

Constructing the Spin Hamiltonian for an N -Electron System*

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The problem of constructing an effective spin Hamiltonian that will have the same eigenvalues as a physical system of N electrons is considered. It is assumed that the eigenvalues are obtained by some other means and the exchange integrals are treated as parameters to be adjusted so as to fit them. It is found that there are definite restrictions on carrying out this scheme with a vector model Hamiltonian, although it can always be done with a spin Hamiltonian containing higher order products of spin functions. These restrictions should be kept in mind when using perturbation theory or some other method to improve the definition of exchange integrals.

I. INTRODUCTION

THE first real progress in explaining the magnetic properties of physical systems (excluding diamagnetism) was made by considering the systems as assemblages of small elementary magnets interacting through the classical magnetic dipole interaction.¹ Although increasing knowledge about the atomic structure of matter led to the realization that this picture could not be quantitatively correct, its qualitative success was such that scientists were unwilling to give it up entirely. For this reason most of the theoretical work on the nature of magnetism has been devoted to deriving a quantum mechanical interaction between the atomic moments which would be similar in form to the classical interaction, but with a different coupling constant.

Heisenberg² pointed out that the exchange interaction between the valence electrons of the atoms in a diatomic molecule which is due to the Pauli principle gives rise to an effective interaction between electron spins. By considering the interaction between pairs of atoms, he derived the effective spin Hamiltonian which gives the energy corresponding to each spin state of an N -electron system,

$$H_{\text{eff}} = C_0 - 2 \sum_{a < b} J_{ab} \mathbf{S}_a \cdot \mathbf{S}_b, \quad (1)$$

where \mathbf{S}_a is the spin operator for electron a , J_{ab} is the exchange integral, and C_0 is a constant usually taken to be zero. This Hamiltonian is the basis for the vector model for magnetic systems. Dirac³ derived it without the assumption of pairwise interactions by considering the effect of symmetry on N -electron wave functions whose spatial part is a product of one-electron orbitals.

The derivations of Heisenberg and Dirac are open

to criticism on several counts.⁴ It has been pointed out that if the one-electron orbitals in Dirac's theory are orthogonal, then the exchange integrals are always positive and the ferromagnetic state always has the lowest energy; while if they are not orthogonal, then the eigenvalues of H_{eff} do not have any meaning. It may be argued on intuitive grounds for systems in which the concentration of paramagnetic ions is low, that the assumption of pairwise interactions in Heisenberg's theory and the nonorthogonality problem in Dirac's theory should not lead to serious difficulties. Even for such a case, however, there is still the objection that the definition of the exchange integral is based on the Heitler-London⁵ theory for the eigenvalues and eigenfunctions of diatomic molecules which is not the most accurate theory available today.

There have been several attempts to use perturbation theory or configuration interactions to obtain more meaningful definitions for the exchange integrals occurring in the effective Hamiltonian either for an isolated pair of atoms⁶ or for the total system.⁷ It has been shown by Löwdin⁸ that the results of any calculation of the eigenvalues and eigenfunctions for a pair of interacting hydrogen-like atoms can be represented by an effective Hamiltonian of the Heisenberg form where the exchange integral is defined in terms of the calculated eigenvalues. The purpose of this paper is to investigate the possibility of defining an effective Hamiltonian for the total system from this same point of view, i.e., we assume that the eigenvalues and eigenfunctions are known beforehand and try to define the exchange integrals in such a way as to match them. This is obviously not a practical approach for treating a large system, but it yields considerable insight into the nature of the vector model. In particular, it is found that there are very definite restrictions on carrying out this scheme even in principle, and these restrictions should be kept in mind when treating the problem by any other method.

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¹ J. A. Ewing, Proc. Roy. Soc. (London) **48**, 342 (1890); R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., New York, 1951), Chap. 10.

² W. Heisenberg, Z. Physik **49**, 619 (1928).

³ P. A. M. Dirac, *The Principles of Quantum Mechanics* (Oxford University Press, New York, 1958), 4th ed., Chap. 9.

⁴ J. C. Slater, Revs. Modern Phys. **25**, 199 (1953).

⁵ W. Heitler and F. London, Z. Physik **44**, 455 (1927).

⁶ R. K. Nesbet, Ann. Phys. (New York) **4**, 87 (1958).

⁷ L. F. Mattheiss, Phys. Rev. **123**, 1219 (1961); D. I. Paul, *ibid.* **118**, 92 (1960); T. Arai, *ibid.* **126**, 471 (1962).

⁸ P. O. Löwdin, Revs. Modern Phys. **34**, 80 (1962).

II. THE PHYSICAL SYSTEM

Let us consider a set of N electrons interacting with each other and with a set of fixed ion cores. Due to the indistinguishability of electrons the Hamiltonian for the system, H , will be invariant under permutation of the electronic coordinates. The magnetic spin interaction is considered negligible in comparison with the Coulomb interaction so that H does not contain the spin operators of the individual electrons explicitly. The N -electron spin operators, S^2 [having eigenvalues $l(l+1)\hbar^2$] and S_z (having eigenvalues $m\hbar$), will commute with H and yield good quantum numbers for the system.

We will denote the energy eigenvalues of the system by $E_k^{l,m}$ and the corresponding eigenfunctions by $\Psi_k^{l,m}$, where the subscript distinguishes between the infinite number of states that will ordinarily exist for each l and m . For convenience we assume that the system is isotropic so that the $E_k^{l,m}$ will have the same value, E_k^l , for every m . We also assume that the set of electrons under consideration does not contain subsets which are constrained by Hund's rule or some other mechanism to preserve a given relative spin orientation. The following work could be extended to cover more general cases if necessary, but these assumptions are consistent with the ones usually made in discussions of the vector model.⁹

It is well known¹⁰ that the $\Psi_k^{l,m}$ can be written in the form

$$\Psi_k^{l,m} = (n_l)^{-\frac{1}{2}} \sum_{i=1}^{n_l} \Phi_{k,i}^l \Theta_i^{l,m}, \quad (2)$$

where $\Phi_{k,i}^l$ are an orthonormal set of spatial eigenfunctions of H , and the $\Theta_i^{l,m}$ are an orthonormal set of spin eigenfunctions of S^2 and S_z . The set of spin eigenfunctions¹¹ that correspond to a given l and m contains n_l functions, where

$$n_l = (2l+1) \frac{N!}{(\frac{1}{2}N+l+1)!(\frac{1}{2}N-l)!}, \quad (3)$$

and these functions form the basis for a unitary irreducible representation of the permutation group. Thus,

$$P^\sigma \Theta_i^{l,m} = \sum_j \Gamma_l(P)_{ji} \Theta_j^{l,m}, \quad (4)$$

where P^σ is a permutation operator on spin coordinates, and $\Gamma_l(P)_{ji}$ is the ji element of the representative of P in the irreducible representation Γ_l . The antisymmetry of $\Psi_k^{l,m}$ is insured by requiring that the $\Phi_{k,i}^l$ transform according to the associated representation of Γ_l . That

is, to say,

$$P^r \Phi_{k,i}^l = \sum_j \Gamma_l'(P)_{ji} \Phi_{k,j}^l, \quad (5)$$

where P^r is a permutation operator on spatial coordinates and Γ_l' is defined by

$$\Gamma_l'(P) = (-1)^P \Gamma_l(P)^*.$$

Using the orthogonality relation

$$\sum_P \Gamma_l(P)_{ij}^* \Gamma_l'(P)_{qr} = (N!/n_l) \delta_{il} \delta_{iq} \delta_{jr}, \quad (6)$$

the eigenfunctions can be written in the following form¹²:

$$\Psi_k^{l,m} = \delta_{il} \delta_{ij} (n_l/N!)^{\frac{1}{2}} \mathcal{A} \Phi_{k,i}^l \Theta_j^{l',m}, \quad (7)$$

where \mathcal{A} is the antisymmetrizing operator

$$\mathcal{A} = (N!)^{-\frac{1}{2}} \sum_P (-1)^P P^r P^\sigma.$$

In the following sections we will consider various methods for constructing a spin operator, H_{eff} , which has the same eigenvalues as the Hamiltonian, H . The domain of H is an infinite dimensional Hilbert space, but the domain of H_{eff} is the space of N -electron spin functions which has the dimension 2^N . This leads to the difficulty that H can have an infinite number of eigenvalues corresponding to a given l and m , whereas H_{eff} can have only n_l [cf. Eq. (3)]. The concept of an effective spin Hamiltonian will not be useful unless there is an excuse for ignoring the eigenvalues of H that cannot be put into correspondence with the finite number of eigenvalues of H_{eff} . A possible excuse for this can be found by considering the application of perturbation theory to the system.

The Hamiltonian, H , can be written as the sum of an independent electron Hamiltonian, H_0 , plus a perturbation, λV , which contains the interactions. The unperturbed eigenfunctions will be antisymmetrized products of orthogonal spin orbitals which are formed by multiplying orthogonal one-electron orbitals with one-electron spin functions. Since a large number of determinants can be formed from the same set of orbitals by choosing different spin functions, the unperturbed eigenvalues will be highly degenerate. In particular, the ground state of H_0 will have a 2^N -fold degeneracy if the one-electron orbitals that are used to form the wave functions are all different and are not members of a degenerate set. This degeneracy can be removed to first order by adapting the ground-state wave functions to the perturbation, λV , in the standard way. This process corresponds to Dirac's derivation of the vector model. As the perturbation series is continued, the excited states mix with the ground state in a complicated way.¹³

If the physical system is such that its eigenvalue spectrum is adequately described by the perturbation

⁹ J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932), Chap. 12.

¹⁰ H. A. Kramers, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1957); M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, *Tables of Molecular Integrals* (Maruzen Company, Tokyo, 1955).

¹¹ G. F. Koster, Massachusetts Institute of Technology Technical Report No. 8, 1956 (unpublished).

¹² D. R. Johnston, *Reports on Progress in Physics* (The Physical Society, London, 1960), Vol. 23, p. 66.

¹³ An example of this appears in L. F. Mattheiss, *Phys. Rev.* **123**, 1209 (1961).

theory result corresponding to a very small λ , the Dirac vector model should give correct results. If the spectrum is like the case where λ is intermediate in size, the Dirac theory will give the wrong splitting, but the 2^N states arising from the perturbation of the ground state should lie much lower than the other states and control the magnetic properties of the system. In the following sections we will consider just these low-lying eigenvalues of H . Of course, if the physical system corresponds to the case where λ is large, no theory based on an effective spin Hamiltonian will be useful.

III. THE EFFECTIVE HAMILTONIAN

We will first investigate the possibility of constructing an effective Hamiltonian whose form is the same as the Heisenberg Hamiltonian [Eq. (1)] and whose eigenvalues are the same as the low-lying eigenvalues of H which we assume are known. It is convenient to use the Dirac identity,¹⁴

$$P_{ab}^\sigma = \frac{1}{2}[1 + (4/\hbar^2)\mathbf{S}_a \cdot \mathbf{S}_b], \quad (8)$$

to rewrite H_{eff} in the form

$$H_{\text{eff}} = C - \hbar^2 \sum_{a < b} J_{ab} P_{ab}^\sigma, \quad (9)$$

where P_{ab}^σ is the permutation operator which interchanges the a and b coordinates in the spin functions. The constant C is given by

$$C = C_0 + \frac{1}{4}N(N-1)\hbar^2\langle J \rangle,$$

where C_0 appears in Eq. (1) and $\langle J \rangle$ is the average over all pairs of the J_{ab} :

$$\langle J \rangle = [2/N(N-1)] \sum_{a < b} J_{ab}. \quad (10)$$

Since the domain of H_{eff} is the space of N -electron spin functions, its eigenvalues can be found by diagonalizing the $2^N \times 2^N$ matrix, \mathbf{H} , whose elements are the matrix elements of H_{eff} between orthonormal spin functions. From the fact that S^2 and S_z commute with H_{eff} it follows that \mathbf{H} can be reduced to a block diagonal form by choosing the orthonormal spin functions to be spin eigenfunctions, $\Theta_i^{l,m}$. The elements of \mathbf{H} on this basis are

$$\begin{aligned} \langle \Theta_i^{l,m} | H_{\text{eff}} | \Theta_j^{l',m'} \rangle \\ = \delta_{ll'} \delta_{mm'} [C \delta_{ij} - \hbar^2 \sum_{a < b} J_{ab} \Gamma_l(P_{ab})_{ij}], \end{aligned} \quad (11)$$

where the $\Gamma_l(P_{ab})_{ij}$ are elements of the irreducible representation of the permutation group that appear in Eq. (4). We see that the block matrices do not depend on m , which is in keeping with the description of an isotropic system.

Suppose we keep the elements $\Gamma_l(P_{ab})_{ij}$ fixed and set \mathbf{H} equal to a diagonal matrix, \mathbf{E} , which has the true eigenvalues of H arranged along the diagonal in the proper order as to the l value of their associated eigenfunctions. This yields a set of linear equations for the

$\frac{1}{2}N(N-1)+1$ unknowns, J_{ab} and C , which can be written in the form $\mathbf{H} = \mathbf{E}$. The solvability of these equations determines the possibility of choosing the J_{ab} and C in such a way as to force H_{eff} to have the same eigenvalues as H .

It should be remarked that the above scheme would also force H_{eff} to have as its eigenvectors the $\Theta_i^{l,m}$ which correspond to the chosen irreducible representations appearing in \mathbf{H} . It will be seen in the following, however, that the freedom to make unitary transformations of the spin eigenfunctions corresponding to a given l and m among themselves does not effect any of the basic arguments.

An investigation of the equations, $\mathbf{H} = \mathbf{E}$, shows that one cannot construct a vector model that would match any possible set of eigenvalues for the physical system under consideration if the number of electrons exceeds three. The reason for this is simply that there are more equations than there are unknowns, but the detailed restrictions can be more readily seen by the following considerations.

Let us denote the submatrix of \mathbf{H} that corresponds to a given l as \mathbf{H}^l , and the corresponding submatrix of \mathbf{E} by \mathbf{E}^l . The dimension of these matrices is n_l , and there is no need to specify the value of m that they correspond to since they are the same for any m . If we divide the trace of \mathbf{E}^l by n_l we get the average energy, $\langle E^l \rangle$. By evaluating the trace of \mathbf{H}^l Van Vleck¹⁵ has shown that

$$\langle E^l \rangle = C - [\frac{1}{4}N^2 - N + l(l+1)]\hbar^2\langle J \rangle, \quad (12)$$

where $\langle J \rangle$ is the average defined in Eq. (10). This result shows that the average energies for only two values of l can be matched exactly since there are only two adjustable parameters, C and $\langle J \rangle$. If the number of electrons exceeds three they can, of course, couple to give more than two values for l . The argument in this paragraph does not depend on the choice of spin functions since the only quantities that occur are matrix traces which are not changed by unitary transformations of the matrices.

Another way to see these restrictions is to count the number of independent equations that occur in $\mathbf{H} = \mathbf{E}$ under the assumption that the spin functions are real. The unitary irreducible representations, $\Gamma_l(P_{ab})$, become orthogonal for this case; and, since $P_{ab}^2 = 1$, they are also symmetric. There will thus be $\frac{1}{2}n_l(n_l+1)$ different equations in the set $\mathbf{H}^l = \mathbf{E}^l$ for each l . Using Eq. (3) it can be seen that a number of equations equal to the number of unknowns is obtained if only the states corresponding to $l = \frac{1}{2}N$ and $l = \frac{1}{2}N - 1$ are considered. This result shows that the energies and eigenfunctions for the ferromagnetic ground state and the spin wave states can be fitted exactly, but then all the parameters in H_{eff} are fixed so that the energies of the

¹⁴ Reference 3, page 222.

¹⁵ J. H. Van Vleck, Phys. Rev. **45**, 405 (1934).

other states, which occur if the number of electrons exceeds three, cannot be adjusted.

An effective Hamiltonian whose eigenvalues are exactly the same as the low-lying eigenvalues of H can be constructed if we give up the requirement that it have the same form as the Heisenberg Hamiltonian [Eq. (1) or (9)]. This operator, which we call $\mathfrak{H}_{\text{eff}}$, is obtained in the following way.

According to the discussion in Sec. II we will consider n_l states for each l (again we ignore m since the system is isotropic), and according to Eq. (2) there are n_l space functions associated with each $\Psi_k^{l,m}$. We will number the states by $k=1, 2, \dots, n_l$ and define a spatial function, F , by

$$F = \sum_{l,k} (n_l/N!) \Phi_{k;l}^l. \quad (13)$$

Using Eq. (7) it can be shown that

$$\Psi_k^{l,m} = \alpha F \Theta_k^{l,m}. \quad (14)$$

This expression has the same form as the expression for the space spin eigenfunctions that are obtained from Dirac's theory, although it refers to exact eigenfunctions and F is not a product of one-electron orbitals. Thus, we can insert F into Dirac's¹⁶ equation for the effective Hamiltonian,

$$\mathfrak{H}_{\text{eff}} = \sum_P \int F^* H P^r F d\mathbf{v} P^\sigma,$$

and obtain

$$\mathfrak{H}_{\text{eff}} = \sum_P \sum_{l,k} (n_l/N!) E_k \Gamma_l(P)_{kk}^* P^\sigma, \quad (15)$$

where we have made use of Eqs. (5) and (6) and the orthogonality of eigenfunctions that correspond to different eigenvalues. From the orthogonality relation given in Eq. (6) it can be shown that the projection operator,

$$\rho_k^l = (n_l/N!) \sum_P \Gamma_l(P)_{kk}^* P^\sigma,$$

will project out a spin function that transforms according to the k th row of the irreducible representation Γ_l .¹¹ Rewriting Eq. (15) in terms of these projection operators shows that this form for $\mathfrak{H}_{\text{eff}}$ corresponds to the spectral representation of an operator whose eigenvalues are E_k^l and whose eigenfunctions are $\Theta_k^{l,m}$.

The $\mathfrak{H}_{\text{eff}}$ of Eq. (15) differs from the H_{eff} of Eq. (9) in that $\mathfrak{H}_{\text{eff}}$ contains all permutation operators whereas H_{eff} contains only the interchange operators. The Dirac identity can be used to write $\mathfrak{H}_{\text{eff}}$ in terms of spin operators because any permutation can be expressed as a product of interchanges, but there will be many terms containing complicated multiple products of the spin operators.

It is interesting to note that the construction of both $\mathfrak{H}_{\text{eff}}$ and H_{eff} yields the same effective Hamiltonian for the case of two electrons. This Hamiltonian has the Heisenberg form and is identical with the one obtained by Löwdin.⁸ Löwdin's derivation actually includes concepts related to both of the constructions described in this section.

IV. DISCUSSION

Although a general distribution of eigenvalues cannot be matched with a spin Hamiltonian of the Heisenberg form by adjusting the parameters, it is certainly conceivable that the distribution obtained for a specific system by perturbation theory or some other method could be matched in that way. Such a result could not be assumed without a detailed investigation, however. It is interesting for ferromagnetic problems that the eigenvalues corresponding to total spins of $\frac{1}{2}N$ and $\frac{1}{2}N-1$ can always be matched by a vector model. If it is assumed that when these eigenvalues are matched exactly the neighboring ones are approximately correct, then a good theory for low temperatures could be constructed on the basis of the vector model at least in principle. The result that all eigenvalues can be matched with a spin Hamiltonian that contains high-order spin products does not seem particularly useful except as a basis for other approximations.

We have said very little about the spin eigenfunctions of the system. It can be seen from Eq. (2) that all spin eigenfunctions corresponding to a given l and m enter into the expression for the exact space-spin eigenfunction in an equivalent way so that the choice of spin eigenfunctions must be made on physical rather than mathematical grounds. They may be chosen to emphasize the crystallographic symmetry of the system if such exists. This could be done within the framework of the vector model, for example, by associating electron a with the lattice site specified by the vector R_a and requiring that $J_{ab} = J_{cd}$, if $R_a - R_b \leftrightarrow R_c - R_d$. (By the symbol, \leftrightarrow , we mean that the vectors are either equal or equivalent under operations of the crystallographic group.) Such a procedure would force H_{eff} to have eigenfunctions similar to the ones obtained from the Dirac theory, and might be convenient in applying group theory to the problem.

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¹⁶ Reference 3, page 218.