COLOPHON

The attached paper has little connection with my current research in Computer Science and Digital Documents. It is very simply an experiment to see how long it would take me to build an electronic version of a paper I published, with George Hall, in the International Journal of Quantum Chemistry (John Wiley Inc.) in 1971. This, of course, was well before the era of desktop publishing and all I had was a reprint of the original paper. I decided against scanned bitmap pages and/or the use of an OCR package, reasoning that the time taken to rebuild the paper to my liking, with something like *Acrobat Capture*, would probably exceed the time taken to re-key the whole thing.

So, the paper was totally re-keyed. UNIX *troff* was used to set up the correct typeface (Baskerville) and to get the line and page breaks as accurate as posssible. Specialist material within the paper was re-set with the *refer*, *eqn*, *tbl* and *psfig* pre-processors for *troff*.

Of course, another candidate for this exercise would have been LATEX but although I use this quite a lot for journal and conference papers I am not very skilled in the tweaks needed to get exact page layout, especially when non-standard fonts such as Baskerville are to be used. Hence the decision to use the *troff* suite.

The three diagrams were scanned in from an original reprint of the paper, cleaned up in Adobe Photoshop and then vectorized using Adobe Streamline. Further small adjustments, including resetting of the 'C' and 'H' characters in the neopentane diagram, were done in Adobe Illustrator before exporting each diagram to version 3.0 of Illustrator's Encapsulated PostScript (but with no TIFF preview). This Encapsulated PostScript was then incorporated into the paper using *psfig*.

This form of "rescue" of an early paper can produce a very pleasing result but the time taken to do it (12 hours for this paper) makes it prohibitively expensive for any publisher to undertake as a general procedure, especially given that you need to be totally familiar with something like *troff/eqn*, or LATEX before you can even begin.

The International Journal of Quantum Chemistry home page is at:
`http://www3.interscience.wiley.com/cgi-bin/jhome/29830`
and PDF versions of more recent papers in that journal (i.e. from 1996 onwards) are available via that site.

Symmetry Properties of One- and Two-Electron Molecular Integrals

D. F. BRAILSFORD AND G. G. HALL

Department of Mathematics, University of Nottingham, England

Abstracts

The maximum numbers of distinct one- and two-electron integrals that arise in calculating the electronic energy of a molecule are discussed. It is shown that these may be calculated easily using the character table of the symmetry group of the set of basis functions used to express the wave function. Complications arising from complex group representations and from a conflict of symmetry between the basis set and the nuclear configuration are considered and illustrated by examples.

On discute les nombres maximaux d'integrales mono- et biélectroniques distinctes qui sont nécessaires pour calculer l'énergie électronique d'une molecule. On montre que ceux-ci peuvent être calculés facilement au moyen du tableau de caractères du groupe de symétrie des fonctions de base employées. Des complications dues aux représentations complexes et au conflit de symétrie entre les fonctions de base et la configuration nucléaire ont été considérées et illustrées par des exemples.

Die maximalen Anzahlen von verschiedenen Ein- und Zweielektronenintegralen, die in der Berechnung der elektronischen Energie eines Moleküls vorkommen, werden diskutiert. Es wird gezeigt, dass diese leicht mittels der Charakterentafel der Symmetriegruppe für den Basissatz berechnet werden können. Komplikationen, die von komplexen Gruppendarstellungen und von dem Symmetriekonflikt zwischen dem Basissatz und der Kernkonfiguration entstehen, werden betrachtet und mit Beispielen illustriert.

1. Introduction

One of the less familiar uses of group theory in molecular studies is its use for predicting the number of independent physical constants needed to describe some molecular property. In this paper we are concerned with the number of independent one- and two-electron integrals that occur between the functions of a basis set used to describe the electronic structure of a molecule. These numbers are important in checking the input data for molecular orbital calculations of various different kinds. To simplify the details of the discussion we restrict our discussion to states where spin properties do not enter explicitly. These include closed shell ground states and states in which all orbitals are singly-occupied with the same spin factor.

657

2. One-Electron Integrals

We first consider the integrals of various one-electron operators between a set of real basis functions $\phi_a, \phi_b, \phi_c \ldots$. These will be the basis functions used to express the molecular orbitals for the molecule. The discussion is independent of the analytical or numerical specification of the functions. Three types of integral have to be considered

$$(1) \qquad\qquad [a \,|\, b] = \int \phi_a \phi_b \, dV$$

$$(2) \qquad\qquad [a \,|{-}\tfrac{1}{2}\nabla^2 \,|\, b] = \int \phi_a (-\tfrac{1}{2}\nabla^2) \phi_b \, dV$$

$$(3) \qquad\qquad [a \,|\, \sum_\alpha \frac{Z_\alpha}{r_\alpha} \,|\, b] = \int \phi_a \left[\sum_\alpha \frac{Z_\alpha}{r_\alpha} \right] \phi_b \, dV$$

The first two involve the unit operator and the operator $(-\tfrac{1}{2}\nabla^2)$ respectively and both of these are invariant under any possible symmetry operation of the molecule or of the basis functions. On the other hand the nuclear attraction integrals (3) depend on the nuclear potential which has the molecular symmetry. Integrals of this type in which the basis functions have a different symmetry from the molecule are considered later.

Because of the Hermitian property of the operators and the reality of the functions

$$(4) \qquad [a|b] = [b|a], \quad [a|{-}\tfrac{1}{2}\nabla^2|b] = [b|{-}\tfrac{1}{2}\nabla^2|a],$$

$$[a|\sum_\alpha \frac{Z_\alpha}{r_\alpha}|b] = [b|\sum_\alpha \frac{Z_\alpha}{r_\alpha}|a]$$

Thus if the functions are unrelated there will be

$$(5) \qquad\qquad \tfrac{1}{2}n(n+1)$$

integrals of each kind between n basis functions.

In general some of the basis functions will permute into one another under a symmetry operation and this will reduce appreciably the number of distinct integrals. To determine this number we consider the reduction of the matrix of integrals to block form by the introduction of symmetry orbitals to replace the original basis functions. This can be conveniently discussed in terms of an example. The electronic structure of the staggered form of ethane can be described in terms of equivalent orbitals, χ_n. Six of these orbitals are asociated with the six CH bonds and have their symmetry, and one with the CC bond. The matrix elements of the self-consistent Hamiltonian with respect to these equivalent orbitals (EO) are the one-electron integrals

$$(6) \qquad\qquad e_{mn} = \int \chi_m \, H_{\text{SCF}} \, \chi_n \, dV$$

In the semi-empirical form of EO theory [1] the distinct integrals are treated as parameters. Thus. for ethane, the six parameters are defined by

(7)
$$e_{mn} = \begin{bmatrix} c & d & d & d & d & d & d \\ d & a & b & b & f & g & g \\ d & b & a & b & g & f & g \\ d & b & b & a & g & g & f \\ d & f & g & g & a & b & b \\ d & g & f & g & b & a & b \\ d & g & g & f & b & b & a \end{bmatrix}$$

The seven EO functions span a permutation representation of the molecular symmetry group (D_{3d}). By considering its character it is easy to find the irreducible representations into which it can be resolved:

(8)
$$\Gamma_{\mathrm{EO}} = 2A_{1g} \oplus A_{2u} \oplus E_g \oplus E_u$$

It is then possible, using the group theoretical projection operators, to find symmetry orbitals which will span each of these representations. Since a matrix element

(9)
$$E_{rs} = \int \psi_r H_{\mathrm{SCF}} \psi_s \, dV$$

between two symmetry orbitals will vanish unless the orbitals ψ_r and ψ_s belong to the same irreducible representation, this change in basis brings E_{rs} into block form. The A_{1g} block has two rows and columns

(10)
$$\begin{bmatrix} E_{11} & E_{12} \\ E_{21} & E_{22} \end{bmatrix} \qquad (2A_{1g})$$

and their values are readily calculated to be

(11)
$$E_{11} = c, \quad E_{22} = a + 2b + f + 2g, \quad E_{12} = E_{21} = \sqrt{6}d$$

The other blocks have only one element each

(12)
$$E_{33} = a + 2b - f - 2g \qquad (A_{2u})$$

(13)
$$E_{44} = E_{55} = a - b + f - g \quad (E_g)$$

(14)
$$E_{66} = E_{77} = a - b - f + g \quad (E_u)$$

Thus, although each degenerate E representation produces two non-zero elements, these are equal and it can be seen that, if an irreducible representation occurs only once, it will yield one distinct matrix element. An irreducible representation occurring twice yields three distinct matrix elements. Thus in total there are 6

distinct matrix elements E_{rs} and, since this number is a symmetry property, it is independent of the basis set and so equals the number of distinct parameters in the equivalent orbital matrix e_{mn} .

In more general terms the number of distinct one-electron integrals over a totally symmetric operator is found by a resolution into irreducible representations. If n basis functions span a reducible representation Γ of the group, the character of the representation can be found from the $n \times n$ matrices and thence the resolution into irreducible representations

$$(15) \qquad\qquad \Gamma = m_1 \Gamma^{(1)} \oplus m_2 \Gamma^{(2)} \oplus \; \cdots$$

The total number of distinct integrals is then

$$(16) \qquad\qquad K = \tfrac{1}{2} \sum_k m_k (m_k + 1)$$

The use of this result in connection with normal modes of vibration has been discussed by Herzberg [2]

In all the one-electron integrals considered above, the operator has been assumed to have at least the full symmetry of the group appropriate to the basis functions. The nuclear attraction integral has the symmetry of the nuclear configuration and this may be lower than the symmetry of the basis set. In this event the same formulae can be used provided that the group concerned is the maximum subgroup common to the group of the nuclei and the group of the basis set. If integrals over the potentials of individual nuclei are considered then the subgroup common to the nucleus and the basis set is required.

3. The Direct Product

An alternative way of discussing these one-electron integrals is in terms of the direct product representation spanned by the functions ϕ_x multiplied together in pairs as in the integrand. The only non-vanishing integrals will then be those corresponding to the identity representation.

The direct product of a representation with itself may be simplified immediately into a symmetric and an anti-symmetric part denoted by $[\Gamma]^2$ and $\{\Gamma\}^2$ respectively. Because the integrals are real and Hermitian, only $[\Gamma]^2$ is here involved. To isolate the symmetric part of the direct product we consider first the character of the representation. The principles involved can be illustrated using a simple example. If the functions χ_1 and χ_2 span a two-dimensional representation then the effect of a group operation produces new functions η_1 and η_2 where

$$(17) \qquad\qquad \begin{bmatrix} \eta_1 \\ \eta_2 \end{bmatrix} = \begin{bmatrix} a & b \\ c & d \end{bmatrix} \begin{bmatrix} \chi_1 \\ \chi_2 \end{bmatrix} = A \begin{bmatrix} \chi_1 \\ \chi_2 \end{bmatrix}$$

so that the group operation is represented by the matrix A. The three distinct

symmetric products η_1^2, $\eta_1\eta_2$, η_2^2 are readily deduced from these equations and the result of the group operation can be written as

$$(18) \qquad \begin{bmatrix} \eta_1^2 \\ \eta_1\eta_2 \\ \eta_2^2 \end{bmatrix} = \begin{bmatrix} a^2 & 2ab & b^2 \\ ac & ad + bc & bd \\ c^2 & 2cd & d^2 \end{bmatrix} \begin{bmatrix} \chi_1^2 \\ \chi_1\chi_2 \\ \chi_2^2 \end{bmatrix}$$

This matrix is the symmetrical direct product, $[A]^2$, of the original matrix. The trace of the matrix is

$$(19) \qquad \operatorname{tr} [A]^2 = a^2 + ad + bc + d^2$$

but the traces of the original matrix and its square are

$$(20) \qquad \operatorname{tr} A = a + d$$

$$(21) \qquad \operatorname{tr} A^2 = a^2 + 2bc + d^2$$

so that

$$(22) \qquad \operatorname{tr}[A]^2 = \tfrac{1}{2}\{(\operatorname{tr} A)^2 + \operatorname{tr} A^2\}$$

This result is proved generally by Murnaghan [3] and extended to higher symmetrized direct powers. Since, for the direct product $A \times A$

$$(23) \qquad \operatorname{tr} (A \times A) = (\operatorname{tr} A)^2$$

it follows that the antisymmetrized direct product will have the trace

$$(24) \qquad \operatorname{tr}\{A\}^2 = \tfrac{1}{2}\{(\operatorname{tr} A)^2 - \operatorname{tr} A^2\}$$

The totally symmetric representation cannot occur in the antisymmetrized direct product spanned by two functions of the same variable so that this representation must occur the same number of times in Γ^2 as in $[\Gamma]^2$.

4. Symmetry Groups Having Complex Representations

Some molecular symmetry groups, such as the cyclic group whose order is at least 3, have representations whose characters are complex. These representations can always be grouped together in conjugate pairs. In the Mulliken notation [4] two singly-degenerate conjugate representations are bracketed together into one "doubly degenerate" representation denoted by E. A representation of a symmetry group spanned by real functions must consist of real matrices and so must have a real character. Consequently, if the representation contains one of these conjugate pairs it must also include the other.

The formula for the number of distinct one-electron integrals needs to be modified to fit groups of this kind. The group C_3, for example, contains the conjugate representations γ and γ^*. The direct products $\gamma \times \gamma$ and $\gamma^* \times \gamma^*$ will not generate the identity representation but the product $\gamma \times \gamma^*$ does do this.

If γ and γ^* each occur p times in the reduction of the representation spanned by the functions then the product of each γ with any of the γ^* will generate an invariant. Thus there will be p^2 distinct products. If the conjugate representations are counted as E representations in Mulliken's nomenclature, the number of distinct integrals will become

$$(25) \qquad K = \tfrac{1}{2} \sum_{k \text{ real}} m_k(m_k + 1) + \sum_{l \text{ complex}} m_l^2$$

where the first sum includes all real representations and the second all pairs of complex representations.

5. Two-Electron Integrals

The two-electron integrals needed to calculate the energy are all of the form

$$(26) \qquad [ab|cd] \equiv \int \phi_a(1)\phi_b(1) \frac{1}{r_{12}} \phi_c(2)\phi_d(2) \, dV_{12}$$

The operator $1/r_{12}$ is totally symmetric. The products $\phi_a(1)\phi_b(1)$ and $\phi_c(2)\phi_d(2)$ have already been discussed as one-electron integrands. The two-electron integral has the further symmetry of an interchange of the two electrons so that $[ab|cd] = [cd|ab]$. Thus the following permutations of indices produce equal integrals

$$[ab|cd], \ [ab|dc], \ [ba|cd], \ [ba|dc], \ [cd|ab], \ [cd|ba], \ [dc|ab], \ [dc|ba]$$

In the absence of any symmetry of the basis set, the number of distinct integrals can be obtained by applying twice the argument used for the number of one-electron integrals (Equation 5). With n functions this gives

$$(27) \qquad \tfrac{1}{2}\{\tfrac{1}{2}n(n+1)\}\{\tfrac{1}{2}n(n+1) + 1\} = \tfrac{1}{8}n(n+1)(n^2 + n + 2)$$

When the basis set possesses some symmetry the arguments already used can be readily adapted. The product representation spanned by $\phi_a\phi_b$ is $[\Gamma]^2$. This can be reduced to a direct sum of irreducible representations by taking the scalar products with the characters given in the character table in the usual way. If this sum is

$$(28) \qquad [\Gamma]^2 = l_1\Gamma^{(1)} \oplus l_2\Gamma^{(2)} \oplus \ \cdots$$

then the number of distinct two-electron integrals is just

$$(29) \qquad M = \tfrac{1}{2}\sum_k l_k(l_k + 1)$$

Alternatively we may find the number of occurrences of the identity representation in $[[\Gamma]^2]^2$, the symmetrized square of $[\Gamma]^2$.

6. The Character of $[\Gamma]^2$ for a Molecular Symmetry Group

The formula (22) for the trace of a matrix of the symmetrized direct product can be used to simplify the task of calculating the character of $[\Gamma]^2$ and hence of reducing it to irreducible representations. The trace of the matrix A representing a group element $\mathbf{A}$ in the representation Γ is usually easily determined. The trace of the matrix A^2 would normally require a knowledge of all the elements of A but we can now use the fact that A represents $\mathbf{A}$ and consequently that A^2 represents $\mathbf{A}^2$. The trace of A^2 is found, therefore, to be the trace of the matrix which represents $\mathbf{A}^2$ in the same representation and so must already be available. The process is now easily explained using some examples.

A. *Neopentane* C_5H_{12}

This molecule has T_d symmetry with the methyl groups placed symmetrically around the centre carbon atom. We consider a representation spanned by basis functions corresponding to each of the CC and CH bonds. This is a 16 dimensional representation and its character is shown in Table I. The characters for the squares of the matrices are deduced from this using the group multiplication properties. Since $I^2 = I$ the identity entry is also 16. In the next class $(C_3)^2 = C_3^2$ which belongs to the same class so the trace is unchanged. The element C_2 gives I
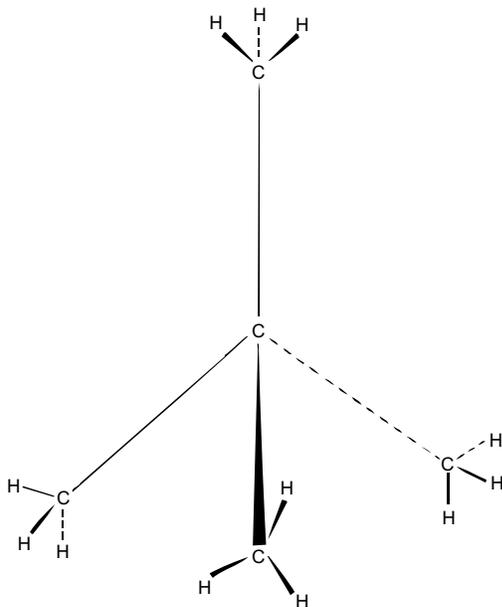

Figure 1. The neopentane molecule (C_5H_{12}). A basis function is associated with each of the C—C and C—H bonds.

Table I. Character of $[\Gamma]^2$ for neopentane

T_d	I	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
tr A	16	1	0	4	0
tr A^2	16	1	16	16	0
tr $[\Gamma]^2$	136	1	8	16	0

when squared and so the next also repeats the entry under I viz. 16 and similarly in the next class since $\sigma_d^2 = I.$ An element S_4 satisfies

$$(30) \qquad\qquad\qquad S_4^2 = C_2$$

so that the final trace will be in the original character. These entries are shown as tr A^2 in Table I. The formula 22 enables the character of $[\Gamma]^2$ to be deduced and this in turn can be reduced using the character table. Thus

$$(31) \qquad\qquad \Gamma = 2A_1 \oplus E \oplus T_1 \oplus 3T_2$$

and using Equation (16), the number of one-electron integrals is

$$(32) \qquad\qquad\qquad K = 11$$

Similarly,

$$(33) \qquad\qquad [\Gamma]^2 = 11A_1 \oplus 3A_2 \oplus 13E \oplus 12T_1 \oplus 20T_2$$

so that the number of two-electron integrals is

$$(34) \qquad\qquad\qquad M = 451$$

B. π electrons of benzene

The π electrons of benzene are often described using six functions each of $2p_z$ type at one of the carbon nuclei. Using the group relations

$$(35) \qquad I^2 = I; \;\; (C_6)^2 = C_3; \;\; (C_3)^2 = C_3^2; \;\; (C_2')^2 = I; \;\; (C_2'')^2 = I; \;\; i^2 = I;$$

$$(S_3)^2 = C_3^2; \;\; (S_6)^2 = C_3; \;\; (\sigma_h)^2 = I; \;\; (\sigma_d)^2 = I; \;\; (\sigma_v)^2 = I$$

the entries for tr A^2 can also be written down (see Table II). The six-dimensional representation reduces as

$$(36) \qquad\qquad \Gamma = A_{2u} \oplus B_{2g} \oplus E_{1g} \oplus E_{2u}$$

while the symmetrized square reduces as

$$(37) \qquad\qquad [\Gamma]^2 = 4A_{1g} \oplus 4E_{2g} \oplus B_{1u} \oplus 2B_{2u} \oplus 3E_{1u}$$

Thus there will be 4 distinct one-electron terms, e.g.

$$(38) \qquad\qquad [1|1],\; [1|2],\; [1|3],\; [1|4]$$

and 30 distinct two-electron terms. This is a known result and a listing of the 30 integrals is given by Parr [5].

Table II. Character of $[\Gamma]^2$ for benzene π electrons

D_{6h}	I	$2C_6$	$2C_3$	C_2	$3C_2{}'$	$3C_2{}''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
tr A	6	0	0	0	0	-2	0	0	0	-6	2	0
tr A^2	6	0	0	6	6	6	6	0	0	6	6	6
tr $[\Gamma]^2$	21	0	0	3	3	5	3	0	0	21	5	3

C. *A hypothetical molecule*

To illustrate the use of complex representations we consider 6 functions grouped as in Figure 2. This has the symmetry C_3 and the character of the representation set up by the 6 functions is given at the bottom of the character table for this group shown in Table II. The reduction can be expressed as
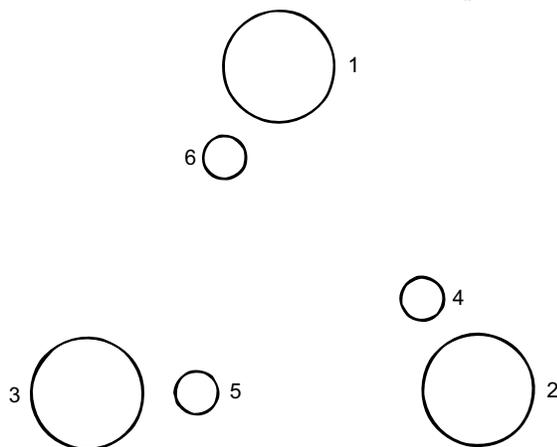

Figure 2. Six basis functions arranged with C_3 symmetry, to describe a hypothetical molecule.

$$(39) \qquad \Gamma = 2A \oplus 2E$$

and using Equation (25) this gives

$$(40) \qquad K = 3 + 2^2 = 7$$

The seven integrals are

$$(41) \qquad [1|1],\ [2|1],\ [4|1],\ [4|2],\ [4|3],\ [4|4],\ [5|4]$$

Similarly, the character of $[\Gamma]^2$ is found using

$$(42) \qquad I^2 = I;\ \ (C_3)^2 = C_3^2;\ \ (C_3^2)^2 = C_3$$

Thus

(43) $$[\Gamma]^2 = 7A \oplus 7E$$

and the number of two-electron integrals is

(44) $$M = 28 + 7^2 = 77$$

Table III. Characters for a C_3 molecule.

C_3	I	C_3	C_3^2	
A	1	1	1	$\varepsilon = \exp 2\pi i /3$
$E \left\{ \begin{array}{c} \\ \\ \end{array} \right.$	1	ε	ε^*	
	1	ε^*	ε	
tr A	6	0	0	
tr A^2	6	0	0	
tr $[\Gamma]^2$	21	0	0	

D. *A conflict of symmetries*

To illustrate the procedure when the nuclear symmetry differs from the symmetry of the basis set we consider, in Figure 3, a basis set consisting of four functions in a square configuration and three nuclei in an equilateral triangle.
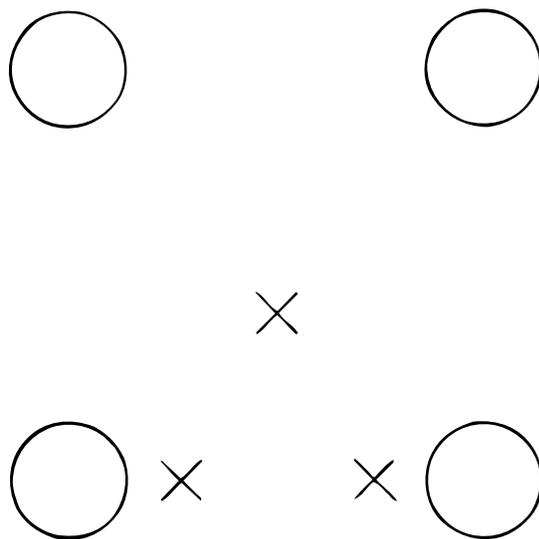

Figure 3. Arrangement of four basis functions ($\bigcirc$) in a square to describe a molecule whose nuclei lie on an equilateral triangle ($\times$).

The square array gives a representation of C_{4v} as

(45) $$\Gamma = A_1 \oplus B_2 \oplus E$$

so that, for totally symmetric operators, there will be 3 distinct one-electron integrals.

The nuclear symmetry is C_{3v} but only operations of a C_{2v} subgroup are common to the two groups and integrals over the nuclear potentials have to be discussed using C_{2v}. This can be done by considering the four functions as spanning a representation of C_{2v} or by examining the splitting of the irreducible representations of C_{4v} into irreducible representations of C_{2v}. Since these splittings are readily derived from the character tables of the two groups we note only the results

(46) $$A_1 \rightarrow A_1 \; ; \;\; A_2 \rightarrow B_1 \; ; \;\; B_1 \rightarrow A_1 \; ; \;\; B_2 \rightarrow B_1 \; ; \;\; E \rightarrow A_1 \oplus B_1$$

where the representation of C_{4v} is listed first. From this

(47) $$\Gamma \rightarrow 2A_1 \oplus 2B_1$$

so that there will be 6 distinct one-electron nuclear potential integrals.

7. Conclusion

The results presented here illustrate the fact that group theory can often be applied very simply to a problem involving symmetry to give some of the required information. Here, the number of distinct one- and two-electron integrals is given but not a listing. On the other hand, it is not too difficult to give a listing, once the precise number is known.

An independent check on all the results mentioned above and on a large number of other examples has been obtained using a program written by Packer [6]. One of the first steps in this program is to list all the distinct one- and two- electron integrals arising in the molecular orbital calculation of a molecular wave function. The list is generated from a list of the basis functions and a table of their permutations. In every instance the number listed agreed with that calculated using the equation given above.

Bibliography

[1] G. G. Hall, *Proc. Roy. Soc. (London)*, **A205**, 541, (1951).

[2] G. Herzberg, *Infra-red and Raman Spectra of Polyatomic molecules,* (D. Van Nostrand, New York, 1945).

[3] F. D. Murnaghan, *The Theory of Group Representations,* (Johns Hopkins Press, Baltimore, 1938).

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

[5] R. G. Parr, *The Quantum Theory of Molecular Electronic Structure,* (Benjamin, New York, 1963).

[6] J. C. Packer, *Science Research Council Report,* (June 1970). unpublished