

Three-dimensional rotational averages in radiation-molecule interactions: an irreducible cartesian tensor formulation

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Abstract. In this paper we present a new method for the calculation of the rotational averages which arise in the theory of spectroscopic radiation-molecule interactions in fluid media. Based upon the principles of irreducible cartesian tensor analysis, the method presented allows us to express results either in the usual reducible form, or directly in terms of linearly independent sets of irreducible tensor products. For interactions up to and including rank 3 in the molecular response (or non-linear susceptibility) tensor, the rotational averages cast in terms of irreducible tensor products are considerably simpler in structure than the corresponding results expressed in reducible form.

1. Introduction

In the study of molecule-radiation interactions it is often the case that the principal observable, for example the quantum transition rate or scattering intensity, depends upon the orientation of sample molecules with respect to the radiation field. Within the framework of molecular quantum electrodynamics, the rate and intensity parameters associated with such interactions are normally described in terms of the Fermi golden rule. Most processes are *incoherent*, in the sense that they do not depend on exact phase-matching between the incident and any emergent photons, and the observable can be expressed in terms of the square modulus of a quantum-mechanical probability amplitude, M_{fi} , constructed from a contraction of two tensors. Adopting the implied summation convention for repeated tensor indices, we can express M_{fi} for a process which involves n photon-molecule interactions occurring at any one centre as a series of the form

$$M_{fi} = S_{i_1 \dots i_n} T_{i_1 \dots i_n} + S'_{i_1 \dots i_{n+1}} T'_{i_1 \dots i_{n+1}} + \dots \quad (1.1)$$

Here the first term, comprising the contraction of two rank- n tensors, represents the leading term, usually the electric dipole approximation, for the n photon-molecule interaction, whilst successive terms involving higher-rank tensor contractions represent higher-order multipolar corrections to the probability amplitude: the tensors $T_{i_1 \dots i_n}$ and $T'_{i_1 \dots i_{n+1}}$ are the corresponding molecular response tensors, and $S_{i_1 \dots i_n}$ and $S'_{i_1 \dots i_{n+1}}$ are the polarisation tensors constructed from products of radiation field vectors [1].

Taking the square modulus of the matrix element gives

$$\begin{aligned} |M_{fi}|^2 = & S_{i_1 \dots i_n} \bar{S}_{j_1 \dots j_n} T_{i_1 \dots i_n} \bar{T}_{j_1 \dots j_n} + S_{i_1 \dots i_n} \bar{S}'_{j_1 \dots j_{n+1}} T_{i_1 \dots i_n} \bar{T}'_{j_1 \dots j_{n+1}} \\ & + \bar{S}_{i_1 \dots i_n} \bar{S}'_{j_1 \dots j_{n+1}} \bar{T}_{i_1 \dots i_n} T'_{j_1 \dots j_{n+1}} + \dots \end{aligned} \quad (1.2)$$

If the sample is a fluid or gas it is necessary to account for the random orientation of the molecules within the sample. To this end it is usually necessary to rotationally average a result derived for the case where the laboratory and molecular frames are fixed with respect to one another. For such systems, the leading term for the observable, $A^{(2n)}$, can be written as

$$A^{(2n)} = \langle T_{i_1 \dots i_n} S_{i_1 \dots i_n} \bar{T}_{i_{n+1} \dots i_{2n}} \bar{S}_{i_{n+1} \dots i_{2n}} \rangle \quad (1.3)$$

where the angle brackets denote the rotational average. Thus, for example, single-photon absorption ($n=1$) requires a rank-2 tensor average, two-photon absorption and Raman scattering ($n=2$) require a fourth-rank rotational average, and three-photon absorption and hyper-Raman scattering ($n=3$) require elucidation of the sixth-rank rotational average [2-9].

In the normal trigonometric method for deriving the appropriate averages, the molecular-fixed parameters are first transformed into a molecular-fixed frame, denoted in this paper by Greek indices, through the relation

$$T_{i_1 \dots i_n} = l_{i_1 \lambda_1} \dots l_{i_n \lambda_n} T_{\lambda_1 \dots \lambda_n} \quad (1.4)$$

where $l_{\lambda_j i_p}$ represents the direction cosine of the angle between the molecule-fixed λ_j axis and the laboratory-fixed i_p axis, as may be expressed in terms of Euler angles φ , θ and ψ . The required even-rank rotational average is then obtained by inserting equation (1.4) into (1.3) and then integrating over the Euler angles, i.e.

$$A^{(2n)} = (8\pi^2)^{-1} T_{i_1 \dots i_n} \bar{T}_{i_{n+1} \dots i_{2n}} S_{\lambda_1 \dots \lambda_n} \bar{S}_{\lambda_{n+1} \dots \lambda_{2n}} \\ \times \int_0^{2\pi} \int_0^\pi \int_0^{2\pi} l_{i_1 \lambda_1} \dots l_{i_{2n} \lambda_{2n}} \sin \theta \, d\varphi \, d\theta \, d\psi. \quad (1.5)$$

As n increases, the trigonometric evaluation of results of this form becomes a problem of rapidly escalating difficulty. Each index can represent either x , y or z , and hence there are 3^{4n} separate integrals to evaluate. The problem of isotropically averaging tensor quantities of this type has often been addressed in the limited context of particular physical processes. In earlier papers, Andrews *et al* [7, 10] developed a systematic, *non*-trigonometric, matrix-based procedure, giving explicit results up to rank 8 ($n=4$) whilst the logistics of the problem recently led Wagnière [8] and McClain *et al* [9] to evaluate the integrals computationally, obtaining results up to rank 10 ($n=5$).

In § 2 of this paper it is shown that, in the *non*-trigonometric method of rotational averaging, expressions of the form of equation (1.3) can be further simplified by casting both the molecular and polarisation tensors into their embedded irreducible cartesian forms. This method has two distinct advantages. First, the results are cast in terms of a linearly independent irreducible basis set in which each component can be characterised by its rotational transformation properties: previous averaging treatments have generally necessitated subsequent irreducible tensor development in order to perform a full symmetry analysis. Second, the transformation to an irreducible basis set means that the rotational averaging matrices are brought into block diagonal form, simplifying the results considerably. In § 3, development of these results illustrates their correspondence with conventional rotational averages, while in § 4 it is demonstrated that the procedure can be extended to tensor averages of odd rank, so facilitating evaluation of the rotational averages of the higher-order correction terms in equation (1.2).

2. Calculational procedure

The procedure for calculation of the rotational averages of the type given in equation (1.3) involves consideration of the linear transformation properties of the tensors involved. Since the integrand in (1.5) must be rotationally invariant, it forms a basis for a totally symmetric irreducible representation of the rotation-inversion group $SO(3)$. We can ascertain the exact form of this basis by expressing each tensor as a sum of its embedded irreducible tensor components [11-13]†.

In general, a reducible tensor of rank n can be written as a sum of irreducible parts of weights j ($0 \leq j \leq n$), each of which is associated with a multiplicity $N_n^{(j)}$ given by [14]

$$N_n^{(j)} = \sum_k (-1)^k \begin{bmatrix} n \\ k \end{bmatrix} \begin{bmatrix} 2n-3k-j-2 \\ n-2 \end{bmatrix} \quad (2.1)$$

where $0 \leq k \leq [(n-j)/3]$. Each irreducible tensor has $(2j+1)$ independent components, so that the total number of components is

$$\sum_j (2j+1) N_n^{(j)} = 3^n \quad (2.2)$$

as required. The reduction of the tensors in (1.2) into irreducible parts thus takes the following form:

$$T_{i_1 \dots i_n} = \sum_{j=0}^n \sum_{p=1}^{N_n^{(j)}} T_{i_1 \dots i_n}^{(j;p)} \quad (2.3)$$

$$\bar{T}_{i_{n+1} \dots i_{2n}} = \sum_{j'=0}^n \sum_{q=1}^{N_n^{(j')}} \bar{T}_{i_{n+1} \dots i_{2n}}^{(j';q)} \quad (2.4)$$

$$S_{i_1 \dots i_n} = \sum_{j''=0}^n \sum_{r=1}^{N_n^{(j'')}} S_{i_1 \dots i_n}^{(j'';r)} \quad (2.5)$$

$$\bar{S}_{i_{n+1} \dots i_{2n}} = \sum_{j'''=0}^n \sum_{s=1}^{N_n^{(j'''')}} \bar{S}_{i_{n+1} \dots i_{2n}}^{(j''';s)} \quad (2.6)$$

We now consider the substitution of these results into (1.2), where there are index contractions involving coupling between the tensors represented by (2.3) and (2.5), and also between those represented by (2.4) and (2.6). It is well known that the coupling of two tensors of weights j and j'' results in a tensor represented by weights j^* in the range $|j-j''| \leq j^* \leq j+j''$. However, the n -fold contraction of two tensors of rank n must give rise to a scalar result; therefore products of the type $T_{i_1 \dots i_n}^{(j;p)} S_{i_1 \dots i_n}^{(j'';r)}$ will only be non-vanishing when $j^*=0$, and this can only occur when $j=j''$. Similar reasoning shows that $j'=j'''$, and hence the substitution of equations (2.3)-(2.6) into (1.2), must give the result

$$\langle |T_{i_1 \dots i_n} S_{i_1 \dots i_n}|^2 \rangle = \sum_{j,j'} \sum_{p,q} \sum_{r,s}^{N_n^{(j)} N_n^{(j')}} \langle T_{i_1 \dots i_n}^{(j;p)} \bar{T}_{i_{n+1} \dots i_{2n}}^{(j';q)} S_{i_1 \dots i_n}^{(j;r)} \bar{S}_{i_{n+1} \dots i_{2n}}^{(j';s)} \rangle \quad (2.7)$$

Equation (2.7) can be re-expressed in a natural form [12, 13] through the use of the

† Note that in [12] the last two column headings of table III should be interchanged, and $T_{(j)n}$ becomes $T_{(n)j}$.

mapping formulae

$$T_{i_1 \dots i_n}^{(j;p)} = G_{i_1 \dots i_n; k_1 \dots k_j}^{(0;p)} t_{k_1 \dots k_j}^{(j;p)} \quad (2.8)$$

$$\bar{T}_{i_{n+1} \dots i_{2n}}^{(j;q)} = G_{i_{n+1} \dots i_{2n}; l_1 \dots l_j}^{(0;q)} \bar{t}_{l_1 \dots l_j}^{(j;q)} \quad (2.9)$$

$$S_{i_1 \dots i_n}^{(j;r)} = G_{i_1 \dots i_n; m_1 \dots m_j}^{(0;r)} s_{m_1 \dots m_j}^{(j;r)} \quad (2.10)$$

$$\bar{S}_{i_{n+1} \dots i_{2n}}^{(j;s)} = G_{i_{n+1} \dots i_{2n}; n_1 \dots n_j}^{(0;s)} \bar{s}_{n_1 \dots n_j}^{(j;s)}. \quad (2.11)$$

Here $G_{i_1 \dots i_n; n_1 \dots n_j}^{(0;s)}$ represents a rank- $(n+j)$ -invariant symmetry preserving mapping from the weight- j , rank- j subspace into a weight- j , rank- n irreducible subspace. Substitution of these identities into (2.7) gives

$$\begin{aligned} \langle |T_{i_1 \dots i_n} S_{i_1 \dots i_n}|^2 \rangle &= \sum_{j,j'=0}^n \sum_{p,q} N_n^{(j)} N_n^{(j')} \langle G_{i_1 \dots i_n; k_1 \dots k_j}^{(0;p)} t_{k_1 \dots k_j}^{(j;p)} G_{i_{n+1} \dots i_{2n}; l_1 \dots l_j}^{(0;q)} \bar{t}_{l_1 \dots l_j}^{(j;q)} \\ &\quad \times G_{i_1 \dots i_n; m_1 \dots m_j}^{(0;r)} s_{m_1 \dots m_j}^{(j;r)} G_{i_{n+1} \dots i_{2n}; n_1 \dots n_j}^{(0;s)} \bar{s}_{n_1 \dots n_j}^{(j;s)} \rangle. \end{aligned} \quad (2.12)$$

In order to develop (2.12) further, we note that by projecting the two invariant mappings given expression in (2.8) and (2.9) to their dual bases, through use of the metric tensor $g_{pq}^{(n;j)}$, i.e.

$$G_{i_1 \dots i_n; k_1 \dots k_j}^{(0;p)} = \sum_{p'} g_{pp'}^{(n;j)} \tilde{G}_{k_1 \dots k_j; i_1 \dots i_n}^{(0;p')} \quad (2.13)$$

$$G_{i_{n+1} \dots i_{2n}; l_1 \dots l_j}^{(0;q)} = \sum_{q'} g_{qq'}^{(n;j')} \tilde{G}_{l_1 \dots l_j; i_{n+1} \dots i_{2n}}^{(0;q')} \quad (2.14)$$

it is possible to conduct an n -fold index contraction to give a new mapping between two rank- j subspaces [12, 13]:

$$\tilde{G}_{k_1 \dots k_j; i_1 \dots i_n}^{(0;p')} G_{i_1 \dots i_n; m_1 \dots m_j}^{(0;r)} = \delta_{p'r} E_{k_1 \dots k_j; m_1 \dots m_j}^{(j)}. \quad (2.15)$$

The invariant tensor mapping operator $E_{k_1 \dots k_j; m_1 \dots m_j}^{(j)}$ represents a mapping from the rank- j space to the natural rank- j , and hence weight- j , subspace. By exploiting the idempotent nature of this operator when it operates upon rank- j natural tensors, substitution of equations (2.13)–(2.15) into (2.12) gives the result

$$\langle |T_{i_1 \dots i_n} S_{i_1 \dots i_n}|^2 \rangle = \sum_{j=0}^n \sum_{p,q} N_n^{(j)} N_n^{(j')} g_{pr}^{(n;j)} g_{qs}^{(n;j')} \langle t_{k_1 \dots k_j}^{(j;p)} \bar{t}_{l_1 \dots l_j}^{(j;q)} s_{k_1 \dots k_j}^{(j;r)} \bar{s}_{l_1 \dots l_j}^{(j;s)} \rangle. \quad (2.16)$$

The isotropic average can now be directly evaluated, by taking the weight-0 isotropic part of the tensor product $t_{k_1 \dots k_j}^{(j;p)} \bar{t}_{l_1 \dots l_j}^{(j;q)}$ and contracting the result with $s_{k_1 \dots k_j}^{(j;r)} \bar{s}_{l_1 \dots l_j}^{(j;s)}$. As before, the isotropic part of such tensor products is only non-vanishing when $j=j'$, and the relation takes the form

$$(t_{k_1 \dots k_j}^{(j;p)} \bar{t}_{l_1 \dots l_j}^{(j;q)})^{(0)} = \delta_{jj'} t_{i_1 \dots i_j}^{(j;p)} \bar{t}_{i_1 \dots i_j}^{(j;q)} (2j+1)^{-1} E_{k_1 \dots k_j; l_1 \dots l_j}^{(j)} \quad (2.17)$$

which on substitution into (2.16) gives

$$\langle |T_{i_1 \dots i_n} S_{i_1 \dots i_n}|^2 \rangle = \sum_{j=0}^n (2j+1)^{-1} \sum_{p,q} N_n^{(j)} N_n^{(j')} g_{pr}^{(n;j)} g_{qs}^{(n;j)} t_{\lambda_1 \dots \lambda_j}^{(j;p)} \bar{t}_{\lambda_1 \dots \lambda_j}^{(j;q)} s_{k_1 \dots k_j}^{(j;r)} \bar{s}_{k_1 \dots k_j}^{(j;s)}. \quad (2.18)$$

This is the central result for the rotational average, as expressed in terms of natural tensors. It is important to note that it is only those tensor products where all weights are the same that contribute to the average.

Equation (2.18) can be suitably embedded in the computationally more convenient rank- n tensor space by use of the following identity proved in appendix 1:

$$t_{\lambda_1 \dots \lambda_j}^{(j;p)} t_{\lambda_1 \dots \lambda_j}^{(j;q)} S_{k_1 \dots k_j}^{(j;r)} S_{k_1 \dots k_j}^{(j;s)} = (g_{pq}^{(n;j)} g_{rs}^{(n;j)})^{-1} T_{\lambda_1 \dots \lambda_n}^{(j;p)} T_{\lambda_1 \dots \lambda_n}^{(j;q)} S_{k_1 \dots k_n}^{(j;r)} S_{k_1 \dots k_n}^{(j;s)} \quad (2.19)$$

which is valid provided no elements of the metric tensor $g^{(n;j)}$ are zero. (In fact zeros only occur for $n > 3$.) Inserting (2.19) into (2.18) gives the desired final result:

$$\begin{aligned} & \langle |T_{i_1 \dots i_n} S_{i_1 \dots i_n}|^2 \rangle \\ &= \sum_{j=0}^n (2j+1)^{-1} \sum_{p,q}^{N_n^{(j)}} \sum_{r,s}^{N_n^{(j)}} \left(\frac{g_{pr}^{(n;j)}}{g_{pq}^{(n;j)}} \frac{g_{qs}^{(n;j)}}{g_{rs}^{(n;j)}} \right) \\ & \quad \times T_{\lambda_1 \dots \lambda_n}^{(j;p)} \bar{T}_{\lambda_1 \dots \lambda_n}^{(j;q)} S_{k_1 \dots k_n}^{(j;r)} \bar{S}_{k_1 \dots k_n}^{(j;s)}. \end{aligned} \quad (2.20)$$

Here the Greek indices indicate, as before, reference to a molecule-fixed frame in which the molecular response tensors are rotation invariant. Since the only matrix elements which are non-zero are those in which the weights of the molecular response tensors and the radiation field tensors are the same, the rotational averaging matrix takes on a block diagonal form. The rotational averaging matrix coefficients can readily be calculated with the aid of table 1 which gives the explicit form for $g_{pp}^{(n;j)}$ up to rank 4 [11-13, 15].

Table 1. Explicit form of the metric $g_{pp}^{(n;j)}$ up to rank 4.

Rank	Weight	$g_{pp}^{(n;j)}$
2	2	1
2	1	2
2	0	3
3	3	1
3	2	$\begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix}$
3	1	$\begin{pmatrix} 3 & 1 & 1 \\ 1 & 3 & 1 \\ 1 & 1 & 3 \end{pmatrix}$
3	0	6
4	4	1
4	3	$\begin{pmatrix} 2 & 1 & -1 \\ 1 & 2 & -1 \\ -1 & -1 & 2 \end{pmatrix}$
4	2	$\begin{pmatrix} 3 & 1 & 1 & 1 & 1 & 0 \\ 1 & 3 & 1 & 1 & 0 & 1 \\ 1 & 1 & 3 & 0 & 1 & 1 \\ 1 & 1 & 0 & 3 & 1 & 1 \\ 1 & 0 & 1 & 1 & 3 & 1 \\ 0 & 1 & 1 & 1 & 1 & 3 \end{pmatrix}$
4	1	$\begin{pmatrix} 6 & 2 & 2 & -2 & -2 & 0 \\ 2 & 6 & 2 & 2 & 0 & -2 \\ 2 & 2 & 6 & 0 & 2 & 2 \\ -2 & 2 & 0 & 6 & 2 & -2 \\ -2 & 0 & 2 & 2 & 6 & 2 \\ 0 & -2 & 2 & -2 & 2 & 6 \end{pmatrix}$
4	0	$\begin{pmatrix} 9 & 3 & 3 \\ 3 & 9 & 3 \\ 3 & 3 & 9 \end{pmatrix}$

As mentioned above, the result given in (2.20) is correct so long as neither $g_{pq}^{(n;j)}$ nor $g_{rs}^{(n;j)}$ is zero. Although this condition is satisfied for $n \leq 3$, for $n = 4$ the result is more complicated. In this case $g_{pq}^{(4;j)}$ are zero when $j = 1, 2$ and $q = N_j^{(n)} + 1 - p$. For these elements the following identity can be used to re-express (2.18) in an alternative embedded irreducible form:

$$\begin{aligned} & t_{\lambda_1 \dots \lambda_j}^{(j;p)} t_{\lambda_1 \dots \lambda_j}^{(j;q)} s_{k_1 \dots k_j}^{(j;r)} s_{k_1 \dots k_j}^{(j;s)} \\ &= \sum_{t,u} \tilde{g}_{(4;j)}^{tp} \tilde{g}_{(4;j)}^{ru} G_{\mu_1 \dots \mu_4; \lambda_1 \dots \lambda_j}^{(0;t)} \tilde{G}_{\lambda_1 \dots \lambda_j; \rho_1 \dots \rho_4}^{(0;q)} G_{k_1 \dots k_4; i_1 \dots i_j}^{(0;u)} \\ & \quad \times \tilde{G}_{i_1 \dots i_j; l_1 \dots l_4}^{(0;s)} T_{\mu_1 \dots \mu_4}^{(j;p)} T_{\rho_1 \dots \rho_4}^{(j;q)} S_{k_1 \dots k_4}^{(j;r)} S_{l_1 \dots l_4}^{(j;s)} \end{aligned} \quad (2.21)$$

where $g_{(4;j)}$ is the inverse metric defined by

$$\sum_q \tilde{g}_{(4;j)}^{pq} g_{qr}^{(4;j)} = \delta_r^p. \quad (2.22)$$

However, the fact that the contributions $T_{\lambda_1 \dots \lambda_4}^{(j;p)} \bar{T}_{\lambda_1 \dots \lambda_4}^{(j; N_j^{(n)} + 1 - p)}$ vanish means that this average *cannot* be expressed in terms of a linear combination of the quadruply contracted tensors of the form $T_{\lambda_1 \dots \lambda_4}^{(j;p)} \bar{T}_{\lambda_1 \dots \lambda_4}^{(j;q)}$. This is verified by the fact that $G_{\mu_1 \dots \mu_4; \lambda_1 \dots \lambda_j}^{(0;r)} \tilde{G}_{\lambda_1 \dots \lambda_j; \rho_1 \dots \rho_4}^{(0;q)}$ does not map the tensor product $T_{\mu_1 \dots \mu_4}^{(j;p)} \bar{T}_{\rho_1 \dots \rho_4}^{(j; N_j^{(n)} + 1 - p)}$ into an irreducible result of the form $T_{\lambda_1 \dots \lambda_4}^{(j;r)} \bar{T}_{\lambda_1 \dots \lambda_4}^{(j;s)}$.

Explicit results for the rotational average of (1.1) up to rank 6 ($n = 3$) are as follows.

Rank 2.

$$\langle |T_i S_i|^2 \rangle = \sum_{j=0}^1 (2j+1)^{-1} T_{\lambda}^{(j)} \bar{T}_{\lambda}^{(j)} S_i^{(j)} \bar{S}_i^{(j)} \quad (2.23)$$

Rank 4.

$$\langle |T_{ij} S_{ij}|^2 \rangle = \sum_{j=0}^2 (2j+1)^{-1} T_{\lambda\mu}^{(j)} \bar{T}_{\lambda\mu}^{(j)} S_{ij}^{(j)} \bar{S}_{ij}^{(j)} \quad (2.24)$$

Rank 6.

$$\langle |T_{ijk} S_{ijk}|^2 \rangle = T_{\lambda\mu\nu}^{(0)} \bar{T}_{\lambda\mu\nu}^{(0)} S_{ijk}^{(0)} \bar{S}_{ijk}^{(0)}$$

$$+ \left(\begin{array}{cc} T_{\lambda\mu\nu}^{(1\alpha)} & \bar{T}_{\lambda\mu\nu}^{(1\alpha)} \\ T_{\lambda\mu\nu}^{(1\alpha)} & \bar{T}_{\lambda\mu\nu}^{(1\beta)} \\ T_{\lambda\mu\nu}^{(1\alpha)} & \bar{T}_{\lambda\mu\nu}^{(1\gamma)} \\ T_{\lambda\mu\nu}^{(1\beta)} & \bar{T}_{\lambda\mu\nu}^{(1\alpha)} \\ T_{\lambda\mu\nu}^{(1\beta)} & \bar{T}_{\lambda\mu\nu}^{(1\beta)} \\ T_{\lambda\mu\nu}^{(1\beta)} & \bar{T}_{\lambda\mu\nu}^{(1\gamma)} \\ T_{\lambda\mu\nu}^{(1\gamma)} & \bar{T}_{\lambda\mu\nu}^{(1\alpha)} \\ T_{\lambda\mu\nu}^{(1\gamma)} & \bar{T}_{\lambda\mu\nu}^{(1\beta)} \\ T_{\lambda\mu\nu}^{(1\gamma)} & \bar{T}_{\lambda\mu\nu}^{(1\gamma)} \end{array} \right)^T \frac{1}{48} \left(\begin{array}{cccccccccc} 16 & 16 & 16 & 16 & 1 & -4 & 16 & -4 & 1 \\ 16 & 256 & -64 & 16 & 16 & 16 & 16 & -64 & -4 \\ 16 & -64 & 256 & 16 & -4 & -64 & 16 & 16 & 16 \\ 16 & 16 & 16 & 256 & 16 & -64 & -64 & 16 & -4 \\ 1 & 16 & -4 & 16 & 16 & 16 & -4 & 16 & 1 \\ -4 & 16 & -64 & -64 & 16 & 256 & 16 & 16 & 16 \\ 16 & 16 & 16 & -64 & -4 & 16 & 256 & -64 & 16 \\ -4 & -64 & 16 & 16 & 16 & 16 & -64 & 256 & 16 \\ 1 & -4 & 16 & -4 & 1 & 16 & 16 & 16 & 16 \end{array} \right)$$

$$\begin{aligned}
& \times \begin{pmatrix} S_{ijk}^{(1\alpha)} & \bar{S}_{ijk}^{(1\alpha)} \\ S_{ijk}^{(1\alpha)} & \bar{S}_{ijk}^{(1\beta)} \\ S_{ijk}^{(1\alpha)} & \bar{S}_{ijk}^{(1\gamma)} \\ S_{ijk}^{(1\beta)} & \bar{S}_{ijk}^{(1\alpha)} \\ S_{ijk}^{(1\beta)} & \bar{S}_{ijk}^{(1\beta)} \\ S_{ijk}^{(1\beta)} & \bar{S}_{ijk}^{(1\gamma)} \\ S_{ijk}^{(1\gamma)} & \bar{S}_{ijk}^{(1\alpha)} \\ S_{ijk}^{(1\gamma)} & \bar{S}_{ijk}^{(1\beta)} \\ S_{ijk}^{(1\gamma)} & \bar{S}_{ijk}^{(1\gamma)} \end{pmatrix} + \frac{1}{20} \begin{pmatrix} T_{\lambda\mu\nu}^{(2\alpha)} & \bar{T}_{\lambda\mu\nu}^{(2\alpha)} \\ T_{\lambda\mu\nu}^{(2\alpha)} & \bar{T}_{\lambda\mu\nu}^{(2\beta)} \\ T_{\lambda\mu\nu}^{(2\beta)} & \bar{T}_{\lambda\mu\nu}^{(2\alpha)} \\ T_{\lambda\mu\nu}^{(2\beta)} & \bar{T}_{\lambda\mu\nu}^{(2\beta)} \end{pmatrix}^T \begin{pmatrix} 4 & 4 & 4 & 1 \\ 4 & 16 & 4 & 4 \\ 4 & 4 & 16 & 4 \\ 1 & 4 & 4 & 4 \end{pmatrix} \begin{pmatrix} S_{ijk}^{(2\alpha)} & \bar{S}_{ijk}^{(2\alpha)} \\ S_{ijk}^{(2\alpha)} & \bar{S}_{ijk}^{(2\beta)} \\ S_{ijk}^{(2\beta)} & \bar{S}_{ijk}^{(2\alpha)} \\ S_{ijk}^{(2\beta)} & \bar{S}_{ijk}^{(2\beta)} \end{pmatrix} \\
& + \frac{1}{7} T_{\lambda\mu\nu}^{(3)} \bar{T}_{\lambda\mu\nu}^{(3)} S_{ijk}^{(3)} \bar{S}_{ijk}^{(3)}. \tag{2.25}
\end{aligned}$$

3. Correspondence with conventional rotational averages

It is possible to use the principles expounded above to generate earlier results obtained in reducible tensor form [2-8]. If we convert the natural tensors in (2.18) into their reducible forms in rank- n space, through the use of the following inverse mapping formulae:

$$t_{\lambda_1 \dots \lambda_j}^{(j;p)} = \tilde{G}_{\lambda_1 \dots \lambda_j; \mu_1 \dots \mu_n}^{(0;p)} T_{\mu_1 \dots \mu_n} \tag{3.1}$$

$$\bar{t}_{\lambda_1 \dots \lambda_j}^{(j;q)} = \tilde{G}_{\lambda_1 \dots \lambda_j; \nu_1 \dots \nu_n}^{(0;q)} \bar{T}_{\nu_1 \dots \nu_n} \tag{3.2}$$

$$s_{k_1 \dots k_j}^{(j;r)} = \tilde{G}_{k_1 \dots k_j; l_1 \dots l_n}^{(0;r)} S_{l_1 \dots l_n} \tag{3.3}$$

$$\bar{s}_{k_1 \dots k_j}^{(j;s)} = \tilde{G}_{k_1 \dots k_j; m_1 \dots m_n}^{(0;s)} \bar{S}_{m_1 \dots m_n} \tag{3.4}$$

we find that on substitution of (3.1)–(3.4) into (2.19) we obtain the necessary average expressed in terms of reducible tensor isomers, i.e.

$$\begin{aligned}
& \langle T_{i_1 \dots i_n} \bar{T}_{i_{n+1} \dots i_{2n}} S_{i_1 \dots i_n} \bar{S}_{i_{n+1} \dots i_{2n}} \rangle \\
& = \sum_{j=0} (2j+1)^{-1} \sum_{p,q} \sum_{r,s} g_{pq}^{(n;j)} g_{rs}^{(n;j)} \tilde{G}_{k_1 \dots k_j; l_1 \dots l_n}^{(0;r)} \tilde{G}_{k_1 \dots k_j; m_1 \dots m_n}^{(0;s)} \tilde{G}_{\lambda_1 \dots \lambda_j; \mu_1 \dots \mu_n}^{(0;p)} \\
& \quad \times \tilde{G}_{\lambda_1 \dots \lambda_j; \nu_1 \dots \nu_n}^{(0;q)} T_{\mu_1 \dots \mu_n} \bar{T}_{\nu_1 \dots \nu_n} S_{l_1 \dots l_n} \bar{S}_{m_1 \dots m_n}. \tag{3.5}
\end{aligned}$$

As an example, we derive the second-rank tensor average ($n=1$). Using the information given in table 2 together with (3.5), and using the affine relation

$$G_{k_1 \dots k_n; l_1 \dots l_n}^{(0;p)} G_{k_1 \dots k_n; m_1 \dots m_n}^{(0;p)} = \prod_{l_1 \dots l_n; m_1 \dots m_n}^{(n;n)} \tag{3.6}$$

Table 2. Tensor mappings for a second-rank tensor.

j	$g_{pq}^{(2;j)}$	$G_{l_1 \dots l_j; k_1 k_2}^{(0;p)}$
2	1	$\frac{1}{2}(\delta_{l_1 k_1} \delta_{l_2 k_2} + \delta_{l_1 k_2} \delta_{l_2 k_1}) - \frac{1}{3} \delta_{l_1 l_2} \delta_{k_1 k_2}$
1	2	$\frac{1}{2} e_{l_1 k_1 k_2}$
0	3	$\frac{1}{3} \delta_{k_1 k_2}$

where the mapping on the right projects out the rank- n , weight- n , tensor representation from the reducible tensor subspace, we obtain the following result:

$$\begin{aligned} \langle |T_{ij}S_{ij}|^2 \rangle = & \left\{ \frac{1}{2} \left[\frac{1}{2} (\delta_{l_1 k_1} \delta_{l_2 k_2} + \delta_{l_1 k_2} \delta_{l_2 k_1}) - \frac{1}{3} \delta_{l_1 l_2} \delta_{k_1 k_2} \right] \left[\frac{1}{2} (\delta_{\mu_1 \nu_1} \delta_{\mu_2 \nu_2} + \delta_{\mu_1 \nu_2} \delta_{\mu_2 \nu_1}) - \frac{1}{3} \delta_{\mu_1 \mu_2} \delta_{\nu_1 \nu_2} \right] \right. \\ & + \frac{4}{3} \left[\left(\frac{1}{2} \varepsilon_{l_1 k_1 k_2} \right) \left(\frac{1}{2} \varepsilon_{l_1 m_1 m_2} \right) \left(\frac{1}{2} \varepsilon_{\lambda_1 \nu_1 \nu_2} \right) \left(\frac{1}{2} \varepsilon_{\lambda_1 \mu_1 \mu_2} \right) \right] \\ & \left. + \frac{1}{3} \delta_{l_1 l_2} \delta_{m_1 m_2} \delta_{\mu_1 \mu_2} \delta_{\nu_1 \nu_2} \right\} T_{\mu_1 \mu_2} \bar{T}_{\nu_1 \nu_2} S_{l_1 l_2} \bar{S}_{m_1 m_2}. \end{aligned} \quad (3.7)$$

By executing the necessary index contractions we find that we can express the result as

$$\frac{1}{30} \begin{pmatrix} \delta_{l_1 l_2} & \delta_{m_1 m_2} \\ \delta_{l_1 m_1} & \delta_{l_2 m_2} \\ \delta_{l_1 m_2} & \delta_{l_2 m_1} \end{pmatrix}^T \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{\mu_1 \mu_2} & \delta_{\nu_1 \nu_2} \\ \delta_{\mu_1 \nu_1} & \delta_{\mu_2 \nu_2} \\ \delta_{\mu_1 \nu_2} & \delta_{\mu_2 \nu_1} \end{pmatrix} T_{\mu_1 \mu_2} \bar{T}_{\nu_1 \nu_2} S_{l_1 l_2} \bar{S}_{m_1 m_2} \quad (3.8)$$

which is the more usual form in which the rotational average appears [7]. Results for higher-rank rotational averages can be obtained through the use of (3.5) and the necessary mapping formulae given by Coope *et al* [11–13]. Although this method affords no calculational advantages over methods employed to evaluate isotropic tensor averages, it serves as a powerful illustration of the use of irreducible cartesian tensor calculus, and may additionally serve as a means of verifying results.

4. Rotational averages involving tensor products of odd rank

Up to this point we have principally been concerned with the calculation of isotropic averages involving only the square of the leading term in the probability amplitude. However, there are certain chiral effects which arise in connection with linear and non-linear light scattering which require the evaluation of odd-rank cross terms [16, 17]. Following a similar method one finds that such averages are given by

$$\begin{aligned} \langle S_{i_1 \dots i_n} S'_{j_1 \dots j_{n+1}} T_{i_1 \dots i_n} T'_{j_1 \dots j_{n+1}} \rangle \\ = \sum_{j=0}^n \sum_{p,q} \sum_{s',r'} (2j+1)^{-1} g_{pq}^{(n;j)} g_{(n+1;j)}^{s'r'} \tilde{G}_{\lambda_1 \dots \lambda_j; \mu_1 \dots \mu_n}^{(0;p)} \tilde{G}_{i_1 \dots i_j; k_1 \dots k_n}^{(0;q)} \\ \times G_{\rho_1 \dots \rho_{n+1}; \lambda_1 \dots \lambda_j}^{(0;r)} G_{i_1 \dots i_{n+1}; i_1 \dots i_j}^{(0;s)} T_{\mu_1 \dots \mu_n} T'_{\rho_1 \dots \rho_{n+1}} S_{k_1 \dots k_n} S'_{i_1 \dots i_{n+1}} \end{aligned} \quad (4.1)$$

which represents the main result in reducible form. The irreducible counterpart of equation (4.1) is found to be

$$\begin{aligned} \langle S_{i_1 \dots i_n} S'_{j_1 \dots j_{n+1}} T_{i_1 \dots i_n} T'_{j_1 \dots j_{n+1}} \rangle \\ = \sum_{j=0}^n \sum_{p,q,r,s} \sum_{s',r'} (2j+1)^{-1} g_{pq}^{(n;j)} g_{(n+1;j)}^{rr'} g_{(n+1;j)}^{ss'} g_{rs}^{(n;j)} \\ \times \tilde{G}_{\lambda_1 \dots \lambda_j; \mu_1 \dots \mu_n}^{(0;p)} \tilde{G}_{i_1 \dots i_j; k_1 \dots k_n}^{(0;q)} G_{\rho_1 \dots \rho_{n+1}; \lambda_1 \dots \lambda_j}^{(0;r)} G_{i_1 \dots i_{n+1}; i_1 \dots i_j}^{(0;s')} \\ \times T_{\mu_1 \dots \mu_n}^{(j;p)} T'_{\rho_1 \dots \rho_{n+1}}^{(j;r)} S_{k_1 \dots k_n}^{(j;p)} S'_{i_1 \dots i_{n+1}}^{(j;r)}. \end{aligned} \quad (4.2)$$

The rank-3 ($n=1$) and the rank-5 ($n=2$) rotational averages have the following explicit forms.

$n=1.$

$$\langle S_{i_1} S'_{j_1 j_2} T_{i_1} T'_{j_1 j_2} \rangle = \frac{1}{6} \varepsilon_{\mu_1 \mu_2 \mu_3} \varepsilon_{l_1 l_2 l_3} T_{\mu_1} T'_{\mu_2 \mu_3} S_{l_1} S'_{l_2 l_3} \quad (4.3)$$

$$= \frac{1}{6} \varepsilon_{l_1 l_2 l_3} \varepsilon_{\mu_1 \mu_2 \mu_3} S_{l_1}^{(1)} S'_{l_2 l_3}^{(1)} T_{\mu_1}^{(1)} T'_{\mu_2 \mu_3}^{(1)}. \quad (4.4)$$

$n=2$.

$$\begin{aligned} & \langle S_{i_1 i_2} S'_{j_1 j_2 j_3} T_{i_1 i_2} T'_{j_1 j_2 j_3} \rangle \\ &= \frac{1}{30} \begin{pmatrix} \varepsilon_{i_1 i_2 i_3} & \delta_{i_4 i_5} \\ \varepsilon_{i_1 i_2 i_4} & \delta_{i_3 i_5} \\ \varepsilon_{i_1 i_2 i_5} & \delta_{i_3 i_4} \\ \varepsilon_{i_1 i_3 i_4} & \delta_{i_2 i_5} \\ \varepsilon_{i_1 i_3 i_5} & \delta_{i_2 i_4} \\ \varepsilon_{i_1 i_4 i_5} & \delta_{i_2 i_3} \end{pmatrix}^T \begin{pmatrix} 3 & -1 & -1 & 1 & 1 & 0 \\ -1 & 3 & -1 & -1 & 0 & 1 \\ -1 & -1 & 3 & 0 & -1 & -1 \\ 1 & -1 & 0 & 3 & -1 & 1 \\ 1 & 0 & -1 & -1 & 3 & -1 \\ 0 & 1 & -1 & 1 & -1 & 3 \end{pmatrix} \begin{pmatrix} \varepsilon_{\lambda_1 \lambda_2 \lambda_3} & \delta_{\lambda_4 \lambda_5} \\ \varepsilon_{\lambda_1 \lambda_2 \lambda_4} & \delta_{\lambda_3 \lambda_5} \\ \varepsilon_{\lambda_1 \lambda_2 \lambda_5} & \delta_{\lambda_3 \lambda_4} \\ \varepsilon_{\lambda_1 \lambda_3 \lambda_4} & \delta_{\lambda_2 \lambda_5} \\ \varepsilon_{\lambda_1 \lambda_3 \lambda_5} & \delta_{\lambda_2 \lambda_4} \\ \varepsilon_{\lambda_1 \lambda_4 \lambda_5} & \delta_{\lambda_2 \lambda_3} \end{pmatrix} \\ & \times T_{\lambda_4 \lambda_5} T'_{\lambda_1 \lambda_2 \lambda_3} S_{i_4 i_5} S'_{i_1 i_2 i_3} \end{aligned} \quad (4.5)$$

$$\begin{aligned} &= \frac{1}{18} \varepsilon_{i_1 i_2 i_3} S_{i_4 i_5}^{(0)} S'_{i_1 i_2 i_3}{}^{(0)} \varepsilon_{\mu_1 \mu_2 \mu_3} T_{\mu_4 \mu_5}^{(0)} T'_{\mu_1 \mu_2 \mu_3}{}^{(0)} \\ &+ \frac{1}{600} S_{i_4 i_5}^{(1)} T_{\mu_4 \mu_5}^{(1)} \begin{pmatrix} \varepsilon_{\mu_1 \mu_4 \mu_5} & \delta_{\mu_2 \mu_3} \\ \varepsilon_{\mu_2 \mu_4 \mu_5} & \delta_{\mu_1 \mu_3} \\ \varepsilon_{\mu_3 \mu_4 \mu_5} & \delta_{\mu_1 \mu_2} \end{pmatrix}^T \begin{pmatrix} 4T'^{(1;1)}_{\mu_1 \mu_2 \mu_3} & -T'^{(1;1)}_{\mu_1 \mu_2 \mu_3} & -T'^{(1;1)}_{\mu_1 \mu_2 \mu_3} \\ -T'^{(1;2)}_{\mu_1 \mu_2 \mu_3} & 4T'^{(1;2)}_{\mu_1 \mu_2 \mu_3} & -T'^{(1;2)}_{\mu_1 \mu_2 \mu_3} \\ -T'^{(1;3)}_{\mu_1 \mu_2 \mu_3} & -T'^{(1;3)}_{\mu_1 \mu_2 \mu_3} & 4T'^{(1;3)}_{\mu_1 \mu_2 \mu_3} \end{pmatrix} \\ &\times \begin{pmatrix} 3 & 1 & 1 \\ 1 & 3 & 1 \\ 1 & 1 & 3 \end{pmatrix} \begin{pmatrix} 4S'^{(1;1)}_{i_1 i_2 i_3} & -S'^{(1;2)}_{i_1 i_2 i_3} & -S'^{(1;3)}_{i_1 i_2 i_3} \\ -S'^{(1;1)}_{i_1 i_2 i_3} & 4S'^{(1;2)}_{i_1 i_2 i_3} & -S'^{(1;3)}_{i_1 i_2 i_3} \\ -S'^{(1;1)}_{i_1 i_2 i_3} & -S'^{(1;2)}_{i_1 i_2 i_3} & 4S'^{(1;3)}_{i_1 i_2 i_3} \end{pmatrix} \begin{pmatrix} \varepsilon_{i_1 i_4 i_5} & \delta_{i_2 i_3} \\ \varepsilon_{i_2 i_4 i_5} & \delta_{i_1 i_3} \\ \varepsilon_{i_3 i_4 i_5} & \delta_{i_1 i_2} \end{pmatrix} \\ &+ \frac{1}{45} S_{i_4 i_5}^{(2)} T_{\mu_4 \mu_5}^{(2)} \begin{pmatrix} E_{(\mu_4 \mu_5; \tau \mu_1)}^{(2)} & \varepsilon_{\tau \mu_2 \mu_3} \\ E_{(\mu_4 \mu_5; \tau \mu_2)}^{(2)} & \varepsilon_{\tau \mu_1 \mu_3} \end{pmatrix}^T \begin{pmatrix} 2T'^{(2;1)}_{\mu_1 \mu_2 \mu_3} & -T'^{(2;1)}_{\mu_1 \mu_2 \mu_3} \\ -T'^{(2;2)}_{\mu_1 \mu_2 \mu_3} & 2T'^{(2;2)}_{\mu_1 \mu_2 \mu_3} \end{pmatrix} \\ &\times \begin{pmatrix} 2 & 1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} 2S'^{(2;1)}_{i_1 i_2 i_3} & -S'^{(2;2)}_{i_1 i_2 i_3} \\ -S'^{(2;1)}_{i_1 i_2 i_3} & 2S'^{(2;2)}_{i_1 i_2 i_3} \end{pmatrix} \begin{pmatrix} E_{(i_4 i_5; i_1)}^{(2)} & \varepsilon_{i_1 i_2 i_3} \\ E_{(i_4 i_5; i_2)}^{(2)} & \varepsilon_{i_1 i_3} \end{pmatrix}. \end{aligned} \quad (4.6)$$

5. Derivation of embedded irreducible isotropic averages from reducible isotropic averages

It is possible to verify the results of §2 by an alternative method using a matrix formalism outlined in part by Andrews and Wilkes [18]. This method expresses each scalar $T_{\lambda_1 \dots \lambda_n}^{(j;p)} \bar{T}_{\lambda_1 \dots \lambda_n}^{(j;q)}$ in terms of the Q_n linearly independent isotropic tensor isomers. First, we write the isotropic average as

$$I_{i_1 \dots i_{2n}; \lambda_1 \dots \lambda_{2n}}^{(2n)} = \sum_{p,q} m_{pq}^{(2n)} f_{i_1 \dots i_{2n}}^{(2n;p)} g_{\lambda_1 \dots \lambda_{2n}}^{(2n;q)} \quad (5.1)$$

where m_{pq} are numerical coefficients and $f^{(2n;p)}$, $g^{(2n;q)}$ denote the rank- $2n$ isotropic tensors in the laboratory and molecular frames respectively. Writing

$$t_q = g_{\lambda_1 \dots \lambda_{2n}}^{(2n;q)} T_{\lambda_1 \dots \lambda_n} \bar{T}_{\lambda_{n+1} \dots \lambda_{2n}} \quad (5.2)$$

and

$$s_p = f_{i_1 \dots i_{2n}}^{(2n;p)} S_{i_1 \dots i_n} \bar{S}_{i_{n+1} \dots i_{2n}} \quad (5.3)$$

it is possible to write the rank- $2n$ average in the form

$$\langle S_{i_1 \dots i_n} \bar{S}_{i_{n+1} \dots i_{2n}} T_{i_1 \dots i_n} \bar{T}_{i_{n+1} \dots i_{2n}} \rangle = \sum_{p,q} m_{pq}^{(2n)} s_p t_q. \quad (5.4)$$

Both the molecular parameters t_q and the polarisation parameters s_p can be re-expressed in terms of *irreducible* tensor products t_r^i and s_s^i by use of (2.3)–(2.6), leading to relations of the form

$$t_r^i = \sum_{q=1}^{Q_n} j_{rq} t_q \quad (5.5)$$

and

$$t_q = \sum_{r=1}^{Q_n} (j^{-1})_{qr} t_r^i \quad (5.6)$$

where j and j^{-1} constitute index-symmetric numerical matrices of rank Q_n . It is thus possible to express the rotational average defined in (5.4) as

$$\langle S_{i_1 \dots i_n} \bar{S}_{i_{n+1} \dots i_{2n}} T_{i_1 \dots i_n} \bar{T}_{i_{n+1} \dots i_{2n}} \rangle = \sum_{r,s} \sum_{p,q} (j^{-1})_{ps} m_{pq}^{(2n)} (j^{-1})_{qr} s_s^i t_r^i. \quad (5.7)$$

For ranks $n=2$ and $n=4$, averaging the result is trivial since there is only one representation for each weight, and consequently $(j^{-1})_{ps}$ and $(j^{-1})_{qr}$ are elements of 2×2 and 3×3 matrices. This is not the case for rank-6 averaging, however, where $(j^{-1})_{ps}$ and $(j^{-1})_{qr}$ are elements of a 15×15 matrix. These elements have previously been calculated by Andrews and Wilkes [16].

As an example we again concentrate on the rank-4 average. From (5.5) and appendix 2 we have

$$\begin{pmatrix} T_{\lambda\mu}^{(0)} & \bar{T}_{\lambda\mu}^{(0)} \\ T_{\lambda\mu}^{(1)} & \bar{T}_{\lambda\mu}^{(1)} \\ T_{\lambda\mu}^{(2)} & \bar{T}_{\lambda\mu}^{(2)} \end{pmatrix} = \frac{1}{6} \begin{pmatrix} 2 & 0 & 0 \\ 0 & 3 & -3 \\ -2 & 3 & 3 \end{pmatrix} \begin{pmatrix} T_{\nu\nu} & \bar{T}_{\tau\tau} \\ T_{\lambda\mu} & \bar{T}_{\lambda\mu} \\ T_{\lambda\mu} & \bar{T}_{\mu\lambda} \end{pmatrix}. \quad (5.8)$$

The inverse relation can be expressed in the form of (5.6) as follows:

$$\begin{pmatrix} 3 & 0 & 0 \\ 1 & 1 & 1 \\ 1 & -1 & 1 \end{pmatrix} \begin{pmatrix} T_{\lambda\mu}^{(0)} & \bar{T}_{\lambda\mu}^{(0)} \\ T_{\lambda\mu}^{(1)} & \bar{T}_{\lambda\mu}^{(1)} \\ T_{\lambda\mu}^{(2)} & \bar{T}_{\lambda\mu}^{(2)} \end{pmatrix} = \begin{pmatrix} T_{\nu\nu} & \bar{T}_{\tau\tau} \\ T_{\lambda\mu} & \bar{T}_{\lambda\mu} \\ T_{\lambda\mu} & \bar{T}_{\mu\lambda} \end{pmatrix}. \quad (5.9)$$

Inserting this relation into (5.7) gives the isotropic average as

$$\frac{1}{30} \begin{pmatrix} S_{ij}^{(0)} & \bar{S}_{ij}^{(0)} \\ S_{ij}^{(1)} & \bar{S}_{ij}^{(1)} \\ S_{ij}^{(2)} & \bar{S}_{ij}^{(2)} \end{pmatrix}^T \begin{pmatrix} 3 & 1 & 1 \\ 0 & 1 & -1 \\ 0 & 1 & 1 \end{pmatrix} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} 3 & 0 & 0 \\ 1 & 1 & 1 \\ 1 & -1 & 1 \end{pmatrix} \begin{pmatrix} T_{\lambda\mu}^{(0)} & \bar{T}_{\lambda\mu}^{(0)} \\ T_{\lambda\mu}^{(1)} & \bar{T}_{\lambda\mu}^{(1)} \\ T_{\lambda\mu}^{(2)} & \bar{T}_{\lambda\mu}^{(2)} \end{pmatrix} \quad (5.10)$$

which reduces to the earlier result

$$\langle |T_{ij} S_{ij}|^2 \rangle = \sum_{j=0}^2 (2j+1)^{-1} T_{\lambda\mu}^{(j)} \bar{T}_{\lambda\mu}^{(j)} S_{ij}^{(j)} \bar{S}_{ij}^{(j)}. \quad (2.23)$$

6. Conclusion

In this paper we have shown how the principles of irreducible cartesian tensor analysis can be used to derive rotational averages for the observables associated with molecular processes described in terms of the Fermi golden rule. It has been demonstrated that the results are considerably simplified by expressing observables directly in terms of

irreducible tensors, thus bringing the rotational averaging matrix into block diagonal form. We also have shown how the principles of cartesian tensor analysis can be used to derive the isotropic averages in a reducible form. This has served to verify results published in earlier papers, and to facilitate future extension to isotropic averages for any higher rank. Although the results given in this paper apply to three-dimensional rotational averaging, it would be relatively simple to adapt these results for two-dimensional systems by a suitable adaptation of the relevant metric tensors.

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Appendix 1. Proof of an identity

$$\begin{aligned} T_{\lambda_1 \dots \lambda_n}^{(j;p)} \bar{T}_{\lambda_1 \dots \lambda_n}^{(j;q)} S_{i_1 \dots i_n}^{(j;r)} \bar{S}_{i_1 \dots i_n}^{(j;s)} \\ = G_{\lambda_1 \dots \lambda_n; \rho_1 \dots \rho_j}^{(0;p)} G_{\lambda_1 \dots \lambda_n; \sigma_1 \dots \sigma_j}^{(0;q)} G_{i_1 \dots i_n; k_1 \dots k_j}^{(0;r)} G_{i_1 \dots i_n; l_1 \dots l_j}^{(0;s)} \\ \times t_{\rho_1 \dots \rho_j}^{(j;p)} \bar{t}_{\sigma_1 \dots \sigma_j}^{(j;q)} s_{k_1 \dots k_j}^{(j;r)} \bar{s}_{l_1 \dots l_j}^{(j;s)}. \end{aligned} \quad (A1)$$

Using the inverse mappings

$$\begin{aligned} G_{i_1 \dots i_n; k_1 \dots k_j}^{(0;r)} &= \sum_{r'} g_{rr'}^{(n;j)} \tilde{G}_{k_1 \dots k_j; i_1 \dots i_n}^{(0;r')} \\ G_{\lambda_1 \dots \lambda_n; \rho_1 \dots \rho_j}^{(0;p)} &= \sum_p g_{pp}^{(n;j)} \tilde{G}_{\rho_1 \dots \rho_j; \lambda_1 \dots \lambda_n}^{(0;p')} \end{aligned} \quad (A2)$$

and the identities

$$\begin{aligned} \tilde{G}_{k_1 \dots k_j; i_1 \dots i_n}^{(0;r')} G_{i_1 \dots i_n; l_1 \dots l_j}^{(0;s)} &= \delta_{r's} E_{k_1 \dots k_j; l_1 \dots l_j}^{(j)} \\ \tilde{G}_{\rho_1 \dots \rho_j; \lambda_1 \dots \lambda_n}^{(0;p')} G_{\lambda_1 \dots \lambda_n; \sigma_1 \dots \sigma_j}^{(0;q)} &= \delta_{p'q} E_{\rho_1 \dots \rho_j; \sigma_1 \dots \sigma_j}^{(j)} \end{aligned}$$

we obtain from (A1)

$$T_{\lambda_1 \dots \lambda_n}^{(j;p)} \bar{T}_{\lambda_1 \dots \lambda_n}^{(j;q)} S_{i_1 \dots i_n}^{(j;r)} \bar{S}_{i_1 \dots i_n}^{(j;s)} = g_{pq}^{(n;j)} g_{rs}^{(n;j)} s_{k_1 \dots k_j}^{(j;r)} \bar{s}_{k_1 \dots k_j}^{(j;s)} t_{\rho_1 \dots \rho_j}^{(j;p)} \bar{t}_{\rho_1 \dots \rho_j}^{(j;q)}$$

or

$$(g_{pq}^{(n;j)} g_{rs}^{(n;j)})^{-1} T_{\lambda_1 \dots \lambda_n}^{(j;p)} \bar{T}_{\lambda_1 \dots \lambda_n}^{(j;q)} S_{i_1 \dots i_n}^{(j;r)} \bar{S}_{i_1 \dots i_n}^{(j;s)} = s_{k_1 \dots k_j}^{(j;r)} \bar{s}_{k_1 \dots k_j}^{(j;s)} t_{\rho_1 \dots \rho_j}^{(j;p)} \bar{t}_{\rho_1 \dots \rho_j}^{(j;q)}. \quad (A3)$$

This is the identity used in (2.20).

Appendix 2. Explicit forms of the rank- n , weight- j , irreducible tensors $T_{s_1 \dots s_n}^{(j;p)}$

Rank 2.

$$\begin{aligned} T_{s_1 s_2}^{(0)} &= \frac{1}{3} \delta_{s_1 s_2} T_{s_p s_p} \\ T_{s_1 s_2}^{(1)} &= \frac{1}{2} (T_{s_1 s_2} - T_{s_2 s_1}) \\ T_{s_1 s_2}^{(2)} &= \frac{1}{2} (T_{s_1 s_2} + T_{s_2 s_1}) - \frac{1}{2} \delta_{s_1 s_2} T_{s_p s_p} \end{aligned}$$

Rank 3.

$$\begin{aligned}
 T_{s_1 s_2 s_3}^{(0)} &= \frac{1}{6} \varepsilon_{s_1 s_2 s_3} \varepsilon_{s_p s_\sigma s_\tau} T_{s_p s_\sigma s_\tau} \\
 T_{s_1 s_2 s_3}^{(1;1)} &= \frac{1}{10} (4\delta_{s_1 s_2} T_{s_p s_p s_3} - \delta_{s_1 s_3} T_{s_p s_p s_2} - \delta_{s_2 s_3} T_{s_p s_p s_1}) \\
 T_{s_1 s_2 s_3}^{(1;2)} &= \frac{1}{10} (-\delta_{s_1 s_2} T_{s_p s_3 s_p} + 4\delta_{s_1 s_3} T_{s_p s_2 s_p} - \delta_{s_2 s_3} T_{s_p s_1 s_p}) \\
 T_{s_1 s_2 s_3}^{(1;3)} &= \frac{1}{10} (-\delta_{s_1 s_2} T_{s_3 s_p s_p} - \delta_{s_1 s_3} T_{s_2 s_p s_p} + 4\delta_{s_2 s_3} T_{s_1 s_p s_p}) \\
 T_{s_1 s_2 s_3}^{(2;1)} &= \frac{1}{6} \varepsilon_{s_1 s_2 s_\tau} (2\varepsilon_{s_p s_\sigma s_\tau} T_{s_p s_\sigma s_3} + 2\varepsilon_{s_p s_\sigma s_3} T_{s_p s_\sigma s_\tau} + \varepsilon_{s_p s_\sigma s_\tau} T_{s_3 s_p s_\sigma} + \varepsilon_{s_p s_\sigma s_3} T_{s_\tau s_p s_\sigma} \\
 &\quad - 2\delta_{s_1 s_\tau} \varepsilon_{s_\pi s_p s_\sigma} T_{s_\pi s_p s_\sigma}) \\
 T_{s_1 s_2 s_3}^{(2;2)} &= \frac{1}{6} \varepsilon_{s_2 s_3 s_\tau} (2\varepsilon_{s_p s_\sigma s_\tau} T_{s_1 s_p s_\sigma} + 2\varepsilon_{s_p s_\sigma s_1} T_{s_\tau s_p s_\sigma} + \varepsilon_{s_p s_\sigma s_\tau} T_{s_p s_\sigma s_1} + \varepsilon_{s_p s_\sigma s_1} T_{s_p s_\sigma s_\tau} \\
 &\quad - 2\delta_{s_1 s_\tau} \varepsilon_{s_\pi s_p s_\sigma} T_{s_\pi s_p s_\sigma}) \\
 T_{s_1 s_2 s_3}^{(3)} &= \frac{1}{6} (T_{s_1 s_2 s_3} + T_{s_1 s_3 s_2} + T_{s_2 s_1 s_3} + T_{s_2 s_3 s_1} + T_{s_3 s_1 s_2} + T_{s_3 s_2 s_1}) \\
 &\quad - \frac{1}{15} [\delta_{s_1 s_1} (T_{s_p s_p s_3} + T_{s_p s_3 s_p} + T_{s_3 s_p s_p}) \\
 &\quad + \delta_{s_1 s_3} (T_{s_p s_p s_2} + T_{s_p s_2 s_p} + T_{s_2 s_p s_p}) + \delta_{s_2 s_3} (T_{s_p s_p s_1} + T_{s_p s_1 s_p} + T_{s_1 s_p s_p})].
 \end{aligned}$$

References

- [1] Craig D P and Thirunamachandran T 1984 *Molecular Quantum Electrodynamics—An Introduction to Molecule–Radiation Interactions* (New York: Academic)
- [2] Kielich S 1961 *Acta Phys. Polon.* **20** 433
- [3] Monson P R and McClain W M 1970 *J. Chem. Phys.* **53** 29
- [4] McClain W M 1972 *J. Chem. Phys.* **57** 2264
- [5] Healy W P 1974 *J. Phys. B: At. Mol. Phys.* **7** 1633
- [6] Power E A and Thirunamachandran T 1974 *J. Chem. Phys.* **60** 3695
- [7] Andrews D L and Thirunamachandran T 1977 *J. Chem. Phys.* **67** 5026
- [8] Wagnière G 1982 *J. Chem. Phys.* **76** 473
- [9] McClain W M, Tian D and Ghoul W A 1987 *J. Chem. Phys.* **87** 4986
- [10] Andrews D L and Ghoul W A 1981 *J. Phys. A: Math. Gen.* **14** 1281
- [11] Coope J A R, Snider R F and McCourt F R 1965 *J. Chem. Phys.* **43** 2269
- [12] Coope J A R and Snider R F 1970 *J. Math. Phys.* **11** 993
- [13] Coope J A R 1970 *J. Math. Phys.* **11** 1591
- [14] Mikhailov V V 1977 *J. Phys. A: Math. Gen.* **10** 147
- [15] Andrews D L and Ghoul W A 1982 *Phys. Rev. A* **25** 2647
- [16] Andrews D L and Thirunamachandran T 1979 *J. Chem. Phys.* **70** 1027
- [17] Andrews D L 1980 *J. Chem. Phys.* **72** 4141
- [18] Andrews D L and Wilkes P J 1985 *J. Chem. Phys.* **83** 2009