Symmetry coordinates for O_h atomic shells

1982 J. Phys. A: Math. Gen. 15 331

(http://iopscience.iop.org/0305-4470/15/2/007)

J. Phys. A: Math. Gen. **15** (1982) 331–341. Printed in Great Britain

Symmetry coordinates for O_h atomic shells

S C Chen and D J Newman
Department of Physics, University of Hong Kong, Hong Kong

Received 20 July 1981

Abstract. The group factorisation and correlation theorem methods used previously to provide a unique labelling of atomic shell symmetry coordinates are shown to give also a simple means for deriving explicit expressions for these coordinates. Results are given for the 12-atom shell and the two types of 24-atom shells in O_h symmetry.

1. Introduction

In calculating the coupling between electronic states of paramagnetic ions and distortions of the surrounding crystal it is necessary to use group-theoretical methods to diagonalise the force matrix. This requires the determination of symmetry-adapted coordinates for the displacements of successive shells of ions surrounding the paramagnetic ion. For a given site symmetry there is a limited number of types of shell, each type corresponding to a distinct subgroup of the full site symmetry group which leaves the position of a single ion in the shell unmoved. In the case of O_h symmetry there are six distinct types of shell, two of which have 24 ions. These two cases, as well as being relevant to local distortion calculations, provide ideal examples to demonstrate our method for obtaining symmetry coordinates. For completeness, we also give the symmetry coordinates for the 12-fold shell.

2. The 24-fold shell with ions in $(p, q, 0)$ positions

The symmetry coordinates of this shell may be classified uniquely (Newman 1981) either according to their relation with the 12-fold shell or with the 6-fold shell. We shall find it instructive to follow the latter alternative in generating an explicit set of symmetry coordinates. The correlation diagram relating C_{4v} subgroups with the O_h group is given by figure 2 of Newman (1981).

Our method is to relate the C_{4v} irreducible representations for the permutation of 4-atom subarrays of the 24-fold shell to simple functions of the coordinate displacements in the 6-fold shell which transform in the same way. The symmetry coordinates of the 24-fold shell permutations can then be deduced directly from the well known displacement symmetry coordinates of the octahedral system (e.g. Bates 1978). Figure 1 shows the labelling for both the 24-fold cubic (O_h) array and the C_{4v} 4-fold subarrays

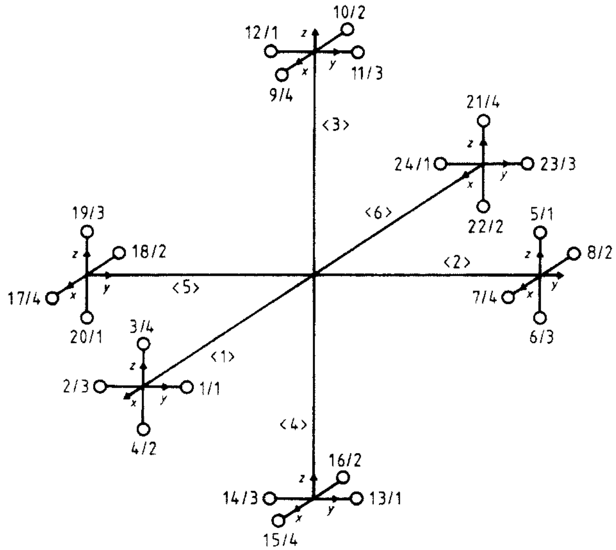

Figure 1. Structure of a 24-fold array of atoms in positions $(p, q, 0)$, showing the labels used in table 1. $\langle a\rangle$ denotes subarray a and b/c denotes atom b of the full 24-fold array and atom c of the 4-fold subarrays.

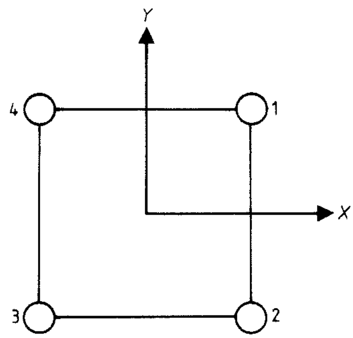

Figure 2. Relation of atom numbering in a 4-fold subarray with X, Y coordinates.

of ions. Symmetry-adapted functions for the C_{4v} irreducible permutation representations are given by (figure 2):

A_1: $\frac{1}{2}(\{1\}+\{2\}+\{3\}+\{4\})$: invariant

B_1: $\frac{1}{2}(\{1\}-\{2\}+\{3\}-\{4\})$: transforming as XY

E_a: $\frac{1}{2}(\{1\}+\{2\}-\{3\}-\{4\})$: transforming as X

E_b: $\frac{1}{2}(\{1\}-\{2\}-\{3\}+\{4\})$: transforming as Y.

It will be convenient to use suffixes to distinguish subarrays in the following argument. Square brackets will be used to denote labels on the 24-fold array so that with the notation in figure 1 $\{c\}_a=[b]$; for example $\{4\}_5\equiv[17]$, $\{3\}_2\equiv[6]$, etc.

In order to make direct substitutions into the octahedral symmetry coordinates these functions must be related (in terms of C_{4v} transformation properties) to the local coordinates at each ion. Figure 1 is drawn with the same local coordinates as figure 1 of Bates (1978), although the subarray labels ⟨4⟩ and ⟨6⟩ have been exchanged. These local coordinates are related by a 45° rotation to the C_{4v} coordinates X and Y shown in figure 2. Examining each of the six subarrays of four ions in turn we obtain the following relationships between C_{4v} transformation properties in the notation of figure 1:

$$\left.\begin{array}{l} z_1, x_2, x_3, x_4, x_5, z_6 \sim (Y-X)/\sqrt{2} \sim (\{4\}-\{2\})/\sqrt{2} \\ y_1, z_2, -y_3, y_4, -z_5, -y_6 \sim (Y+X)/\sqrt{2} \sim (\{1\}-\{3\})/\sqrt{2} \end{array}\right\} \quad \text{E representation}$$

$$x_1, y_2, z_3, -z_4, -y_5, -x_6 \sim \text{invariant} \sim \tfrac{1}{2}(\{1\}+\{2\}+\{3\}+\{4\}) \qquad \text{A}_1 \text{ representation.}$$

The permutation symmetry coordinates corresponding to the A_1 and E representations can thus be obtained from table 5 of Bates (1978) by substituting the C_{4v} symmetry coordinates given above (with labels 4 and 6 interchanged) for the coordinate displacements. For example, using subarray suffixes,

$$\begin{aligned} -z_6 \text{ (Bates's notation)} &\equiv -z_4 \text{ (figure 1)} \\ &\rightarrow \text{the invariant for subarray 4 of figure 1} \\ &\rightarrow \tfrac{1}{2}(\{1\}_4+\{2\}_4+\{3\}_4+\{4\}_4) \\ &\equiv \tfrac{1}{2}([13]+[16]+[14]+[15]), \end{aligned}$$

and

$$\begin{aligned} -y_4 \text{ (Bates's notation)} &\equiv -y_6 \text{ (figure 1)} \\ &\rightarrow (Y+X)/\sqrt{2} \qquad \text{for subarray 6 of figure 1} \\ &\rightarrow (\{1\}_6-\{3\}_6)/\sqrt{2} \end{aligned}$$

Table 1. Symmetry coordinates for permutations of a 24-fold shell with atoms in $(p, q, 0)$ positions. The relative positions of the ions are shown in figure 1, where the numbering accords with the top three rows of the table.

	Subarray:	1				2				3				4				5				6				Normalisation
	Label:	1	3	4	2	1	3	4	2	4	2	3	1	1	3	4	2	4	2	3	1	4	2	3	1	factor
Row	$C_{3v}\|O_h$ No:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	$1/\sqrt{\sim}$
1	$A\|A_{1g}$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	24
2	$E_g\ \epsilon$	+	+	+	+	−	−	−	−									−	−	−	−	+	+	+	+	16
3	θ	−	−	−	−	−	−	−	−	2	2	2	2	2	2	2	2	−	−	−	−	−	−	−	−	48
4	$T_{1u}\ x$	+	+	+	+																	−	−	−	−	8
5	y					+	+	+	+									−	−	−	−					8
6	z									+	+	+	+	−	−	−	−									8
7	$B_1\|A_{2g}$	+	+	−	−	+	+	−	−	+	+	−	−	−	−	+	+	−	−	+	+	−	−	+	+	24
8	$E_g\ \epsilon$	+	+	−	−	−	−	+	+									+	+	−	−	−	−	+	+	16
9	θ	−	−	+	+	−	−	+	+	+2	+2	−2	−2	−2	−2	+2	+2	+	+	−	−	+	+	−	−	48
10	$T_{2u}\ \xi$	+	+	−	−																	+	+	−	−	8
11	η					+	+	−	−									+	+	−	−					8
12	ζ									+	+	−	−	+	+	−	−									8
13	$E\|T_{2g}\ \xi$					+	−					+	−	−	+					−	+					8
14	η			+	−					+	−					−	+					−	+			8
15	ζ	+	−					+	−									−	+					−	+	8
16	$T_{1u}\ x$							+	−	+	−					+	−	+	−							8
17	y	+	−									+	−	+	−									+	−	8
18	z			+	−	+	−													+	−	+	−			8
19	$T_{1g}\ x$	−	+					+	−									−	+					+	−	8
20	y			+	−					−	+					+	−					−	+			8
21	z					−	+					+	−	−	+					+	−					8
22	$T_{2u}\ \xi$							+	−	−	+					−	+	+	−							8
23	η	−	+									+	−	+	−									−	+	8
24	ζ			+	−	−	+													−	+	+	−			8

Griffiths (1962) provides the coupling coefficients required to generate any displacement modes from the permutation modes. The abbreviated notation introduced above allows us to write these very simply as

$$
\begin{aligned}
(A_1|T_{1u}\otimes T_{1u})A_{1g}&: (x^4+y^5+z^6)/2\sqrt{6}\\
E_g\,\varepsilon&: (x^4+y^5-2z^6)/4\sqrt{3}\\
\theta&: -\tfrac{1}{4}(x^4-y^5)\\
T_{1g}\,x&: -\tfrac{1}{4}(y^6-z^5)\\
y&: -\tfrac{1}{4}(z^4-x^6)\\
z&: -\tfrac{1}{4}(x^5-y^4)\\
T_{2g}\,\xi&: -\tfrac{1}{4}(y^6-z^5)\\
\eta&: -\tfrac{1}{4}(z^4-x^6)\\
\zeta&: -\tfrac{1}{4}(x^5-y^4).
\end{aligned}
$$

The $(E|T_{1u}\otimes T_{1u})$ symmetry coordinates follow the same pattern with superfix replacements $4\rightarrow 16$, $5\rightarrow 17$ and $6\rightarrow 18$. We also obtain

$$
\begin{aligned}
(E|T_{2u}\otimes T_{1u})A_{2g}&: (x^{22}+y^{23}+z^{24})/2\sqrt{6}\\
E_g\,\varepsilon&: (x^{22}+y^{23}-2z^{24})/4\sqrt{3}\\
\theta&: \tfrac{1}{4}(x^{22}-y^{23})\\
T_{1g}\,x&: -\tfrac{1}{4}(y^{24}+z^{23})\\
y&: -\tfrac{1}{4}(z^{22}+x^{24})\\
z&: -\tfrac{1}{4}(x^{23}+y^{22})\\
T_{2g}\,\xi&: -\tfrac{1}{4}(y^{24}-z^{23})\\
\eta&: -\tfrac{1}{4}(z^{22}-x^{24})\\
\zeta&: -\tfrac{1}{4}(x^{23}-y^{22}).
\end{aligned}
$$

$(B_1|T_{2u}\otimes T_{1u})$ symmetry coordinates can be obtained with the superfix substitutions $22\rightarrow 10$, $23\rightarrow 11$ and $24\rightarrow 12$.

Explicit symmetry coordinates for all even-parity distortions of the 24-atom shell with ions in $(p, q, 0)$ positions have been given above. These are all that are normally required in calculations. Odd-parity symmetry coordinates can, however, also be simply derived from table 1.

3. The 24-fold shell with ions in (p, p, q) positions

The atom configuration and labelling for this case are shown in figure 3. As can be seen from the figure, we have chosen to use C_{3v} subarrays as a basis for generating the symmetry coordinates of the 24-fold permutation representation. The symmetry

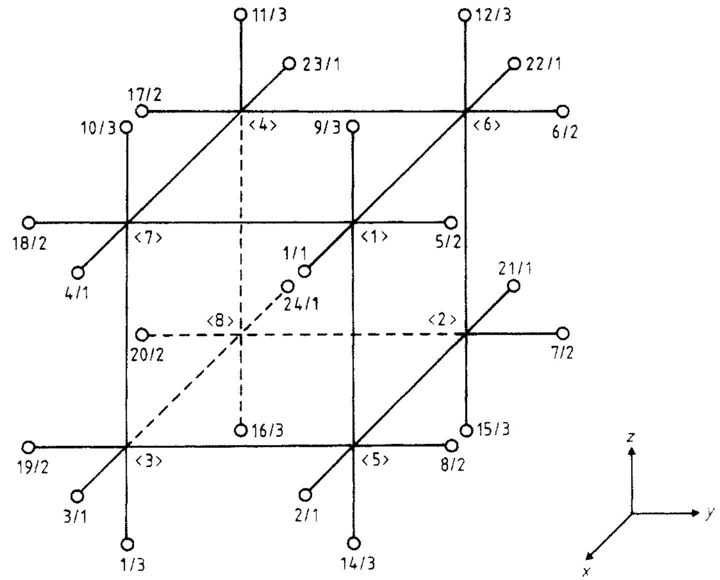

Figure 3. Structure of a 24-fold array of atoms in positions (p, p, q), showing the labels used in table 2. The notation follows that in figure 1.

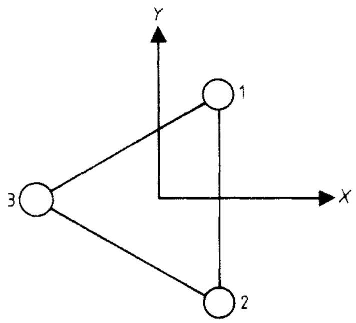

Figure 4. Relation of atom numbering in a 3-fold subarray with X, Y coordinates.

functions for the C_{3v} irreducible permutation representations are given by (see figure 4)

A_1: $(\{1\}+\{2\}+\{3\})/\sqrt{3}$: invariant

E: $(\{1\}-\{2\})/\sqrt{2}$: transforming as Y

: $\frac{1}{2}(\{1\}+\{2\}-2\{3\})$: transforming as X.

The generation of symmetry coordinates then follows exactly the same pattern as that used in the previous section, using table 6 of Bates (1978) to generate symmetry coordinates for the displacements of an 8-fold shell. The 24-fold permutation representations derived are given in table 2. These can then be used to obtain the

Table 2. Symmetry coordinates for permutations of a 24-fold shell with atoms in (p, p, q) positions. The relative positions of the ions are shown in figure 3, where the numbering is in accord with the top three rows of the table.

		Subarray:	1	5	3	7	1	6	2	5	1	7	4	6	3	5	2	8	4	7	3	8	2	6	4	8	Normalisation
		Label:	1	1	1	1	2	2	2	2	3	3	3	3	3	3	3	3	2	2	2	2	1	1	1	1	factor
Row	$C_{3v}\|O_h$	No:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	$1/\sqrt{\sim}$
1	$A_1\|A_{1g}$		+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	24
2	A_{2u}		+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−	+	−	24
3	$T_{1u}\ x$		+	+	+	+																	−	−	−	−	8
4	y						+	+	+	+									−	−	−	−					8
5	z										+	+	+	+	−	−	−	−									8
6	$T_{2g}\ \xi$		+	−	+	−																	−	+	−	+	8
7	η						+	−	+	−									−	+	−	+					8
8	ζ										+	−	+	−	−	+	−	+									8
9	$E\|E_g\ \theta$		+	+	+	+	+	+	+	+	−2	−2	−2	−2	−2	−2	−2	−2	+	+	+	+	+	+	+	+	48
10	ε		+	+	+	+	−	−	−	−									−	−	−	−	+	+	+	+	16
11	$E_u\ \theta$		+	−	+	−	−	+	−	+									−	+	−	+	+	−	+	−	16
12	ε		+	−	+	−	+	−	+	−	−2	+2	−2	+2	−2	+2	−2	+2	+	−	+	−	+	−	+	−	48
13	$T_{1g}\ x$						+	+	−	−	−	+	+	−	−	+	+	−	−	−	+	+					16
14	y		−	+	+	−					+	+	−	−	−	−	+	+					−	+	+	−	16
15	z		+	+	−	−	−	+	+	−									−	+	+	−	−	−	+	+	16
16	$T_{1u}x$						+	−	−	+	+	+	−	−	+	+	−	−	−	+	+	−					16
17	y		+	+	−	−					+	−	−	+	−	+	+	−					+	+	−	−	16
18	z		+	−	−	+	+	+	−	−									+	+	−	−	−	+	+	−	16
19	$T_{2g}\ \xi$						+	+	−	−	+	−	−	+	+	−	−	+	−	−	+	+					16
20	η		+	−	−	+					+	+	−	−	−	−	+	+					+	−	−	+	16
21	ζ		+	+	−	−	+	−	−	+									+	−	−	+	−	−	+	+	16
22	$T_{2g}\ \xi$						+	−	−	+	−	−	+	+	−	−	+	+	−	+	+	−					16
23	η		−	−	+	+					+	−	−	+	−	+	+	−					−	−	+	+	16
24	ζ		+	−	−	+	−	−	+	+									−	−	+	+	−	+	+	−	16

even-parity symmetry coordinates given below:

$$(\mathrm{A}_1|\mathrm{A}_{2u}\otimes\mathrm{T}_{1u})\mathrm{T}_{2g}\ \xi: x^2/2\sqrt{6}$$
$$\eta: y^2/2\sqrt{6}$$
$$\zeta: z^2/2\sqrt{6}$$
$$(\mathrm{A}_1|\mathrm{T}_{1u}\otimes\mathrm{T}_{1u})\mathrm{A}_{1g}: (x^3+y^4+z^5)/2\sqrt{6}$$
$$\mathrm{E}_g\ \theta: (x^3+y^4-2z^5)/4\sqrt{3}$$
$$\varepsilon: -\tfrac{1}{4}(x^3-y^4)$$
$$\mathrm{T}_{1g}\ x: -\tfrac{1}{4}(y^5-z^4)$$
$$y: -\tfrac{1}{4}(z^3-x^5)$$
$$z: -\tfrac{1}{4}(x^4-y^3)$$
$$\mathrm{T}_{2g}\ \xi: -\tfrac{1}{4}(y^5+z^4)$$
$$\eta: -\tfrac{1}{4}(z^3+x^5)$$
$$\zeta: -\tfrac{1}{4}(x^4+y^3)$$
$$(\mathrm{E}|\mathrm{E}_u\otimes\mathrm{T}_{1u})\mathrm{T}_{1g}\ x: \tfrac{1}{8}(x^{11}-x^{12})$$
$$y: \tfrac{1}{8}(y^{11}+y^{12})$$
$$z: -\tfrac{1}{4}z^{11}$$
$$\mathrm{T}_{2g}\ \xi: -\tfrac{1}{8}\sqrt{3}(x^{11}+\tfrac{1}{3}x^{12})$$
$$\eta: \tfrac{1}{8}\sqrt{3}(y^{11}-\tfrac{1}{3}y^{12})$$
$$\zeta: z^{12}/4\sqrt{3}$$
$$(\mathrm{E}|\mathrm{T}_{1u}\otimes\mathrm{T}_{1u})\mathrm{A}_{1g}: (x^{16}+y^{17}+z^{18})/4\sqrt{3}$$
$$\mathrm{E}_g\ \theta: (x^{16}+x^{17}-2z^{18})/4\sqrt{6}$$
$$\varepsilon: -(x^{16}-y^{17})/4\sqrt{2}$$
$$(\mathrm{E}|\mathrm{T}_{1u}\otimes\mathrm{T}_{1u})\mathrm{T}_{1g} x: -(y^{18}-z^{17})/4\sqrt{2}$$
$$y: -(z^{16}-x^{18})/4\sqrt{2}$$
$$z: -(x^{17}-y^{16})/4\sqrt{2}$$
$$\mathrm{T}_{2g}\ \xi: -(y^{18}+z^{17})/4\sqrt{2}$$
$$\eta: -(z^{16}+x^{18})/4\sqrt{2}$$
$$\zeta: -(x^{17}+y^{16})/4\sqrt{2}$$
$$(\mathrm{E}|\mathrm{T}_{2u}\otimes\mathrm{T}_{1u})\mathrm{A}_{2g}: (x^{22}+y^{23}+z^{24})/4\sqrt{3}$$
$$\mathrm{E}_g\ \theta: (x^{22}-y^{23})/4\sqrt{2}$$
$$\varepsilon: (x^{22}+y^{23}-2z^{24})/4\sqrt{6}$$
$$\mathrm{T}_{1g}\ x: -(y^{24}+z^{23})/4\sqrt{2}$$
$$y: -(z^{22}+x^{24})/4\sqrt{2}$$

$$z: -(x^{23}+y^{22})/4\sqrt{2}$$
$$T_{2g}\ \xi: -(y^{24}-z^{23})/4\sqrt{2}$$
$$\eta: -(z^{22}-x^{24})/4\sqrt{2}$$
$$\zeta: -(x^{23}-y^{22})/4\sqrt{2}.$$

4. Symmetry coordinates for displacements of the 12-fold shell

In this section we give the symmetry coordinates for the 12-fold shell corresponding to the unique labelling scheme (Newman 1981), omitting details of the derivation. The irreducible components of the permutation representation are given in table 3, where the atomic labelling corresponds to figure 5. Using the coupling coefficients given by

Table 3. Irreducible components of the representation of O_h based on permutations of atoms in the 12-fold shell. The numbering accords with the labelling in figure 5.

Row Label	Representation	Atom levels 1	2	3	4	5	6	7	8	9	10	11	12	Normalisation factor
1	A_{1g}	+	+	+	+	+	+	+	+	+	+	+	+	$1/2\sqrt{3}$
2	$E_g\ \theta$	+	+	+	+	+	+	+	+	−2	−2	−2	−2	$1/2\sqrt{6}$
3	ε	−	−	−	−	+	+	+	+					$1/2\sqrt{2}$
4	$T_{2u}\ \xi$					−	−	+	+	+	+	−	−	$1/2\sqrt{2}$
5	η	+	−	−	+					−	+	+	−	$1/2\sqrt{2}$
6	ζ	−	−	+	+	+	−	−	+					$1/2\sqrt{2}$
7	$T_{2g}\ \xi$	+	−	+	−									$\frac{1}{2}$
8	η					+	−	+	−					$\frac{1}{2}$
9	ζ									+	−	+	−	$\frac{1}{2}$
10	$T_{1u}\ x$					+	−	−	+	+	−	−	+	$1/2\sqrt{2}$
11	y	+	+	−	−					+	+	−	−	$1/2\sqrt{2}$
12	z	+	−	−	+	+	+	−	−					$1/2\sqrt{2}$

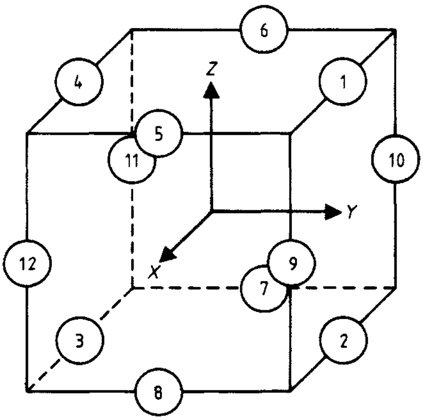

Figure 5. Structure of the 12-fold array of atoms, showing the labels used in table 3.

Griffiths (1962) we derive the following symmetry coordinates:

$$
\begin{aligned}
(A_{1g}\otimes T_{1u})T_{1u}\ x&: x^{1}/2\sqrt{3}\\
y&: y^{1}/2\sqrt{3}\\
z&: z^{1}/2\sqrt{3}\\
(E_{g}\otimes T_{1u})T_{1u}\ x&: (x^{2}-3x^{3})/4\sqrt{6}\\
y&: (y^{2}+3y^{3})/4\sqrt{6}\\
z&: -z^{2}/2\sqrt{2}\\
T_{2u}\ x&: (x^{2}+x^{3})/4\sqrt{2}\\
y&: (y^{3}-y^{2})/4\sqrt{2}\\
z&: -z^{3}/2\sqrt{2}\\
(T_{2u}\otimes T_{1u})A_{2g}&: (x^{4}+y^{5}+z^{6})/2\sqrt{6}\\
E_{g}\ \theta&: \tfrac{1}{4}(x^{4}-y^{5})\\
\varepsilon&: -(2z^{6}-x^{4}-y^{5})/4\sqrt{3}\\
T_{1g}\ x&: -\tfrac{1}{4}(y^{6}+z^{5})\\
y&: -\tfrac{1}{4}(z^{4}+x^{6})\\
z&: -\tfrac{1}{4}(x^{5}+y^{4})\\
T_{2g}\ \xi&: -\tfrac{1}{4}(y^{6}-z^{5})\\
\eta&: -\tfrac{1}{4}(z^{4}-x^{6})\\
\zeta&: -\tfrac{1}{4}(x^{5}-y^{4})\\
(T_{2g}\otimes T_{1u})A_{u}&: (x^{7}+y^{8}+z^{9})/2\sqrt{3}\\
E_{u}\ \theta&: (x^{7}-y^{8})/2\sqrt{6}\\
\varepsilon&: (x^{7}+y^{8}-2z^{9})/2\sqrt{6}\\
T_{1u}\ x&: -(x^{9}+z^{8})/2\sqrt{2}\\
y&: -(z^{7}+x^{9})/2\sqrt{2}\\
z&: -(x^{8}+x^{7})/2\sqrt{2}\\
T_{2u}\ \xi&: -(y^{9}-z^{8})/2\sqrt{2}\\
\eta&: -(z^{7}-x^{9})/2\sqrt{2}\\
\zeta&: -(x^{8}-y^{7})2\sqrt{2}\\
(T_{1u}\otimes T_{1u})A_{1g}&: (x^{10}+y^{11}+z^{12})/2\sqrt{6}\\
E_{g}\ \theta&: -(2z^{12}-x^{10}-y^{11})/4\sqrt{3}\\
\varepsilon&: \tfrac{1}{4}(y^{11}-x^{10})\\
T_{1g}\ x&: -\tfrac{1}{4}(y^{12}-z^{11})\\
y&: -\tfrac{1}{4}(z^{10}-x^{12})
\end{aligned}
$$

$$z: -\tfrac{1}{4}(x^{11} - y^{10})$$
$$T_{2g}\ \xi: -\tfrac{1}{4}(y^{12} + z^{11})$$
$$\eta: -\tfrac{1}{4}(z^{10} + x^{12})$$
$$\zeta: -\tfrac{1}{4}(x^{11} + y^{10}).$$

5. Conclusion

We have used a new technique to derive explicit symmetry coordinates for the two distinct types of 24-atom shell. An advantage of these particular sets of symmetry coordinates is that they are in accord with the unique labelling scheme introduced by Newman (1981). There is, of course, an alternative set of symmetry coordinates generated by the subarrays with C'_{2v} invariance. These can easily be generated using an approach similar to that described in this paper. However, they do not seem to be as useful for calculations as the subarrays are not usually as localised as those chosen in the present work. Various approaches also exist for the 48-atom shell, but we have yet to find a need for these symmetry coordinates in actual calculations. Symmetry coordinates (corresponding to the unique labelling scheme) have also been given for the 12-atom shell.

References

Bates C A 1978 *Phys. Rep.* **35** 187–304
Griffiths J A 1962 *The Irreducible Tensor Method for Molecular Symmetry Groups* (London: Prentice-Hall) pp 109–12
Newman D J 1981 *J. Phys. A: Math. Gen.* **14** 3143–51