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Unique labelling of many-electron states in multicentre systems

K S Chan and D J Newman
Department of Physics, University of Hong Kong

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Abstract. General methods of generating complete sets of states for $l(\leqslant 2n)$ electrons in s-states on n centres are described. It is shown that a unique labelling of these states can always be obtained using a fictitious S_n symmetry of the n centres. Explicit descriptions of eight, seven and four electrons on eight centres are derived and the problem of determining a unique labelling for these states on rigid eight-centre structures with cubic and lower symmetry is solved.

1. Introduction

This paper is a contribution to a programme of work on the general problem of describing the many-electron states and Hamiltonians for multicentre systems in terms of finite group representations. The aim of this programme is to develop finite group theoretical techniques which can be applied to multicentre systems in an analogous way to which the Racah (1949) Lie group scheme has been applied to the many-electron states of paramagnetic ions (i.e. one-centre systems). Our ultimate aim is to set up a general and realistic formalism for the description of phenomena such as the metal–insulator transition and intermediate valency which involve electron-correlation effects in molecules and in finite regions of crystals. In this work we develop a general description of many-electron states on multicentre systems in which the states are uniquely labelled in a way that is related to the symmetry of the system.

The methods used build on group theoretical methods developed by Newman (1981, 1982) and Chan and Newman (1982). The present work extends that of Chan *et al* (1983). In particular, we shall find that there are considerable advantages in replacing the combinatorial methods used by Newman (1982) and Chan *et al* (1983) by induced representation methods. Other applications of these methods have been discussed by Litvin (1982) and Newman (1983).

It should also be remarked that the permutation group labelling of states developed in this work is quite closely related to state labelling using unitary group representations as described, for example, by Harter and Patterson (1976), Paldus (1977) and Condon and Odabasi (1980, ch 7). The unitary group approach is not, however, entirely appropriate for the present type of application in which we wish to relate the state labelling directly to the irreducible representation labels of the finite group describing the real symmetry.

2. State enumeration and labelling

In this section we describe two methods of enumerating the states of n electrons on n-centre systems in general terms, one of which has already been employed by Chan *et al* (1983) for the four-centre system. These techniques will both be employed to enumerate the S_8 states in § 3 and some physically realisable systems with eight electrons on eight centres will be discussed in § 4. Finally, in § 5, we shall show how to enumerate the states of $l \neq n$ electrons on n-centre systems.

Method B is easier to use than method A, although it involves a deeper understanding of the properties of symmetric groups. In particular, we note that it suggests a possible development of the combinatorial approach described by Newman (1982) in a more general context.

Method A. Combinatorial method of obtaining the states of n electrons in s-states on n centres (see also Chan *et al* 1983)

(1) The different possible spin configurations on each site are assigned 'colours': $a \equiv \uparrow$, $b \equiv \downarrow$, $c \equiv \updownarrow$.

(2) Polya's theorem, in the generalisation described by Newman (1982), is used to determine the S_n characters for all possible colourings corresponding to each possible configuration $1^{n-2p}\,2^p$ of p paired electrons and $n-2p$ unpaired electrons. All the characters produced in this way are positive. (Such a procedure could, of course, be employed for any number of electrons.)

(3) Characters for classes involving odd permutations (even cycles) must be modified to allow for the antisymmetry under interchange of the a and b colourings. In configurations of the types 1^n and $1^{n-2}2$ this simply requires the sign of the characters of odd permutation classes to be changed. In the case of the configuration $2^{n/2}$ (i.e. $c^{n/2}$) no change in the characters is required. For all other configurations rather complicated changes may be necessary. The method of finding these character changes is described by means of an example in § 3.

(4) The characters derived in (2) and (3) correspond to specific configuration and M_S values. Total spin characters are obtained by the usual procedure of starting with the highest $M_S \equiv S$ and subtracting off these states from those with $M_S - 1$ to give the states for $S = M_S - 1$, etc until $S = 0$ is reached.

(5) The characters then determine the S_n irreducible representation labels for the states of a given configuration and given total spin.

Note that this procedure suffices to *enumerate* the states but it does not provide a *unique* labelling.

Method B. Group theoretical method of obtaining the states of n electrons in s-states on n centres

(1) List possible configurations in terms of p paired electrons, $n-2p$ unpaired electrons and p unoccupied centres.

(2) Determine the spin (permutation) representations for a given configuration using the standard branching rules shown for n up to 16 in table 1.

(3) The configuration group is defined as $S_{n-2p} \otimes S_p \otimes S_p$. The configuration representation for a given spin state is determined by: (a) taking the appropriate S_{n-2p} space representation (say Γ) for the unpaired electrons conjugate to the spin representation determined in (2); (b) inducing the representation of the symmetric group S_n from the representation $\Gamma \otimes [p] \otimes [p]$ of $S_{n-2p} \otimes S_p \otimes S_p$.

Table 1. Spin states and their multiplicities for up to 16 centres.

n =	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
0		$[1^2]$ 1		$[2^2]$ 2		$[3^2]$ 5		$[4^2]$ 14		$[5^2]$ 42		$[6^2]$ 132		$[7^2]$ 429		$[8^2]$ 1430
$\frac{1}{2}$	[1] 1		[21] 2		[32] 5		[43] 14		[54] 42		[65] 132		[76] 429		[87] 1430	
1		[2] 1		[31] 3		[42] 9		[53] 28		[64] 90		[75] 297		[86] 1001		[97] 3432
$\frac{3}{2}$			[3] 1		[41] 4		[52] 14		[63] 48		[74] 165		[85] 572		[96] 2002	
2				[4] 1		[51] 5		[62] 20		[73] 75		[84] 275		[95] 1001		[10, 6] 3640
$\frac{5}{2}$					[5] 1		[61] 6		[72] 27		[83] 110		[94] 429		[10, 5] 1638	
3						[6] 1		[71] 7		[82] 35		[93] 154		[10, 4] 637		[11, 5] 2548
$\frac{7}{2}$							[7] 1		[81] 8		[92] 44		[10, 3] 208		[11, 4] 910	
4								[8] 1		[91] 9		[10, 2] 54		[11, 3] 273		[12, 4] 1260
$\frac{9}{2}$									[9] 1		[10, 1] 10		[11, 2] 65		[12, 3] 350	
5										[10] 1		[11, 1] 11		[12, 2] 77		[13, 3] 440
$\frac{11}{2}$											[11] 1		[12, 1] 12		[13, 2] 90	
6												[12] 1		[13, 1] 13		[14, 2] 104
$\frac{13}{2}$													[13] 1		[14, 1] 14	
7														[14] 1		[15, 1] 15
$\frac{15}{2}$															[15] 1	
8																[16] 1

(4) If the induced representation of S_n obtained from 3(b) contains repeated irreducible representations then an intermediate group between $S_{n-2p} \otimes S_p \otimes S_p$ and S_n can always be found which provides a unique labelling of the states. A suitable intermediate group is $S_{n-p} \otimes S_p$, because there is only one way of forming each of the representations of the group S_{n-p} from an arbitrary representation of S_{n-2p} and the identity representation $[p]$ of S_p. Similarly the representations of S_n can only be formed in one way from an arbitrary representation of S_{n-p} and the identity representation $[p]$ of S_p.

(5) Finally, the representations of the spatial symmetry group of the n-centre system can be subduced from the S_n representations, again using intermediate groups to make the subduction process unique.

Quite apart from the relative simplicity of the analysis, method B has two distinct advantages over method A. The labelling obtained is unique and the S_n group character table is not needed in the analysis. This latter point is important for large values of n for which explicit character tables have never been derived.

3. State enumeration and labelling for an eight-centre system

We shall employ, in turn, each of the two methods described in § 2. This will show up the shortcomings of the combinatoric approach in relation to electronic states. It will also show how the induced representation method can be adapted for use in problems that have hitherto been treated combinatorially. This will complete the work on the link between combinatorial and group theoretical methods begun by Newman (1982).

Table 2. Characters for the colourings corresponding to eight particles in various configurations on eight centres, where spin occupation is related to colouring by $a \equiv \uparrow$, $b \equiv \downarrow$, $c \equiv \updownarrow$. Bracketed numbers and signs indicate the change in character that occurs when allowance is made for the antisymmetry of the states under particle exchange.

	Class	1^8	1^62	1^53	1^44	1^42^2	1^323	1^35	1^26
	Order	1	28	112	420	210	1120	1344	3360
Configurations	Colourings								
$1^8\ M_S=4$	a^8, b^8	1	(−) 1	1	(−) 1	1	(−) 1	1	(−) 1
3	a^7b, ab^7	8	(−) 6	5	(−) 4	4	(−) 3	3	(−) 2
2	a^6b^2, a^2b^6	28	(−) 16	10	(−) 6	8	(−) 4	3	(−) 1
1	a^5b^3, a^3b^5	56	(−) 26	11	(−) 4	12	(−) 5	1	0
0	a^4b^4	70	(−) 30	10	(−) 2	14	(−) 6	0	0
$1^62\ M_S=3$	a^6c, b^6c	56	(−) 30	20	(−) 12	12	(−) 6	6	(−) 2
2	a^5bc, ab^5c	336	(−) 120	60	(−) 24	24	(−) 6	6	0
1	a^4b^2c, a^2b^4c	840	(−) 210	60	(−) 12	36	(−) 6	0	0
0	a^3b^3c	1120	(−) 240	40	0	48	(−) 12	0	0
$1^42^2\ M_S=2$	a^4c^2, b^4c^2	420	120 (−60)	30	(−) 6	32 (−16)	(+) 6	0	0
1	a^3bc^2, ab^3c^2	1680	300 (−60)	30	0	56 (−40)	(+) 6	0	0
0	$a^2b^2c^2$	2520	360 (0)	0	0	72 (−24)	0	0	0
$1^22^3\ M_S=1$	a^2c^3, b^2c^3	560	140 (100)	20	0	40 (8)	8 (4)	0	0
0	abc^3	1120	(+) 240	40	0	(+) 48	(+) 12	0	0
$2^4\ M_S=0$	c^4	70	30	10	2	14	6	0	0

3.1. Method A: combinatorial approach

Pólya's theorem was applied to each of the five possible electron configurations 1^8, 1^62, 1^42^2, 1^22^3, 2^4 of the group S_8 to obtain the coefficients of $a^rb^sc^t$ shown (unbracketed) in table 2. Mistakes in this table were eliminated by checking that each row corresponds to a single equivalence class (see Newman 1982).

A more direct way of obtaining single entries in the table is possible simply by counting the number of distinct ways a colouring may be fitted to the cycle structures of a class. For example, a^4c^2 may be fitted into the cyclic structure $(1^6)(2)$ in three 'modes': $(a^4)(c^2)$; $(a^4c^2)(1)$; $(a^2c^2)(a^2)$. In the first mode there are $6!/4!\,2! = 15$ ways and in the second and third modes 15 and 90 ways respectively. The total number is thus $15+15+90=120$, corresponding to the result shown in table 2. Although this form of calculation is tedious, it is less prone to error than the method described by Newman (1982). As we shall shortly find, it is also essential to use this approach in order to allow for the antisymmetry of electron exchange.

Following Chan *et al* (1983) we note that each colouring (corresponding to a row in the table) may be associated with a definite M_S value. However, the positive characters shown correspond to colourings, and do not allow for the antisymmetry properties of electron exchange. Before attempting to relate the characters to irreducible representations it is necessary to modify their values to make allowance for this property of the basis functions.

In the study of the system with four electrons on four centres (Chan *et al* 1983), this was simply done by changing the sign of the characters for all odd permutations in the 1^4 and 1^22 configurations. This approach can only be used for the 1^8 and 1^62 configurations of the eight-centre system, giving the signs shown bracketed in table 2. The signs are left unchanged for the 2^4 configuration, as the permutations

Table 2. (continued)

1^224	1^22^3	1^33^2	125	12^23	134	17	8	4^2	2^24	26	23^2	35	2^4
2520	420	1120	4032	1680	3360	5760	5040	1260	1260	3360	1120	2688	105
1	(−) 1	1	(−) 1	1	(−) 1	1	(−) 1	1	(−) 1	1	(−) 1	1	1
2	(−) 2	2	(−) 1	1	(−) 1	1	0	0	0	0	0	0	0
2	(−) 4	1	(−) 1	2	0	0	0	0	(−) 2	1	(−) 1	0	4
2	(−) 6	2	(−) 1	3	(−) 1	0	0	0	0	0	(−) 2	1	0
2	(−) 6	4	0	2	(−) 2	0	0	2	(−) 2	0	0	0	6
2	(−) 2	2	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	(−) 6	0	0	0	0	0	0	0	0	0	0	0	0
0	0	4	0	0	0	0	0	0	0	0	0	0	0
(−) 2	12 (0)	0	0	(+) 2	0	0	0	0	(−) 2	0	0	0	(+) 12
0	(−) 2	0	0	(+) 2	0	0	0	0	0	0	0	0	0
0	24 (0)	0	0	0	0	0	0	0	0	0	0	0	(+) 24
0	(−) 12	2	0	(−) 4	0	0	0	0	0	0	(−) 2	0	0
0	0	4	0	0	0	0	0	0	0	0	0	0	0
2	6	4	0	2	2	0	0	2	2	0	0	0	6

interchange $c \equiv \uparrow\downarrow$ in this case, and no changes of sign occur. The other configurations pose a more difficult problem, however, as some cycles are acting on $a \equiv \uparrow$ and $b \equiv \downarrow$ and some are acting upon $c \equiv \uparrow\downarrow$. The only way of disentangling this situation within the context of the present method is to look individually at all entries for these configurations in those cases where the classes contain one or more *odd* permutations (or *even* cycles). Luckily the non-zero entries are not very numerous.

As an example of this character modification process we consider again the case of the colouring a^4c^2 and the class 1^62. Each of the three modes considered above may be associated with signs according to whether the odd (2) cycle is associated in with the single or double electron occupation:

$$(1^6)(2): (a^4)(c^2) +; (a^4c^2)(1) +; (a^2c^2)(a^2) -.$$

Hence the correct character for this case when the antisymmetry of electron exchange has been allowed for is $+15+15-90=-60$. This figure is shown bracketed in table 2.

When the antisymmetrised characters have been determined we can associate the maximum M_S characters for each configuration with the maximum S value for that configuration. This $(M_S)_{max} = S$ set of characters can then be subtracted from those with a value of M_S less than $(M_S)_{max}$ to determine the characters for $S-1$. Successive applications of this rule then give the characters for each S value of the configuration.

3.2. Method B: direct (induced representation) approach

Each of the five configurations can be associated with a definite number of unpaired electrons and hence, using table 1, with a set of possible total spin values. The table gives S_n representations corresponding to these spin values, as follows.

Configuration 1^8. In this case $n = 8$, so that the possible total spin values are $S = 0$ or $[4^2]$, $S = 1$ or $[53]$, $S = 2$ or $[62]$, $S = 3$ or $[71]$ and $S = 4$ or $[8]$.

Configuration 1^62. The $n = 6$ unpaired electrons have the possible spin values $S = 0$ or $[3^2]$, $S = 1$ or $[42]$, $S = 2$ or $[51]$ and $S = 3$ or $[6]$.

Configuration 1^42^2. In this case $n = 4$, so that $S = 0$ or $[2^2]$, $S = 1$ or $[31]$ and $S = 0$ or $[4]$.

Configuration 1^22^3. This corresponds to the spin values $S = 0$ or $[1^2]$ and $S = 1$ or $[2]$.

Configuration 2^4. There are no unpaired electrons so that $n = 0$ and $S = 0$.

In the case of configuration 1^8 the configuration group is S_8, so that each spin value determines a unique spatial representation conjugate to the spin representation given above: $[4^2] \rightarrow [2^4]$, $[53] \rightarrow [2^31^2]$, $[62] \rightarrow [2^21^4]$, $[71] \rightarrow [21^6]$, $[8] \rightarrow [1^8]$.

The configuration group for 1^62 is $S_6 \otimes S_1 \otimes S_1$ and the S_6 representations $[3^2]$, $[42]$, $[51]$ and $[6]$ corresponding to the possible spin values will each induce several representations of S_8. This induction process, which uses S_7 as a intermediate group, is shown in figures 1 and 2. We only show the genealogy of repeated representations in figure 2 (for $S > 1$). Note that the use of S_7 automatically provides a unique label for every S_8 orbital state. The results obtained in this way agree with those shown in table 3 (previously derived using the combinatorial approach).

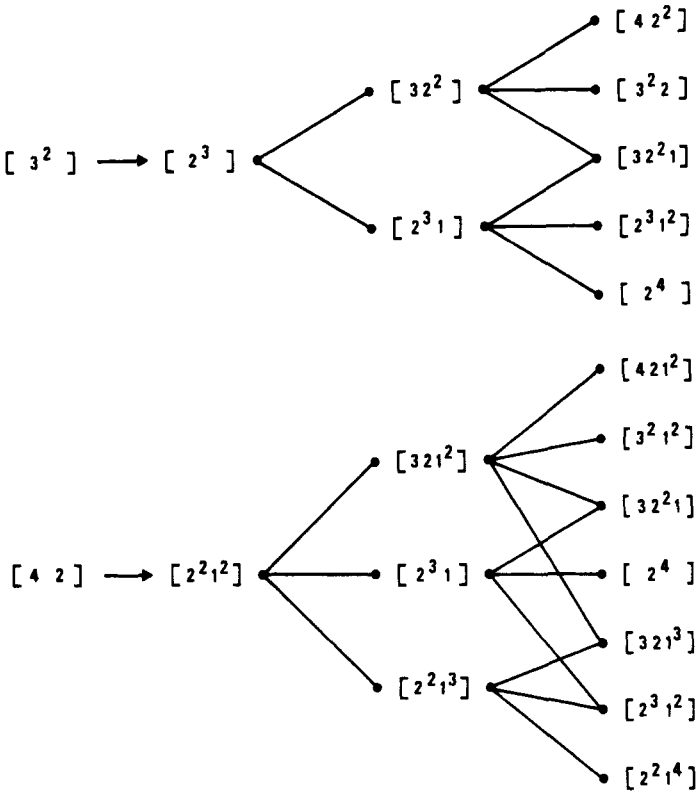

Figure 1. Genealogy of the $S = 0$, 1 representations of the configuration $1^6 2$ using $S_8 \supset S_7 \otimes S_1 \supset S_6 \otimes S_1 \otimes S_1$.

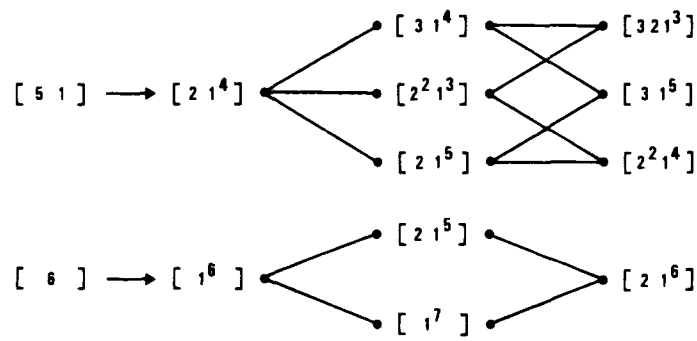

Figure 2. Genealogy of the $S = 2$, 3 repeated representations of the configuration $1^6 2$ using $S_8 \supset S_7 \otimes S_1 \supset S_6 \otimes S_1 \otimes S_1$.

The generation of states for the configurations $1^4 2^2$ and $1^2 2^3$ proceeds in much the same way using respectively the representations of $S_4 \otimes S_2 \otimes S_2$ and $S_2 \otimes S_3 \otimes S_3$ to induce representations of S_8. In all cases only the identity representations $[n]$ of the last two groups are used in this process, together with the spatial representation conjugate to the appropriate spin representation for the first group. Figures 3 and 4 show only the repeated representations of S_8.

Table 3. Irreducible representations (irreps) of S_n corresponding to eight electrons in s-state on eight centres.

Configuration			1^8				1^62				1^42^2			1^22^3		2^4
		$S=0$	1	2	3	4	0	1	2	3	0	1	2	0	1	0
Irrep	Dim															
[8]	1													1		1
[71]	7													2	1	1
[62]	20										1			3	1	1
$[61^2]$	21											1		1	2	
[53]	28										1			3	1	1
[521]	64										2	2		2	2	
$[51^3]$	35											2	1		1	
$[4^2]$	14										1			1	1	1
[431]	70										2	2		2	2	
$[42^2]$	56						1				3	1		1		
$[421^2]$	90							1			1	4	1		1	
$[3^22]$	42						1				1	1		1		
$[3^21^2]$	56							1			1	2	1		1	
$[32^21]$	70						2	2			2	2				
$[2^4]$	14	1					1	1			1					
$[41^4]$	35								1			1	2			
$[321^3]$	64							2	2			2	2			
$[2^31^2]$	28		1				1	2	1			1				
$[31^5]$	21								2	1			1			
$[2^21^4]$	20			1				1	2	1			1			
$[21^6]$	7				1				1	2						
$[1^8]$	1					1				1						
No of states		14	84	100	49	9	280	1512	1400	392	840	3780	2100	560	1680	70

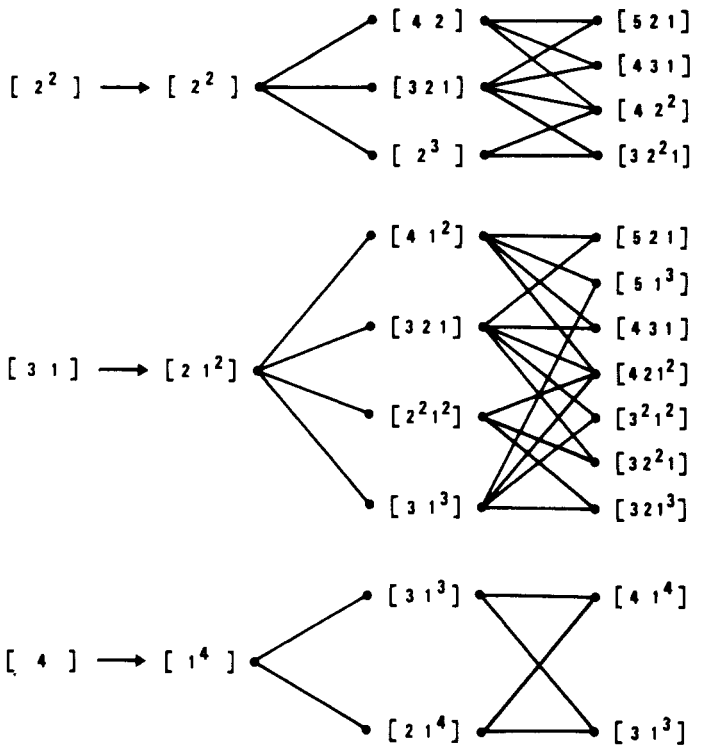

Figure 3. Genealogy of the $S = 0, 1, 2$ repeated representations of the configuration $1^4 2^2$ using $S_8 \supset S_6 \otimes S_2 \supset S_4 \otimes S_2 \otimes S_2$.

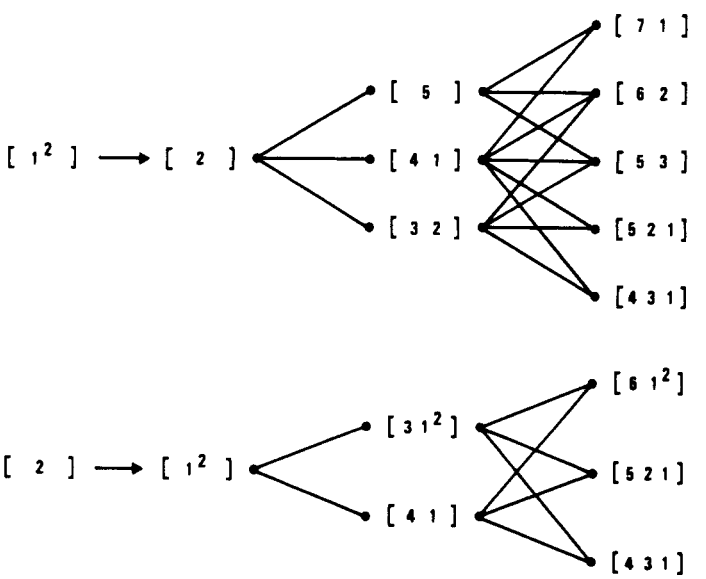

Figure 4. Genealogy of the $S = 0, 1$ repeated representations of the configuration $1^2 2^3$ using $S_8 \supset S_5 \otimes S_3 \supset S_2 \otimes S_3 \otimes S_3$.

As an example consider the case of the $S_2 \otimes S_3 \otimes S_3$ representation $[1^2] \otimes [3] \otimes [3]$ corresponding to total spin $S = 1$ for the configuration $1^2 2^3$. The induced representations may be obtained immediately from the direct product rules for S_n (e.g. see Hamermesh 1964):

$$S_2 \otimes S_3: [1^2] \otimes [3] = [41] + [31^2],$$

$$S_5 \otimes S_3: [41] \otimes [3] = [71] + [62] + [53] + [4^2] + [61^2] + [521] + [431],$$

$$[31^2] \otimes [3] = [61^2] + [521] + [431] + [51^3] + [421^2] + [3^2 1^2].$$

These results correspond to the column of table 3 labelled $1^2 2^3$, $S = 1$. The repeated representations [431], [521] and $[61^2]$ appear in figure 4.

Finally we note that the configuration 2^4 corresponds to the identity representation $[4] \otimes [4]$ of the direct product group $S_4 \otimes S_4$. This induces the representations $[8] + [71] + [62] + [53] + [4^2]$ into S_8 as is shown in the final column of table 3. This completes the analysis.

4. Description of eight-electron states on rigid eight-centre systems

The problem of finding a unique labelling of the many-electron states on a physically realisable rigid array of lattice points of given spatial symmetry is now seen to be equivalent to finding a chain of subgroups relating S_n with the spatial symmetry, so that each group–subgroup relationship leads to a unique subduction. Littlewood (1958) has studied the large subgroups of S_8 and has, in particular, identified a 1344-element subgroup. This will be denoted $G^{(1)}$ here. In Littlewood (1958) it was denoted by the representation induced in S_8 by its identity representation: namely $[8] + [4^2] + [2^4] + [1^8]$. This group contains the 192-element group studied by Chan and Newman (1982). In order to make the subduction between S_8 and $G^{(1)}$ unique for the self-conjugate representations of S_8 it was found to be necessary to insert the alternating group $A_8 = [8] + [1^8]$. The complete subduction for $S_8 \supset A_8 \supset G^{(1)}$ is given in table 4.

It is then easy to show that the subduction for $G^{(1)}$ to the 192-element group (which we shall call $G^{(2)}$) is also unique. The complete set of subduction relations for $G^{(1)} \supset G^{(2)}$ is shown in table 5. This provides a unique labelling for all the 12 870 eight-electron states on eight-centre cyclic regions in a body-centred or face-centred cubic lattice. The unique labelling for a simple cubic lattice is related to that for the $G^{(2)}$ states by the further subduction for $G^{(2)} \supset O$. As is shown in table 6, this subduction is also unique.

5. Enumeration of l-electron states for $l \neq n$

We shall consider only the case $l < n$, as more than half-filled systems ($l > n$) are directly related to those with $l < n$ by particle–hole conjugation. In this case the electron configurations take the form

$$1^l, 1^{l-2}2, \ldots, 1^{l-2r}2^r, \ldots$$

and the possible spin-values range from $\frac{1}{2}$ to $\frac{1}{2}(l-2r)$ for l odd, and 0 to $\frac{1}{2}(l-2r)$ for

Table 4. Branching rules for $S_8 \supset A_8(=[8]+[1^8]) \supset G^{(1)}(=[8]+[4^2]+[2^4]+[1^8])$. Alternating group ($A_8$) representations are shown in the standard notation for S_8 representations. Suffixes α, β distinguish A_8 representations subduced by S_8 self-conjugate representations. The representations of the 1344-element subgroup of A_8 are labelled following the notation of Littlewood (1958, p 276).

A_8 representations	$G^{(1)}$ representations
$[8]\equiv[1^8]$	(a)
$[71]\equiv[21^6]$	(c)
$[62]\equiv[2^21^4]$	(b)+(d)
$[61^2]\equiv[31^5]$	(e)
$[53]\equiv[2^31^2]$	(e)+(c)
$[521]\equiv[321^3]$	(d)+(e)+(g)+(j)
$[51^3]\equiv[41^4]$	(f)+(g)+(h)
$[4^2]\equiv[2^4]$	(a)+(b)+(f)
$[431]\equiv[32^21]$	(c)+(d)+(e)+(g)+(h)
$[42^2]\equiv[3^21^2]$	(b)+(d)+(f)+(g)+(j)
$[421^2]_\alpha$	(e)+(g)+(k)
$[421^2]_\beta$	(e)+(g)+(l)
$[3^22]_\alpha$	(e)
$[3^22]_\beta$	(e)

Table 5. Branching rules for the 1344-element group $G^{(1)}=[8]+[4^2]+[2^4]+[1^8]$ to the 192-element group $G^{(2)}=[8]+[62]+2[4^2]+[42^2]+[3^21^2]+2[2^4]+[2^21^4]+[1^8]$. Character tables for both groups are given by Littlewood (1958, p 276). 192-element group representations are labelled following Chan and Newman (1982).

$G^{(1)}$ representations	$G^{(2)}$ representations
(a)	A_1^Γ
(b)	$A_1^\Gamma+E^\Gamma+T_2^\Gamma$
(c)	$A_1^X+A_1^L$
(d)	$A_1^X+B_2^X+E^L$
(e)	$B_1^X+E^X+A_1^L+E^L$
(f)	$B_2^X+A_2^L$
(g)	$A_2^X+E^X+A_2^L+E^L$
(h)	$T_2^\Gamma+T_1^\Gamma+A_2^\Gamma$
(j)	$T_2^\Gamma+E^\Gamma+T_1^\Gamma$
(k)	T_1^Γ
(l)	T_1^Γ

l even. The configuration group for the general configuration $1^{l-2r}2^r$ is given by

$$S_{l-2r} \otimes S_r \otimes S_{n-l+r}. \tag{5.1}$$

Hence the states of the system of total spin S are formed from direct products of irreducible representations as follows:

$$[2^{(l-2r-2S)/2}, 1^{2S}] \otimes [r] \otimes [n-l+r]. \tag{5.2}$$

The sets of irreducible representations in the first square bracket, corresponding to $l-2r$ unpaired electrons, are given explicitly in table 1 for $l-2r<16$.

Table 6. Branching rules for the 192-element group $G^{(2)} = [8]+[62]+2[4^2]+[42^2]+[3^21^2]+2[2^4]+[2^21^4]+[1^8]$ to the octahedral group O corresponding to a rigid structure of eight labelled points at the corners of a cube or the eight-centre cyclic regions of a simple cubic lattice.

$G^{(2)}$ representations	O representations
A_1^Γ	A_1
T_2^Γ	T_2
E^Γ	E
T_1^Γ	T_1
A_2^Γ	A_2
B_1^X	A_2+E
A_1^X	A_1+E
B_2^X	T_2
A_2^X	T_1
E^X	T_1+T_2
A_1^L	A_1+T_2
A_2^L	A_2+T_1
E^L	$E+T_1+T_2$

Just as in the case $l = n$, a unique labelling of the states can be obtained by using S_{l-r} as an intermediate group, as the direct products of irreducible representations with the identity representations $[n-l+r]$ do not produce any repetitions.

5.1. Seven electrons on eight centres ($n = 8, l = 7$)

In this case the possible configurations and spin states (see table 1) are:

$r = 0, 1^7$: $S = \frac{1}{2}, [2^31]$ $S = \frac{3}{2}, [2^21^3]$ $S = \frac{5}{2}, [21^5]$ $S = \frac{7}{2}, [1^7]$

$r = 1, 1^52$: $S = \frac{1}{2}, [2^21]$ $S = \frac{3}{2}, [21^3]$ $S = \frac{5}{2}, [1^5]$

$r = 2, 1^32^2$: $S = \frac{1}{2}, [21]$ $S = \frac{3}{2}, [1^3]$

$r = 3, 1\,2^3$: $S = \frac{1}{2}, [1]$

(Note that the square brackets are orbital states conjugate to the spin states shown in table 1.)

Forming the direct products shown in equation (5.2) we obtain the induced representations in S_8 shown in table 7. The unique labels are not given in this table, so we illustrate this by considering the case of the configuration 1^32^2 with $S = \frac{1}{2}$. The direct product of the appropriate representations of $S_3 \otimes S_2$ gives S_5 representations as follows:

$$[21]\otimes[2]=[41]+[31^2]+[32]+[2^21].$$

Each representation of S_5 then induces a set of S_8 representations which can be obtained by forming their direct product with the identity representation [3] of S_3:

$$[32]\otimes[3]=[62]+[53]+[521]+[431]+[42^2]+[3^22],$$

$$[31^2]\otimes[3]=[61^2]+[521]+[51^3]+[431]+[421^2]+[3^21^2],$$

$$[2^21]\otimes[3]=[521]+[42^2]+[421^2]+[32^21],$$

$$[41]\otimes[3]=[71]+[62]+[53]+[61^2]+[521]+[4^2]+[431]. \qquad (5.3)$$

Table 7. Enumeration of the 11 440 states for seven electrons on eight centres.

Configuration		1^7				1^52			1^32^2		12^3
	$S=$	1/2	3/2	5/2	7/2	1/2	3/2	5/2	1/2	3/2	1/2
Irrep	Dim										
[8]	1										1
[71]	7								1		2
[62]	20								2		2
$[61^2]$	21								2	1	1
[53]	28								2		2
[521]	64					1			4	1	1
$[51^3]$	35						1		1	2	
$[4^2]$	14								1		1
[431]	70					1			3	1	1
$[42^2]$	56					2			2		
$[421^2]$	90					2	2		2	2	
$[3^22]$	42					1			1		
$[3^21^2]$	56					1	1		1	1	
$[32^21]$	70	1				3	1		1		
$[2^4]$	14	1				1					
$[41^4]$	35						2	1		1	
$[321^3]$	64		1			1	3	1		1	
$[2^31^2]$	28	1	1			1	1				
$[31^5]$	21			1			1	2			
$[2^21^4]$	20		1	1			1	1			
$[21^6]$	7			1	1			1			
$[1^8]$	1				1						
No of states		224	448	288	64	1680	2688	1008	2240	2240	560

We note, for example, that each of the four occurrences of [521] as recorded in table 7 corresponds to a different S_5 representation label. No repeated representations occur in (5.3), showing that the S_5, S_8 labelling is unique for this configuration.

Table 8. Enumeration of the 1820 states for four electrons on eight centres.

Configuration		1^4			1^22		2^2
	$S=$	0	1	2	0	1	0
Irrep	Dim						
[8]	1				1		1
[71]	7				2	1	1
[62]	20	1			2	1	1
$[61^2]$	21		1		1	2	
[53]	28				1		
[521]	64	1	1		1	1	
$[51^3]$	35		1	1		1	
$[42^2]$	56	1					
$[421^2]$	90		1				
$[41^4]$	35			1			
No of states		140	630	350	168	504	28

5.2. Four electrons on eight centres ($n = 8$, $l = 4$)

In this case there are only three configurations and the total spin takes integral values as follows:

$r = 0, 1^4$: $S = 0, [2^2]$ $S = 1, [21^2]$ $S = 2, [1^4]$

$r = 1, 1^2 2$: $S = 0, [2]$ $S = 1, [1^2]$

$r = 2, 2^2$: $S = 0$

Forming the direct products shown in equation (5.2), we obtain the results given in table 8.

In the case $l \neq n$ the reduction of S_8 irreducible representations to irreducible representations of the real symmetry of the system follows exactly the same pattern as given in § 4. Hence we have obtained a unique description of the states for any number of electrons on eight sites.

6. Summary

We have shown that the complete set of l-electron states formed from (one-electron) s-states on n centres can be uniquely labelled if full symmetric group (S_n) symmetry is assumed. Direct group theoretical, rather than combinatorial, methods were found to be easier to use to obtain this result, which holds for all values of n.

In the case $n = 8$ it has been shown that a unique labelling of all l-electron states on rigid arrays of the eight centres in rigid configurations with various spatial symmetries can also be obtained.

These results provide the first step in obtaining a full classification of many-electron states on multicentre systems which is directly related to the finite group symmetry of the real system. Further developments will involve generalisations of the one-electron basis set and finding systematic methods for evaluating many-electron matrix elements of one- and two-particle operators. Many-electron states of this type can then be employed to study the energy structure of multicentre electronic systems with arbitrarily strong correlation effects.

The methods we have described are not restricted to s-states on separate centres. They could, for example, be applied to the Hückel–Hubbard method for planar unsaturated molecules (Matsen 1976), or to more general configuration interaction basis sets (Harter and Patterson 1976).

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