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1984 J. Phys. A: Math. Gen. 17 1755

(http://iopscience.iop.org/0305-4470/17/8/029)

J. Phys. A: Math. Gen. **17** (1984) 1755–1759. Printed in Great Britain

COMMENT

$3jm$ factors and basis functions for $D_{\infty h}$ and $C_{\infty v}$

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Received 6 January 1984

Abstract. The results of earlier work by Butler and Reid for the pure-rotation double group D_∞ are used to obtain algebraic formulae for the $3jm$ factors of the branching $D_{\infty h} \supset C_{\infty v}$. Other branchings involving these groups are trivially related to branchings involving D_∞. The transformations of the group chains $O_3 \supset D_{\infty h} \supset C_{\infty h}$ and $O_3 \supset D_{\infty h} \supset C_{\infty v} \supset C_\infty$ to the standard angular momentum basis are also given.

1. Introduction

The groups $D_{\infty h}$ and $C_{\infty v}$ are important because they are the symmetry groups for diatomic molecules with identical and non-identical atoms, respectively. The application of the Wigner–Eckart theorem to physical problems involving these groups requires a knowledge of their $6j$ symbols and $3jm$ factors (i.e. coupling coefficients). Butler and Reid (1979) have used the building-up method developed by Butler and Wybourne (1976) to obtain algebraic formulae for the $6j$ symbols and $3jm$ factors of the pure-rotation group D_∞. Butler (1981) and Reid and Butler (1982) have shown how to determine the $3jm$ factors and basis functions of groups involving inversions and/or reflections from a knowledge of the related pure-rotational groups. Thus the information needed for the derivation of algebraic formulae for the $3jm$ factors and basis functions of $D_{\infty h}$ and $C_{\infty v}$ exists.

The impetus for gathering this information together here is the subtle difference between the standard notation for $D_{\infty h}$ and the notation used by Butler (1981). The source of the difference is that $D_{\infty h}$ may be considered to be the direct product

$$D_{\infty h} = D_\infty \times C_i \tag{1}$$

or

$$D_{\infty h} = C_{\infty v} \times C_i. \tag{2}$$

The notation for $D_{\infty h}$ used by Butler (1981), and in this work, adds parity labels (superscript $\pm$) to D_∞ irrep labels, favouring the structure of equation (1), whereas the standard notation adds parity labels (subscript u and g) to $C_{\infty v}$ labels (Tinkham 1964) favouring the structure of equation (2). $C_{\infty v}$ is *isomorphic* to D_∞, but the branching $D_{\infty h} \supset C_{\infty v}$ is different from $D_{\infty h} \supset D_\infty$ for irreps of odd parity.

The relationship between our notation and the standard notation is given in table 1. Character tables appear in Butler and Reid (1979) and Tinkham (1964). The labelling 'problem' involves only the two odd-parity one-dimensional irreps of $D_{\infty h}$. Of course, merely changing the labels cannot change branching rules or values of $3jm$ factors. However, confusion of the notations is likely to lead to mislabelling of operators and basis functions and hence to completely incorrect results.

0305-4470/84/081755+05\$02.25

Table 1. Notation for irreps of D_∞, $C_{\infty v}$ and $D_{\infty h}$.

(a) D_∞, $C_{\infty v}$					
This work:	0	$\tilde{0}$	$\frac{1}{2}$	1	...
Standard:	Σ^+	Σ^-	$E\frac{1}{2}$	π	...

(b) $D_{\infty h}$									
This work:	0^+	0^-	$\tilde{0}^+$	$\tilde{0}^-$	$\frac{1}{2}^+$	$\frac{1}{2}^-$	1^+	1^-	...
Standard:	Σ_g^+	Σ_u^-	Σ_g^-	Σ_u^+	$E\frac{1}{2}_g$	$E\frac{1}{2}_u$	π_g	π_u	...

2. The chain $O_3 \supset D_{\infty h} \supset C_{\infty h}$

All the groups in this chain are products of a pure-rotation group with C_i: $O_3 = SO_3 \times C_i$, $D_{\infty h} = D_\infty \times C_i$ and $C_{\infty h} = C_\infty \times C_i$. The chain $O_3 \supset D_{\infty h} \supset C_{\infty h}$ is therefore trivially related to $SO_3 \supset D_\infty \supset C_\infty$, because the C_i part may be factorised off. Therefore the pure-rotation results of Butler and Reid (1979) (which have been conveniently tabulated by Piepho and Schatz (1983)) are directly applicable to $O_3 \supset D_{\infty h} \supset C_{\infty h}$. Thus there is no need to introduce $C_{\infty v}$ in order to treat a system with $D_{\infty h}$ symmetry.

3. $3jm$ factors for $D_{\infty h} \supset C_{\infty v}$

If the group chain $O_3 \supset D_{\infty h} \supset C_{\infty v} \supset C_\infty$ is required then we must extend the work of Butler and Reid (1979). Since $C_{\infty v}$ is isomorphic to D_∞ the $6j$ symbols are identical and the $3jm$ factors for $C_{\infty v} \supset C_\infty$ are just those for $D_\infty \supset C_\infty$. In § 2 we noted that the branching $O_3 \supset D_{\infty h}$ is trivially related to $SO_3 \supset D_\infty$. Thus the only extra information we need is the $3jm$ factors for $D_{\infty h} \supset C_{\infty v}$. The branching rules for this embedding are

$$0^+ \to 0, \qquad 0^- \to \tilde{0}, \qquad \tilde{0}^+ \to \tilde{0}, \qquad \tilde{0}^- \to 0, \qquad a^+ \to a, \qquad a^- \to a, \tag{3}$$

where $a \neq 0, \tilde{0}$.

Butler (1981) describes a method for calculating the $3jm$ factors for such an embedding, based on the work of Butler and Ford (1979). The $2jm$ factors, and all $3jm$ factors involving only even-parity irreps, may be chosen to have the value $+1$. Those involving two odd-parity irreps are given by (Butler 1981, equation (5.2.9))

$$\begin{pmatrix} a^- & b^- & c^+ \\ \tilde{a} & \tilde{b} & c \end{pmatrix}^{D_{\infty h}}_{C_{\infty v}} = |a|^{1/2}|b|^{1/2}\{b\}\{a\ b\ c\}\{\tilde{b}\ b\ \tilde{0}\} \begin{Bmatrix} \tilde{a} & \tilde{b} & c \\ b & a & \tilde{0} \end{Bmatrix}_{D_\infty}, \tag{4}$$

where $\tilde{a} \equiv a \times \tilde{0}$ (and is just a unless $a = 0$ or $\tilde{0}$). In (4), a, b and c are any irreps of D_∞. The algebraic formulae given by Butler and Reid (1979) lead to the following $3jm$ factors which do *not* change sign under odd column permutations:

$$\begin{pmatrix} a^- & b^- & (a+b)^+ \\ a & b & (a+b) \end{pmatrix} = -1, \qquad \begin{pmatrix} (b+c)^- & b^- & c^+ \\ (b+c) & b & c \end{pmatrix} = +1,$$
$$\begin{pmatrix} a^- & a^- & \tilde{0}^+ \\ a & a & \tilde{0} \end{pmatrix} = +1, \qquad \begin{pmatrix} 0^- & \tilde{0}^- & \tilde{0}^+ \\ \tilde{0} & 0 & \tilde{0} \end{pmatrix} = +1, \tag{5}$$

and the following, which *do* change sign under odd column permutations:

$$\begin{pmatrix} 0^- & b^- & b^+ \\ \tilde{0} & b & b \end{pmatrix} = +1, \qquad \begin{pmatrix} \tilde{0}^- & b^- & b^+ \\ 0 & b & b \end{pmatrix} = -1. \tag{6}$$

In (5) and (6), a, b and $c \neq 0, \tilde{0}$.

4. Basis functions

The building-up method of calculation requires only character theory results (Butler 1981), knowledge of irrep matrices or basis functions being unnecessary. However, it is often useful to know the actual form of at least some of the basis functions. To construct these functions we perform a transformation to the standard angular momentum ('*JM*') basis, and then use the spherical harmonic functions. Butler and Reid (1979) give the transformation between the pure-rotation chain $SO_3 \supset D_\infty \supset C_\infty$ and the *JM* basis:

$$\langle J\ 0 | J\ 0\ 0\rangle = 1\ (J \text{ even}), \qquad \langle J\ 0 | J\ \tilde{0}\ 0\rangle = 1\ (J \text{ odd}),$$
$$\langle J\ a | J\ a\ a\rangle = (-1)^{J-a}, \qquad \langle J\ -a | J\ a\ -a\rangle = 1, \tag{7}$$

where $a \neq \tilde{0}, 0$. The transformation coefficients could all be +1 *only* if the Condon and Shortley phases for the *JM* basis were modified (Butler and Reid 1979). The above transformations are obviously directly applicable to the chain $O_3 \supset D_{\infty h} \supset C_{\infty h}$.

For the chain $O_3 \supset D_{\infty h} \supset C_{\infty v} \supset C_\infty$ we use the method described by Reid and Butler (1982). The even-parity transformation coefficients are identical to the pure-rotation transformations of (7). The odd-parity coefficients may be related to those of even parity by coupling on the transformation between $|0^-(O_3)0(SO_2 = C_\infty)\rangle$ and $|0^-(O_3)0^-(D_{\infty h})\tilde{0}(C_{\infty v})0(C_\infty)\rangle$. Complex conjugation symmetry shows that the transformation coefficient $\langle 0^-\ 0|0^-\ 0^-\ \tilde{0}\ 0\rangle$ is imaginary because the $2jm$ factor $\binom{\tilde{0}}{0}$ for $C_{\infty v} \supset C_\infty$ (i.e. $D_\infty \supset C_\infty$) has been chosen to be -1 (Butler and Reid 1979), and the other $2jm$ factors are +1. From Reid and Butler (1982) we have

$$\langle J^-\ \pm a | J^-\ a^-\ \tilde{a}\ \pm a\rangle = \langle J^+\ M | J^+\ a^+\ a\ \pm a\rangle\langle 0^-\ 0|0^-\ 0^-\ \tilde{0}\ 0\rangle$$
$$\times(-)^{2J}|J|^{1/2}\begin{pmatrix} J^- & J^+ & 0^- \\ a^- & a^+ & 0^- \\ \tilde{a} & a & \tilde{0} \\ \mp a & \pm a & 0 \end{pmatrix}\begin{pmatrix} J^- \\ a^- \\ \tilde{a} \\ \pm a \end{pmatrix}, \tag{8}$$

where a is any irrep of D_∞. Using the formulae of Butler and Reid (1979) and (5) and (6), and choosing $\langle 0^-\ 0|0^-\ 0^-\ \tilde{0}\ 0\rangle = +\mathrm{i}$, we obtain

$$\langle J^-\ 0 | J^-\ 0^-\ \tilde{0}\ 0\rangle = \mathrm{i}(-1)^{2J},$$
$$\langle J^-\ 0 | J^-\ \tilde{0}^-\ 0\ 0\rangle = \mathrm{i}(-1)^{2J+1},$$
$$\langle J^-\ a | J^-\ a^-\ a\ a\rangle = \mathrm{i}(-1)^{J-a+1},$$
$$\langle J^-\ -a | J^-\ a^-\ a\ -a\rangle = \mathrm{i}(-1)^{2J+2a}, \tag{9}$$

where $a \neq 0, \tilde{0}$.

Tables 2 and 3 contain a short list of basis functions for the chains $O_3 \supset D_{\infty h} \supset C_{\infty h}$ and $O_3 \supset D_{\infty h} \supset C_{\infty v} \supset C_\infty$, derived from (7) and (10). Note that particular care is

Table 2. Selected basis functions for $O_3 \supset D_{\infty h} \supset C_{\infty h}$.

$\|O_3D_{\infty h}C_{\infty h}\rangle$ket	$\|JM\rangle$ equivalent	Basis functions
$\|0^+\ 0^+\ 0^+\rangle$	$\|0^+\ 0^+\rangle$	1
$\|0^-\ 0^-\ 0^-\rangle$	$\|0^-\ 0^-\rangle$	1
$\|\frac{1}{2}^+\ \frac{1}{2}^+\ \pm\frac{1}{2}^+\rangle$	$\|\frac{1}{2}^+\ \pm\frac{1}{2}^+\rangle$	
$\|\frac{1}{2}^-\ \frac{1}{2}^-\ \pm\frac{1}{2}^-\rangle$	$\|\frac{1}{2}^-\ \pm\frac{1}{2}^-\rangle$	
$\|1^+\ \tilde{0}^+\ 0^-\rangle$	$\|1^+\ 0^+\rangle$	R_z
$\|1^-\ \tilde{0}^-\ 0^-\rangle$	$\|1^-\ 0^-\rangle$	z
$\|1^+\ 1^+\ \pm1^+\rangle$	$\|1^+\ \pm1^+\rangle$	$\mp(R_x \pm iR_y)/\sqrt{2}$
$\|1^-\ 1^-\ \pm1^-\rangle$	$\|1^-\ \pm1^-\rangle$	$\mp(x \pm iy)/\sqrt{2}$

Table 3. Selected basis functions for $O_3 \supset D_{\infty h} \supset C_{\infty v} \supset C_\infty$.

$\|O_3D_{\infty h}C_{\infty v}C_\infty\rangle$ ket	$\|JM\rangle$ equivalent	Basis function
$\|0^+\ 0^+\ 0\ 0\rangle$	$\|0^+\ 0\rangle$	1
$\|0^-\ 0^-\ \tilde{0}\ 0\rangle$	$i\|0^-\ 0\rangle$	i
$\|\frac{1}{2}^+\ \frac{1}{2}^+\ \frac{1}{2}\ \pm\frac{1}{2}\rangle$	$\|\frac{1}{2}^+\ \pm\frac{1}{2}\rangle$	
$\|\frac{1}{2}^-\ \frac{1}{2}^-\ \frac{1}{2}\ \pm\frac{1}{2}\rangle$	$\mp i\|\frac{1}{2}^-\ \pm\frac{1}{2}\rangle$	
$\|1^+\ \tilde{0}^+\ \tilde{0}\ 0\rangle$	$\|1^+\ 0\rangle$	R_z
$\|1^-\ \tilde{0}^-\ 0\ 0\rangle$	$-i\|1^-\ 0\rangle$	$-iz$
$\|1^+\ 1^+\ 1\ \pm1\rangle$	$\|1^+\ \pm1\rangle$	$\mp(R_x \pm iR_y)/\sqrt{2}$
$\|1^-\ 1^-\ 1\ \pm1\rangle$	$\mp i\|1^-\ \pm1\rangle$	$+i(x \pm iy)/\sqrt{2}$

needed for $O_3 \supset D_{\infty h} \supset C_{\infty v} \supset C_\infty$, where, for example, $0(C_{\infty v})$ transforms as iz, and $\tilde{0}(C_{\infty v})$ transforms as R_z (in agreement with Tinkham (1964)).

5. Conclusions

The results given here, along with those of Butler and Reid (1979), provide algebraic formulae for all the $6j$ symbols and $3jm$ factors necessary for the application of the Wigner–Eckart theorem to physical problems involving $D_{\infty h}$ or $C_{\infty v}$ symmetry. Coupling coefficients for $C_{\infty v}$ or $D_{\infty h}$ are not particularly difficult to calculate (see e.g. Schatz *et al* 1978). However, the factorised results given here have much greater applicability because they can be used with the $3jm$ factors for $O_3 \supset D_{\infty h}$ and for finite subgroups of $D_{\infty h}$ and $C_{\infty v}$ (Butler and Reid 1979, Butler 1981).

It is obvious from the transformation coefficients given in § 4 that the basis functions for the chains $SO_3 \supset D_\infty \supset C_\infty$, $O_3 \supset D_{\infty h} \supset C_{\infty h}$, and $O_3 \supset D_{\infty h} \supset C_{\infty v} \supset C_\infty$ are very similar to those for the *JM* basis. They could, in fact, be made identical if the Condon and Shortley phase choices were modified. However, these phases, along with the standard labelling of $D_{\infty h}$, cannot be ignored. It is hoped that by emphasising these differences we have eliminated any possibility of confusion.

Acknowledgments

The author wishes to thank Dr S B Piepho and Professor P N Schatz, who pointed out the differences in notation for $D_{\infty h}$ and made several useful suggestions regarding the presentation of this paper. Financial support from the National Science Foundation (NSF grant CHE-8215815) is also gratefully acknowledged.

References

Butler P H 1981 *Point Group Symmetry Applications: Methods and Tables* (New York: Plenum)
Butler P H and Ford A M 1979 *J. Phys. A: Math. Gen.* **12** 1357–65
Butler P H and Reid M F 1979 *J. Phys. A: Math. Gen.* **12** 1655–66
Butler P H and Wybourne B G 1976 *Int. J. Quantum Chem.* **10** 581–98
Piepho S B and Schatz P N 1983 *Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism* (New York: Wiley) Appendix F
Reid M F and Butler P H 1982 *J. Phys. A: Math. Gen.* **15** 2327–35
Schatz P N, Mowery R L and Krausz E R 1978 *Mol. Phys.* **35** 1537–57
Tinkham M 1964 *Group Theory and Quantum Mechanics* (New York: McGraw-Hill) p 329