

Calculating Spin-Orbit Matrix Elements with RACAH

HUGHAN J. ROSS,* LUKE F. MCAVEN,* KIMINARI SHINAGAWA,† AND PHILIP H. BUTLER*

**Department of Physics and Astronomy, University of Canterbury, Private Bag 4800, Christchurch, New Zealand; and*

†*Department of Physics, Toho University, Funabashi-City, Chiba, 274 Japan*

Received December 29, 1995; revised May 29, 1996

RACAH is a computer program developed to simplify calculations involving generalized coupling coefficients. As a demonstration of its usefulness in doing this, we apply it to calculating the spin-orbit matrix elements of CrBr_3 . From those matrix elements we can derive the spin-orbit coupling coefficients, vital to discussing Kerr rotation. We base our calculations on a cluster consisting of a Cr^{3+} ion, surrounded by six Br^- ions in an octahedral configuration. The Racah–Wigner calculus, useful for doing such calculations, is built into RACAH in such a way as to provide a natural approach to choosing between possible group chains. © 1996 Academic Press, Inc.

1. INTRODUCTION

Many spectroscopic problems require the evaluation of matrix elements. To calculate these matrix elements, a sophisticated mathematical formalism, the Racah–Wigner calculus is extremely useful [3, 8]. However, this formalism is not familiar to experimentalists and is still tiresome in long calculations. A software package, called RACAH, has been developed at Canterbury. RACAH is a much more versatile and general version of the program which produced the tables of Butler [3]. We demonstrate, with a specific example, how useful RACAH is for simplifying general matrix elements to reduced matrix elements.

RACAH is not restricted to this problem, however, and contains the necessary structure for a broad range of uses. All point groups are recognized and the programming structure of RACAH is versatile enough to allow many open shells, as we have seen in this application. All $3jm$, $6j$, and $9j$ can be calculated for all point groups, and the Wigner–Eckart theorem can be used in collaboration with those coupling coefficients to reduce matrix elements. Specific information about the normalization of the operators is not considered by the current version of RACAH. That is, the actual values of the reduced matrix elements of some operator cannot be obtained. Therefore the only restriction on the operators is that the group irrep labels associated with the operators can be specified.

The development of RACAH is an ongoing and long-term project (see Butler [3]). The core development is at the stage where it should largely be driven by feedback from

applied users. RACAH has been distributed to a number of such persons, who are finding it useful. Knowledge about what applications and capabilities users would like RACAH to have would allow us to build into the core program the appropriate calculations relevant to other applications and, perhaps, to develop libraries for special one-off calculations. Details about obtaining RACAH are given after the summary.

The approach we take to the analysis of Kerr rotation in CrBr_3 , requires the calculation of matrix elements of spin-orbit operators, of known symmetry, between electron configurations with many open shells. From those the magnitudes of the spin-orbit coupling constants can be derived, the spin-orbit effect being the dominate cause of magneto-optical effects in ferromagnetic materials. Ferromagnetic materials with high magneto-optical effects have been applied to devices such as optical isolators, magnetic sensors, and rewritable optical memories [1, 5]. In recent years there has been an increasing demand for materials with higher magneto-optical effects. This is therefore an example of practical significance.

The new aspects of this calculation are the presence of RACAH to take the labor out of calculating the vector coupling coefficients (vcc's) [3] and the way that choosing the right group chain to classify states reduces the calculation of matrix elements, even very complicated ones, to the calculation of vcc. In one view, RACAH is just a convenient way of doing the tedious bits of calculating matrix elements. Thus many of the calculations in Piepho and Schatz [8] are trivially reduced to finding values for the reduced matrix elements. The conceptual advantage of using RACAH is exactly analogous to the tensor calculus and serves to unify all group theory calculations that arise in evaluating matrix elements. Contrary to the previous viewpoint, RACAH allows one to think in a structurally simple way *and* provides a means to calculate within that structure. RACAH allows the operators and symmetries of the physical problem to be retained throughout the calculation. The $6j$ and $9j$ that appear in more traditional reductions of matrix elements appear as special cases of $3jm$, whose labels are trivially constructed from those of the states and the operators.

TABLE I

Schönflies (S) and Butler (B) Labelling for the Irreps of O on the Left and D₃ on the Right

S	B	S	B	S	B	S	B
A ₁	0	A ₂	$\tilde{0}$ or ~ 0	A ₁	0	E'	$\frac{1}{2}$ or s0
E	2	T ₁	1	A ₂	$\tilde{0}$ or ~ 0	E	1
					$\frac{3}{2}$ or s1		
T ₂	$\tilde{1}$ or ~ 1	E'	$\frac{1}{2}$ or s0	E''			
					$-\frac{3}{2}$ or -s1		
E'	$\frac{5}{2}$ or $\sim s0$	U'	$\frac{3}{2}$ or s1				

Note. The second label in the Butler columns is the form of the Butler notation that RACAH recognizes.

In Section 2 we discuss the labelling of the cluster and the ground state configuration and outline how RACAH recognizes group chains. Section 3 extends the group chain to allow such effects as trigonal distortion to be taken into account. Section 4 demonstrates the transformation of the spin-orbit to a form compatible with the group chain we choose. In Section 5 we step through the calculation of a particular matrix element, utilizing the Wigner–Eckart theorem to its full potential.

The multicenter reduced matrix elements which we have derived at that stage are unable to be calculated by RACAH so in Section 6 we give the results of reducing to single-center reduced matrix elements.

Section 7 shows the results of applying RACAH to finding the relationship between matrix element and reduced matrix element, as examined in Section 5. Finally, bringing together the results of Sections 6 and 7, we calculate the spin-orbit coupling coefficients. Those spin-orbit coupling coefficients are required to investigate the Kerr–rotation spectra of CrBr₃. This work will be followed by a calculation of the Kerr effect, again using a cluster approach.

1.1. The Butler Irrep Labelling Scheme

The Butler notation, used extensively in both Butler [3] and Piepho and Schatz [8], is based on a simple numerical labelling scheme for irreps. The program RACAH takes advantage of this notation, while still recognizing many other labelling schemes. See Table I for the relation between Schönflies and Butler irrep labels in the case of the groups O, and D₃. It is of particular importance to note that an *s* is prefixed to a number to indicate half integer, allowing RACAH to express fractional irrep labels. For example, s1 = $\frac{3}{2}$ and s5 = $\frac{11}{2}$. This is particularly noticeable when dealing with SU₂ and SO₃. In this work we tend

toward using the Schönflies notation which is more familiar to spectroscopists.

2. LABELLING THE CLUSTER AND THE GROUND STATE CONFIGURATION

The molecular orbitals which are largely of Br composition are fully occupied in the clusters ground state. Those molecular orbitals with a mainly Cr composition are empty in the ground state, with the exception of the *t*_{2g} orbital, which is occupied by three electrons with parallel spins. High Kerr rotations have been observed [7] and are attributed to the spin-orbit splitting of particular excited states. Those excited states arise from the transition of an electron in a *t*_{1u} or *t*_{2u} orbital to the *e*_g orbital, a molecular orbital which consists mainly of 3*d* orbitals of the chromium [9]. Since this transition represents a transition from a non-bonding π orbital, of mainly Br character, to an antibonding orbital, of mainly Cr character, it is known as a “charge transfer” transition.

The ground state has the *e*_g shell empty and the various shells of the Br₆ that we shall consider, *t*_{1u}⁶(ρ) and *t*_{2u}⁶(ρ), full. So, with the three up-spin electrons in the *t*_{2g} shell the ground state has the configuration

$$(t_{2g}^3)(e_g^0)(t_{2u}^6)(t_{1u}^6).$$

Given that the octahedral field is “strong,” we classify the orbital parts of the chromium orbitals using O_h = O × C_i. Similarly the orbitals on the individual bromine atoms are classified using O_h. The atomic orbitals of the Cr³⁺ ion which contribute to the relevant molecular orbitals of the complex are the 3*d*, 4*s*, and 4*p* orbitals. The electronic configurations of the complex are assumed to be given by a linear combination of atomic orbitals (LCAO).

The 4*p* orbitals on the single Br[−] ions are first combined into molecular orbitals for the octahedral complex of six bromines. The symmetry types of the Br-molecular orbitals we obtain are given in Table II. The third column of the table contains the linear combinations of the orbital spaces

TABLE II

Molecular Orbitals for the Six Br[−] Ions

	Schönflies notation	Butler notation	Factorised states
σ -orbital	<i>a</i> _{1g}	0 ⁺	(1 [−] , 1 [−])0 ⁺
π -orbital	<i>t</i> _{1g}	1 ⁺	(1 [−] , 1 [−])1 ⁺
π -orbital	<i>t</i> _{2g}	$\tilde{1}^+$	(1 [−] , 1 [−]) $\tilde{1}^+$
σ -orbital	<i>e</i> _g	2 ⁺	(1 [−] , 1 [−])2 ⁺
σ -orbital	<i>t</i> _{1u}	1 [−]	$\frac{1}{\sqrt{3}} (0^+, 1^-)1^- - \frac{\sqrt{2}}{\sqrt{3}} (2^+, 1^-)1^- $
π -orbital	<i>t</i> _{1u}	1 [−]	$\sqrt{2}/\sqrt{3} (0^+, 1^-)1^- + 1/\sqrt{3} (2^+, 1^-)1^- $
π -orbital	<i>t</i> _{2u}	$\tilde{1}^-$	(2 ⁺ , 1 [−]) $\tilde{1}^-$

obtained by coupling the irreps of the permutation representation of O and the irrep of O given by the $4p$ orbitals on an individual bromine. The details of this combination process need not concern us at the moment, but they are important when we come to relate the reduced matrix elements of the molecular orbitals to the matrix elements of the bromide ions.

The Br_6 orbitals are characterized not only by the symmetry properties under the O_h group, but also by the extent to which they partake in the bonding of the bromides to the chromium. We have σ -type bonding orbitals and π -type antibonding orbitals. The σ and π molecular orbitals are the only nontrivial linear combinations.

With the addition of spin our classifying group becomes $SU_2 \times O_h$.

We now want to obtain a labelling scheme for the excited states of the cluster. In the charge transfer states there are three open shells, two on the Cr center and one on the Br_6 "molecule." The overall symmetry of the state of the cluster must be $SU_2 \times O_h$, before the inclusion of the trigonal distortion, and so we couple these three orbitals at the $SU_2 \times O_h$ level. Although we can couple the shells in any order it is natural to couple the two Cr orbitals together first, and then to couple the Br_6 orbital to the result. Thus our group chain currently looks like

$$\begin{aligned} & \{((SU_2 \times O_h)_{t_{2g}}, (SU_2 \times O_h)_{e_g}) \downarrow (SU_2 \times O_h)_{Cr}, \\ & (SU_2 \times O_h)_{Br_6}\} \downarrow (SU_2 \times O_h)_{Cluster}, \end{aligned} \quad (1)$$

where \downarrow denotes a branching. This completes the classification of states imposed by the terms in the Hamiltonian that have O_h symmetry. The remaining terms are the spin-orbit contribution, the trigonal term, and the magnetic exchange interaction.

We consider two possible branching schemes, or chains, below $(SU_2 \times O_h)_{Cluster}$, in which two of the perturbing terms are diagonal. The trigonal distortion term of the Hamiltonian will be diagonal in the scheme

$$\begin{aligned} (SU_2 \times O_h)_{Cluster} & \downarrow O^S \times O_h^I \downarrow D_3^S \times D_{3d}^I \\ & \downarrow C_3^S \times C_{3i}^I \downarrow C_3^S \times C_3^I \downarrow C_3^I \end{aligned}$$

and the spin-orbit interaction will be diagonal in

$$(SU_2 \times O_h)_{Cluster} \downarrow O^S \times O_h^I \downarrow O_h^I \downarrow D_{3d}^I \downarrow C_{3i}^I \downarrow C_3^I.$$

The inclusion of those branching schemes will be considered in Section 3, but first we demonstrate how RACAH recognizes a branch.

2.1. Branching with RACAH

Once RACAH has been started our first action is to describe the group chain using the branch command. We do

this first for the chain, in Eq. (1), down to $(SU_2 \times O_h)_{Cluster}$ using brackets and commas in exactly the way we have written the chain:

```
Racah v3.1          Fri Apr 28 08:37:12 1995
>branch ((su2*oh, su2*oh) su2*oh, su2*oh)
su2*oh
((su2 * oh), (su2 * oh)) to (su2 * oh),
(su2 * oh) to (su2 * oh)
```

The output confirms we have entered the chain correctly and indicates where to put the irreps when we come to describe the states. The options for the chains below $(SU_2 \times O_h)_{Cluster}$ are entered thus

```
>branch su2*oh o*oh d3*d3d c3*c3i c3*c3 c3
(su2 to o, oh) to (o to d3, (o to d3, ci))
to (d3 to c3, (d3 to c3, ci))
to (c3, c3i to c3) to c3
```

or

```
>branch (su2 o d3 c3, oh d3d c3i c3) c3
(su2 to o to d3 to c3, (o to d3, ci) to
(d3 to c3, ci) to c3) to c3
```

for the scheme in which the trigonal term is diagonal. The second option branches the spin chain separately from the orbital chain, until they both reach C_3 , at which point they are joined by a coupled branching. At the second level of this chain, the product of $O \times O_h$, there is an ambiguity about the branch to the O_h below. Depending on whether the product $O \times O_h$ is bracketed as $(O \times (O \times C_i))$ or $((O \times O) \times C_i)$ we have a different interpretation for the coupling. We need the later form, so that we can branch the SU_2 down to an O and then combine the product $O \times O$ into a single O by coupling them together. Two ways to implement such a scheme, within RACAH, are

```
>branch (su2*o, ci) (o*o, ci) (o, ci) d3d
c3i c3
((su2 to o, o), ci) to ((o, o) to o, ci)
to (o to d3, ci) to (d3 to c3, ci)
to c3
```

and

```
>branch (su2*o o*o o d3 c3, ci) c3
((su2 to o, o) to o to d3 to c3, ci) to c3
```

It is both physically reasonable, and RACAH compatible, to drop the parity label at the earliest opportunity, thus obtaining a simpler branching,

>branch su2*oh o*o o d3 c3
(su2 to o, oh to o) to o to d3 to c3

which we can take advantage of. Initially we will include explicit parity labels at the $O \times O_h$ level since RACAH is quite capable of dealing with them.

3. EXTENDING THE SYMMETRY SCHEME

Although we are only concerned with calculating the spin-orbit coupling constant, and therefore do not need a definite symmetry scheme below the octahedral group (O'), we would like to exhibit one that could be used in a calculation that went beyond spin-orbit effects, for instance taking into account the trigonal distortion of the lattice.

We choose a group chain to classify the states that reflect the environment of the Cr^{3+} ion. Since the point group symmetry of the Cr site is C_3 , due to the trigonal distortion of the octahedral arrangement of bromines, the natural choice is the chain $O \supset D_3 \supset C_3$. Therefore the kets are essentially labeled with the following group structure

$$\begin{aligned} & \{(\text{SU}_2 \times \text{O}_h, \text{SU}_2 \times \text{O}_h) \downarrow \text{SU}_2 \times \text{O}_h, \text{SU}_2 \times \text{O}_h\} \\ & \downarrow \text{SU}_2 \times \text{O}_h \downarrow O \times O \downarrow O \downarrow D_3 \downarrow C_3, \end{aligned}$$

for states with three open shells. The branching $\text{SU}_2 \times \text{O}_h \downarrow O \times O$ is a product branching of $\text{SU}_2^S \downarrow O^S$ and $O_h^L \downarrow O^L$, while $O^S \times O^L \downarrow O'$ is a coupled branching.

By virtue of having only one open shell, the ground state of the cluster need not include labels for the closed shells t_{1u} and t_{2u} . Thus the ground state can be written in a simpler form, as

$$|t_{2g}^3(^4A_{2g})U' \cdot A_2U'E^{n\frac{3}{2}}\rangle.$$

The excited states are referred to as ‘‘charge transfer states’’ due to their connection with the ground state through the charge transfer transitions. The designations of these states, within the symmetry scheme given at the start of this section, are

$$|\mathcal{P}\{(t_{2g}^3(^4A_{2g}), e_g(^2E_g))^5E_g, t_{1u}^5(^2T_{1u})\}^4T_{2u}U' \cdot T_{2u}r \lambda \mu l\rangle$$

and

$$|\mathcal{P}\{(t_{2g}^3(^4A_{2g}), e_g(^2E_g))^5E_g, t_{2u}^5(^2T_{2u})\}^4T_{2u}U' \cdot T_{2u}r \lambda \mu l\rangle$$

for excitations from the t_{1u} and t_{2u} open shells, respectively, and for the various values of r , λ , μ , and l that occur. λ , μ , and l are labels for the irreps of O , D_3 , and C_3 , respectively. r is a multiplicity label for the coupled branching $O^S \times O^L \downarrow O'$. In these states the \mathcal{P} [8, Section 19.7]

indicates that the electrons in the separate shells are anti-symmetrized, as well as those within the same shells.

4. THE SPIN-ORBIT HAMILTONIAN

The matrix elements we seek are

$$\begin{aligned} & \langle \mathcal{P}\{(t_{2g}^3(^4A_{2g}), e_g(^2E_g))^5E_g, t_{1u}^5(^2T_{1u})\}^4T_{2u}U' \cdot T_{2u}r \lambda \alpha \mu l | \\ & \quad \times \mathcal{H}_{\text{so}} | \mathcal{P}\{(t_{2g}^3(^4A_{2g}), e_g(^2E_g))^5E_g, t_{1u}^5(^2T_{1u})\}^4T_{2u}U' \\ & \quad \cdot T_{2u}r \lambda \alpha \mu l \rangle, \end{aligned} \quad (2)$$

where

$$\mathcal{H}_{\text{so}} = \zeta_{t_{2g}}(\mathbf{S} \cdot \mathbf{L})_{t_{2g}} + \zeta_{e_g}(\mathbf{S} \cdot \mathbf{L})_{e_g} + \zeta_{t_{1u}}(\mathbf{S} \cdot \mathbf{L})_{t_{1u}},$$

a sum of the spin-orbit operators for the electrons in the three open shells that are present. The spin-orbit operator for each shell contains a parameter or coupling constant, ζ , which depends on the particular radial character of that molecular orbital and, hence, on which atomic orbitals it is a linear combination.

4.1. Facing Up to the Group Chain

It is more enlightening to denote the three operators in the sum by

$$\begin{aligned} & \zeta_{t_{2g}}(\mathbf{S} \cdot \mathbf{L})_{t_{2g}} \otimes (\mathbf{1} \cdot \mathbf{1})_{e_g} \otimes (\mathbf{1} \cdot \mathbf{1})_{t_{1u}}, \\ & \zeta_{e_g}(\mathbf{1} \cdot \mathbf{1})_{t_{2g}} \otimes (\mathbf{S} \cdot \mathbf{L})_{e_g} \otimes (\mathbf{1} \cdot \mathbf{1})_{t_{1u}} \end{aligned}$$

and

$$\zeta_{t_{1u}}(\mathbf{1} \cdot \mathbf{1})_{t_{2g}} \otimes (\mathbf{1} \cdot \mathbf{1})_{e_g} \otimes (\mathbf{S} \cdot \mathbf{L})_{t_{1u}}$$

which is equivalent to the prior equation, since the operators have trivial action on the spaces that they do not apply to.

To apply the full power of the Wigner–Eckart theorem (Section 5) we need to classify the operator \mathcal{H}_{so} using all groups of the group chain labelling the states. The set of three spin operators, $\{s_x, s_y, s_z\}$, forms a basis for irrep 1 of SU_2 , which branches uniquely to t_1 of O . The same analysis applies to the three orbital angular momentum operators, $\{l_x, l_y, l_z\}$, although there is a parity label present as well. For the lower part of the chain, $\text{SU}_2 \times \text{O}_h \supset O \times \text{O}_h \supset \text{O}_h \supset O \supset D_3 \supset C_3$, the irrep labels for the spin-orbit operators are ${}^3T_{1g}T_1 \cdot T_{1g}A_{1g}000$. With the complete chain the labels for the t_{1u} term are

$$\zeta_{t_{1u}}[({}^1A_{1g}, {}^1A_{1g}){}^1A_{1g}, {}^3T_{1g}]{}^3T_{1g}T_1 \cdot T_{1g}A_{1g}a_1.$$

There are similar expressions for the t_{2g} and e_g terms which differ only in the position of the ${}^3T_{1g}$ inside the nested brackets (and the ζ factor):

$$\begin{aligned}\zeta_{t_{2g}} [({}^3T_{1g}, {}^1A_{1g})^3T_{1g}, {}^1A_{1g}]^3T_{1g}T_1 \cdot T_{1g}A_1a_1 \\ \zeta_{e_g} [({}^1A_{1g}, {}^3T_{1g})^3T_{1g}, {}^1A_{1g}]^3T_{1g}T_1 \cdot T_{1g}A_1a_1.\end{aligned}$$

We follow the conventions of Butler [3] in defining the coupling of two operators. We adopt as a basis of the space of operators

$$\{s^1T_1A_2^0, s^1T_1e^1, s^1T_1e^{-1}\} \quad \text{for } \mathbf{S}, \quad (4)$$

$$\{l^{1+}T_{1g}T_1A_2^0, l^{1+}T_{1g}T_1e^{-1}, l^{1+}T_{1g}T_1e^1\} \quad \text{for } \mathbf{L}, \quad (5)$$

and couple those bases using the coupling coefficients for the chain $O \supset D_3 \supset C_3$, treating the parity and SU_2 labels as parentage labels:

$$\begin{aligned}(\mathbf{S} \otimes \mathbf{L})^3T_{1g}T_1 \cdot T_{1g}A_1A_1A_1^0 \\ = \sum_{\alpha, \beta} \langle T_1\alpha, T_1\beta | 000 \rangle (s^{T_1\alpha} \otimes l^{T_1\beta}).\end{aligned} \quad (6)$$

Expanding the right-hand side we obtain

$$\begin{aligned}(\mathbf{S} \otimes \mathbf{L})^3T_{1g}T_1 \cdot T_{1g}A_1A_1A_1^0 &= \frac{1}{\sqrt{3}} (s^{T_1^1} \otimes l^{T_1^{-1}}) \\ &\quad - \frac{1}{\sqrt{3}} (s^{T_1^0} \otimes l^{T_1^0}) \\ &\quad + \frac{1}{\sqrt{3}} (s^{T_1^{-1}} \otimes l^{T_1^1})\end{aligned} \quad (7)$$

which differs from the expression we seek,

$$\mathcal{H}_{so} = (s_x \otimes l_x) + (s_y \otimes l_y) + (s_z \otimes l_x), \quad (8)$$

in that it is expressed in a different basis. We follow Butler [3] and Piepho and Schatz [8] in relating the $\{x, y, z\}$ basis to the $\{T_11, T_1 - 1, T_10\}$ basis. We have

$$\begin{aligned}o^{T_1^1} &= \frac{1}{\sqrt{2}} o_x + \frac{i}{\sqrt{2}} o_y \\ o^{T_1^{-1}} &= -\frac{1}{\sqrt{2}} o_x + \frac{i}{\sqrt{2}} o_y \\ o^{T_1^0} &= o_z\end{aligned} \quad (9)$$

which implies that

$$\begin{aligned}(\mathbf{S} \otimes \mathbf{L})^3T_{1g}T_1 \cdot T_{1g}A_1A_1A_1^0 &= -\frac{1}{\sqrt{3}} ((s_x \otimes l_x) + (s_y \otimes l_y) \\ &\quad + (s_z \otimes l_z)).\end{aligned} \quad (10)$$

Using this we transliterate \mathcal{H}_{so} into a form that transforms under the same group chain as the states,

$$\begin{aligned}\mathcal{H}_{so} &= -\sqrt{3} [\zeta_{t_{2g}} (\mathbf{S} \otimes \mathbf{L}) [({}^3T_{1g}, {}^1A_{1g})^3T_{1g}, {}^1A_{1g}]^3T_{1g}T_1 \cdot T_{1g}A_1A_1a_1 \\ &\quad + \zeta_{e_g} (\mathbf{S} \otimes \mathbf{L}) [({}^1A_{1g}, {}^3T_{1g})^3T_{1g}, {}^1A_{1g}]^3T_{1g}T_1 \cdot T_{1g}A_1A_1a_1 \\ &\quad - \zeta_{t_{1u}} (\mathbf{S} \otimes \mathbf{L}) [({}^1A_{1g}, {}^1A_{1g})^1A_{1g}, {}^3T_{1g}]^3T_{1g}T_1 \cdot T_{1g}A_1a_1].\end{aligned} \quad (11)$$

Now that the spin-orbit Hamiltonian is in a compatible basis we can proceed with the reduction of the matrix element using the Wigner–Eckart theorem. It is at this stage that $3jm$ (and other coefficients disguised as $3jm$) appear and RACAH shows its worth.

5. APPLICATION OF THE WIGNER–ECKART THEOREM

In this section we apply the Wigner–Eckart theorem several times to the matrix elements we wish to calculate. The Wigner–Eckart theorem [3, Eq. (4.2.3)],

$$\begin{aligned}\langle x_1\lambda_1l_1 | T^\lambda | x_2\lambda_2l_2 \rangle \\ = \sum_r \begin{pmatrix} \lambda_1 \\ l_1 \end{pmatrix} \begin{pmatrix} \lambda^* & \lambda & \lambda_2 \\ l_1^* & l & l_2 \end{pmatrix} \langle x_1\lambda_1 || T^\lambda || x_2\lambda_2 \rangle_r\end{aligned} \quad (12)$$

relates the matrix elements of some operator to a $3jm$ of the transforming group, multiplied by a normalizing factor. This normalizing factor is called a reduced matrix element. This reduced matrix element contains the properties of the operators, T^λ , reduced by the extraction of their transformation properties. In many applications, states and operators transform according to irreps of groups in some chain, $G \supset H$. The Wigner–Eckart theorem may be applied to either group, and the reduced matrix elements with respect to each group may be related to each other. This allows, for example, octahedral reduced matrix elements to be related to SO_3 reduced matrix elements.

Before considering the t_{1u} -shell contribution to \mathcal{H}_{so} we need to introduce some notation. Since we are dealing with matrix elements that are diagonal, except for the multiplicity label r , we denote the bra by $\langle * |$ on the understanding that it has the same labels as the ket, with the possible exception of the multiplicity label. Furthermore, we use $(\mathbf{S} \otimes \mathbf{L})_{t_{1u}}$ to denote what would otherwise be written

$$[(\mathbf{1}^0A_{1g}, \mathbf{1}^0A_{1g})^1A_{1g}, \mathbf{S}^1\mathbf{L}^T_{1g}]^3T_{1g}T_1 \cdot T_{1g}A_1a_1,$$

although we often superscript the last few labels so that we know how far back the operator has been reduced. Through the use of these expedients and the Wigner–

Eckart theorem the t_{1u} -shell contribution to the matrix elements in Eq. (2) can be reduced to the $SU_2 \times O_h$ level in one step, with the result

$$\begin{aligned} & \langle * | \zeta_{t_{1u}}(\mathbf{S} \otimes \mathbf{L})_{t_{1u}}^3 T_{1g} T_1 \cdot T_{1g} A_1 a_1 | \{({}^4A_{2g}, {}^2E_g)^5E_g, {}^2T_{1u}\}^4 T_{2u} U' \\ & \cdot T_{2u} r \lambda \rangle \\ & = \sum_s \begin{pmatrix} {}^4T_{2u} \\ U' \cdot T_{2u} \\ r' \\ \lambda \\ l \end{pmatrix} \begin{pmatrix} {}^4T_{2u} & {}^3T_{1g} & {}^4T_{2u} \\ U' \cdot T_{2u} & T_1 \cdot T_{1g} & U' \cdot T_{2u} \\ r' & 0 & r \\ \lambda & A_1 & \lambda \\ l^* & a_1 & l \end{pmatrix} s_0 \quad (13) \\ & \times \langle * | \zeta_{t_{1u}}(\mathbf{S} \otimes \mathbf{L})_{t_{1u}}^{(1A_{1g}, 1A_{1g})^1 A_{1g}, {}^3T_{1g} \}^3 T_{1g} | \\ & \{({}^4A_{2g}, {}^2E_g)^5E_g, {}^2T_{1u}\}^4 T_{2u} \rangle. \end{aligned}$$

This expression is analogous to Eq. (18.4.6) of Piepho and Schatz [8]. To see this clearly we use a relation between the $3jm$ of a coupled branching, $G \times G \downarrow G$, and a $9j$ for G ,

$$\begin{aligned} & \begin{pmatrix} \lambda_1 \lambda_2 \\ r_1 \\ \lambda \end{pmatrix} \begin{pmatrix} \lambda_1^* \lambda_2^* & \kappa_1 \cdot \kappa_2 & \mu_1 \cdot \mu_2 \\ r_1 & t & r_2 \\ \lambda^* & \kappa & \mu \end{pmatrix}^{s_1 s_2} \\ & = H(\lambda_1 \lambda_2 \lambda) H(\kappa_1 \kappa_2 \kappa) H(\mu_1 \mu_2 \mu) |\lambda|^{1/2} |\kappa|^{1/2} |\mu|^{1/2} \quad (14) \\ & \begin{Bmatrix} \lambda_1 & \lambda_2 & \lambda^* \\ \kappa_1^* & \kappa_2^* & \kappa \\ \mu_1^* & \mu_2^* & \mu \end{Bmatrix} \begin{matrix} r_1 \\ t \\ r_2 \end{matrix} \\ & \begin{matrix} s_1 & s_2 & s \end{matrix} \end{aligned}$$

Since, in the case we are considering κ is restricted to A_1 , we can, after cyclicly permuting the rows of the $9j$, apply Eq. (3.3.36) of Butler [3], yielding a $6j$ plus phase and dimension factors:

$$\begin{aligned} & \begin{pmatrix} U' \cdot T_{2u} \\ r' \\ \lambda \end{pmatrix} \begin{pmatrix} U' \cdot T_{2u} & T_1 \cdot T_{1g} & U' \cdot T_{2u} \\ r' & 0 & r \\ \lambda & A_1 & \lambda \end{pmatrix} s_0 \\ & = |\lambda| \begin{Bmatrix} U' & T_2 & \lambda \\ U' & T_2 & \lambda \\ T_1 & T_1 & A_1 \end{Bmatrix} \begin{matrix} r \\ r' \\ 0 \end{matrix} \\ & \begin{matrix} s & 0 & 0 \end{matrix} \quad (15) \end{aligned}$$

$$\begin{aligned} & = |\lambda|^{1/2} |T_1|^{-1/2} \{T_2\} \{T_2 T_2 T_1\} \{U' T_2 \lambda\} \\ & \begin{Bmatrix} U' & U' & T_1 \\ T_2 & T_2 & \lambda \end{Bmatrix} r' r_0 s. \end{aligned}$$

Returning to the matrix element, Eq. (13), we factor the $3jm$ and substitute the above expression involving the $6j$. Doing this the matrix element can be expressed as

$$\begin{aligned} & \sum_s |\lambda|^{1/2} |T_1|^{-1/2} \{T_2\} \{T_2 T_2 T_1\} \{U' T_2 \lambda\} \begin{Bmatrix} U' & T_2 & \lambda \\ T_2 & U' & T_1 \end{Bmatrix} s_0 r r' \quad (16) \\ & \times \begin{pmatrix} \frac{3}{2} \\ U' \end{pmatrix} \begin{pmatrix} \frac{3}{2} & 1 & \frac{3}{2} \\ U' & T_1 & U' \end{pmatrix} s_0 \begin{pmatrix} \lambda \\ l \end{pmatrix} \begin{pmatrix} \lambda & A_1 & \lambda \\ l^* & a_1 & l \end{pmatrix}. \end{aligned}$$

The last $3jm$ can be written as a $2jm$ times the square root of the dimension of l , one in this case, and divided by the square root of the dimension of λ (Eq. (3.3.8) of Butler [3]). This means the last $2jm$ and $3jm$ become a simple $|\lambda|^{-1/2}$, which cancels one of the dimension factors at the beginning of the expression. The $2j$ phase $\{T_2\}$ is +1 because T_2 is a true irrep. Since the $SO_3 \downarrow O$ $2jm$ is unity, the only obstruction preventing favorable comparison of our expression with Eq. (18.4.6) of Piepho and Schatz [8] is the dimension factor $|T_1|^{-1/2}$. This is explained by the different operators in the reduced matrix element. Since $s_1 u^1 = (1/\sqrt{3}) \zeta(\mathbf{S} \otimes \mathbf{L})$ the two expressions are indeed in agreement ($|T_1| = 3$).

So the final form for this step of the reduction is either Eq. (13) or

$$\begin{aligned} & \langle * | \zeta_{t_{1u}}(\mathbf{S} \otimes \mathbf{L})_{t_{1u}}^3 T_{1g} T_1 \cdot T_{1g} A_1 a_1 | \{({}^4A_{2g}, {}^2E_g)^5E_g, {}^2T_{1g}\} \\ & {}^4T_{2u} U' \cdot T_{2u} r \lambda \rangle \\ & = \sum_s |T_1|^{-1/2} \{T_2 T_2 T_1\} \{U' T_2 \lambda\} \begin{Bmatrix} U' & T_2 & \lambda \\ T_2 & U' & T_1 \end{Bmatrix} s_0 r r' \quad (17) \\ & \begin{pmatrix} \frac{3}{2} & 1 & \frac{3}{2} \\ U' & T_1 & U' \end{pmatrix} s_0 \\ & \times \langle * | \zeta_{t_{1u}}(\mathbf{S} \otimes \mathbf{L})_{t_{1u}}^{(1A_{1g}, 1A_{1g})^1 A_{1g}, {}^3T_{1g} \}^3 T_{1g} | \\ & \{({}^4A_{2g}, {}^2E_g)^5E_g, {}^2T_{1u}\}^4 T_{2u} \rangle. \end{aligned}$$

The next step in the reduction is very like the previous one, except that the group is not O but $SU_2 \times O_h$. Applying the Wigner-Eckart theorem to the partly reduced matrix element gives

Because the matrix elements do not depend on irrep labels lower than the octahedral group we do not take the chain any lower. The matrix element we want to calculate, Eq. (2), can be expressed as a sum over coefficients multiplying reduced matrix elements of the type found on the right-hand side of Eq. (22). RACAH gives us the coefficients of the reduced matrix elements in this expression. The reduced matrix elements themselves are calculated using the procedure outlined in Section 6.

Now we simply ask for the Wigner–Eckart coefficients, with question marks in the place of irreps or multiplicities we wish to range freely. The output is such that, for example, $1/8.5\#2.3 = +1/8 \times 5\sqrt{2} \times 3$

```
weme ((s1.~0+,s0.2+)2.2+,s0.1-)s1.~1-
(s1 s1,~1- ~1) ? %
%>((0.0+,0.0+)0.0+,1.1+)1.1+ (1 1,1+ 1)
0 %
%>((s1.~0+,s0.2+)2.2+,s0.1-)s1.~1- (s1
s1,~1- ~1) ?
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1, ~1- ~1) s0 | ((0.0+, 0.0+) 0.0+,
1.1+) 1.1+(1 1, 1+ 1) 0, ((s1.~0+,
s0.2+) 2.2+, s0.1-) s1.~1-(s1 s1, ~1-
~1) s0) + +1/8.5#2.3
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1, ~1- ~1) \0 s1 | ((0.0+, 0.0+)
0.0+, 1.1+) 1.1+(1 1, 1+ 1) 0,
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1,
~1- ~1) \0 s1) + +1/4.3.5#3
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1, ~1- ~1) \0 s1 | ((0.0+, 0.0+)
0.0+, 1.1+) 1.1+(1 1, 1+ 1) 0,
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1,
~1- ~1) \1 s1) + +1/4.3.5#3
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1, ~1- ~1) \1 s1 | ((0.0+, 0.0+)
0.0+, 1.1+) 1.1+(1 1, 1+ 1) 0,
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1,
~1- ~1) \0 s1) + +1/4.3.5#3
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1, ~1- (s1, ~1- ~1) ~s0 | ((0.0+, 0.0+)
0.0+, 1.1+) 1.1+(1 1, 1+ 1) 0,
((s1.~0+, s0.2+) 2.2+, s0.1-) s1.~1-(s1
s1,
~1- ~1) ~s0) + -1/8.3#2.3
```

This process is repeated for each state with each operator, using the following strings to represent the stated labels. The results are given in Table III.

shell states.

```
eg ((s1.~0+,0.0+)s1.~0+,0.0+)s1.~0+ (s1
s1,~0+ ~0) ?
t1u ((s1.~0+,s0.2+)2.2+,s0.1-)s1.~1- (s1
s1,~1- ~1) ?
t2u ((s1.~0+,s0.2+)2.2+,s0.~1-) (s1
s1,~1- ~1) ?
t2g^* ((1.~1+,0.0+)1.~1+,s0.~1-)s1.~1-
(s1 s1,~1- ~1) ?
```

operator states.

```
t2g ((1.1+,0.0+)1.1+,0.0+)1.1+ (1 1,1+
1) 0
t1u ((0.0+,0.0+)0.0+,1.1+)1.1+ (1 1,1+
1) 0
eg ((0.0+,1.1+)1.1+,0.0+)1.1+ (1 1,1+
1) 0
```

7.1. The State Energies

The matrices obtained by RACAH are not diagonal, and so we must find the eigenvalues of the two by two blocks to obtain the contribution of the spin-orbit interaction to the energy of these states. We multiply those values by the reduced matrix elements of Section 6 to give the energies of the various states.

Those state energies are given in Table IV. We use the notation $|t_{1u}s0\rangle$, for example, to represent the energy of the $s0$ projection state of the t_{1u} level. We give the energies in terms of the ζ 's as well as the explicit values. The values of the free ζ parameters,

$$\zeta_{3d}^{\text{Cr}} = 290 \text{ cm}^{-1}$$

$$\zeta_{4p}^{\text{Cr}} = 50 \text{ cm}^{-1}$$

$$\zeta_{4p}^{\text{Br}} = 2460 \text{ cm}^{-1},$$

are taken from Dillon *et al.* [6]

7.2. The Spin-Orbit Coupling Constant

The spin-orbit coupling constants are defined by

$$\lambda = -\frac{\langle {}^4T_2 || \mathcal{H}_{so} || {}^4T_2 \rangle}{\langle L || L || L \rangle \langle S || S || S \rangle}, \quad (25)$$

where, for this case, $\langle L || L || L \rangle = -\sqrt{6}$ and $\langle S || S || S \rangle = \sqrt{S(S+1)(2S+1)}$.

In this case we need to calculate the reduced matrix elements for \mathcal{H}_{so} as found on the left-hand side of Eq. (22).

We give below examples of how we would input requests to RACAH, for the various factors appearing on the right-hand side of that equation, and how RACAH returns the result. To the right we briefly explain each step.

```
Racah v3.1          Fri Dec 15 09:51:06 1995

>group su2          Selecting a group.
su2

>irrep s1           Obtaining
4 s1 s1 3 - +4      information about
                    and irrep, e.g.
                    dimension=+4

>3j 2 s1 s0         Asking for a 3j
2 s1 s0 +           phase
>3j s1 s1 1
s1 s1 1 +

>6j s0 s0 1 s1 s1 2 Asking for a 6j
s0 s0 1 s1 s1 2 +
+1/2#2.5
```

Putting those values together with Eq. (23) and (24) gives

$$\lambda_{1u} = -\frac{1}{20} \zeta_{4p}^{\text{Br}}. \quad (26)$$

The complete set of spin-orbit coupling coefficients is given in Table V.

8. SUMMARY

We have demonstrated the power and convenience with which RACAH can calculate reduced matrix elements. Extensions of RACAH are planned to take in the simplification of the multicenter reduced matrix elements to single-center reduced matrix elements.

We have given the spin-orbit energies of the charge-transfer states and the spin-orbit coupling constants associated with this. The results of this paper are being used to investigate the Kerr rotation of CrBr_3 , an effect which hinges on the spin-orbit coupling.

A copy of RACAH can be obtained by emailing a message to racah-help@phys.canterbury.ac.nz. RACAH has been compiled and tested under MS-Dos, Unix, and VMS.

REFERENCES

1. M. Abe, and M. Gomi, *J. Magn. Mat.* **84**, 222 (1990).
2. P. M. Argyres, *Phys. Rev.* **97**, 334 (1955).
3. P. H. Butler, *Point Group Symmetry Applications* (Plenum, New York, 1981).
4. P. H. Butler, A. M. Ford, and M. F. Reid, *J. Phys. B: At. Mol. Phys.* **16**, 967 (1983).
5. J. F. Dillon Jr., *J. Magn. Mat.* **84**, 213 (1990).
6. J. F. Dillon Jr., H. Kamimura, and J. P. Remika, *J. Phys. Chem. Solids* **27**, 1531 (1966).
7. W. Jung, *J. Appl. Phys.* **36**, 2422 (1965).
8. S. B. Piepho and P. N. Schatz, *Group Theory in Spectroscopy* (Wiley, New York, 1983).
9. K. Shinagawa, T. Suzuki, T. Saito, and T. Tsushima, *J. Magn. Mat.* **140-144**, 171 (1995).