(To appear in "The Quantum Theory of Atoms, Molecules and the Solid State", dedicated to J. C. Slater, edited by P. O. Löwdin, to be published by Academic Press, 1966).

ON THE FACTORIZATION OF SECULAR EQUATIONS BY GROUP THEORY *

by

W. Byers Brown

Theoretical Chemistry Institute, University of Wisconsin
Madison, Wisconsin

17069

ABSTRACT

The factor equations are obtained in an explicitly invariant form which does not involve the matrix elements of degenerate irreducible representations of the group, but only the group characters.

Author

* This research was supported by the following grant: National Aeronautics and Space Administration Grant NsG-275-62.

I. INTRODUCTION

One of the most fundamental and practical problems in the quantum mechanics of atoms, molecules and crystals is to solve secular equations of the form

$$(\underset{\sim}{H} - E\underset{\sim}{S})\,\underset{\sim}{c} = 0 \qquad (1)$$

where $\underset{\sim}{H}$ and $\underset{\sim}{S}$ are the matrix representatives of the Hamiltonian $\mathcal{H}$ and unity in some basis set $\underset{\sim}{\phi}$, and $\underset{\sim}{c}$ is a column vector of coefficients. It is well known that if the system of interest possesses symmetry, a knowledge of the irreducible representations of the symmetry group can be used to factorise equation (1) into a set of secular equations of lower order.

Professor Slater has been closely associated with this problem, particularly in the field of atoms. One of his major contributions was the theory of the central-field approximation for atoms (Slater, 1929), which leads to secular equations of type (1). The striking feature of his method was that he showed how to factorise and solve the secular equations <u>without</u> the use of group theory. Slater's method works well in the cases in which the irreducible representations occur no more than once in the basis and the degeneracies are low. However, when this is no longer true, he acknowledges the value of group theory techniques (Slater, 1960).

The group theory methods described in the literature have, however, an unnecessary weakness. In the general case in which degenerate irreducible representations occur more than once, they require actual matrix realizations of the representations. Yet the factorised secular equations are independent of any particular matrices, and depend only on the invariant characteristics, all of which are contained in the character table of the group.

The object of this paper is to derive the explicitly invariant forms of the factor equations. It gives me great pleasure to dedicate it to Professor Slater, who has contributed so much to the problem of factorising secular equations.

II. DESCRIPTION OF PROBLEM

Let the basis consist of n linearly independent functions $\phi_1, \phi_2, \ldots \phi_n$. The matrices $\underset{\sim}{H}$ and $\underset{\sim}{S}$ occurring in Eq. (1) are defined by

$$\underset{\sim}{H} = \langle \underset{\sim}{\phi}^{\dagger}, \mathcal{H} \underset{\sim}{\phi} \rangle \quad \text{and} \quad \underset{\sim}{S} = \langle \underset{\sim}{\phi}^{\dagger}, \underset{\sim}{\phi} \rangle, \tag{2}$$

where the row vector $\underset{\sim}{\phi} = (\phi_1, \phi_2, \ldots, \phi_n)$. Let $\mathcal{G}$ be the symmetry group of order g, and with h classes, associated with the system of interest. By definition the Hamiltonian commutes with all the symmetry operators R belonging to the group,

$$\mathcal{R}\mathcal{H} = \mathcal{H}\mathcal{R} . \tag{3}$$

It will be assumed that the space of the functions ϕ is closed under the operations of the group, so that ϕ forms the basis for a matrix representation Γ , in general reducible, of $\mathcal{G}$. The matrices $\underset{\sim}{\Gamma}(R)$ are defined in the usual way by

$$\mathcal{R}\underset{\sim}{\phi} = \underset{\sim}{\phi}\,\underset{\sim}{\Gamma}(R). \tag{4}$$

The completely reduced form of Γ may be written formally as

$$\Gamma = \sum_{\alpha=1}^{h} m_\alpha \Gamma^{(\alpha)}, \tag{5}$$

where $\Gamma^{(\alpha)}$ is the α th irreducible representation of of dimension ℓ_α .

The essential step in solving Eq. (1) is to find the n roots (eigenvalues) of the determinantal equation

$$\det(\underset{\sim}{H} - E\underset{\sim}{S}) = 0 . \tag{6}$$

Equation (1) may then be solved for the corresponding eigenvectors $\underset{\sim}{c}$. The structure of Γ implies that there are m_α distinct eigenvalues $E_i^{(\alpha)}(i = 1,2,\ldots, m_\alpha)$, each ℓ_α-fold degenerate, belonging to the representation $\Gamma^{(\alpha)}$; the total number of eigenvalues is

$$n = \sum_{\alpha=1}^{h} m_\alpha l_\alpha \ . \qquad (7)$$

It follows that a transformation matrix $\underset{\sim}{U}$ exists, depending only on the properties of G , which will reduce the determinant of (6) to a block diagonal form[1] which can be factorised in the following manner:

$$\det(\underset{\sim}{U}\underset{\sim}{H}\underset{\sim}{U}^{\dagger} - E\underset{\sim}{U}\underset{\sim}{S}\underset{\sim}{U}^{\dagger}) = \prod_{\alpha=1}^{h} \{\det(\underset{\sim}{H}_\alpha - E\underset{\sim}{S}_\alpha)\}^{l_\alpha} , \qquad (8)$$

where the matrices $\underset{\sim}{H}_\alpha$ and $\underset{\sim}{S}_\alpha$ are of order $m_\alpha \times m_\alpha$. The roots of Eq. (6) are unaltered by the transformation, and the m_α eigenvalues $E_i^{(\alpha)}$ are therefore given by the factor determinantal equation

$$\det(\underset{\sim}{H}_\alpha - E\underset{\sim}{S}_\alpha) = 0 \ . \qquad (9)$$

The aim of the present paper is to construct irreducible factor equations (9) involving only the characters $\chi^{(\alpha)}$ of the irreducible representations $\Gamma^{(\alpha)}$ of G . It is not feasible in general to determine a transformation matrix $\underset{\sim}{U}$ which will do the job directly. The first step is to use the well known procedure of projecting symmetry adapted functions $\Phi^{(\alpha)}$ out of the basis $\emptyset$.

The number of sets of such functions required is equal to the number of generators, p , in the basis. From the new (redundant) basis $\underset{\sim}{\Phi}$, matrices $\underset{\sim}{H}^{(\alpha)}$ and $\underset{\sim}{S}^{(\alpha)}$ of order $pl_\alpha \times pl_\alpha$ and rank m_α are constructed; these involve the irreducible matrices $\underset{\sim}{\Gamma}^{(\alpha)}$. The final step is to sum over the appropriate principal minors of order m_α of $\underset{\sim}{H}^{(\alpha)} - E\underset{\sim}{S}^{(\alpha)}$, which yields the explicitly invariant form of Eq. (9).

III. FACTORISATION WITH SIMPLE BASIS

Consider first the simplest case in which the space of the basis ϕ can be generated by the action of the g symmetry operators $\mathcal{R}$ of the group on one member, say ϕ_1. This is only possible if $n \leqslant g$, or more precisely $m_\alpha \leqslant l_\alpha$. A new basis, $\underset{\sim}{\Phi}^{(1)}$, $\underset{\sim}{\Phi}^{(2)}$, ... , $\underset{\sim}{\Phi}^{(k)}$ of g symmetry functions may then be defined by[2]

$$\Phi_{ik}^{(\alpha)} = g^{-1} \sum_R \Gamma_{ik}^{(\alpha)}(R)\, \mathcal{R}\phi_1 , \qquad (10)$$

where the sum is over all ements R of $\mathcal{G}$. The significance of the Φ's follows from the orthogonality theorem for irreducible representations (Wigner, 1959), which leads to the result

$$\langle \Phi_{ik}^{(\alpha)}, \mathcal{D}\Phi_{j\ell}^{(\beta)} \rangle = \delta_{\alpha\beta}\delta_{ij}(g l_\alpha)^{-1} \sum_R \Gamma_{k\ell}^{(\alpha)}(R)\, \mathcal{D}_R , \qquad (11)$$

where $\mathcal{D}$ is any operator which commutes with the operators of $\mathcal{G}$, and

$$D_R = \langle \phi_1, \mathcal{D} R \phi_1 \rangle . \tag{12}$$

Let the members $\Phi_{ik}^{(\alpha)}$ of the new basis be ordered lexicographically, first by the representation superscript α, then by the row suffix i, and finally by the column suffix k. Then it follows from Eq. (11) that the new g x g matrix representative of $\mathcal{D} = \mathcal{H} - E$, which commutes with $\mathcal{G}$, will have a block form of the kind illustrated in Figure 1. The ℓ_α blocks $\underset{\sim}{D}^{(\alpha)} = \underset{\sim}{H}^{(\alpha)} - E\underset{\sim}{S}^{(\alpha)}$ of order $\ell_\alpha \times \ell_\alpha$, belonging to representation $\Gamma^{(\alpha)}$, are identical, since the expression on the right hand side of Eq. (11) is independent of i for i = j. The block sub-matrix $\underset{\sim}{D}^{(\alpha)}$ may be conveniently defined by summing Eq. (11) over i and j to give[3]

$$\underset{\sim}{D}^{(\alpha)} = \langle \underset{\sim}{\Phi}^{(\alpha)}, (\mathcal{H} - E) \underset{\sim}{\Phi}^{(\alpha)} \rangle = g^{-1} \sum_R \underset{\sim}{\Gamma}^{(\alpha)}(R) D_R \tag{13}$$

where

$$D_R = H_R - E S_R . \tag{14}$$

The matrix $\underset{\sim}{D}^{(\alpha)}$ of order $\ell_\alpha \times \ell_\alpha$ is of rank m_α. This follows from the fact that the ℓ_α^2 functions $\underset{\sim}{\Phi}^{(\alpha)}$ span a subspace of dimension $m_\alpha \ell_\alpha$, belonging to $\Gamma^{(\alpha)}$, of the n-dimensional space of the basis $\underset{\sim}{\phi}$. Since functions belonging to different rows of $\underset{\sim}{\Phi}^{(\alpha)}$ are orthogonal, only m_α functions in any row are linearly independent. Nevertheless, the m_α roots $E_i^{(\alpha)}$ could be obtained from the determinantal equation

$$\det(\underset{\sim}{D}^{(\alpha)}) \equiv \det(\underset{\sim}{H}^{(\alpha)} - E\underset{\sim}{S}^{(\alpha)}) = 0 . \qquad (15)$$

This has two disadvantages, however. In the first place, if $m_\alpha < \ell_\alpha$ Eq. (15) will have $\ell_\alpha - m_\alpha$ irrelevant zero roots. Secondly, to construct $\underset{\sim}{D}^{(\alpha)}$ it is necessary to have particular realizations of the $\underset{\sim}{\Gamma}^{(\alpha)}(R)$. These disadvantages are removed in the next section.

IV. INVARIANT FACTOR EQUATIONS

Possible forms for the irreducible factor equations (9) are obtained by equating to zero any non-vanishing minor of $\underset{\sim}{D}^{(\alpha)}$ of order m_α. However, such forms contain the elements of the irreducible matrices $\underset{\sim}{\Gamma}^{(\alpha)}(R)$ explicitly. A form involving only the group characters can be obtained by equating to zero the <u>sum</u>

of all the principal minors of $\underset{\sim}{D}^{(\alpha)}$ of order m_α. Since $\underset{\sim}{D}^{(\alpha)}$ is hermitian, at least one of the principal minors must be non-vanishing ($m_\alpha \neq 0$). Furthermore, the non-vanishing minors must be proportional to each other, since they all yield the same roots.

For convenience in deriving the explicitly invariant form, the representation number α will be dropped everywhere temporarily. The matrix $\underset{\sim}{D}^{(\alpha)}$ given by Eq. (13) will therefore be written, ignoring the factor g^{-1},

$$\underset{\sim}{D} = \sum_R \underset{\sim}{\Gamma}(R) D_R . \tag{16}$$

A typical principal minor of $\underset{\sim}{D}$ of order m is

$$M_{ij\ldots k} \equiv \begin{vmatrix} \sum\limits_R D_R \Gamma_{ii}(R), & \sum\limits_R D_R \Gamma_{ij}(R), & \ldots & \sum\limits_R D_R \Gamma_{ik}(R) \\ \sum\limits_R D_R \Gamma_{ji}(R), & \sum\limits_R D_R \Gamma_{jj}(R), & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \sum\limits_R D_R \Gamma_{ki}(R), & \ldots & \ldots & \sum\limits_R D_R \Gamma_{kk}(R) \end{vmatrix} . \tag{17}$$

By the rule for addition of determinants this may be written

$$M_{ij\ldots k} = \sum_R \sum_Q \ldots \sum_K D_R D_Q \cdots D_K \begin{vmatrix} \Gamma_{ii}(R), & \Gamma_{ij}(R), & \ldots & \Gamma_{ik}(R) \\ \Gamma_{ji}(Q), & \Gamma_{jj}(Q), & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \Gamma_{ki}(K), & \ldots & \ldots & \Gamma_{kk}(K) \end{vmatrix} . \tag{18}$$

The sum of the principal minors is

$$\sum_{i>}^{\ell}\sum_{j>}^{\ell}\cdots\sum_{>k=1}^{\ell} M_{ij\ldots k} = \sum_{R}\sum_{Q}\cdots\sum_{K} D_R D_Q \ldots D_K \, X_m(R,Q,..,K) \tag{19}$$

where

$$X_m(R,Q,..,K) = (m!)^{-1}\sum_{i=1}^{\ell}\sum_{j=1}^{\ell}\cdots\sum_{k=1}^{\ell} \left|\begin{matrix} \Gamma_{ii}(R), & \Gamma_{ij}(R), & \ldots & \Gamma_{ik}(R) \\ \Gamma_{ji}(Q), & \Gamma_{jj}(Q), & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots \\ \Gamma_{ki}(K), & \ldots & \ldots & \Gamma_{kk}(K) \end{matrix}\right|_m \tag{20}$$

The importance of the coefficients X defined above lies in the fact that they can be expressed directly in terms of the characters $\chi(R)$, $\chi(RQ)$, etc., of the α th irreducible representation. That this is possible can be seen immediately by comparing a typical term from the determinant of (20) with the formulae for the characters:

$$\chi(R) = \sum_i \Gamma_{ii}(R) ,$$

$$\chi(RQ) = \sum_i\sum_j \Gamma_{ij}(R)\,\Gamma_{ji}(Q),$$

$$\chi(RQK) = \sum_i\sum_j\sum_k \Gamma_{ij}(R)\,\Gamma_{jk}(Q)\,\Gamma_{ki}(K), \text{ etc.}$$

Every system in the <u>compound character</u> X_m , as it may be called, corresponds to a permutation belonging to the symmetric group of degree m . Therefore

$$X_m(R_1, R_2, .., R_m) = (m!)^{-1} \sum_P \pm T_P(R_1, R_2, .., R_m) \quad (21)$$

where the summation is over all $m!$ permutations, and the + or - sign is taken according to whether P is even or odd. The correspondence between the permutations P and the individual terms of equation (21) is illustrated by the following example: if m = 5 and P=(1)(3)(254), then

$$T_P(R_1, .., R_5) = \chi(R_1)\,\chi(R_3)\,\chi(R_2 R_5 R_4)\ ;$$

the form of T_P in the general case is clear from this example. The first three compound characters are

$$X(R) = \chi(R),$$

$$X(R,Q) = \tfrac{1}{2}\left[\chi(R)\chi(Q) - \chi(RQ)\right],$$

$$X(R,Q,K) = \tfrac{1}{6}\Big[\chi(R)\chi(Q)\chi(K) - \chi(R)\chi(QK) - \chi(Q)\chi(KR) - \chi(K)\chi(RQ)$$
$$+ \chi(RQK) + \chi(QRK)\Big]. \quad (22)$$

The X_m are not defined for $m > \ell$, the dimension of the representation. Some elementary properties are as follows.

(a) $X_m(R,Q,\ldots, K)$ is symmetric in $R, Q, \ldots, K$.

(b) $\sum_R X_m(R,Q,\ldots, K) = 0$, except for the unit representation.

(c) $X_\ell(R,R,\ldots, R) = \det\{\underset{\sim}{\Gamma}(R)\} = \pm 1$, since $\underset{\sim}{\Gamma}$'s unitary.

The explicitly invariant form of the irreducible factor equations can be obtained by equating (19) to zero. By substituting for D_R from Eq. (14), introducing $R_1, R_2, \ldots, R_m$ as the element summation symbols and restoring the representation number α , Eq. (19) can be written in the polynomial form:

$$\sum_{r=0}^{m_\alpha} \binom{m_\alpha}{r} (-E)^{m_\alpha - r} \sum_{R_1} \sum_{R_2} \cdots \sum_{R_m} H_{R_1} H_{R_2} \cdots H_{R_r} S_{R_{r+1}} \cdots S_{R_m} X_m^{(\alpha)}(R_1, \ldots, R_m) = 0 . \qquad (23)$$

For the cases $m_\kappa = 1$, 2 and 3, Eq. (23) for the $E_i^{(\alpha)}$ has the form

$$\sum_R (H_R - E S_R) X^{(\alpha)}(R) = 0,$$

$$\sum_R \sum_Q (H_R H_Q - 2E H_R S_R + E^2 S_R S_Q) X^{(\alpha)}(R,Q) = 0,$$

$$\sum_R \sum_Q \sum_K (H_R H_Q H_K - 3E H_R H_Q S_K + 3E^2 H_R S_Q S_K - E^3 S_R S_Q S_K) X^{(\alpha)}(R,Q,K) = 0, \qquad (24)$$

where $X^{(\alpha)}(R,Q)$ and $X^{(\alpha)}(R,Q,K)$ are given by Eq. (22).

V. GENERAL BASIS

Consider now the general case in which the basis $\emptyset$ possesses p generators, say $\emptyset_1$, $\emptyset_2$, ..., $\emptyset_p$. That is, the gp functions $R\emptyset_1$, $R\emptyset_2$, ..., $R\emptyset_b$ where R ranges over the group $\mathcal{G}$, span the n-dimensional space of the basis. The functions produced from the generators may be linearly dependent ($n \leqslant gp$). Let the sub-basis ${}^{\mu}\emptyset$, consisting of the g functions $R\emptyset_{\mu}$ ($R \subset \mathcal{G}$), be of rank ${}^{\mu}m$, so that

$$n = \sum_{\mu=1}^{p} {}^{\mu}m \,.$$

The ${}^{\mu}\emptyset$ form the basis for a representation ${}^{\mu}\Gamma$ of the group of order ${}^{\mu}m$, in general reducible. Let

$$^{\mu}\Gamma = \sum_{\alpha=1}^{h} {}^{\mu}m_{\alpha}\, \Gamma^{(\alpha)}. \tag{25}$$

Then it follows from Eq.(5) that

$$m_{\alpha} = \sum_{\mu=1}^{p} {}^{\mu}m_{\alpha} \,, \quad \text{and} \quad {}^{\mu}m = \sum_{\alpha=1}^{h} {}^{\mu}m_{\alpha}\, l_{\alpha} \,. \tag{26}$$

To factorise the secular equation (1) in the general case it is necessary to introduce a set of g symmetry functions ${}^{\mu}\Phi = {}^{\mu}\underset{\sim}{\Phi}^{(1)}, {}^{\mu}\underset{\approx}{\Phi}^{(2)}, \ldots, {}^{\mu}\Phi^{(h)}$ for each sub-basis ${}^{\mu}\emptyset$, defined by

$$ {}^{\mu}\underset{\sim}{\Phi}^{(\alpha)} = g^{-1} \sum_{R} \underset{\sim}{\Gamma}^{(\alpha)}(R)\, R\phi_{\mu} . \qquad (27)$$

Let the new basis of gp functions ${}^{\mu}\Phi^{(\alpha)}_{ik}$ be ordered lexicographically by α , μ , i , k . The matrix representative of the operator $\mathcal{D} = \mathcal{H} - E$ will consist of l_{α} diagonal blocks $\underset{\sim}{D}^{(\alpha)}$ for each representation $\Gamma^{(\alpha)}$, as in the simple case of section III. However, the $\underset{\sim}{D}^{(\alpha)}$ are now of order pl_{α} x pl_{α} , a nd consists of sub-matrices ${}^{\mu\nu}\underset{\sim}{D}^{(\alpha)}$,

$$ \underset{\sim}{D}^{(\alpha)} = [{}^{\mu\nu}\underset{\sim}{D}^{(\alpha)}] . \qquad (28)$$

The sub-matrices may be defined, by analogy with Eq. (13), by

$$ \begin{aligned} {}^{\mu\nu}\underset{\sim}{D}^{(\alpha)} &= \langle {}^{\mu}\underset{\sim}{\Phi}^{(\alpha)}, \mathcal{D}\, {}^{\nu}\underset{\sim}{\Phi}^{(\alpha)} \rangle , \\ &= g^{-1} \sum_{R} \underset{\sim}{\Gamma}^{(\alpha)}(R)\, {}^{\mu\nu}D_{R} , \end{aligned} \qquad (29)$$

where

$$ \begin{aligned} {}^{\mu\nu}D_{R} &= \langle \phi_{\mu}, \mathcal{D} R\, \phi_{\nu} \rangle , \\ &= {}^{\mu\nu}H_{R} - E\, {}^{\mu\nu}S_{R} . \end{aligned} \qquad (30)$$

By introducing new p x p matrices $\underset{\sim}{D}_R$, whose elements are the ${}^{\mu\nu}D_R$, the matrix $\underset{\sim}{D}^{(\alpha)}$ may be defined succinctly by

$$\underset{\sim}{D}^{(\alpha)} = g^{-1} \sum_R \underset{\sim}{\Gamma}^{(\alpha)}(R) \times \underset{\sim}{D}_R , \qquad (31)$$

where $\times$ indicates a direct product.

The required form of the irreducible factor equations is obtained by taking the sum of certain of the principal minors of $\underset{\sim}{D}^{(\alpha)}$ of order m_α . These minors must contain ${}^{\mu}m_\alpha$ rows and columns from the sub-matrix ${}^{\mu\mu}\underset{\sim}{D}^{(\alpha)}$ of rank ${}^{\mu}m_\alpha$, as any non-vanishing minor of $\underset{\sim}{D}^{(\alpha)}$ of order m_α must consist of linearly independent rows and columns. Let $M_{ij} \ldots k\,({}^1m, {}^2m, \ldots, {}^pm)$ be a principal minor of $\underset{\sim}{D}^{(\alpha)}$ of order $m = {}^1m + {}^2m + \ldots + {}^pm$ which satisfies the above condition. By the rule for the addition of determinants, it can be written

$$M_{ij\ldots k}({}^1m, {}^2m, \ldots, {}^pm) =$$

$$\sum_R \sum_Q \ldots \sum_K \left| \begin{array}{c:c:c} {}^{11}D_R \Gamma_{ii}(R) \;,\; {}^{11}D_R \Gamma_{ij}(R), \ldots & \ldots & \ldots {}^{1p}D_R \Gamma_{ik}(R) \\ {}^{11}D_Q \Gamma_{ji}(Q) \;,\; {}^{11}D_Q \Gamma_{jj}(Q), \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots \\ \hdashline \ldots & \ldots & \ldots \\ \hdashline \ldots & \ldots & \ldots \\ {}^{p1}D_K \Gamma_{ki}(K), \ldots & \ldots & \ldots {}^{pp}D_K \Gamma_{kk}(K) \end{array} \right| \qquad (32)$$

where the representation superscript α has been dropped from Γ. The determinant in Eq. (32) differs from that in the corresponding Eq. (18) of the previous section, in that it is not possible to factor the ${}^{\mu\nu}D_R$'s out of it. An explicitly invariant form of the irreducible factor equation is still obtained by taking the sum over all such minors, but in this general case must be left in the form[4]

$$\sum_{i=1}^{l}\sum_{j=1}^{l}\cdots\sum_{k=1}^{l} M_{ij\ldots k}({}^{1}m,\ldots,{}^{p}m) = 0. \tag{33}$$

It can be seen, however, that the coefficient of any product of the ${}^{\mu\nu}D_R$'s will be directly expressible in terms of the simple characters $\chi^{(\alpha)}$; the compound characters $\chi_m^{(\alpha)}$ do not appear in general. The invariant form of the factor equations can be illustrated best by means of simple examples in which the basis ϕ possesses $p = 2$ generators, ϕ_1 and ϕ_2.

(a) Consider the case ${}^{1}m = {}^{2}m = 1$. The general principal minor of $\underset{\sim}{D}^{(\alpha)}$ of order 2 is

$$M_{ij}(1,1) = \sum_R\sum_Q \left| \begin{array}{c|c} {}^{11}D_R\Gamma_{ii}(R) & {}^{12}D_R\Gamma_{ij}(R) \\ \hline {}^{21}D_Q\Gamma_{ji}(Q) & {}^{22}D_Q\Gamma_{jj}(Q) \end{array} \right| .$$

taking the sum of the principal minors, Eq. (33) is

$$\sum_{R}\sum_{Q}\left[{}^{11}D_R\,{}^{22}D_Q\,\chi(R)\chi(Q) - {}^{12}D_R\,{}^{21}D_Q\,\chi(RQ)\right] = 0. \qquad (34)$$

(b) Consider the case ${}^{1}m = 1$, ${}^{2}m = 2$. The principal minor is

$$M_{ijk}(1,2) = \sum_{R}\sum_{Q}\sum_{K}\left|\begin{array}{c|cc} {}^{11}D_R\,\Gamma_{ii}(R) & {}^{12}D_R\,\Gamma_{ij}(R) & {}^{12}D_R\,\Gamma_{ik}(R) \\ \hline {}^{21}D_Q\,\Gamma_{ji}(Q) & {}^{22}D_Q\,\Gamma_{jj}(Q) & {}^{22}D_Q\,\Gamma_{jk}(Q) \\ {}^{21}D_K\,\Gamma_{ki}(Q) & {}^{22}D_K\,\Gamma_{kj}(K) & {}^{22}D_K\,\Gamma_{kk}(K) \end{array}\right| .$$

Expanding the determinant and taking the sum over all i, j, k this becomes

$$\sum_{R}\sum_{Q}\sum_{K} {}^{22}D_K\left\{{}^{11}D_R\,{}^{22}D_Q\left[\chi(Q)\chi(K) - \chi(QK)\right]\chi(R) + \right.$$

$$\left. + 2\,{}^{12}D_R\,{}^{21}D_Q\left[\chi(RQK) - \chi(RQ)\chi(K)\right]\right\} = 0. \qquad (35)$$

These equations may be put in the form of polynomials in E by substituting for ${}^{\mu\nu}D_R$ from Eq. (30).

VI. EPILOGUE

It would seem incredible if the mathematical problem solved in this paper had not been tackled and solved at least fifty years ago by the mathematicians of group representation theory. However, a reasonably diligent search of the literature, and much questioning of mathematicians, has not yet brought such a discussion to light. Rather than engage in further historical research, it seemed more sensible to publish the author's treatment of the problem within the context of quantum mechanics.

ACKNOWLEDGEMENTS

I would like to thank Professor H. C. Longuet-Higgins for suggesting the problem discussed in this paper, and for supervizing my work on it some years ago. I am also very grateful to Professor P. O. Löwdin, whose interest and enthusiasm have led to its resuscitation, for valuable discussion and criticism. Lastly, I would like to thank the Department of Scientific and Industrial Research (U.K.) for a grant, during the tenure of which most of the work was carried out.

REFERENCES

Slater, J. C. (1929). Phys. Rev. 34, 1293.

Slater, J. C. (1960). In "Quantum Theory of Atomic Structure", Vol. II. McGraw-Hill, New York.

Wigner, E. P. (1959). "Group Theory and its Applications to the Quantum Mechanics of Atomic Spectra". Academic Press, New York.

FOOTNOTES

1. Note that $\underset{\sim}{U}$ is not the same as the matrix which reduces the matrices of Γ simultaneously to the block form (5).

2. The usual definition involves the complex imaginary of the matrix element $\underset{\sim}{\Gamma}$, which is a nuisance in the present work.

3. The notation in Eq. (13) requires that the adjoint be taken of a matrix in the left half of a bracket expression. This definition of $\underset{\sim}{D}^{(\alpha)}$ is ℓ_α times that occurring in Figure 1.

4. Eq. (33) is actually $({}^{1}m!\ {}^{2}m!\ \ldots {}^{p}m!)$ times the sum of the appropriate principal minors of $\underset{\sim}{D}^{(\alpha)}$.

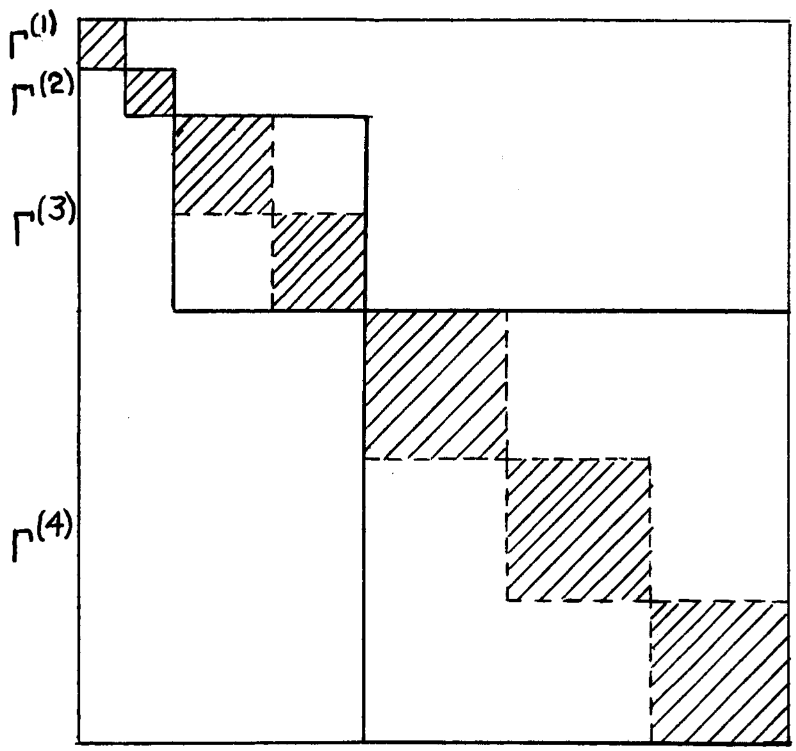

Figure 1

LEGEND FOR FIGURE 1

Figure 1. Block form of $\underset{\sim}{D} = \underset{\sim}{H} - E\underset{\sim}{S}$ in the symmetry basis Φ for a group of order 15 with 4 irreducible representations with dimensions 1,1,2 and 3. Non-zero matrix elements are shaded.