functions be singlets. This is equivalent to requiring that the interchange operators P_{12}^σ, P_{34}^σ, $\cdots$ $P_{(2\nu-1)2\nu}^\sigma$ have diagonal matrices, the diagonal elements being ± 1. Serber has described a method for constructing the basis for this representation.[6] We assume that the basis functions $\theta_i(N,S,M_s)$ have been ordered such that first the -1's (singlets) and then the $+1$'s (triplets) of $\mathbf{\Gamma}_s'(P_{12})$ occur along the diagonal. Then, those functions with diagonal elements of (-1) for $\mathbf{\Gamma}_s'(P_{12})$ are arranged so that the -1's for $\mathbf{\Gamma}_s'(P_{34})$ occur first, then the $+1$'s, and so on.

It will be necessary to work through some of the details of the Dirac vector model in order to obtain the results of interest. This serves a useful purpose in that it permits the approximations inherent in the present treatment to be pointed out explicitly. The general expression for the matrix elements of the Hamiltonian operator connecting the μ and μ' configurations (now denoted by a single index) can be written

$$\mathbf{H}_s^{\mu\mu'} = \sum_P \mathbf{\Gamma}_s(P)V(P)^{\mu\mu'}, \quad (13)$$

where

$$V(P)^{\mu\mu'} = (2)^{-(\nu_\mu+\nu_{\mu'})/2}\langle\Phi^{\nu_\mu m_\mu}|HP^s|\Phi^{\nu_{\mu'} m_{\mu'}}\rangle, \quad (14a)$$

$$\mathbf{\Gamma}_s(P) = (-1)^P\mathbf{\Gamma}_s'(P). \quad (14b)$$

For the ground configuration, Eq. (13) reduces to

$$\mathbf{H}_s^{00} = [\sum_i Q_i + \sum_{i>j} K_{ij}]\mathbf{1}_s + \sum_{i>j} J_{ij}\mathbf{\Gamma}_s(P_{ij}), \quad (15)$$

where $\mathbf{1}_s$ is a unit matrix of appropriate order and Q_i, K_{ij}, and J_{ij} are the one-electron, Coulomb, and exchange integrals given by the expressions

$$Q_i = \left\langle w_i(\mathbf{r}_1)\left| -\tfrac{1}{2}\nabla_1^2 + \sum_\alpha \frac{Z_\alpha}{|\mathbf{r}_1 - R_\alpha|}\right| u_i(\mathbf{r}_1)\right\rangle, \quad (16a)$$

$$K_{ij} = \left\langle w_i(\mathbf{r}_1)w_j(\mathbf{r}_2)\left|\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right| w_i(\mathbf{r}_1)w_j(\mathbf{r}_2)\right\rangle, \quad (16b)$$

$$J_{ij} = \left\langle w_i(\mathbf{r}_1)w_j(\mathbf{r}_2)\left|\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right| w_j(\mathbf{r}_1)w_i(\mathbf{r}_2)\right\rangle. \quad (16c)$$

Neglecting an additive constant to the energy, Eq. (15) can be written as

$$\mathbf{H}_s^{00} = \sum_{i>j} J_{ij}\mathbf{\Gamma}_s(P_{ij}). \quad (17)$$

At larger distances, Eq. (17) can be further simplified by assuming that all but the nearest-neighbor exchange integrals (J_1) can be neglected. Then, Eq. (17) reduces to

$$\mathbf{H}_s^{00} = J_1[N\mathbf{1}_s + \sum_i \mathbf{\Gamma}_s(P_{i\,i+1})]. \quad (18)$$

The eigenvalue spectrum of the secular equation resulting from Eq. (18) is known to be identical with that of the Heisenberg exchange operator of Eq. (1).[7] The zero of energy in Eqs. (1) and (18) has been adjusted to coincide with that of the ferromagnetic state.

We are now interested in obtaining an expression for $\mathbf{H}_{01}$ in Eq. (7). The matrix $\mathbf{H}_{01}$ represents that part of the complete Hamiltonian matrix which connects the ground and ionic configuration portions. For the present, we consider only that part of $\mathbf{H}_{01}$ which connects the ground configuration with those states containing a single doubly filled orbital and hole located at adjacent lattice sites. There are a total of $2N$ configurations involving such states. One such configuration can be represented by the spatial function,

$$\Phi^{11} = w_1(\mathbf{r}_1)w_1(\mathbf{r}_2)w_3(\mathbf{r}_3)w_4(\mathbf{r}_4)\cdots w_N(\mathbf{r}_N). \quad (19)$$

The entire set of $2N$ functions similar to this one can be obtained by applying the $2N$ operations in the group of the Hamiltonian (C_{Nv}) to this function. These operations are equivalent to the rotations and rotations followed by reflections which send a regular N-sided polygon into itself.

It is quite straightforward to show that the matrix connecting the ground configuration states with those states having a spatial part equivalent to $R_i\Phi^{11}$ (R_i representing one of the $2N$ operations in the group of the Hamiltonian) is given by $\mathbf{D}_s^{0i}$, where

$$\begin{aligned}\mathbf{D}_s^{0i} = (2)^{-\frac{1}{2}}M_1[\mathbf{\Gamma}_s(R_i)+\mathbf{\Gamma}_s(R_i)\mathbf{\Gamma}_s(P_{12})] \\ +(2)^{-\frac{1}{2}}\sum_k L_k[\mathbf{\Gamma}_s(R_i)\mathbf{\Gamma}_s(P_{2k}) \\ +\mathbf{\Gamma}_s(R_i)\mathbf{\Gamma}_s(P_{2k})\mathbf{\Gamma}_s(P_{12})]. \quad (20)\end{aligned}$$

M_r is a generalization of the quantity M defined by Paul[3]:

$$\begin{aligned}M_r \equiv \langle w_{p+r}(\mathbf{r}_i)|H(i) \\ +\sum_{q\neq p}\langle w_q(\mathbf{r}_2)\left|\frac{1}{|\mathbf{r}_i-\mathbf{r}_2|}\right| w_q(\mathbf{r}_2)\rangle w_p(\mathbf{r}_i)\rangle. \quad (21)\end{aligned}$$

In this expression, $H(i)$ is the one-electron operator for the ith electron and L_k is a three-center exchange integral:

$$L_k \equiv \left\langle w_1(\mathbf{r}_1)w_k(\mathbf{r}_2)\left|\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right| w_k(\mathbf{r}_1)w_2(\mathbf{r}_2)\right\rangle. \quad (22)$$

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[6] R. Serber, Phys. Rev. 45, 461 (1934).

[7] G. F. Koster, Technical Report No. 8, Solid-State and Molecular Theory Group, M.I.T., 1956 (unpublished), Chapter 4.

For the matrices $\mathbf{\Gamma}_s(R_i)$ in Eq. (20), the permutations R_i have the following significance. If we consider the ground configuration function Φ^{01} which contains a single orbital localized about each atomic site, then the permutation R_i^s is defined such that $R_i^sR_i\Phi^{01}=\Phi^{01}$. Similarly, $\mathbf{\Gamma}_s(P_{2k})$ is the matrix which represents the interchange operator P_{2k}^s.

Since the second term in Eq. (20) involves a sum over the three-center integrals L_k which are expected to be considerably smaller than M_1, we can neglect these terms. Then, Eq. (20) can be reduced to

$$\mathbf{D}_s^{0i}=(2)^{-\frac{1}{2}}M_1[\mathbf{\Gamma}_s(R_i)+\mathbf{\Gamma}_s(R_i)\mathbf{\Gamma}_s(P_{12})]. \tag{23}$$

In this approximation, the matrix $\mathbf{H}_{01}$ of Eq. (7) has the form

$$\mathbf{H}_{01}=\begin{bmatrix} \times & & \times & & \times & & & \times & \\ \times & \mathbf{D}_s^{01} & \times & \mathbf{D}_s^{02} & \times & \mathbf{D}_s^{03} & \cdots & \times & \mathbf{D}_s^{0(2N)} \\ \times & & \times & & \times & & & \times & \end{bmatrix}. \tag{24}$$

The $\times$'d columns of Eq. (24) represent the nonvanishing columns of $\mathbf{D}_s^{0i}$; these correspond to the $+$'s in the matrix $\mathbf{\Gamma}_s(P_{12})$ [or to the $-$'s in the matrix $\mathbf{\Gamma}_s'(P_{12})$]. For the spin-wave states where $S=N/2-1$, this corresponds to a single column. In this case, the matrix $1/(E\mathbf{1}-\mathbf{H}_{11}^d)$ may be written

$$\frac{1}{E\mathbf{1}-\mathbf{H}_{11}^d}=\frac{1}{2(E-H_1^1)}\left[\begin{array}{ccccc} 1 & 2 & 3 & \cdots & 2N \\ \mathbf{\Gamma}_s(E)+\mathbf{\Gamma}_s(P_{12}) & & & & \\ & \mathbf{\Gamma}_s(E)+\mathbf{\Gamma}_s(P_{12}) & & 0 & \\ & & \mathbf{\Gamma}_s(E)+\mathbf{\Gamma}_s(P_{12}) & & \\ & & & \ddots & \\ & 0 & & & \mathbf{\Gamma}_s(E)+\mathbf{\Gamma}_s(P_{12}) \end{array}\right], \tag{25}$$

where H_1^k denotes the diagonal element of $\mathbf{H}_{11}^d$ for which the electron and hole are separated by k lattice sites. The matrices $\mathbf{\Gamma}_s(E)+\mathbf{\Gamma}_s(P_{12})$ contain a single nonvanishing element in the upper left-hand corner, but we choose to write them in this form for convenience in the following discussion. Using the relation given by Eq. (25) for $1/(E\mathbf{1}-\mathbf{H}_{11}^d)$, it is quite straightforward to show that

$$\mathbf{H}_{01}\frac{1}{E\mathbf{1}-\mathbf{H}_{11}^d}\mathbf{H}_{01}^\dagger=\frac{1}{4}\frac{M_1^2}{E-H_1^1}\times\{\textstyle\sum_i[\mathbf{\Gamma}_s(R_i)+\mathbf{\Gamma}_s(R_i)\mathbf{\Gamma}_s(P_{12})]\times[\mathbf{\Gamma}_s(E)+\mathbf{\Gamma}_s(P_{12})]\times[\mathbf{\Gamma}_s(R_i)^\dagger+\mathbf{\Gamma}_s(P_{12})\mathbf{\Gamma}_s(R_i)^\dagger]\}. \tag{26}$$

Equation (26) reduces to

$$\mathbf{H}_{01}\frac{1}{E\mathbf{1}-\mathbf{H}_{11}^d}\mathbf{H}_{01}^\dagger=\frac{M_1^2}{2(E-H_1^1)}\times[4N\mathbf{1}_s+2\textstyle\sum_i\mathbf{\Gamma}_s(R_i)\mathbf{\Gamma}_s(P_{12})\mathbf{\Gamma}_s(R_i)^\dagger]. \tag{27}$$

If one makes use of the identity

$$\sum_{i=1}^{2N}\mathbf{\Gamma}_s(R_i)\mathbf{\Gamma}_s(P_{12})\mathbf{\Gamma}_s(R_i)^\dagger=2\sum_{i=1}^{N}\mathbf{\Gamma}_s(P_{i\,i+1}), \tag{28}$$

Eq. (27) can be written

$$\mathbf{H}_{01}\frac{1}{E\mathbf{1}-\mathbf{H}_{11}^d}\mathbf{H}_{01}^\dagger=\frac{2M_1^2}{(E-H_1^1)}[N\mathbf{1}_s+\textstyle\sum_i\mathbf{\Gamma}_s(P_{i\,i+1})]. \tag{29}$$

Thus, using this relation along with Eq. (18), the first two terms of Eq. (7) can be written

$$\mathbf{H}_{00}'=\left(J_1+\frac{2M_1^2}{E-H_1^1}\right)[N\mathbf{1}_s+\textstyle\sum_i\mathbf{\Gamma}_s(P_{i\,i+1})]. \tag{30}$$

The result of Eq. (30) cannot be extended to include those states containing a hole which is located two atomic sites away from the doubly filled orbital. For this case, the equivalent to Eq. (29) contains the term

$$\frac{2M_2^2}{(E-H_1^2)}\textstyle\sum_i\mathbf{\Gamma}_s(P_{i\,i+2}). \tag{31}$$

From this result, the nature of the general term representing an arbitrary separation of the hole and doubly filled orbital is obvious.

The generalization of the result given by Eq. (30) to states of lower multiplicity involves an additional approximation. For these lower multiplicities, the matrix $\mathbf{\Gamma}_s(E)+\mathbf{\Gamma}_s(P_{12})$ contains, in general, more than one nonvanishing diagonal element. In order to write the matrix $1/(E\mathbf{1}-\mathbf{H}_{11}{}^{d})$ in the form of Eq. (25), it is necessary to assume that the non-vanishing elements of $\mathbf{H}_{11}{}^{d}$ are degenerate. This should correspond to a reasonable approximation at large separations since these diagonal elements differ only by multiples of J_1, and these exchange integrals become quite small at large lattice spacings. For these states of lower multiplicity, a reasonable approximation is to use the average energy of $\mathbf{H}_{11}{}^{d}$ for $H_1{}^1$.

Similarly, it is not possible to extend Eq. (30) to include the effects of states containing more than one pair of doubly filled orbitals. For configurations containing three or more doubly filled orbitals, the corresponding portion of $\mathbf{H}_{01}$ vanishes identically. For two doubly filled orbitals, the coefficient of the term equivalent to Eq. (23) would be a four-center integral. The corresponding coefficient arising from

$$\mathbf{H}_{01}\frac{1}{E\mathbf{1}-\mathbf{H}_{11}{}^{d}}\mathbf{H}_{01}{}^{\dagger}$$

would be proportional to the square of a four-center integral divided by an energy denominator which is approximately twice that of Eq. (29). Since it has been necessary to neglect the three-center integrals L_k in obtaining Eq. (29), it is reasonable to expect that the terms involving two doubly filled orbitals will be negligible when the approximate techniques described here are valid.

IV. EFFECTIVE EXCHANGE INTEGRAL

According to Eq. (30), the effective exchange integral J' can be represented quite accurately by the relation

$$J'=J_1+(2M_1{}^2/E-H_1{}^1), \tag{32}$$

if the most important interaction between the ground and excited configurations occurs for those ionic states which contain a single doubly filled orbital and hole located at adjacent lattice sites. Physically, one would certainly expect that the Coulomb attraction between the negative ion and positive hole would lower the energy of such a pair and thereby increase the importance of its interaction with the ground configuration states. It is interesting to note that the validity of Eq. (30) depends not on the fact that the second-nearest neighbor exchange integral J_2 is small, but rather on the assumption that the *effective* second-nearest neighbor exchange integral

$$J_2{}'=J_2+\frac{2M_2{}^2}{E-H_1{}^2}, \tag{33}$$

is small compared to J'.

For the spin wave states, $H_1{}^1$ can be written in a more explicit form. If we introduce ϵ as the difference between the eigenvalue E and the energy of the ferromagnetic state, then

$$\epsilon=E-\sum_i Q_i-\sum_{i>j} K_{ij}+NJ_1, \tag{34}$$

and

$$J'=J_1+\frac{2M_1{}^2}{\epsilon-3J_1-W+C_1}. \tag{35}$$

W and C_1 are one- and two-center Coulomb integrals between Wannier functions,

$$W=\left\langle w_p(\mathbf{r}_1)w_p(\mathbf{r}_2)\left|\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right|w_p(\mathbf{r}_1)w_p(\mathbf{r}_2)\right\rangle, \tag{36a}$$

$$C_q=\left\langle w_p(\mathbf{r}_1)w_{p+q}(\mathbf{r}_2)\left|\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\right|w_p(\mathbf{r}_1)w_{p+q}(\mathbf{r}_2)\right\rangle \tag{36b}$$

C_q is an obvious generalization of Paul's C.[3]

For states of lower multiplicity, Eq. (35) is replaced by

$$J'=J_1+\frac{2M_1{}^2}{\epsilon-B(S)J_1-W+C_1}. \tag{37}$$

In Eq. (37), $B(S)$ is a coefficient which depends on the multiplicity; it results from the averaging process which is necessary to obtain the equivalent to Eq. (25) for states with a multiplicity lower than $S=N/2-1$.

In those situations where the unperturbed energy difference between the ground and excited states is large compared to the ground configuration splittings, there exist several approximate methods for evaluating the parameter J' of Eq. (37). The simplest approximation is to set ϵ equal to zero. This corresponds to replacing E in Eq. (7) by the energy of the ferromagnetic state. Another approach involves substituting the exact value of ϵ into Eq. (37). However, this naturally requires that the full configuration interaction calculation be carried through. Finally, one can evaluate this relation for the kth eigenvalue by setting ϵ_k equal to A_kJ', where A_k represents the eigenvalue of the secular equation

$$\det[N\mathbf{1}_s+\textstyle\sum_i \boldsymbol{\Gamma}_s(P_{i\,i+1})-E\mathbf{1}_s]=0$$

for this kth state. In this case, Eq. (37) can be solved for J', yielding the relation

$$\begin{aligned}J'=&-\frac{1}{2A_k}[(-B(S)J_1-W+C)-A_kJ_1]\\&\pm\frac{1}{2A_k}\{[(-B(S)J_1-W+C_1)-A_kJ_1]^2\\&\qquad+4A_k[J_1(-B(S)J_1-W+C_1)+2M_1{}^2]\}^{\frac{1}{2}}.\end{aligned} \tag{38}$$

Equation (38) implies that the spin degeneracy problem for the ground configuration has been solved. While this problem can be handled for short chains, a branching diagram analysis shows that this would become prohibitively difficult for longer chains.

Table I. The values of parameters involved in the evaluation of the effective exchange integral J' for the six-atom chain.

	$R=1$	$R=2$	$R=3$	$R=5$
W	0.900605	0.753950	0.677537	0.630948
C_1	0.574682	0.413099	0.310011	0.199007
J_1	0.006274	0.010178	0.005404	0.000833
M_1	−0.725720	−0.239759	−0.107455	−0.026094

Table III. Values of J' obtained by setting $\epsilon=0$ in Eq. (37). This is equivalent to replacing E by the energy of the ferromagnetic state in Eq. (32).

	$R=1$	$R=2$	$R=3$	$R=5$
${}^5J'$	−3.049149	−0.299393	−0.055093	−0.002302
${}^3J'$	−2.941844	−0.283307	−0.053427	−0.002290
${}^1J'$	−2.890969	−0.275875	−0.052628	−0.002284

V. EVALUATION OF J' FOR THE SIX-ATOM CHAIN

The expression for the effective exchange integral given by Eq. (37) involves a number of integrals between Wannier functions, the values of which are listed in Table I for the six-atom chain. In this system, the factor $B(S)$ in Eq. (37) assumes the values of 3, 5, and 6 for S values of 2, 1, and 0, respectively. While the fact that Eq. (37) is valid only at large separations has been stressed, this relation will be evaluated at all four internuclear separations where configuration calculations have been carried out, namely 1, 2, 3, and 5 atomic units.[4] This permits the variation in the accuracy of the results to be evaluated as a function of the lattice spacing.

For reference purposes, the values of the effective exchange integrals J' which are obtained by fitting the eigenvalues of Eq. (1) to the results of the configuration interaction calculations are contained in Table II. The ordering of states is equivalent to that of Table IV in reference 4.

The approximation of setting ϵ equal to zero in Eq. (37) produces values of J' which are functions only of the multiplicity [through $B(S)$], so that at each internuclear separation for the six-atom chain, we obtain the three values of ${}^{(2S+1)}J'$ listed in Table III.

If the value of ϵ which is obtained from the configuration interaction calculations described in reference (4) is substituted into Eq. (37), J' becomes a function of both the multiplicity and the eigenvalue ϵ. The results obtained by evaluating Eq. (37) using the actual values for ϵ are contained in Table IV. The ordering of states is equivalent to that of Table II. It is clear that at small lattice spacings where ϵ is appreciable, the results of Table IV are in much better agreement with the fitted values of Table II than those of Table III, where ϵ is set equal to zero.

Finally, we present in Table V the results of evaluating the expression for J' as given by Eq. (38). Again, the ordering of states is equivalent to Tables II and IV. The results of Tables III, IV, and V are in good agreement with those of Table II at a lattice spacing of 5 atomic units. At this separation, the values of J' are relatively constant since their dependence on $B(S)$ and ϵ is relatively small. At the smaller separations, it is felt that the agreement between the results of Table IV and V and Table II is fortuitous since the higher terms in the expansion of $\mathbf{H}_{00}'$ in Eq. (7) undoubtedly become more important in this limit. Furthermore, the values of J' at these separations vary considerably for the different states.

The calculations described in reference 4 provide further reasons for suspicion regarding the agreement between the results of Tables IV and V and Table II except at large separations. Figure 5 of reference 4 indicates that the doubly and triply ionized states make an important contribution to the wave function of the ground state at the smaller lattice spacings. To emphasize this point, let us examine the decomposition of this ground state wave function for the six-atom chain in terms of its different ionic components. In Table VI, we tabulate the sums of squares of the combining coefficients for the different degrees of ionization for the six-atom ground-state wave function. At a separation of 5 atomic units, it is found that the ground and singly ionized configurations represent 99.89% of the total wave function. (Actually, the ground configuration and singly ionized states with a neighboring hole and doubly filled orbital represent 99.83% of the total wave function.) At smaller separations, the doubly ionized states assume a significantly greater role. Since we have shown that the direct interaction of these doubly ionized states with the ground configuration is small, the indirect interaction represented by the higher order terms of Eq. (7) must become significant at these separations. In any case, the parameterization of the spin degeneracy problem in terms of a single effective exchange integral is no longer possible.

Table II. Values of J' obtained by fitting the results of the configuration interaction calculations described in reference 4 to the eigenvalue spectrum of the Heisenberg exchange operator of Eq. (1).

Symmetry	k_{spin}	$R=1$	$R=2$	$R=3$	$R=5$
${}^5\Gamma_6$	$\pi/3R$	−1.382231	−0.216346	−0.050459	−0.002275
${}^1\Gamma_1$	π/R	−2.032575	−0.268761	−0.055809	−0.002302
${}^3\Gamma_5$	$2\pi/3R$	−1.588595	−0.174419	−0.054274	−0.002296
${}^3\Gamma_2$	π/R	−1.414510	−0.268449	−0.053374	−0.002294
${}^3\Gamma_3$	0	−0.819750	−0.174419	−0.046444	−0.002283
${}^5\Gamma_5$	$2\pi/3R$	−0.808411	−0.168544	−0.044901	−0.002275
${}^5\Gamma_1$	π/R	−0.753644	−0.171096	−0.045111	−0.002272
${}^1\Gamma_6$	$\pi/3R$	−0.806216	−0.177750	−0.046453	−0.002284
${}^3\Gamma_6$	$\pi/3R$	−0.659192	−0.153252	−0.043222	−0.002277
${}^3\Gamma_5$	$2\pi/3R$	−0.701888	−0.170279	−0.045846	−0.002283
${}^1\Gamma_4$	0	−0.640063	−0.155451	−0.043916	−0.002285
${}^3\Gamma_3$	0	−0.543572	−0.138335	−0.041463	−0.002280
${}^1\Gamma_1$	π/R	−0.568831	−0.149660	−0.043779	−0.002286

TABLE IV. Values of J' which are obtained by using the actual calculated values of ϵ from reference 4.

Symmetry	k_{spin}	$R=1$	$R=2$	$R=3$	$R=5$
${}^5\Gamma_6$	$\pi/3R$	-0.604231	-0.185439	-0.048030	-0.002286
${}^1\Gamma_1$	π/R	-0.323279	-0.112921	-0.042886	-0.002261
${}^3\Gamma_5$	$2\pi/3R$	-0.392600	-0.137534	-0.043668	-0.002266
${}^3\Gamma_2$	π/R	-0.324474	-0.138134	-0.040849	-0.002258
${}^3\Gamma_3$	0	-0.290701	-0.121393	-0.038930	-0.002247
${}^5\Gamma_5$	$2\pi/3R$	-0.374219	-0.120914	-9.039314	-0.002254
${}^5\Gamma_1$	π/R	-0.307352	-0.098719	-0.035675	-0.002238
${}^1\Gamma_6$	$\pi/3R$	-0.287396	-0.093129	-0.034156	-0.002220
${}^3\Gamma_6$	$\pi/3R$	-0.282183	-0.089105	-9.032539	-0.002211
${}^3\Gamma_5$	$2\pi/3R$	-9.241032	-9.075700	-0.030261	-0.002202
${}^1\Gamma_4$	0	-0.244382	-0.075966	-0.029510	-0.002189
${}^3\Gamma_3$	0	-0.239318	-0.072372	-0.027941	-0.002176
${}^1\Gamma_1$	π/R	-0.194093	-0.057859	-0.024402	-0.002150

TABLE VI. Decomposition of the ground-state wave function for the six-atom chain into the various degrees of ionization.

R	$\Sigma_i\,\alpha_i^2(0)$	$\Sigma_i\,\alpha_i^2(1)$	$\Sigma_i\,\alpha_i^2(2)$	$\Sigma_i\,\alpha_i^2(3)$
1	0.099360	0.456733	0.390393	0.053514
2	0.175390	0.487485	0.304811	0.032314
3	0.411802	0.445978	0.134148	0.008072
5	0.940599	0.058314	0.001081	0.000006

VI. DISCUSSION AND CONCLUSIONS

The results of the previous sections serve to supplement a discussion given by Slater in a paper concerned with cohesion in monovalent metals.[8] Slater showed that a monovalent metal had little likelihood of becoming ferromagnetic in the limit where the energy band approximation was valid. However, the situation at large lattice spacings was not quite clear. A multitude of states with multiplicities ranging from $S=N/2$ to $S=0$ (or $\frac{1}{2}$) approach the same limiting energy (which corresponds to the non-ionized separated atoms) and it was not clear then which of these states would lie lowest. The present analysis indicates that it is unlikely that the ferromagnetic state would have the lowest energy at large separations. Certainly, the calculations on a six atom chain[4] substantiate this conclusion. The ground state for this six-atom system is a singlet at all internuclear separations. This fact does not mean, however, that the Heisenberg exchange operator of Eq. (1) is valid at all internuclear separations. Rather, it implies that there is a gradual transition from the energy band to the orthogonalized atomic orbital approximations which are valid at small and large lattice spacings respectively. The results of Table VI trace this transition for the ground-state wave function of the six-atom chain.

TABLE V. Values of J' which are obtained by setting $\epsilon=A_kJ'$, where A_k is the eigenvalue of the Heisenberg exchange operator for this kth state.

Symmetry	k_{spin}	$R=1$	$R=2$	$R=3$	$R=5$
${}^5\Gamma_6$	$\pi/3R$	-0.864674	-0.193390	-0.048298	-0.002286
${}^1\Gamma_1$	π/R	-0.744890	-0.169821	-0.044760	-0.002262
${}^3\Gamma_5$	$2\pi/3R$	-0.736921	-0.170365	-0.045086	-0.002267
${}^3\Gamma_2$	π/R	-0.638361	-0.154086	-0.042879	-0.002258
${}^3\Gamma_3$	0	-0.552619	-0.138341	-0.040399	-0.002246
${}^5\Gamma_5$	$2\pi/3R$	-0.534439	-0.136853	-0.040490	-0.002254
${}^5\Gamma_1$	π/R	-0.468485	-0.122990	-0.037898	-0.002238
${}^1\Gamma_6$	$\pi/3R$	-0.466321	-0.120117	-0.036921	-0.002222
${}^3\Gamma_6$	$\pi/3R$	-0.421276	-0.111158	-0.035211	-0.002213
${}^3\Gamma_5$	$2\pi/3R$	-0.400903	-0.106594	-0.034218	-0.002205
${}^1\Gamma_4$	0	-0.386440	-0.102728	-0.033250	-0.002193
${}^3\Gamma_3$	0	-0.354317	-0.095794	-0.031720	-0.002181
${}^1\Gamma_1$	π/R	-0.326062	-0.088578	-0.029859	-0.002157

It is reasonable to conclude that at large lattice spacings, the Heisenberg exchange operator of Eq. (1) provides an accurate description of the magnetic interaction between *s*-type electrons of a linear chain. However, it is clear that this description is only approximate; the necessary approximations appear to break down quite seriously at smaller lattice spacings. While the extrapolation from this simplified one-dimensional example to a more physical three-dimensional magnetic system involves serious difficulties, the present discussions serve to emphasize one fact. The magnetic interaction is not *exactly* described by the Heisenberg exchange operator. In a given problem, it may prove to be desirable (or perhaps even necessary) to choose a more fundamental approach.

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[8] J. C. Slater, Phys. Rev. **35**, 509 (1931).