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The influence of abstract group theory on molecular symmetry

L. L. Boyle
Vine Cottage, Patrixbourne, Kent CT4 5BX, UK

E-mail: Laurence.Boyle@gmail.com

Abstract. It is shown that the identification of the double groups required for treating molecular problems involving an odd number of electrons can be solved using abstract group theory without consideration of explicit matrices as in Pauli's discussion using spin matrices. This presupposes that the character tables are arrays of invariant numbers which alone are sufficient to specify the relevant properties of the spin systems. Consideration of subduction from infinite groups such as SU(2) is thus avoided and the criteria used to identify abstract groups as suitable double groups for the odd-electron spin problem include the need for subduction from finite symmetry groups of higher order as well as the requirement to produce closed shells of electrons in which no two electrons can have the same quantum numbers. Explicit calculations are provided for groups of orders 1, 2 and 4 and these provide the underlying principles for any molecular symmetry group. Novel aspects include the consideration of the separable four-fold degeneracies which occur in molecules having a single four-fold axis of symmetry. It is also shown that the treatment required for threefold symmetries is consistent with the principles derived from the study by abstract group theory of 1-, 2- and 4-fold symmetries.

1. Introduction

Abstract groups are described by presentations. These provide information about the order of the generators of the group and the relationships between them. A character table and an automorphism group can be defined for each abstract group. The following are some simple examples of presentations:-

1. The cyclic groups of order *n*. These can be expressed in terms of a single generator, A, such that $A^n = E$ where E is the unit element of the group. A is said to be of order *n* where *n* is the smallest power of A which generates E.
2. The direct product group of order *mn*. Such a group can be expressed in terms of 2 generators, A and B, such that $A^m = E$ and $B^n = E$. The elements A and B have to commute, *i.e.* BA=AB. In some notations this would be written [A,B] = E.
3. The dihedral group of order 2*n*. This may be presented as $\{A^n = E; B^2 = E; BA = A^{-1}B\}$ so that the commutator $[A,B] = A^{-1}B^{-1}AB = A^{n-2}$.

The above examples are the simplest possible and it should be recorded that in more complicated groups such as the icosahedral rotation group the choice of generators to produce elements labelled by words which contain the powers of the generators in alphabetical order should not be regarded as completely free if one also aspires to mechanise the process of identifying the product of any two elements by use of the relationships given between the generators. In some cases analysis of the product will unfortunately lead to an infinite sequence of generators.

2. Some aspects of character tables

2.1 *The non-uniqueness of character tables*

Every abstract group has a character table which is a number-theoretical array. Not all character tables are different, however, but it will be demonstrated that the irreducible representations of two different groups which have identical arrays of numbers as their character tables may well differ in some of their derived properties.

To illustrate this point we may study the simplest case which happens to occur with groups of order 8. The dihedral group $\mathbf{D}_4 := \{A^4=B^2=E;\ BA=A^3B\}$ and the quaternion group $\mathbf{Q} := \{A^4=B^4=E;\ B^2=A^2;\ BA=A^3B\}$ have the same character table:-

D_4 / **Q**	E	A^2	A, A^3	B, A^2B	AB, A^3B
Γ_1	1	1	1	1	1
Γ_2	1	1	1	−1	−1
Γ_3	1	1	−1	1	−1
Γ_4	1	1	−1	−1	1
Γ_5	2	−2	0	0	0

The conjugacy-class structures are identical but the order structures are not. Apart from the identity, $\mathbf{D}_4$ has five elements of order 2 and two of order 4 while **Q** has one element of order 2 and six of order 4. The differences produced in the squares of the elements, ε_i , are reflected in the calculation of the symmetric and antisymmetric squares of the 2-dimensional irreducible representation, Γ_5 , of each group. The character of the symmetric square for a representation, Γ, and an element, ε_i , is defined as $[\Gamma^2] = \frac{1}{2}[\{\chi(\varepsilon_i)\}^2 + \chi(\varepsilon_i^2)]$ while for the antisymmetric square, $\{\Gamma^2\}$, it is defined as $\frac{1}{2}[\{\chi(\varepsilon_i)\}^2 - \chi(\varepsilon_i^2)]$. The sum of these two components is the square Γ^2 and both the symmetric and antisymmetric parts are reducible representations of the group.

When we calculate the symmetric and antisymmetric squares of the 2-dimensional irreducible representation, Γ_5, of each group we obtain the following results:-

Group $\mathbf{D}_4$

ε_i / ε_i^2	E / E	A^2 / E	A, A^3 / A^2	B, A^2B / E	AB, A^3B / E	
Γ_5	2	−2	0	0	0	
$[\Gamma_5^2]$	3	3	−1	1	1	$= \Gamma_1+\Gamma_3+\Gamma_4$
$\{\Gamma_5^2\}$	1	1	1	−1	−1	$= \Gamma_2$

Group Q

ε_i / ε_i^2	E / E	A^2 / E	A, A^3 / A^2	B, A^2B / A^2	AB, A^3B / A^2	
Γ_5	2	−2	0	0	0	
$[\Gamma_5^2]$	3	3	−1	−1	−1	$= \Gamma_2+\Gamma_3+\Gamma_4$
$\{\Gamma_5^2\}$	1	1	1	1	1	$= \Gamma_1$

It is to be noticed that the totally-symmetric representation, Γ_1 , occurs in the symmetric square of Γ_5 of $\mathbf{D}_4$ but in the antisymmetric square of Γ_5 of **Q**.

2.2 *Single- and double-valued representations*

When, as in these two cases, a group possesses an invariant subgroup of index 2 (*i.e.* a halving subgroup) the concept of single and double value can be defined. In such cases the single-valued representations have the same character for the commuting twofold element as for the identity while the double-valued representations have minus the character for the identity as the character for the commuting twofold element. This leads to the statement that

the products of two single-valued representations or two double-valued representations are single-valued while the product of a single-valued representation with a double-valued representation is double-valued.

In the above two examples, all characters of Γ_5 happened to be real numbers. According to the definition above, the irreducible representations Γ_5 of both $\mathbf{D_4}$ and **Q** can both be regarded as double-valued. The fundamental difference, however, is that Γ_5 of $\mathbf{D_4}$ is such that the totally-symmetric representation, Γ_1 , occurs in the symmetric part of its square while in the case of Γ_5 of **Q**, Γ_1 occurs in the antisymmetric part of its square.

2.3 *Complex representations*

Another type of representation is characterised by having some characters which are complex numbers. For this type the above formulæ for the square and its parts cannot be used without further information. This can be illustrated with reference to the tetrahedral rotation group, **T**, which is isomorphic to the alternating group, $\mathbf{A_4}$. **T** may be presented in terms of three generators, A, B and C, such that $\{A^2=B^2=C^3=E; BA=AB; CA=ABC; CB=AC\}$. The character table is:-

T	E	A, B, AB	C, AC, BC, ABC	C^2, BC^2, ABC^2, AC^2
Γ_1	1	1	1	1
Γ_2	1	1	ω	ω^2
Γ_2^*	1	1	ω^2	ω
Γ_3	3	−1	0	0

where ω and ω^2 are the complex cube roots of unity. If one simply squares the characters of either of the complex representations the other is obtained and this will not lead to a useful implementation in quantum mechanics. However, if one takes the real, reducible, representation $\Gamma_2+\Gamma_2^*$ and applies the formulæ above the direct product will be $2\Gamma_1+\Gamma_2+\Gamma_2^*$ with the totally-symmetric representation, Γ_1 , occurring in both the symmetric, $\Gamma_1+\Gamma_2+\Gamma_2^*$, and the antisymmetric, Γ_1 , parts. That Γ_1 should appear twice is logical since $\Gamma_2+\Gamma_2^*$ consists of two representations. Γ_2 and Γ_2^* are normally described as a complex-conjugate pair of representations because, for each element their characters are related by complex conjugation. In another terminology the reducible representation $\Gamma_2+\Gamma_2^*$ would be said to be a separably-degenerate representation.

A more abstract description derives from the group-theoretical concept of the inverse automorphism rather than the algebraic concept of complex conjugation. This automorphism has the effect of replacing each element by its inverse. In this example the class {C, AC, BC, ABC} will be interchanged with the class $\{C^2, BC^2, ABC^2, AC^2\}$ and the characters are replaced by their complex conjugates. The invariance of the character table to this automorphism is assured by permuting Γ_2 and Γ_2^* at the same time as interchanging the two classes of threefold elements.

Another example of a group with complex representations is the cyclic group of four elements, $\mathbf{C_4}$. The presentation is $\{A^4=E\}$ and the character table may be written as follows:-

$\mathbf{C_4}$	E	A^2	A	A^3
Γ_1	1	1	1	1
Γ_2	1	1	−1	−1
Γ_3	1	−1	i	−i
Γ_3^*	1	−1	−i	i

Unlike **T** this group has an invariant subgroup of order 2, $\{E, A^2\}$, and the characters for the twofold element, A^2, are ± those for the identity. Γ_1 and Γ_2 could therefore be regarded as single-valued representations and Γ_3 and Γ_3^* as double-valued representations. It should be stressed, however, that this is not a necessary distinction: in applications where double-valued representations are not needed as such, all four representations of $\mathbf{C_4}$ can be used as ordinary

representations. The above character table of $\mathbf{C_4}$ illustrates one further point which is true for groups where the terms single-valued and double-valued are applicable. The weight of any double-valued representations, defined as the sum of the squares of their dimensions, has to equal the weight of the single-valued representations. In the case of $\mathbf{C_4}$ the weights of both single- and double-valued representations are $1^2+1^2=2$. In the case of **T**, however, the weight of the Γ_2 and Γ_2* representations is $1^2+1^2=2$ while that of the Γ_1 and Γ_3 representations is $1^2+3^2=10$. In such a case the criterion of having an invariant subgroup of order two is not satisfied and so the abstract group **T** could not be used in a context where double-valued representations are required.

3. The problem of electron spin

In order to explain the Stern−Gerlach effect and the anomalous Zeeman effect it was necessary to introduce the concept of spin. Unlike electronic orbital functions, the one-electron spin-functions transform as double-valued representations of a so-called "double group" which has double the order of the group used to describe the orbital functions. Unlike orbital functions, however, the spin functions of degeneracy 2*n* have to be such that the fully-antisymmetrised 2*n*-th power of the representation they span contains the totally-symmetric representation[1]. The problem is to identify what abstract groups could satisfy these requirements and hence provide information from their structure about the transformation properties of spins and spin-orbitals. Rather than assume that the special unitary group of all 2×2 matrices is involved and then reduce the symmetry to the often finite symmetry involved in molecules, the approach taken here is the converse, *viz.* to go from low-order groups to groups of higher symmetry without any mention of matrices.

4. Construction of double groups of abstract groups suitable for electron-spin problems

The principles will be illustrated by constructing the double groups of the two abstract groups of orders 1, 2 and 4. These must be groups of orders 2, 4 and 8 respectively. There are just five distinct abstract groups of order 8 which can be enumerated as:-

Order	Group	Presentation
2	$\mathbf{C_2}$	$\{A^2=E\}$
4	$\mathbf{C_4}$	$\{A^4=E\}$
	$\mathbf{C_2\times C_2}$	$\{A^2=B^2=E;\ BA=AB\}$
8	$\mathbf{C_8}$	$\{A^8=E\}$
	$\mathbf{C_4\times C_2}$	$\{A^4=B^2=E;\ BA=AB\}$
	$\mathbf{D_4}$	$\{A^4=B^2=E;\ BA=A^3B\}$
	$\mathbf{Q}$	$\{A^4=B^4=E;\ B^2=A^2;\ BA=A^3B\}$
	$\mathbf{C_2\times C_2\times C_2}$	$\{A^2=B^2=C^2=E;\ BA=AB;\ CA=AC;\ CB=BC\}$

The presentations are each given in terms of a minimum number of generators: this is noteworthy for the quaternion group where a more symmetric set is obtained using a third generator. The reason for using minimal sets is that a double group will then contain no more than one additional generator relative to the single group.

It will also be useful to enumerate the abstract halving subgroups in each case:-

Order	Group	Halving subgroups
2	$\mathbf{C_2}$	$\mathbf{C_1}\{E\}$
4	$\mathbf{C_4}$	$\mathbf{C_2}\{A^2=E\}$
	$\mathbf{C_2\times C_2}$	$\mathbf{C_2}\{A^2=E\}$
8	$\mathbf{C_8}$	$\mathbf{C}_4\{A^4=E\}$
	$\mathbf{C_4\times C_2}$	$\mathbf{C}_4\{A^4=E\};\ \mathbf{C_2\times C_2}\{A^2=B^2=E;\ BA=AB\}$
	$\mathbf{D_4}$	$\mathbf{C}_4\{A^4=E\};\ \mathbf{C_2\times C_2}\{A^2=B^2=E;\ BA=AB\}$
	$\mathbf{Q}$	$\mathbf{C}_4\{A^4=E\};\ \mathbf{C_2\times C_2}\{A^2=B^2=E;\ BA=AB\}$
	$\mathbf{C_2\times C_2\times C_2}$	$\mathbf{C_2\times C_2}\{A^2=B^2=E;\ BA=AB\}$

4.1 *The double group of the group of order one*

This case is trivial but does serve to illustrate that real representations can serve as the symmetries of electronic spin-orbitals. The double group of $\mathbf{C_1}$ has to be $\mathbf{C_2}$ and the Γ_2 representation of $\mathbf{C_2}$ is the only available double-valued representation. Taking a pair of these the symmetric square will be $3\Gamma_1$ and the antisymmetric square will be Γ_1. $\mathbf{C_2}$ is therefore an acceptable spin double group for $\mathbf{C_1}$.

4.2 *The double group of the group of order two*

Both abstract groups of order four are candidates to be the double group of the abstract group of order two. Superimposing the character tables illustrates this point well. If $\mathbf{C_4}$ is to be the double group, the table below shows that Γ_3 and Γ_3* behave as double-valued representations for $\mathbf{C_2}$. Further the antisymmetric square of this complex-conjugate pair is the totally-symmetric representation so $\mathbf{C_4}$ is a suitable double group for studying the spin-½ problem.

	$\mathbf{C_4}$	E	A^2	A	A^3
$\mathbf{C_2}$		E		A	
Γ_1	Γ_1	1	1	1	1
Γ_2	Γ_2	1	1	−1	−1
	Γ_3	1	−1	i	−i
	Γ_3*	1	−1	−i	i

Turning now to Klein's four-group as a possible double group of $\mathbf{C_2}$ the character tables can be matched up as

	$\mathbf{C_2\times C_2}$	E	B	A	AB
$\mathbf{C_2}$		E		A	
Γ_1	Γ_1	1	1	1	1
Γ_2	Γ_3	1	1	−1	−1
	Γ_2	1	−1	1	−1
	Γ_4	1	−1	−1	1

so that Γ_2 and Γ_4 of $\mathbf{C_2\times C_2}$ can serve as double-valued representations. Even though they are real and independently have no antisymmetric squares, taken as the pair $\Gamma_2+\Gamma_4$ they have Γ_3 as their antisymmetric square and so are not suitable for studying the spin problem. This means that only the cyclic group of twice the order can serve as the spin double group.

4.3 *The double group of the cyclic group of order four*

Cyclic groups are 1-generator groups by definition hence the double group of a cyclic group must be presentable in terms of not more than two generators: $\mathbf{C_2\times C_2\times C_2}$ cannot therefore be regarded as a candidate. Further, $\mathbf{D_4}$ and $\mathbf{Q}$ cannot be candidates because their character tables do not contain any complex numbers and hence their single-valued representations cannot be mapped onto the representations of the single group, $\mathbf{C_4}$. In the case of $\mathbf{C_8}$ the only twofold element, A^4, is in the invariant subgroup of order 2 and so the character tables map as:-

	$\mathbf{C_8}$	E	A^4	A^2	A^6	A	A^5	A^3	A^7
$\mathbf{C_4}$		E		A^2		A		A^3	
Γ_1	Γ_1	1	1	1	1	1	1	1	1
Γ_2	Γ_2	1	1	1	1	−1	−1	−1	−1
Γ_3	Γ_3	1	1	−1	−1	i	i	−i	−i
Γ_3*	Γ_3*	1	1	−1	−1	−i	−i	i	i
	Γ_4	1	−1	i	−i	√i	−√i	i√i	−i√i
	Γ_4*	1	−1	−i	i	−i√i	i√i	−√i	√i
	Γ_5	1	−1	i	−i	−√i	√i	−i√i	i√i
	Γ_5*	1	−1	−i	i	i√i	−i√i	√i	−√i

where $\sqrt{i}=(i+1)/\sqrt{2}$ and $i\sqrt{i}=(i-1)/\sqrt{2}$. This case is unusually interesting as it merits further examination. If one takes the antisymmetric square of either of the complex-conjugate pairs of double-valued representations one obtains Γ_1. If one takes the pair $\Gamma_4 + \Gamma_5$ one obtains the complex, single-valued, representation Γ_3* for the antisymmetric square while Γ_4* + Γ_5* produce its complex conjugate Γ_3. However, if one takes either the pair $\Gamma_4 + \Gamma_5$* or the pair Γ_4* + Γ_5 one obtains Γ_2 . This unexpected result is best understood by a consideration of the automorphisms of the group $\mathbf{C_8}$. These form a group of four elements isomorphic with Klein's four-group and generated by the inverse transformation, $A^n \rightarrow A^{7n}$, (which produces complex conjugation in the irreducible representations) and the transformation produced by replacing the generator A by A^3. The product of these two transformations is equivalent to replacing A^n by A^{5n}. The effect on the representations can be summarised in the following table:-

A^n	A^{7n}	A^{3n}	A^{5n}
Γ_3	Γ_3*	Γ_3	Γ_3*
Γ_3*	Γ_3	Γ_3*	Γ_3
Γ_4	Γ_4*	Γ_5*	Γ_5
Γ_4*	Γ_4	Γ_5	Γ_5*
Γ_5	Γ_5*	Γ_4*	Γ_4
Γ_5*	Γ_5	Γ_4	Γ_4*

The character table is invariant to the same transformations as those of the elements of the group. Mathematically the four irreducible representations {Γ_3 , Γ_3*, Γ_4 , Γ_4*} are distinct 1-dimensional representations which form an orbit under the action of the automorphism group of the group, $\mathbf{C_8}$. Physically they form a separable quadruply-degenerate state so that they would all be associated with states of the same energy. In the presence of a linear magnetic field, however, the quadruple degeneracy is lifted into two pairs of complex-conjugate double degeneracies.

To consider $\mathbf{C_4 \times C_2}$ as a potential double group of $\mathbf{C_4}$ the character tables may be matched as follows:-

$\mathbf{C_4}$	$\mathbf{C_4 \times C_2}$	E E	B	A^2 A^2	A^2B	A A	AB	A^3 A^3	A^3B
Γ_1	Γ_1	1	1	1	1	1	1	1	1
Γ_2	Γ_2	1	1	1	1	−1	−1	−1	−1
Γ_3	Γ_3	1	1	−1	−1	i	i	−i	−i
Γ_3*	Γ_3*	1	1	−1	−1	−i	−i	i	i
	Γ_4	1	−1	1	−1	1	−1	1	−1
	Γ_5	1	−1	1	−1	−1	1	−1	1
	Γ_6	1	−1	−1	1	i	−i	−i	i
	Γ_6*	1	−1	−1	1	−i	i	i	−i

The relevant invariant subgroup of order 2 is {E, B}. Γ_4 , Γ_5 , Γ_6 and Γ_6* are then the double-valued representations as they have characters for B which are minus those for E. The problem is, however, that the real double-valued representations, Γ_4 and Γ_5 , cannot be used to construct states which have an antisymmetric square equal to Γ_1. Hence they cannot represent spin-orbitals involving spin-½ functions even though the complex-conjugate pair, Γ_6 and Γ_6*, satisfy this criterion.

The spin double group of the cyclic group of order 4 must therefore be the cyclic group of order 8.

4.4 *The double group of Klein's four-group,* $\mathbf{C_2 \times C_2}$

Since Klein's four-group is a two-generator group, the cyclic group $\mathbf{C_8}$ can immediately be ruled out as a possible double group. The elementary group $\mathbf{C_2 \times C_2 \times C_2}$ and the dihedral

group $\mathbf{D_4}$ are both ineligible as they only contain representations which cannot be used to produce an antisymmetric square containing the identity representation.

This leaves just $\mathbf{C_4{\times}C_2}$ and **Q** and we shall see that both are possible structures for double groups of Klein's four-group. To justify $\mathbf{C_4{\times}C_2}$ it is helpful to rearrange the rows and columns of the character table without changing the labelling of the representations of $\mathbf{C_4{\times}C_2}$ above to produce:-

$\mathbf{C_2{\times}C_2}$	$\mathbf{C_4{\times}C_2}$	E E	A^2	A A	A^3	B B	A^2B	AB AB	A^3B
Γ_1	Γ_1	1	1	1	1	1	1	1	1
Γ_2	Γ_4	1	1	1	1	−1	−1	−1	−1
Γ_3	Γ_2	1	1	−1	−1	1	1	−1	−1
Γ_4	Γ_5	1	1	−1	−1	−1	−1	1	1
	Γ_3	1	−1	i	−i	1	−1	i	−i
	Γ_3*	1	−1	−i	i	1	−1	−i	i
	Γ_6	1	−1	i	−i	−1	1	−i	i
	Γ_6*	1	−1	−i	i	−1	1	i	−i

from which it can be seen that the four complex representations of $\mathbf{C_4{\times}C_2}$ now serve as double-valued representations of the double group of Klein's four-group. Further, the antisymmetric squares of the sum of either of the complex-conjugate pairs is the totally-symmetric representation, Γ_1, and hence $\mathbf{C_4{\times}C_2}$ appears to be a suitable double group for application to the electron-spin problem.

When the corresponding table for **Q** is constructed the doubly-degenerate representation Γ_5 of **Q** has all the required properties and so **Q** is also a possible structure for the spin double group of Klein's four-group.

$\mathbf{C_2{\times}C_2}$	**Q**	E E	A^2	A, A^3 A	B, A^2B B	AB, A^3B AB
Γ_1	Γ_1	1	1	1	1	1
Γ_2	Γ_2	1	1	1	−1	−1
Γ_3	Γ_3	1	1	−1	1	−1
Γ_4	Γ_4	1	1	−1	−1	1
	Γ_5	2	−2	0	0	0

Comparison of the conjugacy-class structures provides an elegant demonstration of the 2:1 homomorphism between the double group and the single group as well as the identification of Γ_5 of **Q** as the double-valued representation.

To decide which of the two possible groups to use as the spin double group we have to consider the relationship between the double groups of $\mathbf{C_2}$ and $\mathbf{C_4}$. On subduction from the double group of $\mathbf{C_4}$ to that of $\mathbf{C_2}$ we would have to choose which of the generators of $\mathbf{C_4{\times}C_2}$ was to remain a four-fold element and which was to become a two-fold element. But it has been seen that any two-fold generator of $\mathbf{C_2}$ becomes a four-fold generator in the double group of $\mathbf{C_2}$ which must be a subgroup of the double group of $\mathbf{C_4}$.

In considerations of spin-free molecular symmetry there are just three types of two-fold element, *viz.* space inversion, two-fold rotations and reflections. Space inversion is treated separately for this purpose as it is assumed that the spin problems are independent of whether we use a right-handed or a left-handed set of coördinates. Hence space inversion is included by factorising a symmetry group containing space inversion into a $\mathbf{C_2}$ group consisting of the identity and space inversion and a group which may contain rotations, reflections and combinations of these. Symmetry groups containing space inversion are thus best considered as direct product groups and the space inversion operation is taken to commute with all elements of the double group of the inversion-free part. Further, spin functions are taken to be invariant to space inversion, *i.e.* they are *gerade* or g-type.

This leaves the quaternion group **Q** as the only acceptable spin double group of Klein's four-group.

5. Construction of spin orbitals for the double group of C_4

This example is sufficiently interesting to merit inclusion here as it provides the key to the general problem and has probably not been published elsewhere. We know very little about electronic spin functions except that they are characterised by two quantum numbers, S and S_z, which are related to the eigenvalues of the spin operators $\hat{\mathbf{S}}^2$ and $\hat{\mathbf{S}}_z$ by the familiar relationships $\hat{\mathbf{S}}^2\sigma(S,S_z) = S(S+1)\sigma(S,S_z)$ and $\hat{\mathbf{S}}_z\sigma(S,S_z) = S_z\sigma(S,S_z)$. Converting functions with given values of S and S_z to those with neighbouring values of S_z is effected by the ladder operators $\hat{\mathbf{S}}_+$ and $\hat{\mathbf{S}}_-$ which have the effects $\hat{\mathbf{S}}_\pm\sigma(S,S_z) = \{(S\mp S_z)(S\pm S_z+1)\}^{½}\sigma(S,S_z\pm1)$. It is usual to abbreviate $\sigma(½,½)$ as α and $\sigma(½,-½)$ as β.

For group-theoretical analysis the effects of the symmetry operators on the spin functions are required. This is given in the case of one-dimensional representations by the character tables. Thus the generator A of $\mathbf{C_8}$ acting on the spin function α produces α multiplied by one of the four eighth roots of unity. Which of the four is chosen is entirely a matter of convention and the customary choice is to take that which is the lowest power of $\exp(2\pi i)$. In this case it will be $\exp(\pi i/4)=\sqrt{i}$. Correspondingly the effect of A on β must produce the complex conjugate $-i\sqrt{i}\beta$. These definitions assign the 1-electron spin functions to the Γ_4 and Γ_4* representations respectively.

Now suppose that we have two electrons labelled 1 and 2 with spin functions $\alpha(1)$, $\alpha(2)$, $\beta(1)$ and $\beta(2)$. The antisymmetric square of $\Gamma_4+\Gamma_4$* is Γ_1 so that $\alpha(1)\beta(2)-\beta(1)\alpha(2)$ is totally-symmetric and of S_z-value zero. The symmetric square produces the un-normalised functions $\alpha(1)\alpha(2)$, $\alpha(1)\beta(2)+\beta(1)\alpha(2)$ and $\beta(1)\beta(2)$ for the triplet (*i.e.* S=1) state with S_z values +1, 0 and −1 respectively. These states are of symmetries Γ_3, Γ_1 and Γ_3* respectively. These are single-valued representations as is to be expected for states involving an even number of electrons.

To find spin functions spanning the double-valued representations Γ_5 and Γ_5* it is necessary to consider functions for 3 or more electrons[2]. The four un-normalised three-electron functions having $S=^3/_2$ and $S_z = {}^3/_2$, ½, −½ and $-^3/_2$ are respectively $\alpha(1)\alpha(2)\alpha(3)$, $\alpha(1)\alpha(2)\beta(3)+\alpha(1)\beta(2)\alpha(3)+\beta(1)\alpha(2)\alpha(3)$, $\beta(1)\beta(2)\alpha(3)+\beta(1)\alpha(2)\beta(3)+\alpha(1)\beta(2)\beta(3)$ and $\beta(1)\beta(2)\beta(3)$ and span the irreducible representations Γ_5*. Γ_4, Γ_4* and Γ_5. To show that these four spin functions form a "closed shell" requires that the determinantally-antisymmetric fourth power of $\{\Gamma_4, \Gamma_4^*, \Gamma_5, \Gamma_5^*\}$ contains the identity representation which is the case.

6. Three-fold symmetry

The other chain of symmetry groups which is important in crystallographic symmetries although not exclusively fir free molecules is that deriving from the ascent $\mathbf{C_1}\rightarrow\mathbf{C_3}$. In this case the double group of $\mathbf{C_3}$ will be a group of order 6. There are just two abstract groups of this order. The central extension produces the cyclic group $\mathbf{C_6}$ defined by $\{A^6=E\}$ while a splitting extension produces the dihedral group $\mathbf{D_3}$ defined by $\{A^3=B^2=E;\ BA=A^2B\}$. The dihedral group of six elements cannot be chosen as the spin double group because it has no complex representations which can be matched onto the single-valued complex representations Γ_2 and Γ_3 of $\mathbf{C_3}$.

The character tables of $\mathbf{C_3}$ and $\mathbf{C_6}$ may be matched as

	$\mathbf{C_6}$	E	A^3	A	A^4	A^2	A^5
$\mathbf{C_3}$		E		A		A^2	
Γ_1	Γ_1	1	1	1	1	1	1
Γ_2	Γ_2	1	1	ω*	ω*	ω	ω
Γ_3	Γ_3	1	1	ω	ω	ω*	ω*
	Γ_4	1	−1	−1	1	1	−1
	Γ_5	1	−1	−ω*	ω*	ω	−ω
	Γ_6	1	−1	−ω	ω	ω*	−ω*

where $\omega=\exp(2\pi i/3)=(-1+i\sqrt{3})/2$ and its complex conjugate, ω^*, are the complex cube roots of unity as in section 2.3 above. Antisymmetric squares can only be formed from the complex-conjugate pairs $\Gamma_2+\Gamma_3$ and $\Gamma_5+\Gamma_6$. In both cases the antisymmetric square will be Γ_1 .

If Γ_5 rather than Γ_6 of $\mathbf{C_3}$ is chosen as the symmetry of the α-spin function, the pattern established in section 5 above can be followed. The effect of the operator A of the double group is to multiply the α-spin function by $\exp(\pi i/3)=-\omega^*$ and the β-spin function, which will have the symmetry of Γ_6 , by its inverse, $\exp(-\pi i/3)=-\omega$.

7. References

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