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Reduced matrix elements of a coupled tensor in a subgroup basis

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Abstract. The reduced matrix elements of a coupled tensor between (i) uncoupled kets and (ii) coupled kets are derived in a group–subgroup basis using the phase choices of Butler.

1. Introduction

The central problem in quantum mechanical calculations, using group theory, is the obtaining of the matrix elements of operators (Wybourne 1974). Most of the operators whose matrix elements we wish to evaluate are expressible in terms of one of the special cases of the coupled tensor operators (Griffith 1962). Butler (1975) derived the reduced matrix elements of coupled tensors in terms of the reduced matrix elements of uncoupled tensors in two cases: (1) the basis states are ordinary (uncoupled) kets; (2) the kets are coupled. Using the Racah factorisation lemma, he related the reduced matrix elements of a tensor between uncoupled subgroup basis kets to the reduced matrix elements of the tensor between uncoupled group basis kets, considering a group–subgroup chain.

In the present paper we extend the work of Butler (1975) to evaluate the reduced matrix elements of a coupled tensor in a group–subgroup basis. The reduced matrix elements of a coupled tensor between the coupled kets of a subgroup H are expressed in terms of $9j$ symbols, $3jm$ factors of $G\supset H$ and the reduced matrix elements of uncoupled tensors between uncoupled kets of the group G. As in the case with the equations given by Butler (1975), the equations derived here are applicable for finite or compact groups. The various special cases of the coupled tensor are discussed. These results can be used to obtain the reduced matrix elements of any tensor between the basis kets of any molecular symmetry group $G\subset SO_3$, since it is easy to obtain the reduced matrix elements of many operators for SO_3. For example, the equations derived in this paper are useful for calculating the reduced matrix elements of spin-independent one-electron operators and the spin-orbit coupling operator for any molecular symmetry group $G\subset SO_3$. As an illustration, we obtain the spin-orbit coupling energy matrix elements for the d^2 configuration under octahedral symmetry.

The notation used throughout this paper is that of Butler (1975). The summation labels are given inside the parentheses immediately next to Σ.

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1. Reduced matrix element (RME) of a coupled tensor between ordinary kets

Let $P^{K_1c_1\epsilon_1}_{\kappa_1}$ and $Q^{K_2c_2\epsilon_2}_{\kappa_2}$ be two tensor operators transforming according to the representations K_1, K_2 of a group G and ϵ_1, ϵ_2 of its subgroup H. c_1, c_2 are the branching multiplicities of ϵ_1, ϵ_2. Then the coupled tensor with respect to H is defined by

$$\{P^{K_1c_1\epsilon_1}Q^{K_2c_2\epsilon_2}\}^{n\epsilon}_{\kappa} = \sum (\kappa_1\kappa_2)|\epsilon|^{1/2}\phi_\epsilon(\epsilon_1\epsilon_2\epsilon)^{n\kappa_1\kappa_2}{}_{\kappa}P^{K_1c_1\epsilon_1}_{\kappa_1}Q^{K_2c_2\epsilon_2}_{\kappa_2} \tag{1.1}$$

where n is the Kronecker multiplicity of ϵ in the product $\epsilon_1\times\epsilon_2$, ϕ_ϵ is the $2j$ phase (§ 4 of Butler 1975) whose value is ± 1, fixed by character theory, and $(\epsilon_1\epsilon_2\epsilon)^{n\kappa_1\kappa_2}{}_{\kappa}$ is a $3jm$ symbol with two of its indices raised (§ 8 of Butler 1975). Let $|x_1\lambda_1a_1\mu_1i_1\rangle$ and $|x_2\lambda_2a_2\mu_2i_2\rangle$ be bases respectively in the representation spaces μ_1 and μ_2 of H. Using Butler (1975) phase choices, the RME of the coupled tensor in (1.1) between these basis states is given by

$$\begin{aligned}&\langle x_1\lambda_1a_1\mu_1\|\{P^{K_1c_1\epsilon_1}Q^{K_2c_2\epsilon_2}\}^{n\epsilon t}\|x_2\lambda_2a_2\mu_2\rangle\\ &\quad=\sum (t_1t_2x\lambda a\mu)|\epsilon|^{1/2}\phi_{\mu_1}\theta(\mu^*\epsilon_2\mu_2t_2)\theta(\mu_1^*\epsilon_1\mu t_1)\begin{Bmatrix}\epsilon_2 & \epsilon^* & \epsilon_1\\ \mu_1 & \mu & \mu_2\end{Bmatrix}_{t_2tt_1n}\\ &\quad\times\langle x_1\lambda_1a_1\mu_1\|P^{K_1c_1\epsilon_1t_1}\|x\lambda a\mu\rangle\langle x\lambda a\mu\|Q^{K_2c_2\epsilon_2t_2}\|x_2\lambda_2a_2\mu_2\rangle,\end{aligned} \tag{1.2}$$

where $\theta(\mu^*\epsilon_2\mu_2t_2)$ is a $3j$ symbol which occurs in the reordering of the $3jm$ symbols; its value is ± 1 (§ 6 of Butler 1975). This equation (1.2) is nothing but equation (19.5) of Butler (1975) written in group–subgroup notation for the subgroup H. Because the tensors in (1.2) are also tensors with respect to G, the RMEs of the uncoupled tensor operators in the subgroup basis can be transformed into RMEs in the group basis using (20.5) of Butler (1975). After using permutational symmetries of $3jm$ factors, (1.2) reads

$$\begin{aligned}&\langle x_1\lambda_1a_1\mu_1\|\{P^{K_1c_1\epsilon_1}Q^{K_2c_2\epsilon_2}\}^{n\epsilon t}\|x_2\lambda_2a_2\mu_2\rangle\\ &\quad=\sum (t_1t_2r_1r_2x\lambda a\mu)|\epsilon|^{1/2}\phi_{\mu_1}\theta(\lambda_1^*\lambda K_1r_1)\\ &\quad\times\theta(K_2\lambda^*\lambda_2r_2)(\lambda_1)^{a_1\mu_1,a_1^*\mu_1^*}(\lambda)^{a\mu,a^*\mu^*}\\ &\quad\times\begin{Bmatrix}\epsilon_2 & \epsilon^* & \epsilon_1\\ \mu_1 & \mu & \mu_2\end{Bmatrix}_{t_2tt_1n}\begin{pmatrix}\lambda_1^* & \lambda & K_1\\ a_1^*\mu_1^* & a\mu & c_1\epsilon_1\end{pmatrix}^{r_1}_{t_1}\begin{pmatrix}K_2 & \lambda^* & \lambda_2\\ c_2\epsilon_2 & a^*\mu^* & a_2\mu_2\end{pmatrix}^{r_2}_{t_2}\\ &\quad\times\langle x_1\lambda_1\|P^{K_1r_1}\|x\lambda\rangle\langle x\lambda\|Q^{K_2r_2}\|x_2\lambda_2\rangle,\end{aligned} \tag{1.3}$$

where $(\lambda_1)^{a_1\mu_1,a_1^*\mu_1^*}$ is a $2jm$ factor whose magnitude is one, and which relates a group $2jm$ symbol to a subgroup $2jm$ symbol (§ 13 of Butler 1975). The $6j$ symbols of a group and its subgroup are related by $3jm$ factors (equation (40) of Butler and Wybourne 1976):

$$\begin{aligned}&\sum (r_4)\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda_3\\ a_1\sigma_1 & a_2\sigma_2 & a_3\sigma_3\end{pmatrix}^{r_4}_{s_4}\begin{Bmatrix}\lambda_1 & \lambda_2 & \lambda_3\\ \mu_1 & \mu_2 & \mu_3\end{Bmatrix}_{r_1r_2r_3r_4}\\ &\quad=\sum (s_1s_2s_3b_1b_2b_3\rho_1\rho_2\rho_3)(\mu_1)^{b_1\rho_1,b_1^*\rho_1^*}(\mu_2)^{b_2\rho_2,b_2^*\rho_2^*}\\ &\quad\times(\mu_3)^{b_3\rho_3,b_3^*\rho_3^*}\begin{pmatrix}\lambda_1 & \mu_2^* & \mu_3\\ a_1\sigma_1 & b_2^*\rho_2^* & b_3\rho_3\end{pmatrix}^{r_1}_{s_1}\begin{pmatrix}\mu_1 & \lambda_2 & \mu_3^*\\ b_1\rho_1 & a_2\sigma_2 & b_3^*\rho_3^*\end{pmatrix}^{r_2}_{s_2}\\ &\quad\times\begin{pmatrix}\mu_1^* & \mu_2 & \lambda_3\\ b_1^*\rho_1^* & b_2\rho_2 & a_3\sigma_3\end{pmatrix}^{r_3}_{s_3}\begin{Bmatrix}\sigma_1 & \sigma_2 & \sigma_3\\ \rho_1 & \rho_2 & \rho_3\end{Bmatrix}_{s_1s_2s_3s_4}.\end{aligned} \tag{1.4}$$

Using the orthogonality of $3jm$ factors, (1.4) can also be written as

$$\sum (r_2r_4\lambda_2a_2)\frac{|\lambda_2|}{|\sigma_2|}\begin{pmatrix}\mu_1 & \lambda_2 & \mu_3^*\\ b_1\rho_1 & a_2\sigma_2 & b_3^*\rho_3^*\end{pmatrix}^{*r_2}_{s_2}\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda_3\\ a_1\sigma_1 & a_2\sigma_2 & a_3\sigma_3\end{pmatrix}^{r_4}_{s_4}\begin{Bmatrix}\lambda_1 & \lambda_2 & \lambda_3\\ \mu_1 & \mu_2 & \mu_3\end{Bmatrix}_{r_1r_2r_3r_4}$$

$$=\sum (s_1s_3b_2\rho_2)(\mu_1)^{b_1\rho_1,b_1^*\rho_1^*}(\mu_2)^{b_2\rho_2,b_2^*\rho_2^*}(\mu_3)^{b_3\rho_3,b_3^*\rho_3^*}$$

$$\times\begin{pmatrix}\lambda_1 & \mu_2^* & \mu_3\\ a_1\sigma_1 & b_2^*\rho_2^* & b_3\rho_3\end{pmatrix}^{r_1}_{s_1}\begin{pmatrix}\mu_1^* & \mu_2 & \lambda_3\\ b_1^*\rho_1^* & b_2\rho_2 & a_3\sigma_3\end{pmatrix}^{r_3}_{s_3}\begin{Bmatrix}\sigma_1 & \sigma_2 & \sigma_3\\ \rho_1 & \rho_2 & \rho_3\end{Bmatrix}_{s_1s_2s_3s_4}. \tag{1.5}$$

In the light of (1.5), (1.3) becomes

$$\langle x_1\lambda_1a_1\mu_1\|\{P^{K_1c_1\epsilon_1}Q^{K_2c_2\epsilon_2}\}^{n\epsilon\eta}\|x_2\lambda_2a_2\mu_2\rangle$$

$$=\sum (r_1r_2rsx\lambda K^*c^*)\phi_{\mu_1}|K||\epsilon|^{-1/2}(\lambda_2)^{a_2\mu_2,a_2^*\mu_2^*}\theta(\lambda_1^*K_1\lambda r_1)\theta(\lambda^*K_2\lambda_2r_2)$$

$$\times\begin{pmatrix}K_2 & K^* & K_1\\ c_2\epsilon_2 & c^*\epsilon^* & c_1\epsilon_1\end{pmatrix}^{r}_{n}\begin{pmatrix}\lambda_1 & K^* & \lambda_2^*\\ a_1\mu_1 & c^*\epsilon^* & a_2^*\mu_2^*\end{pmatrix}^{*s}_{t}\begin{Bmatrix}K_2 & K^* & K_1\\ \lambda_1 & \lambda & \lambda_2\end{Bmatrix}_{r_2sr_1r}$$

$$\times\langle x_1\lambda_1\|P^{K_1r_1}\|x\lambda\rangle\langle x\lambda\|Q^{K_2r_2}\|x_2\lambda_2\rangle. \tag{1.6}$$

2. Reduced matrix element (RME) of a coupled tensor between coupled kets

Let $|(\lambda_1a_1\sigma_1;\lambda_2a_2\sigma_2)m_1\sigma i\rangle$ and $|(\mu_1b_1\rho_1;\mu_2b_2\rho_2)m_2\rho j\rangle$ be bases belonging to the product spaces $\sigma_1\times\sigma_2$ and $\rho_1\times\rho_2$ of H respectively and m_1, m_2 be the Kronecker multiplicities of σ and ρ. Then the RME of the coupled tensor $\{P^{K_1c_1\epsilon_1}Q^{K_2c_2\epsilon_2}\}^{m\epsilon}_{\kappa}$ between the coupled states is given by

$$\langle(\lambda_1a_1\sigma_1;\lambda_2a_2\sigma_2)m_1\sigma\|\{P^{K_1c_1\epsilon_1}Q^{K_2c_2\epsilon_2}\}^{m\epsilon n}\|(\mu_1b_1\rho_1;\mu_2b_2\rho_2)m_2\rho\rangle$$

$$=\sum (n_1n_2)|\sigma\epsilon\rho|^{1/2}\begin{Bmatrix}\sigma_1 & \sigma_2 & \sigma^*\\ \epsilon_1^* & \epsilon_2^* & \epsilon\\ \rho_1^* & \rho_2^* & \rho\end{Bmatrix}^{m_1\,m\,m_2}_{n_1\,n_2\,n}$$

$$\times\langle\lambda_1a_1\sigma_1\|P^{K_1c_1\epsilon_1n_1}\|\mu_1b_1\rho_1\rangle\langle\lambda_2a_2\sigma_2\|Q^{K_2c_2\epsilon_2n_2}\|\mu_2b_2\rho_2\rangle. \tag{2.1}$$

This equation is nothing but equation (19.9) of Butler (1975) written in group–subgroup notation for the subgroup H.

Using (20.5) of Butler (1975), (2.1) can be written as

$$\sum (s_1s_2n_1n_2)|\sigma\epsilon\rho|^{1/2}(\lambda_1)^{a_1\sigma_1,a_1^*\sigma_1^*}(\lambda_2)^{a_2\sigma_2,a_2^*\sigma_2^*}$$

$$\times\begin{pmatrix}\lambda_1^* & K_1 & \mu_1\\ a_1^*\sigma_1^* & c_1\epsilon_1 & b_1\rho_1\end{pmatrix}^{s_1}_{n_1}\begin{pmatrix}\lambda_2^* & K_2 & \mu_2\\ a_2^*\sigma_2^* & c_2\epsilon_2 & b_2\rho_2\end{pmatrix}^{s_2}_{n_2}\begin{Bmatrix}\sigma_1 & \sigma_2 & \sigma^*\\ \epsilon_1^* & \epsilon_2^* & \epsilon\\ \rho_1^* & \rho_2^* & \rho\end{Bmatrix}^{m_1\,m\,m_2}_{n_1\,n_2\,n}$$

$$\times\langle\lambda_1\|P^{K_1s_1}\|\mu_1\rangle\langle\lambda_2\|Q^{K_2s_2}\|\mu_2\rangle. \tag{2.2}$$

The $9j$ symbols of a group and its subgroup are related by

$$\sum (s_3)\begin{pmatrix} \lambda_3 & \mu_3 & \nu_3 \\ a_3\sigma_3 & b_3\rho_3 & c_3\epsilon_3 \end{pmatrix}_{n_3}^{s_3} \begin{Bmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ \mu_1 & \mu_2 & \mu_3 \\ \nu_1 & \nu_2 & \nu_3 \end{Bmatrix}^{r_1 r_2 r_3}_{s_1 s_2 s_3}$$

$$= \sum (m_1 m_2 m_3 n_1 n_2 a_1\sigma_1 a_2\sigma_2 b_1\rho_1 b_2\rho_2 c_1\epsilon_1 c_2\epsilon_2)$$
$$\times \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ a_1\sigma_1 & a_2\sigma_2 & a_3\sigma_3 \end{pmatrix}_{m_1}^{r_1} \begin{pmatrix} \mu_1 & \mu_2 & \mu_3 \\ b_1\rho_1 & b_2\rho_2 & b_3\rho_3 \end{pmatrix}_{m_2}^{r_2}$$
$$\times \begin{pmatrix} \nu_1 & \nu_2 & \nu_3 \\ c_1\epsilon_1 & c_2\epsilon_2 & c_3\epsilon_3 \end{pmatrix}_{m_3}^{r_3} \begin{pmatrix} \lambda_1 & \mu_1 & \nu_1 \\ a_1\sigma_1 & b_1\rho_1 & c_1\epsilon_1 \end{pmatrix}_{n_1}^{*s_1} \begin{pmatrix} \lambda_2 & \mu_2 & \nu_2 \\ a_2\sigma_2 & b_2\rho_2 & c_2\epsilon_2 \end{pmatrix}_{n_2}^{*s_2}$$
$$\times \begin{Bmatrix} \sigma_1 & \sigma_2 & \sigma_3 \\ \rho_1 & .\rho_2 & \rho_3 \\ \epsilon_1 & \epsilon_2 & \epsilon_3 \end{Bmatrix}^{m_1 m_2 m_3}_{n_1 n_2 n_3}. \tag{2.3}$$

An alternative form of this equation is

$$\sum (s_3 r_1 r_2 r_3 \lambda_3 \mu_3 \nu_3 a_3 b_3 c_3) \frac{|\lambda_3\mu_3\nu_3|}{|\sigma_3\rho_3\epsilon_3|} \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ a_1\sigma_1 & a_2\sigma_2 & a_3\sigma_3 \end{pmatrix}_{m_1}^{*r_1} \begin{pmatrix} \mu_1 & \mu_2 & \mu_3 \\ b_1\rho_1 & b_2\rho_2 & b_3\rho_3 \end{pmatrix}_{m_2}^{*r_2}$$
$$\times \begin{pmatrix} \nu_1 & \nu_2 & \nu_3 \\ c_1\epsilon_1 & c_2\epsilon_2 & c_3\epsilon_3 \end{pmatrix}_{m_3}^{*r_3} \begin{pmatrix} \lambda_3 & \mu_3 & \nu_3 \\ a_3\sigma_3 & b_3\rho_3 & c_3\epsilon_3 \end{pmatrix}_{n_3}^{s_3} \begin{Bmatrix} \lambda_1 & \lambda_2 & \lambda_3 \\ \mu_1 & \mu_2 & \mu_3 \\ \nu_1 & \nu_2 & \nu_3 \end{Bmatrix}^{r_1 r_2 r_3}_{s_1 s_2 s_3}$$

$$= \sum (n_1 n_2) \begin{pmatrix} \lambda_1 & \mu_1 & \nu_1 \\ a_1\sigma_1 & b_1\rho_1 & c_1\epsilon_1 \end{pmatrix}_{n_1}^{*s_1}$$
$$\times \begin{pmatrix} \lambda_2 & \mu_2 & \nu_2 \\ a_2\sigma_2 & b_2\rho_2 & c_2\epsilon_2 \end{pmatrix}_{n_2}^{*s_2} \begin{Bmatrix} \sigma_1 & \sigma_2 & \sigma_3 \\ \rho_1 & \rho_2 & \rho_3 \\ \epsilon_1 & \epsilon_2 & \epsilon_3 \end{Bmatrix}^{m_1 m_2 m_3}_{n_1 n_2 n_3}. \tag{2.4}$$

Using (2.4) and complex conjugation of $3jm$ factors (Butler and Wybourne 1976) in (2.2), the RME of the coupled tensor between the coupled kets is given by

$$\langle(\lambda_1 a_1\sigma_1; \lambda_2 a_2\sigma_2) m_1\sigma \| \{P^{K_1c_1\epsilon_1} Q^{K_2c_2\epsilon_2}\}^{m\epsilon n} \| (\mu_1 b_1\rho_1; \mu_2 b_2\rho_2) m_2\rho\rangle$$
$$= \sum (r_1 r_2 r s s_1 s_2 \lambda^* K \mu a^* bc) |\lambda\mu K| \, |\sigma\epsilon\rho|^{-1/2} (\mu)^{b\rho, b^*\rho^*}$$
$$\times (K)^{c\epsilon, c^*\epsilon^*} \begin{pmatrix} \lambda^* & K & \mu \\ a^*\sigma^* & c\epsilon & b\rho \end{pmatrix}_n^{s} \begin{pmatrix} \mu_1 & \mu_2 & \mu^* \\ b_1\rho_1 & b_2\rho_2 & b^*\rho^* \end{pmatrix}_{m_2}^{r_2}$$
$$\times \begin{pmatrix} K_1 & K_2 & K^* \\ c_1\epsilon_1 & c_2\epsilon_2 & c^*\epsilon^* \end{pmatrix}_m^{r} \begin{pmatrix} \lambda_1 & \lambda_2 & \lambda^* \\ a_1\sigma_1 & a_2\sigma_2 & a^*\sigma^* \end{pmatrix}_{m_1}^{*r_1} \begin{Bmatrix} \lambda_1 & \lambda_2 & \lambda^* \\ K_1^* & K_2^* & K \\ \mu_1^* & \mu_2^* & \mu \end{Bmatrix}^{r_1 r r_2}_{s_1 s_2 s}$$
$$\times \langle\lambda_1 \| P^{K_1 s_1} \| \mu_1\rangle \langle\lambda_2 \| Q^{K_2 s_2} \| \mu_2\rangle. \tag{2.5}$$

There are two special cases of a coupled tensor which are of interest for applications. The first case occurs when one of the tensors $P^{K_1c_1\epsilon_1}$, $Q^{K_2c_2\epsilon_2}$ is a unit operator, and the second case occurs when they are coupled to give an overall scalar.

The expression for the RME in (2.5) when $P^{K_1c_1\epsilon_1}$ is the unit operator 1 is

$$\begin{aligned}
&\langle(\lambda_1a_1\sigma_1;\lambda_2a_2\sigma_2)m_1\sigma\|\{1Q^{K_2c_2\epsilon_2}\}^{1\epsilon_2n}\|(\mu_1b_1\rho_1;\mu_2b_2\rho_2)m_2\rho\rangle\\
&\quad=\sum(r_1r_2ss_1\lambda^*\mu a^*b)|\lambda\mu|\,|\sigma\rho|^{-1/2}(\mu)^{b\rho,b^*\rho^*}\phi_\lambda\\
&\quad\times\theta(\mu\lambda^*K_2s)\theta(\lambda_2\lambda^*\lambda_1r_1)\begin{pmatrix}\lambda^* & K_2 & \mu\\ a^*\sigma^* & c_2\epsilon_2 & b\rho\end{pmatrix}^s_n\\
&\quad\times\begin{pmatrix}\mu_1 & \mu_2 & \mu^*\\ b_1\rho_1 & b_2\rho_2 & b^*\rho^*\end{pmatrix}^{r_2}_{m_2}\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda^*\\ a_1\sigma_1 & a_2\sigma_2 & a^*\sigma^*\end{pmatrix}^{*r_1}_{m_1}\begin{Bmatrix}\mu_2 & \lambda_2^* & K_2\\ \lambda & \mu & \lambda_1\end{Bmatrix}^*_{r_2r_1ss_1}\\
&\quad\times\langle\lambda_2\|Q^{K_2s_1}\|\mu_2\rangle\delta_{\lambda_1\mu_1}\delta_{a_1b_1}\delta_{\sigma_1\rho_1}.
\end{aligned}\tag{2.6}$$

Similarly, when $Q^{K_2c_2\epsilon_2}$ is the unit operator one obtains

$$\begin{aligned}
&\langle(\lambda_1a_1\sigma_1;\lambda_2a_2\sigma_2)m_1\sigma\|\{P^{K_1c_1\epsilon_1}1\}^{1\epsilon_1n}\|(\mu_1b_1\rho_1;\mu_2b_2\rho_2)m_2\rho\rangle\\
&\quad=\sum(r_1r_2ss_1\lambda^*\mu a^*b)|\lambda\mu|\,|\sigma\rho|^{-1/2}\phi_{\mu_1}(\mu)^{b\rho,b^*\rho^*}\\
&\quad\times\theta(\mu_1^*\lambda_1K_1^*s_1)\theta(\lambda_1\lambda_2\lambda^*r_1)\begin{pmatrix}\mu^* & \mu_1 & \mu_2\\ b^*\rho^* & b_1\rho_1 & b_2\rho_2\end{pmatrix}^{r_2}_{m_2}\\
&\quad\times\begin{pmatrix}\lambda^* & K_1 & \mu\\ a^*\sigma^* & c_1\epsilon_1 & b\rho\end{pmatrix}^s_n\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda^*\\ a_1\sigma_1 & a_2\sigma_2 & a^*\sigma^*\end{pmatrix}^{*r_1}_{m_1}\begin{Bmatrix}\mu & \lambda^* & K_1\\ \lambda_1 & \mu_1 & \lambda_2^*\end{Bmatrix}_{r_2r_1s_1s}\\
&\quad\times\langle\lambda_1\|P^{K_1s_1}\|\mu_1\rangle\delta_{\lambda_2\mu_2}\delta_{a_2b_2}\delta_{\sigma_2\rho_2}.
\end{aligned}\tag{2.7}$$

In the second case, when the tensors are coupled to a scalar, the RME in (2.5) is given by

$$\begin{aligned}
&\langle(\lambda_1a_1\sigma_1;\lambda_2a_2\sigma_2)m_1\sigma\|\{P^{K_1c_1\epsilon_1}Q^{K_1^*c_1^*\epsilon_1^*}\}^{111}\|(\mu_1b_1\rho_1;\mu_2b_2\rho_2)m_2\sigma\rangle\\
&\quad=\sum(r_1r_2s_1s_2\lambda^*a^*)\frac{|\lambda|}{|K_1|}\frac{|\epsilon_1|^{1/2}}{|\sigma|^{1/2}}(K_1)^{c_1\epsilon_1,c_1^*\epsilon_1^*}\\
&\quad\times\phi_{\mu_1}\phi_{\epsilon_1}\theta(\lambda_1\mu_1^*K_1^*s_1)\theta(\mu_1^*\mu_2^*\lambda r_2)\begin{pmatrix}\mu_1 & \mu_2 & \lambda^*\\ b_1\rho_1 & b_2\rho_2 & a^*\sigma^*\end{pmatrix}^{r_2}_{m_2}\\
&\quad\times\begin{pmatrix}\lambda_1 & \lambda_2 & \lambda^*\\ a_1\sigma_1 & a_2\sigma_2 & a^*\sigma^*\end{pmatrix}^{*r_1}_{m_1}\begin{Bmatrix}\lambda_1^* & \mu_1 & K_1\\ \mu_2 & \lambda_2 & \lambda\end{Bmatrix}^*_{r_1r_2s_2s_1}\\
&\quad\times\langle\lambda_1\|P^{K_1s_1}\|\mu_1\rangle\langle\lambda_2\|Q^{K_1^*s_2}\|\mu_2\rangle.
\end{aligned}\tag{2.8}$$

When one of the tensors is the unit operator, equation (1.6) reduces to (20.5) of Butler (1975). In the second case, for the RME in (1.6) one has

$$\begin{aligned}
&\langle x_1\lambda_1a_1\mu_1\|\{P^{K_1c_1\epsilon_1}Q^{K_1^*c_1^*\epsilon_1^*}\}^{111}\|x_1\lambda_1a_1\mu_1\rangle\\
&\quad=\sum(r_1x\lambda)\phi_{\lambda_1}|\lambda_1,K_1|^{-1}|\epsilon_1,\mu_1|^{1/2}(K_1)^{c_1\epsilon_1,c_1^*\epsilon_1^*}\theta(\lambda_1^*\lambda K_1r_1)\\
&\quad\times\langle x_1\lambda_1\|P^{K_1r_1}\|x\lambda\rangle\langle x\lambda\|Q^{K_1^*r_1}\|x_1\lambda_1\rangle.
\end{aligned}\tag{2.9}$$

As an example, consider the spin-orbit coupling energy matrices for the d^2 configuration under octahedral symmetry. They were calculated and tabulated by Griffith (1971, p 418). Here we calculate two matrix elements using some of the equations derived in this section.

The RME of the coupled tensor $\{P^{K_1c_1\epsilon_1}Q^{K_1^*c_1^*\epsilon_1^*}\}_1^{11}$ between the coupled states, when the tensors are coupled to a scalar, is given by, using equation (2.1),

$$\begin{aligned}
&\langle(\lambda_1a_1\sigma_1;\ \lambda_2a_2\sigma_2)m_1\sigma\|\{P^{K_1c_1\epsilon_1}Q^{K_1^*c_1^*\epsilon_1^*}\}^{111}\|(\mu_1b_1\rho_1;\ \mu_2b_2\rho_2)m_2\sigma\rangle\\
&\quad=\sum(s_1s_2)|\sigma|^{1/2}|\epsilon|^{-1/2}\phi_{\rho_1}\theta(\sigma_1\rho_1^*\epsilon_1^*s_1)\\
&\quad\times\theta(\rho_1^*\rho_2^*\sigma m_2)\begin{Bmatrix}\sigma_1 & \rho_1^* & \epsilon_1^*\\ \rho_2^* & \sigma_2^* & \sigma^*\end{Bmatrix}_{m_1m_2s_2s_1}\\
&\quad\times\langle\lambda_1a_1\sigma_1\|P^{K_1c_1\epsilon_1s_1}\|\mu_1b_1\rho_1\rangle\langle\lambda_2a_2\sigma_2\|Q^{K_1^*c_1^*\epsilon_1^*s_2}\|\mu_2b_2\rho_2\rangle. \qquad (2.10)
\end{aligned}$$

Consider the matrix element

$$\langle t_2^2(^1A_1)A_1i|\mathscr{H}_S|t_2^2(^3T_1)A_1i\rangle=2\zeta\langle t_2^2(^1A_1)A_1\|\boldsymbol{l}(1)\cdot\boldsymbol{s}(1)\|t_2^2(^3T_1)A_1\rangle$$

where

$$\mathscr{H}_S=\sum_{i=1}^{2}\zeta\boldsymbol{l}(i)\cdot\boldsymbol{s}(i)$$

(using the Wigner–Eckart theorem). Writing this RME in the group–subgroup notation and $l(1)\cdot s(1)=\sqrt{3}\{\boldsymbol{l}_{(1)}^{1T_1}\boldsymbol{s}_{(1)}^{1T_1}\}^{0A_1}$, and applying equation (2.10), we obtain

$$\begin{aligned}
&\langle t_2^2(0A_1;\ 0A_1)A_1\|\mathscr{H}_S\|t_2^2(1T_1;\ 1T_1)A_1\rangle\\
&\quad=\zeta 2\phi_{T_1}\theta(A_1T_1T_1)\theta(T_1T_1A_1)\begin{Bmatrix}A_1 & T_1 & T_1\\ T_1 & A_1 & A_1\end{Bmatrix}\\
&\quad\times\langle t_2^2 0A_1\|\boldsymbol{l}^{1T_1}(1)\|t_2^2 1T_1\rangle\langle 0A_1\|\boldsymbol{s}^{1T_1}(1)\|1T_1\rangle\\
&\quad=\zeta(2/\sqrt{3})\langle t_2^2 0A_1\|\boldsymbol{l}^{1T_1}(1)\|t_2^2 1T_1\rangle\langle 0A_1\|\boldsymbol{s}^{1T_1}(1)\|1T_1\rangle. \qquad (2.11)
\end{aligned}$$

The kets on the right-hand side of equation (2.11) are again coupled kets, and hence we can use equations (2.6) and (2.7) to evaluate them. Thus

$$\begin{aligned}
&\langle 0A_1\|\boldsymbol{s}^{1T_1}(1)\|1T_1\rangle=\langle(\tfrac{1}{2}E';\ \tfrac{1}{2}E')0A_1\|\boldsymbol{s}^{1T_1}(1)\|(\tfrac{1}{2}E';\ \tfrac{1}{2}E')1T_1\rangle\\
&\quad=\frac{3}{\sqrt{3}}\theta(101)\theta(\tfrac{1}{2}0\tfrac{1}{2})\begin{pmatrix}0 & 1 & 1\\ A_1 & T_1 & T_1\end{pmatrix}\begin{pmatrix}\tfrac{1}{2} & \tfrac{1}{2} & 1\\ E' & E' & T_1\end{pmatrix}\\
&\quad\times\begin{pmatrix}\tfrac{1}{2} & \tfrac{1}{2} & 0\\ E' & E' & A_1\end{pmatrix}\begin{Bmatrix}\tfrac{1}{2} & \tfrac{1}{2} & 1\\ 0 & 1 & \tfrac{1}{2}\end{Bmatrix}\langle\tfrac{1}{2}\|\boldsymbol{s}(1)\|\tfrac{1}{2}\rangle\\
&\quad=-\sqrt{3}\times(1/\sqrt{6})\times(\sqrt{3}/\sqrt{2})=-\sqrt{3}/2.
\end{aligned}$$

Before calculating the RME of $\boldsymbol{l}$, we have to rewrite the two electron states as (Griffith 1962)

$$|a^2h\theta\rangle=|a(1)a(2)h\theta\rangle \qquad (2.12)$$

and

$$|abh\theta\rangle=(1/\sqrt{2})|a(1)b(2)h\theta\rangle+(1/\sqrt{2})(-1)^{S+h+a+b}|b(1)a(2)h\theta\rangle$$

and then apply equation (2.7).

Because we do not have all the $3jm$ factors for $SO_3\supset O$ which are necessary to make use of (2.7), we use the step previous to it, namely a particular case of (2.2) when $Q^{K_2c_2\epsilon_2}$

is the unit operator:

$$
\begin{aligned}
\langle(\lambda_1 a_1\sigma_1;\lambda_2 a_2\sigma_2)r_1\sigma\|\{P^{K_1c_1\epsilon_1}1\}^{1K_1c_1\epsilon_1 s}\|(\mu_1 b_1\rho_1;\mu_2 b_2\rho_2)r_2\rho\rangle
&=\sum(s_1s_2)|\sigma\rho|^{1/2}\phi_{\sigma_1}\theta(\rho_1^*\sigma_1\epsilon_1^*s_1)\theta(\sigma^*\sigma_1\sigma_2r_1)\\
&\quad\times(\lambda_1)^{a_1\sigma_1,a_1^*\sigma_1^*}\begin{pmatrix}\lambda_1^* & K_1 & \mu_1\\ a_1^*\sigma_1^* & c_1\epsilon_1 & b_1\rho_1\end{pmatrix}_{s_1}^{s_2}\begin{Bmatrix}\rho & \sigma^* & \epsilon_1\\ \sigma_1 & \rho_1 & \sigma_2^*\end{Bmatrix}_{r_2r_1s_1s}\\
&\quad\times\langle\lambda_1\|P^{K_1s_2}\|\mu_1\rangle\delta_{\lambda_2\mu_2}\delta_{a_2b_2}\delta_{\sigma_2\rho_2}.
\end{aligned}
\tag{2.13}
$$

We obtain

$$
\begin{aligned}
\langle t_2^2 0A_1\|l^{1T_1}(1)\|t_2^2 1T_1\rangle&=\langle(2t_2(1)2t_2(2))A_1\|l^{1T_1}(1)\|(2t_2(1)2t_2(2))T_1\rangle\\
&=\sqrt{3}\phi_{T_1}\phi_{T_1}\theta(T_2T_2T_1)\theta(T_2T_2A_1)\begin{pmatrix}2 & 1 & 2\\ T_2 & T_1 & T_2\end{pmatrix}\\
&\quad\times\langle 2\|l(1)\|2\rangle\begin{Bmatrix}T_1 & A_1 & T_1\\ T_2 & T_2 & T_2\end{Bmatrix}\\
&=-\sqrt{3}(-1/\sqrt{5})\sqrt{30}(-1/3)=-\sqrt{2}.
\end{aligned}
$$

Thus

$$
\langle t_2^2(^1A_1i)A_1|\mathscr{H}_S|t_2^2(^3T_1)A_1i\rangle=\zeta(2/\sqrt{3})(\sqrt{3}/2)(-\sqrt{2})=\sqrt{2}\zeta.
$$

Similarly,

$$
\begin{aligned}
\langle t_2^2(^1A_1)A_1i|\mathscr{H}_S|t_2e(^3T_1)A_1i\rangle&=(2/\sqrt{3})\zeta\langle t_2^2A_1\|l^{1T_1}(1)\|t_2eT_1\rangle\langle 0A_1\|s^{1T_1}(1)\|1T_1\rangle\\
&=\zeta(2/\sqrt{3})(-\sqrt{3}/2)\langle t_2^2A_1\|l^{1T_1}(1)\|t_2eT_1\rangle\\
&=(-1/\sqrt{2})\zeta\langle 2t_2(1)2t_2(2)A_1\|l^{1T_1}(1)\|2t_2(1)2e(2)T_1\rangle\\
&\quad-(1/\sqrt{2})\zeta(-1)^{1+T_1+T_2+E}\langle 2t_2(1)2t_2(2)A_1\|l^{1T_1}(1)\|2e(1)2t_2(2)T_1\rangle\\
&\qquad\qquad\text{(using equations (2.12))}\\
&=-(1/\sqrt{2})\zeta\langle 2t_2(1)2t_2(2)A_1\|l^{1T_1}(1)\|2e(1)2t_2(2)T_1\rangle
\end{aligned}
$$

(where the first matrix element disappeared because of the delta function occurring in equation (2.13))

$$
\begin{aligned}
&=-(1/\sqrt{2})\sqrt{3}\zeta\phi_{T_1}\phi_{T_1}\theta(ET_2T_1)\theta(T_2T_2A_1)\begin{pmatrix}2 & 1 & 2\\ T_2 & T_1 & E\end{pmatrix}\\
&\quad\times\langle 2\|l(1)\|2\rangle\begin{Bmatrix}T_1 & A_1 & T_1\\ T_2 & E & T_2\end{Bmatrix}\\
&=\zeta(\sqrt{3}/\sqrt{2})\times(\sqrt{2}/\sqrt{5})\times\sqrt{30}\times(-1/3)=-\sqrt{2}\zeta.
\end{aligned}
$$

Similarly the other matrix elements can be calculated.

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