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The Relation Between Vector and Bond Eigenfunction Methods for Spin Degeneracy

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A method previously developed for the calculation of matrix components for problems in which spin degeneracy only is important is shown to be equivalent to an operator method derivable from the vector approach of Dirac. Complete rules for the simple construction of matrices for all possible cases which can arise under these conditions of spin degeneracy are given. An especially simple way of

determining secular equations for states of the identical representation is described, and the method is applied to the calculation of the energy of an infinite linear extension of sodium atoms. An inspection method of resolving a crossed six bond eigenfunction in terms of the uncrossed set is given.

INTRODUCTION

RECENTLY Van Vleck² and Serber³ have extended the vector method of Dirac,⁴ applying it to the calculation of matrix coefficients of exchange integrals. Van Vleck was chiefly concerned in demonstrating the value of the vector approach in single-atom systems, but indicated its utility in molecular problems. A more generally useful approach to the latter, however, is that employing bond eigenfunctions.⁵ This paper considers relations between the vector and bond eigenfunction methods for configurations of orbits in which spin degeneracy only is important. In addition certain improvements in the mechanics of calculation with bond eigenfunctions are described and applied to a consideration of the energy of an infinite linear extension of sodium atoms.

THE VECTOR AND BOND EIGENFUNCTION METHODS

In considering a system of N electrons distributed among an equal number of orbits a, b, \dots in the many centered field of a molecule or group of atoms one proceeds as follows. A complete set of antisymmetric eigenfunctions is constructed for the configuration in a manner

elaborated by Slater.⁶ One of these can be written

$$\varphi_i = \frac{1}{(N!)^{\frac{1}{2}}} \sum_P (-1)^P P(a\alpha(1), b\beta(2), \dots), \quad (1)$$

in which $a\alpha(1)$ expresses the orbit-spin eigenfunction occupied by electron 1, $b\beta(1)$ that of electron 2, and so on. The sum of the P 's permutes the electrons in $N!$ ways among the orbit-spin combination orbitals, and $(-1)^P$ is positive for even, negative for odd permutations. There are 2^N eigenfunctions of the type φ_i obtained by taking all possible combinations of the two spin eigenfunctions α or β for each electron. The φ 's formed in this manner are all independent, and though in general not orthogonal, they form a convenient set in terms of which we suppose any state arising when perturbations are introduced can be expanded. Because of the method of formation, the φ 's are already eigenfunctions of the operator S_z for spin momentum quantized along an optional z axis. A convenient way of expressing all φ 's with a particular eigenvalue for S_z is the following:

$$\begin{aligned} \varphi_r &= \frac{Q_r}{(N!)^{\frac{1}{2}}} \sum_P (-1)^P P(a\alpha(1), b\beta(2), \dots) \\ &= Q_r \varphi_I. \end{aligned} \quad (2)$$

Here φ_I is a particular one of the antisymmetric eigenfunctions with the required eigenvalue of S_z . The operator Q_r permutes the spins of φ_I with respect to the orbits in such a way as to give rise to a new function φ_r .

⁶ Slater, *Phys. Rev.* **34**, 1293 (1929).

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² Van Vleck, *Phys. Rev.* **45**, 405 (1934).

³ Serber, *Phys. Rev.* **45**, 461 (1934).

⁴ Dirac, *Proc. Roy. Soc. A123*, 714 (1929).

⁵ (a) Slater, *Phys. Rev.* **38**, 1109 (1931);

(b) Kimball and Eyring, *J. Am. Chem. Soc.* **54**, 3876 (1932);

(c) Eyring and Kimball, *J. Chem. Phys.* **1**, 239 (1933);

(d) Pauling *J. Chem. Phys.* **1**, 280 (1933).

Frequently it is useful to consider another set of independent functions instead of the φ 's. These will be linear combinations of φ 's which have the same eigenvalue of S_z :

$$\psi_r = \sum_i c_{ri} \varphi_i = \sum_i c_{ri} Q_i \varphi_1, \quad (3)$$

where c_{ri} is the coefficient of φ_i in the expansion of ψ_r .

If one now applies the perturbations of electron interactions, H , new states arise which can be expanded in terms of the set of ψ 's. Perturbation theory then shows that the matrix of $H-W$, for the set of ψ 's can be used as a secular determinant whose solutions for W , the energy, when equated to zero will be the required energy levels of the perturbed system. The only matrix components which will be different from zero are those between ψ 's with the same eigenvalues for S_z . Hence we can write nonvanishing components as follows:

$$\int \psi_r^* (H-W) \psi_i d\tau = \int \sum_u c_{ru}^* Q_u \varphi_1^* \times (H-W) \sum_v c_{iv} Q_v \varphi_1 d\tau. \quad (4)$$

Consider the integral

$$Q_{ri, i} = \int \left(\sum_u c_{ru} Q_u \varphi_1^* \right) Q_i \left(\sum_v c_{iv} Q_v \varphi_1 \right) d\tau. \quad (5)$$

The integrals of the type $\int (Q_u \varphi_1^*) Q_i (Q_v \varphi_1) d\tau$ are unity if $Q_u \varphi = Q_i \varphi$, otherwise they are zero, providing we neglect non-orthogonality of the orbitals as we shall do here.

The integral, $Q_{ri, i}$, defined in (5) is the coefficient of an expression $(K_{Q_i} - W \Delta_{Q_i})$ in the expansion of (4), where K_{Q_i} is an exchange integral between spin-orbit products which differ in permutation of their spins by the permutation Q_i . Δ_{Q_i} is the corresponding integral with unity instead of H between the spin-orbit products. Because we neglect non-orthogonality of our orbitals $\Delta_{Q_i} = 0$ unless $i=1$, i.e., unless Q_i is the identical permutation. The particular identical permutation Q_1 gives rise to the quantity $(J-W)$, where J is the familiar sum of coulombic integrals. The usual designation of exchange integrals, however, is with respect to a permutation, P_i , of the orbits in relation to the spins,

such that for the corresponding integrals we have $P_{ri, i} = \pm Q_{ri, i}$, the positive or negative sign occurring when the permutation is even or odd, respectively. We have, therefore, the expansion of (4):

$$\int \psi_r (H-W) \psi_i d\tau = (J-W) P_{ri, i} + \sum_{P_i} K_{P_i} P_{ri, i} \quad (6)$$

The expression (6) is similar to Eq. (14) of Serber.³ We can also write (6) in the form

$$\int \psi_r (H-W) \psi_i d\tau = (J-W) I_{ri} + \sum_{i < j} K_{ij} P_{ri, ij}, \quad (7)$$

where the subscript ij indicates an exchange between orbits i and j . The quantities I_{ri} and $P_{ri, ij}$ are the matrix components of unity and P_{ij} between the states ψ_r and ψ_i . K_{ij} is the exchange integral between the orbitals i and j .

Bond eigenfunctions have the important property of being eigenfunctions of S^2 , the operator for the square of the total spin angular momentum, as well as for S_z . They are formed from the antisymmetric functions (φ 's) which are eigenfunctions with a particular eigenvalue for S_z .

$$\psi_{a-b \dots c-d \dots} = \sum_u \delta_{ab} \delta_{cd} \dots \varphi_u,$$

where δ_{ij} is $+1$ for any φ_u which has α on the orbit i and β on j ; it is -1 when β is on i and α on j ; or it is 0 when both i and j are associated with the same spins. Convenient methods of determining an independent set of bond eigenfunctions have been developed.⁷

In order to work directly with these ψ 's which we call bond eigenfunctions it is necessary to have an operator for P_{ij} . Dirac⁴ has shown that (in $\hbar/2\pi$ units)

$$Q_{ij} = -P_{ij} = \frac{1}{2}(1 + 4s_i \cdot s_j). \quad (8)$$

Since $2s_i \cdot s_j = (s_i + s_j)^2 - (s_i^2 + s_j^2)$

and $s_i + s_j = S_{ij}$, $s_i^2 = s_j^2 = \frac{1}{2}(\frac{1}{2} + 1) = \frac{3}{4}$,

we have $2s_i \cdot s_j = S_{ij}^2 - \frac{3}{2}$.

Here s_i and s_j are the operators for spin vectors

⁷ Rumer, Nachr. Ges. Wiss. Gottingen, M. P. Kl., p. 337 (1932).

of electrons i and j , and S_{ij}^2 is the operator for total spin angular momentum associated with the two electrons. As a result of substitution in (8) we find:

$$P_{ij} = (1 - S_{ij}^2). \quad (9)$$

Methods have been developed (reference 5c) for operating with S^2 on any antisymmetric function φ_u . These are readily adapted to S_{ij}^2 in the following way. As in the case of S^2 ,

$$S_{ij}^2 = (S_{z, ij} - iS_{y, ij})(S_{z, ij} + iS_{y, ij}) + S_{z, ij} + S_{z, ij}^2. \quad (10)$$

Here all operations are to be carried out on the electrons i and j only. The coefficient $\hbar/2\pi$ is omitted on $S_{z, ij}$, since we are dealing in $\hbar/2\pi$ units. The i 's multiplying $S_{y, ij}$ are, of course, the square root of -1 .

The effect of the operation $(1 - S_{ij}^2)$ on any φ is to interchange the spins of electrons i and j and multiply the result by -1 , as is easily verified. Consequently, the effect of P_{ij} in the integral (5) is to pick out from ψ_r and ψ_t the number of times that φ 's of the two differ only by a single exchange of spins on the electrons i and j . The negative sign corresponds to the fact that single-exchange integrals occur with signs opposite to that of the coulombic one. These results, of course, were to be expected, but the considerations just stated constitute a simple verification of the vector method of determining matrix coefficients.

One could, of course, proceed to calculate coefficients of exchange integrals occurring in matrix components between bond eigenfunctions by the laborious process expressed in (5) and (9). However, complete and simpler rules have been found already from entirely equivalent reasoning. The reader is referred to previous papers^{5c, 8, 9} where methods have been given for determining the coefficients from "sequences," each of which is related to the two bond eigenfunctions of a particular matrix component. The vector method, however, does lead to the interesting comparison with the sequences which follows.

The vector form of the operator P_{ij} suggests rewriting (7) as

$$\int \psi_r(H - W)\psi_t d\tau = (J - W - \frac{1}{2} \sum_{i < j} K_{ij}) I_{rt} - 2 \sum_{i < j} K_{ij}(s_i \cdot s_j)_{rt}. \quad (11)$$

We now write the sequence in an equivalent although formally somewhat different form than was used in previous work. Some simple conventions permit us to write the matrix component between two bond eigenfunctions of any multiplicity. Unless the two eigenfunctions are of the same multiplicity, i.e., have the same number of bonds the matrix component is zero. Where they do have the same number of bonds we classify the orbitals in the following way. If two orbitals are bound together in one eigenfunction we put them into two different groups. Now if in the second eigenfunction either or both of these orbitals are bound to new orbitals the new orbitals are assigned to the group not containing the bond partner. This process is continued until the assignment of orbitals starts repeating itself or until a new orbital found is not bound to a partner. If the first case (repetition) arises the two groups are said to form a cycle and in the second case they are said to form a chain. After completing a cycle or chain the process is then repeated with some orbital not yet appearing until all orbitals in the two bonds are classified as cycles or chains. Orbitals not bound in either bond eigenfunction are counted as chains of one link. Any such matrix component can then be written as

$$(-1)^{p/2m} [\delta_{u0} \{ J - W - 1/2 \sum_{i < j} K_{ij} + \sum_{m \text{ cycles}} 3/2(K_{ij} - K_{ij}') + \sum_{i \text{ odd chains}} 3/2(K_{ij} - K_{ij}') + 1/2(K_{ij}'' - K_{ij}''') \} + \delta_{u2} \sum_{u \text{ even chains}} (K_{ij}'' - K_{ij}''')]. \quad (12)$$

The symbol δ_{ui} is, of course, 1 if $u = i$, and 0 if $u \neq i$ where u is the number of even chains. For the unprimed exchange integrals, K_{ij} , the i orbital is to be taken from one group in a particular cycle or chain and j is to be taken from the other group. In K_{ij}' both orbital i and j are

⁸ Eyring, Frost and Turkevich, J. Chem. Phys. 1, 777 (1933).

⁹ Stearn, Lindsley and Eyring, J. Chem. Phys. 2, 410 (1934).

to be from the same group. For K_{ij}'' the i and j must be from different chains and if one is from the first group of a chain the other must be from the second group. For K_{ij}''' the i and j must be from different chains and either both from first or both from second groups. It is immaterial which group in a cycle or even chain is counted as first or second. For an odd chain an orbit unbound in either eigenfunction belongs to the first group. This determines the second group. Having chosen the second groups we use them to determine p in the following way. The exponent p is the total number of times that second group orbitals are written as the first letter of a bond in either eigenfunction. J is the sum of the coulombic integrals; W is the energy and $\sum_{i < j} K_{ij}$ is the sum of all possible single exchange integrals. The exponent m is the number of cycles. The justification of (12) is readily obtained along the lines developed in reference (5c) for singlet states. Since for singlet states there are no chains (12) then reduces to $(-1)^{p/2m} [M + \sum_{m \text{ cycles}} 3/2(K_{ij} - K_{ij}')] (13)$ where the expression has been simplified by making the substitution $M = Q - W - 1/2 \sum_{i < j} K_{ij}$.

We now give two matrix components as examples of (12). First $\mathcal{J}(ab\ cd\ ef\ gh\ ij\ kl\ mn) \times (H - W)(ac\ bd\ ef\ gh\ ij\ kl\ mn) d\tau = (ad/bc, fg/e, h, m, n, (i/j)(k/l)) = (-1)^{1/2} [il + kj - ik - jl]$. Secondly $\mathcal{J}(ab\ cd\ ef\ gh\ ij\ kl\ mn)(H - W)(ac\ bd\ ef\ gh\ ij\ kl\ mn) d\tau = (ad/bc, i/j, fg/e, h, k, l, m, n) = (-1)^{1/2} [M + 3/2\{ab + ac + bd + cd + ij + ef + eg - ad - bc - fg\} + 1/2\{eh + ek + el + em + en - fk - fl - fm - fh - fn - gk - gl - gm - gn - kl - km - kh - kn - lm - ln - mn - hk - hl - hm - hn\}]$. In the bond eigenfunctions two letters written with no space between are understood to be bound together. A letter separated by spaces from both neighbors is not bonded. In the first case a is bound to b in the first eigenfunction so they are assigned to different groups in the sequence. Now in the second eigenfunction b is bound to d so they are assigned to different groups and finally in the first eigenfunction d is bound to c . Continuing we simply repeat our letters so that we have the cycle ad/bc . Similarly we have the odd chains fg/e and h and m , etc., and finally the two even chains (i/j) and (k/l) . The paren-

theses are used to distinguish even chains from cycles. The application of (12) to our expression (sequence) which classifies our orbitals into cycles and chains leads immediately to the expanded matrix component. In the expanded form two letters written together signify the corresponding exchange integral between the two orbitals.

The simple ratios between the coefficients of W and the coefficients of the various primed and unprimed exchange integrals K_{ij} in (12) could in fact have been deduced from (11). Remembering that S_x , S_z and S_y have the forms $\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}^{1/2}$, $\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}^{1/2}$ and $\begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix}^{1/2}$, respectively, when written as the matrices operating on the¹⁰ eigenfunctions α and β of S_x . We obtain for the corresponding operators S_{xi}, S_{zi}, S_{yi} , S_{xi}, S_{zi}, S_{yi} and their sum $S_i \cdot S_j$ operating on $\alpha_i\beta_j$, $\alpha_i\beta_j$, $\beta_i\alpha_j$, $\beta_i\alpha_j$ the matrices

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}^{1/4}, \quad \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}^{1/4},$$

$$\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}^{1/4}, \quad \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 2 & 0 \\ 0 & 2 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}^{1/4}.$$

Our problem is the comparison of matrix components for twice the last operator with those for the unit matrix for bond eigenfunctions. The subscripts i and j on the spin eigenfunctions α and β are to indicate that these are the spin eigenfunctions associated with the i th and j th orbitals. As we have seen bond eigenfunctions are linear combinations of the antisymmetric configuration eigenfunctions φ_i of Eq. (1) with coefficients of ± 1 or 0. Because of the symmetry of the energy operator H with respect to interchange of electrons we have the well-known equality

$$\int \varphi_u H \varphi_v d\tau = \int (N)! \varphi_u H Q_v (a\alpha(1)b\beta(2)\cdots) d\tau, \quad (13)$$

where $Q_v(a\alpha(1)b\beta(2)\cdots)$ is simply the diagonal element of φ_v . To calculate the coefficient of the

¹⁰ Pauli, Zeits. f. Physik **43**, 601 (1927).

exchange integral ab in (13) we need simply replace H by $-2S_1 \cdot S_2$ with a similar procedure for any other coefficient. To calculate the matrix component of unity H is replaced by 1. Now the matrix components for bond eigenfunctions is clearly a sum of terms like (13). An examination yields the following results for the various cases. The coefficients of K_{ij} for cycles arises from the sum of matrix components of the operator $-2S_i \cdot S_j$ for four types of integrals (13) occurring equally often. We give the spin eigenfunctions associated with the i th and j th orbital for both φ_u and φ_v for the four types (1) $\alpha_i\beta_j, \alpha_i\beta_j$; (2) $\alpha_i\beta_j, -\beta_i\alpha_j$; (3) $-\beta_i\alpha_j, \alpha_i\beta_j$ and (4) $-\beta_i\alpha_j, -\beta_i\alpha_j$. The only contributions to I_{rt} arises from the first and last of the four pairs so that the ratio $-2(S_i \cdot S_j)_{rt} + I_{rt}$ is readily seen to be $3/2$. For K_{ij} in odd chains two types of integrals are different from zero. Here as in all other cases all integrals occurring at all occur equally often, i.e., 2^m times. The spin eigenfunctions for φ_u and φ_v are $\alpha_i\beta_j, -\alpha_i\beta_j$ and $-\beta_i\alpha_j, -\alpha_i\beta_j$ so that again $-2(S_i \cdot S_j)_{rt} + I_{rt} = 3/2$. For K_{ij}' in a cycle four types occur $\alpha_i\alpha_j, \alpha_i\alpha_j; \beta_i\beta_j, \beta_i\beta_j; \alpha_i\beta_j, \beta_i\alpha_j; \beta_i\alpha_j, \alpha_i\beta_j$ giving a ratio $-3/2$. For K_{ij}' in an odd chain there are the two types $\alpha_i\alpha_j, -\alpha_i\alpha_j$ and $-\beta_i\alpha_j, \alpha_i\beta_j$ again giving the ratio $-3/2$. For K_{ij}'' between two odd chains we get $\beta_i\alpha_j, \beta_i\alpha_j$, giving the ratio $1/2$; for K_{ij}''' between two odd chains $\alpha_i\alpha_j, \alpha_i\alpha_j$ giving the ratio $-1/2$. Finally for K_{ij}''' between two even chains we have $-\beta_i\alpha_j, -\alpha_i\beta_j$ giving zero for the matrix component of I_{rt} and 1 for the matrix component of $-2S_i \cdot S_j$; and for K_{ij}'''' we have $-\beta_i\alpha_j, -\alpha_i\beta_j$ giving the values 0 and -1 for the respective matrix components. The coefficients in all cases are of course multiplied by the common factor $(-1)^{r2^m}$.

An additional feature of the present method of calculating matrix coefficients is the ease with which multiple exchange coefficients can be calculated. Any multiple permutation of orbits can always be expressed as the product of single exchanges; for example $P_{ijk} = P_{ki}P_{ij}$. The coefficient of $K_{ijk} - W\Delta_{ijk}$ is most conveniently found by taking advantage of the observation, similar to that used by Heitler,¹¹ that P_{ij} exchanges the orbits i and j in the bond eigenfunction upon

which it operates, changing the sign of the function as well. One can then use $P_{ki} = -1/2 \times (1 + 4s_k \cdot s_i)$ to determine the multiple exchange coefficient after the usual method of sequences. In the second matrix component given consider $P_{abc} = P_{ca}P_{ab}$. Then $P_{ab}(ac\,bd\,ef\,g\,h\,ij\,k\,l\,m\,n) = -(bc\,ad\,ef\,g\,h\,ij\,k\,l\,m\,n)$ determines the sequence with $(ab\,cd\,ef\,g\,h\,ij\,k\,l\,m\,n)$ to be now $-(ac/bd, i/j, fg/e, h, k, l, m, n)$, from which $-1/2(1 + 4s_c \cdot s_a)_{rt}$ is seen to be $2(-1)^{42}$. Hence in this instance the coefficient multiplying $(K_{abc} - W\Delta_{abc})$ is 8. More complex changes in the sequence arise when the exchanges involve interchanges of orbits coming from different cycles or from a cycle and a chain, but the procedure is the same.

SINGLET ENERGY CALCULATIONS FOR SYMMETRICAL SYSTEMS

Most stable chemical systems are in singlet states, and energy levels of this multiplicity assume particular importance therefore. By combining bond eigenfunctions into new ones in a way indicated by group theory from the atomic configuration, it is possible to factor the singlet secular equation into subdeterminants of smaller degree (for examples see reference 8). Usually, however, one is most interested in the lowest energy level, and then much simpler methods, involving no very great use of group theory, are available. Usually also the lowest level results from solution of the determinant related to the combinations of bond eigenfunctions belonging to the identical representation.

Seitz and Sherman¹² have indicated a fairly simple way to determine eigenfunctions of the identical representation. An equivalent and somewhat simpler method is described by Stearn, Lindsley and Eyring.⁹ The expression $\Phi = \sum_R \chi_R R\psi$ where χ_R is the group theory character belonging to the symmetry operation R for a given one-dimensional representation and where ψ is any bond eigenfunction, can be used to determine the required number of Φ 's of this symmetry. For the particular identical representation all χ_R 's are unity, and the determination of Φ 's is extremely simple: $\Phi = \sum_R R\psi$. The procedure is to determine

¹¹ Heitler, Zeits. f. Physik 79, 143 (1932).

¹² F. Seitz and Albert Sherman, J. Chem. Phys. 2, 11 (1934).

all possible Φ 's, one from each of the independent set of singlet bond eigenfunctions. Some of the resulting eigenfunctions (Φ 's) will be the same, except possibly for sign, while others though different may not all be independent. It is a simple matter, however, to pick out from these an independent set of Φ 's.

This procedure can be further improved by drawing the independent bond eigenfunctions on a figure which has the symmetry of the problem under consideration. When this is done it becomes apparent immediately that certain ψ 's, with the same pattern of bonds, differ from each other by permitted symmetry operations. These, then, when given the proper sign and summed will form part of a particular Φ , though not necessarily all of it. Certain other eigenfunctions with the same bond pattern will also enter the Φ function, and these additional ones will correspond to "crossed-bond" functions when drawn on the circle of orbits used to determine the independent set. These can be resolved in terms of the independent ψ 's, and from all Φ 's so found, equal in number to the number of different patterns formed by the independent set when drawn on the figure with the symmetry of the problem, the largest number of independent functions (Φ 's) is selected for the construction of the secular equation.

RULES FOR RESOLVING CROSSED BOND EIGENFUNCTIONS

Simple empirical rules for the uncrossing of bond patterns containing as many as five bonds have been given.¹³ It is possible in the simple way which follows to extend these methods to twelve-electron eigenfunctions. For these six-bond cases one traces along bonds of the crossed eigenfunction A (never traversing the same bond twice) the shortest connections between the extreme points of the bonds in the uncrossed eigenfunction B . If this is possible the expansion of A contains B at least once. If three or more paths pass through a common point the coefficient of B is $p-2+q$. What is meant by the number of paths p passing through a common

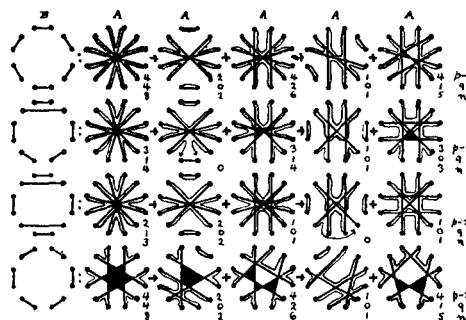


FIG. 1. Examples of the methods of tracing bond paths on crossed-bond eigenfunctions (A) in order to determine the number of times ($n=p-2+q$) a given uncrossed eigenfunction (B) is contained therein. The value of $p-2$ is to be taken as unity for values of $p \leq 3$. Filled in areas are those bounded by unused sections of bonds and are to be regarded as essentially points in determining p and q . Pairs of A eigenfunctions connected by plus signs are those obtained by uncrossing one of the crosses of the function immediately preceding the pair.

point needs to be defined. Frequently parts of the bond lines in A are not traversed in drawing the required shortest paths. All points connected by untraversed lines are for this purpose to be counted as one point. Also any path which passes through a point and which with the perimeter circle separates other paths common to the point into two groups is omitted in determining p for the point. This discarding is continued until there are no more such paths. Since q is zero in cases of five or fewer bonds, it will also be zero when the six bonds of A can be divided into two or more non-intersecting groups. Otherwise q is determined by the number of pairs of diametrically opposite bonds on the perimeter of B which when drawn on A have the following properties. For a given pair to be counted in the determination of q each member of the pair must have its path as drawn on A terminate along two bond lines which cross; the paths for members of such a pair must touch at some point, either directly or by the "shrinking" of untraversed lines as discussed in the previous rules; and the pair members must not be separated by the traced path of another bond, for one or two such pairs q is 1 or 2, respectively. For three such pairs q is 4. Self-explanatory examples are given in Fig. 1.

¹³ Eyring and Sun, *J. Chem. Phys.* 2, 299 (1934).

ENERGIES FOR HIGHER MULTIPLICITIES

The method of using bond eigenfunctions drawn on a figure with the symmetry of the actual problem at hand combined with the above rapid method of resolving crossed eigenfunctions thus becomes a simple one for the determination of singlet levels of the identical representation. A similar procedure is valid for levels of higher multiplicity and the identical representation. The method for selecting independent sets of bond eigenfunctions for higher multiplicities follows.¹⁴ Between two of the orbits in the usual circular arrangement one inserts an additional orbit. One then draws non-crossing bonds within the circle, leaving the extra orbit and $\nu-1$ others unbonded, where ν is the multiplicity. If it is possible in a particular eigenfunction to draw lines between the extra orbit and all other unbonded ones without crossing any of the bonds, the eigenfunction is a member of the complete set. After selecting in this manner a complete set, the extra orbit is, of course, discarded. The "pattern" method of determining Φ 's as combinations of members of this set can then be applied, but in general the levels thus determined may not contain the lowest level of the system.

USEFULNESS OF SPACIAL SUPERPOSITION PATTERNS

It is possible to use the patterns to determine Φ 's belonging to other representations as well if the group theory characters are known. The method is then still superior to an experimental choice of ψ 's from which to build the Φ 's by use of the symmetry operations and characters. In fact one immediately sees that the Φ 's will always be composed of bond eigenfunctions of the same pattern with coefficients depending upon the representation.

Having selected an independent set of Φ 's for the problem in hand, one now finds that the use of the patterns is of further value in the calculation of matrix components. For this purpose it is more convenient to use the Φ 's expressed in terms of bond eigenfunctions which are of the

same pattern, irrespective of whether they are members of the independent set or not. One then, in a manner introduced by Pauling^{5d} for orbits arranged in a circle, superimposes bond eigenfunctions upon each other in order to determine matrix components as follows. Suppose Φ_r and Φ_t are the two of the Φ 's for which a component is to be determined and ψ_{ru} and ψ_{tv} are typical bond eigenfunctions composing the two, respectively. Then the matrix component $\int \Phi_r \times (H - W) \Phi_t d\tau = \int \sum_u c_{ru} \psi_{ru} (H - W) \sum_v c_{tv} \psi_{tv} d\tau$ is the sum of ones for which coefficients can be found by the sequence method. The superposition patterns of ψ_{ru} and ψ_{tv} are simply diagrammatic ways of writing the sequences, the parts of which will be recognized as follows. Certain "islands" composed of a broken closed line with an even number of bonds are cycles. Unclosed lines of no bonds or of an even or odd number of bonds are chains. First group orbitals are alternate ones starting with the first orbital in an odd chain and any arbitrary orbital in an even chain or cycle (island). The other orbitals belong to second groups. As long as one is dealing with "canonical" eigenfunctions, i.e., those formed according to the previous definition with orbits of each bond written in alphabetical order, it is unnecessary to consider the quantity $(-1)^p$ in (12) as other than positive. The coefficients of J , W , and the exchange integrals are then directly determinable for each superposition pattern from (12). The advantages of the spatial superposition patterns thus employed are that (1) any one of the ψ_{ru} 's, apart from the coefficients c_{ru} and c_{tv} , gives the same types of superposition patterns with all of the ψ_{tv} 's as does any other ψ_{ru} , hence the same coefficients of J , W , and the exchange integrals; and (2) it is possible to allow directly for several exchange integrals being equal as may be indicated by the spacial arrangement of orbits. These factors result in reduction of the labor of calculating matrix components.

The application of the above methods of obtaining eigenfunctions and matrix components for the identical representation from figures drawn according to the symmetry of the problem is particularly simple when the atoms are arranged in one or two-dimensional configura-

¹⁴ Rumer, Teller and Weyl, Nach. Ges. Wiss. Gottingen, M. P. Kl. p. 519 (1932).

tions, such as a straight line, circle, square, etc. Then it is possible to draw an independent set of bond eigenfunctions directly on this configuration, and no symmetry operation on any one of these will give rise to eigenfunctions outside of the complete set. The number of different Φ 's is then equal to the number of patterns that arise, and all of them are independent. When three-dimensional figures are necessary no way of determining the independent bond functions directly is possible because of the two-value nature of the spin eigenfunctions. In such cases Φ 's will contain bond eigenfunctions other than those of the independent set, and these will need to be resolved in order to pick out independent Φ 's.

ENERGIES OF FILAMENTS OF SODIUM ATOMS

In order to apply the foregoing considerations in a simple way we have calculated the lowest singlet level for the identical representation for various even-numbered configurations of sodium atoms arranged on straight lines or in circles. The object was to find a limiting value for the energy per atom approached as the number of atoms increases. This energy would then be that of a single atom in an infinite linear extension of atoms, a one-dimensional lattice. The circle as well should show the same energy per atom in the limit, and since the circle has the greater symmetry it was hoped that the greater simplification of the secular equations thereby introduced would allow closer approach to the limiting value by permitting determination of energies for larger numbers of atoms. Actually, however, the straight line of atoms more quickly shows a trend which indicates the desired energy in the limit.

In Fig. 2 the independent sets for six atoms are shown as drawn on linear and circular models. The method in the linear case is to draw non-crossing bonds on the line connecting the atoms or to one side of that line. It becomes obvious immediately that a quadratic equation will give the energies for the circle, while one of fourth degree arises for the linear configuration. The Φ 's in the circular case are $\Phi_1 = I + II$, $\Phi_2 = III + IV + V$; and for the linear model $\Phi_1 = I$, $\Phi_2 = II$, $\Phi_3 = III + IV$, and $\Phi_4 = V$.

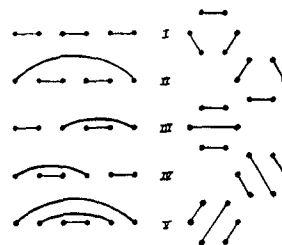


FIG. 2.

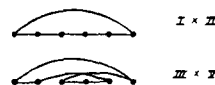


FIG. 3.

Pauling^{5d} has given superposition patterns for the circular configuration, and in Fig. 3 are given several for the linear set. The examples have been chosen to illustrate the existence of apparently different superposition patterns which, however, are easily recognizable as giving the same expansion in terms of the coulombic and exchange integrals. All of the examples given yield $F = 2^4 [M + 3/2(5\alpha + 3\gamma + \epsilon) - 3/2(4\beta + 2\delta)]$, where α , β , γ , δ and ϵ are the exchange integrals between orbits or atoms separated, respectively, by 1, 2, 3, 4 and 5 times the distance between adjacent atoms. The matrix component $\int \Phi_1 (H - W) \Phi_2 d\tau = F$ and $\int \Phi_3 (H - W) \Phi_4 d\tau = 2F$. The other matrix components are determined similarly.

In this manner the secular equations for circular and linear configurations up to 12 and 8 orbits, respectively, have been set up. These are of twelfth degree for the largest circle considered and of tenth degree for 8 atoms on a line. Beyond these numbers of atoms the determinants are entirely too large to be handled with reasonable labor. We shall not repeat the matrix components here, since the determinants are of limited application.

For estimation of coulombic and exchange integrals we have employed the method previously used in similar investigations.^{15, 9} The dissociation energy of the Na_2 molecule, D , is

¹⁵ Taylor, Eyring and Sherman, J. Chem. Phys. 1, 68 (1933).

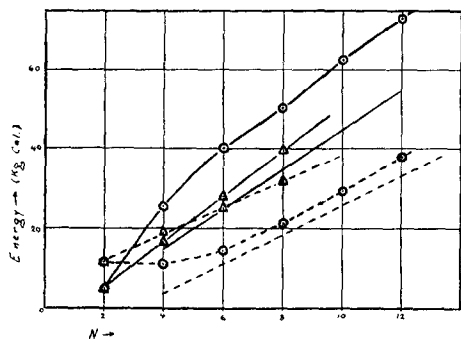


FIG. 4. Energies of various sodium atom configurations. — Coulombic contributions. - - - Exchange contributions. \odot atoms arranged in circle. \triangle atoms arranged on line. Curves without circles or triangles after Slater. N is the number of atoms.

17.5 kg cal., $D'=17.7$ kg cal., $\omega_0=159$ cm $^{-1}$, and $r^0=3.15$ Å. From these constants a Morse curve was constructed. For the coulombic binding between two atoms at a given distance from each other we have employed Rosen's value¹⁶ of 28.3 percent of the total binding energy as determined from the Morse curve. The corresponding exchange integral then is 71.7 percent of the binding energy. Energies have been calculated only for configurations in which the distance between adjacent atoms is r_0 for the Na_2 molecule. This is sufficiently close to the equilibrium configuration in each case.

TABLE I.

N	Circle				Line			
	$J(\text{circle})$	$W-J$	W	W/N	J	$W-J$	W	W/N
2			17.7	8.85			17.7	8.85
4	25.6	11.2	36.8	9.20	16.5	19.1	35.6	8.90
6	40.1	14.5	54.6	9.10	28.0	25.4	53.4	8.90
8	50.4	21.3	71.7	8.96	39.5	31.8	71.3	8.91
10	62.6	29.5	92.1	9.21				
12	73.0	38.0	111.0	9.25				

The results are given in Table I and plotted in Fig. 4. It will be noticed that the coulombic and exchange energies for the linear configurations increase by practically constant amounts for each pair of atoms added. Hence the total energy per atom for these cases rapidly approaches the constant value of about 8.91 kg cal., which is the desired limiting energy value. The

¹⁶ Rosen, Phys. Rev. **38**, 255 (1931).

circular configurations possess greater coulombic energy than do the linear ones. On account of the unusual importance of coulombic energy, the circular arrangements of the atoms appear to be the stabler ones.

The straight lines for coulombic and exchange energy plotted against N for the linear configurations enable one to express the total energy by the following equation:

$$W=5.0+5.7(N-2)+3.2(N+2). \quad (14)$$

The first two terms arise from coulombic origins, those of the third from exchange contributions. It becomes apparent from (14) that the energy per atom for infinite N is composed of 5.7 kg cal. from coulombic sources and 3.2 kg cal. from electron exchanges.

These results can be compared with those of Slater,¹⁷ who found for an infinite linear lattice of identical atoms to the approximation of including only interactions between adjacent atoms:

$$W=(N-1)J'+0.290(N-3)K, \quad (15)$$

where J' is the coulombic attraction between adjacent atoms and K the exchange integral between adjacent orbits. By using the values 5.0 and 12.7 for J' and K , respectively, the results of (15) have been calculated for small values of N and plotted in Fig. 3. Though it appears that Slater's equation is not very good for small values of N , it may be written

$$W=5.0(N-1)+3.7(N-3), \quad (15b)$$

and it then becomes evident that radical differences between (14) and (15b) disappear for large N . At such large values of N the Slater equation indicates somewhat less coulombic energy and a little more exchange energy than the method used here gives, but these differences nearly cancel to give the limiting value for the total energy per atom of 8.7 kg cal. as compared to the 8.9 determined by including interactions between atoms further apart than neighbors. The higher value is, however, greater than the energy per atom in the diatomic molecule, while the lower is not.

¹⁷ Slater, Phys. Rev. **35**, 509 (1930).