The Resolution of Bond Eigenfunctions in Terms of a Linearly Independent Set

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By means of simple operators derived from the anti-symmetrical configuration eigenfunctions a method is devised for obtaining the coefficients in the expansion of a bond eigenfunction in terms of a linearly independent set. This method eliminates any necessity of drawing diagrams and removes the unique advantage of the uncrossed set. It is applied to the determination of the coefficients of eigenfunctions expanded in terms of the Rumer (uncrossed) set for as many as six bonds. For three and four bonds crossed sets are given for which the process of resolving eigenfunctions is simpler than for the Rumer set. A convenient method of expansion in terms of the Rumer set is extended to include eigenfunctions of as many as six bonds of any multiplicity.

I. INTRODUCTION AND GENERAL METHOD

IN order to take advantage of molecular symmetry in reducing the secular determinants of many atom problems it is necessary to be able to expand bond eigenfunctions in terms of a complete set. Until quite recently the calculation of the coefficients in such an expansion offered considerable difficulty. A solution of this problem, complete from the theoretical point of view, has been given by Rumer, Teller and Weyl[2] who developed a geometric method of determining such a complete set and also show how by the laborious method of successive uncrossing of bonds, any eigenfunction can be expanded in terms of an uncrossed set. Their methods have been applied to the less complicated symmetrical molecules. As the number of bonds considered is increased the process rapidly reaches Herculean dimensions. Preceding papers from this laboratory have given rules for getting the coefficients in the expansions of eigenfunctions containing as many as six bonds in terms of the Rumer set.[3] These methods, however, enable one to use only one of the many possible independent sets. For systems of atoms having some other symmetry than that corresponding to rotations in a plane it is advantageous to use instead of the Rumer, that independent set which most nearly possesses the symmetry of the atomic configuration. We, therefore, considered it desirable to develop some method which would make more easy the

expansion of a bond eigenfunction in terms of any l.i.s. (linearly independent set).

An analytical solution of this problem is suggested when one considers the function space of higher dimensions which underlies that of the bond eigenfunctions. A bond eigenfunction ψ_j can be represented as a linear combination of the antisymmetric configuration eigenfunctions φ_i which have the same eigenvalue for S_z the total z-component of spin. The φ_i are the determinants defined by[4]

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

Here N is the number of orbitals a, b, etc.; so that $1/(N!)^{\frac{1}{2}}$ is the factor which just normalizes the $N!$ terms of (1) to the approximation of neglecting non-orthogonality of the orbitals. The quantities α and β are the two eigenfunctions for the S_z for a single electron with the corresponding eigenvalues $h/4\pi$ and $-h/4\pi$. The operation P permutes the electrons among the orbitals. Such an eigenfunction can be represented symbolically in a very simple fashion, by indicating which spin eigenfunction is associated with each orbital. Thus for the singlet state of the four electron problem we write $\begin{pmatrix} a & b & c & d \\ \alpha & \beta & \alpha & \beta \end{pmatrix}$ for the eigenfunction which has the eigenvalue $S_z = 0$, and which has β's in the b and d columns of its determinant.

These φ_i's are all linearly independent, whereas the ψ's are not. Furthermore, the coefficients of the φ_i's that combine to give a ψ_j can be only ± 1

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[1] Parker Fellow of Harvard University.
[2] (a) Rumer, Nach. Ges. Wiss. Gott. M. P. K. **1932**, 332; (b) Rumer, Teller and Weyl, ibid. **1932**, 499.
[3] (a) Eyring and Sun, J. Chem. Phys. **2**, 299 (1934); (b) Bear and Eyring, ibid. **3**, 98 (1935).

[4] These are simply the antisymmetrical determinants used by (a) Slater, Phys. Rev. **34**, 1293 (1929). For a more complete discussion see (b) Eyring and Kimball, J. Chem. Phys. **1**, 246 (1933); and (c) Bear and Eyring, reference 3(b).

or 0, while in the expansion of a ψ_j in terms of ψ's that are linearly independent, the coefficients are not thus restricted. Let us now suppose that we have an independent set $\psi_1, \psi_2, \cdots \psi_s$ and expand ψ_k in terms of this set.[5]

$$\psi_k = \sum_{r=1}^{s} a_{rk} \psi_r. \qquad (2)$$

But we have also $$\psi_k = \sum_{i=1}^{l} b_{ik} \varphi_i \qquad (3a)$$

and $$\psi_r = \sum_{i=1}^{l} b_{ir} \varphi_i. \qquad (3b)$$

Therefore, substituting in (2) the expansions of ψ_k and ψ_r from (3a) and (3b) and equating the coefficients of φ_i we get

$$b_{ik} = \sum_{r=1}^{s} a_{rk} b_{ir}. \qquad (4)$$

It is convenient to think of the φ's (antisymmetric configuration eigenfunctions) as constituting a set of mutually orthogonal unit vectors. The ψ's (bond eigenfunctions) are then vectors in this space with one end at the origin and the other given by adding and subtracting vectorially an equal number of these orthogonal* unit vectors. The coefficient b_{ik} in (3a) is then just the scalar product $\varphi_i \cdot \psi_k$ (4a). This scalar product is not to be confused with the integral $\int \varphi_i^* \psi_k d\tau$, with which it agrees if $\int \varphi_i^* \varphi_j d\tau = \delta_{ij}$. The use of (4a) is of course not a limitation on our method of determining linear dependence.

It is clear that b_{ik} and b_{ir} can also be expressed as the simple operators $D_i = (\partial/\partial \varphi_i) = \varphi_i \cdot$, acting on ψ_k and ψ_r, respectively, whence

$$D_i \psi_k = \sum_{r=1}^{s} a_{rk} D_i \psi_r. \qquad (5)$$

We evaluate $D_i \psi_r$ for our independent set and substitute in (5), which process gives l equations ($l > s$) from any s of which we can solve for the s unknowns (the a_{rk}) in terms of the $D_i \psi_k$. It is always possible to choose a set of s equations in such a way that one obtains linear equations of the form:

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[5] In all that follows the subscript k refers to the specific bond function in which we are interested, and does not change, while r may be any one of the s linear independent bond functions and i any one of the l Slater functions.

$$a_{rk} = (D_m + D_n + \cdots - D_p - D_q - \cdots) \psi_k. \qquad (6)$$

The operator in the brackets is independent of k. We can therefore write

$$a_{rk} = A_r \psi_k, \qquad (7)$$

where $A_r = (D_m + D_n + \cdots - D_p - D_q - \cdots)$. (8)

The operation A_r on ψ_k of course amounts simply to taking a sum of scalar products. We have then a convenient method of obtaining the coefficients in the expansion of *any* bond eigenfunction. We need determine only once the operator A_r for each ψ_r and then the coefficient of that ψ_r in the expansion of any ψ_k is given by A_r operating on that ψ_k. The simplest coefficients for any independent set will be found by picking the s equations properly. In the applications that follow it will be shown how easily this may be done.

II. Applications to Singlet Eigenfunctions

A. Three bonds

Let us consider in detail the resolution of six electron bond eigenfunctions for the singlet state. For this case there are twenty φ_i's and fifteen ψ_j's, of which five of the latter are linearly independent. We shall arrange the φ_i's as follows. We shall write at the top of a column $a\,b\,c\,d\,e\,f$ representing the six orbitals involved. Then we shall distribute three α's and three β's in all the twenty possible ways among these orbitals by arranging them as one would in constructing a dictionary. Thus $\varphi_1 = \begin{pmatrix} a\,b\,c\,d\,e\,f \\ \alpha\,\alpha\,\alpha\,\beta\,\beta\,\beta \end{pmatrix}$, $\varphi_2 = \begin{pmatrix} a\,b\,c\,d\,e\,f \\ \alpha\,\alpha\,\beta\,\alpha\,\beta\,\beta \end{pmatrix}$ and $\varphi_{20} = \begin{pmatrix} a\,b\,c\,d\,e\,f \\ \beta\,\beta\,\beta\,\alpha\,\alpha\,\alpha \end{pmatrix}$. When we arrange the φ_i's in this manner we see that φ_{20} through φ_{11} are the reflections of φ_1 through φ_{10}, i.e., they have α's where β's were and *vice versa*. Thus the coefficients of φ_{20} through φ_{11} in any expansion of a bond eigenfunction will be the negative of those of φ_1 through φ_{10}. Therefore in our further work we need only consider φ_1 through φ_{10}. In the expansion of any bond eigenfunction ψ_j the coefficients of the φ_i's can be determined in the following manner. Corresponding to each φ_i we define an operator D_i of the form $[def]$ in which the letters simply list the orbitals in the corresponding φ_i which are

associated with β's. Operating on a bond eigenfunction such as $\psi_4 = ab\ cd\ ef$, D_i gives 0 if any two of the orbitals occur in any one bond; otherwise it gives $+1$ if the number of letters in it which are first letters of bonds is even and -1 if this number is odd. The following convention is to be understood for the ψ's. In each bond the letter coming first in the alphabet is written first and this eigenfunction we indicate by plus ψ_k. Interchanging the order of the letters in one bond changes the sign of ψ_k.

Thus $[def]\psi_4 = 0$; $[bce]\psi_4 = 1$; $[bcf]\psi_4 = -1$, etc. We consider, therefore, ten such operators, $D_1 = [def]$, $D_2 = [cef]$, $\cdots D_{10} = [bcd]$. For our five linearly independent ψ's let us first choose the Rumer set.

$$\begin{array}{ll}
\psi_1 = af\ bc\ de, & \psi_4 = ab\ cd\ ef, \\
\psi_2 = ad\ bc\ ef, & \psi_5 = ab\ cf\ de. \\
\psi_3 = af\ be\ cd,
\end{array} \quad (9)$$

Now any other eigenfunction ψ_k can be written as

$$\psi_k = a_{1k}\psi_1 + a_{2k}\psi_2 + a_{3k}\psi_3 + a_{4k}\psi_4 + a_{5k}\psi_5 \quad (10)$$

and we are interested in finding the a_{ik}'s. Operating on ψ_k with the brackets defined above we obtain:

$$\begin{array}{l}
d_{1k} = [def]\psi_k = a_{3k}, \\
d_{2k} = [cef]\psi_k = a_{1k} - a_{3k}, \\
d_{3k} = [cdf]\psi_k = -a_{1k} + a_{2k}, \\
d_{4k} = [cde]\psi_k = -a_{2k}, \\
d_{5k} = [bef]\psi_k = -a_{1k} + a_{5k}, \\
d_{6k} = [bdf]\psi_k = a_{1k} - a_{2k} - a_{3k} + a_{4k} - a_{5k}, \\
d_{7k} = [bde]\psi_k = a_{2k} - a_{4k}, \\
d_{8k} = [bcf]\psi_k = a_{3k} - a_{4k}, \\
d_{9k} = [bce]\psi_k = a_{4k} - a_{5k}, \\
d_{10k} = [bcd]\psi_k = a_{5k},
\end{array} \quad (10a)$$

where

$$d_{ik} = D_i\psi_k. \quad (10b)$$

From the five equations for d_{1k}, d_{2k}, d_{4k}, d_{9k} and d_{10k} we get the following solutions for the a's.

$$\begin{array}{ll}
a_{1k} = d_{1k} + d_{2k}, & a_{4k} = d_{9k} + d_{10k}, \\
a_{2k} = -d_{4k}, & a_{5k} = d_{10k}. \\
a_{3k} = d_{1k},
\end{array} \quad (11)$$

For the expansion of any three-bond eigenfunction ψ_k in terms of the Rumer set we, therefore, have,

$$\psi_k = [\psi_1(D_1 + D_2) - \psi_2 D_4 + \psi_3 D_1$$
$$+ \psi_4(D_9 + D_{10}) + \psi_5 D_{10}]\psi_k. \quad (12)$$

It is possible to pick an independent set in which not more than one operator is required to calculate each coefficient. This can be done by letting the ten D_i's operate on all fifteen ψ's and then picking out five suitable ψ's. When this is done we find that such a set is given by $\psi_1' = ab\ cd\ ef$, $\psi_2' = af\ bc\ de$, $\psi_3' = ab\ ce\ df$, $\psi_4' = ae\ bc\ df$, $\psi_5' = af\ be\ cd$. The coefficients are $A_1' = D_9$, $A_2' = -D_3$, $A_3' = D_{10}$, $A_4' = -D_4$, $A_5' = D_1$, where A_i was defined in Eqs. (7) and (8) and D_i was defined in (10b). The expansion of any ψ_k in terms of this set then becomes

$$\psi_k = [\psi_1' D_9 - \psi_2' D_3 + \psi_3' D_{10}$$
$$- \psi_4' D_4 + \psi_5' D_1]\psi_k. \quad (13)$$

Thus we see that it is a very simple matter to expand any bond eigenfunction in terms of any complete set. Even for the Rumer set it is no longer necessary to draw diagrams and repeated superposition patterns each time an eigenfunction is expanded. Eqs. (12) or (13) need be obtained only once and then can be applied to any ψ_k.

Eq. (12) may be written in a simpler form by taking advantage of the symmetry properties of the Rumer set. The five eigenfunctions form only two patterns which can be represented by rotation (or permutation) groups of order two and three. Thus ψ_1 is carried into $-\psi_4$ by the odd permutation $R = (abcdef)$ and $-\psi_4$ into ψ_1 by repeating this permutation. The sign of an eigenfunction obtained by applying to a positive eigenfunction the permutation $(abcdef)$ p times is $(-)^p$. The same permutation changes ψ_2 into $-\psi_3$, $-\psi_3$ into ψ_5, and ψ_5 into $-\psi_2$. As stated before the operation D_i is simply φ_i·, so that the odd permutation $R = (abcdef)$ applied p times gives $(-)^p\varphi_j$· $= (-)^p D_j$.[6] Furthermore, if the operator D_i is one used to determine the coefficient of ψ_r, then $(-)^p R^p D_i$ is the operator associated with $(-)^p R^p \psi_r$. Thus we can rewrite (12) as

[6] This follows because any permutation applied to a φ_i gives some other Slater eigenfunction φ_j, and hence this permutation applied to the operator φ_i· (which symbolizes the taking of a scalar product of φ_i with the eigenfunction that is operated upon) gives the operator $(-)^P - \varphi_j$·, which in our alternate notation is the operator $(-)^P D_j$. If it should so happen that the permutation carries the given operator into one belonging to the set φ_{11}· to φ_{20}· inclusive (such as $[aef]$, for example), one can either keep it or replace it by the negative of its reflection from the set φ_i· to φ_{10}· (i.e. $-[bcd]$).

$$\psi_k = \left\{ \sum_{i=0}^{1} R^i [\psi_1([def]+[cef])] \right.$$

$$\left. - \sum_{i=0}^{2} R^i (\psi_2[cde]) \right\} \psi_k. \quad (14)$$

This simple way of writing the expansion does not diminish the actual labor of carrying out the operation itself but will be found very convenient for the representation of eigenfunctions of more bonds where the number of those in the l.i.s. becomes quite large. Furthermore it does reduce the amount of labor needed to determine the operators since it is now necessary to find the operator for only one bond eigenfunction of each pattern. When the Rumer set is used it is found that those operators D_i give the simplest coefficients a_{ik} which have the largest number of β's associated with neighboring orbitals (successive letters). With these simplifications it becomes possible to determine quickly the expansions for eigenfunctions of many bonds.

Another advantage of the notation employed in Eq. (14) is perceived when we proceed to determine the character of a representation. If we let some operator B act upon our independent set we get the character χ of the corresponding transformation from the equation

$$\chi = \sum_{r=1}^{s} A_r B \psi_r. \quad (15)$$

If ψ_1 to ψ_n can be obtained from ψ_1 by the permutation P^i and ψ_{n+1} to ψ_r by a permutation Q^i on ψ_{n+1} we have

$$\chi = \sum_{i=1}^{n} A_i B P^i \psi_1 + \sum_{i=n+1}^{r} A_i B Q^i \psi_{n+1}. \quad (16)$$

In the particular cases for which B and P and B and Q commute it is seen that (16) can be much further simplified.

B. Four bonds

The Rumer set of four-bond eigenfunctions has fourteen members which fall into three groups of orders two, four and eight. These groups can be generated by the permutation $R = (abcdefgh)$ operating on $\psi_1 = ab\ cd\ ef\ gh$; $\psi_2 = ad\ bc\ eh\ fg$ and $\psi_3 = ab\ cd\ eh\ fg$, respectively. The coefficients of these eigenfunctions are readily found to be

$$a_{1k} = ([bcfg]-[bcde]-[defg])\psi_k = A_1\psi_k,$$
$$a_{2k} = ([cdef]\psi_k = A_2\psi_k, \quad (17)$$
$$a_{3k} = ([bdef]+[cdef])\psi_k = A_3\psi_k.$$

The eleven other coefficients are obtained from these by repeated application of the cyclic permutation R. We have then for the expansion of any four bond singlet eigenfunction in terms of the Rumer set,

$$\psi_k = \left\{ \sum_{i=0}^{1} R^i(\psi_1 A_1) + \sum_{i=0}^{3} R^i(\psi_2 A_2) \right.$$

$$\left. + \sum_{i=0}^{7} R^i(\psi_3 A_3) \right\} \psi_k. \quad (18)$$

In the above set only four coefficients have one term, while eight have two terms and two have three terms. There exists a set for which eleven coefficients have one term, two have two terms, and one has three terms. It is the following:

$$\psi_1 = ab\ cd\ eg\ fh, \quad A_1 = [bdgh],$$
$$\psi_2 = ab\ ce\ dg\ fh, \quad A_2 = [begh],$$
$$\psi_3 = ab\ cf\ dg\ eh, \quad A_3 = [bfgh],$$
$$\psi_4 = ac\ bd\ ef\ gh, \quad A_4 = [cdfh],$$
$$\psi_5 = ac\ be\ df\ gh, \quad A_5 = [cefh],$$
$$\psi_6 = ad\ bg\ ce\ fh, \quad A_6 = [degh],$$
$$\psi_7 = ad\ bg\ cf\ eh, \quad A_7 = [dfgh],$$
$$\psi_8 = ac\ be\ dg\ fh, \quad A_8 = [cegh],$$
$$\psi_9 = ac\ af\ bg\ eh, \quad A_9 = [cfgh],$$
$$\psi_{10} = af\ ce\ bg\ dh, \quad A_{10} = [efgh],$$
$$\psi_{11} = ad\ be\ cf\ gh, \quad A_{11} = [defh],$$
$$\psi_{12} = ab\ ce\ df\ gh, \quad A_{12} = [befh]+[efgh],$$
$$\psi_{13} = ac\ bd\ eg\ fh, \quad A_{13} = [cdef]-[cegh],$$
$$\psi_{14} = ab\ cd\ ef\ gh, \quad A_{14} = [bdeg]-[befh]-[efgh].$$

C. Five bonds

There are 42 linearly independent five-bond eigenfunctions. The members of the Rumer set, however, form only six rotation groups, one of order two, two of order five and three of order ten. These six groups can be generated by the cyclic permutation from the eigenfunctions

$$\psi_1 = ab\ cd\ ef\ gh\ ij \quad \text{(order 2)},$$
$$\psi_2 = ab\ cj\ di\ eh\ fg \quad \text{(order 5)},$$
$$\psi_3 = aj\ bc\ di\ ef\ gh \quad \text{(order 5)},$$
$$\psi_4 = ab\ cj\ di\ ef\ gh \quad \text{(order 10)},$$
$$\psi_5 = ab\ cj\ dg\ ef\ hi \quad \text{(order 10)},$$
$$\psi_6 = ab\ ej\ de\ fg\ hi \quad \text{(order 10)}.$$

The following are the coefficients of these eigenfunctions from which the others may be gener-

ated by the cyclic permutation $R = (abcdefghij)$:

$$a_{1k} = ([cdefg] + [bdefg] - [bcdef] - [bcdeg] + [bcehi] \\ + [bedhi] + [dfghi] + [efghi])\psi_k = A_1\psi_k,$$

$$a_{2k} = [bcdef]\psi_k = A_2\psi_k,$$

$$a_{3k} = ([bcdef] + [bcdeg] + [acdeg] + [acdef])\psi_k = A_3\psi_k,$$

$$a_{4k} = ([bcdef] + [bcdeg])\psi_k = A_4\psi_k,$$

$$a_{5k} = ([bcdef] + [bcdeg] + [bcdeh])\psi_k = A_5\psi_k,$$

$$a_{6k} = ([bcdef] + [defgh] + [cefgh] \\ - [bcdgh] + [befgh])\psi_k = A_6\psi_k.$$

D. Six bonds

There are 132 linearly independent six-bond singlet eigenfunctions. The symmetry properties of the Rumer set reduce these to 14 rotation groups, one of order 2, one of order 4, three of order 6 and eight of order 12. We shall give in some detail the method of obtaining the coefficients in this case as it throws some light on the way in which symmetry properties may be used to reduce enormously the labor of the calculation. Thus the operators for this set were obtained in several hours, whereas the method of uncrossing a single much crossed eigenfunction takes a time of an entirely different order of magnitude. Even to expand an eigenfunction by the simplified methods previously suggested[3] would take longer than this operator method since in the former method to determine each coefficient it is necessary to draw a new diagram.

Let us assume that twelve points $a, b, c \cdots, l$, representing the orbitals, are arranged in order on the circumference of a circle (8). A bond between two of the orbitals is represented by the chord connecting the two points. Following a definition of Rumer, Teller and Weyl,[2b] we shall measure the length of the arc subtended by this chord, by the number of points on the arc, the two terminal points each counting one-half. We have already noted that the simplest coefficients are given by those operators representing antisymmetric configuration eigenfunctions in which all the β's are on adjacent orbitals. We see at once that such an operator will give zero when acting on any bond eigenfunction except one of that symmetry group in which there are just two arcs of unit length. (Such an eigenfunction is $ab\ cl\ dk\ ej\ fi\ gh$.) The next simplest operator is that with five β's on adjacent orbitals. Such an operator will give zero when acting on all eigenfunctions except one of the symmetry group

already mentioned and one of a group with just three arcs of length one. When one proceeds to choose the operators in such an orderly manner one finds that the solution of the fourteen simultaneous equations that are needed is made quite easy, since each new equation involved only the quantities that have occurred in previous equations. Thus, the fourteen eigenfunctions which follow are those of the Rumer set of 132 for which we require the corresponding operators.

	Order of rot. group
$\psi_1 = ab\ cl\ dk\ ej\ fi\ gh$	6
$\psi_2 = ab\ cl\ dk\ ej\ fg\ hi$	12
$\psi_3 = ab\ cl\ dk\ eh\ fg\ ij$	12
$\psi_4 = ab\ cl\ dk\ ef\ gj\ hi$	12
$\psi_5 = ab\ cl\ dk\ ef\ gh\ ij$	12
$\psi_6 = ab\ cl\ dg\ ef\ hk\ ij$	4
$\psi_7 = ab\ cl\ di\ ef\ gh\ jk$	12
$\psi_8 = ab\ cl\ de\ fk\ gb\ ij$	12
$\psi_9 = ab\ cl\ dg\ ef\ hi\ jk$	12
$\psi_{10} = ab\ cd\ el\ fk\ gh\ ij$	6
$\psi_{11} = ab\ cl\ de\ fi\ gh\ jk$	6
$\psi_{12} = ab\ cl\ de\ fg\ hi\ jk$	12
$\psi_{13} = ab\ cd\ ej\ fg\ hi\ kl$	12
$\psi_{14} = ab\ cd\ ef\ gh\ ij\ kl$	2

The fourteen eigenfunctions given above are in the order of complexity of their operators. Thus the operator associated with ψ_1 has one term, that of ψ_2 two terms, etc. Furthermore, their symmetry relations are such that each one contains the operator associated with the eigenfunctions that have gone before. This will be made clear by the following table. In this we give the operator coefficients of the eigenfunctions (A_r), not explicitly in terms of the D_r's, but in terms of the A's of the preceding eigenfunctions and whatever other D's are necessary. In the actual expansion the labor is reduced if the coefficients are determined in this same order. This order can be followed with advantage in the cases of three, four and five-bond eigenfunctions.

In order to get these relations in the simplest form it was necessary to use besides the operators for the fourteen eigenfunctions given above some of the others which are obtained by the repeated cyclic permutation. Thus in the expression for A_9 the symbol R^4A_3 means that one repeats four times the permutation $R = (abcdefghijkl)$ on A_3. The expression R^4A_3 is the operator associated with the eigenfunction $R^4\psi_3$, which is $ab\ ch\ dg\ ef\ il\ jk$.

$A_1 = [bcdefg]$,
$A_2 = [bcdefh] + A_1$,
$A_3 = [bcdefi] + A_2$,
$A_4 = [bcdegh] + A_2$,
$A_5 = [bcdegi] - A_2$,
$A_6 = [bcdehi] + A_5$,
$A_7 = [bcdegj] - [bcdefj] + A_6$,
$A_8 = [bcdfgi] - [bcdfgh] + A_6$,
$A_9 = [bcdeij] + A_4 + R^4 A_3$,
$A_{10} = [bcefhi] + A_8 + R^8 A_7 - R^8 A_9$,
$A_{11} = [bcdfgj] + A_1 - A_6 + A_7 + A_8$,
$A_{12} = [bcdghj] + [aefjkl] + R^4 A_7 + A_2 + R^8 A_4$,
$A_{13} = [bcgijk - A_1 + A_2 + R^8 A_5 - R^2 A_6 + R^{10} A_9$,
$A_{14} = [bcfgjk] - A_1 - R^2 A_1 + A_5 + R^2 A_5$
$\qquad\qquad + R^4 A_5 + R^6 A_5 + R^8 A_5 + R^{10} A_5 - A_6 - R^2 A_6$.

III. The Expansion of Bond Eigenfunctions of Higher Multiplicities

The resolution of bond eigenfunctions of higher multiplicity could also be carried through by this same method of operators. However, for high multiplicities the number of linearly independent bond eigenfunctions becomes so large that the method begins to become unwieldy. For such cases one may use to advantage a combination of the geometric and analytic methods. The l.i.s. for higher multiplicities may be obtained in the following way.[2b] The n orbitals a_1 to a_n are arranged in order on a circle. Since we are concerned with higher multiplicities, not all of these orbitals are bound to others. A reference orbital is inserted on the circumference between a_1 and a_n. The independent set is that one composed of eigenfunctions in which no lines cross, when, beside the lines representing actual bonds, one adds additional straight lines connecting the unbound orbitals with the reference orbital.

The first step in the resolution of bond eigenfunctions of higher multiplicities is to disregard all orbitals that are not connected by bonds and to expand the resulting eigenfunction in terms of an uncrossed set by the methods of the preceding section for the singlet state. These resulting uncrossed eigenfunctions will not in general be members of the l.i.s. We must, then, expand each of them.

It has been shown[7] that there is a vector-like relationship between eigenfunctions which are exactly the same except for a single bond. If these differing bonds when superposed on the same circle form a closed polygon any one of the

[7] Eyring, Frost and Turkevich, J. Chem. Phys. **1**, 777 (1933).

eigenfunctions can be represented as the vector sum of the rest. This principle, together with the definition of a l.i.s. given above, enables us to expand our uncrossed eigenfunction in terms of the l.i.s.

The method of expanding an eigenfunction of any number of bonds and of any multiplicity is now summarized. After one has applied to a crossed eigenfunction the method for obtaining an uncrossed set, as previously described, each one of the set is separately expanded. First we introduce some definitions. We speak of the bond which has one of its ends farthest from our reference orbital as B_0 the one next to it as B_1, etc. By the arc subtended by B_1 is meant the arc which does not contain the reference orbital. We next define a quantity which we will call the weight of a bond. The weight of B_0 is equal to the length of its arc n_0 (defined previously). The weight of B_i is its length minus $2i$. The product of the weights for all bonds of an eigenfunction ψ gives the number of eigenfunctions of the l.i.s., which will occur in the expansion of ψ. If for every eigenfunction the orbital in a bond with the lower ordinal number is written first all these eigenfunctions will occur with a coefficient $+1$. This is the convention of sign which has been employed throughout the paper.

To resolve the eigenfunction ψ one first expresses it as the sum of eigenfunctions which differ from ψ only in having B_0 replaced in turn by each possible bond B_0' lying along the arc subtended by B_0. Each of the resulting new functions is in turn replaced by a sum. This sum is obtained by replacing B_1, successively, by all the bonds which add vectorially to give B_1 and which follow along the arc of B_1 at all points except at the two points corresponding to the extremities of the B_0' for this eigenfunction. These points are omitted. This same process is continued for all the bonds up to B_{n-1} (there being assumed to be n bonds). In expanding a particular eigenfunction by successive replacements of the bond B_i we proceed as for B_1 except that we now omit the $2i$ points on the arc of B_i which coincide with the two extremities of the i bonds $B_0'B_1'\cdots B'_{i-1}$. Thus eigenfunctions for higher multiplicities, for any number of bonds n, are readily resolved in terms of the linear independent set.