

Antiferromagnetic Linear Chain*

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Many-electron configuration interaction calculations have been carried out on a system of six hydrogen atoms arranged in a regular hexagonal array with a variable lattice spacing. The approximate wave functions for this system have been expressed as linear combinations of the $(2 \times 6)!/(6!)^2 = 924$ determinantal functions which can be formed from atomic $1s$ functions. In this manner, the effects of ionic configurations containing as many as three pairs of doubly filled orbitals have been introduced into the calculations. All three- and four-center integrals have been taken into account. The nonorthogonality of hydrogenic $1s$ orbitals localized about different atomic sites has been removed by transforming to a set of orthonormal Wannier functions. The principal result of these calculations is the fact that the effects of configura-

tion interaction can be represented quite accurately at large internuclear separations in terms of a parameter J' (analogous to a nearest-neighbor exchange integral) which assumes a negative value in a nonferromagnetic system such as this one. This provides a justification for the use of the Heisenberg exchange operator, $-2J'(\sum_i \mathbf{s}_i \cdot \mathbf{s}_{i+1} - \frac{1}{4})$, to describe the magnetic interaction at large separations in this system. In addition, these results show that this system of hydrogen atoms is bound with respect to six separated atoms, but not with respect to three molecules. The ground-state wave function is a singlet at all internuclear separations. The general form of the curves representing energy as a function of internuclear separation show a striking similarity to those obtained for the hydrogen molecule.

I. INTRODUCTION

THE electrical and magnetic properties of a linear chain of monovalent atoms containing s -type electrons outside of closed inner shells have been subject to a considerable amount of discussion since the early days of quantum mechanics. The essentials of the problem were first outlined by Slater¹ in an early paper on cohesion in monovalent metals. Slater considered a three-dimensional monovalent crystal with a variable lattice spacing. By utilizing the fact that the molecular orbital or energy-band functions represent a good approximation to the ground-state wave function at small lattice spacings, while the Heitler-London type shows the correct behavior in the limit of large separations, he was able to discuss the nature of the transition region in fairly definite terms. Most important, he emphasized the fact that while this intermediate region can be described equally well either in terms of the molecular orbital or Heitler-London schemes, it is necessary to supplement both methods by configuration interaction. In the Heitler-London theory, the excited configurations insert the ionic states which are necessary to obtain conductivity at small lattice spacings. On the other hand, the role of configuration interaction in the molecular orbital or energy-band scheme is to modify the nature of the wave functions of the various states so they reduce to a definite degree of ionization for the separated atoms. Finally, Slater pointed out that if the complete configuration interaction calculation is carried out, the final results are independent of whether the unperturbed functions are chosen in either the molecular orbital or Heitler-London schemes.

About the same time, the magnetic properties of a linear chain of monovalent atoms were considered by Bloch,² who approached this problem from the Heitler-London point of view. He described the interaction of the ferromagnetic state (having a parallel spin alignment) with those states containing a small number of reversed spins in terms of spin waves. While Bloch's treatment was exact for a single reversed spin, it was only approximate for more than one. Bethe³ found an exact solution to the problem of a linear chain containing an arbitrary number of reversed spins, again using a Heitler-London approach. Using Bethe's solutions, Hulthén⁴ found the ground-state energy of a linear chain under the assumption that the nearest-neighbor exchange integral was negative. The arbitrariness in sign for the exchange integral was attributed to the effects of the ionized states, which were completely neglected in the treatments of Bloch and Bethe.

More detailed studies of the effects of ionized configurations on magnetic phenomena have been carried out by Schubin and Wonsowsky,⁵ Slater,⁶ and Paul.⁷ Slater reconsidered the problem of spin waves originally treated by Bloch. He included in his more exact treatment not only states where a single spin was reversed, but also those states where this electron with reversed spin was free to move to neighboring lattice sites. By means of a perturbation expansion, he was able to indicate those terms in the energy which compete in determining whether or not a particular material is ferromagnetic. Paul extended Slater's treatment by considering the more general system which contains an arbitrary number of reversed spins, again including ionic configurations. He solved the problem of a single reversed spin exactly, so that his results for this case are

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¹ J. C. Slater, Phys. Rev. **35**, 509 (1931).

² F. Bloch, Z. Physik **61**, 206 (1930).

³ H. Bethe, Z. Physik **71**, 205 (1931).

⁴ L. Hulthén, Arkiv Mat. Astron. Fysik **26A**, 1 (1938).

⁵ S. Schubin and S. Wonsowsky, Proc. Roy. Soc. (London) **A145**, 159 (1934).

⁶ J. C. Slater, Phys. Rev. **52**, 198 (1937).

⁷ D. I. Paul, Phys. Rev. **118**, 92 (1960).

valid for large as well as small interactions between the ground and ionic configurations. His results include an approximate expression for an effective exchange integral J' in terms of integrals between Wannier functions.

The purpose of the present investigation is to provide further insight into these and other closely related problems. It is well known that the approximate solution to the hydrogen molecular problem involving $1s$ orbitals has provided a simple but sound basis for comparing the various approaches to a theoretical understanding of the electronic structure of molecules and solids. This system has been used as an example to point out the essential similarities and differences between the Heitler-London, orthogonalized atomic orbital, and energy-band methods. As a result, it has been possible to recognize the difficulties and limitations inherent in each of these different approaches. The results of this analysis have been applied not only to the study of more complicated molecules, but also to investigations concerned with the electrical and magnetic properties of solids.

The transition from the diatomic hydrogen molecule to a solid made up of a large number of atoms is admittedly a vast one. The purpose of the present study is to provide calculations on a system of intermediate size which is large enough so that the wave functions and energy levels begin to resemble those of a solid and yet small enough so that the calculations can be carried through with an accuracy equivalent to that obtained for the hydrogen molecule. As a compromise between these two extremes, calculations have been carried out on a system of six hydrogen atoms arranged in a regular hexagonal array with a variable lattice spacing. This system is qualitatively similar to that of a linear chain of six hydrogen atoms with periodic boundary conditions, since the group of the Hamiltonian (C_{6v}) is the same for both systems. The approximate, many-electron wave functions are expanded as linear combinations of the $(6 \times 2)!/(6!)^2 = 924$ determinantal functions which can be formed from hydrogenic $1s$ functions localized at the various atomic sites. These determinantal functions represent not only states which arise from the ground configuration (where there is a single electron associated

with each atomic site), but also those ionized states which contain as many as three pairs of doubly filled orbitals and an equal number of holes. The effects of configurations which include excited atomic states ($2s, 2p, \dots$, etc.) have been neglected.

All one-, two-, three-, and four-center integrals have been included in the formulation of the problem. The computational difficulties resulting from the non-orthogonality of hydrogenic $1s$ functions centered about different atomic sites have been removed by transforming to an orthonormal set of localized Wannier functions.⁸ This requires that the nearest-neighbor exchange integral be positive definite. The results of these calculations verify that the ground state of the system is a singlet at all internuclear separations. Furthermore, they reveal that in a nonmagnetic system such as this one, the effects of ionized configurations on the ground configuration can be parameterized quite accurately in terms of a negative effective exchange integral J' , especially at large lattice spacings where the overlap between the hydrogenic $1s$ functions is small (of the order of 0.1).

II. METHOD

The secular equation for this hexagonal ring of hydrogen atoms has been set up using symmetrized determinantal functions which are eigenfunctions of the square of the total spin angular momentum operator S^2 and its z component S_z and which transform irreducibly under the operations in the group of the Hamiltonian. The method of computing matrix elements of the Hamiltonian and identity operators is essentially that of the Dirac vector model.⁹ The symmetrized determinantal functions are designated by $\Omega_k^\nu(N, S, M_s; \beta, i, j)$, where

$$\Omega_k^\nu(N, S, M_s; \beta, i, j) = C \sum_P (-1)^P P^s P^\sigma O_{ij} \Phi^\nu \theta_k(N, S, M_s). \quad (1)$$

The normalization constant is designated by C 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.

In Eq. (1), Φ^ν is a product of one-electron Wannier functions, the single superscript ν enumerating the various configurations which contain different numbers and arrangements of doubly filled orbitals and holes. The various types of functions considered in these calculations are represented graphically in Fig. 1; in this figure, the relative positions of doubly filled orbitals and holes are indicated by $-$ and $+$ signs, respectively. The ground configuration function, which has a single electron localized about each atomic site, is designated by Φ^0 .

The functions $\theta_k(6, S, M_s)$ of Eq. (1) represent the six electron spin product functions which diagonalize S^2, S_z and form a basis for an irreducible representation

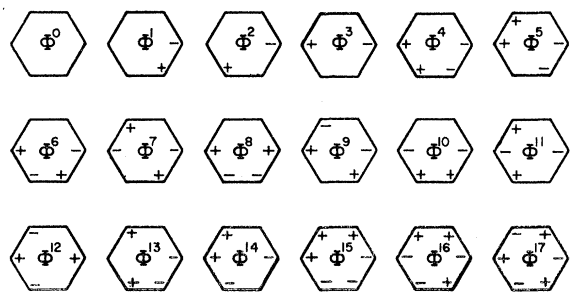


FIG. 1. Graphical representation of the 18 types of configurations included in these calculations. The $-$'s and $+$'s correspond to the relative distribution of doubly filled orbitals and holes, respectively. The non-ionic ground configuration function is represented by Φ^0 .

⁸ G. Wannier, Phys. Rev. **52**, 191 (1937).

⁹ P. A. M. Dirac, Proc. Roy. Soc. (London) **A123**, 714 (1929).

of the group of spin coordinate permutations. From this property, it follows that

$$P^s \theta_{k'}(N, S, M_s) = \sum_k \Gamma'^s(P)_{kk'} \theta_k(N, S, M_s). \quad (2)$$

The coefficients $\Gamma'^s(P)_{kk'}$ form the columns of an irreducible representation. When considering doubly filled orbitals, it is necessary to use basis functions for which the individual spin angular momentum operators are compounded according to a scheme due to Serber.¹⁰ In this method, electrons 1 and 2, 3 and 4, and 5 and 6 are first coupled through the use of Clebsch-Gordan coefficients to form singlets and triplets. These are then combined in a similar manner to form the six electron functions $\theta_k(6, S, M_s)$. From the usual branching diagram analysis, it is found that one septet, five quintets, nine triplets, and five singlets with $M_s = S$ can be formed in this manner. The subscript k distinguishes between these linearly independent functions of the same multiplicity.

The spatial symmetry of the Hamiltonian operator is introduced through the use of the projection operators O_{ij}^β of Eq. (1), where

$$O_{ij}^\beta = \sum_{R_m} \gamma^\beta(R_m)_{ij}^* R_m, \quad m=1, \dots, 12; i, j=1, 2, \dots, n_\beta. \quad (3)$$

$$\langle \Omega_k^\nu(N, S, M_s; \beta, i, j) | H | \Omega_{k'}^{\nu'}(N, S', M_{s'}; \beta', i', j') \rangle$$

$$= \frac{\delta_{SS'} \delta_{M_s M_{s'}} \delta_{\beta\beta'} \delta_{ii'} \sum_P (-1)^P \Gamma'^s(P)_{kk'} \langle \Phi^\nu | H | P^s \sum_{R_m} \gamma^\beta(R_m)_{jj}^* R_m \Phi^{\nu'} \rangle}{[\sum_P (-1)^P \Gamma'^s(P)_{kk'} \langle \Phi^\nu | P^s \sum_{R_m} \gamma^\beta(R_m)_{jj}^* R_m \Phi^\nu \rangle]^{1/2} [\sum_P (-1)^P \Gamma'^s(P)_{k'k'} \langle \Phi^{\nu'} | P^s \sum_{R_m} \gamma^\beta(R_m)_{j'j'}^* R_m \Phi^{\nu'} \rangle]^{1/2}}. \quad (4)$$

The $\delta_{SS'} \delta_{M_s M_{s'}} \delta_{\beta\beta'} \delta_{ii'}$ results from the orthonormal properties of the spin functions $\theta_k(N, S, M_s)$. The additional delta functions indicate that there are no matrix elements connecting either functions corresponding to different irreducible representations for the group of the Hamiltonian ($\delta_{\beta\beta'}$) or partners of the same irreducible representation ($\delta_{ii'}$). The form of Eq. (4) indicates the close relationship between this method and that of the Dirac vector model.

The delta functions of Eq. (4) factor the original secular equation into noncombining portions, each of which can be solved separately. The results of this reduction for the six-atom chain are contained in Table I. This table indicates the manner in which the various configurations represented by Fig. 1 contribute to the factored secular equations. The irreducible representations and multiplicities are designated by subscripts and superscripts, respectively. The blank portions of this table represent functions which fail to satisfy the exclusion principle. A zero entry indicates that the function corresponding to Eq. (1) vanishes identically for that symmetry. For the one-dimensional representations Γ_1 through Γ_4 , the nonzero entries of a given column denote the number of spin functions for each multiplicity which can be combined with the spatial function indicated at the top of the column. The entries do not include functions which

Here, the sum is over the twelve operations R_m contained in C_{6v} , the group of the Hamiltonian. $\gamma^\beta(R_m)_{ij}^*$ is the complex conjugate of the ij th matrix element in the β irreducible representation for C_{6v} and n_β is its dimension. The operations R_m include all the physical rotations and rotations followed by reflections which send a regular hexagon into itself. The group C_{6v} contains four one-dimensional and two two-dimensional irreducible representations which we denote by Γ_1 through Γ_6 , respectively.¹¹ These irreducible representations are closely associated with the wave vector \mathbf{k} which describes the properties of crystal wave functions under translation. The irreducible representations Γ_1 and Γ_2 represent functions which translate like $k=0^+$ and 0^- , respectively, the $+$ and $-$ indicating the manner in which the functions transform under operations which include a translation followed by a reflection. Similarly, Γ_3 and Γ_4 represent functions which translate like $k=\pi^+/R$ and π^-/R , where R is the distance between two adjacent atoms. Finally, Γ_5 and Γ_6 are equivalent to k values of $\pi/3R$ and $2\pi/3R$, respectively.

Using the Dirac notation, the matrix elements of the Hamiltonian operator between the functions $\Omega_k^\nu(N, S, M_s; \beta, i, j)$ can be written¹²

transform as partners for the two-dimensional irreducible representations Γ_5 and Γ_6 . However, they do include functions which transform according to different columns of the same irreducible representation. The results of Table I indicate that the largest secular equation which results from the use of the symmetrized determinantal functions of Eq. (1) is a 33×33 equation.

III. INTEGRALS

The calculations described in the previous sections have been carried out at four internuclear separations, namely 1, 2, 3, and 5, atomic units.¹³ At each lattice spacing, the orbital exponents for the hydrogenic functions have been set equal to unity; there has been no variation of these parameters.

The calculational difficulties involved with the use of nonorthogonal one-electron functions have been reduced through the use of the orthonormal Wannier functions $w_n(\mathbf{r})$; the subscript n indicates the nuclear site about which the particular function is localized. The transformation from the nonorthogonal hydrogenic type

¹¹ G. F. Koster, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 173.

¹² L. F. Mattheiss, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Quarterly Progress Report No. 33, July 15, 1959 (unpublished).

¹³ D. R. Hartree, *The Calculation of Atomic Structures* (John Wiley and Sons, Inc., New York, 1957), p. 5.

¹⁰ R. Serber, Phys. Rev. 45, 461 (1934).

TABLE I. Enumeration of the contributions to the various factored secular equations by determinantal functions with spatial parts represented by Fig. 1. A zero entry in this table signifies that the corresponding symmetrized determinantal function vanishes identically.

| | 0 Φ^0 | 1 Φ^1 | Φ^2 | Φ^3 | Φ^4 | Φ^5 | Φ^6 | Φ^7 | Φ^8 | 2 Φ^9 | Φ^{10} | Φ^{11} | Φ^{12} | Φ^{13} | Φ^{14} | 3 Φ^{15} | Φ^{16} | Φ^{17} | Dimension/ No. of doubly filled orbitals |
|-----------|---------------|---------------|----------|----------|----------|----------|----------|----------|----------|---------------|-------------|-------------|-------------|-------------|-------------|------------------|-------------|-------------|------------------------------------------------|
| 7T_3 | 1 | | | | | | | | | | | | | | | | | | 1 |
| 5T_1 | 1 | 1 | 1 | 1 | | | | | | | | | | | | | | | 4 |
| 5T_2 | 0 | 1 | 1 | 0 | | | | | | | | | | | | | | | 2 |
| 5T_3 | 0 | 1 | 1 | 1 | | | | | | | | | | | | | | | 3 |
| 5T_4 | 0 | 1 | 1 | 0 | | | | | | | | | | | | | | | 2 |
| 5T_5 | 1 | 2 | 2 | 1 | | | | | | | | | | | | | | | 6 |
| 5T_6 | 1 | 2 | 2 | 1 | | | | | | | | | | | | | | | 6 |
| 3T_1 | 0 | 3 | 3 | 1 | 1 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | | | | 12 |
| 3T_2 | 1 | 3 | 3 | 2 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | | | | 18 |
| 3T_3 | 2 | 3 | 3 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | | | | 18 |
| 3T_4 | 0 | 3 | 3 | 2 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 1 | 1 | 1 | 1 | | | | 15 |
| 3T_5 | 2 | 6 | 6 | 3 | 2 | 1 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | | | | 33 |
| 3T_6 | 1 | 6 | 6 | 3 | 2 | 1 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | | | | 30 |
| 1T_1 | 2 | 2 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 22 |
| 1T_2 | 0 | 2 | 2 | 0 | 1 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 10 |
| 1T_3 | 0 | 2 | 2 | 2 | 1 | 0 | 1 | 0 | 0 | 1 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 16 |
| 1T_4 | 1 | 2 | 2 | 0 | 1 | 1 | 1 | 0 | 1 | 0 | 1 | 0 | 0 | 1 | 1 | 0 | 1 | 0 | 13 |
| 1T_5 | 0 | 4 | 4 | 2 | 2 | 1 | 2 | 0 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 1 | 2 | 0 | 27 |
| 1T_6 | 1 | 4 | 4 | 2 | 2 | 1 | 2 | 2 | 1 | 1 | 1 | 1 | 1 | 2 | 2 | 1 | 2 | 0 | 30 |

functions $a_n(\mathbf{r})$ to the Wannier representation can be expressed by the relation⁸

$$w_n(\mathbf{r}) = \sum_p A(p) a_{n+p}(\mathbf{r}). \quad (5)$$

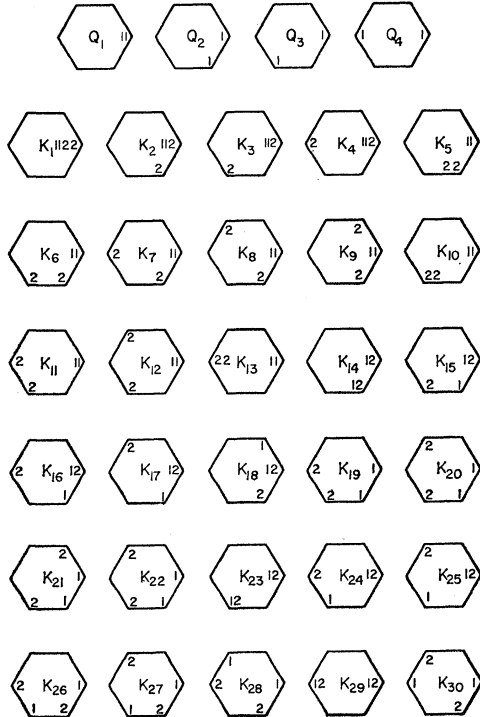


FIG. 2. Pictorial representation of the 4 one-electron integrals (Q_i , $i=1, \dots, 4$) and 30 two-electron integrals (K_i , $i=1, 2, \dots, 30$) involved in these calculations. The 1's and 2's represent the location of the orbitals corresponding to electrons 1 and 2.

The coefficients $A(p)$ are functions of the overlap between the different neighbors, and they determine the degree to which the Wannier functions are localized. These coefficients are symmetric about the central atomic site so that $A(1)=A(-1)$ and $A(2)=A(-2)$. The values of these coefficients at the four internuclear separations are given in Table II along with the values of the nearest neighbor, second nearest neighbor, and third nearest neighbor overlap integrals S_1 , S_2 , and S_3 , respectively. From the results of Table II, it is apparent that the Wannier functions are orthogonal not because they do not overlap appreciably, but rather because there is a cancellation of positive and negative contributions coming from the oscillating terms of the functions.

In evaluating the matrix elements of Eq. (4), the one- and two-electron integrals between Wannier functions are required. If we denote these by Q_{ij} and K_{ijlm} , respectively, where

$$Q_{ij} = \int w_i^*(\mathbf{r}_1) \left[-\frac{1}{2} \nabla_1^2 - \sum_{\alpha} (Z_{\alpha}/|\mathbf{r}_1 - \mathbf{R}_{\alpha}|) \right] \times w_j(\mathbf{r}_1) dv_1, \quad (6)$$

$$K_{ijlm} = \int \int w_i^*(\mathbf{r}_1) w_j(\mathbf{r}_1) (1/|\mathbf{r}_1 - \mathbf{r}_2|) \times w_l^*(\mathbf{r}_2) w_m(\mathbf{r}_2) dv_1 dv_2, \quad (7)$$

it is clear that Q_{ij} and K_{ijlm} are represented by double and quadruple sums when expressed in terms of integrals between the nonorthogonal hydrogenic functions through the transformation of Eq. (5). The integrals Q_{ij} and K_{ijlm} have a high degree of symmetry. The independent integrals can be obtained by considering

TABLE II. Atomic overlap integrals (a.u.) and Wannier function coefficients at internuclear separations of 1, 2, 3, and 5 atomic units.

| S_1 | S_2 | S_3 | $A(0)$ | $A(1)$ | $A(2)$ | $A(3)$ |
|----------|----------|----------|----------|-----------|----------|-----------|
| 0.858385 | 0.660279 | 0.586453 | 3.049879 | -1.615410 | 0.490163 | -1.334329 |
| 0.586453 | 0.264936 | 0.189262 | 1.391708 | -0.439078 | 0.061628 | -0.048781 |
| 0.348509 | 0.084159 | 0.047096 | 1.103790 | -0.196940 | 0.012731 | -0.012257 |
| 0.096578 | 0.006080 | 0.002031 | 1.007062 | -0.048710 | 0.000618 | -0.000726 |

the symmetry properties of Eqs. (6) and (7) as expressed by Eqs. (8) and (9):

$$Q_{ij} = Q_{ji}, \quad (8)$$

$$K_{ijlm} = K_{jilm} = K_{ijml} = K_{jiml} = K_{lmij} = K_{mlji} = K_{lmji} = K_{mlji}, \quad (9)$$

as well as the fact that the values of the integrals are dependent only on the relative values of the respective indices. Using these symmetry properties, the distinct integrals are found to be those represented by Fig. 2. In this figure, a total of 4 one-electron and 30 two-electron integrals are represented graphically. The 1's and 2's represent the relative locations of the orbitals corresponding to the coordinates of electrons 1 and 2.

The values of the independent integrals of Fig. 2 at separations of 1, 2, 3, and 5 atomic units are given in Table III, in terms of the Wannier functions as well as of the nonorthogonal hydrogenic orbitals. The two-, three-, and four-center integrals between the hydrogenic orbitals were obtained by means of the zeta-function expansion technique proposed by Barnett and Coulson.^{14,15} From the results of this table, it is evident that there is little similarity between the integrals in the two representations. The three- and four-center integrals are, in general, significantly smaller in the Wannier representation.

The one-, two-, and three-center integrals between hydrogenic orbitals have been obtained with an accuracy of approximately six decimal figures. The four-center integrals are accurate to between three and five decimal figures. The corresponding integrals between Wannier functions are less accurate, due to round-off errors. This is especially true at $R=1$ where the estimated error is approximately ± 0.01 . It should be noted that the positive-definite exchange integral K_{23} has a negative value at this separation.

IV. RESULTS

The results of the calculations described in the previous sections are too numerous to be reproduced here in their entirety. Under these circumstances, it is appropriate to begin this discussion with a description of their general nature. The form of the energy levels for the six-atom ring of hydrogen atoms has been plotted as a function of internuclear separation in Fig. 3. Due to the

large number of states involved, the individual levels have not been drawn. Rather, the envelopes of the curves for the various states which reduce to the same degree of ionization at infinity have been plotted. The line which forms the lower limit of the ground configuration envelope represents the ground state of the system and has a symmetry corresponding to 1T_1 . The upper limit to the ground configuration envelope is the ferromagnetic state with symmetry 7T_3 . These two states, along with the first three excited states arising from the ground configuration, have been plotted in Fig. 4 with a larger scale.

The general behavior of the energy of the various states as a function of internuclear separation reveals a striking similarity to that found for the hydrogen molecule. An interesting aspect of these curves concerns the rate with which the various levels converge to their correct values at infinity. While the ground configuration levels have an energy which is a few hundredths of the infinite separation value of -3.0 atomic units (a.u.)

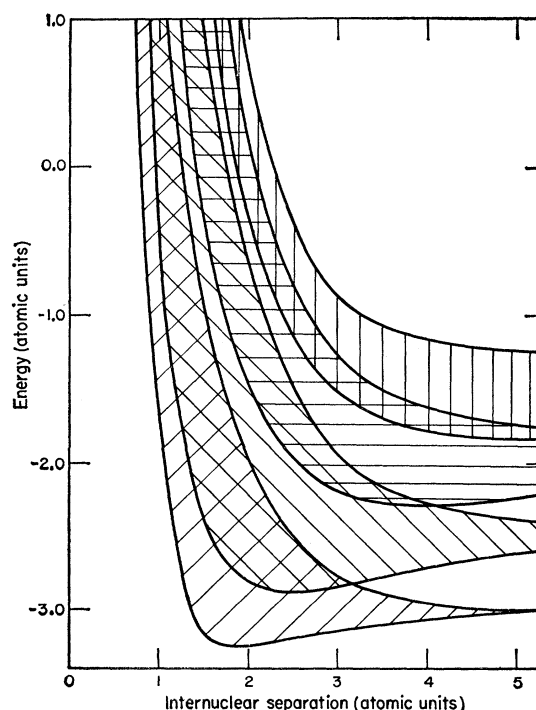


FIG. 3. Envelopes of the curves of energy as a function of internuclear separation for the states which reduce to the different degrees of ionization at infinite separation.

¹⁴ C. A. Coulson, Proc. Cambridge Phil. Soc. **33**, 104 (1937).

¹⁵ M. P. Barnett and C. A. Coulson, Phil. Trans. Roy. Soc. London **A243**, 221 (1951).

TABLE III. Tabulation of the values (a.u.) for the one- and two-electron integrals in both the nonorthogonal atomic and orthonormal Wannier representations. The notation of Fig. 2 is used in identifying the integrals of this table.

| Integral | Wannier | Hydrogenic | Integral | Wannier | Hydrogenic |
|-----------------------------------------------------------------|-----------|------------|----------|-----------|------------|
| (A) Integrals between Wannier and hydrogenic functions, $R=1$. | | | | | |
| Q_1 | -2.407211 | -3.487140 | K_{14} | 0.006274 | 0.436651 |
| Q_2 | -0.675058 | -3.104501 | K_{15} | 0.004956 | 0.315489 |
| Q_3 | 0.151021 | -2.490330 | K_{16} | -0.002270 | 0.264265 |
| Q_4 | -0.205367 | -2.249271 | K_{17} | 0.005157 | 0.294973 |
| K_1 | 0.900605 | 0.625000 | K_{18} | -0.013178 | 0.404162 |
| K_2 | -0.003141 | 0.507044 | K_{19} | 0.000748 | 0.351717 |
| K_3 | 0.001811 | 0.358781 | K_{20} | -0.000475 | 0.274859 |
| K_4 | -0.005742 | 0.308036 | K_{21} | -0.000843 | 0.262708 |
| K_5 | 0.574682 | 0.554521 | K_{22} | 0.003471 | 0.330490 |
| K_6 | -0.014338 | 0.434811 | K_{23} | -0.000872 | 0.240192 |
| K_7 | 0.011847 | 0.326396 | K_{24} | 0.000779 | 0.205430 |
| K_8 | 0.005334 | 0.305159 | K_{25} | -0.001264 | 0.224506 |
| K_9 | -0.015245 | 0.374425 | K_{26} | -0.003310 | 0.234807 |
| K_{10} | 0.387778 | 0.459927 | K_{27} | 0.003224 | 0.205454 |
| K_{11} | -0.009423 | 0.382475 | K_{28} | 0.001384 | 0.219244 |
| K_{12} | 0.011991 | 0.311226 | K_{29} | 0.000779 | 0.184156 |
| K_{13} | 0.344402 | 0.425974 | K_{30} | -0.001625 | 0.183672 |
| (B) Integrals between Wannier and hydrogenic functions, $R=2$. | | | | | |
| Q_1 | -2.010509 | -2.269458 | K_{14} | 0.010178 | 0.184156 |
| Q_2 | -0.224322 | -1.456287 | K_{15} | -0.000337 | 0.071821 |
| Q_3 | 0.020981 | -0.701687 | K_{16} | 0.000214 | 0.044959 |
| Q_4 | -0.036765 | -0.511531 | K_{17} | 0.000849 | 0.060993 |
| K_1 | 0.753950 | 0.625000 | K_{18} | -0.001412 | 0.149267 |
| K_2 | -0.007075 | 0.308036 | K_{19} | 0.000532 | 0.107335 |
| K_3 | 0.001379 | 0.115160 | K_{20} | 0.000453 | 0.051189 |
| K_4 | -0.004076 | 0.076982 | K_{21} | 0.000338 | 0.043632 |
| K_5 | 0.413099 | 0.425974 | K_{22} | -0.000197 | 0.094837 |
| K_6 | -0.005739 | 0.205210 | K_{23} | 0.000442 | 0.032258 |
| K_7 | 0.004504 | 0.090467 | K_{24} | 0.000157 | 0.021115 |
| K_8 | 0.001891 | 0.073329 | K_{25} | -0.000185 | 0.027267 |
| K_9 | -0.003478 | 0.126366 | K_{26} | 0.000089 | 0.030504 |
| K_{10} | 0.256295 | 0.282540 | K_{27} | 0.000351 | 0.021186 |
| K_{11} | 0.001558 | 0.158329 | K_{28} | -0.000142 | 0.025587 |
| K_{12} | 0.003756 | 0.081054 | K_{29} | 0.000212 | 0.015627 |
| K_{13} | 0.222430 | 0.247554 | K_{30} | -0.000124 | 0.015453 |
| (C) Integrals between Wannier and hydrogenic functions, $R=3$. | | | | | |
| Q_1 | -1.643441 | -1.711543 | K_{14} | 0.005404 | 0.058508 |
| Q_2 | -0.098392 | -0.678072 | K_{15} | -0.000155 | 0.011392 |
| Q_3 | 0.005259 | -0.174530 | K_{16} | 0.000107 | 0.005279 |
| Q_4 | -0.008623 | -0.098917 | K_{17} | 0.000243 | 0.008942 |
| K_1 | 0.677537 | 0.625000 | K_{18} | -0.000255 | 0.041920 |
| K_2 | -0.006871 | 0.160742 | K_{19} | 0.000072 | 0.026394 |
| K_3 | 0.000181 | 0.029801 | K_{20} | 0.000175 | 0.006949 |
| K_4 | -0.001839 | 0.015311 | K_{21} | 0.000087 | 0.004968 |
| K_5 | 0.312011 | 0.319803 | K_{22} | -0.000890 | 0.022785 |
| K_6 | -0.002433 | 0.087055 | K_{23} | 0.000093 | 0.002775 |
| K_7 | 0.001485 | 0.020723 | K_{24} | 0.000028 | 0.001363 |
| K_8 | 0.000690 | 0.013857 | K_{25} | -0.000041 | 0.002148 |
| K_9 | -0.001046 | 0.033602 | K_{26} | 0.000028 | 0.002550 |
| K_{10} | 0.185801 | 0.192144 | K_{27} | 0.000069 | 0.001393 |
| K_{11} | 0.001337 | 0.063971 | K_{28} | -0.000043 | 0.001942 |
| K_{12} | 0.001233 | 0.017959 | K_{29} | 0.000045 | 0.000814 |
| K_{13} | 0.160915 | 0.166593 | K_{30} | -0.000015 | 0.000797 |
| (D) Integrals between Wannier and hydrogenic functions, $R=5$. | | | | | |
| Q_1 | -1.226793 | -1.230831 | K_{14} | 0.000833 | 0.003717 |
| Q_2 | -0.020931 | -0.139498 | K_{15} | -0.000012 | 0.000169 |
| Q_3 | 0.000441 | -0.009118 | K_{16} | 0.000004 | 0.000043 |
| Q_4 | -0.000406 | -0.003045 | K_{17} | 0.000012 | 0.000119 |
| K_1 | 0.630948 | 0.625000 | K_{18} | 0.000063 | 0.002201 |
| K_2 | -0.005033 | 0.034953 | K_{19} | -0.000117 | 0.001117 |
| K_3 | -0.000038 | 0.001529 | K_{20} | 0.000022 | 0.000092 |
| K_4 | -0.000186 | 0.000461 | K_{21} | 0.000001 | 0.000039 |
| K_5 | 0.199007 | 0.199569 | K_{22} | -0.000132 | 0.000953 |
| K_6 | -0.000469 | 0.014730 | K_{23} | 0.000001 | 0.000011 |
| K_7 | 0.000078 | 0.000912 | K_{24} | 0.0000002 | 0.000003 |
| K_8 | 0.000043 | 0.000381 | K_{25} | 0.000002 | 0.000007 |
| K_9 | 0.000031 | 0.001760 | K_{26} | 0.000001 | 0.000010 |
| K_{10} | 0.115163 | 0.115469 | K_{27} | 0.000003 | 0.000005 |
| K_{11} | 0.000404 | 0.010784 | K_{28} | -0.000003 | 0.000006 |
| K_{12} | 0.000059 | 0.000776 | K_{29} | 0.0000004 | 0.000001 |
| K_{13} | 0.099702 | 0.099999 | K_{30} | 0.0000004 | 0.000001 |

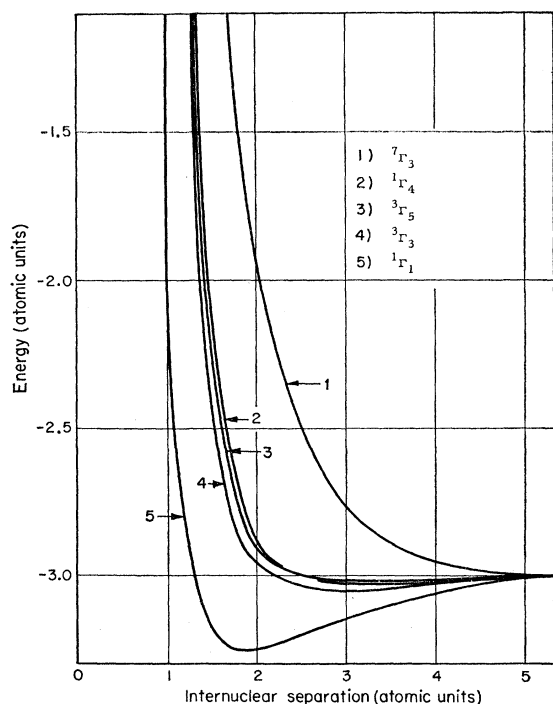


FIG. 4. Energy of the ground configuration states as a function of internuclear separation.

at a distance of 5 a.u., the ionized configurations show a much slower convergence. Clearly, this is due to the long-range Coulomb interaction which takes place between the negative ion-positive hole pairs contained in these ionic configurations.

From Fig. 4, the ground-state energy as a function of internuclear separation shows a definite minimum somewhere in the vicinity of 2 a.u. This indicates that the system is bound with respect to six separated hydrogen atoms by an energy of approximately 0.25 a.u. It is interesting to compare this value of the binding energy with the energy of three separated hydrogen molecules. Using the results of a configuration interaction calculation on the hydrogen molecule which includes all states arising from $1s$ orbitals,¹⁶ it is found that the three separated molecules have an energy which is lower by approximately 0.1 a.u. Thus, the dissociation of this six-atom system into the more stable configuration of three separated molecules is correctly predicted.

The energy minimum for the hydrogen molecule occurs at a lattice spacing of approximately 1.4 a.u. While it would require additional calculations to determine the precise position of this minimum for the six-atom system, Figs. 3 and 4 indicate that it has been shifted to a larger internuclear separation. This agrees with the conclusion of Ruffa and Griffing¹⁷ who have

¹⁶ J. C. Slater, Technical Report No. 3, Solid-State and Molecular Theory Group, M. I. T. (1953) (unpublished), p. 58.

¹⁷ A. R. Ruffa and V. Griffing (private communication).

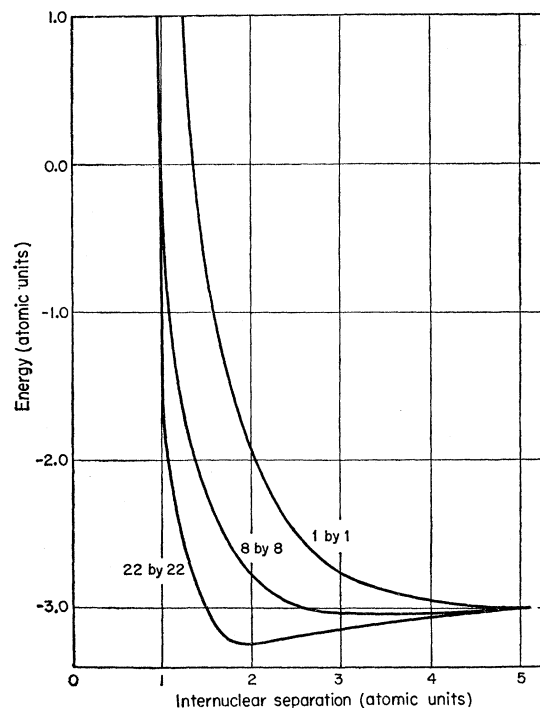


FIG. 5. Energy of the ground state as a function of internuclear separation and the dimension of the secular equation.

carried out self-consistent field calculations on a linear configuration of six hydrogen atoms. They find that the energy minimum occurs at approximately 1.8 a.u., a value which is certainly consistent with the present results.

It is important to emphasize the fact that the position of the energy minimum and the value of the binding energy are to a large extent affected by the amount of configuration interaction which is included. To illustrate this point, calculations have been carried out on the ground state in which portions of the full secular equation have been solved. The results of these calculations are contained in Fig. 5. The lowest curve of this figure represents the lowest root of the complete ground-state secular equation. The intermediate curve represents the lowest root of the secular equation which involves only the ground configuration in addition to singly ionized states. The upper curve represents the lowest root of the secular equation involving only the un-ionized configurations. It is evident from this figure that doubly and triply ionized configurations contribute significantly to the ground-state wave function, especially at smaller internuclear separations. It must be expected, therefore, that further changes in the shapes of the curves shown in Figs. 3 and 4 will occur when the effects of additional configurations involving excited atomic states are included. Similarly, by permitting the screening parameter of the hydrogen $1s$ functions to vary as a function of internuclear separation, the scale of the curves presented here will undoubtedly undergo quantitative changes;

however, it is expected that their qualitative nature will remain the same.

V. DISCUSSION

Let us now proceed to a more quantitative discussion of the results of the previous section. Perhaps the most important result of these calculations is the fact that they provide a justification for the use of the Heisenberg exchange operator given by Eq. (10) to describe the magnetic interaction between s -type electrons:

$$H = -2 \sum_{i>j} J_{ij} (\mathbf{s}_i \cdot \mathbf{s}_j - \frac{1}{4}), \quad (10)$$

at least in situations where the nearest-neighbor overlap is small. Equation (10) is valid under the following conditions. If one considers only the un-ionized ground configuration wave functions, then the effective Hamiltonian of Eq. (10) produces the same Hamiltonian matrix with spin product functions (eigenfunctions of S^2 and S_z) as the true Hamiltonian operator does with determinantal functions which are eigenfunctions of S^2 and S_z (neglecting an additive constant along the diagonal).

A frequent approximation to Eq. (10) neglects all but nearest-neighbor exchange integrals J , so that

$$J_{ij} = J \delta_{i(i+1)}. \quad (11)$$

Then, Eq. (10) becomes

$$H = -2J \sum_i (\mathbf{s}_i \cdot \mathbf{s}_{i+1} - \frac{1}{4}). \quad (12)$$

Equation (12) is considered by many to be a fundamental relation in magnetic theory. A serious difficulty results from the fact that this approximate relation is derived through the use of orthonormal one-electron functions. This requires that J be positive definite. A value of J greater than zero predicts that the ferromagnetic state will lie lowest in this approximation. This difficulty has been discussed by Slater,¹⁸ who emphasizes the need to include the interaction of the ground configuration functions with those representing ionized configurations.

To account for the existence of nonmagnetic, anti-ferromagnetic, ferrimagnetic, as well as ferromagnetic systems, it is assumed frequently that J is a parameter which can take on positive or negative values in particular systems. This can be justified through the introduction of a perturbation technique due to Kramers.¹⁹ In essence, this method projects the effects of the ionized configurations into the ground configuration through the introduction of an effective Hamiltonian operator. Associated with this effective Hamiltonian operator is an effective exchange integral which can take on positive or negative values. The details of this method will be discussed in a future paper. Comparison will be made

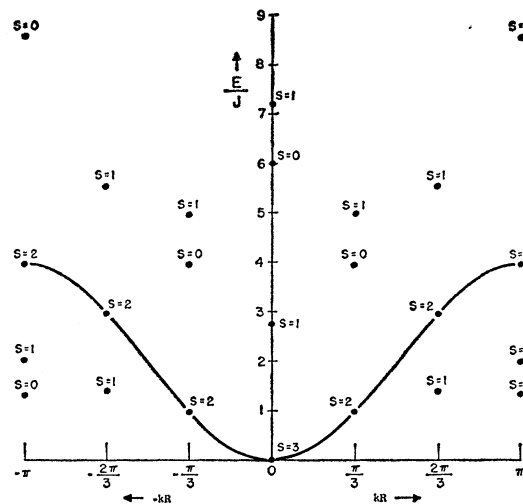


FIG. 6. Energy as a function of kR for eigenvalues of the Heisenberg exchange operator representing a six-atom linear chain with periodic boundary conditions.

with a similar technique for including the effects of ionic configurations which has been introduced by Paul.⁷

The eigenvalues and eigenfunctions for the effective Hamiltonian operator of Eq. (12) have been obtained for short chains by Orbach²⁰ and also independently by the present author.²¹ The energy (in units of J') of the various states arising from the six-atom chain have been plotted as a function of kR in Fig. 6. This figure is drawn with the assumption that J' is positive. A negative J' would cause the figure to be inverted. The multiplicity of the individual states is indicated. The translational symmetry index k results from the periodic boundary conditions which have been imposed on the chain (or from the rotational symmetry of the hexagonal ring of atoms). The symmetry index k in Fig. 6 identifies the translational symmetry of the spin functions, which turns out to be quite different from that of the determinantal functions as a whole. As a matter of fact, there is a reciprocal relationship which exists between the translational symmetry of these determinantal functions and their spin portions. Determinantal functions which translate like k equal to 0, $\pi/3R$, $2\pi/3R$, and π/R have spin portions which translate like k equal to π/R , $2\pi/3R$, $\pi/3R$, and 0, respectively. In Fig. 6, a solid line has been drawn through the spin-wave states which contain a single reversed spin and obey the simple dispersion relationship

$$E_{J'} = 2J'(1 - \cos kR). \quad (13)$$

In an attempt to compare the results of Fig. 6 with those obtained from the more accurate configuration interaction calculations, the following procedure has been used. The energy difference between the ferro-

²⁰ R. Orbach, Phys. Rev. **115**, 1181 (1959).

²¹ L. F. Mattheiss, Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Quarterly Progress Report No. 31, January 15, 1959 (unpublished).

¹⁸ J. C. Slater, Revs. Modern Phys. **25**, 199 (1953).

¹⁹ H. A. Kramers, Physica **1**, 182 (1934).

magnetic state and the ground state has been used to determine an effective exchange integral J' . Using this parameter, the relative values of the intermediate states of Fig. 6 have been computed. These energy values are denoted by $E_{J'}$. The results of these calculations are contained in Table IV. In this table, the values of E represent the actual energies of the various states as obtained from the configuration interaction calculations. $|\Delta E|$ is the magnitude of the difference between E and $E_{J'}$.

The results of Table IV indicate the extent to which we are able to parameterize the spin degeneracy problem in terms of a single effective exchange integral J' . At a separation of 5 a.u., E and $E_{J'}$ are in agreement to better than four decimal figures. The ordering of levels is identical in each case. At smaller internuclear separations, the agreement becomes quite poor. Discrepancies occur in the ordering of levels as predicted by the two methods. This is obvious from the results of Fig. 4 and Table IV where a number of levels corresponding to states of different symmetry are shown to cross. No such crossing of levels is predicted for the eigenvalues of the Heisenberg exchange operator of Eq. (10).

VI. ANTIFERROMAGNETIC SPIN WAVES

While the ferromagnetic ground state and low-lying excited states are well understood in terms of spin-wave theory, the situation is quite unsatisfactory as far as our understanding of the antiferromagnetic ground state is concerned. This term is generally associated with the lowest eigenvalue of Eq. (12) when J' is less than zero, although the wave function for this state by no means shows the long- or short-range order which is generally implied in the term antiferromagnetic. The results of the previous section indicate that the antiferromagnetic ground state for the six-atom chain is a singlet at all internuclear separations; this is in agreement with the result of Marshall²² who showed in general that the lowest eigenfunction of the Heisenberg exchange operator of Eq. (12) with $J' < 0$ is a singlet. Anderson²³ has proposed a semiclassical theory of the antiferromagnetic ground and spin-wave states. Kubo²⁴ and Oguchi²⁵ have presented quantum mechanical treatments of these states which lead to results which are quite similar to those obtained by Anderson.

For our purposes, the most interesting result of these treatments is the dispersion relationship for antiferromagnetic spin waves. Anderson predicts that the dispersion relation for these waves is given by $2JS \sin kR$. The results of Kubo and Oguchi merely add small correction factors to the coefficient multiplying $\sin kR$. The low-lying states of Fig. 6 ($J' < 0$) do exhibit a dependence on kR which is quite similar to that of a sine

TABLE IV. Energy (in atomic units) of states arising from the ground configuration as compared with those predicted by the Heisenberg exchange operator. The effective exchange integral J' is obtained by setting the energy difference between the ferromagnetic and ground states (as obtained from the configuration interaction calculations) equal to $8.6055 J'$, the ground-state energy of the Heisenberg exchange operator. The quantities $E_{J'}$ correspond to the intermediate energy levels of the Heisenberg exchange operator which are computed using this value of J' . The quantity $|\Delta E|$ represents the absolute value of the difference between the intermediate eigenvalues E and the quantities $E_{J'}$.

| Symmetry | k_{spin} | $E_{J'}$ | E | $ \Delta E $ |
|--------------------------------------------------------|-------------------|-----------|-----------|--------------|
| (A) Internuclear separation = 1 a.u.; $J' = -0.568831$ | | | | |
| $^7\Gamma_3$ | 0 | 3.294055 | 3.294055 | 0.0 |
| $^6\Gamma_6$ | $\pi/3R$ | 2.725224 | 1.911824 | 0.813400 |
| $^1\Gamma_1$ | π/R | 2.500849 | 0.459733 | 2.041116 |
| $^3\Gamma_5$ | $2\pi/3R$ | 2.475821 | 1.008944 | 1.466877 |
| $^3\Gamma_2$ | π/R | 2.156393 | 0.465034 | 1.691359 |
| $^3\Gamma_3$ | 0 | 1.721845 | 1.028323 | 0.693522 |
| $^6\Gamma_5$ | $2\pi/3R$ | 1.587562 | 0.868823 | 0.718739 |
| $^5\Gamma_1$ | π/R | 1.018731 | 0.279480 | 0.739251 |
| $^1\Gamma_6$ | $\pi/3R$ | 1.018731 | 0.069190 | 0.949541 |
| $^3\Gamma_6$ | $\pi/3R$ | 0.449900 | -0.001905 | 0.451805 |
| $^3\Gamma_5$ | $2\pi/3R$ | 0.130471 | -0.609535 | 0.740006 |
| $^1\Gamma_4$ | 0 | -0.118931 | -0.546324 | 0.427393 |
| $^3\Gamma_3$ | 0 | -0.822045 | -0.639266 | 0.182779 |
| $^1\Gamma_1$ | π/R | -1.601047 | -1.601047 | 0.0 |
| (B) Internuclear separation = 2 a.u.; $J' = -0.149660$ | | | | |
| $^7\Gamma_3$ | 0 | -1.961706 | -1.961706 | 0.0 |
| $^6\Gamma_6$ | $\pi/3R$ | -2.111366 | -2.178052 | 0.066686 |
| $^1\Gamma_1$ | π/R | -2.170399 | -2.493751 | 0.323352 |
| $^3\Gamma_5$ | $2\pi/3R$ | -2.176984 | -2.348305 | 0.171321 |
| $^3\Gamma_2$ | π/R | -2.261026 | -2.498603 | 0.237577 |
| $^3\Gamma_3$ | 0 | -2.375355 | -2.443789 | 0.068434 |
| $^6\Gamma_5$ | $2\pi/3R$ | -2.410685 | -2.467338 | 0.056653 |
| $^5\Gamma_1$ | π/R | -2.560345 | -2.646089 | 0.085744 |
| $^1\Gamma_6$ | $\pi/3R$ | -2.560345 | -2.672706 | 0.112361 |
| $^3\Gamma_6$ | $\pi/3R$ | -2.710005 | -2.727964 | 0.017959 |
| $^3\Gamma_5$ | $2\pi/3R$ | -2.794046 | -2.908720 | 0.114674 |
| $^1\Gamma_4$ | 0 | -2.859664 | -2.894415 | 0.034751 |
| $^3\Gamma_3$ | 0 | -3.044654 | -2.962705 | 0.081949 |
| $^1\Gamma_1$ | π/R | -3.249610 | -3.249610 | 0.0 |
| (C) Internuclear separation = 3 a.u.; $J' = -0.043779$ | | | | |
| $^7\Gamma_3$ | 0 | -2.769443 | -2.769443 | 0.0 |
| $^6\Gamma_6$ | $\pi/3R$ | -2.813222 | -2.819902 | 0.006680 |
| $^1\Gamma_1$ | π/R | -2.830490 | -2.849721 | 0.019231 |
| $^3\Gamma_5$ | $2\pi/3R$ | -2.832416 | -2.847514 | 0.015098 |
| $^3\Gamma_2$ | π/R | -2.857001 | -2.876192 | 0.019191 |
| $^3\Gamma_3$ | 0 | -2.890445 | -2.897811 | 0.007366 |
| $^6\Gamma_5$ | $2\pi/3R$ | -2.900779 | -2.904147 | 0.003368 |
| $^5\Gamma_1$ | π/R | -2.944558 | -2.949889 | 0.005331 |
| $^1\Gamma_6$ | $\pi/3R$ | -2.944558 | -2.955257 | 0.010699 |
| $^3\Gamma_6$ | $\pi/3R$ | -2.988337 | -2.985551 | 0.002786 |
| $^3\Gamma_5$ | $2\pi/3R$ | -3.012021 | -3.024418 | 0.011497 |
| $^1\Gamma_4$ | 0 | -3.032116 | -3.032938 | 0.000822 |
| $^3\Gamma_3$ | 0 | -3.086230 | -3.069471 | 0.016759 |
| $^1\Gamma_1$ | π/R | -3.146184 | -3.146184 | 0.0 |
| (D) Internuclear separation = 5 a.u.; $J' = -0.002286$ | | | | |
| $^7\Gamma_3$ | 0 | -2.988816 | -2.988816 | 0.0 |
| $^6\Gamma_6$ | $\pi/3R$ | -2.991102 | -2.991091 | 0.000011 |
| $^1\Gamma_1$ | π/R | -2.992004 | -2.992026 | 0.000022 |
| $^3\Gamma_5$ | $2\pi/3R$ | -2.992104 | -2.992120 | 0.000016 |
| $^3\Gamma_2$ | π/R | -2.993388 | -2.993403 | 0.000015 |
| $^3\Gamma_3$ | 0 | -2.995134 | -2.995125 | 0.000009 |
| $^6\Gamma_5$ | $2\pi/3R$ | -2.995673 | -2.995641 | 0.000032 |
| $^5\Gamma_1$ | π/R | -2.997959 | -2.997903 | 0.000056 |
| $^1\Gamma_6$ | $\pi/3R$ | -2.997959 | -2.997952 | 0.000007 |
| $^3\Gamma_6$ | $\pi/3R$ | -3.000244 | -3.000201 | 0.000043 |
| $^3\Gamma_5$ | $2\pi/3R$ | -3.001528 | -3.001511 | 0.000017 |
| $^1\Gamma_4$ | 0 | -3.002530 | -3.002526 | 0.000004 |
| $^3\Gamma_3$ | 0 | -3.005355 | -3.005315 | 0.000040 |
| $^1\Gamma_1$ | π/R | -3.008485 | -3.008485 | 0.0 |

²² W. Marshall, Proc. Roy. Soc. (London) A232, 48 (1955).

²³ P. W. Anderson, Phys. Rev. 86, 694 (1952).

²⁴ R. Kubo, Phys. Rev. 87, 568 (1952).

²⁵ T. Oguchi, Phys. Rev. 117, 117 (1960).

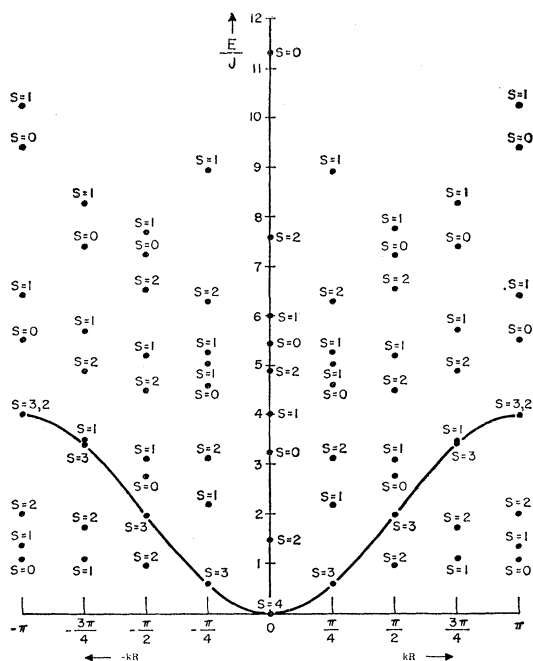


FIG. 7. Energy as a function of kR for eigenvalues of the Heisenberg exchange operator representing an eight-atom linear chain with periodic boundary conditions.

function. This is even more striking when one considers the results of a similar calculation for an eight-atom chain, shown in Fig. 7. The coefficient $2JS$ has a magnitude which is too small, approximately by a factor of three; this is not too surprising since Anderson points out that his method is most accurate in the limit of large S .

It is interesting to consider a plot of the inverse of the energy difference between the ground state and the first excited state ($J/\Delta E$) as a function of N , where N is the number of atoms in the chain. Such a plot was given by Orbach²⁰ for chains containing as many as ten atoms. The energy difference was found to be nearly proportional to $1/N$. In terms of Figs. 6 and 7, the energy of the

antiferromagnetic spin-wave states appears to be approaching a more sine-like dependence for large N . Orbach interpreted this linear dependence between ΔE and $1/N$ in a different manner. He reasoned that since ΔE was proportional to $\sin kR$, and k was given by $2\pi q/NR$ (q an integer), ΔE should be proportional to $1/N$ for small k . However, from Figs. 6 and 7, ΔE does not correspond to an energy difference between the ground state and the excited state with smallest k , as he assumes. Plotting the correct energy differences as a function of $1/N$ produces a scatter of points, which might be expected for short chains, since replacing $\sin kR$ by kR is certainly not justified for kR values of $\pi/4$, $\pi/3$, etc.

One curious aspect of Figs. 6 and 7 concerns the alternation of the translational symmetry of the antiferromagnetic ground-state spin-wave function as a function of N . For chains of 2 (not shown) and 6 atoms, these functions transform like $k=\pi/R$ under translation. For chains of 4 (not shown) and 8 atoms, they transform like $k=0$. Presumably, this alternation continues with longer chains. It appears to have no obvious physical significance.

ACKNOWLEDGMENTS

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