Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
This journal is © the Owner Societies 2015

Supporting Information to "Three-photon circular dichroism: Towards a generalization of chiroptical non-linear light absorption"

Daniel H. Friese, Kenneth Ruud

1 Rotational averaging procedure

Fundamental expressions for the rotational averaging of 7th rank tensors have been published by Andrews and Thirunamachandran in 1977[1] and five years later by Wagnière[2]. We will use the theory by Andrews and Thirunamachandran in the so-called reducible form. This form has not been encouraged by the authors as the involved matrices and vectors are longer than the ones of the irreducible form.[1] Their advantage is, however, that the expressions are very clearly structured which also leads to clearly structured results using a bit of computational support (which was not available when the fundamental work was presented).

According to Andrews and Thirunamachandran the universal orientational average of a 7th rank tensor $\langle \mathbf{T}^{(7)} \rangle$ is

$$\langle \mathbf{T}^{(7)} \rangle = \frac{1}{840} \cdot \mathbf{A} \cdot \mathbf{f} \cdot \mathbf{M} \cdot \mathbf{g} \cdot \mathbf{\Pi}, \tag{1}$$

where $\mathbf{A}$ is a 7th-rank tensor describing the incident field (in our case: the polarization tensor) and $\mathbf{\Pi}$ is a 7th-rank tensor describing the molecular property (in our case: the transition strength tensor). While the tensor $\mathbf{A}$ is evaluated in a laboratory-fixed coordinate system, the tensor $\mathbf{\Pi}$ is evaluated in a molecule-fixed coordinate system and orientational averaging is about finding a connection between these two coordiate systems. The vectors $\mathbf{f}$ and $\mathbf{g}$ are 105-dimensional and contain strings of one Levi-Civita tensor and two Kronecker deltas which refer either to the laboratory or the molecule-fixed coordinate system.

These strings are set up according to the following rules:[3]

1. On all three symbols indices have to be in ascending order.
2. The first indices on the Kronecker deltas have to be in ascending order.

These strings can be interpreted as operators that act on either $\mathbf{A} \cdot \mathbf{f}$ or $\mathbf{g} \cdot \mathbf{\Pi}$.[3] The matrix $\mathbf{M}$ is of dimension 105×105 and has the shape

$$\mathbf{M} = \mathbf{E}_{35} \otimes \begin{pmatrix} 6 & -1 & -1 \\ -1 & 6 & -1 \\ -1 & -1 & 6 \end{pmatrix}, \tag{2}$$

where $\mathbf{E}_{35}$ is a 35×35 unit matrix and the symbol $\otimes$ denotes an outer product of these two matrices. For the evaluation of the orientational averaging it is most convenient to first carry out

[0a] *Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø—The Arctic University of Norway, N-9037 Tromsø, Norway. Tel: +47 77623103; E-mail: daniel.h.friese@uit.no*

the matrix-vector multiplication $\mathbf{M}\cdot\mathbf{g}$ according to

$$\mathbf{M}\cdot\mathbf{g} = \begin{pmatrix} 6 & -1 & -1 & 0 & 0 & 0 & \cdots \\ -1 & 6 & -1 & 0 & 0 & 0 & \cdots \\ -1 & -1 & 6 & 0 & 0 & 0 & \cdots \\ 0 & 0 & 0 & 6 & -1 & -1 & \cdots \\ 0 & 0 & 0 & -1 & 6 & -1 & \cdots \\ 0 & 0 & 0 & -1 & -1 & 6 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} \epsilon_{123}\delta_{45}\delta_{67} \\ \epsilon_{123}\delta_{46}\delta_{57} \\ \epsilon_{123}\delta_{47}\delta_{56} \\ \epsilon_{124}\delta_{35}\delta_{67} \\ \epsilon_{124}\delta_{36}\delta_{57} \\ \epsilon_{124}\delta_{37}\delta_{56} \\ \vdots \end{pmatrix}, \tag{3}$$

$$= \begin{pmatrix} 6\epsilon_{123}\delta_{45}\delta_{67} - \epsilon_{123}\delta_{46}\delta_{57} - \epsilon_{123}\delta_{47}\delta_{56} \\ -\epsilon_{123}\delta_{45}\delta_{67} + 6\epsilon_{123}\delta_{46}\delta_{57} - \epsilon_{123}\delta_{47}\delta_{56} \\ -\epsilon_{123}\delta_{45}\delta_{67} - \epsilon_{123}\delta_{46}\delta_{57} + 6\epsilon_{123}\delta_{47}\delta_{56} \\ +6\epsilon_{124}\delta_{35}\delta_{67} - \epsilon_{124}\delta_{36}\delta_{57} - \epsilon_{124}\delta_{37}\delta_{56} \\ -\epsilon_{124}\delta_{35}\delta_{67} + 6\epsilon_{124}\delta_{36}\delta_{57} - \epsilon_{124}\delta_{37}\delta_{56} \\ -\epsilon_{124}\delta_{35}\delta_{67} - \epsilon_{124}\delta_{36}\delta_{57} + 6\epsilon_{124}\delta_{37}\delta_{56} \\ \vdots \end{pmatrix}. \tag{4}$$

This result vector will determine the elements of the transition strength tensor that contribute to the rotational averaging.

In the following we will evaluate the result of the operators in $\mathbf{f}$ on the polarization tensor $\mathbf{A}$ which is constructed from the polarization and propagation vectors of the photons. These vectors are defined as

$$\boldsymbol{\lambda} = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}, \quad \boldsymbol{\lambda}^* = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix}, \quad \mathbf{k} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}, \tag{5}$$

where $\boldsymbol{\lambda}$ denotes a circularly left polarized photon and $\boldsymbol{\lambda}^*$ a circularly right polarized photon.[4, 5]

The operator strings in $\mathbf{f}$ look the same as the ones in $\mathbf{g}$. In general we find that evaluating the three polarization tensors under consideration, namely $\boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*$, $\boldsymbol{\lambda}\boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*$ and $\boldsymbol{\lambda}\boldsymbol{\lambda}\boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*$ constructed from the vectors in Eq. (5) in the three cases under consideration only terms where the Levi-Civita tensor contains 2, 3 and 4, respectively, will survive as these are the positions where the only z components in the respective tensors are located. From the operator string it follows furthermore that for a non-zero contribution to the rotational averaging both the coordinates x and y have to occur in an odd number of times. So we have either tensor elements with two index triples and one single index (always z in this case) or with one quintuple of indeces and two single indices. As the imaginary unit is always in y position in the definitions in Eq. (5) and the number of y-indices is always odd this means that only imaginary tensor elements can contribute to the rotational averaging. Using computationally supported evaluation we find furthermore that all elements that finally survive have the following characteristics:

1. The Levi-Civita tensor contains at least one index larger than 4 and one index smaller than four.

2. Terms where one index on the Levi-Civita tensor is lower than the index of z and one is higher than the index of z are positive, all other terms are negative.

3. There are no strings where all the indices of the two Kronecker deltas are in direct ascending order (e.g. $\delta_{45}\delta_{67}$ never survives but $\delta_{46}\delta_{57}$ and $\delta_{47}\delta_{56}$ do).

4. All contributions have a prefactor of 8 which compensates against the prefactor of $\frac{1}{8}$ in the tensor elements (see prefactor in Eq. (5)).

The Levi-Civita tensors for the surviving contributions and their signs are listed in Tab. 1. We

Table 1: Levi-Civita tensors which contribute to non-zero elements of the product $\mathbf{A}\cdot\mathbf{f}$.

$\boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\cdot\mathbf{f}$	$\boldsymbol{\lambda}\boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\cdot\mathbf{f}$	$\boldsymbol{\lambda}\boldsymbol{\lambda}\boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\cdot\mathbf{f}$
ϵ_{125}	ϵ_{135}	ϵ_{145}
ϵ_{126}	ϵ_{136}	ϵ_{146}
ϵ_{127}	ϵ_{137}	ϵ_{147}
$-\epsilon_{235}$	ϵ_{235}	ϵ_{245}
$-\epsilon_{236}$	ϵ_{236}	ϵ_{246}
$-\epsilon_{237}$	ϵ_{237}	ϵ_{247}
$-\epsilon_{245}$	$-\epsilon_{345}$	ϵ_{345}
$-\epsilon_{246}$	$-\epsilon_{346}$	ϵ_{346}
$-\epsilon_{247}$	$-\epsilon_{347}$	ϵ_{347}

now have to combine the products $\mathbf{A}\cdot\mathbf{f}$ and $\mathbf{M}\cdot\mathbf{g}$. Both these results are vectors and therefore we get

$$\boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\cdot\mathbf{f}\cdot\mathbf{M}\cdot\mathbf{g} = \tag{6}$$

$$\begin{pmatrix} \vdots \\ 0 \\ \epsilon_{125}\delta_{36}\delta_{47} \\ \epsilon_{125}\delta_{37}\delta_{46} \\ 0 \\ \epsilon_{126}\delta_{35}\delta_{47} \\ \epsilon_{126}\delta_{37}\delta_{45} \\ 0 \\ \epsilon_{127}\delta_{35}\delta_{46} \\ \epsilon_{127}\delta_{36}\delta_{45} \\ 0 \\ -\epsilon_{235}\delta_{16}\delta_{47} \\ -\epsilon_{235}\delta_{17}\delta_{46} \\ 0 \\ -\epsilon_{236}\delta_{15}\delta_{47} \\ -\epsilon_{236}\delta_{17}\delta_{45} \\ 0 \\ -\epsilon_{237}\delta_{15}\delta_{46} \\ -\epsilon_{237}\delta_{16}\delta_{45} \\ \vdots \end{pmatrix} \begin{pmatrix} \vdots \\ 6\epsilon_{125}\delta_{34}\delta_{67} - \epsilon_{125}\delta_{36}\delta_{47} - \epsilon_{125}\delta_{37}\delta_{46} \\ -\epsilon_{125}\delta_{34}\delta_{67} + 6\epsilon_{125}\delta_{36}\delta_{47} - \epsilon_{125}\delta_{37}\delta_{46} \\ -\epsilon_{125}\delta_{34}\delta_{67} - \epsilon_{125}\delta_{36}\delta_{47} + 6\epsilon_{125}\delta_{37}\delta_{46} \\ 6\epsilon_{126}\delta_{34}\delta_{57} - \epsilon_{126}\delta_{35}\delta_{47} - \epsilon_{126}\delta_{37}\delta_{45} \\ -\epsilon_{126}\delta_{34}\delta_{57} + 6\epsilon_{126}\delta_{35}\delta_{47} - \epsilon_{126}\delta_{37}\delta_{45} \\ -\epsilon_{126}\delta_{34}\delta_{57} - \epsilon_{126}\delta_{35}\delta_{47} + 6\epsilon_{126}\delta_{37}\delta_{45} \\ 6\epsilon_{127}\delta_{34}\delta_{56} - \epsilon_{127}\delta_{35}\delta_{46} - \epsilon_{127}\delta_{36}\delta_{45} \\ -\epsilon_{127}\delta_{34}\delta_{56} + 6\epsilon_{127}\delta_{35}\delta_{46} - \epsilon_{127}\delta_{36}\delta_{45} \\ -\epsilon_{127}\delta_{34}\delta_{56} - \epsilon_{127}\delta_{35}\delta_{46} + 6\epsilon_{127}\delta_{36}\delta_{45} \\ 6\epsilon_{235}\delta_{14}\delta_{67} - \epsilon_{235}\delta_{16}\delta_{47} - \epsilon_{235}\delta_{17}\delta_{46} \\ -\epsilon_{235}\delta_{14}\delta_{67} + 6\epsilon_{235}\delta_{16}\delta_{47} - \epsilon_{235}\delta_{17}\delta_{46} \\ -\epsilon_{235}\delta_{14}\delta_{67} - \epsilon_{235}\delta_{16}\delta_{47} + 6\epsilon_{235}\delta_{17}\delta_{46} \\ 6\epsilon_{236}\delta_{14}\delta_{57} - \epsilon_{236}\delta_{15}\delta_{47} - \epsilon_{236}\delta_{17}\delta_{45} \\ -\epsilon_{236}\delta_{14}\delta_{57} + 6\epsilon_{236}\delta_{15}\delta_{47} - \epsilon_{236}\delta_{17}\delta_{45} \\ -\epsilon_{236}\delta_{14}\delta_{57} - \epsilon_{236}\delta_{15}\delta_{47} + 6\epsilon_{236}\delta_{17}\delta_{45} \\ 6\epsilon_{237}\delta_{14}\delta_{57} - \epsilon_{237}\delta_{15}\delta_{46} - \epsilon_{237}\delta_{16}\delta_{45} \\ -\epsilon_{237}\delta_{14}\delta_{57} + 6\epsilon_{237}\delta_{15}\delta_{46} - \epsilon_{237}\delta_{16}\delta_{45} \\ -\epsilon_{237}\delta_{14}\delta_{57} - \epsilon_{237}\delta_{15}\delta_{46} + 6\epsilon_{237}\delta_{16}\delta_{45} \\ \vdots \end{pmatrix} = \begin{matrix} \cdots - 2\epsilon_{125}\delta_{34}\delta_{67} + 5\epsilon_{125}\delta_{36}\delta_{47} + 5\epsilon_{125}\delta_{37}\delta_{46} \\ -2\epsilon_{126}\delta_{34}\delta_{57} + 5\epsilon_{126}\delta_{35}\delta_{47} + 5\epsilon_{126}\delta_{37}\delta_{45} \\ -2\epsilon_{127}\delta_{34}\delta_{56} + 5\epsilon_{127}\delta_{35}\delta_{46} + 5\epsilon_{127}\delta_{36}\delta_{45} \\ -2\epsilon_{235}\delta_{14}\delta_{67} + 5\epsilon_{235}\delta_{16}\delta_{47} + 5\epsilon_{235}\delta_{17}\delta_{46} \\ -2\epsilon_{236}\delta_{14}\delta_{57} + 5\epsilon_{236}\delta_{15}\delta_{47} + 5\epsilon_{236}\delta_{17}\delta_{45} \\ -2\epsilon_{237}\delta_{14}\delta_{57} + 5\epsilon_{237}\delta_{15}\delta_{46} + 5\epsilon_{237}\delta_{16}\delta_{45}\cdots \end{matrix} .$$

Therefore we are left with 27 terms per polarization tensor. Applying these rules to the three combinations of polarization tensors and transition strength tensors we presented in the main

article and re-substituting the perturbation operators we get

$$
\begin{aligned}
\langle \boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^* : (\mathbf{gh})\mathbf{bcdef}\alpha\bar{\alpha}\rangle = \frac{1}{840}\cdot\Big\{ & -2[\mathbf{p}_{fl_4}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{fl_4}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{fl_4}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}] \\
& -2[\mathbf{p}_{l_4l_3}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{l_4l_3}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_4l_3}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]-2[\mathbf{p}_{l_3i}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}] \\
& +5[\mathbf{p}_{l_3i}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]+5[\mathbf{p}_{l_3i}\cdot(\mathbf{p}\times\mathbf{r})_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}] \\
& +2[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\mathbf{p}_{l_3i}]-5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}] \\
& -5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]+2[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}] \\
& -5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]-5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}] \\
& +2[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]-5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}] \\
& -5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]+2[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}] \\
& -5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]-5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}] \\
& +2[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]-5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}] \\
& -5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]+2[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}] \\
& -5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]-5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}].\Big\}\alpha\bar{\alpha},
\end{aligned}
\tag{7}
$$

$$
\begin{aligned}
\langle \boldsymbol{\lambda}\boldsymbol{\lambda}\mathbf{k}_\lambda\boldsymbol{\lambda}\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\mathbf{a}(\mathbf{jk})\mathbf{cdef}\alpha\bar{\alpha}\rangle = \frac{1}{840}\cdot\Big\{ & -2[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}] \\
& -2[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]-2[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}] \\
& +5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]+5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}] \\
& -2[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]-2[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}] \\
& -2[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+5[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}] \\
& +5[\mathbf{p}_{l_2l_1}\times\mathbf{r}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]+2[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}] \\
& -5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}]-5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}] \\
& +2[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]-5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}] \\
& -5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}]+2[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}] \\
& -5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}]-5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}]\Big\}\alpha\bar{\alpha}
\end{aligned}
\tag{8}
$$

$$
\begin{aligned}
\langle \boldsymbol{\lambda}\boldsymbol{\lambda}\boldsymbol{\lambda}\mathbf{k}_\lambda \boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\boldsymbol{\lambda}^*\mathbf{ab}(\mathbf{lm})\mathbf{def}\alpha\bar{\alpha}\rangle = \frac{1}{840}\cdot\Big\{ & -2[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]+5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}] \\
& -2[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}] \\
& +5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]-2[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}] \\
& +5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]+5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}] \\
& -2[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}] \\
& +5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}]-2[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}]+5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}] \\
& -2[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+5[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}] \\
& +5[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}]-2[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}] \\
& -2[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+5[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}] \\
& +5[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]-2[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}] \\
& +5[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]+5[\mathbf{p}_{l_1i}\times\mathbf{r}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]\Big\}\alpha\bar{\alpha}
\end{aligned}
\tag{9}
$$

Evaluating these expressions we note that there are the following classes of terms:

1. Negative terms with a prefactor of 2 where the cross product is between a $\mathbf{p}$ and a $\mathbf{r}$ of the same characteristic (e.g. $(\mathbf{p}\times\mathbf{r})_{fl_2}$))
2. Positive terms with a prefactor of 5 where the cross product is between a $\mathbf{p}$ and a $\mathbf{r}$ of the same characteristic (e.g. $(\mathbf{p}\times\mathbf{r})_{fl_2}$))
3. Terms with a prefactor of 2 where the cross product is between $\mathbf{p}$ and $\mathbf{r}$ of different characteristic. These terms are either positive or negative.
4. Terms with a prefactor of 5 where the cross product is between $\mathbf{p}$ and $\mathbf{r}$ of different characteristic. These terms are either positive or negative.

In the following we will evaluate these classes of terms separately.

1.1 Class 1 terms

All terms of class 1 contain two contractions of $\mathbf{p}$ terms from the same intermediate state manifold (either l_1/l_2 or l_3/l_4). The term with the cross product can easily be evaluated by introducing the magnetic dipole moment according to

$$
(\mathbf{p}\times\mathbf{r})_{fl_2} = 2\mathbf{m}_{fl_2}. \tag{10}
$$

Gathering now all terms from this class, reordering the perturbation tensors by excitation manifolds and changing from the sum-over-states to the response theory framework acoording to

$$
\begin{aligned}
-\frac{4}{840}\cdot\Big(&[\mathbf{p}_{fl_4}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+[\mathbf{p}_{l_4l_3}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+\\
&[\mathbf{p}_{l_3i}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+\\
&[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+\\
&[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+\\
&[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]\Big)\alpha\bar{\alpha}= \qquad (11)\\
-\frac{4}{840}\cdot\Big(&(\mathbf{m}_{fl_2}\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i})(\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}+\mathbf{p}_{l_4l_3}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}+\mathbf{p}_{l_3i}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3})+\\
&(\mathbf{m}_{l_2l_1}\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i})(\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}+\mathbf{p}_{l_4l_3}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}+\mathbf{p}_{l_3i}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3})+\\
&(\mathbf{m}_{l_1i}\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1})(\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}+\mathbf{p}_{l_4l_3}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}+\mathbf{p}_{l_3i}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3})\Big)\alpha\bar{\alpha}=\\
\frac{4}{840}\cdot\frac{1}{\omega^5}\cdot\sum_{abc}&\Big(M^{p,0f}_{a_pa_pb}P^{f0}_{bcc}\Big), \qquad (12)
\end{aligned}
$$

we get a formulation for this class of terms using tensors which can easily be obtained from response theory calculations. Here ω is the frequency of the incident photons, $\mathbf{M}$ is the magnetic dipole–electric dipole–electric dipole transition moment tensor while $\mathbf{P}$ is the electric dipole–electric dipole–electric dipole transition moment tensor. These tensors are defined according to

$$
M^{p,0f}_{abc}=\mathcal{P}^{0l_1,l_1l_2,l_2f}\sum_{l_2l_1}\frac{\mathbf{m}_{a,0l_1}\mathbf{p}_{b,l_1l_2}\mathbf{p}_{l_2f}}{\alpha}=\frac{1}{\omega^2}\mathcal{P}^{0l_1,l_1l_2,l_2f}\sum_{l_2l_1}\frac{\mathbf{m}_{a,0l_1}\boldsymbol{\mu}^p_{b,l_1l_2}\boldsymbol{\mu}^p_{c,l_2f}}{\alpha}, \qquad (13)
$$

$$
P^{0f}_{abc}=\mathcal{P}^{0l_1,l_1l_2,l_2f}\sum_{l_2l_1}\frac{\mathbf{p}_{a,0l_1}\mathbf{p}_{b,l_1l_2}\mathbf{p}_{l_2f}}{\bar{\alpha}}=-\sum_{l_2l_1}\frac{1}{\omega^3}\frac{\boldsymbol{\mu}^p_{a,0l_1}\boldsymbol{\mu}^p_{b,l_1l_2}\boldsymbol{\mu}^p_{c,l_2f}}{\bar{\alpha}}. \qquad (14)
$$

In these expressions $\boldsymbol{\mu}^p$ is the electric dipole velocity operator which is also used in origin independent formulations of TPCD by Tinoco and Rizzo.[4, 6] The operator $\mathcal{P}^{0l_1,l_1l_2,l_2f}$ permutes the indices $0l_1, l_1l_2$ and l_2f. The electric dipole velocity operator is defined as

$$
\boldsymbol{\mu}^p_{0l_1}=-\mathbf{p}_{0l_1}, \qquad (15)
$$

$$
\boldsymbol{\mu}^p_{0l_1}=\frac{2\pi i}{m_e}e\nu_{0i}\boldsymbol{\mu}_{0l_1}, \qquad (16)
$$

where ν_{0i} is the excitation energy for state i and $\boldsymbol{\mu}$ is the electric dipole length operator. Note that Eq. (16) is only fulfilled in the case of a complete one-electron basis set. For the reason of this definition the introduction of the dipole velocity operator requires a minus sign in front of the expression in Eq. (12). The term involving $\frac{1}{\omega^5}$ comes from the relation between the dipole length and velocity operators.

The notation $M_{a_pa_pb}$ denotes that the paired indices of $\mathbf{M}^{p,0f}$ in the contraction have to be indices that refer to the electric dipole operator.

1.2 Class 2 terms

Terms of this class can be evaluated completely analog to class one. The major difference is that this class contains contractions of terms from different intermediate state manifolds which has an impact on the pairing of the indices. Also in this case we gather the corresponding terms, introduce the magnetic dipole operator and reorder the tensors according to intermediate state

manifolds and get

$$\frac{5\cdot 2}{840}\cdot\Big([\mathbf{p}_{fl_4}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]+[\mathbf{p}_{fl_4}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}] \tag{17}$$
$$+[\mathbf{p}_{l_4l_3}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]+[\mathbf{p}_{l_4l_3}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]$$
$$+[\mathbf{p}_{l_3i}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]+[\mathbf{p}_{l_3i}\cdot\mathbf{m}_{fl_2}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]$$
$$+[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]+[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]$$
$$+[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]+[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]$$
$$+[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]+[\mathbf{m}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]$$
$$+[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]+[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]$$
$$+[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]+[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]$$
$$+[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]+[\mathbf{m}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]\Big)\alpha\bar{\alpha}=$$

$$\frac{10}{840}\cdot\Big((\mathbf{m}_{fl_2}\mathbf{p}_{l_2l_1}\mathbf{p}_{l_1i}+\mathbf{p}_{fl_2}\mathbf{m}_{l_2l_1}\mathbf{p}_{l_1i}+\mathbf{p}_{fl_2}\mathbf{p}_{l_2l_1}\mathbf{m}_{l_1i}) \tag{18}$$
$$(\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}\mathbf{p}_{l_3i}+\mathbf{p}_{fl_4}\mathbf{p}_{l_3i}\mathbf{p}_{l_4l_3}+\mathbf{p}_{l_4l_3}\mathbf{p}_{fl_4}\mathbf{p}_{l_3i}+$$
$$\mathbf{p}_{l_4l_3}\mathbf{p}_{l_3i}\mathbf{p}_{fl_4}+\mathbf{p}_{l_3i}\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}+\mathbf{p}_{l_3i}\mathbf{p}_{l_4l_3}\mathbf{p}_{fl_4})\Big)\alpha\bar{\alpha}=,$$

$$\frac{10\cdot 6}{840}\cdot\Big((\mathbf{m}_{fl_2}\mathbf{p}_{l_2l_1}\mathbf{p}_{l_1i}+\mathbf{p}_{fl_2}\mathbf{m}_{l_2l_1}\mathbf{p}_{l_1i}+\mathbf{p}_{fl_2}\mathbf{p}_{l_2l_1}\mathbf{m}_{l_1i})(\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}\mathbf{p}_{l_3i})\Big)= \tag{19}$$

$$-\frac{60}{840}\cdot\frac{1}{\omega^5}\cdot\sum_{abc}\Big(M^{p,0f}_{abc}P^{f0}_{abc}\Big). \tag{20}$$

1.3 Class 3 terms

In the class 3 and class 4 terms the cross product cannot be formulated such that it connects two operators of the same intermediate state manifold. Futhermore evaluating Eqs. (7) to (9) we note that there are both terms with positive and negative sign. In the negative term the cross product is between terms of different intermediate state manifold, however this can be changed by exchanging the two terms in the contraction after the cross product which yields sign inversion. Hence we have all terms positive and with the cross product between two operators of the same intermediate state manifold.

Gathering these terms, and reordering the tensors we get

$$\frac{2}{840}\Big([\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\mathbf{p}_{l_3i}]+[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+ \tag{21}$$
$$[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+$$
$$[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+$$
$$[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+$$
$$[\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+$$
$$[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+$$
$$[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+$$
$$[\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]+[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}]+$$
$$[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}]+[\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3}]\Big)\alpha\bar{\alpha}=$$

$$\frac{2}{840}\Big((\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_2}\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}+\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_2}\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}+ \tag{22}$$
$$\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_2l_1}\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}+\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2l_1}\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}+$$
$$\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_1i}\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}+\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1i}\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1})$$
$$(\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_3i}+\mathbf{p}_{l_4l_3}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3i}+\mathbf{p}_{l_3i}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4l_3})\Big)\alpha\bar{\alpha}.$$

We are then left with terms of the pattern $\mathbf{p}\cdot(\mathbf{pr})\times\mathbf{p}$. We note that the tensor $(\mathbf{pr})$ is not symmetric, however we would like to express it in terms of symmetric tensors. We therefore substitute

$$(\mathbf{pr}) = \frac{(\mathbf{pr})^+ - i(\mathbf{pr})^-}{2}, \tag{23}$$

$$(\mathbf{pr})^+ = \mathbf{pr} + \mathbf{rp} = \mathbf{q}^p, \tag{24}$$

$$(\mathbf{pr})^- = \mathbf{pr} - \mathbf{rp} = 2i\mathbf{I}\times\mathbf{m}, \tag{25}$$

where $\mathbf{q}^p$ is the electric quadrupole moment operator in velocity gauge representation[4, 6], $\mathbf{I}$ is the unit matrix and i is the imaginary unit. Hence we will express the operator $(\mathbf{pr})$ in terms of both the electric quadrupole and the magnetic dipole operator.

The terms with the electric quadrupole operator contain the cross product $\mathbf{q}^p\times\mathbf{p}$, which is evaluated according to[6]

$$\mathbf{q}^p\times\mathbf{p} = \boldsymbol{\mathcal{T}}^+, \tag{26}$$

$$\mathcal{T}^+_{ab} = \epsilon_{b\sigma\rho} q^p_{a\sigma} p_\rho, \tag{27}$$

where $\epsilon_{b\sigma\rho}$ is the Levi-Civita tensor. The tensor $\boldsymbol{\mathcal{T}}^+$ is the electric quadrupole–electric dipole transition moment tensor used in Rizzo's origin independent formulation of TPCD.[6]

For the other cross product we find

$$2i(\mathbf{I}\times\mathbf{m})\times\mathbf{p} = 2i(-\mathbf{mp} + \mathbf{m}\cdot\mathbf{p}). \tag{28}$$

Inserting these findings into the initial pattern we find

$$\mathbf{p}\cdot(\mathbf{pr})\times\mathbf{p} = \frac{1}{2}\mathbf{p}\cdot\boldsymbol{\mathcal{T}}^+ - \mathbf{p}\cdot\mathbf{mp} + \mathbf{p}\cdot(\mathbf{m}\cdot\mathbf{p}). \tag{29}$$

With these definitions we find

$$\frac{2}{840}\Big(\mathbf{p}_{l_1 i}\cdot\mathbf{p}_{fl_2}\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2 l_1} + \mathbf{p}_{l_2 l_1}\cdot\mathbf{p}_{fl_2}\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1 i} + \tag{30}$$

$$\mathbf{p}_{l_1 i}\cdot\mathbf{p}_{l_2 l_1}\mathbf{r}_{l_2 l_1}\times\mathbf{p}_{fl_2} + \mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_2 l_1}\mathbf{r}_{l_2 l_1}\times\mathbf{p}_{l_1 i} +$$

$$\mathbf{p}_{l_2 l_1}\cdot\mathbf{p}_{l_1 i}\mathbf{r}_{l_1 i}\times\mathbf{p}_{fl_2} + \mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_1 i}\mathbf{r}_{l_1 i}\times\mathbf{p}_{l_2 l_1})$$

$$(\mathbf{p}_{fl_4}\mathbf{p}_{l_4 l_3}\cdot\mathbf{p}_{l_3 i} + \mathbf{p}_{l_4 l_3}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_3 i} + \mathbf{p}_{l_3 i}\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_4 l_3})\Big)\alpha\bar{\alpha} = \tag{31}$$

$$\frac{2}{840}\cdot\frac{1}{\omega^5}\cdot\sum_{abc}\Big(-\frac{1}{2}Q^{p,+,0f}_{a_p a_Q b}P^{f0}_{bcc} + M^{p,0f}_{a_p a_p b}P^{f0}_{bcc} - M^{p,0f}_{a_p a_m b}P^{f0}_{bcc}\Big),$$

where $\mathbf{Q}^{p,+,0f}$ is the electric quadrupole–electric dipole–electric dipole transition moment tensor and the notation $Q^{p,+0f}_{a_p a_Q b}$ denotes that the paired index has to correspond to one electric dipole operator and to one index of the electric quadrupole operator. The elements of the tensor $\mathbf{Q}^{+,0f}$ are defined as

$$Q^{p,+,0f}_{abc} = \frac{1}{3}\mathcal{P}^{0l_1,l_1 l_2,l_2 f}\sum_{l_1 l_2}\epsilon_{b\gamma\delta}\frac{\mathbf{q}^p_{a\gamma,0l_1}\boldsymbol{\mu}^p_{\delta,l_1 l_2}\boldsymbol{\mu}^p_{c,l_2 f}}{\alpha} \tag{32}$$

1.4 Class 4 terms

For the Class 4 terms we find in general the same behaviour as for the class 3 terms concerning signs and the shapes of the cross products. Doing the same modifications as for class 3 we gather the terms and write them as transition strength tensors according to their intermediate state

manifolds

$$\frac{5}{840}\cdot\Big\{-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}] \tag{33}$$

$$\begin{aligned}
&-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]\\
&-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]\\
&-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]\\
&-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]\\
&-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{fl_2}][\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]\\
&-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]\\
&-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}]-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]\\
&-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}]-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}]\\
&-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}]-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}]\\
&-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}]-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}]\\
&-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}]-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_2l_1}][\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}]\\
&-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]\\
&-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}]\\
&-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}]-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}]\\
&-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}]-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{fl_4}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}]\\
&-[\mathbf{p}_{l_3i}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}]-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_4l_3}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_3i}]\\
&-[\mathbf{p}_{l_4l_3}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{fl_4}]-[\mathbf{p}_{fl_4}\cdot\mathbf{p}_{l_1i}][\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\cdot\mathbf{p}_{l_3i}][\mathbf{p}_{fl_2}\cdot\mathbf{p}_{l_4l_3}]\Big\}\alpha\bar{\alpha}=
\end{aligned}$$

$$\begin{aligned}
&-\frac{5}{840}\Big(\mathbf{p}_{fl_2}\mathbf{r}_{fl_2}\times\mathbf{p}_{l_2l_1}\mathbf{p}_{l_1i}+\mathbf{p}_{fl_2}\mathbf{r}_{fl_2}\times\mathbf{p}_{l_1i}\mathbf{p}_{l_2l_1}+\mathbf{p}_{l_2l_1}\mathbf{r}_{l_2l_1}\times\mathbf{p}_{fl_2}\mathbf{p}_{l_1i}+ \qquad (34)\\
&\quad\mathbf{p}_{l_2l_1}\mathbf{r}_{l_2l_1}\times\mathbf{p}_{l_1i}\mathbf{p}_{fl_2}+\mathbf{p}_{l_1i}\mathbf{r}_{l_1i}\times\mathbf{p}_{fl_2}\mathbf{p}_{l_2l_1}+\mathbf{p}_{l_1i}\mathbf{r}_{l_1i}\times\mathbf{p}_{l_2l_1}\mathbf{p}_{fl_2}\Big)\\
&\Big(\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}\mathbf{p}_{l_3i}+\mathbf{p}_{fl_4}\mathbf{p}_{l_3i}\mathbf{p}_{l_4l_3}+\mathbf{p}_{l_4l_3}\mathbf{p}_{fl_4}\mathbf{p}_{l_3i}+\\
&\quad\mathbf{p}_{l_4l_3}\mathbf{p}_{l_3i}\mathbf{p}_{fl_4}+\mathbf{p}_{l_3i}\mathbf{p}_{fl_4}\mathbf{p}_{l_4l_3}+\mathbf{p}_{l_3i}\mathbf{p}_{l_4l_3}\mathbf{p}_{fl_4}\Big)\alpha\bar{\alpha}=
\end{aligned}$$

$$\frac{30}{840}\cdot\frac{1}{\omega^5}\cdot\sum_{abc}\Big(\frac{1}{2}Q^{p,+,0f}_{abc}P^{f0}_{abc}-M^{p,0f}_{abc}P^{f0}_{abc}+M^{p,0f}_{a_ma_pb}P^{f0}_{bcc}\Big) \tag{35}$$

2 Definition of transition moment tensors in length gauge

The definitions of the transition moment tensors in length gauge are:

$$M_{abc}^{0f} = \mathcal{P}^{0l_1,l_1l_2,l_2f} \sum_{l_1l_2} \frac{m_{a,0l_1}\mu_{b,l_1l_2}\mu_{c,l_2f}}{\alpha}, \tag{36}$$

$$S_{abc}^{0f} = \mathcal{P}^{0l_1,l_1l_2,l_2f} \sum_{l_1l_2} \frac{\mu_{a,0l_1}\mu_{b,l_1l_2}\mu_{c,l_2f}}{\alpha}, \tag{37}$$

$$Q_{abc}^{0f} = \mathcal{P}^{0l_1,l_1l_2,l_2f} \sum_{l_1l_2} \epsilon_{b\gamma\delta} \frac{q_{a\gamma,0l_1}\mu_{\delta,l_1l_2}\mu_{c,l_2f}}{\alpha} \tag{38}$$

3 Tabulated values

3.1 Hydrogen peroxide

3.1.1 Basis set behaiour

Table 2: Complete magnetic contributions and photon frequencies for the basis set behaviour of the third excited state of the hydrogen peroxide molecule.

pVXZ	aug			d-aug			t-aug	
	ΔE	Velo	London	ΔE	Velo	London	ΔE	Velo
2	0.108758	-2.94E+007	-2.86E+007	0.108588	1.39E+007	-3.02E+007	0.10857	1.65E+007
3	0.108715	-1.03E+009	-8.04E+008	0.108648	-1.54E+009	-1.47E+009	0.108639	-1.63E+009
4	0.108716	-1.69E+009	-1.56E+009	0.108686	-2.13E+009	-2.11E+009	0.108684	-2.21E+009
5	0.10872	-2.09E+009	-1.94E+009	0.108703	-2.40E+009			
6	0.108714	-2.25E+009						

Table 3: Complete quadrupole contributions for the basis set behaviour of the third excited state of the hydrogen peroxide molecule.

pVXZ	aug		d-aug		t-aug
	Velo	London	Velo	London	Velo
2	1.30E+006	-1.82E+004	6.45E+005	3.89E+004	6.99E+005
3	4.48E+006	-1.69E+006	-3.38E+006	-2.30E+006	-3.34E+006
4	-4.21E+005	-3.01E+006	-4.47E+006	-3.49E+006	-4.52E+006
5	-1.71E+006	-3.62E+006	-4.62E+006		
6	-2.55E+006				

3.1.2 Origin dependence

Table 4: Complete magnetic contributions to 3PCD calculated using the length gauge approach without London orbitals at different diplacements in x-direction. All numbers are in atomic units.

Displacement	auc-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	aug-cc-pV5Z
0	39306065.0269138	910457101.066788	1747018024.64319	2167812002.71147
5	36959534.6434756	908532386.111407	1743770637.80453	2164977632.77072
15	32266474.27525	904682944.441446	1737275815.34762	2159307825.08694
30	25226881.2098218	898908813.677926	1727533672.60836	2150805105.65867

3.2 3-Methylcyclopentanone

3.3 4-helicene

Table 5: Magnetic and quadrupole contribution as well as photon energies for 3-Methylcyclopentanone. All numbers are in atomic units. The column marked ω contains the photon energies.

	Singly augmented			Doubly augmented		
	ω	magnetic	quadrupole	ω	magnetic	quadrupole
State 1						
2	0.051324	-2083751.96087199	-905025.442459084	0.0513	-1745480.91533936	-724468.246182452
3	0.051566	-1007652.0262027	-32226.2340340788	0.051555	-1028640.06212205	4944.376413665
4	0.051545	-911215.351952581	-3965.2759306404			
State 2						
2	0.068956	40544300.2847298	-883102.127206097	0.068411	38402105.1411886	-61340.7578969598
3	0.069127	20015024.5526992	-1087451.16602324	0.068805	21964829.7223039	-627678.847763609
4	0.069082	19423919.2716241	-935668.428603362			
State 3						
2	0.074939	33953920.1129771	-40742.7875845544	0.073836	23770017.753463	-1378855.69676159
3	0.074873	17593377.9962969	-1333647.81830498	0.074205	11110093.4019021	-1310581.4631255
4	0.07475	16354596.3523775	-1355382.17594674			
State 4						
2	0.07536	-68149300.2837003	367925.913005214	0.074254	-47220617.7457942	1686642.20464309
3	0.075313	-59200622.5772428	1304090.44535512	0.074633	-50082828.8615628	1718676.88094057
4	0.075192	-58198084.4431487	1634527.29110489			
State 5						
2	0.076903	14366396889.4578	-1427682412.526	0.075341	-72861653.7269248	-10297056.9782662
3	0.076726	-397154915.493218	-11081253.418662	0.075739	-176168665.936144	-2866668.72429844
4	0.076551	-342483780.538171	-7331696.28991826			
State 6						
2	0.083916	-56656378.6003517	-2596415.86683345	0.079775	-43931089.1202126	-1630610.9575217
3	0.083287	-75859502.4906078	-1151641.96590259	0.080023	-42882424.1484699	-326235.112996945
4	0.082859	-74294099.5929215	-1051923.4955114			

Table 6: Magnetic and quadrupole contribution to 3PCD as well as photon energies for 4-helicene. All numbers are in atomic units. The column marked ω contains the photon energies.

Irrep	State	ω	magnetic	quadrupole
		aug-cc-pVDZ		
a	1	0.0497391933	-29044792.3809502	34239193.6464837
a	2	0.05904814	-7080050.37897043	14507995.0144435
a	3	0.0614171067	-200754663.9981	7409938.50424558
a	4	0.0690760267	-33528205.5360227	20757028.5777473
a	5	0.0694978767	275839939.866661	3753959.42598702
a	6	0.07182234	-28943446126.7419	-3000273766.12203
a	7	0.0720035967	-23724493258.2785	-3801019698.61199
a	8	0.07352795	602195232.790145	30313241.7130679
b	1	0.0480233133	16673928.7453367	41048212.1030163
b	2	0.0577753933	-11193042.6345159	32760387.6129496
b	3	0.06284153	13224385.8676239	15752275.1699851
b	4	0.0670089067	-113781920.020349	23522851.989875
b	5	0.0681185933	343686896.444121	-2257825.14578294
b	6	0.0707828333	180680753.92935	2883073.90605842
b	7	0.0710642067	-162599045.77415	8402139.82682588
b	8	0.0728617133	-32647319.3866499	14905521.141489
		aug-cc-pVTZ		
a	1	0.0495977	-46943717.6493857	-245008.335118743
a	2	0.0589707333	-4836420.27561938	96545.1316995348
a	3	0.0613005667	-66284655.602522	1010357.96317482
a	4	0.0689240333	-21407527.0566096	10794836.207214
a	5	0.0693574	292786559.658895	431714.707636832
a	6	0.0716021667	-10417498729.86	-1163496340.94582
a	7	0.0717583667	384059178.133251	2307842.35978119
a	8	0.0733393667	639009028.885636	27061825.0275283

References

[1] D. L. Andrews and T. Thirunamachandran. On three-dimensional rotational averages. *J. Chem. Phys.*, 67(11):5026–5033, 1977.

[2] G. Wagnière. The evaluation of three-dimensional rotational averages. *J. Chem. Phys.*, 76(1):473–480, 1982.

[3] D. H. Friese, M. T. P. Beerepoot, and K. Ruud. Rotational averaging of multiphoton absorption cross sections. *J. Chem. Phys.*, 141:204103, 2014.

[4] Ignacio Tinoco. Twophoton circular dichroism. *J. Chem. Phys.*, 62(3):1006–1009, 1975.

[5] W J Meath and E A Power. Differential multiphoton absorption by chiral molecules and the effect of permanent moments. *J. Phys. B*, 20(9):1945, 1987.

[6] Antonio Rizzo, Branislav Jansík, Thomas Bondo Pedersen, and Hans Ågren. Origin invariant approaches to the calculation of two-photon circular dichroism. *J. Chem. Phys.*, 125(6):064113, 2006.