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The Use of Symmetry in the Self-Consistent Field Theory of the Localised Molecular Orbital

David Peters
Royal Holloway College, University of London

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It is shown how symmetry may be used in the context of the self-consistent field theory of the localised molecular orbital of the chemical bond. The results are (1) a reduction of the order of the secular determinant of the localised molecular orbital: (2) the classifying of the localised and canonical molecular orbitals under the various symmetry groups of the bonds and the molecule: (3) a clarification of the various types of symmetry group which are involved with the localised molecular orbitals.

Es wird gezeigt, wie Symmetrieeigenschaften im Zusammenhang mit der SCF-Theorie lokalisierter Molekülorbitale benutzt werden kann. Die Ergebnisse sind: 1. eine Reduktion der Ordnung der Säkulardeterminante des lokalisierten Molekülorbitals; 2. die Klassifizierung der lokalisierten und kanonischen Molekülorbitale nach den verschiedenen Symmetriegruppen der Bindungen und des Moleküls; 3. eine Klärung der verschiedenen Typen von Symmetriegruppen, die im Zusammenhang mit lokalisierten Molekülorbitalen stehen.

When we deal with the localised molecular orbitals (l.m.o.) which describe the chemical bond [1], it is not clear just what role symmetry plays in this type of theory. It is well known that the l.m.o.s transform as a reducible representation of the molecule's point group and it is less easy to deal with the reducible representations than with the irreducible ones. In addition, the nature of the relevant symmetry group is not obvious because l.m.o.s are confined in large measure to one part of a molecule and so it may seem that the symmetry group should be that of this part of the molecule. On the other hand, no l.m.o. is ever perfectly localised in one region of a molecule because it will generally have small but finite amplitude in all parts of the molecule.

In thinking about chemical bonds and l.m.o.s, we may either begin with an isolated bond and then expand our viewpoint to encompass the whole molecule or we may begin with the whole molecule and then narrow down our attention to the bond in question. The latter method is simpler and is generally used in this paper.

1. Introduction

The first step in applying symmetry to any molecule is to select the point group of the molecule in the usual way [2]. This group is now referred to as the "molecule group", G, and is of order g. If we are dealing with a closed shell ground state of a $2n$ electron molecule, then we have immediately

$$H\Psi = E\Psi \qquad R\Psi = +1\Psi \qquad = |\phi_1 \dots \phi_n \bar{\phi}_1 \dots \bar{\phi}_n| \tag{1}$$

where $\boldsymbol{H}$ is the hamiltonian of the molecule, Ψ is the many electron wavefunction of the Hartree-Fock approximation, $\boldsymbol{R}$ is any operation of the molecule group, the vertical bars denote a determinant and the ϕ are the familiar canonical m.o.s. In Eq. (1), we have labeled the m.o.s $1 \ldots n$. We may equally use three labels, one for the irreducible representation to which the m.o. belongs (i), one for the row of this representation (r) and a third label to distinguish m.o.s which are not distinguished by symmetry. This is a common notation and the standard sequence is a, i, r.

The equations which describe the symmetry of the canonical m.o.s are

$$\boldsymbol{R}\phi_{air} = \sum_{s=1}^{d_i} D_i(\boldsymbol{R})_{sr}\phi_{ais} \tag{2}$$

together with the basic eigenvalue equation

$$\boldsymbol{F}\phi_{air} = e_{ai}\phi_{air} \tag{3}$$

and the equations which result from the fact that $\boldsymbol{R}$ and $\boldsymbol{F}$ commute

$$\begin{aligned} \boldsymbol{R}(\boldsymbol{F}\phi_{air}) = \boldsymbol{F}(\boldsymbol{R}\phi_{air}) = \boldsymbol{F}\sum_{s=1}^{d_i} D_i(\boldsymbol{R})_{rs}\phi_{ais} = \sum_{s=1}^{d_i} D_i(\boldsymbol{R})_{rs}\boldsymbol{F}\phi_{ais} \\ = e_{ai}\sum_{s=1}^{d_i} D_i(\boldsymbol{R})_{rs}\phi_{ais}\,. \end{aligned} \tag{4}$$

In these three equations, $\boldsymbol{R}$ is the operator of the molecule group G, and $D_i(\boldsymbol{R})_{rs}$ is the element of the r^{th} row and s^{th} column of the matrix $\boldsymbol{D}$ of the i^{th} irreducible representation.

The secular equation for the l.m.o.s is

$$\sum_{q=1}^{t-n+1} [c_{qi}(F_{pq} - e_{ii}S_{pq})] = 0 \qquad p = 1-(t-n+1) \tag{5}$$

where the c_{qi} are coefficients of the expansion of the l.m.o. over suitable basis functions earlier written [3] as $\chi_1 \ldots \chi_{(t-n+1)}$. In the earlier work [3] we chose these basis functions by guessing the final form of the eigenfunctions as well as possible and using these basis functions $u_1 \ldots u_{(t-n+1)}$ to form the secular determinant as in Fig. 1. Full details are given in the earlier work [3].

The two nuclei of the chosen bond establish a unique axis in the molecule. This is the "bond axis". We select from all the operations of the molecule group those operations which leave unchanged the two nuclei of the bond. Should we be dealing with a homopolar bond, A–A, we must extent this selection to include those operations which exchange the two nuclei.

Two possibilities arise now. If the bond in question is unique in the molecule, such as the C–Cl bond of methyl chloride, the selected operations will be the whole molecule group G. If there are other bonds in the molecule which are equivalent to the bond in question under the operations of the molecule group, such as the C–H bonds of methyl chloride, then the selected operations will be a subgroup, H, of the molecule group. The order of this subgroup is h. We refer to this group as the "bond-molecule" group (Table 1) to stress that this group is concerned with both the bond and the whole molecule. If we identify each bond in

$$\begin{array}{c|cc|ccc|}
 & u_1 & u_1^* & u_2^* & u_3^* & u_4^* \ldots \\ \hline
u_1 & -0.5 & \delta & & \text{small} & \\
u_1^* & \delta & 0.5 & & & \\ \hline
u_2^* & & & 0.5 & & \\
u_3^* & \text{small} & & & 0.5 & \ldots \\
\vdots & & & & & \\ \hline
\end{array}$$

Fig. 1. The $\boldsymbol{F}$ matrix for the localised m.o.s before the use of symmetry. The quantity δ is a small quantity in general

Table 1. The bond-molecule groups

C_1	C_2	C_3	C_4	C_5	C_6	
	C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	
C_{1h}	C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	
	$S_2(C_i)$		S_4		S_6	
	D_2	D_3	D_4	D_5	D_6	
	D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	
	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	
						$C_{\infty v}$
						$D_{\infty h}$

Taking the 37 groups in this table, removing the ten groups C_5, C_{5v}, C_{5h}, D_5, D_{5h}, D_{4d}, D_{5d}, D_{6d}, $C_{\infty v}$ and $D_{\infty h}$ and adding the groups T, T_d, O, O_h and T_h gives the familiar 32 point groups which occur in crystals. In a few molecules, other symmetries such as D_{7h} may occur.

the molecule with a label, α say, then we have H^α for a bond molecule group and S^α for its operations. The irreducible representations of H^α are either one dimensional or two dimensional.

Looking now at the forms of the m.o.s (not l.m.o.s) of the bond-molecule group, it is clear that we get the same m.o.s when we use the bond-molecule group as when we use the molecule group. This must be so if we use Eq. (3) to calculate the m.o.s since this equation uniquely determines the m.o.s regardless of any manipulation of symmetry groups. Some care is required with any degenerate levels but suitable choice of the functions spanning a degenerate level will make the above statement a valid one.

The formal equations for the use of symmetry with the bond-molecule group are straightforward. The equation which refer to the many electron wave function are essentially as before (Eq. (1)) while the equations which refer to the individual

Table 2. Examples of bond-molecule groups and bond groups

Molecule	Molecule group	Bond	Bond-molecule group	Bond group
H_2	$D_{\infty h}$	H–H	$D_{\infty h}$	$D_{\infty h}$
HF	$C_{\infty v}$	H–F	$C_{\infty v}$	$C_{\infty v}$
H_2O	C_{2v}	O–H	$C_{\infty v}$	$C_{\infty v}$
NH_3	C_{3v}	N–H	C_s	$C_{\infty v}$
CH_4	T_d	C–H	C_{3v}	$C_{\infty v}$
C_2H_4	D_{2h}	C–H	C_{1h}	$C_{\infty v}$
C_6H_6	D_{6h}	C–H	C_{2v}	$C_{\infty v}$
PCl_5	D_{3h}	P–Cl (axial)	C_{3v}	$C_{\infty v}$
PCl_5	D_{3h}	P–Cl (equatorial)	C_{2v}	$C_{\infty v}$
BF_3	D_{3h}	B–F	C_{2v}	$C_{\infty v}$
H_2O_2	C_2	O–H	C_1	$C_{\infty v}$
C_2H_6	D_{3h}	C–H	C_{1h}	$C_{\infty v}$
C_2H_6	D_{3h}	C–C	D_{3h}	$D_{\infty h}$

Table 3. Correlation tables for the bond groups $C_{\infty v}$ and $D_{\infty h}$

Heteronuclear case $C_{\infty v}$

$C_{\infty v}$	C_{6v}	C_{5v}	C_{4v}	C_{3v}	C_{2v}	C_6	C_5	C_4	C_3	C_2	C_s
a_1	a_1	a_1	a_1	a_1	a_1	a	a	a	a	a	a'
e_1	e_1	e_1	e	e	b_1+b_2	e_1	e_1	e	e	$2b$	$a'+a''$

Homonuclear case $D_{\infty h}$

$D_{\infty h}$	D_{6h}	D_{5h}	D_{4h}	D_{3h}	D_{2h}	D_{3d}	D_{2d}	S_6	S_4
a_{1g}	a_{1g}	a_1'	a_{1g}	a_1'	a_g	a_{1g}	a_1	a_g	a
a_{2u}	a_{2u}	a_2''	a_{2u}	a_2''	b_{1u}	a_{2u}	b_2	a_u	b
e_{1u}	e_{1u}	e_1'	e_u	e'	$b_{2u}+b_{3u}$	e_u	e	e_u	e
e_{1g}	e_{1g}	e_1''	e_g	e''	$b_{2g}+b_{3g}$	e_g	e	e_g	e

$D_{\infty h}$	D_6	D_5	D_4	D_3	D_2	C_{6h}	C_{5h}	C_{4h}	C_{3h}	C_{2h}
a_{1g}	a_1	a_1	a_1	a_1	a	a_g	a'	a_g	a'	a_g
a_{2u}	a_2	a_2	a_2	a_2	b_1	a_u	a''	a_u	a''	a_u or b_u
e_{1u}	e_1	e_1	e	e	b_2+b_3	e_{1u}	e_1'	e_u	e'	$2b_u$ or a_u+b_u
e_{1g}	e_1	e_1	e	e	b_2+b_3	e_{1g}	e_1''	e_g	e''	$2b_g$ or a_g+b_g

$D_{\infty h}$	C_{6v}	C_{5v}	C_{4v}	C_{3v}	C_{2v}	C_6	C_5	C_4	C_3	C_2	C_s	C_i
a_{1g}	a_1	a_1	a_1	a_1	a_1	a	a	a	a	a	a'	a_g
a_{2u}	a_1	a_1	a_1	a_1	a_1 or b_2	a	a	a	a	a or b	a'' or a_2'	a_u
e_{1u}	e_1	e_1	e	e	a_1+b_1 or b_1+b_2	e_1	e_1	e	e	$2b$ or $a+b$	$2a'$ or $a'+a''$	$2a_u$
e_{1g}	e_1	e_1	e	e	a_2+b_2 or b_1+b_2	e_1	e_1	e	e	$2b$ or $a+b$	$2a''$ or $a'+a''$	$2a_g$

The $C_{\infty v}$ table was worked from first principles as were the D_{6h}, D_{5h}, and D_{4h} components of the $D_{\infty h}$ table. The remainder of the latter table was constructed from the correlation tables of Ref. [4] via the D_{6h}, D_{5h}, and D_{4h} components. The choices which arise in the $D_{\infty h}$ table arise from different selections of axes and the correct choice will be obvious from context in a given problem.

m.o.s are

$$S^{\alpha}\phi_{bjs} = \sum_{t=1}^{d_j} B_j(S^{\alpha})_{tr}\phi_{bjt} \qquad F\phi_{bjs} = e_{jb}\phi_{bjs} \tag{6}$$

together with the analogue of Eq. (4).

Some relevant examples are given in Table 2. In working with the molecule group and its subgroups, we will need the correlation tables between a group and its subgroups. These are available in the standard texts [4] apart from those for $C_{\infty v}$ and $D_{\infty h}$ which are given in Table 3.

2. The l.m.o.s and the Molecule Group

The l.m.o.s are now given three labels. The first (k) is a serial label denoting the position of the bond in the molecule, the second (w) being a distinguishing label between the equivalent bonds of one set and the third (p) distinguishing between the members of a degenerate set. An example is the molecule of Fig. 2a.

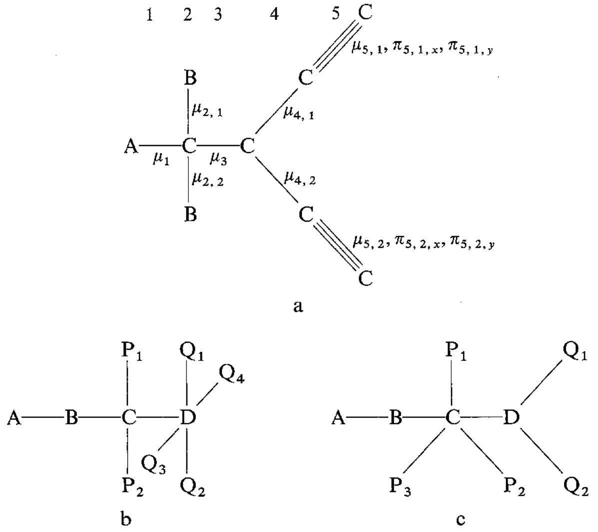
The l.m.o.s are related to the canonical m.o.s by an orthogonal transform given by

$$\boldsymbol{\mu} = \boldsymbol{\phi} A \qquad \boldsymbol{\phi} = \boldsymbol{\mu} A^{-1} = \boldsymbol{\mu}\tilde{A} \tag{7}$$

where $\boldsymbol{\mu}$ is the row vector of the l.m.o.s, $\boldsymbol{\phi}$ is the row vector of the canonical m.o.s and A is an orthogonal (more generally, unitary) $n \times n$ matrix. In components, we have

$$\mu_{kwp} = \sum_{bjs} \phi_{bjs} A_{bjs}^{kwp} \qquad \phi_{bjs} = \sum_{kwp} \mu_{kwp} A_{kwp}^{bjs}\,. \tag{8}$$

It is well known that this transformation does not change the total wave function of the molecule [1, 3].



a

b

c

Fig. 2

The type of symmetry which occurs with the l.m.o.s is different from that of the canonical m.o.s. The former is a generalised type of permutational symmetry which is based on the physical assumption that equivalent bonds have l.m.o.s which are equivalent. By "equivalent" is meant differing only on their positions in space and not in the essentials of their functional form.

This type of permutational symmetry (more correctly perhaps pseudo-permutational symmetry) is important in the development of this work. In these permutational matrices, unity occurs once in each row and once in each column. Such matrices are orthogonal matrices. It is generally true that not all possible permutations between equivalent bonds are physically possible under the usual symmetry operations (e.g., the six C–H bonds of benzene) although exceptionally the molecule group and the permutation group are isomorphous (methane, T_d, is the permutation group on four objects). It follows that we are not concerned with the permutation groups themselves.

These matrices are block diagonal, each block clearly corresponding to a set of equivalent bonds in the molecule. An important property of such matrices is that one may strike out certain rows and columns in such a way as to remove the entire block and still have a permutational matrix. It is *not* generally possible to strike out the *same* rows and columns from all the matrices and still have a set of permutational matrices when dealing with the molecule group.

The above remarks apply to single bonds. If two dimensional π bonds are involved, the theory is readily extended to deal with such an example.

We may now write

$$R\mu_{kwp} = \sum_{w'p'} C^{kwp}_{kw'p'}\mu_{kw'p'} \tag{9}$$

where $C^{kwp}_{kw'p'}$ is the matrix element. Notice that we cannot assume $p = p'$ as a few simple examples show.

3. The l.m.o.s and the Bond-Molecule Group

Suppose that we are concerned with the bond μ_1. We select from the g matrices of the molecule group those matrices which correspond to the operations S^1 of the bond-molecule group H^1. There will be h^1 such matrices which form a representation of the bond-molecule group. The l.m.o.s form a basis for this representation in the usual way. The h^1 matrices differ from the entire set of g matrices in that the matrix element corresponding to the bond μ_1 is particularly simple. If μ_1 is a σ bond, then the top left element of the permutation matrices is $+1$ for *all* the matrices of the bond-molecule group. That is, all the h^1 matrices have the partial structure

$$S^1(\mu_1 \ldots \mu_n) = (\mu_1 \ldots \mu_n) \begin{bmatrix} +1 & 0 & 0\ldots \\ 0 & & \\ 0 & & \\ \ldots & \ldots & \end{bmatrix} . \tag{10}$$

This result is only true for the bond-molecule group and not for the molecule group.

It follows that the l.m.o. μ_1 belongs to an irreducible representation of the bond-molecule group H^1. We have then

$$S^1 \mu_{1js} = \sum_{t=1}^{d_j} B_j(S^1)_{jt} \mu_{1jt} \,. \tag{11}$$

Equations such as (10) and (11) will clearly hold for all the bonds in the molecule. If a doubly degenerate π bond is being dealt with, then the theory is extended in a straightforward way. Notice that all the functions $\mu_1 \ldots \mu_n$ will occur in each case but that different selections of the set of g matrices will be needed for the different bonds and bond-molecule groups.

Now we focus attention on the bond μ_1 again. The h^1 matrices of Eq. (10) are already partly reduced but we may if we wish reduce them completely. It is convenient to do this in two steps. First, we reduce each block under the "block group" which consists of μ_1 plus the block under discussion. Thus in the example of Fig. 2b, we have C_{2v} and C_{4v} block groups present. If we reduce the blocks in this way, we must of course replace the set of functions spanning each block with symmetrised functions as usual. That is, we replace the set of functions μ_{kwp} with the set of functions ϱ_{kjs} where now the second and third labels denote the s^{th} row of the j^{th} irreducible of the block group. Second, we reduce *all* the blocks under the *one* bond-molecule group. This bond-molecule group will clearly be the block group of lowest order or, in some cases, a group of lower order than any of the block groups. As an example of these two steps, we take the molecule of Fig. 2b and first reduce the P block under C_{2v} and the Q block under C_{4v}. Then both are classified under the bond-molecule group C_{2v}. A contrasting example is the molecule of Fig. 2c where we have both a C_{2v} and a C_{3v} block group while the bond-molecule group is C_s.

4. The Transformation between the l.m.o.s and the Canonical m.o.s

At this point we settle the question of the extent to which the matrix elements of the A matrix are determined by symmetry alone. We consider the reverse transformation between $\boldsymbol{\mu}$ and $\boldsymbol{\phi}$ of Eq. (7)

$$\boldsymbol{\phi} = \boldsymbol{\mu} A \,. \tag{7}$$

Suppose that we are given the $\boldsymbol{\mu}$ and we then reduce this set of functions under the molecule group in the usual way to generate a set of functions v_{air}. That is

$$\boldsymbol{v} = \boldsymbol{\mu} \boldsymbol{B} \tag{12}$$

where $\boldsymbol{v}$ is the n dimensional row of the symmetry adapted functions v_{air}. The matrix $\boldsymbol{B}$ is determined by symmetry alone. To convert the $\boldsymbol{v}$ to the $\boldsymbol{\phi}$ requires the solution of the secular equation and we think of this as a transformation with the orthogonal matrix $\boldsymbol{C}$ where

$$\boldsymbol{\phi} = \boldsymbol{v} \boldsymbol{C} \tag{13}$$

and

$$C_{bjs}^{air} = \delta_{ij} \delta_{rs} C_{bir}^{air} \tag{14}$$

and the elements of $\boldsymbol{C}$ are otherwise arbitrary as far as symmetry is concerned.

The complete transformation is then

$$\boldsymbol{\phi} = \boldsymbol{\mu} \boldsymbol{B} \boldsymbol{C} \qquad \boldsymbol{\mu} = \boldsymbol{\phi} \tilde{\boldsymbol{C}} \tilde{\boldsymbol{B}} . \tag{15}$$

As an example of this process, consider the methyl chloride molecule with the four l.m.o.s written as $\mu_{\mathrm{CCl}}, \mu_{\mathrm{CH}}, \mu_{\mathrm{CH'}}, \mu_{\mathrm{CH''}}$. The $\boldsymbol{B}$ and $\boldsymbol{C}$ matrices are then

$$\boldsymbol{B} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/3 & 0 & 2/3 \\ 0 & 1/3 & 1/2 & -1/6 \\ 0 & 1/3 & -1/2 & -1/6 \end{bmatrix} \qquad \boldsymbol{C} = \begin{bmatrix} c & s & & \\ -s & c & & \\ & & 1 & \\ & & & 1 \end{bmatrix} \tag{16}$$

where $c = \cos(\gamma)$ and $s = \sin(\gamma)$ and γ is arbitrary.

5. l.m.o.s of the Truncated Molecule and the Bond Groups

The formal theory of the symmetry of the l.m.o.s which has been developed so far is complete in itself but it must be taken further is symmetry is to be of practical value in computing l.m.o.s. In particular, we must be able to truncate the secular equations and the secular determinant of Sect. 1 in ways suggested by chemical experience. We know, for example, that the properties of a given bond in a large molecule will be affected only slightly by the nature of a remote bond or group of atoms.

Suppose that we are again concerned with the bond whose l.m.o. is μ_1. We truncate the molecule by removing an atom or atoms and we clearly remove the atomic orbitals which are centred on the deleted atoms from the basis set of orbitals. In general, the symmetry of the bond-molecule group will change when atoms are deleted although cases do arise in which there is no such change in symmetry. Indeed, to change the symmetry an atom must be removed from an off-axis position as in the case of atom P in examples such as the molecule of Fig. 3a. If there is a set of several off-axis atoms which are equivalent, it is clear

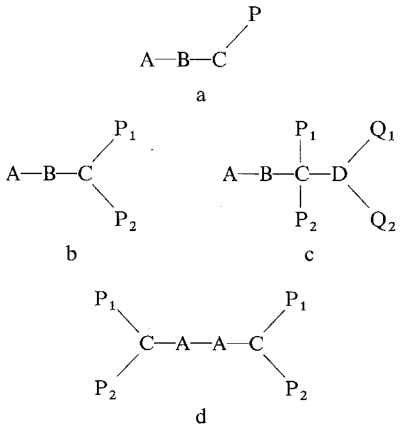


Fig. 3

that we must remove all of them at the same time. A simple example of an increase of symmetry resulting from the removal of a set of atoms is the removal of atoms P_1 and P_2 from the molecule of Fig. 3b.

As the symmetry of the molecule is increased by truncation of the molecule, operations must be added to the bond-molecule group. If the bond is $C_{\infty v}$, then as we truncate the molecule we can add only rotations (C_n) and reflections in a place which contains the bond axis (σ_v). If the bond is $D_{\infty h}$, we may add the same operations as before plus two fold rotations about the axis perpendicular to the bond axis together with σ_h, the inversion i and the rotary reflections (S_n). Some of these operations are interconnected and they cannot be added in arbitrary sets.

We now have the extended bond group. The matrices which we had before the truncation are dealt with by striking out the appropriate rows and columns. We strike out the appropriate functions from the row of l.m.o.s together with the contributions of the deleted atoms' atomic orbitals to the remaining l.m.o.s. We also write down by inspection the new matrices for the new operations which are now present in the extended bond group. We now have a set of permutation matrices which represent the extended bond group and all of these matrices have the partial structure

$$\begin{bmatrix} +1 & 0 & 0 & 0 \\ 0 & 0 \ldots\ldots\ldots & & \\ 0 \ldots\ldots\ldots\ldots & & & \\ \ldots\ldots\ldots\ldots\ldots & & & \end{bmatrix}.$$

The extension of this process to such cases as the molecules of Figs. 3c and 3d is straightforward.

Table 4. Matrices of the irreducible representations of the bond groups

Heteronuclear bond $C_{\infty v}$

Bond		E	$2C_\alpha$	σ_v
σ or σ^*	a_1	1	1	1
π or π^*	e_1	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}c_\alpha & -s_\alpha\\s_\alpha & c_\alpha\end{bmatrix}$	$\begin{bmatrix}c_{2\alpha} & s_{2\alpha}\\s_{2\alpha} & -c_{2\alpha}\end{bmatrix}$

Homonuclear bond $D_{\infty h}$

Bond		E	$2C_\alpha$	σ_v	i	S_α	C_2'
σ	a_{1g}	1	1	1	1	1	1
σ^*	a_{2u}	1	1	1	-1	-1	-1
π	e_{1u}	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}c_\alpha & -s_\alpha\\s_\alpha & c_\alpha\end{bmatrix}$	$\begin{bmatrix}c_{2\alpha} & s_{2\alpha}\\s_{2\alpha} & -c_{2\alpha}\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\0 & -1\end{bmatrix}$	$\begin{bmatrix}c_\alpha & -s_\alpha\\s_\alpha & c_\alpha\end{bmatrix}$	$\begin{bmatrix}-c_{2\alpha} & -s_{2\alpha}\\-s_{2\alpha} & c_{2\alpha}\end{bmatrix}$
π^*	e_{1g}	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}c_\alpha & -s_\alpha\\s_\alpha & c_\alpha\end{bmatrix}$	$\begin{bmatrix}c_{2\alpha} & s_{2\alpha}\\s_{2\alpha} & -c_{2\alpha}\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}-c_\alpha & s_\alpha\\-s_\alpha & -c_\alpha\end{bmatrix}$	$\begin{bmatrix}c_{2\alpha} & s_{2\alpha}\\s_{2\alpha} & -c_{2\alpha}\end{bmatrix}$

The symbols c_α and s_α denote cosine(α) and sine(α) respectively.

Returning now to the truncation of the molecule, we continue this until there remains only the bond in question and its two nuclei. The bond group is thus $C_{\infty v}$ or $D_{\infty h}$. Throughout the truncation we deal with a chain of subgroups each of which is contained in a larger group. The chain begins with the bond-molecule group and ends with the bond group $C_{\infty v}$ or $D_{\infty h}$. When we have only the two nuclei of the bond μ_1 remaining then we have only one function left in the row of l.m.o.s. The corresponding matrices will be 1×1. They correspond to a row of the $C_{\infty v}$ or $D_{\infty h}$ character tables (Table 4). If a two dimensional π bond is being discussed, then the theory is extended in a natural way.

As an example of this truncation process, consider the methyl chloride molecule again. Taking the C–Cl bond as μ_1, the bond-molecule group is C_{3v} and the bond group $C_{\infty v}$. We must use the top line of the $C_{\infty v}$ character table. Or, were we interested in the π bond of methyl acetylene, we must end the truncation with the e_{1u} matrices of the $D_{\infty h}$ table.

6. Solution of the Secular Equations

We now show how symmetry simplifies the solution of the secular equation of the l.m.o.s. Before symmetry is considered, the matrix of Fig. 1 contains no zeros although matrix elements between functions which are far apart in space will clearly be small. It is convenient to divide this section into three subsections. In the first subsection, we examine the solution of the 2×2 secular determinant where the bond is perfectly localised and the operators which make up the **F** operator are confined to the two atoms forming the bond. In the second subsection, we expand the **F** operator until the entire molecule is represented in this operator while at the same time the secular determinant remains a 2×2 one. This is the stage in which the chemical ideas of polarisation and induction are incorporated into the theory and given a rigorous definition. In the third subsection, we allow the delocalisation of the bond μ_1 say over the entire molecule. This is the quantitative formulation of the chemical idea of hyperconjugation.

a) Operator and Orbital Localised

Here we suppose that we are solving a 2×2 secular determinant with a fully symmetrical operator. There are some questions about the detailed formulation of this operator but we leave these aside for the moment. If we are concerned with a σ bond, the matrix of the **F** operator over the basis functions u_1 and u_1^* is then [3]

$$\begin{bmatrix} F_{1,1} & F_{1,1^*} \\ F_{1,1^*} & F_{1^*,1^*} \end{bmatrix} \qquad F_{1,1} = \langle u_1 | \boldsymbol{F} | u_1 \rangle \text{ etc.} \tag{17}$$

We naturally choose the two basis functions to transform under $C_{\infty v}$ or $D_{\infty h}$ just as we would in dealing with a diatomic molecule. We will emerge at the end with the a_1 or e_1 m.o.s of the $C_{\infty v}$ case or with the a_{1g}, a_{1u}, e_{1u} or e_{1g} m.o.s of the $D_{\infty h}$ case.

b) Extended Operator, Localised Function

At the end of the previous section, we were left with a diagonalised 2×2 matrix. We now allow the $\boldsymbol{F}$ operator to expand until it encompasses the entire molecule. Physically, this means that the two electrons of the bond μ_1 can see the attraction and repulsion of all the nuclei and electrons of distant atoms. The $\boldsymbol{F}$ operator now has the symmetry of the extended molecule but the electron is confined to the vicinity of the chosen bond μ_1 and this situation is just that of an external static electric field with the symmetry of the $\boldsymbol{F}$ operator. All we require is that the l.m.o. μ_1 transforms as the irreducible representation of the bond molecule group H^1. This may require the use of an extended basis set for the two atoms of the bond μ_1.

c) Extended Operator and Extended Orbital

In this section we consider the extension of the secular determinant until finally the complete μ_1 is reached. We begin with the two atoms of the bond and then add atoms to the molecule and add functions to the row of functions in Eq. (10) at the same time as we add the new μ^* to the basis of the secular equation. We also increase the size of the matrices while reducing the number of them. For convenience, we may replace the μ^* with the set of symmetry adapted functions ϱ^* each of which transforms as the s^{th} row of the j^{th} irreducible representation of the extended group. Then we may use the familiar theorem that the matrix elements of the $\boldsymbol{F}$ operator will vanish unless both functions belong to the same irreducible representation and to the same row of this representation. That is

$$\langle \varrho^*_{kjs} | \boldsymbol{F} | \varrho^*_{k'j's'} \rangle = \delta_{ss'} \delta_{jj'} \langle \varrho^*_{kjs} | \boldsymbol{F} | \varrho^*_{k'js} \rangle \,. \tag{18}$$

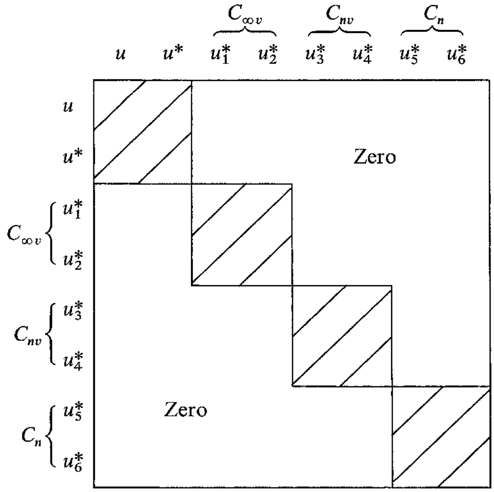


Fig. 4. An example of the $\boldsymbol{F}$ matrix over the l.m.o. after the use of symmetry (AB case)

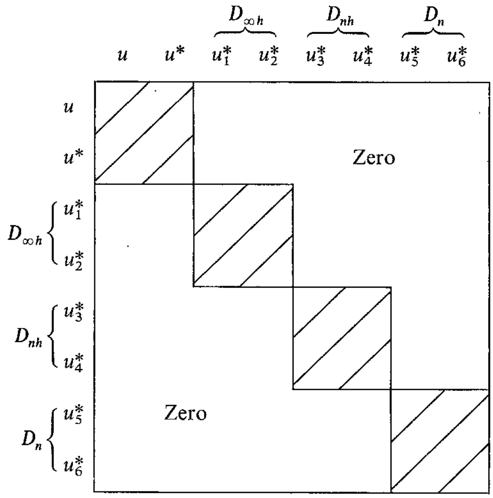


Fig. 5. An example of the $\boldsymbol{F}$ matrix over the l.m.o. after the use of symmetry (AA case)

This result will reduce the dimension of the secular determinant in nearly all cases. In the general case, the $\boldsymbol{F}$ matrix will take the form shown in Fig. 4 for a $C_{\infty v}$ bond and that shown in Fig. 5 for a $D_{\infty h}$ bond. The ordering of the blocks is the natural order for $C_{\infty v}$ but is somewhat arbitrary in the $D_{\infty h}$ case.

7. Summary and Comments

To summarise this work, we may say that the following points have been established:

1. The nature of the various symmetry groups with which we are concerned in dealing with the l.m.o.s is established (Table 5).

Table 5. Summary of the different groups involved with the bonds of a molecule

Molecule group	Bond-molecule groups	Bond groups
1) One group, G, order g, operations R	n groups, H^α, order h^α operations S^α	n groups, all $C_{\infty v}$ or $D_{\infty h}$
2) n occupied m.o.s, either localised or canonical	n m.o.s for each bond-molecule group	one or three m.o.s for each bond
3) Number of matrices is g	Number of matrices h^α for each bond	Number of matrices is infinite
4) All matrices may appear in permutational or reduced form	All matrices may appear in permutational or reduced form	All matrices fixed once and for all
5) Example of methyl chloride C_{3v}, 6th order, operations are E, C_3, and σ_v	Four groups, C_{3v} and C_s (three times)	$C_{\infty v}$ for all four bonds

2. The nature of the relevant reducible and irreducible representations of these groups is established.
3. The nature of the basis functions of these representations is clarified.
4. The order of the secular determinant is reduced.

Taken in conjunction with the theory of l.m.o.s reported earlier [3] this work and some other results to be reported later on perturbation methods establish a complete theory of the l.m.o. at the restricted Hartree-Fock level of approximation.

Extension of this work to deal with subsystems consisting of three or more atoms is quite feasible and can be made by inspection given the earlier work. Typical situations which will require this extension are the hydrogen bonding problem and the general chemical reactivity problem.

Finally, it should be noted that symmetry is of much greater use in l.m.o. theory where it is almost always useful for all bonds and not for just a small proportion of cases as is true of the theory of symmetry and canonical m.o.s.

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Dr. David Peters
Royal Holloway College
University of London
Englefield Green, Surrey, England