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The Solution of Problems Involving Permutation Degeneracy

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Matrix methods are developed for calculating the energy levels of many electron systems. These methods are based on the intimate relation between the energy matrix and the irreducible representations of the symmetric permutation group. Part I deals with the "pure matrix method," which involves explicit calculation of the matrices representing the permutations. The permutation matrices are given for states of various multiplicities arising from configurations of eight or fewer electrons. From these we obtain a very convenient orthogonal representation of the energy matrix. In particular, for symmetrical polyatomic molecules, it is shown that correct labelling of the orbits leads directly to a partial factorization of the secular determinant. A systematic procedure is given for determining just how this factorization can be achieved. Part II takes up the "algebraic method," which makes use of algebraic relations satisfied by the permutations. Explicit representations of the permutations are not required if this method is employed. The procedure is illustrated by the four electron problem, including non-orthogonality corrections. The interactions between configurations can also be calculated by the algebraic method. For symmetrical polyatomic molecules, the group of symmetry operators which commute with the Hamiltonian function can be used to obtain the secular equation in a factored form. The factorization is complete in the group theory sense. A number of illustrative examples are worked out, the energy levels of all multiplicities being found for the hexagonal (benzene) configuration, the configuration of eight similar orbits at cube corners, and the body-centered cube. The singlet levels of the tetrahedral (methane) configuration are also given.

§1. INTRODUCTION

TWO types of attack have been developed for calculating energy levels in problems involving permutation degeneracy. The more commonly employed, the wave method, is based on the use of Slater wave functions, or of "bond eigenfunctions." The second type, comprising the matrix methods, is based upon the fact that the portion of the Hamiltonian function arising from a single configuration of n non-identical electrons and having a given characteristic value, S, of the total spin, is of the form[1]

$$H = \Sigma_P H_P P. \qquad (1)$$

Here the permutation integrals, H_P, are numerical constants, and the matrices P are irreducible representations of the elements of the symmetric permutation group of n objects. The particular irreducible representation to be used is determined by the value assigned to S. The modifications of (1) required when pairs of orbits are identical, as well as the extension of the method to include interactions between configurations, have been treated by the writer in a previous paper,[2] which will be referred to as I.

The fundamental equation, (1), can be employed in a variety of ways. The most direct method, of course, is to calculate the matrices P explicitly and solve the resulting secular determinant. This will be termed the "pure matrix method." It has been discussed in I, and will be further considered in Part I of this paper.

Instead of actually calculating the P's, as contemplated in the pure matrix method, one may utilize the Dirac vector model, which expresses the P's in terms of spin variables. This vector model has been very ingeniously applied by Van Vleck to problems of complex and molecular spectra and of ferromagnetism.[3] Of course, if it were actually necessary to find the matrices representing the spin variables, the distinction between the pure matrix method and the vector model would be entirely trivial. However, as Van Vleck has shown, many problems can be solved very simply by use of algebraic relations satisfied by the spins. Van Vleck's method may accordingly be more properly classified as an algebraic, rather than as a pure matrix one, the elements of the algebra being the electronic spin vectors.

Much the same sort of simplification can be achieved by considering the algebra whose ele-

[1] P. A. M. Dirac, *The Principles of Quantum Mechanics*, Chapter XI; E. Wigner, Zeits. f. Physik **40**, 883 (1927).
[2] R. Serber, Phys. Rev. **45**, 461 (1934).

[3] J. H. Van Vleck, Phys. Rev. **45**, 405 (1934); *The Theory of Electric and Magnetic Susceptibilities*, Chapter XII.

ments are the permutations P. The use of this algebra, which will be discussed in Part II of this paper, is more convenient than the use of the spin algebra when permutations of higher order than simple interchanges are involved, or when group theory can be employed to factor the secular determinant.

Before proceeding with the applications of (1), a brief description will be given of some results of the theory of the symmetric permutation group which are of particular importance in our work.[4]

§2. THE PRIMITIVE CHARACTERS OF THE SYMMETRIC PERMUTATION GROUP

The usual cyclic notation for the permutations will be employed.[5] Thus, I is the identity element, (12) represents the interchange of orbits one and two, (123) the permutation which replaces orbit one by two, two by three, and three by one, and so forth. The primitive character of a permutation belonging to the class specified by the partition[6] $a_1 + a_2 + \cdots + a_p = n$, for any given irreducible representation of the symmetric permutation group, will be denoted by $[a_1 a_2 \cdots]$, only the a's different from unity being written down. Thus the primitive character of (12) is written $[2]$, while that of (123)(45) is written $[32]$. The primitive character of the identity element will be symbolized by $[I]$. It should be borne in mind that the primitive character of a permutation P is simply the spur of the matrix representing P, and is the same for all permutations belonging to a given class.

The primitive characters of the P's appearing in (1) are given by the following rule:[7]

The primitive character of a permutation belonging to the class $a_1 + a_2 + \cdots + a_p = n$ is the coefficient of x^k in

$$(-1)^{n-p}(1-x)(1+x^{a_1})(1+x^{a_2})\cdots(1+x^{a_p}),$$

where $k = \frac{1}{2}n - S$. The explicit appearance in this formula of S, the characteristic value of the total spin, is a consequence of the fact that the value

[4] For a more complete account of the theory of this group, the reader is referred to E. Wigner, *Gruppentheorie*, Chapter XIII.
[5] E. Wigner, reference 4, p. 134.
[6] E. Wigner, reference 4, p. 135.
[7] E. Wigner, reference 4, pp. 149, 196.

assigned to S determines the particular irreducible representation to be used in (1).

It follows immediately from this rule and (1) that the number of states of multiplicity $2S+1$ arising from a configuration of n non-identical orbits is

$$[I] = \binom{n}{k} - \binom{n}{k-1}. \qquad (2)$$

If the configuration contains r pairs of identical orbits, n in this formula must be replaced by $n - 2r$.

I. THE PURE MATRIX METHOD

§3. THE IRREDUCIBLE REPRESENTATIONS OF THE PERMUTATION GROUP FOR $n \leq 8$

The matrices P, representing the permutations, have been calculated for the singlet states of an eight electron system by the method described in I. The results for a number of simple interchanges, i.e., permutations of the form (12), are listed on the following page. The interchanges (12), (34), (56) and (78) are diagonal in the representation we have employed, hence it suffices simply to list their characteristic values. The interchanges which are not tabulated can very easily be obtained from the ones we have given. For example, (23) can be found by use of the relation $(23) = (12)(13)(12)$, which, in view of the diagonal form of (12), tells us how to obtain (23) simply by changing certain signs in (13). Similar relations, involving only changes in sign, suffice to determine all the remaining interchanges. Any permutation of higher order can of course be written as a product of interchanges.[8]

The representation has been so chosen that the matrices P for $n < 8$ can also be read directly from the ones given. The interchanges corre-

Characteristic Values of the Diagonalized Interchanges													
						States							
1	2	3	4	5	6	7	8	9	10	11	12	13	14
(12) −1	−1	−1	1	−1	1	−1	−1	1	−1	−1	1	−1	1
(34) −1	−1	1	−1	−1	1	−1	1	−1	−1	1	−1	−1	1
(56) −1	−1	−1	−1	1	−1	1	1	1	−1	−1	−1	1	1
(78) −1	−1	−1	−1	−1	−1	−1	−1	−1	1	1	1	1	1

[8] In taking the product of two permutations, PP', the convention we adopt is that P' operates first on any function of the orbits. For example, (12)(23) = (123).

(15)

(17)

(57)

(13)

(35)

(37)

sponding to $n=7$, $S=\frac{1}{2}$ are identical with those for $n=8$, $S=0$ if all interchanges referring to orbit 8 are omitted. Such a relation always holds between the representations for n, $S=0$ and those for $n-1$, $S=\frac{1}{2}$. It will be observed that each of the fifteen interchanges involving only orbits one to six factors into two parts. The larger, containing states one to nine, gives the representation for $n=6$, $S=1$. The smaller, containing the last five states, gives the representation for $n=6$, $S=0$. Similarly, for the six interchanges involving only orbits one to four, the representations for $n=6$, $S=0$ factor into the representations for $n=4$, $S=1$, and for $n=4$, $S=0$, the former corresponding to states 10, 11, 12, the latter to states 13 and 14.

Substitution of any of these representations of the P's into (1) leads to an orthogonal representation of the energy matrix, i.e., if permutation integrals of unity are neglected, W and the Coulomb integrals appear in the secular determinant only on the main diagonal. The representations of H obtained in this way have several advantages over the orthogonal representations used by Eyring and his co-workers.[9] For one thing, the energy matrix is normalized, and the very convenient spur theorem can consequently be employed. Also, our representation is well adapted to the use of perturbation theory when electron pair bonding is nearly a good approximation, e.g., for $n=8$, $S=0$, when four exchange integrals are much larger than all the others. This follows from the fact that (12), (34), (56), (78) are all diagonal, hence, if the orbits are labelled so that the large exchange integrals are H_{12}, H_{34}, $\cdots$, only small terms appear off the diagonal. It should be noted that state 14 corresponds to pure electron pair bonding, (12), (34), (56) and (78) all being 1 for this state, and the average value of all other interchanges being $-\frac{1}{2}$. It is essential to have (12), (34) $\cdots$ diagonal in considering the interactions between configurations if pairs of orbits of any configuration are identical. And finally, as will be shown in the following section, partial factorization of the secular determinant can readily be obtained for symmetrical molecules. Taylor, Eyring and Sherman[9] have

[9] H. S. Taylor, H. Eyring and A. Sherman, J. Chem. Phys. 1, 68 (1933); H. Eyring and G. E. Kimball, J. Chem. Phys. 1, 239 (1933).

pointed out that for such molecules correct labelling of the orbits sometimes leads to factorization. The use of our representations greatly increases the possibilities along this line, and in addition a systematic method is afforded for determining how the factorization may be achieved.

§4. Symmetrical Molecules

In dealing with symmetrical molecules, the secular determinant can usually be factored if a little attention is paid the group of symmetry operations (rotations and reflections) which commute with the Hamiltonian function. For a single configuration of similar orbits, these symmetry elements form a subgroup of the symmetric permutation group. It should be noted that by "permutation" we always mean a permutation of the orbits. It we were thinking of permutations of the coordinates, the remark that the elements of a subgroup of such permutations commute with the Hamiltonian function would be entirely trivial, as, in fact, all permutations of the coordinates commute with the Hamiltonian function. However, the situation is very different when we refer to permutations of the orbits, since it is obvious from (1) that permutations of this type in general do not commute with H. The existence, in a particular problem, of certain permutations which do, is consequently a real aid. When interactions between configurations must be considered, symmetry elements may correspond to permutations of the configurations among themselves, as well as to permutations of orbits within a configuration.

The procedure to be followed can best be explained by reference to a specific example. Let us consider the model of the benzene molecule consisting of six similar orbits placed at the vertices of a regular hexagon. The symmetry operations form the holohedral hexagonal group D_{6h}. However, since inclusion of the inversion element leads to no added simplification, it is sufficient to consider only the twelve elements of the hemohedral group, D_6. The primitive characters for this group may be found in Mulliken's convenient tables.[10] We shall follow Mulliken's terminology for the irreducible representations; thus the let-

[10] R. S. Mulliken, Phys. Rev. 43, 279 (1933).

ters A and B are used for irreducible representations of the first degree, E and T for representations of the second and third degrees, respectively. The classes will be labelled C_1, C_2, $\cdots$ in the order in which they appear in Mulliken's tables.

Proceeding around the hexagon in a clockwise direction, denote the orbits by 1,6,4,2,5,3. Each symmetry operation is evidently equivalent to a permutation of the orbits. For example, a clockwise rotation through $\pi/3$ around the sixfold axis induces the permutation (164253), while a rotation through π about the line through 1 and 2 induces the permutation (36)(45). A typical element of each class is: C_1, I; C_2, (12)(34)(56); C_3, (145)(623); C_4, (164253); C_5, (36)(45); C_6, (16)(34)(25).

Consider first the singlet states. The irreducible representation of the symmetric permutation group corresponding to $n=6$, $S=0$ is, of course, a reducible representation of the group D_6. The character in this representation, $\chi(C_i)$, of an element of C_i is given by the rule of §2. Thus $\chi(C_1)=[I]=5$, $\chi(C_2)=[222]=3$, $\chi(C_3)=[33]=2$, $\chi(C_4)=[6]=0$, $\chi(C_5)=[22]=1$, $\chi(C_6)=[222]=3$. The number of times each irreducible representation of D_6 appears in our fifth degree representation of the symmetric permutation group can now be determined in the usual way.[11] One finds that A_1 appears twice, B_2 and E^* each once.

We shall not attempt to obtain immediately complete factorization of the secular determinant into a quadratic factor and three linear factors, but content ourselves with the partial factorization which results directly from the fact that (12), (34) and (56) are diagonal. It will be observed that the scheme of labelling orbits we have employed diagonalizes the symmetry element (12)(34)(56), belonging to C_2. Relabelling the orbits in any way of course corresponds to a canonical transformation of the energy matrix, the transformation matrix being simply the representation of the permutation which changes the old labelling scheme into the new one. Since the square of (12)(34)(56), is unity, its characteristic values are ± 1. Referring to the values given in Mulliken's table for the primitive characters $\chi^j(C_2)$ ($j = A_1, B_2, E^*$) of an element of C_2, we see

[11] E. Wigner, reference 4, p. 95.

that (12)(34)(56) must be 1 for the states $^1A_1$ and $^1E^*$, and -1 for $^1B_2$. The superscript indicates the multiplicity, $2S+1$. Since the secular determinant can have no matrix elements between states having different characteristic values of (12)(34)(56), it consequently factors into a linear factor, corresponding to $^1B_2$, and a quartic, containing the remaining levels. Reference to the explicit representations of (12), (34), and (56) given in §3 shows that (12)(34)(56) is -1 for state 10, which therefore is $^1B_2$, and 1 for states 11,12,13, and 14, which thus give rise to the quartic. We shall write α for exchange integrals of the type H_{16}, β for the type H_{14}, γ for the type H_{12}. Higher order permutation integrals will be neglected. Setting up the secular determinant, we find the energy of the $^1B_2$ state is, omitting the Coulomb term, $^1B_2 = -3\gamma$, and the quartic is

$A-W$	$-C$	$-C$	$-\sqrt{3}C$
$-C$	$A-W$	C	$\sqrt{3}C$
$-C$	C	$A-W$	$\sqrt{3}C$
$-\sqrt{3}C$	$\sqrt{3}C$	$\sqrt{3}C$	$B-W$

with $A = -\alpha - \beta - \gamma$, $B = -3\alpha - 3\beta + 3\gamma$, $C = \alpha - \beta$. A double root of this equation is obviously given by $A - W = C$. Hence $^1E^* = -2\alpha - \gamma$. The energies of the $^1A_1$ levels can now be found by use of the spur theorem. The sum of the $^1A_1$ energies is found by subtracting the known energies of the remaining levels from Sp H. Similarly the sum of the squares of the $^1A_1$ level is found by subtracting the squares of the known energies from Sp H^2. The energies of the $^1A_1$ levels are then given by

$$W = \tfrac{1}{2}a \pm \tfrac{1}{2}(2b - a^2)^{\frac{1}{2}}, \qquad (3)$$

where a is the sum of the energies, b is the sum of their squares. We find

$$^1A_1 = -\alpha - 3\beta + \gamma \pm [9(\alpha - \beta)^2 + 4(\alpha - \gamma)^2]^{\frac{1}{2}}. \qquad (4)$$

This result has previously been obtained by Seitz and Sherman.[12]

Examining the typical elements of the classes, we see that by suitable labelling of the orbits it would alternatively be possible to make an element of C_5 or an element of C_6 diagonal. The latter choice would factor out a $^1E^*$ level, since

[12] F. Seitz and A. Sherman, J. Chem. Phys. 2, 11 (1934).

$\chi^{E^*}(C_6) = 0$, and hence (12)(34)(56) has the value 1 for one $^1E^*$ level, -1 for the other. The former choice leads to a quadratic factor, containing $^1B_2$ and $^1E^*$, and a cubic factor.

Joint use of two or more labelling schemes is often helpful, since some levels may be most easily found by using one scheme, some by using another.

§5. CUBIC CONFIGURATION

As another example, consider the configuration of eight similar orbits located at the corners of a cube. Proceeding clockwise around the top face of the cube, label the orbits by the numbers 1,6,2,5. Label the orbits directly under these by 7,4,8,3, respectively. The forty-eight symmetry operations form the cubic holohedral group, O_h. Typical elements of the interesting classes are: C_2, (12)(34)-(56)(78); C_4, (17)(28)(36)(45); J, (18)(27)(36)(45); JC_2, (17)(28)(35)(46); JC_4, (12)(78). Any of these elements may be diagonalized by suitable labelling of the orbits. The choice we have made diagonalizes (12)(34)(56)(78) of class C_2, and (12)(78) of class JC_4. The energy matrix can accordingly have nonvanishing elements only between states for which both of these symmetry elements have the same characteristic values.

The irreducible representations of O_h to which the fourteen singlet states belong, together with the number of times each appears, are: A_1 (3 times), E (twice), T_2 (once), JA_1 (once), JT_2 (once). From the table of primitive characters for O_h we see that the characteristic values of our diagonal symmetry elements corresponding to these representations are

	A_1	E	T_2	JA_1	JT_2
(12)(34)(56)(78)	1	1, 1	1, -1, -1	1	1, -1, -1
(12)(78)	1	1, -1	1, -1, 1	-1	-1, -1, 1

There is an ambiguity in the columns for T_2 and JT_2 which cannot be settled by reference to the table of primitive characters alone; namely, we are uncertain which of the values in the first row correspond to which in the second row. For example, the correct assignment for one of the $^1T_2$ states may be (12)(34)(56)(78) = 1, (12)(78) = 1, the corresponding values for the second state may be $-1, -1$, and for the third state $-1,1$. But it is equally possible that the values for the first state should be $1, -1$, and for the second and third states $-1,1$. This question can only be settled by reference to the actual representations of the permutations given in §3. From the matrices there given, we see that the characteristic values of the symmetry elements for the states of this representation (labelled "Initial States") are

(12)(34)(56)(78)	(12)(78)	Initial States	Final States
1	1	1, 2, 5, 8, 12, 14	$^1A_{1a}$, $^1A_{1b}$, $^1A_{1c}$, ^1E_a, ^1E_b, $^1T_2$
1	-1	6, 9, 11, 13	$^1JA_1$, ^1E_a, ^1E_b, $^1JT_2$
-1	1	3, 7	$^1T_2$, $^1JT_2$
-1	-1	4, 10	$^1T_2$, $^1JT_2$

Thus the secular determinant breaks up into two identical quadratics, a quartic, and a sixth degree factor. The last column gives the irreducible representations corresponding to the various roots of these factors. The subscripts a,b,c have been introduced to distinguish between the three different $^1A_1$ levels and the two different ^1E levels. This identification of the levels follows from a comparison of the table just given with the preceding one. Consistency of the two tables requires us, for T_2 and JT_2 of the first table, to put into correspondence with each number in the first row the number directly beneath it in the second row.

The quartic factor can be handled in the same way as the quartic encountered in the preceding

section. Three roots of the sixth degree factor will then be known. The secular equation satisfied by the remaining roots, the three $^1A_1$ levels, can consequently be determined by using the three invariants Sp H, Sp H^2, Sp H^3. The equation can be written

$$W^3 - aW^2 + \tfrac{1}{2}(a^2 - b)W - \tfrac{1}{6}(a^3 - 3ab + 2c) = 0, \tag{5}$$

where a is the sum of the three roots, b is the sum of their squares, and c is the sum of their cubes.

We shall not carry out the explicit calculations here, since the problem will be discussed in Part II by a different method.

II. THE ALGEBRAIC METHOD

§6. The Four Electron Problem, Including Non-Orthogonality Corrections

In order to illustrate the workings of the algebraic method we shall, as a first example, discuss the energies of the singlet states of four electrons in non-identical orbits. The orbits need not be orthogonal, accordingly two kinds of non-orthogonality corrections must be considered. The first kind, due to the nonvanishing values of exchange and higher order permutation integrals of unity, will play no rôle in our formal procedure, for, as Van Vleck has pointed out,[3] the most convenient way of treating this correction is to disregard it completely in obtaining formulas for the energy levels, which subsequently can easily be modified to allow for the correction. The second type of correction requires us to retain in (1) third and higher order permutation integrals. The Hamiltonian function (1) thus takes the form

$$
\begin{aligned}
H = {} & H_{12}(12) + H_{13}(13) + H_{14}(14) + H_{23}(23) + H_{24}(24) + H_{34}(34) + H_{123}[(123) + (132)] \\
& + H_{124}[(124) + (142)] + H_{134}[(134) + (143)] + H_{234}[(234) + (243)] + H_{(12)(34)}(12)(34) \\
& + H_{(13)(24)}(13)(24) + H_{(14)(23)}(14)(23) + H_{1234}[(1234) + (1432)] + H_{1243}[(1243) + (1342)] \\
& + H_{1324}[(1324) + (1423)]. \tag{6}
\end{aligned}
$$

In writing (6), we have omitted the Coulomb integral H_I, which contributes only an additive term to the energy, and, since without loss of generality we may suppose the permutation integrals are real, we have set $H_P = H_{P^{-1}}$. Using the rule given in §2 we find for the primitive characters $[I] = 2$, $[2] = 0$, $[3] = -1$, $[22] = 2$, $[4] = 0$. The spur of H is obtained by replacing each permutation in (6) by its primitive character; we thus find

$$\text{Sp } H = -2(H_{123} + H_{124} + H_{134} + H_{234}) + 2(H_{(12)(34)} + H_{(13)(24)} + H_{(14)(23)}).$$

In a similar way the spur of H^2 can be found by squaring (6) and then replacing each permutation by its primitive character. In squaring (6) it is of course unnecessary to actually multiply out term by term, for many of the resulting terms will be of a similar type. For example, the term $H_{12}(12)$ is typical of the first six terms of (6), and the contribution of interchanges to Sp H^2 can be determined by examination of the product Sp $H_{12}(12)H$. The first term of this product gives $H_{12}^2[I]$, the second is $2H_{12}H_{13}[3]$. The factor 2 is included since each cross-term appears twice in taking the square. It should be noted in this connection that the class to which the product of two permutations belongs is unchanged if the product is taken in the reverse order, as is shown by the relation $P_b(P_aP_b)P_b^{-1} = P_bP_a$. The third, fourth and fifth terms of the product are of the same type as the second, since in each case one integer in the first permutation is repeated in the second. The sixth term, however, is of a different type, and gives $2H_{12}H_{34}[22]$. Collecting the above results we see that, aside from higher order permutation integrals, the spur of H^2 is

$$2[H_{12}^2 + H_{13}^2 + \cdots] - 2[H_{12}H_{13} + H_{12}H_{14} + \cdots] + 4[H_{12}H_{34} + H_{13}H_{24} + \cdots].$$

Continuing the multiplication of Sp $H_{12}(12)H$, the next two terms are of the type $2H_{12}H_{123}(2[2])$, and the following two of the type $2H_{12}H_{134}(2[4])$. Terms involving products of double and triple

permutations consequently vanish. After completing the $H_{12}(12)$ product, we begin with $H_{123}[(123)$ $+(132)]$, which need be multiplied only the by terms in H which follow the interchanges, since products with interchanges have already been considered. Proceeding in this way, all terms of the spur are readily obtained. Knowing Sp H and Sp H^2 the energy levels can be found by using (3). This formula of course does not include non-orthogonality corrections of the first kind mentioned above.

In our case, (3) leads to the result

$$W = -(H_{123}+H_{124}+H_{134}+H_{234})+(H_{(12)(34)}+H_{(13)(24)}+H_{(14)(23)})$$
$$\pm\{\tfrac{1}{2}[(\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2]\}^{\frac{1}{2}} \quad (7)$$

with $\alpha=H_{12}+H_{34}+2H_{1324}$, $\beta=H_{13}+H_{24}+2H_{1234}$, $\gamma=H_{14}+H_{23}+2H_{1243}$. Slater[13] has obtained this formula by use of the wave method.

The method of obtaining the energy levels illustrated above is, of course, applicable whatever the number of electrons, and whatever the degree of the resulting secular determinant. However, unless other simplifying factors enter, the practical scope of the method is limited to secular problems of small degree, since for a secular problem of degree t it is in general necessary to evaluate t invariants, the spurs of $H, H^2, \cdots H^t$. If t is at all large, the pure matrix method of solving (1) is likely to afford a less tedious attack. Fortunately, simplifying factors do enter in important classes of problems. Such simplifications are usually due to the existence of symmetry elements, in addition to permutations of the coordinates, which commute with the Hamiltonian function. Cases of this sort arising in molecular spectra will be discussed in §§8 to 11. In complex spectra, some of the roots of the secular determinant will be already known since they may be obtained by the method of diagonal sums. The number of invariants we are required to compute is consequently greatly reduced. However, in such problems it is imperative to include the interactions between configurations. These will be considered in the following section.

§7. Interactions between Configurations

If we wish to consider interactions between configurations, or if the orbits of a configuration are not all different, (1) must be replaced by the more general formula

$$H^{R_iR_j} = \sqrt{2^{-r_i-r_j}} \Sigma_P H^{R_iR_j} {}_P P. \quad (8)$$

Here $H^{R_iR_j}$ is the portion of the energy matrix in which the states arising from the configuration R_i, which has r_i pairs of identical orbits, intersect the states arising from the configuration R_j, which has r_j pairs of identical orbits. It should be understood that in (8) we may have $i=j$. Eq. (8) differs in two respects from the corresponding equation, (13), given in I. The summation in (8) is over all permutations, rather than only over a subset, as in (13). This accounts for the appearance of the normalization factor $\sqrt{2^{-r_i}}$, instead of $\sqrt{2^{r_i}}$. And the P's themselves appear in (8), rather than the matrices $P^{R_iR_j}$, from which were omitted rows and columns corresponding to states which vanish in virtue of the identity of pairs of orbits. The inclusion of these rows and columns in (8) does no harm, for an obvious modification of the argument following (10) of I shows that the elements of the rows and columns so included are all zero, and hence will in no way affect the values of our spurs.

Instead of using the expression (8) for the energy matrix, $H^{R_iR_i}$, of a configuration having r_i pairs of identical orbits, it is simpler to use (1) for the configuration of $n-2r_i$ electrons obtained by omitting the identical pairs, replacing, however, H_I by H_I+C. The explicit equation for C, the additive constant due to paired electrons, is given in Van Vleck's paper.[3]

The spur of H^2 may be obtained from (8) and the relation

$$\text{Sp } H^2 = \Sigma_{ij} \text{ Sp } H^{R_iR_j} H^{R_jR_i}. \quad (9)$$

Analogous formulas hold for the higher invariants.

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[13] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

As an illustration of the use of (8) and (9), let us find the contribution to Sp H^2 of the interaction between a configuration A, consisting of three non-identical orbits, and a configuration B, which has orbits 1 and 2 identical. All non-orthogonality corrections will be neglected. As orbits 1 and 2 of B are the same, $H^{BA}{}_{P'} = H^{BA}{}_P$ if $P' = (12)P$. Hence, (8) gives

$$H^{BA} = \sqrt{\tfrac{1}{2}}\{H^{BA}{}_I[I+(12)]+H^{BA}{}_{13}[(13)+(132)]+H^{BA}{}_{23}[(23)+(123)]\},$$
$$H^{AB} = \sqrt{\tfrac{1}{2}}\{H^{BA}{}_I[I+(12)]+H^{BA}{}_{13}[(13)+(123)]+H^{BA}{}_{23}[(23)+(132)]\}.$$

The second of these relations follows from the fact that H^{AB} is the matrix adjoint to H^{BA}. Since the permutations are unitary operators, H^{AB} may accordingly be obtained by replacing each permutation in H^{BA} by its reciprocal. The interaction between A and B contributes to Sp H^2 the terms

$$\begin{aligned}
\text{Sp } H^{BA}H^{AB}+\text{Sp } H^{AB}H^{BA} &= 2 \text{ Sp } H^{BA}H^{AB}\\
&= (H^{BA}{}_I{}^2+H^{BA}{}_{13}{}^2+H^{BA}{}_{23}{}^2)(2[I]+2[2])\\
&\quad +2(H^{BA}{}_I H^{BA}{}_{13}+H^{BA}{}_I H^{BA}{}_{23}+H^{BA}{}_{13}H^{BA}{}_{23})(2[2]+2[3])\\
&= 2[(H^{BA}{}_I - H^{BA}{}_{13})^2+(H^{BA}{}_I - H^{BA}{}_{23})^2+(H^{BA}{}_{13}-H^{BA}{}_{23})^2].
\end{aligned} \tag{10}$$

This algebraic solution of the problem offers an interesting alternative to the pure matrix solution given in I in connection with the calculation of the ^2D levels arising from the atomic configuration d^3. It is interesting to observe that if the values of the characters appropriate to $S=\tfrac{3}{2}$ are used in (10), the spur reduces, as it must, to zero.

§8. SYMMETRICAL MOLECULES

The algebraic method is very well adapted for Heitler-London calculations of the energy levels of symmetrical polyatomic molecules, since the aid of the group of symmetry operations which commute with the Hamiltonian function can be invoked to factor the secular equation. The number and complexity of the invariants which must be evaluated are consequently greatly reduced. Consider, for example, the hexagonal configuration discussed in §4. Proceeding clockwise around the hexagon, label the orbits 1,2,3,4,5,6. The twelve symmetry operations are

$$\begin{array}{ll}
C_1 : I & C_4 : (123456),\ (165432)\\
C_2 : (14)(25)(36) & C_5 : (26)(35),\ (13)(46),\ (15)(24)\\
C_3 : (135)(246),\ (153)(264) & C_6 : (12)(36)(45),\ (14)(23)(56),\ (16)(25)(34).
\end{array} \tag{11}$$

We now introduce the operators χ_j, used by Dirac,[1] which are defined by

$$\chi_j = (1/n_j)\Sigma_{P_{c_j}} P_{c_j},$$

where the summation is over all elements in class C_j, and n_j is the number of such elements. For example $\chi_3 = \tfrac{1}{2}[(135)(246)+(153)(264)]$. We shall call these operators "Dirac characters." They must not be confused with the ordinary characters and primitive characters, which are not operators, but spurs of matrices. The Dirac characters, χ_j, commute with all elements of the symmetry group, consequently the matrices representing them must be constants (multiples of the unit matrix) within an irreducible representation of this group. Since the spur of χ_j equals the spur of one of the elements P_{c_j}, the characteristic value of χ_j for a given irreducible representation may be obtained by dividing the primitive character of P_{c_j}, for that representation, by the degree of the representation. The characteristic values of the χ_j, for the three irreducible representations to which the singlet states belong, are given in the following table.

	χ_1	χ_2	χ_3	χ_4	χ_5	χ_6
A_1	1	1	1	1	1	1
B_2	1	-1	1	-1	-1	1
E^*	1	1	$-\tfrac{1}{2}$	$-\tfrac{1}{2}$	0	0

Consider a representation in which the energy matrix, H, is diagonal, and in which the matrices representing the symmetry elements are completely reduced. Since the irreducible representation A_1 occurs twice, the characteristic values of H may be written $^1A_{1+}$, $^1A_{1-}$, $^1B_2$, $^1E^*$, $^1E^*$. The corresponding characteristic values of χ_4, for example,

are $1, 1, -1, -\frac{1}{2}, -\frac{1}{2}$. From the table given above we see that the characteristic values of $\frac{1}{2}(\chi_1 - \chi_2)$ are $0, 0, 1, 0, 0$. Hence the characteristic values of $\frac{1}{2}(\chi_1 - \chi_2)H$ are $0, 0, {}^1B_2, 0, 0$, and the energy of the ${}^1B_2$ state is simply the spur of this matrix. It follows that in any representation ${}^1B_2 = \mathrm{Sp}\ \frac{1}{2}(\chi_1 - \chi_2)H$. In a similar way we prove that the sum of the energies of the ${}^1E^*$ levels is $2{}^1E^* = \mathrm{Sp}\ (\chi_1 - \chi_6)H$. The sum of the ${}^1A_1$ energies which we denote by $[{}^1A_1]$ can now be obtained from the relation $[{}^1A_1] + {}^1B_2 = \mathrm{Sp}\ \chi_6 H$. In order to separate the ${}^1A_1$ levels, it is necessary to find the sum of their squares, which we write $[{}^1A_1{}^2]$. This can be obtained most simply by subtracting the squares of the energies of the other levels from $\mathrm{Sp}\ H^2$. The explicit expression for ${}^1A_{1+}$ and ${}^1A_{1-}$ are then found by use of (3). It is evident that there are a variety of other ways in which the factorization of the secular determinant could be executed. Which one is chosen is solely a matter of convenience.

The calculations indicated above are readily carried out. The energy matrix, neglecting non-orthogonality corrections, and omitting the additive Coulomb term is,

$$H = \alpha\{(12) + (23) + (34) + (45) + (56) + (61)\}$$
$$+ \beta\{(13) + (15) + (24) + (26) + (35) + (46)\} + \gamma\{(14) + (25) + (36)\}, \quad (12)$$

with $\alpha = H_{12}$, $\beta = H_{13}$, $\gamma = H_{14}$. One readily verifies that H commutes with the symmetry elements (11).

As remarked in §6, it is by no means necessary to evaluate all the terms appearing in the various spurs. In fact, it is obvious from the symmetry of the problem that

$$\mathrm{Sp}\ \chi_j H = \mathrm{Sp}\ \chi_j \{6\alpha(12) + 6\beta(13) + 3\gamma(14)\}.$$

Of course $\chi_1 H$ is simply H itself. Thus

$$\mathrm{Sp}\ H = (6\alpha + 6\beta + 3\gamma)[2] = -6a - 6\beta - 3\gamma, \quad (13)$$

upon evaluating $[2]$ by means of the rule given in §2, while

$$\mathrm{Sp}\ \chi_2 H = \mathrm{Sp}\ (14)(25)(36)\{6\alpha(12) + 6\beta(13) + 6\gamma(14)\}$$
$$= 6\alpha[42] + 6\beta[42] + 3\gamma[22] = -6\alpha - 6\beta + 3\gamma, \quad (14)$$

and

$$\mathrm{Sp}\ \chi_6 H = \mathrm{Sp}\ \tfrac{1}{3}\{(12)(36)(45) + (14)(23)(56) + (16)(25)(34)\}\{6\alpha(12) + 6\beta(13) + 3\gamma(14)\}$$
$$= 2\alpha\{[22] + 2[42]\} + 2\beta\{3[42]\} + \gamma\{2[42] + [22]\} = -2\alpha - 6\beta - \gamma. \quad (15)$$

Half the difference of (13) and (14) gives ${}^1B_2 = -3\gamma$ and half the difference of (13) and (15) gives ${}^1E^* = -2\alpha - \gamma$. The sum of the ${}^1A_1$ levels is then found to be $[{}^1A_1] = -2\alpha - 6\beta + 2\gamma$.

Let A, B, C be the coefficients of α, β, γ in (12). In finding $\mathrm{Sp}\ H^2$ it is sufficient to write

$$H^2 = \{6\alpha(12) + 6\beta(13) + 3\gamma(14)\}\{\alpha A + \beta B + \gamma C\}$$
$$= 6\alpha^2(12)A + 6\beta^2(13)B + 3\gamma^2(14)C + 12\alpha\beta(12)B + 12\alpha\gamma(12)C + 12\beta\gamma(13)C.$$

As we will require $\mathrm{Sp}\ \chi_5 H^2$ in finding the triplet levels, we shall not lump together all permutations belonging to the same class, but develop H^2 in a more complete form suitable for multiplication with a χ. Since only products of H^2 with χ's are of interest, the abbreviated form of multiplication given above is still permissible. Thus, beginning the multiplication of $(12)A$, the first term is I, the second is (123), and the third is $(12)(34)$. The fourth term, $(12)(45)$, must be considered of a different type than the third in spite of the fact that it belongs to the same class, for referring to a diagram of the hexagon, we see that vertices 4 and 5 are diagonally opposite 1 and 2, while 3 is opposite neither. The fifth term, $(12)(56)$ is evidently of the same type as $(12)(34)$, while the sixth, (162) is of the type (123). Proceeding in this way, we obtain the expression

$$H^2 = 6\alpha^2\{I + 2(123) + 2(12)(34) + (12)(45)\} + 6\beta^2\{I + 2(153) + 2(13)(24) + (13)(46)\}$$
$$+ 3\gamma^2\{I + 2(14)(25)\} + 12\alpha\beta\{2(123) + 2(152) + 2(12)(35)\} + 12\alpha\gamma\{2(152) + (12)(36)\}$$
$$+ 12\beta\gamma\{2(152) + (13)(25)\}. \quad (16)$$

Replacing each permutation by its character gives

$$\mathrm{Sp}\ H^2 = 36\alpha^2 + 36\beta^2 + 21\gamma^2 - 24\alpha\beta - 12\alpha\gamma - 12\beta\gamma.$$

We can now substitute $a = [^1A_1]$, $b = [^1A_1{}^2] = \mathrm{Sp}\ H^2 - (^1B_2)^2 - 2(^1E^*)^2$ in (3) and again obtain the result (4).

The nine triplet states can be handled in the same way. The states $^3A_2$ and $^3E^*$ each occur once, $^3B_1$ and $^3E_*^*$ each twice. The only new spurs it is necessary to calculate are $\mathrm{Sp}\ \chi_5 H$ and $\mathrm{Sp}\ \chi_5 H^2$. The latter is needed because there are now two representations which occur twice: $\mathrm{Sp}\ \chi_5 H^2$, which is readily obtained with the aid of (16), can be used to find $^3B_{1\pm}$, and then $\mathrm{Sp}\ H^2$ to find $^3E_{*\pm}^*$. The other spurs required are obtained simply by substituting the appropriate values of the characters in (13), (14), (15), and (16). The quintet and septet energies can be obtained in a similar way from (13), (14), and (15). The energies are found to be

$$
\begin{aligned}
&^3A_2 = -4\alpha - \gamma, && ^3B_1 = -(\alpha + 3\beta + \gamma) \pm [5(\alpha-\beta)^2 + 4(\beta-\gamma)^2]^{\frac{1}{2}}, \\
&^3E^* = -\alpha - 3\beta - \gamma, && ^3E_*^* = -\tfrac{1}{2}(5\alpha + 3\beta + 2\gamma) \pm \tfrac{1}{2}[5(\alpha-\beta)^2 + 12(\alpha-\gamma)^2 + 4(\beta-\gamma)^2]^{\frac{1}{2}}, \\
&^5A_1 = -2\alpha - 6\beta - \gamma, && ^5E^* = -5\alpha - 3\beta - \gamma, \\
&^5E_*^* = -3\alpha - 3\beta - 3\gamma, && ^7B_1 = -6\alpha - 6\beta - 3\gamma.
\end{aligned}
$$

The method illustrated above is applicable whenever the Hamiltonian function possesses symmetry elements in addition to the permutations of the coordinates. The orthogonality relations satisfied by the primitive characters of the symmetry group assure us that complete factorization of the secular determinant can always be obtained. This method is particularly convenient when the energies of states of all multiplicities are desired, since the same expressions for the spurs are involved in all cases, only the particular values of the characters changing in passing from one value of S to another.

A very convenient running check on the calculations is afforded by noting that when all the exchange integrals are made equal the energies of all the states of a given multiplicity are the same, and are given by[3]

$$^{2S+1}W = -\tfrac{1}{4}H_{12}[n(n-4) + 4S(S+1)],$$

where H_{12} is the common value of the exchange integrals, and n is the number of electrons. Thus in the benzene problem considered above, if we put $\alpha = \beta = \gamma$ the singlet energies all reduce to $^1W = -3\alpha$. $\mathrm{Sp}\ \chi_2 H$, which is the sum of the energies of four states minus the energy of one, must consequently reduce to $3\,^1W$, i.e., to -9α, while, to pick another example, $\mathrm{Sp}\ H^2$ must become $5(^1W)^2$ or $45\alpha^2$.

§9. Cubic Configuration

The problem considered in §5 also can be readily handled by the algebraic method. The orbits will be labelled as shown in Fig. 1. The Hamiltonian function for this configuration is

$$
\begin{aligned}
H = {}&\alpha\{(12)+(13)+(15)+(24)+(26)+(34)+(37)+(48)+(56)+(57)+(68)+(78)\} \\
&+\beta\{(14)+(16)+(17)+(23)+(25)+(28)+(35)+(38)+(46)+(47)+(58)+(67)\} \\
&+\gamma\{(18)+(27)+(36)+(45)\}. \quad (17)
\end{aligned}
$$

The symmetry group of this Hamiltonian function is the cubic holohedral group, O_h.

There are twenty-eight triplet states; as these offer the most complicated problem, we shall treat them first. The number of times each representation of the cubic group occurs, and the corresponding characteristic values of the Dirac characters, are given in the following table.

It will be seen from this table that the determination of the energies can be carried out through the evaluation of the following spurs: $\mathrm{Sp}\ H$, $\mathrm{Sp}\ \chi_2 H$, $\mathrm{Sp}\ \chi_3 H$, $\mathrm{Sp}\ \chi_4 H$, $\mathrm{Sp}\ JH$, $\mathrm{Sp}\ J\chi_4 H$, $\mathrm{Sp}\ H^2$, $\mathrm{Sp}\ \chi_2 H^2$, $\mathrm{Sp}\ \chi_4 H^2$, $\mathrm{Sp}\ JH^2$, $\mathrm{Sp}\ H^3$. In finding $\mathrm{Sp}\ H^3 = \mathrm{Sp}\ \{12\alpha(12) + 12\beta(14) + 4\gamma(18)\}H^2$, the labor is materially shortened if we note that, since the order of multiplication is immaterial for our purposes, H^3 is of the form $(A+B+C)^3 = A^3 + B^3 + C^3 + 3(A^2B + A^2C + AB^2 + B^2C + AC^2 + BC^2) + 6ABC$. The cubic equation satisfied by the $^3JT_1$ levels is obtained by the use of (5).

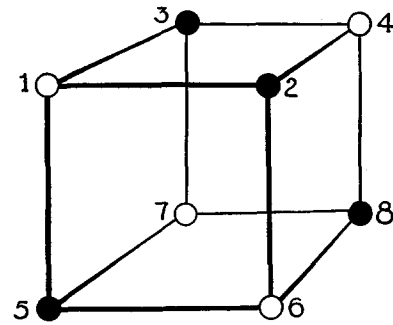|	χ_1	χ_2	χ_3	χ_4	χ_5	J	$J\chi_2$	$J\chi_3$	$J\chi_4$	$J\chi_5$
$(2)T_1$	1	$-\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	0	1	$-\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	0
$(2)T_2$	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	0	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	0
$(2)JA_2$	1	1	-1	-1	1	-1	-1	1	1	-1
$(1)JE$	1	1	0	0	$-\frac{1}{2}$	-1	-1	0	0	$\frac{1}{2}$
$(3)JT_1$	1	$-\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	0	-1	$\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	0
$(1)JT_2$	1	$-\frac{1}{3}$	$-\frac{1}{3}$	$\frac{1}{3}$	0	-1	$\frac{1}{3}$	$\frac{1}{3}$	$-\frac{1}{3}$	0

Fig. 1.

The spurs calculated in connection with the triplet levels also suffice to determine the energies of the levels of other multiplicities. Carrying out the algebra, we find

$$^1T_2 = -4(\alpha+\beta),$$
$$^1JA_1 = -2(3\alpha+\gamma),$$
$$^1JT_2 = -2(\alpha+2\beta+\gamma),$$
$$^3JE = -2(2\alpha+2\beta+\gamma),$$
$$^3JT_2 = -2(3\alpha+\beta+\gamma),$$

$$^1E = -2(2\alpha+\beta+\gamma)\pm2[(\alpha-\beta)^2+(\alpha-\gamma)^2]^{\frac{1}{2}},$$
$$^3T_1 = -(5\alpha+3\beta+2\gamma)\pm[(\alpha-\beta)^2+4(\alpha-\gamma)^2]^{\frac{1}{2}},$$
$$^3T_2 = -(3\alpha+5\beta+2\gamma)\pm[5(\alpha-\beta)^2+4(\beta-\gamma)^2]^{\frac{1}{2}},$$
$$^3JA_2 = -2(\alpha+4\beta)\pm\{2[7(\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2]\}^{\frac{1}{2}},$$
$$^3JT_1 = W,$$

$$W^3+2(7\alpha+7\beta+\gamma)W^2+4(13\alpha^2+14\beta^2-\gamma^2+37\alpha\beta+7\alpha\gamma+5\beta\gamma)W$$
$$+8(5\alpha^3+8\beta^3-\gamma^3+42\alpha^2\beta+8\alpha^2\gamma+41\alpha\beta^2+5\beta^2\gamma-2\beta\gamma^2+19\alpha\beta\gamma)=0,$$

$$^5JE = -2(3\alpha+3\beta+\gamma),$$
$$^5JT_1 = -2(2\alpha+4\beta+\gamma),$$
$$^5JT_2 = -2(4\alpha+2\beta+\gamma),$$
$$^7A_2 = -2(3\alpha+6\beta+\gamma),$$
$$^7JT_1 = -2(5\alpha+4\beta+\gamma),$$

$$^5A_1 = -2(2\alpha+4\beta+\gamma)\pm\{2[(\alpha+\gamma-2\beta)^2+3(\alpha-\beta)^2+(\beta-\gamma)^2]\}^{\frac{1}{2}},$$
$$^5E = -(7\alpha+5\beta+2\gamma)\pm[(\alpha-\beta)^2+4(\alpha-\gamma)^2]^{\frac{1}{2}},$$
$$^5T_2 = -2(3\alpha+3\beta+\gamma)\pm\{2[(\alpha-\beta)^2+(\alpha-\gamma)^2+(\beta-\gamma)^2]\}^{\frac{1}{2}},$$
$$^7T_2 = -4(2\alpha+2\beta+\gamma),$$
$$^9A_1 = -4(3\alpha+3\beta+\gamma).$$

The cubic equation satisfied by the $^1A_1$ levels has been omitted from the above results, since it has already been given by Seitz and Sherman.[12]

§10. Body-Centered Cube

The addition of a ninth electron in a spherically symmetric orbit in the center of the cube simply adds to each energy level of multiplicity $2S+1$ given in the preceding section the term[3] $W_9=Q_9-\delta[(13/4)+S'(S'+1)-S(S+1)]$, where Q_9 is a Coulomb term, δ is the exchange integral between the central orbit and a corner orbit, and S' is the characteristic value of the total spin of all nine electrons. Each singlet energy level of the simple cube is thus augmented by $Q_9-4\delta$, while, for $S\neq0$, the resultant states with $S'=S-\frac{1}{2}$ differ from their parent states by $Q_9-\delta(3-S)$. The case of eight sodium atoms at the corners of a cube has been considered by Taylor, Eyring and Sherman,[9] and by Seitz and Sherman.[12] If, following them, we use Rosen's value for the Coulomb integral, namely, 28.3 percent of the Na_2 Morse curve, we find $Q_9=8\times(28.3/71.7)\delta=3.16\delta$. Hence, since δ is negative, addition of the ninth electron raises the energies of the singlet states of the cube, but lowers the energies of states of higher multiplicity. If δ is sufficiently small, the normal state of the body-centered cube is still $^2A_1$, arising from the normal state, $^1A_1$, of the cube. For a larger value of δ, the normal state becomes $^2JA_2$, arising from the lowest triplet state of the cube, $^3JA_2$. For this state the body-centered cube will be larger than the simple cube in its normal state, since the magnitude of δ is maximized by making the distance from a corner to the center of the cube, rather than the cube edge, equal to the equilibrium distance of the Morse curve. Actually, explicit calculation shows that δ is sufficiently

large to make $^2JA_2$ the normal state. The numerical results will not be given here, since they are contained in a recent paper by Stearn, Lindsley and Eyring.[14]

The energies of a number of the excited states which are derived from triplet states of the simple cube are given incorrectly by the latter authors. Their formulas for the simple cube states $^3T_1$ (Γ_4 in their notation), $^3T_2(\Gamma_5)$, and $^3JT_1(\Gamma_9)$, which disagree with ours, are certainly in error, since they do not reduce properly in the limiting cases considered by Seitz and Sherman[12] by means of the vector model. The source of the error lies in the fact that their "method II," which they used in finding the energies of the triplet states, is incorrect when applied to irreducible representations of higher than the first degree which appear more than once in the secular determinant. Suppose, for example, that an irreducible representation of degree r ($r > 1$) occurs twice, and let the corresponding wave functions be ψ_1, ψ_2, $\cdots \psi_r$, and ψ'_1, ψ'_2, $\cdots \psi'_r$. The subscript tells to which row of a particular irreducible representation of the symmetry elements, $D(R)$, the wave function belongs. This representation is of course not unique, since if S is any canonical transformation, $S^{-1}D(R)S$ is also a representation. If the subscripts in the two sets of wave functions refer to the same representation, the secular determinant will factor into r quadratics. It is clear that if a canonical transformation S is applied to the first set of wave functions, and a transformation S' is applied to the second set, the secular equation will remain in a factored form only provided $S = S'$. The formula (7) used by Stearn, Lindsley and Eyring determines the ψ_i only within a numerical factor, i.e., if we use ψ_i to denote the normalized wave functions, (7) gives $\alpha_i\psi_i$, rather than ψ_i itself. The summation involved in passing from (7) to (8) thus amounts to taking a certain linear combination of the ψ_i. Similarly, the passage from (7) to (8) leads to a linear combination of the ψ'_i, a linear combination however, which is not the same as that applied to the ψ_i. The factorization of the secular determinant is consequently destroyed, and it is not possible to obtain the energies merely by solution of the quadratic equation resulting from consideration only of the two linear combinations given by (8). The occurrence of such a difficulty might have been anticipated from the fact that the factorization of the secular determinant is contingent upon the use of a definite representation, whereas the Eq. (8) employed by Stearn, Lindsley and Eyring involves only the primitive characters, which are independent of the representation.

§11. Tetrahedral Configuration

The tetrahedral configuration exemplified by methane is equivalent to the configuration shown in Fig. 1 if orbits 1,4,6 and 7 are considered different from 2,3,5 and 8. The Hamiltonian function for this configuration is

$$H = \alpha\{(12)+(13)+(15)+(24)+(26)+(34)+(37)+(48)+(56)+(57)+(68)+(78)\}$$
$$+\beta\{(14)+(16)+(17)+(46)+(47)+(67)\}+\beta'\{(23)+(25)+(28)+(35)+(38)+(58)\}$$
$$+\gamma\{(18)+(27)+(36)+(45)\}. \quad (18)$$

It is readily shown with the aid of the vector model that the singlet energies of the tetrahedral configuration involve β and β' only in the combination $\beta+\beta'$. For, in a representation in which the resultant spins of the electrons in orbits 1,4,6 and 7, and of the electrons in orbits 2,3,5 and 8 are "good quantum numbers," with characteristic values S_1 and S_2, respectively, β and β' appear in the energy matrix only in the diagonal elements, and their contribution to these elements is[12] $-S_1(S_1+1)\beta - S_2(S_2+1)\beta'$. The singlet states of the tetrahedral configuration necessarily have $S_1 = S_2$, which proves the proposition stated above. If we write (18) in the form

$$H = \alpha A + \beta B + \beta'B' + \gamma C = \alpha A + \tfrac{1}{2}(\beta+\beta')(B+B') + \gamma C + \tfrac{1}{2}(\beta-\beta')(B-B'), \quad (19)$$

it follows that the last term of (19) vanishes for the singlet states. Comparing the first three terms of (19) with (17), we see that the formulas for the singlet levels of the tetrahedral configuration may be obtained from those for the singlet levels of the cubic configuration simply by replacing β by $\tfrac{1}{2}(\beta+\beta')$.

[14] A. E. Stearn, C. H. Lindsley and H. Eyring, J. Chem. Phys. 2, 410 (1934).

The Hamiltonian function (18) is invariant under the twenty-four operations of the tetrahedral group, T_d. It remains to determine to which irreducible representations of this group the singlet states belong. The symmetry of the energy matrix in β and β' introduces another symmetry element, the inversion $J = (18)(27)(36)(45)$, which, applied to (18), interchanges β and β'. The resultant group of forty-eight elements is evidently isomorphic to the cubic holohedral group, O_h. Referring to Mulliken's tables for the group T_d, we see that it differs from the cubic group O only by the inclusion of an inversion in classes C_3 and C_4. The group obtained by adding an inversion to T_d consequently differs from O_h only in that classes C_3 and JC_3, C_4 and JC_4 are interchanged. It follows immediately that the states of the cube labelled $^1A_1$, ^1E, $^1T_2$, $^1JA_1$, $^1JT_2$, correspond to the states $^1A_1$, ^1E, $^1T_2$, $^1A_2$, $^1T_1$, respectively, of the tetrahedron.

The energies of the $^1A_1$ levels of the tetrahedron have also been computed by Seitz and Sherman,[12] while Eyring, Frost and Turkevich[15] have given formulas for the singlet states. A typographical error should be noted in the latter authors' formula for $^1A_2$ (Γ_2 in their notation). Their results for $^1E(\Gamma_3)$ are also in error.

I am deeply in debt to Professor J. H. Van Vleck, both for the interest he has taken in this work, and for his kindness in criticizing the manuscript.

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

The Heat Capacity Curves of the Simpler Gases, VI. A Correction

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IN our paper of the above title a contribution of $R \ln 2$, resulting from the electron spin of the deuterium atom, was omitted from the free energy values of atomic deuterium, through an oversight. To correct for this omission all entries in the fourth column of Table IV (p. 392) should be increased by 1.377 units. This correction also influences Table X (p. 394). The corrected Table X is as follows:

TABLE X. *Dissociation constants and percentage dissociation of hydrogen.*

T, °K	K — H¹H¹	H¹H²	H²H²
1000	64.49 $\times 10^{-19}$	24.78 $\times 10^{-19}$	37.08 $\times 10^{-19}$
1500	36.00 $\times 10^{-11}$	15.66 $\times 10^{-11}$	26.99 $\times 10^{-11}$
2000	29.60 $\times 10^{-7}$	13.62 $\times 10^{-7}$	24.91 $\times 10^{-7}$
2500	6.915 $\times 10^{-4}$	3.276 $\times 10^{-4}$	6.168 $\times 10^{-4}$
3000	26.87 $\times 10^{-3}$	12.95 $\times 10^{-3}$	24.75 $\times 10^{-3}$

T, °K	Percent dissociation (1 atmosphere) H¹H¹	H¹H²	H²H²
1000	13 $\times 10^{-8}$	7.9 $\times 10^{-8}$	9.6 $\times 10^{-8}$
1500	9.5 $\times 10^{-4}$	6.3 $\times 10^{-4}$	8.2 $\times 10^{-4}$
2000	8.6 $\times 10^{-2}$	5.8 $\times 10^{-2}$	7.8 $\times 10^{-2}$
2500	1.31	0.91	1.24
3000	8.1	5.66	7.9

Except for a portion of the discussion in the paragraph which begins five lines below Table X, no other portions of our paper are influenced by this correction.