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# Symmetrisation of molecular Dirac eigenfunctions

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**Abstract.** A systematic method for the symmetry adaptation of molecular Dirac spinors is presented that avoids the use of the double group of a point group  $G$ . Projective representations of  $G$  are instead used in a manner that fixes all phase factors unambiguously and automatically. Properties of the Euclidean group are exploited in order to simplify the work.

## 1. Introduction

It is well known (see e.g. Jansen and Boon 1967) that the symmetry group of the Dirac Hamiltonian for a molecule with point group symmetry  $G$  is the double group  $\tilde{G}$  of this group. Various methods of symmetrisation with respect to this group  $\tilde{G}$  have been proposed (Onodera and Okasaki 1966, Oreg and Malli 1974, 1976a,b, 1979, Toivonen and Pyykkö 1977, Pyykkö and Desclaux 1977, Hafner 1980). It has recently been pointed out, however, (Altmann 1979, Altmann and Palacio 1979, Altmann and Herzig 1982) that it is advantageous to replace  $\tilde{G}$  by the single group  $G$ , as long as projective, rather than ordinary (vector) representations are used. There are two advantages in this approach. First, the order of the group that is handled is halved, thus considerably reducing the amount of work necessary. In fact, once the correct tables are formed, the user handles the projective representations exactly as if they were ordinary ones. Secondly, and more importantly, major advantages of precision are gained since ambiguities in the multiplication rules of the double group are eliminated at the same time as all phase factors are fixed once for all in a consistent manner by means of closed formulae. This is an important point, of course, for the development of computer programs to carry out the symmetrisation.

Although we refer here to molecular Dirac Hamiltonians, the procedure that we shall present in this paper can be used for cluster calculations in solids and it can easily be extended to space groups.

We shall summarise here the notation used in this paper.

$G \subset O(3)$ , point group of elements  $g$  (proper or improper rotations).

$R \in SO(3)$ , proper rotation.

$R_g$ , Euler–Rodrigues parameters corresponding to  $g$ .

$\hat{G}(g)$ , vector representation of  $G$ .

$\check{G}(g)$ , projective representation of  $G$  for some stated factor system.

$\hat{S}^j(R)$ ,  $\check{S}^j(R)$ , irreducible vector and projective representations of  $SO(3)$  in the  $(2j+1)$ -dimensional Condon and Shortley basis,  $j$  integral and half-integral, respectively,

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the latter in the Pauli gauge (Altmann and Herzig 1982).

$\check{U}(g)$  is  $S^{1/2}(R_g)$ .

$\check{\mathcal{G}}(g)$ , three-dimensional orthogonal representation of  $\mathbf{G}$  on the basis  $x, y, z$ , components of a vector  $\mathbf{r}$ .

$\langle \phi_1 \dots \phi_n |, | \phi_1 \dots \phi_n \rangle$ , row and column vector of components  $\phi_1 \dots \phi_n$ . (Bras and kets are given in light brackets.)

$[g_i, g_j]$ , phase (projective) factor for product  $g_i g_j$ . (Commutators are given in light brackets.)

$\mathbf{g}$ , Hilbert space operator corresponding to  $g$ . All operators are given in sans serif and no notational distinction is made between Hilbert and configuration space operators since they can always be identified in this paper through their operands.

$\mathbf{1}_n, \mathbf{1}_n$ , unit matrix and operator, respectively of dimension  $n$ .

$\alpha, \beta, \rho$ , labels of irreducible vector bases;  $\alpha$  representation,  $\beta$  column,  $\rho$  multiplicity.

$a, b, r$ , labels of irreducible projective bases;  $a$  representation,  $b$  column,  $r$  multiplicity.

## 2. The projective representation method

Given a group  $\mathbf{G}$ , a set of matrices  $\check{\mathbf{G}}(g)$  given for all  $g \in \mathbf{G}$  forms a projective representation if

$$\check{\mathbf{G}}(g_i) \check{\mathbf{G}}(g_j) = [g_i, g_j] \check{\mathbf{G}}(g_i g_j), \quad (2.1)$$

where the brackets are phase factors (projective factors) that must be uniquely determined by each pair  $g_i, g_j$ . If all the phase factors are unity then the representation is a vector representation (denoted with the symbol  $\hat{\mathbf{G}}$ ). In the double group approach  $g_i g_j$  is allowed to be an operation  $g'_k$  in the double group  $\hat{\mathbf{G}}$  but not in  $\mathbf{G}$ , whereas now it must always be an operation  $g_k$ , say, belonging to  $\mathbf{G}$ , the phase factor carrying the former distinction between  $g_k$  and  $g'_k$ .

The basic feature of the method is a procedure to determine the phase factors uniquely. Call  $R(\phi, \mathbf{n})$  a rotation of  $SO(3)$  with angle of rotation ( $-\pi < \phi \leq \pi$ ) and axis of rotation  $\mathbf{n}$ . The rotation must be parametrised by the Euler-Rodrigues (quaternion) parameters

$$\lambda = \cos \frac{1}{2} \phi, \quad \mathbf{\Lambda} = \sin \frac{1}{2} \phi \mathbf{n}, \quad (2.2)$$

which are written into the symbol  $\{\lambda, \mathbf{\Lambda}\}$ , such that two rotations multiply by the simple rule (Rodrigues 1840)

$$\{\lambda_1, \mathbf{\Lambda}_1\} \{\lambda_2, \mathbf{\Lambda}_2\} = \{\lambda_1 \lambda_2 - \mathbf{\Lambda}_1 \cdot \mathbf{\Lambda}_2, \lambda_1 \mathbf{\Lambda}_2 + \lambda_2 \mathbf{\Lambda}_1 + \mathbf{\Lambda}_1 \times \mathbf{\Lambda}_2\}. \quad (2.3)$$

This is the quaternion multiplication rule, the braces being Hamilton's quaternions.

The next step is to denote all rotations by poles on the unit sphere, from which the rotation is always seen as positive. Given a point group  $\mathbf{G}$  the unit sphere is divided in two (not necessarily connected) hemispheres, one of which is chosen to be positive. All positive rotations are given poles on the positive hemisphere and all negative rotations poles on the negative hemisphere. Thus, the axis  $\mathbf{n}$  is uniquely defined for each rotation. If  $g$  is an improper rotation, it is written as  $\mathbf{i} R_g$ , with  $\mathbf{i}$  the inversion and  $R_g \in SO(3)$ , whence we can always assume that for each  $g \in \mathbf{G}$ , proper or improper, its Euler-Rodrigues parameters  $R_g$  are uniquely determined. The rule that fixes the phase factors (Altmann 1979) is the following: when two rotations are multiplied by (2.3), if either the scalar on the right-hand quaternion is positive definite

or it is zero and the vector belongs to the positive hemisphere, then the phase factor is +1. Otherwise, it is -1. The inversion  $i$  entails some problems, since two phase factors are in use for the product  $i i$ , namely +1 in the Pauli gauge universally used for spinors, and -1 in the Cartan gauge which is used to build bases of the vector representations through Kronecker products of spinors (Altmann and Herzog 1982).

Once a phase factor system is constructed, tables of irreducible projective representations and their corresponding Clebsch-Gordan coefficients can be given, as done in Altmann and Palacio (1979) and Altmann and Herzog (1982). Such tables guarantee correct subductions along group chains and they can be used exactly as tables of vector representations are used, without reference to the underlying phase factor system. It should be noticed that the usual choice of Pauli matrices entails a choice of phases that may or may not be compatible with the choice of phases that is implicit in the definition of a double group through the choice of multiplication rules. The projective representation method, on the other hand, fully guarantees this consistency, a point of vital importance in relativistic work where the Pauli matrices play a fundamental role.

An essential feature of the procedure outlined above is that the parametrisation of  $SO(3)$  through Euler angles is replaced by the quaternion parametrisation. The reason for this is important. The topology of  $SO(3)$  is based on the fact that although  $R(\phi, \mathbf{n})$  and  $R(-\phi, -\mathbf{n})$  are the same rotation, the poles of the identical binary rotations  $R(\pi, \mathbf{n})$ ,  $R(\pi, -\mathbf{n})$  must be identifiable in order to classify correctly the classes of homotopy of the group, from which classification the phase factors arise. Whereas the Euler angles cannot recognise the distinction between these poles, their respective quaternion parameters are  $\{0, \mathbf{n}\}$  and  $\{0, -\mathbf{n}\}$  and it is seen at once from the rule given before that distinct phase factors +1 and -1 respectively correspond to them. It is important to notice, moreover, that when the  $SU(2)$  and rotation matrices are expressed in terms of the quaternion parameters their phase factors are correctly given without further work, whereas this is not so when their more usual form in terms of Euler angles is employed.

### 3. The Dirac Hamiltonian and its Hilbert space

We review here the basic principles of the relativistic notation that we shall need. Although we follow as far as possible the notation of Messiah (1961) in order to facilitate comparison, we shall require a somewhat more compact notation.

The Hilbert space  $\mathcal{H}$ ,  $L^2(\mathbb{R}^3) \otimes \mathbb{C}^4$ , is the carrier space for time-independent Dirac Hamiltonians that describe the motion of a charged particle. The unit four-spinors in this space are constructed as follows. Let us call  $|\frac{1}{2}\rangle$  and  $|\frac{1}{2}\rangle$  the unit spinors  $|10\rangle$  and  $|01\rangle$  (column vectors) that correspond to the Pauli spinors  $|\frac{1}{2}\frac{1}{2}\rangle$  and  $|\frac{1}{2}\frac{1}{2}\rangle$  respectively. The four column vectors  $|\lambda\rangle \otimes |\mu\rangle$ , for  $\lambda$  and  $\mu$  equal to  $\pm\frac{1}{2}$ , are the unit four-spinors designated in dictionary order by  $|\frac{1}{2}\frac{1}{2}\rangle$ ,  $|\frac{1}{2}\frac{1}{2}\rangle$ ,  $|\frac{1}{2}\frac{1}{2}\rangle$ ,  $|\frac{1}{2}\frac{1}{2}\rangle$ , where double angular brackets are used in order to differentiate four-spinors from two-spinors. A typical four-spinor of  $\mathcal{H}$ ,  $\Psi(\mathbf{x})$ , will be written as

$$\Psi(\mathbf{x}) = \sum_{\lambda\mu} \psi(\mathbf{x})_{\lambda\mu} |\lambda\mu\rangle, \quad \psi(\mathbf{x}) \in L^2(\mathbb{R}^3), \quad (3.1)$$

where  $\lambda$  and  $\mu$  here and henceforward range over  $\pm\frac{1}{2}$  in dictionary order.

The Dirac Hamiltonian  $\mathbf{H}_D$  that describes the motion of a charged particle in a

scalar potential field  $\varphi(\mathbf{x})$  has the form

$$\mathbf{H}_D = ic\boldsymbol{\gamma}_4 \boldsymbol{\gamma} \cdot \mathbf{p} + mc^2\boldsymbol{\gamma}_4 - e\varphi(\mathbf{x})\mathbf{1}_4. \quad (3.2)$$

The  $\mathbf{p}_j$  here are the usual linear momentum operators and the  $\boldsymbol{\gamma}_j$  are the operators that correspond to the matrices

$$\gamma_j = \begin{bmatrix} & \sigma_j \\ \sigma_j & \end{bmatrix}, \quad \gamma_4 = \begin{bmatrix} \mathbf{1}_2 & \\ & -\mathbf{1}_2 \end{bmatrix}. \quad (3.3)$$

The  $\sigma_j$  are the standard Pauli matrices.

We assume that the function  $\varphi(\mathbf{x})$  is invariant under a point group  $\mathbf{G}$  and its corresponding magnetic (grey) point group, i.e. that the time reversal operator  $\boldsymbol{\theta}$  belongs to the group of  $\mathbf{H}_D$ . The four-inversion operator  $\mathbf{l}$  (parity) is defined in terms of the usual inversion  $\mathbf{i}$  by

$$\mathbf{l} = \mathbf{i} \otimes \boldsymbol{\gamma}_4. \quad (3.4)$$

It acts on the functions (3.1) as follows:

$$\mathbf{l}\Psi(\mathbf{x}) = \sum_{\lambda\mu} \psi(-\mathbf{x})_{\lambda\mu} (-1)^{1/2-\lambda} \|\lambda\mu\rangle. \quad (3.5)$$

The states of all atoms of the system will be described by atomic spinors. In order to consider their transformation properties we first consider all atomic spinors to be centred at the origin, but they will be shifted to the correct atomic sites at a later stage. The atomic spinors for half-integral  $J$  centred at the origin are of the form (Messiah 1961, p 927)

$$\Psi_{J\pm}^{M\tilde{\omega}} = R_{1/2} \sum_{m\mu} (lm\frac{1}{2}\mu | JM) Y_{lm} \|\frac{1}{2}\mu\rangle \pm iR_{1/2} \sum_{m\mu} (l'm\frac{1}{2}\mu | JM) Y_{l'm} \|\frac{1}{2}\mu\rangle. \quad (3.6)$$

The integers  $l$  and  $l'$  here are

$$l = J + \frac{1}{2}\tilde{\omega}, \quad l' = J - \frac{1}{2}\tilde{\omega}, \quad (3.7)$$

where  $\tilde{\omega}$  is the eigenvalue of the four-inversion operator  $\mathbf{l}$  defined in (3.5) and the brackets and the  $Y_{lm}$  are the usual Clebsch–Gordan coefficients and spherical harmonics respectively. The functions  $R$  in (3.6) are the radial functions  $F$  and  $G$  of Messiah divided by the radius. They, as well as  $\Psi$ , depend on an integral quantum number  $n$  that is left implicit.

If, as in (3.1), we call  $\lambda$  the first label of the four-spinors in (3.6) then  $l$  and  $l'$  in (3.7) are functions of  $\lambda$  (and, of course, of  $J$ ) which, in order to emphasise their dependence on this label, will be written as

$$\bar{\lambda} = J + (-1)^{1/2-\lambda} \frac{1}{2}\tilde{\omega}. \quad (3.8)$$

This allows us to write down the spin harmonics in (3.6) in the form

$$\mathcal{Y}_{\lambda J}^M = \sum_{m\mu} (\bar{\lambda} m \frac{1}{2} \mu | JM) Y_{\bar{\lambda} m} |\mu\rangle. \quad (3.9)$$

Correspondingly, the atomic spinors (3.6) can be rewritten in a more compact notation as

$$\Psi_{J\pm}^{M\tilde{\omega}} = \sum_{\lambda} (\pm i)^{1/2-\lambda} R_{\lambda} \mathcal{Y}_{\lambda J}^M |\lambda\rangle, \quad (3.10)$$

where it must be remembered that the summation over  $\lambda$  also entails  $\bar{\lambda}$  through (3.8). The effect of  $\mathbf{l}$  on these functions can now be written from (3.5),

$$\mathbf{l}\Psi_{J\pm}^{M\tilde{\omega}} = (-1)^{J+\tilde{\omega}/2} \Psi_{J\pm}^{M\tilde{\omega}}. \quad (3.11)$$

#### 4. Projective representation of $\mathbf{G}$ and symmetrisation of the centred states

We assume in this section that  $\mathbf{G}$  has been embedded in  $\text{SO}(3)$  or  $\text{O}(3)$ , as the case might be, by the method described in § 2 and that its irreducible projective and vector representations have been tabulated. The operator  $\mathbf{g}$ ,  $g \in \mathbf{G}$  acts on the atomic spinors (3.1) as follows (see Jansen and Boon 1967):

$$\mathbf{g}\Psi(\mathbf{x}) = \sum_{\lambda\mu} \psi(\hat{\mathcal{G}}(g)^{-1}\mathbf{x})_{\lambda\mu} \delta_{\lambda} \sum_{\mu'} \|\lambda\mu'\rangle \check{U}(g)_{\mu'\mu}, \quad (4.1)$$

where

$$\delta_{\lambda} = 1, \quad \lambda = \frac{1}{2}, \quad (4.2)$$

$$= \det \hat{\mathcal{G}}(g), \quad \lambda = -\frac{1}{2}. \quad (4.3)$$

It should be clear that this operator entails a representation of  $\mathbf{G}$  given by the Kronecker product of a vector representation on  $\mathbf{G}$  with the projective representation  $\check{U}(g)$ . This representation, therefore, is a projective representation of  $\mathbf{G}$  with the correct factor system, since  $\check{U}(g)$  has been so chosen. It follows that the atomic spinors (3.10), now to be written with argument  $\mathbf{0}$  in order to emphasise that they are centred at the origin, span a projective representation  $\check{\mathbf{G}}^J$ ,

$$\mathbf{g}\Psi_{J\pm}^{M\tilde{\omega}}(\mathbf{0}) = \sum_{M'} \Psi_{J\pm}^{M'\tilde{\omega}}(\mathbf{0}) \check{\mathbf{G}}^J(g)_{M'M}, \quad (4.4)$$

with

$$\check{\mathbf{G}}^J(g) = \check{S}^J(\mathbf{R}_g), \quad g \text{ proper}, \quad (4.5)$$

$$= (-1)^{J+\tilde{\omega}/2} \check{S}^J(\mathbf{R}_g), \quad g \text{ improper}. \quad (4.6)$$

Equation (4.6) results from writing  $g$  as the product of the rotation parametrised by  $\mathbf{R}_g$  times  $\mathbf{I}$  and applying (3.11). It should also be noticed that the notation  $\check{\mathbf{G}}^J$  is oversimplified, since this representation depends on  $\tilde{\omega}$  as well.

$\check{\mathbf{G}}^J$  is a reducible projective representation over  $\mathbf{G}$ . We reduce it by means of a matrix  $W^J$ ,

$$W^{J\dagger} \check{\mathbf{G}}^J(g) W^J = \sum_a \oplus m_{Ja} \check{\mathbf{G}}^a(g), \quad (4.7)$$

where  $a$  ranges over all the irreducible projective representations of  $\mathbf{G}$  for the chosen factor system. Therefore, the functions belonging to the  $b$  column of the  $a$ th irreducible basis with multiplicity index  $r$  belong to the basis

$$\langle \Psi_b^{ar}(\mathbf{0}) | = \langle \Psi_{J\pm}^{M\tilde{\omega}}(\mathbf{0}) | W^J, \quad (4.8)$$

where  $a, r$  range as on the right-hand side of (4.7) and  $b$  ranges for each  $a$ . The irreducible basis on the left depends on  $\tilde{\omega}, J, \pm$  and it should be remembered that  $M$  labels the functions of the basis on the right of (4.7) as well as the rows of  $W^J$ .

#### 5. Orbits

Once the symmetrised centred states described in § 4 are formed, they can be translated to the various atomic sites within the molecule by means of a translation operator  $\mathbf{t}$  that acts only on the space part of a Dirac spinor,

$$\mathbf{t}\Psi(\mathbf{x}) = \Psi(\mathbf{x} - \mathbf{t}). \quad (5.1)$$

We must first note that in a molecular system there are, in general, sets of identical atoms that occupy equivalent sites, i.e. sites that are permuted amongst themselves under the operations of the molecular group  $\mathbf{G}$ . Such a set of sites is called an *orbit*. In the molecule  $\text{NH}_3$ , for example, the three hydrogen atoms occupy one such orbit. An orbit  $O(\mathbf{t}_0)$  is the set of all sites that are generated from  $\mathbf{t}_0$  under all the group operations,

$$O(\mathbf{t}_0) = \{\mathbf{t} \mid \mathbf{t} = \hat{\mathcal{G}}(h)\mathbf{t}_0\}. \quad (5.2)$$

Some operations of  $\mathbf{G}$ , in general, leave  $\mathbf{t}_0$  invariant and the set formed by such operations is a group called the *little group* of  $\mathbf{t}_0$ ,  $\mathbf{G}_{\mathbf{t}_0}$ ,

$$\mathbf{G}_{\mathbf{t}_0} = \{g \mid \hat{\mathcal{G}}(g)\mathbf{t}_0 = \mathbf{t}_0\} \subseteq \mathbf{G}. \quad (5.3)$$

It should be noticed that the little groups of different sites of the same orbit are not identical in general but isomorphic. Once the little group is defined, it is convenient to express  $\mathbf{G}$  as an expansion in left cosets of  $\mathbf{G}_{\mathbf{t}_0}$ ,

$$\mathbf{G} = \sum_g g\mathbf{G}_{\mathbf{t}_0}. \quad (5.4)$$

The set of coset representatives  $\{g\}$  is neither unique nor closed in general. We assume henceforth, however, that it has been chosen once for all, to emphasise which fact the coset representatives are denoted with bold type.

It is clear from (5.2) and (5.3) that each orbit site is uniquely generated by a coset representative  $g$  on forming  $\hat{\mathcal{G}}(g)\mathbf{t}_0$ . It is thus appropriate to label these sites in terms of the corresponding  $g$  by means of the symbol

$$\hat{\mathcal{G}}(g)\mathbf{t}_0 = \mathbf{t}_0^g. \quad (5.5)$$

We shall now prove that the operator corresponding to (5.5),  $\mathbf{t}_0^g$ , is given by

$$\mathbf{t}_0^g = g\mathbf{t}_0g^{-1}. \quad (5.6)$$

The proof is as follows. Because

$$\mathbf{t}\mathbf{r} = \mathbf{r} + \mathbf{t}, \quad (5.7)$$

it follows from (5.5) that

$$\mathbf{t}_0^g\mathbf{r} = \mathbf{r} + \hat{\mathcal{G}}(g)\mathbf{t}_0. \quad (5.8)$$

The operator on the right of (5.6), on the other hand, is

$$g\mathbf{t}_0g^{-1}\mathbf{r} = g\mathbf{t}_0\hat{\mathcal{G}}(g^{-1})\mathbf{r} \quad (5.9)$$

$$= g\{\hat{\mathcal{G}}(g^{-1})\mathbf{r} + \mathbf{t}_0\} = \mathbf{r} + \hat{\mathcal{G}}(g)\mathbf{t}_0, \quad (5.10)$$

and on comparing (5.10) with (5.8) the result follows. The following relation is an important consequence of (5.6),

$$\mathbf{t}_0^{g'} = g'g^{-1}\mathbf{t}_0(g')^{-1} = g'g^{-1}\mathbf{t}_0(g')^{-1}g^{-1}g = \mathbf{t}_0^{gg'}. \quad (5.11)$$

## 6. Shifted states and their transformation properties

The centred atomic spinors  $\Psi_g^{gr}(\mathbf{0})$  which span the basis on the left of (4.8) can now be systematically shifted to each of the sites of an orbit by acting on them with the shifting operators  $\mathbf{t}_0^g$ , for each of the coset representatives  $g$  in (5.4). Because each

orbit site can uniquely be labelled by each  $\mathbf{g}$ , the shifted atomic spinors will be denoted with the symbol  $\Psi_{b\mathbf{g}}^{ar}$ :

$$\Psi_{b\mathbf{g}}^{ar} = \mathbf{t}_0^{\mathbf{g}} \Psi_b^{ar}(\mathbf{0}) = \Psi_b^{ar}(-\mathbf{t}_0^{\mathbf{g}}). \quad (6.1)$$

In order to find the symmetry behaviour of these functions, we must obtain the action of the operator  $\mathbf{g}$  on them, for all  $\mathbf{g} \in \mathbf{G}$ ,

$$\mathbf{g} \Psi_{a\mathbf{g}'}^{ar} = \mathbf{g} \mathbf{t}_0^{\mathbf{g}'} \Psi_b^{ar}(\mathbf{0}) = \mathbf{t}_0^{\mathbf{g}\mathbf{g}'} \mathbf{g} \Psi_b^{ar}(\mathbf{0}) \quad (6.2)$$

$$= \mathbf{t}_0^{\mathbf{g}\mathbf{g}'} \Sigma_b \cdot \Psi_b^{ar}(\mathbf{0}) \check{\mathbf{G}}^a(\mathbf{g})_{b'b} \quad (6.3)$$

$$= \Sigma_b \cdot \Psi_{b',\mathbf{g}\mathbf{g}'}^{ar} \check{\mathbf{G}}^a(\mathbf{g})_{b'b}. \quad (6.4)$$

Here we have used (5.11) in (6.2) and (6.3) follows from the definition of the centred spinors in (4.7). It is convenient to rewrite (6.4) as follows,

$$\mathbf{g} \Psi_{b\mathbf{g}'}^{ar} = \Sigma_{\mathbf{g}''} \delta(\mathbf{g}'', \mathbf{g}\mathbf{g}') \Sigma_b \cdot \Psi_{b'\mathbf{g}''}^{ar} \check{\mathbf{G}}^a(\mathbf{g})_{b'b}, \quad (6.5)$$

where

$$\delta(\mathbf{g}'', \mathbf{g}\mathbf{g}') = 1 \quad \text{if } (\mathbf{g}'')^{-1} \mathbf{g}\mathbf{g}' \in \mathbf{G}_0, \quad (6.6)$$

$$= 0 \quad \text{otherwise.} \quad (6.7)$$

Notice that, for a given pair  $\mathbf{g}, \mathbf{g}'$ , the element  $\mathbf{g}''$  is uniquely determined, since the set  $\{\mathbf{g}\}$  is fixed. Equations (6.6) and (6.7) thus determine a permutation representation  $\hat{\mathbf{P}}$  for each orbit  $O(\mathbf{t}_0)$ ,

$$\hat{\mathbf{P}}(\mathbf{g})_{\mathbf{g}''\mathbf{g}'} = \delta(\mathbf{g}'', \mathbf{g}\mathbf{g}'). \quad (6.8)$$

On substituting (6.8) into (6.5), we have

$$\mathbf{g} \Psi_{b\mathbf{g}'}^{ar} = \Sigma_{\mathbf{g}''} \Psi_{b'\mathbf{g}''}^{ar} \check{\mathbf{G}}^a(\mathbf{g})_{b'b} \hat{\mathbf{P}}(\mathbf{g})_{\mathbf{g}''\mathbf{g}'} \quad (6.9)$$

$$= \Sigma_{\mathbf{g}''} \Psi_{b'\mathbf{g}''}^{ar} \{ \check{\mathbf{G}}^a(\mathbf{g}) \otimes \hat{\mathbf{P}}(\mathbf{g}) \}_{b'\mathbf{g}''\mathbf{g}'}. \quad (6.10)$$

This means that the set of all shifted functions of an orbit transforms under the projective representation  $\check{\mathbf{G}}^a(\mathbf{g}) \otimes \hat{\mathbf{P}}(\mathbf{g})$ , which satisfies precisely the stated factor system for  $\mathbf{G}$ :

$$\{ \check{\mathbf{G}}^a(\mathbf{g}) \otimes \hat{\mathbf{P}}(\mathbf{g}) \} \{ \check{\mathbf{G}}^a(\mathbf{g}') \otimes \hat{\mathbf{P}}(\mathbf{g}') \} = \check{\mathbf{G}}^a(\mathbf{g}) \check{\mathbf{G}}^a(\mathbf{g}') \otimes \hat{\mathbf{P}}(\mathbf{g}) \hat{\mathbf{P}}(\mathbf{g}') \quad (6.11)$$

$$= [\mathbf{g}, \mathbf{g}'] \check{\mathbf{G}}^a(\mathbf{g}\mathbf{g}') \otimes \hat{\mathbf{P}}(\mathbf{g}\mathbf{g}'). \quad (6.12)$$

The basis spanned by all the shifted functions of an orbit is in general reducible:

$$\mathbf{g} \langle \Psi_{b\mathbf{g}}^{ar} | = \langle \Psi_{b\mathbf{g}}^{ar} | \{ \check{\mathbf{G}}^a(\mathbf{g}) \otimes \hat{\mathbf{P}}(\mathbf{g}) \}. \quad (6.13)$$

Our task is therefore to reduce the direct product on the right of (6.13), which we shall do in two steps, of which the first will be the reduction of  $\hat{\mathbf{P}}$ . Because this is a vector representation, it must reduce into the irreducible vector representations  $\hat{\mathbf{G}}^\alpha$  of  $\mathbf{G}$ ,

$$B^\dagger \hat{\mathbf{P}}(\mathbf{g}) B = \Sigma_\alpha \oplus m_\alpha \hat{\mathbf{G}}^\alpha(\mathbf{g}) = \Sigma_\rho \oplus \hat{\mathbf{G}}^{\alpha\rho}(\mathbf{g}). \quad (6.14)$$

In the last step here we rewrite the previous expression in a notation that will be useful later on,  $\rho$  being a multiplicity index such that for a fixed  $\alpha$  and variable  $\rho$ ,  $\hat{\mathbf{G}}^{\alpha\rho}$  defines precisely the same representation as  $\hat{\mathbf{G}}^\alpha$ .

The representation (6.13) will thus be reduced by the matrix  $\mathbf{1}_\alpha \otimes B$ , where the dimension of  $\mathbf{1}_\alpha$  equals that of  $\hat{\mathbf{G}}^\alpha$ . Since an irreducible vector basis is labelled by  $\Psi_\beta^{\alpha\rho}$



( $\alpha$  representation,  $\beta$  column,  $\rho$  multiplicity index), we define the reduced basis resulting from (6.13) as shown on the left-hand side of the following equation,

$$\langle \Psi_{b\beta}^{ar\alpha\rho} | = \langle \Psi_{bg}^{ar} | \mathbf{1}_a \otimes B. \tag{6.15}$$

(It must be remembered that, like the functions  $\Psi_b^{ar}$  in (4.8), this basis also depends on  $\tilde{\omega}, J, \pm$ .) In fact, on introducing (6.15) into (6.13), we have

$$\mathbf{g} \langle \Psi_{b\beta}^{ar\alpha\rho} | \mathbf{1}_a \otimes B^\dagger = \langle \Psi_{b\beta}^{ar\alpha\rho} | (\mathbf{1}_a \otimes B^\dagger) \{ \hat{\mathbf{G}}^a(g) \otimes \hat{\mathbf{P}}(g) \}, \tag{6.16}$$

and it follows from (6.16) that

$$\mathbf{g} \langle \Psi_{b\beta}^{ar\alpha\rho} | = \langle \Psi_{b\beta}^{ar\alpha\rho} | \hat{\mathbf{G}}^a(g) \otimes \{ B^\dagger \hat{\mathbf{P}}(g) B \} \tag{6.17}$$

$$= \langle \Psi_{b\beta}^{ar\alpha\rho} | \hat{\mathbf{G}}^a(g) \otimes \hat{\mathbf{G}}^{\alpha\rho}(g), \tag{6.18}$$

the summation over  $\rho$  in (6.14) now being implicit through the use of the row vector and matrix notation.

The basis  $\langle \Psi_{b\beta}^{ar\alpha\rho} |$  is not yet fully reduced, because  $\hat{\mathbf{G}}^a \otimes \hat{\mathbf{G}}^{\alpha\rho}$  on the right-hand side of (6.18) will not in general be irreducible. Thus our second step in the reduction process must be the reduction of this representation over the projective representations of  $\mathbf{G}$ . Let us denote the irreducible projective representations that appear in this reduction with the labels  $A, B, R$  for representation, column and multiplicity respectively. Since the multiplicity indices of the basis in (6.18) do not affect its reduction, we shall denote a *single* function of this basis with the ket

$$\Psi_{b\beta}^{ar\alpha\rho} = |a\alpha b\beta\rangle, \tag{6.19}$$

whereas the irreducible basis obtained by coupling  $\hat{\mathbf{G}}^a$  with  $\hat{\mathbf{G}}^{\alpha\rho}$  will be denoted with the ket  $|a\alpha ABR\rangle$ . (This notation, of course, is used in order to parallel the usual notation for angular momentum coupling.) The final irreducible basis is thus made up of functions of the form

$$|a\alpha ABR\rangle = \Sigma |a\alpha b\beta\rangle \langle a\alpha b\beta | a\alpha ABR\rangle. \tag{6.20}$$

The brackets on the right-hand side of this equation are Clebsch–Gordan coefficients that are available from tables.

### 7. Time reversal

The time reversal operator  $\theta$  is defined as follows for time-independent states (see e.g. Jansen and Boon 1967),

$$\theta = \left\{ \mathbf{1}_L \otimes \begin{pmatrix} \sigma_2 & \\ & -\sigma_2 \end{pmatrix} \right\} \mathbf{K}, \tag{7.1}$$

where  $\mathbf{1}_L$  is the unit operator in  $L^2(\mathbb{R}^3)$  and  $\mathbf{K}$  is the complex conjugation operator. It is well known that

$$[\mathbf{g}, \theta] = 0, \quad \forall \mathbf{g} \in \mathbf{G}, \tag{7.2}$$

and that

$$\theta^2 = -\mathbf{1}_L. \tag{7.3}$$

Given the abstract group  $\mathbf{G}$ , the group  $\mathbf{G}^\theta$  (magnetic group) including time reversal  $\theta$  is given by

$$\mathbf{G}^\theta = \mathbf{G} + \theta\mathbf{G} = \mathbf{G} \otimes (E + \theta), \quad (7.4)$$

where  $\theta$  is the abstract element represented by the antiunitary operator  $\Theta$  in (7.1). In order to adopt the very convenient direct product form shown, it is sufficient to take

$$\theta^2 = E, \quad [\theta, \theta] = -1. \quad (7.5)$$

The operators  $\mathbf{g}\theta^m$  represent the elements  $g\theta^m$  of  $\mathbf{G}^\theta$  ( $m = 1, 2$ ) and are unitary/antiunitary operators that define a projective corepresentation.

The action of  $\Theta$  on the spinors (3.1) is given, after some simple manipulation, by the relation

$$\Theta\Psi(\mathbf{x}) = i\sum_{\lambda\mu}\psi(-\mathbf{x})_{\lambda\mu}^*(-1)^{1/2-\lambda}\|\lambda, -\mu\rangle, \quad (7.6)$$

from which their effect on the atomic spinors (3.10) can be seen to be

$$\Theta\Psi_{J\pm}^{M\tilde{\omega}} = (-1)^{M+1}(-1)^{1/2+\tilde{\omega}/2}\Psi_{J\mp}^{-M\tilde{\omega}}. \quad (7.7)$$

(Notice the exchange of the  $\pm$  index.)

Once the states have been symmetrised with respect to  $\mathbf{G}$  as discussed in § 4, they must be symmetry adapted with respect to the unitary projective corepresentations of  $\mathbf{G}^\theta$ . For this purpose, the classification of the unitary representations in the well known types I, II and III (see e.g. Jansen and Boon 1967) is still valid for the projective representations (Dirl 1981) and for types II and III the functions  $\Theta\Psi_b^{gr}(\mathbf{0})$  must be linearly independent of the basis  $\langle\Psi_b^{gr}(\mathbf{0})|$ , in which case a further unitary transformation can be performed (Dirl 1981). Type II representations, however, are exceptional for point groups. In type I nothing is added by time reversal whereas in type II or type III a straight doubling of the degeneracy arises (Jansen and Boon 1967). In practice no further work is necessary owing to this doubling.

## 8. Example for $C_{3v}$ group

We shall consider an example of the method discussed above for a molecule  $C_{3v}$  symmetry, a group which has been treated from the point of view of the projective representations by Altmann and Herzog (1982). We give in table 1 the quaternion parameters that correspond to the setting and positive hemisphere used by these authors and in table 2 the matrices for the generators in all vector and projective representations.

There is only one non-trivial physically significant orbit in this case, generated by a vector  $\mathbf{t}_0$  on the  $\sigma_{v1}$  ( $yz$ ) plane, the little group of which is  $\mathbf{C}_s = E + \sigma_{v1}$ . We choose

**Table 1.** Quaternion parameters.  $\lambda = \cos \frac{1}{2}\phi$ ,  $\Lambda = \sin \frac{1}{2}\phi\mathbf{n}$ ,  $\mathbf{n} = (n_x, n_y, n_z)$ .

Operation	$E$	$C_3^+$	$C_3^-$	$\sigma_{v1} = iC_{21}$	$\sigma_{v2} = iC_{22}$	$\sigma_{v3} = iC_{23}$
$\lambda$	1	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0
$\Lambda$	(0 0 0)	(0 0 $\sqrt{3}/2$ )	(0 0 $-\sqrt{3}/2$ )	(1 0 0)	(0 $\frac{1}{2}\sqrt{3}/2$ )	(0 $\frac{1}{2}-\sqrt{3}/2$ )

**Table 2.** Representations.  $\omega = \exp(2\pi i/6)$ .

Rep Short symbol	$A_1$ $1_0$	$A_2$ 3	$E$ 1	$\bar{E}_{1/2}$ $\frac{1}{2}$	${}^1\bar{E}_{3/2}$ $\frac{3}{2}^+$	${}^2\bar{E}_{3/2}$ $\frac{3}{2}^-$
$C_3^+$	1	1	$\begin{pmatrix} \bar{\omega} & \\ & \bar{\omega}^* \end{pmatrix}$	$\begin{pmatrix} \omega^* & \\ & \omega \end{pmatrix}$	-1	-1
$\sigma_{v1}$	1	-1	$\begin{pmatrix} & 1 \\ 1 & \end{pmatrix}$	$\begin{pmatrix} & -i \\ -i & \end{pmatrix}$	i	-i

for it the following coset decomposition:

$$C_{3v} = EC_s + C_3^+ C_s + C_3^- C_s, \tag{8.1}$$

The coset representatives here label the rows and columns of the permutation matrix which, from (6.6) and (6.8), is given by the condition

$$\hat{P}(g)_{g''g'} = 1 \quad \text{if } (g'')^{-1} g g' \in C_s, \tag{8.2}$$

being zero otherwise. This representation, again listed by generators only, is as follows:

$$g: \quad C_3^+ \quad \sigma_{v1}$$

$$\hat{P}(g): \begin{bmatrix} & & 1 \\ 1 & & \\ & 1 & \end{bmatrix} \begin{bmatrix} 1 & \\ & 1 \end{bmatrix}. \tag{8.3}$$

This representation decomposes into  $A_1 \oplus E$  and the matrix  $B$  that reduces it as in (6.14) is given by

$$B = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 & 1 & 1 \\ 1 & \bar{\omega}^* & \bar{\omega} \\ 1 & \bar{\omega} & \bar{\omega}^* \end{pmatrix}, \quad \omega = \exp(2\pi i/6), \quad \bar{\omega} = -\omega. \tag{8.4}$$

We are now ready to symmetrise the centred states  $\Psi_{j\pm}^{M\bar{\omega}}(\mathbf{0})$  that span the representation  $\hat{G}^J$  as in (4.4). We take for our example  $J = \frac{3}{2}$  and consider the functions

$$\Psi_{3/2\pm}^{M,\pm 1}(\mathbf{0}), \quad \frac{3}{2} \geq M \geq -\frac{3}{2}. \tag{8.5}$$

Since the representation  $\hat{G}^J$  depends on  $\bar{\omega}$  we shall label the corresponding representations with the symbol  $\hat{G}^{J\pm}$ . From (4.5) and (4.6),

$$\hat{G}^{3/2\pm}(g) = \hat{S}^{3/2}(R_g), \quad g \text{ proper}, \tag{8.6}$$

$$= \pm \check{S}^{3/2}(R_g), \quad g \text{ improper}, \tag{8.7}$$

where the  $R_g$  are the quaternion parameters for  $g$  as listed in table 1. The matrices  $\hat{S}^j$  or  $\check{S}^j$  for  $j$  integral and half-integral respectively are given in terms of the quaternion parameters  $R_g$  equal to  $\{\lambda, \Lambda\}$  by the expression

$$S^j\{\lambda, \Lambda\}_{m'm} = \{(j+m')!(j-m')!(j+m)!(j-m)!\}^{1/2}$$

$$\times \sum_k (-1)^k \frac{(\lambda + i\Lambda_z)^{j-m'-k} (\lambda - i\Lambda_z)^{j+m-k} (-\Lambda_y - i\Lambda_x)^{m'-m+k} (-\Lambda_y + i\Lambda_x)^k}{(j-m'-k)!(j+m-k)!(m'-m+k)!k!}, \tag{8.8}$$

where the embellishment on  $S$  must be chosen in accordance to  $j$ . With (8.8) in (8.6)

and (8.7) we obtain the following matrices

$$\begin{matrix} \mathbf{G}^{3/2\pm}(C_3^+) & \mathbf{G}^{3/2\pm}(\sigma_{v1}) \\ \begin{bmatrix} -1 & & & \\ & \omega^* & & \\ & & \omega & \\ & & & -1 \end{bmatrix} & \pm \begin{bmatrix} & & & i \\ & & & i \\ & & i & \\ & i & & \\ i & & & \end{bmatrix}, \end{matrix} \quad (8.9)$$

which reduce as follows,

$$\mathbf{G}^{3/2\pm} = {}^1\bar{E}_{3/2} \oplus \bar{E}_{1/2} \oplus {}^2\bar{E}_{3/2}. \quad (8.10)$$

The subduction matrices  $W^j$  in (4.8) are readily obtained. Since they depend on  $\tilde{\omega}$  they will be denoted with  $W^\pm$ :

$$W^\pm = \begin{matrix} & \begin{matrix} \frac{3}{2}+ & \frac{1}{2} & \frac{1}{2} & \frac{3}{2}- \\ \frac{3}{2}+ & \frac{1}{2} & \frac{1}{2} & \frac{3}{2}- \end{matrix} & \begin{matrix} a \\ b \end{matrix} \\ M & & \\ \begin{matrix} \frac{3}{2} \\ \frac{1}{2} \\ -\frac{1}{2} \\ -\frac{3}{2} \end{matrix} & \left| \begin{matrix} \pm 1/\sqrt{2} & & & 1/\sqrt{2} \\ & 1 & & \\ & & \pm 1 & \\ 1/\sqrt{2} & & & \mp 1/\sqrt{2} \end{matrix} \right| & \end{matrix}. \quad (8.11)$$

In using this matrix to write the symmetrised centred states on the left of (4.8), attention must be paid to the precise order in which the irreducible projective matrices appear along the diagonal, which is in our case that stated in (8.10). The rows of  $W^\pm$ , as follows from (4.8), correspond to each of the functions  $\Psi_{j^{\pm 1}}^M$  in (8.5) in the stated order of  $M$ . We shall consider henceforth the case  $\tilde{\omega} = +1$ , so that functions of this basis can conveniently be abbreviated with the ket  $|JM\rangle$ , the  $+$  sign (as well as  $\tilde{\omega}$  value) being implicit. The reduced basis on the left of (4.8) is labelled by  $a$  (projective representation) and  $b$  (column) and these labels are shown at the top of (8.11) and correspond to the specific reduction form stated. Notice that the labels of the representations are the short symbols in table 2. As is now usual in this field (cf e.g. Pyykkö and Toivonen 1983) these labels are chosen to coincide with the  $j$  of the lowest spherical harmonic that belongs to the representation and, when appropriate, we also use the sequence  $j$  to  $-j$  to label the columns. For consistency of the notation, for one-dimensional representations the column label is given as a repeat of the representation label. Since the multiplicity index in (4.8) can be dispensed with in our case, a symmetrised centred state will be written as  $\Psi_{3/2^+}^{3/2^+}$  but it must be remembered that these must be understood as representation and not as  $j$  labels. The centred symmetrised spinors follow at once from (8.11) and (4.8). They are for the case  $\tilde{\omega} = +1$  in hand,

$$\Psi_{3/2^+}^{3/2^+} = (1/\sqrt{2})|\frac{3}{2}\frac{3}{2}\rangle + (1/\sqrt{2})|\frac{3}{2}\frac{3}{2}\rangle, \quad (8.12)$$

$$\Psi_{1/2}^{1/2} = |\frac{3}{2}\frac{1}{2}\rangle, \quad (8.13)$$

$$\Psi_{1/2}^{1/2} = -|\frac{3}{2}\frac{1}{2}\rangle, \quad (8.14)$$

$$\Psi_{3/2^-}^{3/2^-} = (1/\sqrt{2})|\frac{3}{2}\frac{3}{2}\rangle - (1/\sqrt{2})|\frac{3}{2}\frac{3}{2}\rangle. \quad (8.15)$$

The shifted states are obtained, as on the right-hand side of (6.15), by considering the centred states  $\Psi_b^a$  in (8.12) to (8.15) and adding to them the  $g$  label, this being

one of the three coset representatives  $E, C_3^+, C_3^-$  in (8.1). For simplicity, the latter will be denoted as  $E, +, -$  respectively. The reducible basis on the right-hand side of (6.15) will thus contain 12 states. Since the multiplicity indices  $r$  and  $\rho$  in (6.15) can be dispensed with, a function of the reduced bases on its left will be denoted as follows,

$$\Psi_{b\beta}^{a\alpha} = |a\alpha b\beta\rangle. \quad (8.16)$$

Again, the vector representation symbols  $\alpha \beta$  will be identified with the short symbols of table 2, the columns of the representation 1 being labelled 1 and  $\bar{1}$  respectively. The partly symmetrised shifted states (8.16) are given, on introducing  $B$  from (8.4) into (6.15), by

$$|a1_0b1_0\rangle = (1/\sqrt{3})(\Psi_{bE}^a + \Psi_{b+}^a + \Psi_{b-}^a), \quad (8.17)$$

$$|a1b1\rangle = (1/\sqrt{3})(\Psi_{bE}^a - \omega^*\Psi_{b+}^a - \omega\Psi_{b-}^a), \quad (8.18)$$

$$|a1b\bar{1}\rangle = (1/\sqrt{3})(\Psi_{bE}^a - \omega\Psi_{b+}^a - \omega^*\Psi_{b-}^a). \quad (8.19)$$

Here the indices  $a, b$  range over the four pairs listed at the top of (8.11) and the states on the right-hand side are obtained from (8.12) to (8.15).

The fully symmetrised shifted spinors are the states on the left of (6.20). The symbols here must be first written in full in order to extract the Clebsch–Gordan coefficients from the tables of Altmann and Herzog (1982) whose notation we follow precisely. The symmetrised states  $|a\alpha ABR\rangle$  can be shortened to  $|AB\rangle$  since there is no multiplicity here and, once the coupling is performed, the relevant piece of information is the irreducible projective representation  $A$  and the column  $B$  to which the symmetrised spinor belongs. The symmetrised states are the following twelve, of which the first eight are four degenerate pairs corresponding to the representation  $\bar{E}_{1/2}$ , each pair given in a single line. The next two states belong to  ${}^1\bar{E}_{3/2}$  and the last two to  ${}^2\bar{E}_{3/2}$ .

$$|\frac{1}{2}\frac{1}{2}\rangle = |\frac{1}{2}1_0\frac{1}{2}1_0\rangle, \quad |\frac{1}{2}\bar{1}\bar{2}\rangle = |\frac{1}{2}1_0\frac{1}{2}\bar{1}\bar{2}\rangle, \quad (8.20)$$

$$|\frac{1}{2}\frac{1}{2}\rangle = |1\frac{1}{2}1\frac{1}{2}\rangle, \quad |\frac{1}{2}\bar{1}\bar{2}\rangle = |1\frac{1}{2}\bar{1}\bar{2}\rangle, \quad (8.21)$$

$$|\frac{1}{2}\frac{1}{2}\rangle = -|1\frac{3}{2}+\bar{1}\frac{3}{2}+\rangle, \quad |\frac{1}{2}\bar{1}\bar{2}\rangle = |1\frac{3}{2}+1\frac{3}{2}+\rangle, \quad (8.22)$$

$$|\frac{1}{2}\frac{1}{2}\rangle = |1\frac{3}{2}-\bar{1}\frac{3}{2}-\rangle, \quad |\frac{1}{2}\bar{1}\bar{2}\rangle = |1\frac{3}{2}-1\frac{3}{2}-\rangle, \quad (8.23)$$

$$|\frac{3}{2}+\frac{3}{2}+\rangle = |\frac{3}{2}+1_0\frac{3}{2}+1_0\rangle, \quad (8.24)$$

$$|\frac{3}{2}+\frac{3}{2}+\rangle = -2^{-1/2}|\frac{1}{2}1\frac{1}{2}1\rangle + 2^{-1/2}|\frac{1}{2}1\frac{1}{2}\bar{1}\rangle, \quad (8.25)$$

$$|\frac{3}{2}-\frac{3}{2}-\rangle = |\frac{3}{2}-1_0\frac{3}{2}-1_0\rangle, \quad (8.26)$$

$$|\frac{3}{2}-\frac{3}{2}-\rangle = 2^{1/2}|\frac{1}{2}1\frac{1}{2}1\rangle + 2^{-1/2}|\frac{1}{2}1\frac{1}{2}\bar{1}\rangle. \quad (8.27)$$

The twelve states listed on the right-hand sides here are those given in (8.17)–(8.19).

## 9. Discussion

When double group representations are constructed in the usual Euler parametrisation, the procedure adopted is roughly as follows.  $SU(2)$  matrices are chosen for  $\mathbf{G}$  and their negatives for the remaining operations of  $\tilde{\mathbf{G}}$ . This establishes the multiplication rules of  $\tilde{\mathbf{G}}$ . Once this is done, bases for the other representations are chosen and their matrices constructed from the  $SO(3)$  matrices in terms of the Euler angles. The

matrices resulting do not automatically satisfy the multiplication rules and phases have to be skilfully chosen so as to achieve this. Excellent tables for a large number of point groups have recently been produced in this or a similar way by Pyykkö and Toivonen (1983). The procedure we have given and the representation formulae in quaternion parameters ensure complete consistency of phase factors and multiplication rules and it is thus eminently suited for automatic computation. A program has now been written that produces the irreducible representations and Clebsch–Gordan coefficients for all point groups (P Herzig, private communication).

Even when consistent tables of representations are used, two problems remain. The first is that the representations chosen must also be consistent with the standard form of the Pauli matrices, having to satisfy the relation (see Jansen and Boon 1967, p 318)

$$\check{U}(g)\sigma_j\check{U}(g)^\dagger = \sum_k \sigma_k \hat{\mathcal{G}}(R_g)_{kj} \quad (9.1)$$

Even otherwise good tables, like those of Bradley and Cracknell (1972), fail sometimes to satisfy this relation, which is automatically satisfied by our method. We have checked extensively the tables of Pyykkö and Toivonen (1983) in this respect and have found no inconsistencies.

The second problem is the following. In order to symmetrise the centred spinor states the matrices  $\check{G}^J(g)$  defined in (4.5) and (4.6) must be constructed. Again, if Euler angles are used, skilful adaptation to the multiplication rules is required, whereas this is not so when these equations are used together with the quaternion parametrisation in (8.8). Pyykkö and Toivonen (1983) include expressions for these matrices for the dihedral groups that are admirably correct, but anyone dealing with the cubic and icosahedral groups would find it very hard to proceed in this way. It should finally be mentioned that attention must be paid to the Clebsch–Gordan coefficients used to ensure phase consistency.

As regards the symmetrisation procedure itself, it must be pointed out that owing to the large size of the matrices required in practice, the two-step method presented here reduces considerably the amount of work required by existing methods.

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