On the Symmetric States of Atomic Configurations

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In the secular equations used by Eyring and his school the equations are of high order in general. When cognizance is taken of the symmetry of the configuration considered the secular equation may factor considerably. It is to be expected that the wave function for the lowest state will be invariant under the group which expresses the symmetry of the atomic configuration. This expectation is fulfilled in all cases considered. A general method is set forth upon which a derivation of such symmetric states may be carried out, and the reduced secular equation obtained. Several interesting applications of this method are carried through, including the case of eight identical orbits, centered at the corners of a cube, and eight orbits possessing tetrahedral symmetry, as in methane. The vector model is discussed and applied to the cases considered.

§1. Introduction

THE problem of determining the lowest electronic energy-states associated with a given arrangement of atomic nuclei is of considerable importance for purposes of calculating the binding and activation energies of molecules and crystal nuclei. On the basis afforded by Slater's[1] development for the construction of approximate wave functions, with which this paper is solely concerned,[2] such calculations have been carried out in a number of cases.[3]

In all such work attention is focussed upon a number, say n, of electrons between which interactions are considered, and all others, for example electrons in closed shells or valence electrons involved in bonds that are not appreciably altered by changes in the variable parameters met with in the problem, are neglected. Moreover, all terms which arise from spin in the Hamiltonian operator, describing the interactions of these n electrons, are generally neglected so that spin degeneracy is incurred. Under these conditions the Slater eigenfunctions for the n electrons are of the forms

$$\frac{1}{(n!)^{\frac{1}{2}}} \begin{vmatrix} a\zeta_a(1) & b\zeta_b(1) & \cdots & l\zeta_l(1) \\ a\zeta_a(2) & \cdots & & \cdots & \cdots \\ \cdot & & & \\ \cdot & & & \\ \cdot & & & \\ a\zeta_a(n) & \cdots & & \cdots & l\zeta_l(n) \end{vmatrix} \quad (1)$$

where a, b . . . 1 are n one-electron atomic orbital eigenfunctions which depend only upon the space variables and refer to the same or to different atoms. ζ_a is the Kronecker delta-function $\delta(m_s^a, \sigma_i)$, where σ_i is the spin variable of the ith electron, and $m_s^a = +\frac{1}{2}$ or $-\frac{1}{2}$ refers to the z component of spin momentum and the integer in parenthesis refers to the electron of whose variables the product $g\zeta_g$ is a function. In the following we shall also refer to $\delta(\frac{1}{2}, \sigma_i)$ as $\alpha(i)$ and $\delta(-\frac{1}{2}, \sigma_i)$ as $\beta(i)$. These eigenfunctions are clearly eigenfunctions of the operator S_z corresponding to the z component of total spin momentum, and although S^2, the operator corresponding to the squared magnitude of the total spin momentum vector is not diagonal for this representation a simple method of specifying the proper linear combinations has been given by Slater[1] and more generally by Eyring and Kimball,[4] and leads to the concept of bond eigenfunctions, arising as follows:

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[1] Slater, Phys. Rev. 38, 1109 (1931).

[2] There are several other viewpoints from which qualitative investigations of similar problems have been made. Most notable are those of Hund, Mulliken and Van Vleck.

[3] Sherman and Eyring, J. Am. Chem. Soc. 54, 2661 (1932). Kimball and Eyring, ibid. 54, 3876 (1932). Taylor, Eyring and Sherman, J. Chem. Phys. 1, 68 (1933). Pauling and Wheland, ibid. 1, 362 (1933). Pauling and Sherman, ibid. 1, 606 (1933).

[4] Eyring and Kimball, J. Chem. Phys. 1, 239 (1933).

If we consider the entire set of $(n+1)n!$ functions derived from (1) by taking all possible arrangements of columns of α and β these may be divided into $n+1$ sets in each of which functions possessing an equal number of α's and β's are gathered so that each set may be assigned a definite value of S_z. In the set corresponding to $k\alpha$'s there will clearly be $n!/k!(n-k)!$ different[5] Slater functions, all of which shall be assumed to be linearly independent. Now to form an electron pair bond, electrons with antiparallel spins must be present, whence the bond-forming possibilities within any given set are the same for all functions, and the largest number of possible bonds is the smaller of the two quantities k and $n-k$. In any one set a bond function associated with the bonds a–b, c–d $\cdots$ g–h and a preassigned value of S_z is given by the sum

$$\sum \delta_{ab}(j)\delta_{cd}(j)\cdots\delta_{gh}(j)\psi_j,$$

where j ranges over all Slater functions in the set and $\delta_{rs}(j)$ is a function which is 1 if $\zeta_r(j)=\alpha$, $\zeta_s(j)=\beta$, is -1 if $\zeta_r(j)=\beta$ and $\zeta_s(j)=\alpha$, and is zero otherwise.

These functions possess the important property that S^2 is diagonal with respect to them and different values of $S(S+1)$ are associated with functions corresponding to different numbers of bonds so that the matrix components in the Hamiltonian for the system connecting two of these is zero. In particular, the set corresponding to the maximum number of bonds corresponds to the lowest value of S, that is, the state of lowest multiplicity, and since we may generally select n to be even by augmenting each odd case with an electron at infinity, this will be a singlet state.

In practically all problems met with the state of lowest energy is a singlet so that we need only be concerned with the secular determinant corresponding to $S=0$. For even n the dimensionality of this will be

$$\frac{n!}{\left[\left(\dfrac{n}{2}\right)!\right]^2} \frac{n!}{\left(n+1-\dfrac{n}{2}\right)\left(n-1-\dfrac{n}{2}\right)!}$$

$$=\frac{n!}{\left(\dfrac{n}{2}\right)!\left(\dfrac{n}{2}+1\right)!},$$

so that only this number of the

$$(n-1)(n-3)(n-5)\cdots 1 = n!/2^{n/2}(n/2)!$$

possible singlet bond functions are linearly independent. There are obviously many ways in which the proper number of independent bond functions may be chosen but for our purposes that so-called canonical set of Rumer[6] will be of principal interest in view of the additional developments of Pauling.[7]

It was found by Rumer that if the n orbits are arranged at the corners of an n-sided polygon the $n!2^{n/2}(n/2)!$ bond functions corresponding to a non-crossing bond pattern form an independent set,—the so-called canonical one. Moreover, any non-canonical bond eigenfunction may be resolved into a linear combination of canonical ones by successive application of the rule that

$$\diagdown\kern-0.8em\diagup \; = \; \downarrow\uparrow \; - \; \underrightarrow{}\kern-0.9em\underleftarrow{}. \tag{2}$$

Simple rules for writing matrix components between bond eigenfunctions have been given by both Pauling[7] and Eyring and Kimball.[8]

In addition to the fact that the lowest energy level is found in the secular determinant corresponding to $S=0$ it is also to be expected on general grounds that the lowest state will be invariant under the group which expresses the symmetry of the atomic configuration. The basis for this expectation lies in the fact that symmetric states generally possess a lower mean value of kinetic energy for all electrons than other states, and as the mean value of potential energy does not differ greatly for neighboring states the total energy will be lowest for symmetric states. Hence for the purposes of the

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[5] Assuming that none of the orbital functions are present more than once. This assumption does not appreciably affect the generality of the following discussion.

[6] Rumer, Nachr. d. Ges. d. Wiss. zu Göttingen, M. P. Klasse, 337 (1932).

[7] Pauling, J. Chem. Phys. 1, 280 (1933).

[8] Eyring and Kimball, J. Chem. Phys. 1, 626 (1933).

aforementioned applications it is necessary to consider only that part of the secular determinant associated with symmetric states. The purpose of this article is to set forth a general method upon which a derivation of such symmetric states may be carried out. Several interesting applications of this method will be carried through.[9]

§2. THEORETICAL DEVELOPMENTS

The ideal basis upon which to found a discussion of the symmetry properties of functions consists in geometrizing the functions associated with our problem. Thus, with the $n!/2^{n/2}(n/2)!$ canonical bond functions, B_i, we associate a $n!/2^{n/2}(n/2)!$ dimensional *bond-space* which may be regarded as being spanned by this system of linearly independent coordinate vectors. In general, these bond eigenfunctions will not be mutually orthogonal so that the coordinate system is not a unitary one. To each symmetry element $\delta^{(q)}$ of the group describing the symmetry of the atomic configuration under discussion it will be shown that there corresponds a representative matrix $\Delta^{(q)}$ in bond-space. Hence to each transformation

$$\delta^{(q)} \cdot \mathbf{x} = \mathbf{x}', \tag{3}$$

where $\mathbf{x}$ is a vector in ordinary space and $\delta^{(9)}$ is a symmetry operator, there corresponds the equation

$$\Delta^{(q)}\psi = \psi',$$

where ψ is a vector in bond-space. In particular, if ψ is expressed in terms of canonical vectors so that

$$\psi = \sum_i a_i B_i, \tag{4}$$

where the a's are constants and the summation extends over all i then

$$\Delta^{(q)}\psi = \sum_i a_i \Delta^{(q)} B_i$$
$$\sum_i a_i \sum_j \alpha_{ji}^{(q)} B_j$$
$$= \sum_j (\sum_i \Delta_{ji}^{(q)} a_i) B_j \tag{5}$$
$$= \sum_j a_j' B_j,$$

so that

$$a_j' = \sum_i \Delta_{ji}^{(q)} a_i, \tag{6}$$

where $\Delta_{ji}^{(q)}$ is a representation of $\delta^{(q)}$. For the purposes of the present discussion, we are not interested in all of bond-space but only in that part which is spanned by the complete system of vectors satisfying the relation

$$\Delta^{(q)}\psi = \psi, \tag{7}$$

where q runs through all elements of the group, —that is, in the invariant sub-space associated with the symmetry group. Since the representations of any group may be easily found for a canonical coordinate system by use of the rule (2) the determination of the sub-space may be found directly by solving the equations

$$a_j = \sum_i \Delta_{ji}^{(q)} a_i. \tag{8}$$

In actual practice we need only be concerned with the generating elements of the group since any vector which is invariant under these will be invariant under the entire group.

Concerning the construction of the representation of a given symmetry operation, this may be easily carried out if each operation, which corresponds to a rearrangement of orbits, sends canonical functions into bond functions, for if this is true the elements in the column associated with each bond function in the representation of a given operator are just the coefficients of the canonical functions when the equivalent bond-function is resolved in terms of the canonical set. It is easily shown, however, that the required condition is satisfied. For example, if $a\ b\ c\ \ldots\ 1$ is a normal arrangement of orbit-columns as shown in (1), which arrangement will appear in all Slater functions occurring in a given bond-function, and a given symmetry operation is carried out, these columns will undergo a permutation. All determinants will be brought back to the normal form by the same number of permutations of their columns, which will introduce a factor $(-1)^p$ where p is the order of the required permutation. This is equivalent to a rearrangement of electron-orbit columns accompanied by a possible change of sign. Because each of the electron-function columns in the different Slater functions comprising a given bond function

[9] Mulliken, J. Chem. Phys. **1**, 492 (1933), considers symmetric states for the purposes of his viewpoint. His methods of arriving at these are, however, essentially different from those used in this paper.

are permuted in exactly the same way, the new function, to within a sign, is the bond function corresponding to the rearrangement of bonds induced in a bond pattern by the symmetry operation.

Although the states of lowest multiplicity are kept uppermost in this discussion, the foregoing development is by no means restricted so as to be applicable to these alone, but is as general as the concept of bond-eigenfunctions.[10]

With these facts at our disposal we may now proceed with the construction of the group-representations and the solving of the equations (8) in particular cases.[11]

§3. APPLICATIONS

(1) Polygonal configurations

The simplest non-trivial examples of the use of the foregoing theory occurs when the configuration of orbits under consideration form a ring structure possessing the symmetry of one of the dihedral groups D_n (i.e., the symmetry of a plane polygon). In the case for which n is even, which is the only interesting one since, for example, it corresponds to the six free orbits of C_6H_6 or the eight free electrons of C_8H_8, the group may be generated by a rotation of angle $2\pi/n$ about the axis of symmetry and a reflecting plane passing through diametrically situated centers. The Rumer polygon in this case may be selected to coincide with the structure polygon

so that the manner in which the symmetry operators affect the bonds will be closely connected with the manner in which the orbits are rearranged by the same operators. Since the case $n=6$ is a typical example and is also of particular interest we shall consider it in detail. The five canonical bond patterns for this problem are illustrated in Fig. 1, where the arrowhead
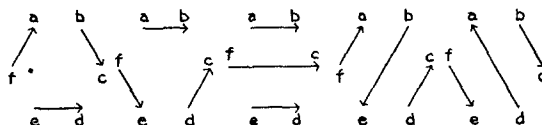

FIG. 1. Canonical bond eigenfunctions for 6 electrons.

marks the electron with spin α and the tail that with spin β. A simple rotation through an angle $\pi/3$ corresponds to an odd permutation of orbits, whence the resultant bond function in any one case is the negative of that obtained by rotating the bond pattern. The reversal of the direction of one arrow in the bond pattern is equivalent to changing the sign of the associated function so it follows at once that B_I is sent into B_{II}, and B_{II} into B_I. Similarly B_{III} is sent into B_{IV}, B_{IV} into B_V and B_V into B_{III}. On the other hand, a reflection in a line passing through fc corresponds to an even permutation so that under this operation B_I and B_{II} are interchanged, B_{III} is sent into itself, while B_{IV} and B_V are also interchanged. From these properties it is clear without further investigation that the invariant subspace in this five dimensional bond-space is two dimensional and is spanned by all vectors of the form

$$\Phi = a(B_I + B_{II}) + b(B_{III} + B_{IV} + B_V), \quad (9)$$

where a and b are arbitrary to within normalization. The secular equation in terms of the two functions $B_I + B_{II}$, and $B_{III} + B_{IV} + B_V$ is, after simplification[12]

$$\begin{vmatrix} Q - 4\alpha + \gamma - E & 2(\alpha - \gamma) \\ 2(\alpha - \gamma) & Q + 2\alpha - 6\beta + \gamma - E \end{vmatrix} = 0, \quad (10)$$

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[10] Eyring, Frost and Turkevich in a forthcoming paper have treated several cases for all possible multiplicities, but from a somewhat different viewpoint. We are indebted to them for the opportunity of seeing their manuscript.

[11] A general and straightforward method of obtaining the functions going with all of the representations is had by making use of the equation

$$(h/l_j)\psi_k{}^j = \Sigma_R \mathfrak{D}_{kk}{}^{(j)}(R)\mathbf{P}_R F$$

(see E. Wigner, *Gruppentheorie*, 1931, page 123, Eq. (6)) in which ψ_k belongs to the kth row of the jth irreducible representation of dimensionality l_j, whose elements are $\mathfrak{D}_{ik}{}^{(j)}(R)$, R runs through all h elements of the group. $\mathbf{P}_R$ is the operator associated with R and F is an arbitrary function. The representations are assumed known or may be derived by reduction of the generating elements of the group in a spherical harmonic coordinate system under the guiding knowledge afforded by Bethe's work (Ann. d. Physik **3**, 133 (1929)).

[12] This corresponds to the usual procedure where overlap terms and multiple exchanges are neglected. In the following we shall evaluate coulombic and exchange integrals empirically by the use of Morse P.E. curves for pairs of electrons on different atoms (H. Eyring, Naturwiss. **18**, 915 (1930)).

where Q is the coulombic energy for the system and α, β and γ are the interchange integrals between a and b, a and c, and a and d, respectively.

Solving Eq. (10) algebraically we find

$$E = Q - \alpha - 3\beta + \gamma$$
$$\pm (13\alpha^2 + 9\beta^2 + 4\gamma^2 - 18\alpha\beta - 8\alpha\gamma)^{\frac{1}{2}}. \quad (11)$$

The lowest of the two possible values corresponds to the $+$ sign in (11). Using $Q = 78.7$, $\alpha = 64.8$, $\beta = 12.9$, and $\gamma = 5.8$ kg cal. gives $E = 176.4$ kg cal. That this is actually the lowest possible eigenvalue associated with these values of α, β and γ was shown by a direct investigation of the 5th order secular equation. The values of a and b in (9) are found to be 0.450 and 0.147, respectively, for Φ normalized to 1. Thus the expectation that the lowest state is symmetric is fully borne out.

(2) Eight identical orbits centered at the corners of a cube

For the configuration consisting of eight identical orbits situated at the corners of a cube the symmetry group is O^h and possesses 48 elements. It may be generated, however, by a 3-fold axis passing through C of Fig. 2, a 4-fold axis passing orthogonally through the center of the square $cdef$, and an inversion at the center of the cube. There are 14 canonical bond eigenfunctions in this case, illustrated in Fig. 3.
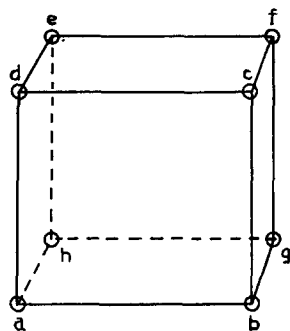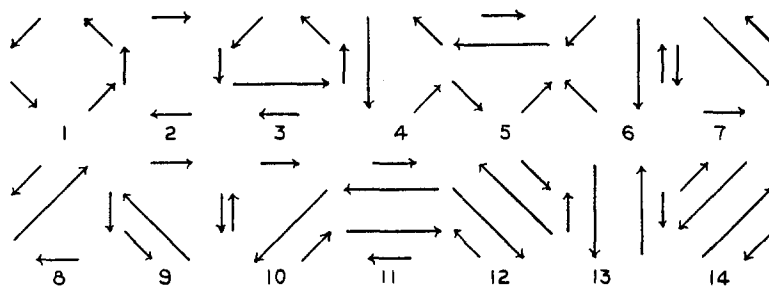

FIG. 2. 8 identical orbits centered at cube corners.

FIG. 3. Canonical bond eigenfunctions for 8 electrons, e.g., 2 is the bond eigenfunction ab, cd, ef, gh.

The three representations of the generating elements in this coordinate system are as follows:

0	0	0	0	0	0	1	0	1	0	-1	0	-1	0
0	0	-1	-1	0	0	-2	0	0	0	0	0	0	1
0	0	0	0	0	0	-1	0	0	0	0	0	1	0
0	0	-1	0	0	1	-1	0	0	0	0	0	1	0
0	0	0	-1	1	0	-1	0	0	0	1	0	0	0
0	0	0	0	0	0	-1	0	0	0	1	0	0	0
0	0	1	0	0	0	1	1	0	0	0	0	-1	0
0	0	0	0	0	0	1	0	0	0	0	0	0	0
0	0	0	1	0	0	1	0	0	1	-1	0	0	0
1	0	1	1	0	0	1	0	0	0	0	0	0	0
0	0	0	1	0	0	1	0	0	0	0	0	0	0
0	1	0	0	0	0	0	0	0	0	1	0	1	0
0	0	1	0	0	0	1	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1	0	0

(12)

Three-fold

0	0	0	0	0	0	1	0	1	0	−1	0	−1	0
0	0	0	0	−1	−1	0	0	−2	0	0	0	0	1
0	0	0	0	0	0	0	0	−1	0	0	0	1	0
0	0	0	0	0	0	0	0	−1	0	1	0	0	0
0	0	1	0	0	−1	0	0	−1	0	1	0	0	0
0	0	0	1	−1	0	0	0	−1	0	0	0	1	0
0	0	0	0	0	0	0	0	1	0	0	0	0	0
0	0	0	0	1	0	0	0	1	1	0	0	−1	0
1	0	0	0	1	1	0	0	1	0	0	0	0	0
0	0	0	0	0	1	0	1	1	0	−1	0	0	0
0	0	0	0	0	1	0	0	1	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1	0	0
0	0	0	0	1	0	0	0	1	0	0	0	0	0
0	1	0	0	0	0	0	0	0	0	1	0	1	0

(13)

Four-fold

1	0	0	0	0	0	0	0	0	0	0	0	0	0
−2	1	−1	−1	−1	−1	0	0	0	0	0	0	0	0
−1	0	0	0	−1	0	0	0	0	0	0	0	0	0
−1	0	0	0	0	−1	0	0	0	0	0	0	0	0
−1	0	−1	0	0	0	0	0	0	0	0	0	0	0
−1	0	0	−1	0	0	0	0	0	0	0	0	0	0
1	0	0	0	1	1	0	0	1	0	0	0	0	0
1	0	0	1	1	0	0	0	0	1	0	0	0	0
1	0	1	1	0	0	1	0	0	0	0	0	0	0
1	0	1	0	0	1	0	1	0	0	0	0	0	0
1	0	1	0	1	0	0	0	0	0	1	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1	0	0
1	0	0	1	0	1	0	0	0	0	0	0	1	0
0	0	0	0	0	0	0	0	0	0	0	0	0	1

(14)

Inversion

By solving the Eqs. (8) we find the relations

$$a_1 = 2a_7 - 2a_{11}, \quad a_3 = a_4 = a_5 = a_6 = -a_7 + a_{11}, \quad a_8 = a_9 = a_{10} = a_7, \quad a_{12} = a_{14} = a_2 + 2a_{11}, \quad a_{13} = a_{11}, \quad (15)$$

so that the invariant sub-space is of dimensionality three and is spanned by the vectors

$$\Psi_1 = B_2 + B_{12} + B_{14},$$
$$\Psi_2 = -2B_1 + B_3 + B_4 + B_5 + B_6 - B_7 - B_8 - B_9 - B_{10}, \quad (16)$$
$$\Psi_3 = -2B_1 + B_3 + B_4 + B_5 + B_6 + B_{11} + 2B_{12} + B_{13} + 2B_{14},$$

which yields after suitable reduction the following secular equation

$$\begin{vmatrix} Q + 2\alpha - 8\beta - 2\gamma - E & -(4/7)^{\frac{1}{2}}(\alpha + 2\beta - 3\gamma) & (20/7)^{\frac{1}{2}}(2\alpha - 3\beta + \gamma) \\ -(4/7)^{\frac{1}{2}}(\alpha + 2\beta - 3\gamma) & Q - (46\alpha + 32\beta - 22\gamma)/7 - E & (20/49)^{\frac{1}{2}}(4\alpha - 3\beta - \gamma) \\ (20/7)^{\frac{1}{2}}(2\alpha - 3\beta + \gamma) & (20/49)^{\frac{1}{2}}(4\alpha - 3\beta - \gamma) & Q - (24\alpha + 24\beta + 8\gamma)/7 - E \end{vmatrix} = 0, \quad (17)$$

when Q is the coulombic integral for the system, α denotes the exchange integral between a and b, β that between a and c, and γ that between a and f.

That this eigenvalue is really the one for the lowest state may be seen if one computes the energy for eight Na atoms at the corners of a cube, and compares the value with that given by Taylor, Eyring and Sherman[13] which was obtained by a direct solution of the 14th order secular equation. For a cube edge of 3.15A the following values of Q, α, β and γ were used:

$$Q = 94.4 \text{ kg cal.}; \qquad \alpha = 12.69; \qquad \beta = 6.88; \qquad \gamma = 3.37.$$

Eq. (17) gives $E = 69.9$ kg cal., which is to be compared with the value 68.1 kg cal. found by the other authors. This difference is within their computational error.

(3) Eight orbits possessing tetrahedral symmetry

The next case which we shall consider is that in which the arrangement of orbits possesses the symmetry group of a tetrahedron (T^d). This arrangement is met with, for example, in methane in which the four hydrogen atoms are situated at the four corners of a tetrahedron relative to the carbon atom at the center. A schematic diagram of the orbits is given in Fig. 4 in which the carbon orbits are designated by circles in circles and those of hydrogen atoms by dots in circles. The line connecting neighboring circles and dots is understood to be a prolongation of a body diagonal. The generating elements of the group T^d may be taken to be a three-fold rotation about the body diagonal through c and a vertical reflecting plane passing through df. With the canonical set of bond functions taken to be associated with Fig. 4 the representation of the threefold rotation is the same as (12), while that of the reflecting plane is

$$
\begin{bmatrix}
1 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 1 & 1 & 0 & 1 & 1 & 1 \\
0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 & 0 & -1 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & -1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & -1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & -1
\end{bmatrix}
\qquad (18)
$$

Plane

The invariant subspace associated with this group is three dimensional and consists of the space spanned by the vectors

$$\psi_1 = B_5, \qquad \psi_2 = -3B_1 + B_4 + B_6 - 2B_9 - 2B_{10} + B_{11} + B_{12} + B_{14},$$

$$\psi_3 = -B_1 - 2B_2 + B_3 - B_4 - B_6 + B_7 + B_8 + 2B_{13},$$

and the secular determinant after suitable reduction is found to be[14]

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[13] Taylor, Eyring and Sherman, J. Chem. Phys. 1, 68 (1933). Eyring and Kimball, J. Chem. Phys. 1, 626 (1933).

[14] This equation has also been independently obtained by Eyring, Frost and Turkevich.

$$\begin{vmatrix} Q+4\alpha-3\beta-3\gamma-6\delta-E & 0 & (9/2)^{\frac{1}{2}}(-\beta-\gamma+2\delta) \\ 0 & Q-4\alpha-\beta-\gamma-2\delta-E & (5/2)^{\frac{1}{2}}(-\beta-\gamma+2\delta) \\ (9/2)^{\frac{1}{2}}(-\beta-\gamma+2\delta) & (5/2)^{\frac{1}{2}}(-\beta-\gamma+2\delta) & Q-4\beta-4\gamma-E \end{vmatrix} = 0, \qquad (19)$$

where α, β, γ and δ are the exchange integrals between ch, ah, bc and ac, respectively.
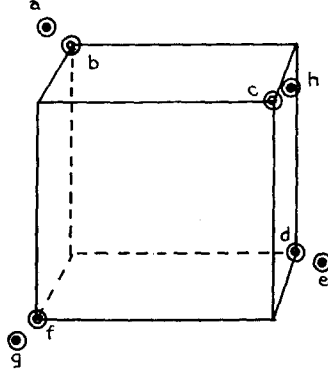

FIG. 4. 8 orbits possessing tetrahedral symmetry.

§4. VECTOR MODEL

As pointed out to us by Professor Van Vleck, our secular Eqs. (17) and (19) may be checked in various limiting cases with the aid of the vector model.[15] Use of the model is possible because the secular problem connected with the permutation degeneracy is formally equivalent, except for an additive constant, to that of cosine coupling between the spin vectors. This has been shown by Dirac, who demonstrated that the exchange effects between two states i and j are equivalent to a potential $-\frac{1}{2}J_{ij}[1+4s_i\cdot s_j]$, where J_{ij} is the exchange integral connecting i and j. The complete Hamiltonian function is therefore $Q-\frac{1}{2}\sum J_{ij}(1+4s_i\cdot s_j)$. The determination of the characteristic values of this function is in general quite complex, but if J_{ij} has the same value J for all pairs it may be taken outside the summation. Now consider the configuration of 8 orbits centered at cube corners, for the following cases:

(1) $\alpha=\beta=\gamma$. There are 8 electrons, 28 pairs.

$$\therefore \quad E=Q-\frac{1}{2}\sum_1^{28}\alpha-2\alpha\sum_{j>i}s_i\cdot s_j=Q-14\alpha-2\alpha\sum_{j>i}s_i\cdot s_j.$$

Since $\sum s_i=0$, and $s_i^2=\frac{3}{4}$, we have $\sum s_i^2+2\sum s_i\cdot s_j=S(S+1)=0$, and $2\sum s_i\cdot s_j=-\frac{3}{4}\times 8=-6$.

$$\therefore \quad E=Q-14\alpha+6\alpha=Q-8\alpha.$$

(2) $\alpha=\gamma=0$. Here the eight electron problem reduces to two identical four electron problems and the J can be taken outside the summation. From Fig. 2 it is clear that there are six β's,—i.e., six surface diagonals,—associated with each group of four electrons. Therefore,

$$E=Q-2[\frac{1}{2}\beta\sum(1+4s_i\cdot s_j)]=Q-2[3\beta+\beta\{S(S+1)-\frac{3}{4}\cdot 4\}],$$

where S is the total spin of the four electrons, which may equal 2, 1 or 0 in this case.

[15] See Dirac, Proc. Roy. Soc. **A123**, 714 (1929) or Dirac, *Quantum Mechanics*, Chapter XI, and Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, Chapter XII. The vector model will also be discussed in forthcoming papers by Van Vleck and Serber.

$$\therefore \quad E = Q - 2[3\beta + \beta(6-3)] = Q - 12\beta \qquad \text{for } S = 2,$$
$$E = Q - 2[3\beta + \beta(2-3)] = Q - 4\beta \qquad \text{for } S = 1,$$
$$E = Q - 2[3\beta + \beta(0-3)] = Q \qquad \text{for } S = 0.$$

These are all roots of (17) in this case.

(3) $\alpha = \beta = 0$. Referring to Fig. 2, there is only one body diagonal leaving any one corner, so that the problem obviously falls into four two-electron problems. The exchange energy in each of the four cases may be either $+\gamma$ or $-\gamma$, but since the total spin of the eight electrons is zero, E may equal either $Q \pm 4\gamma$, Q, or $Q - 2\gamma$. These are not all necessarily roots of (17) because this secular equation is associated with a symmetric wave function. Actually, the first three values of E are roots of (17).

Consider now the case of 8 orbits possessing tetrahedral symmetry, for the following cases:

(1) $\alpha = \beta = \gamma = \delta$. This will obviously give the same result as 1 above.

(2) $\beta = \gamma = \delta = 0$. The secular problem is the same as 3 above, the characteristic values of each two-electron problem being either $+\alpha$ or $-\alpha$. E may equal $Q \pm 4\alpha$, Q or $Q - 2\alpha$. The first three values are all roots of (19) in this case.

(3) $\alpha = \delta$, β and $\gamma \neq 0$. Here the Hamiltonian function becomes

$$Q - 8\alpha - 3\beta - 3\delta - 2\alpha \mathbf{S}_C \cdot \mathbf{S}_{4H} - 2\beta \sum \mathbf{s}_i \mathbf{s}_j - 2\gamma \sum \mathbf{s}_i \mathbf{s}_j$$
$$= Q - 8\alpha - 3\beta - 3\delta - \alpha[\mathbf{S}^2_{CH_4} - \mathbf{S}^2_C - \mathbf{S}^2_{4H}] - \beta[\mathbf{S}^2_{4H} - \tfrac{3}{4} \cdot 4] - \gamma[\mathbf{S}^2_C - \tfrac{3}{4} \cdot 4],$$

where $\mathbf{S}_C = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \mathbf{s}_4$ denotes the spin of the carbon electrons and $\mathbf{S}_{4H} = \mathbf{s}_5 + \mathbf{s}_6 + \mathbf{s}_7 + \mathbf{s}_8$ the collective spin of the four hydrogen electrons. In other words, the total spin of the carbons, and of the four hydrogen electrons, are good quantum numbers. The characteristic values of $\mathbf{S}^2_{CH_4} = S_{CH_4}(S_{CH_4} + 1)$, $\mathbf{S}^2_C = S_C(S_C + 1)$, $\mathbf{S}^2_{4H} = S_{4H}(S_{4H} + 1)$, where S_{CH_4}, S_C and S_{4H} are the total spins of CH_4, C and 4H's, respectively. The resultant spin of CH_4 is 0. Therefore S_C and S_{4H} must be equal and may of course be equal to 2, 1 or 0, corresponding to the values $Q + 4\alpha - 6(\beta + \gamma)$, $Q - 4\alpha - 2(\beta + \gamma)$ and $Q - 8\alpha$ for the Hamiltonian, respectively.