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Molecular Symmetry and the Reduction of the Secular Equation

HENRY EYRING, ARTHUR A. FROST AND JOHN TURKEVICH, *Frick Chemical Laboratory, Princeton University*

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A method is given for expressing a bond eigenfunction of any multiplicity in terms of a linear independent set. The independent sets for the multiplicities corresponding to one bond and to two bonds for an arbitrary number of electrons are given. A method recently given for obtaining matrix components for singlet bond eigenfunctions is generalized to include all multiplicities. Group theory is

applied to the bond eigenfunctions for symmetrical molecules to reduce the secular equation and examples are worked out for all multiplicities. The possible reasons for the approximate additivity of bond energies for molecules is examined in connection with the chemist's custom of ignoring all but the strongest bonds.

INTRODUCTION

IN the calculation of activation energies for reactions involving complicated molecules it is important to know at least approximately how nearly the experimental bond strength corresponds to a simple exchange integral between the paired electrons. In the many reactions for which this is approximately the case the electrons not actually changing partners may be ignored or considered as causing only small steric effects. The binding energy for a few typical molecules is given here. We hope later to extend the cases examined to include more complicated molecules and to supplement these considerations by calculations of the integrals involved.

REDUCTION OF BOND EIGENFUNCTIONS TO A LINEARLY INDEPENDENT SET

Rumer¹ has shown how a linearly independent set of singlet bond eigenfunctions may be chosen. Points representing the atomic eigenfunctions are drawn as a polygon without reentrant angles. Straight lines representing bonds are then drawn. Only bond eigenfunctions for which no bonds cross are included in the linearly independent set. To express any singlet eigenfunction in terms of this linear independent set we require but one relationship. This may be expressed diagrammatically as follows:

$$\begin{array}{c} \nearrow \quad \nwarrow \\ \nwarrow \quad \nearrow \end{array} = \begin{array}{c} \longrightarrow \\ \longleftarrow \end{array} + \begin{array}{c} \uparrow \\ \uparrow \end{array} \quad (1)$$

¹ G. Rumer, *Nach. d. Ges. d. Wiss zu Göttingen, M. P. Klasse*, p. 337 (1932).

This relationship holds not only for bond eigenfunctions involving four electronic eigenfunctions but for those involving an arbitrary number providing the bonding not indicated in our diagram is identical for all three bond eigenfunctions. This same relationship holds even when an arbitrary number of the electronic eigenfunctions are connected by no bonds, i.e., for all multiplicities having as many as two bonds. For multiplets higher than singlets one additional relationship is required. If n bond eigenfunctions are identical except for a single bond in each and if these n unequal bonds added together vectorially have a resultant equal to zero then the sum of the bond eigenfunctions is zero. Diagrammatically this is simply

$$\begin{array}{c} \longrightarrow \\ \cdot \quad \cdot \end{array} = \begin{array}{c} \downarrow \\ \cdot \quad \cdot \end{array} + \begin{array}{c} \cdot \quad \cdot \\ \longrightarrow \end{array} + \begin{array}{c} \cdot \quad \cdot \\ \uparrow \end{array} \quad (2)$$

These two relationships enable us to express any bond eigenfunction in terms of a linearly independent set. Both propositions are readily verified by expressing the bond eigenfunctions in terms of Slater functions. A recent article by Rumer, Teller and Weyl^{1a} is of interest in this connection.

If our $2n$ electronic eigenfunctions (n an integer) be thought of as arranged in the polygon described above, a linearly independent set of one bond eigenfunctions is formed by $2n - 1$ of the $2n$ eigenfunctions around the perimeter which then requires but one bond to form a closed figure.

^{1a} Rumer, Teller and Weyl, *Nach. d. Ges. d. Wiss. zu Göttingen, M. P. Klasse*, p. 449 (1932).

Since any other bond will form a closed figure it is clear all other bond eigenfunctions can be expressed in terms of the set selected, and as there are $(2n-1)$ independent eigenfunctions we have a linearly independent set. An equally satisfactory set corresponds to the $2n-1$ bonds connecting a particular electronic eigenfunction with each of the others.

A linear independent set of two bond eigenfunctions corresponds to the $n(2n-3)$ ways that two bonds can be drawn on the perimeter, never of course using the same electronic eigenfunction in both bonds of the pair. Our two propositions enable us to express any other two bond eigenfunction in terms of this set. The independent set for more than two bonds will involve bonds not falling on the perimeter and is, therefore, slightly more difficult to describe. The two propositions given are, however, all that are required to single out a satisfactory set for any number of bonds.

Kimball and Eyring² defined an operator which acting on all the antisymmetric Slater functions for which M_s (the z component of spin) is zero gives the particular bond eigenfunction with $M_s=0$. To form a bond function with $M_s \neq 0$ proceed exactly as before. Take the linear combination of all Slater functions, with the proper M_s , which associate opposite spin eigenfunctions with each pair of electronic eigenfunctions bound together. Give the Slater function the positive sign if it associates negative spins an even number of times (or not at all) with the first letters in each bond as written, otherwise give it a negative sign. The proof that the functions so formed are eigenfunctions for the operator S^2 , the total angular momentum, proceeds exactly as in the case $M_s=0$.³

The secular equations for a particular independent set of bond eigenfunctions is the same for each value of M_s except for a constant factor multiplying every term in the equations. This factor is smallest for the largest possible M_s for each multiplet. This factor of course divides out of the secular equations and we get the same eigenvalue repeated in a multiplet for each M_s .

² G. E. Kimball and H. Eyring, J. Am. Chem. Soc. **54**, 3876 (1932).

³ H. Eyring and G. E. Kimball, J. Chem. Phys. **1**, 239 (1933).

CALCULATION OF MATRIX COMPONENTS BETWEEN BOND EIGENFUNCTIONS OF ALL MULTIPLICITIES

Bond eigenfunctions with a different number of bonds belong to different multiplets and are noncombining for the energy operator considered in which magnetic terms are neglected. Consider two eigenfunctions with the same number of bonds

$$\psi_1 = a-b \ c-d \ e-g \ f-h \ i-j \ k-l \ m-n,$$

$$\psi_2 = a-c \ b-d \ e-f \ g-h \ i-j \ k-l \ m-n.$$

Now to calculate the matrix component write down the electronic eigenfunctions in order

$$\begin{array}{cccccccccccccccc} a & b & c & d & e & f & g & h & i & j & k & l & m & n \\ +\alpha_1 & \beta_1 & \beta_1 & \alpha_1 & \beta_i & \alpha_i & \alpha_i & \alpha & \alpha_f & \beta_f & \alpha_s & \beta_s & \alpha & \alpha \end{array}$$

and below each letter an α or β is written. We shall call this array of α 's and β 's a sequence. Assign an α or β to an electronic eigenfunction in the following way. If there is a bond in the first eigenfunction between two letters neither of which form part of a bond in the second eigenfunction write α_f under one letter and β_f under the other. The letters $i \ j$ are an example. For a similar bond in the second eigenfunction, as $k \ l$, do the same except use the subscript s . If either eigenfunction has more than one such bond the matrix component is zero to the approximation of first order exchange integrals. If of two letters forming a bond in one of the eigenfunctions for example $e-g$ only one, e , is bonded in the second eigenfunction write α_i under the unbonded letter and β_i under the bonded one. Now continue assigning successively α_i and β_i to the chain of letters connected to these by bonds (connected first in one function and then in the other) until you again come to one which forms part of a bond in one function but not in the other. Here the chain terminates. We shall use the word chain for such a series of atoms to distinguish them from a cycle defined below. The chain $g \ e \ f$ is an example. If there is another chain of this sort do the same using the subscript j . Continue until all chains have been assigned. Now if a letter forms part of a bond in both functions, for example a , write α_1 below it and write β_1 below the letter to which it is bound, b in our example, and below the companion of b

in the second function write α_1 alternating thus around the cycle until you return to the initial letter. Such a cycle in the example is $abcd$. A cycle may contain as few as two letters or as many as all of them. Now if there is a second cycle proceed exactly in the same way using the subscript 2 and so on until all the cycles have been assigned. Finally below letters which are not bonded in either eigenfunction write α without any subscript. We next write a + or - sign before our sequence of α 's and β 's depending on whether to the totality of first letters of bonds in the two functions an even or odd number of β 's have been assigned. In this example four β 's have been assigned so the sign is +. In general if β 's have been assigned p times this sign is $(-1)^p$.

From our sequence we may now tell immediately how many Slater eigenfunctions are common to the two eigenfunctions. If the subscript f or s occurs obviously there are none. If these subscripts do not occur there are 2^m where m is the largest subscript used for numbering the cycles. This is because for each cycle there was really an arbitrary choice of α or β to be assigned to the first letter while outside of cycles there was no choice. The coefficient of the coulombic integral is zero if the subscript f or s occurs otherwise it is $(-1)^p 2^m$. The corresponding coefficient of the energy W in the secular equation is always just the negative of the coefficient of Q .

Case I

If either the subscript f or s occurs on an α as many as two times in a sequence the matrix component is identically zero.

Case II

If both f and s occur as subscripts on but one bond only the four exchange integrals occur which may be formed by taking one of the letters from each of these two bonds. The two integrals corresponding to letters to which like spins have been assigned occur with a plus sign the other two with minus signs. It is to be understood in addition that these quantities are multiplied by the factor $(-1)^p 2^m$. Thus for the two eigenfunctions written down the matrix component is $2(ik+jl-kj-il)$ since $(-1)^p 2^m = 2$.

Case III

Next consider the case where either the subscript f or s does not appear while the other subscript appears only on a single bond. If the bond $k-l$ in eigenfunction ψ_2 is replaced by $g-h$ we have such an example. The sequence would then differ from the former one only in having β_i assigned to h while to k and l are assigned α 's without subscripts. The value of $(-1)^p 2^m$ is unchanged. For this case the only terms appearing will be exchange integrals between one of the two letters in this bond (when the subscript f has been assigned) and a second letter from a chain. All such integrals where like spins have been assigned in the sequence enter with the coefficient 1 while the others have the coefficients -1. All are multiplied by the factor $(-1)^p 2^m$ as before. For the two eigenfunctions just described the matrix component is

$$(-1)^{p+1} 2^m (if + ig + ej + jh - ie - ih - jf - jg).$$

Case IV

Finally consider the case where neither the subscript f or s appears. An example is obtained if in eigenfunction ψ_2 we replace the bond $k-l$ by $i-j$. The sequence would then differ from the one written down in that to both k and l would be assigned α 's with no subscripts and the subscripts associated with i and j would be changed from f to 2. Again it is to be understood that the coefficients given below are all to be multiplied by $(-2)^p 2^m$. The coefficients of the coulombic integral Q and all exchange integrals between letters to which opposite spins with identical subscripts are assigned is then 1; integrals between letters with like spins and like subscripts have coefficients -2; those between letters with positive spin and no subscripts have the coefficient -1; those between letters in cycles and any letter outside the cycle have the coefficient $-\frac{1}{2}$; any integral between a letter in one chain and a second letter outside this chain but not in a cycle with spins alike has the coefficient -1, if the spins are unlike the coefficient is zero.

This gives the general scheme for all multiplicities. For singlets the sequence contains only cycles and the rules reduce to the very simple form already given.^{3, 4, 5} The proof of the rules given follow from the sequence by inspection

using considerations of the type found in the article³ just referred to.

We now consider the simplifications arising in secular equations from molecular symmetry.

GENERAL GROUP THEORETICAL CONSIDERATIONS

We shall state the few group theory propositions required without proof and refer the reader to standard treatises for more detail.^{6, 7, 8} If we have a molecule containing like atoms symmetrically placed certain bonds are equal and the matrix components in the secular equation are entirely unchanged by any rotation or interchange of atoms which simply changes like bonds into like bonds. These operations can be expressed as a group of permutations which acting on any bond eigenfunction changes it into another bond eigenfunction which may or may not be a member of our linear independent set. It can in any case be readily expressed in terms of such a set. The effect of such a permutation on our linear independent set of bond eigenfunctions can be expressed as a matrix and the sum of the terms on the principal diagonal, called its character, is denoted by χ_i . Now the group of operations breaks up into classes such that all members of a class C_i have the same character χ_i . We denote by h_i the number of members in this class. If all the members of a class C_i be multiplied into the members of a class C_j we get a relationship of the type $C_i C_j = \sum_k c_{ijk} C_k$ (3) where c_{ijk} is some integer or zero. The identity, c_1 always constitutes a class by itself; so that χ_1 is the degree of our representation, being simply the number of functions operated upon. For a particular group there is only a limited number of irreducible representations possible, i.e., representations for which no linear combinations of the functions can be found such that they break into two or more sets not transforming into each other for any of the group operations. These may be found by using the relationship $h_i h_j \chi_i \chi_j = \chi_1 \sum_k c_{ijk} h_k \chi_k$ (4) in connection with the set of re-

lationships (3).^{6, 9} The possible choices of the characters in (4) which are consistent with (3) fix the characters of the irreducible representations. Examples will be given later.

Now in molecular problems for each multiplicity we have a linear independent set of bond eigenfunctions as a representation of the group corresponding to the molecular symmetry. This representation, unless especially chosen, is in general reducible for a symmetrical molecule. By taking suitable linear combinations we may break up our representation into equivalent irreducible representations of the group any one of which may fail to appear or may appear once or more times. There is a simple way of determining how often each irreducible representation will appear, however. If for each class we multiply the character, χ_i' , of our reducible representation by the character of the irreducible representation in question, χ_i , and multiply this by the number of members of the class, h_i , the sum of all such quantities divided by the number of members in the group, N , gives the number of times, n , the irreducible representation will appear $1/N \sum_i h_i \chi_i' \chi_i = n$ (5). One other theorem is frequently useful. The average value over all members of the group of the square of the character of the irreducible representation equals the sum of the squares, G , of the number of times each irreducible representation will appear in the reduced representation. $1/N \sum_i h_i \chi_i'^2 = G$ (6).

The advantage of using irreducible representations is that they are non-combining and if a particular one of degree χ_1 occurs but once all χ_1 roots are equal; so that only a linear equation must be solved to get the energy. If a particular irreducible representation occurs l times we must solve an equation of the l -th degree.

Having determined a particular irreducible representation is to appear, very simple means suffice to obtain it. Beginning with any bond eigenfunction from the reducible representation we apply an operation to it and add to it the eigenfunctions which give the proper character for this class. Should this turn out to be impossible this eigenfunction does not occur in this representation and we start with a new one. Having found eigenfunctions which transform

⁴ H. Eyring and G. E. Kimball, J. Chem. Phys. 1, 626 (1933).

⁵ L. Pauling, J. Chem. Phys. 1, 280 (1933).

⁶ A. Speiser, *Theorie der Gruppen*, 2nd edition.

⁷ E. Wigner, *Gruppentheorie*.

⁸ H. Weyl, *The Theory of Groups and Quantum Mechanics*, tr. by H. P. Robertson.

⁹ H. Bethe, Ann. d. Physik 3, 133, 19 (1929).

properly for a member of one class we adjust it to have the proper character for a member of a second class adding functions which do not spoil the first transformation. This is repeated for a member of each class. In some cases it was found easier to start with the most general representation which had the proper character for the first class and specialize it for successive classes. For the identical representation we begin with any eigenfunction and add together all the quantities obtained by operating on it with each member of the group. The linear independence of two representations of the same irreducible representation (equivalent representations) is readily investigated by expressing them in terms of the linear independent set.

AMMONIA

We assume the molecule has one three-fold axis of symmetry and three planes of symmetry. We take the three electronic eigenfunctions on the nitrogen atom as b, d, f and assume they are bonded respectively to the three hydrogen eigenfunctions a, c and e . Our symmetry operations are then C_1 : identity; C_2 : $(ac)(bd), (ae)(bf), (ce)(df)$; C_3 : $(ace)(bdf), (aec)(bfd)$. The relationships (3) are $C_2^2 = 3C_1 + 3C_4$; $C_4^2 = 2C_1 + C_4$ and $C_2C_4 = 2C_2$. These with Eq. (4) give for the characters of the classes of the three irreducible representations:

	C_1	C_2	C_3
Γ_1	1	1	1
Γ_2	1	-1	1
Γ_3	2	0	-1

We take as the linear independent set for the singlets the Rumer set of bond functions: $a-f, b-c, d-e, a-b, c-d, e-f, a-f, b-e, c-d, a-d, b-c, e-f$ and $a-b, c-f, d-e$. The group of operations transform these five eigenfunctions among themselves with only one new eigenfunction appearing $d-a, b-e, c-f$ which by the method of resolving crossed bond functions is readily shown to be just the negative of the sum of the five Rumer functions. We write for the five Rumer eigenfunctions ψ_1 to ψ_5 respectively and ψ_6 for the other eigenfunction. The members of the group are represented by the letters $E, A, B,$

C, D, F respectively. When the operations act on the eigenfunctions in the first line of the table we get the eigenfunctions in the line with the operation.

E	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	5
A	ψ_6	ψ_2	ψ_5	ψ_4	ψ_3	1
B	ψ_6	ψ_2	ψ_3	ψ_5	ψ_4	1
C	ψ_6	ψ_2	ψ_4	ψ_3	ψ_5	1
D	ψ_1	ψ_2	ψ_4	ψ_5	ψ_3	2
F	ψ_1	ψ_2	ψ_5	ψ_3	ψ_4	2

Here the operations in the first column acting on the first row of eigenfunctions give the subsequent rows with the character given in the last column. Using proposition (5) we find there are two irreducible representations of Γ_1 ; one of Γ_2 and one of Γ_3 . These are found almost by inspection to be respectively: $\psi_1 + \psi_6, \psi_2$; $\psi_1 - \psi_6$; and $\psi_3 - \psi_4$ with $\psi_5 - \psi_4$, the latter of course being a two-dimensional representation. The five energies are, respectively, $Q + \alpha - \frac{3}{2}\beta - \frac{3}{2}\gamma - \delta \pm [(2\alpha - 2\delta)^2 + (3\delta - \frac{3}{2}\gamma - \frac{3}{2}\beta)^2]^{\frac{1}{2}}$; $Q - 3\alpha$; and two equal energies with the value $Q - \alpha - 2\delta$. Here the interchange integrals $ab = cd = ef = \alpha$; $ac = ae = ce = \beta$; $bd = bf = df = \gamma$; $ad = af = bc = be = cf = de = \delta$.

TRIPLET STATES

Next consider the triplet terms. These are two bond eigenfunctions and the method of selecting the linear independent set of nine eigenfunctions has been described. In specifying the bond eigenfunctions only the bonded electronic eigenfunctions are written down. Also to further simplify the notation a bond will be indicated by simply writing the two bonded eigenfunctions next to each other leaving a space between atoms not bound together. Thus $ab\ cd$ indicates the bond eigenfunction with a bonded to b and with c bonded to d it being understood that e and f are unbound. A line will be used, however, for one bond eigenfunction to prevent confusing this notation with that for interchange integrals. The linear independent set is then $ab\ cd, ab\ ef, cd\ ef, ab\ de, af\ bc, af\ cd, af\ de, bc\ de, bc\ ef$. By going through precisely the same sort of considerations as for singlets these eigenfunctions break up into two representations of Γ_1 , $\phi_1 = ab\ cd + ab\ ef + cd\ ef$

and $\phi_2 = af\ bc + af\ bd + cb\ de + cb\ df + ed\ fb + ed\ fa$; one representation of Γ_2 , $\phi_3 = ab\ de + dc\ be + ab\ cf + dc\ af + ef\ ad + fe\ cb$; and three representations of Γ_3 , $\phi_4 = ab\ cd + ab\ fe$ with $\phi_5 = ab\ cd + cd\ fe$, $\phi_6 = ac\ bd + fb\ ae$ with $\phi_7 = ac\ bd + ec\ df$, and finally $\phi_8 = ab\ cf + ab\ de + ef\ cb + ef\ da$ with $\phi_9 = dc\ be + dc\ af + ef\ cb + ef\ da$.

These energies lie considerably higher than the lowest singlet and so are not particularly interesting. The matrix components can be readily calculated by the scheme outlined.

QUINTET STATES

For the quintet states we can conveniently take for the five linearly independent single bond functions $[a-b]$, $[a-c]$, $[a-d]$, $[a-e]$ and $[a-f]$. Proceeding as before we get one representation of Γ_1 , $\Omega_1 = [a-b] + [c-d] + [e-f]$; two representations of Γ_3 , $\Omega_2 = [a-e] + [a-f] + [b-f] + [b-e]$ with $\Omega_3 = [c-e] + [c-f] + [d-f] + [d-e]$ and $\Omega_4 = [e-f] + [b-a]$ with $\Omega_5 = [e-f] + [d-c]$.

SEPTET STATES

These states correspond to no bonds and there is a single eigenfunction for each M_s corresponding to this multiplicity, namely the sum of all Slater functions for each M_s . For the largest M_s this eigenfunction is simply the single Slater function with all spins positive and the energy is $Q - 3(\alpha + \beta + \gamma + 2\delta)$. This is the highest possible energy for such a system if all the interchange integrals are negative.

It is interesting to consider under what circumstances the lowest energy for the system corresponds to the energy which would be calculated from ψ_2 , the bond function chemists ordinarily assume. This happens when $\delta = \frac{1}{2}(\beta + \gamma)$ and of course for the much more specialized case when these three integrals are zero. The results given for ammonia apply to all cases of three equivalent bonds, such as might be expected in $C \equiv N$, unless in addition we have symmetry about the plane perpendicular to the triple bond as for example in the case of the nitrogen molecule.

NITROGEN

The additional symmetry in nitrogen over ammonia just doubles the number of group

operations and also the number of classes; so that proceeding exactly as in the case of ammonia we find the characters of the six irreducible representations given in the following table.

	C_1	C_2	C_3	C_4	C_5	C_6
Γ_1	1	1	1	1	1	1
Γ_2	1	1	-1	1	-1	-1
Γ_3	1	-1	-1	1	1	-1
Γ_4	1	-1	1	1	-1	1
Γ_5	2	0	2	-1	0	-1
Γ_6	2	0	-2	-1	0	1
h_i	1	3	1	2	3	2

The last line of the table gives the number of operations in each class. The operations of classes C_1 , C_2 , C_4 are the same, respectively, as C_1 , C_2 , C_3 for ammonia. The other classes may be specified by one operation taken from each; $C_3(ab)(cd)(ef)$; $C_5(ad)(bc)(ef)$; $C_6(adebcf)$. Each of the irreducible representations of ammonia have split into two representations; the first one into the first pair and so on. Exactly the same eigenfunctions form irreducible representations for nitrogen as for ammonia but with the difference that certain eigenfunctions now belong to different representations and are non-combining. The energies are exactly as written for ammonia if we remember that now $\beta = \gamma$. The following is the assignment of eigenfunctions to representations for nitrogen. For the singlets Γ_1 , $\psi_1 + \psi_6$ and ψ_2 ; Γ_3 , $\psi_1 - \psi_6$; Γ_5 , $\psi_3 - \psi_4$ with $\psi_5 - \psi_4$. Triplets Γ_2 , ϕ_1 , and ϕ_2 ; Γ_4 , ϕ_3 ; Γ_5 , ϕ_8 with ϕ_9 ; Γ_6 , ϕ_4 with ϕ_5 and ϕ_6 with ϕ_7 . Quintets Γ_1 , Ω_1 ; Γ_5 , Ω_4 with Ω_5 ; Γ_6 , Ω_2 with Ω_3 .

METHANE

The group of twenty-four symmetry operations includes all the rotations of a regular tetrahedron into itself plus the interchange of two hydrogen atoms, the rest of the molecule remaining fixed. The method of procedure is precisely the same as before. The five irreducible representations have the characters given in the table.

	C_1	C_2	C_3	C_4	C_5
Γ_1	1	1	1	1	1
Γ_2	1	-1	1	1	-1
Γ_3	2	0	2	-1	0
Γ_4	3	1	-1	0	-1
Γ_5	3	-1	-1	0	1
h_i	1	6	3	8	6

The four hydrogen eigenfunctions are indicated by the letters b, d, f, h and they are supposed bound, respectively, to the four carbon eigenfunctions a, c, e, g . The five classes are identified by the five permutations given in order: identity; $(eg)(fh)$; $(ae)(bf)(cg)(dh)$; $(ceg)(dfh)$; $(aceg)(bdfh)$. The representations for the fourteen singlet states are then: three representations of Γ_1 , $\psi_1 = \text{II}$ and $\psi_2 = \text{III} + \text{V} + \text{XIX}$ and $\psi_3 = \text{IV} + \text{VI} + \text{VIII} + \text{XI} + \text{XII} + \text{XIV}$; one of Γ_2 , $\psi_4 = \text{IV}$

—VI—VII—IX+X+XIII; two of Γ_3 , $\psi_5 = \text{V}$ —III with $\psi_6 = \text{V} - \text{XIX}$ and $\psi_7 = \text{XI} + \text{XII} - \text{IV}$ —VI with $\psi_8 = \text{XI} + \text{XII} - \text{XIV} - \text{VIII}$; one representation of Γ_4 , $\psi_9 = \text{VI} - \text{IV}$, $\psi_{10} = \text{VIII} - \text{XIV}$, $\psi_{11} = \text{XII} - \text{XI}$; and finally one representation of Γ_5 , $\psi_{12} = \text{I} - \text{XX}$, $\psi_{13} = \text{XV} - \text{XVII}$, $\psi_{14} = \text{XVI} - \text{XVIII}$. The bond eigenfunctions indicated by the Roman numerals are: I = $ah\ bc\ de\ gf$; II = $ab\ cd\ ef\ gh$; III = $ah\ bg\ cf\ de$; IV = $ab\ ch\ dg\ fe$; V = $ad\ bc\ eh\ fg$; VI = $af\ be\ cd\ hg$; VII = $ah\ bc\ dg\ ef$; VIII = $ah\ bg\ cd\ fe$; IX = $ab\ ch\ de\ fg$; X = $af\ bc\ de\ gh$; XI = $ab\ cd\ eh\ gf$; XII = $ad\ bc\ ef\ hg$; XIII = $ah\ be\ cd\ fg$; XIV = $ab\ cf\ de\ hg$; XV = $ah\ be\ cf\ dg$; XVI = $ad\ be\ ch\ fg$; XVII = $af\ bg\ ch\ de$; XVIII = $af\ bc\ dg\ eh$; XIX = $af\ be\ ch\ dg$; XX = $ad\ bg\ cf\ he$. The last six can be expressed in terms of the first fourteen but nothing is gained by this after linear independence of the eigenfunctions for each representation has been established.

The lowest energy lies in the symmetrical eigenfunctions, Γ_1 , which involves the solution of the cubic:

$$\begin{vmatrix} 4\alpha - 3(\beta + \gamma) - 6\delta - W & 3\alpha - (9/2)(\beta + \gamma) - 3W/4 & 12\alpha - (27/2)(\beta + \gamma) - 9\delta - 3W \\ 3\alpha - (9/2)(\beta + \gamma) - 3W/4 & -9\alpha - 18(\beta + \gamma) + 9\delta - 9W/2 & 9\alpha - (63/2)(\beta + \gamma) + 18\delta - 9W/2 \\ 12\alpha - (27/2)(\beta + \gamma) - 9\delta - 3W & 9\alpha - (63/2)(\beta + \gamma) + 18\delta - 9W/2 & 36\alpha - 72(\beta + \gamma) - 27W/2 \end{vmatrix} = 0.$$

α is the energy of one of the four exchange integrals corresponding to principal bonds; β corresponds to the interaction between hydrogen atoms; γ to the interaction between two bond electrons on carbon and δ to the interaction of an electron on hydrogen with one on carbon to which it is not bound. Examining the cubic it can be seen that if $\delta = (\beta + \gamma)/2$ one root of the equation, the lowest, is the upper principal diagonal element. This is the energy corresponding to ψ_1 the bond function regularly assigned to methane. This eigenfunction is, therefore, probably a rather good approximation. The letter W as written includes only the interchange energy.

The energy corresponding to Γ_2 is $Q - 2\alpha - 6\beta$ where Q is the coulombic binding. The four energies for Γ_3 correspond to taking the plus and minus sign each twice in $Q - (2/3\alpha + 5/3(\beta + \gamma) + 4\delta) \pm 2/3[\alpha^2 + 1/4(\beta + \gamma)^2 + 6\delta^2 + 2(\beta + \gamma)\alpha - 6\alpha\delta - 3(\beta + \gamma)\delta]^{\frac{1}{2}}$. For Γ_4 we have a triple root with energy $Q - 2\beta - 2\gamma - 4\delta$ and for Γ_5 we have a triple root $Q - 2(\alpha + \beta + \gamma + \delta)$.

These results offer some justification for

Woods¹⁰ use of the lowest bond eigenfunction in an approximate calculation. For more accurate results a cubic should of course be used. Van Vleck's¹¹ very interesting papers on methane treat the whole question from a somewhat different point of view.

Instead of using the symmetry group on the bond functions one could first apply it to get representations in terms of Slater functions with subsequent separation of the multiplets. This was carried through for certain of the cases given here but there seemed to be no real advantage and the labor of calculating the final matrix components is greatly increased. The method as outlined seems readily applicable to all symmetrical systems of bond functions.

F. Seitz, A. Sherman and A. E. Stearn have considered this problem from a somewhat different point of view and we wish to thank them for helpful joint discussions.

¹⁰ H. J. Woods, Trans. Faraday Soc. **28**, 877 (1932).

¹¹ J. H. Van Vleck, J. Chem. Phys. **1**, 177 (1933); **1**, 219 (1933).