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Rotational averaging of multiphoton absorption cross sections

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Rotational averaging of tensors is a crucial step in the calculation of molecular properties in isotropic media. We present a scheme for the rotational averaging of multiphoton absorption cross sections. We extend existing literature on rotational averaging to even-rank tensors of arbitrary order and derive equations that require only the number of photons as input. In particular, we derive the first explicit expressions for the rotational average of five-, six-, and seven-photon absorption cross sections. This work is one of the required steps in making the calculation of these higher-order absorption properties possible. The results can be applied to any even-rank tensor provided linearly polarized light is used.
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I. INTRODUCTION

Established as a theoretical concept by Göppert-Mayer,¹ multiphoton absorption has gained a lot of interest in the last three decades. After its first experimental realization,² two-photon absorption was the first nonlinear absorption effect to receive large interest. Promising applications of two-photon absorption include 3D optical storage³ and multiphoton microscopy.⁴ Also higher-order absorption properties up to five-photon absorption have been realized experimentally.⁵ These effects are of particular interest for frequency upconversion of infrared lasers to the visible and UV parts of the spectrum.⁶

Applications of multiphoton absorption require not only strong lasers but also molecular materials with large nonlinear optical absorption cross sections.^{7,8} To support the design of these materials, the development of theoretical methods for the treatment of nonlinear absorption is of large interest. The first quantum-chemical treatment of two-photon absorption dates back to the 1980s.^{9,10} Olsen and Jørgensen introduced the two- and three-photon transition moments as residues of the quadratic and cubic response functions, respectively.¹⁰ Expressions for four-photon absorption were reported by Andrews and Ghoul.¹¹

The calculation of two-photon absorption properties has been implemented for single- and multiconfigurational self-consistent field (SCF) theory,¹² density-functional theory¹³ as well as for coupled-cluster theory.^{14–16} Implementations of three-photon absorption have also been realized.^{17–19} An implementation of higher-order multiphoton absorption properties at the SCF level of theory is in preparation in our group.²⁰

Calculations treat molecules fixed in space, whereas experiments on multiphoton absorption are usually carried out in solution and thus involve a dynamic ensemble of randomly oriented molecules. The molecule can be oriented in a large number of different ways on the timescale of the experiment. Comparison of theory and experiment therefore requires that also the computed values are averaged over all possible ori-

entations. This rotational averaging is a general problem in the treatment of n th-order response properties calculated as n th-rank tensors.^{21–23} The rotational averaging of such tensors has been thoroughly investigated, leading to expressions for up to eighth-rank tensors by Andrews and co-workers.^{11,24,25} Wagnière has discussed even-rank tensors up to rank ten.²⁶ From these studies, formulas for the rotational average of two-, three-, and four-photon absorption cross sections have been derived.¹¹

In the following, we will present a general scheme for rotational averaging of multiphoton absorption tensors. The approach builds on the work by Andrews and co-workers^{24,25} and the work by Wagnière.²⁶ The main aim of the present work is to combine existing theories in a way that can easily be implemented and extended to higher-rank tensors. We will in this paper therefore focus on the derivation of simple and compact equations. Even though the focus will be on rotational averaging of multiphoton absorption cross sections, our findings will also be useful for the averaging of other even-rank tensors because most of the assumptions that we will make are of general nature. An example of another application of our results is in the rotational averaging of m -photon-induced fluorescence tensors²⁷ with no limitation on m . Our approach is limited to linearly polarized photons. For other polarizations, rotational averaging of the absorption properties becomes more involved as will become clear in Sec. IV.

The remainder of this article is organized as follows: In Secs. II and III, we will present the basic theory of multiphoton absorption and rotational averaging of tensors. In Sec. IV, we will treat the polarization tensor for the special case of linearly polarized photons. In Secs. V and VI, we will present the ingredients for the rotational averaging of m -photon absorption cross sections of arbitrary order. Concluding remarks are given in Sec. VII.

II. MULTIPHOTON ABSORPTION THEORY

In this section, we will review the necessary theory of multiphoton absorption. Following Andrews and Thirunamachandran,²⁴ a general observable δ of a molecule

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is obtained from a product of the elements of two tensors

$$\delta = \sum_{i_1 \dots i_n} A_{i_1 \dots i_n}^{[n]} P_{i_1 \dots i_n}^{[n]}, \quad (1)$$

where $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ is an n th-rank tensor in three-dimensional space representing an external influence on a molecule whose response to this influence is described by an n th-rank tensor in three-dimensional space $\mathbf{P}_{i_1 \dots i_n}^{[n]}$. Expressing this in terms of light absorption by a molecule, $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ describes the polarization of the incident photon(s) and $\mathbf{P}_{i_1 \dots i_n}^{[n]}$ is the corresponding transition strength tensor. The indices i on $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ and $\mathbf{P}_{i_1 \dots i_n}^{[n]}$ here denote that the tensors are defined in a space-fixed coordinate system and can be either x , y or z .

In the following, we will represent the number of absorbed photons in multiphoton absorption with m , whereas the rank of the corresponding transition strength tensor $\mathbf{P}_{i_1 \dots i_n}^{[n]}$ is n , with $n = 2m$.

Multiphoton-absorption properties can be calculated from residues of response functions as shown by Olsen and Jørgensen.¹⁰ They can also be expressed using quasienergy derivative theory (see, e.g., Ref. 28). A density-based formalism for calculating residues at the level of time-dependent density-functional theory has been developed by Thorvaldsen *et al.*²⁹ The general expression for the transition strength tensor $\mathbf{P}_{i_1 \dots i_n}^{[n]}$ for m -photon absorption in response theory is

$$\mathbf{P}_{i_1 \dots i_n}^{[n]} = \lim_{\omega_{m+1} + \dots + \omega_n \rightarrow \omega_f} (\omega_{m+1} + \dots + \omega_n - \omega_f) \times \langle \langle X_{i_1}; X_{i_2} \dots X_{i_n} \rangle \rangle_{\omega_1 \dots \omega_n}, \quad (2)$$

where $X_{i_1} \dots X_{i_n}$ are perturbations with corresponding frequencies $\omega_1 \dots \omega_n$, with the frequencies being related through

$$\omega_2 + \omega_3 + \dots + \omega_{2m} = -\omega_1, \quad (3)$$

and therefore sum to zero. $\hbar\omega_f$ is the excitation energy from the electronic ground state to an excited state f . For details on multiphoton-absorption response theory, we refer to the literature.³⁰

The m -photon absorption strength corresponds to the residue of the response function of order n . However, as shown in Ref. 29, the expression for the transition strength $\mathbf{P}^{[n]}$ decomposes to a product of two transition moments $\mathbf{S}^{[m]}$, which are tensors of rank m in three-dimensional space. These transition moments $\mathbf{S}^{[m]}$ are complex conjugates of each other in SCF-based theory and correspond to the residues of the response function of order $m + 1$, significantly reducing the complexity of the expressions. The elements of the transition strength tensor $\mathbf{P}^{[n]}$ can thus be expressed as a product of the

elements of $\mathbf{S}^{[m]}$ and $\bar{\mathbf{S}}^{[m]}$

$$P_{i_1 \dots i_{2m}}^{[n]} = S_{i_1 \dots i_m}^{[m]} \bar{S}_{i_{m+1} \dots i_{2m}}^{[m]}, \quad (4)$$

where the bar indicates complex conjugation. This was also shown by Olsen and Jørgensen in 1985.¹⁰

It is important to note that the response function of order $m + 1$ suffices for the calculation of the transition moments of m -photon absorption for SCF-based theories. However, when it comes to rotational averaging we have to treat the product of two complex conjugate transition moments, which is a tensor of rank n . We will therefore throughout this paper discuss rotational averaging of even-rank tensors in general.

III. ROTATIONAL AVERAGING OF TENSORS

In this section, we will review the basic theory of rotational averaging of tensors.

In Eq. (1) we assumed that the polarization tensor and the transition strengths are described in the same coordinate system. This is only appropriate if the molecules are fixed in space, e.g., in a crystal. If we are dealing with an isotropic sample (e.g., a solution, a neat liquid or a gas), the transition strength $\mathbf{P}^{[n]}$ is described in a molecule-fixed coordinate system. In this case, calculated and experimental results can only be compared if the calculated numbers have been rotationally averaged as discussed in the Introduction. The final result of rotational averaging will be an expression in which the dependence of the transition tensor $\mathbf{P}^{[n]}$ on the molecule-fixed coordinate system has been eliminated and where all quantities are expressed in a space-fixed coordinate system.

Before performing the rotational averaging, we express the two components of Eq. (1) in two different coordinate systems: a space-fixed one for the polarization tensor $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ with the indices i_p , and a molecule-fixed one for the transition strength tensor $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$ with the indices λ_q . Elements of the tensors in the two coordinate systems are connected by a string of L_{i_p, λ_q} -variables²⁴ such that

$$P_{i_1 \dots i_n}^{[n]} = \sum_{\lambda_1 \dots \lambda_n} L_{i_1 \lambda_1} \dots L_{i_n \lambda_n} P_{\lambda_1 \dots \lambda_n}^{[n]}. \quad (5)$$

The string of L -type variables is a product of direction cosines of the angle between the space- and the molecule-fixed coordinate systems.²⁴ The string has n elements: one for every molecule-fixed index of the tensor $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$ that needs a transformation to the space-fixed coordinate system. We note that also elements L_{i_p, λ_q} with $p \neq q$ can appear. The elements L_{i_p, λ_q} can be expressed as elements of the Euler angle matrix \mathbf{L} as used for rotational averaging in Ref. 31

$$\mathbf{L} = \begin{pmatrix} \cos(\phi)\cos(\theta)\cos(\psi) & \sin(\phi)\cos(\theta)\cos(\psi) & -\sin(\theta)\cos(\psi) \\ -\sin(\phi)\sin(\psi) & +\cos(\phi)\sin(\psi) & \\ -\cos(\phi)\cos(\theta)\sin(\psi) & -\sin(\phi)\cos(\theta)\sin(\psi) & \sin(\theta)\sin(\psi) \\ -\sin(\phi)\cos(\psi) & +\cos(\phi)\cos(\psi) & \\ \cos(\phi)\sin(\theta) & \sin(\phi)\sin(\theta) & \cos(\theta) \end{pmatrix}, \quad (6)$$

where the first index of L_{i_p, λ_q} refers to the polarization tensor $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ and the second index to the transition strength tensor $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$. Therefore, for light polarized in the z -direction ($\forall p : i_p = z$), only the elements L_{zx} , L_{zy} , and L_{zz} are needed.

Following Monson and McClain,²¹ we can rewrite Eq. (1) using Eq. (5)

$$\delta = \sum_{i_1 \dots i_n, \lambda_1 \dots \lambda_n} A_{i_1 \dots i_n}^{[n]} L_{i_1 \lambda_1} \dots L_{i_n \lambda_n} P_{\lambda_1 \dots \lambda_n}^{[n]}, \quad (7)$$

where the first factor contains elements of the n th-rank tensor $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ with polarization information, the last factor contains elements of the n th-rank tensor $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$ with the molecular information and the factor in the middle $L_{i_1 \lambda_1} \dots L_{i_n \lambda_n}$ contains the orientational information.²¹

We note that the variable δ in Eq. (7) has not been rotationally averaged yet. To compute the rotational average (which we will denote as $\langle \delta \rangle$ in the following), we have to perform rotational averaging over each string of L -type variables. This can be done by integrating the string $L_{i_1 \lambda_1} \dots L_{i_n \lambda_n}$ over all three rotational angles²⁴

$$I_{i_1 \dots i_n, \lambda_1 \dots \lambda_n}^{(n)} = \frac{1}{8\pi^2} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{\psi=0}^{2\pi} L_{i_1 \lambda_1} \dots L_{i_n \lambda_n} \sin\theta \, d\phi \, d\theta \, d\psi, \quad (8)$$

yielding rotational averages of strings of L -type variables, which are elements of the $2n$ th-rank tensor $\mathbf{I}^{(n)}$. We here distinguish between the superscript $[n]$ for a tensor of rank n and the superscript (n) for a quantity that is used for the rotational averaging of a tensor of rank n .

Andrews and Thirunamachandran have shown how elements of $\mathbf{I}^{(n)}$ can be obtained as a product of one vector with space-fixed coordinates $\mathbf{f}^{(n)}$, one coefficient matrix $\mathbf{M}^{(n)}$, and one vector with molecule-fixed coordinates $\mathbf{g}^{(n)}$ ²⁴

$$I_{i_1 \dots i_n, \lambda_1 \dots \lambda_n}^{(n)} = (\mathbf{f}^{(n)})^T \mathbf{M}^{(n)} \mathbf{g}^{(n)}. \quad (9)$$

The elements of the two vectors $\mathbf{f}^{(n)}$ and $\mathbf{g}^{(n)}$ are both strings of m Kronecker deltas. The number of Kronecker delta strings in $\mathbf{f}^{(n)}$ and $\mathbf{g}^{(n)}$ (i.e., the length of the vectors $\mathbf{f}^{(n)}$ and $\mathbf{g}^{(n)}$) increases rapidly with the rank of the tensor. The number of strings N_n is listed in Table I and determines the number of elements of the two vectors and of the matrix $\mathbf{M}^{(n)}$, which is

TABLE I. Number of Kronecker delta strings N_n to be evaluated for different tensor ranks n , i.e., the length of the vectors $\mathbf{f}^{(n)}$ and $\mathbf{g}^{(n)}$.

n	N_n	Corresponding absorption property
2	1	One-photon
4	3	Two-photon
6	15	Three-photon
8	105	Four-photon
10	945	Five-photon
12	10 395	Six-photon
14	135 135	Seven-photon

an $N_n \times N_n$ matrix, and can be calculated as

$$N_n = \frac{n!}{2^m (m)!} \quad (10)$$

$$= \prod_{i=1}^m (2i-1), \quad (11)$$

which is a product of all odd numbers smaller than n . Equation (11) is useful for our aim of finding a simple and universal approach for rotational averaging of any even-rank tensor.

To obtain the indices of the Kronecker delta strings, Andrews and Thirunamachandran introduced a scheme using so-called standard tableaux.²⁴ This method is very appropriate for a thorough mathematical understanding of the fundamental theory. However, we choose to reformulate their scheme in a different way:

- Generate all permutations of a row containing all indices from 1 to n once.
- Select all strings that fulfill the following conditions:
 1. The numbers in every index pair are in ascending order, e.g., 5, 1; 2, 3; 4, 6; 7, 8 vanishes and 1, 5; 2, 3; 4, 6; 7, 8 remains.
 2. All indices in odd-numbered positions are in ascending order, e.g., 1, 2; 4, 5; 3, 6; 7, 8 vanishes and 1, 2; 3, 6; 4, 5; 7, 8 remains.
- Interpret every index pair as the two indices of one Kronecker delta, e.g., 1, 2; 3, 5; 4, 6; 7, 8 $\rightarrow \delta_{12} \delta_{35} \delta_{46} \delta_{78}$.

In principle, all allowed permutations can be generated computationally using this scheme. However, such an implementation is inefficient since it generates and tests also a large number of permutations that do not fulfill the two conditions and are therefore superfluous. We will later show that an explicit evaluation of all possible permutations is not needed to derive explicit expressions for the rotational averaging of higher-order cross sections for multiphoton absorption. Nevertheless, this scheme is very helpful for setting up the rules needed for the determination of the contraction coefficients, which will be done in Sec. VI.

The coefficients of the matrix $\mathbf{M}^{(n)}$ in Eq. (9) can be determined by evaluating the Kronecker delta strings in $\mathbf{f}^{(n)}$ and $\mathbf{g}^{(n)}$ as explained in Ref. 24.

For a fourth-rank tensor, Andrews' approach yields the following expression for the elements of $\mathbf{I}^{(n)}$:

$$I^{(4)} = \begin{pmatrix} \delta_{i_1 i_2} \delta_{i_3 i_4} \\ \delta_{i_1 i_3} \delta_{i_2 i_4} \\ \delta_{i_1 i_4} \delta_{i_2 i_3} \end{pmatrix}^T \frac{1}{30} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{\lambda_1 \lambda_2} \delta_{\lambda_3 \lambda_4} \\ \delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_4} \\ \delta_{\lambda_1 \lambda_4} \delta_{\lambda_2 \lambda_3} \end{pmatrix}, \quad (12)$$

whereas for a sixth-rank tensor we obtain²⁴

$$I^{(6)} = (\mathbf{f}^{(6)})^T \mathbf{M}^{(6)} \mathbf{g}^{(6)}, \quad (13)$$

where $\mathbf{M}^{(6)}$ is a 15×15 matrix and where the 15 elements of the vectors $\mathbf{f}^{(6)}$ and $\mathbf{g}^{(6)}$ are Kronecker delta strings. The expressions of $\mathbf{f}^{(6)}$, $\mathbf{M}^{(6)}$, and $\mathbf{g}^{(6)}$ from Ref. 24 are given in the Appendix.

We can think of the vectors $\mathbf{f}^{(n)}$ and $\mathbf{g}^{(n)}$ as operators that act on the elements of $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ and $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$, respectively. Indeed, the matrix $\mathbf{M}^{(n)}$ and the vectors $\mathbf{f}^{(n)}$ and $\mathbf{g}^{(n)}$ in Eq. (9) have the same form for every element of $\mathbf{I}^{(n)}$. Each Kronecker delta in $\mathbf{f}^{(n)}$ and $\mathbf{g}^{(n)}$ evaluates whether two of the indices of $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ and $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$ are equal or not. For instance, the string $\delta_{\lambda_1 \lambda_3} \delta_{\lambda_2 \lambda_4} \delta_{\lambda_5 \lambda_6}$ is 1 only if the first and the third, the second and the fourth and the fifth and the sixth index of the transition tensor $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$ are the same. This holds for the elements $P_{ababcc}^{[n]}$ where the first Kronecker delta describes the positions of the indices a , the second the positions of the indices b and the third the positions of the indices c . The indices a , b and c can independently of each other be either x , y or z .

The indices on $P^{[n]}$ determine the indices on S and \bar{S} as shown in Eq. (4), for instance,

$$P_{ababcc}^{[n]} \rightarrow S_{aba}^{[m]} \bar{S}_{bcc}^{[m]}. \quad (14)$$

We note that this procedure leads to the same number of pairs of equal indices on $S^{[m]}$ as on $\bar{S}^{[m]}$ (one pair in the example above). For three indices on $S^{[m]}$ and three indices on $\bar{S}^{[m]}$ (corresponding to three-photon absorption) the number of index pairs can be either 0 or 1. This will be relevant in Sec. VI.

$\mathbf{I}^{(n)}$ can thus be interpreted as an interface between the polarization tensor $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ on the left-hand side and the transition moments $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$ on the right-hand side. A rotationally averaged variable can thus be written as Eq. (9) multiplied from the left by elements of $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ and from the right by elements of $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$

$$\langle \delta \rangle = \sum_{i_1 \dots i_n, \lambda_1 \dots \lambda_n} A_{i_1 \dots i_n}^{[n]} I^{(n)} P_{\lambda_1 \dots \lambda_n}^{[n]} \quad (15)$$

$$= \sum_{i_1 \dots i_n, \lambda_1 \dots \lambda_n} A_{i_1 \dots i_n}^{[n]} (\mathbf{f}^{(n)})^T \mathbf{M}^{(n)} \mathbf{g}^{(n)} P_{\lambda_1 \dots \lambda_n}^{[n]}, \quad (16)$$

where $A_{i_1 \dots i_n}^{[n]} (\mathbf{f}^{(n)})^T$ and $\mathbf{g}^{(n)} P_{\lambda_1 \dots \lambda_n}^{[n]}$ are evaluated first.

IV. THE POLARIZATION TENSOR FOR LINEARLY POLARIZED PHOTONS

In this section, we will show how the use of linearly polarized light simplifies Eq. (16) for the rotational averaging of tensors. In particular, we will use the theory of rotational averaging from Sec. III to derive the well-established expressions for the rotationally averaged one-photon (OPA) and two-photon absorption (TPA) cross sections.

The n th-rank polarization tensor $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ is obtained as the tensor product of all involved polarization vectors and their complex conjugates.³² Therefore, it is the tensor product of outer form of n three-dimensional vectors. For photons that are linearly polarized perpendicular to the propagation direction, the polarization vector \mathbf{p} is a unit vector in the z direction and equal to its complex conjugate. For $\mathbf{A}_{i_1, i_2}^{[2]}$, corresponding to one-photon absorption, we obtain

$$\mathbf{A}_{i_1, i_2}^{[2]} = \mathbf{p} \otimes \bar{\mathbf{p}} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \otimes \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (17)$$

which yields a matrix with just one nonzero element $A_{zz}^{[2]}$. For $\mathbf{A}_{i_1 \dots i_4}^{[4]}$, corresponding to two-photon absorption, the resulting fourth-rank tensor also has only one nonzero element, $A_{zzzz}^{[4]}$. In general, only one element of $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ is nonzero when all photons are linearly polarized. If all photons are polarized perpendicular to the propagation direction, this element is $A_{z^n}^{[n]}$. This leads to a major simplification in the following. If there are more nonzero elements of the tensor $\mathbf{A}_{i_1 \dots i_n}^{[n]}$, the expressions become much longer and the evaluation becomes more complex.

We recall at this point that the tensor $\mathbf{I}^{(n)}$ is of rank $2n$ and has two sets of indices i_p and λ_q , which correspond to the space-fixed and the molecule-fixed coordinate systems, respectively. The elements of $\mathbf{A}_{i_1 \dots i_n}^{[n]} \mathbf{f}^{(n)}$ can only be nonzero for nonzero elements of $\mathbf{A}_{i_1 \dots i_n}^{[n]}$, i.e., for element $A_{z^n}^{[n]}$. For the one-photon absorption case, this corresponds to

$$\sum_{i_1, i_2} A_{i_1, i_2}^{[2]} \mathbf{f}^{(2)} = \sum_{i_1, i_2} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \delta_{i_1, i_2} = 1. \quad (18)$$

In general, summation over all elements of $\mathbf{A}_{i_1 \dots i_n}^{[n]}$ for the case of completely linearly polarized light results in only one non-vanishing contribution. In this contribution, all indices i_n are z and thus all elements of the vector $\mathbf{f}^{(n)}$ are unity.²¹ Thus, when evaluating Eq. (16), $A_{z^n}^{[n]} (\mathbf{f}^{(n)})^T$ reduces to a summation of all the elements of the product of the matrix $\mathbf{M}^{(n)}$, the right-hand side vector $\mathbf{g}^{(n)}$ and the molecular tensor $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$, so that

$$A_{z^n}^{[n]} (\mathbf{f}^{(n)})^T \mathbf{M}^{(n)} \mathbf{g}^{(n)} \mathbf{P}^{[n]} = \sum_{i=1, \lambda_1 \dots \lambda_i} (\mathbf{M}^{(n)} \mathbf{g}^{(n)} \mathbf{P}_{\lambda_1 \dots \lambda_i}^{[n]})_i. \quad (19)$$

Exploiting these properties of the tensor $\mathbf{A}_{i_1 \dots i_n}^{[n]}$, we can formulate expressions for the rotational averaging of the different multiphoton absorption properties. Rotational averaging of the one-photon absorption strength thus gives us the following expression:

$$\langle \delta^{\text{OPA}} \rangle = \sum_a (1)^T \frac{1}{3} (1) (S_a \bar{S}_a) \quad (20)$$

$$= \frac{1}{3} \sum_a S_a \bar{S}_a, \quad (21)$$

which is equal to the familiar expression of taking the trace of $\mathbf{P}_{\lambda_1, \lambda_2}^{[2]}$ and dividing by three. The factor $\frac{1}{3}$ results from solving the integral in Eq. (8) using the elements L_{zx} , L_{zy} or L_{zz} for the L -type variables.

Using Eq. (12) we obtain for the rotationally averaged two-photon absorption strength

$$\langle \delta^{\text{TPA}} \rangle = \sum_{ab} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}^T \frac{1}{30} \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} S_{aa} \bar{S}_{bb} \\ S_{ab} \bar{S}_{ab} \\ S_{ab} \bar{S}_{ba} \end{pmatrix} \quad (22)$$

$$= \frac{1}{15} \sum_{ab} (S_{aa} \bar{S}_{bb} + S_{ab} \bar{S}_{ab} + S_{ab} \bar{S}_{ba}). \quad (23)$$

This is the expression for the rotational average of two-photon absorption cross sections as introduced by Monson and McClain.²¹ Assuming that the transition moments \mathbf{S} and $\bar{\mathbf{S}}$ are symmetric, this expression can be further simplified to¹¹

$$\langle \delta^{\text{TPA}} \rangle = \frac{1}{15} \sum_{ab} (2S_{ab} \bar{S}_{ab} + S_{aa} \bar{S}_{bb}). \quad (24)$$

Corresponding expressions for 3PA and 4PA have been derived in the literature.¹¹

Comparing Eqs. (21) and (24), we note that in both cases the expressions for the rotationally averaged observable have been reduced to a sum of contractions of the tensor $\mathbf{P}_{\lambda_1 \dots \lambda_n}^{[n]}$ and multiplication with a prefactor, which we will call ζ_n . In Secs. V and VI, we will treat the prefactor and the contractions separately, with the goal of obtaining an expression for rotational averaging of even-rank tensors of arbitrary order.

V. THE PREFACTOR ζ_n

The prefactor ζ_n can be obtained from either of two equivalent approaches: from the summation of the elements of each column of $\mathbf{M}^{(n)}$ as shown in Eq. (19), or from the integral in Eq. (8). We will use the latter approach, following Wagnière,²⁶ to derive an expression for the prefactor for rotational averaging of even-rank tensors of arbitrary order assuming linearly polarized light in the z -direction.

If all L -type variables in the integral in Eq. (8) are the elements L_{zz} of the Euler matrix in Eq. (6), the integral reduces to

$$\begin{aligned} I_{z^n, z^n}^{(n)} &= \frac{1}{8\pi^2} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{\psi=0}^{2\pi} \cos^n \theta \sin \theta \, d\phi \, d\theta \, d\psi \quad (25) \\ &= \frac{1}{n+1}. \quad (26) \end{aligned}$$

In principle, the string of L -type variables that needs to be integrated can be a combination of the elements L_{zx} , L_{zy} , and L_{zz} of the Euler matrix in Eq. (6) for linearly polarized light in the z -direction. However, for many combinations, the outcome of the integral is zero. The nonzero elements are those in which all indices λ_p occur as pairs, e.g., $xyyz$ and not $xxzyz$. The combinations that give zero are automatically identified and discarded by interpreting every index pair as the two indices of one Kronecker delta, as described in Sec. III, and can thus be disregarded here. For all combinations of L_{zx} , L_{zy} , and L_{zz} that lead to a nonzero outcome, the element of $\mathbf{I}^{(n)}$ can be written as

$$I_{z^n, \lambda_1 \dots \lambda_n}^{(n)} = \frac{1}{n+1} \frac{k_{\lambda_1 \dots \lambda_n}}{N_n}, \quad (27)$$

with $k_{\lambda_1 \dots \lambda_n}$ being the number of Kronecker delta strings in $\mathbf{g}^{(n)}$ that are one for the indices $\lambda_1 \dots \lambda_n$. For the special case in Eqs. (25) and (26), all Kronecker delta strings give one and $k_{\lambda_1 \dots \lambda_n} = N_n$.

To obtain an expression for ζ_n , we have to divide the element of $\mathbf{I}^{(n)}$ by $k_{\lambda_1 \dots \lambda_n}$ to avoid double-counting terms in the contractions in Sec. VI. The prefactor ζ_n can thus be obtained from n and N_n (Eq. (11)) giving an expression that can be used

for even-rank tensors of any order:

$$\zeta_n = \frac{I_{z^n, \lambda_1 \dots \lambda_n}^{(n)}}{k_{z^n, \lambda_1 \dots \lambda_n}} = \frac{1}{N_n(n+1)} = \prod_{i=1}^m \frac{1}{(2i+1)}, \quad (28)$$

where the only input needed is the number of involved photons m . Note the similarity between Eqs. (11) and (28). The denominator of the prefactor ζ_n is the product of all odd numbers equal or less than $n+1$.

VI. THE CONTRACTION COEFFICIENTS

Having evaluated the expression for the prefactor ζ_n for any order n , we now consider the contraction of the transition tensor elements for the different levels of multiphoton absorption. For TPA, only a very slight degree of systematization is required based on the assumption that the transition tensors are symmetric (see Eqs. (23) and (24)). The contractions for higher-rank tensors are more involved.

The number of contractions involved in the rotational averaging of an n th-rank tensor is N_n and this number increases dramatically with n , see Eq. (11) and Table I. Nevertheless, the number of *different* contractions is reasonably small due to the index symmetry of the transition tensors.¹¹ Indeed, we end up with two different contractions for TPA and 3PA, three different contractions for 4PA and 5PA, four different contractions for 6PA and 7PA, and so on. The different contractions can be distinguished by the number of pairs of equal indices on S or \bar{S} . For instance, S_{abc} has one pair of equal indices a while S_{abcd} has none. In Eq. (24), the first term $S_{ab} \bar{S}_{ab}$ gives the contractions with all different indices on S and \bar{S} (with contraction coefficient 2) whereas the second term $S_{aa} \bar{S}_{bb}$ gives the contractions with one pair of the same indices on both S and \bar{S} (with contraction coefficient 1). In the following, the coefficient for the contraction will be named C_i^m , with i the number of pairs with equal indices in S and \bar{S} so that the coefficients for 4PA for instance will be C_0^4 , C_1^4 and C_2^4 .

The determination of the contraction coefficients C_i^m can be performed using a simple mathematical scheme as explained below, using the two formulas

$$C_0^m = m!, \quad (29)$$

$$C_i^m = \frac{m! \prod_{j=0}^{2i-1} (m-j)}{(2^i)^2 (i!)^2} \quad 1 \leq i \leq \frac{m+1}{2}, i \in \mathbb{N}, \quad (30)$$

where the only input needed is the number of involved photons m . To explain this scheme, we will first reformulate the conditions for the contributing Kronecker delta strings to conditions for the indices on S and \bar{S} using the relation between the Kronecker delta strings and the indices on S and \bar{S} (see Sec. III). Condition 1 ensures that we cannot interchange the indices in a pair, e.g., there is just one allowed permutation $S_{aa} \bar{S}_{bb}$. Condition 2 ensures that the first of the two occurrences of every index are in ascending order, e.g., $S_{ba} \bar{S}_{ab}$ vanishes and $S_{ab} \bar{S}_{ab}$ remains as the first a needs to come before the first b .

The number of pairs of the same indices i on S and \bar{S} is always the same. However, the positions of the indices on S are more constrained than those on \bar{S} . Indeed, when we know

the *positions* of the index pairs on S , there is only one way of arranging the indices that are not part of a pair: in ascending order (condition 2). For the number of permutations of the indices on S we thus need to consider only the positions of the paired indices. The positions of the indices on \bar{S} , on the other hand, are more free. Condition 2 only holds for the first occurrence of an index and thus only for the indices that occur as a pair on \bar{S} . There is no constraint on the indices on \bar{S} that are not part of a pair because these are the second occurrences of the index. It is thus convenient to calculate the number of allowed permutations of S and \bar{S} separately. The total number of contractions is the product of the number of allowed permutations of S and \bar{S} .

For C_0^m — where S and \bar{S} contain no pair with the same indices — it follows from condition 2 that the indices of S can be written in only one way, which is in ascending order. The number of permutations of the indices for \bar{S} is $m!$ giving $1 \cdot m!$ for C_0^m . For C_1^m — where S and \bar{S} contain one pair with the same indices — S can be written in $m(m-1)/2$ ways: $m(m-1)$ is the number of positions where the pair can be and the division by 2 follows from condition 1. The only constraint on the indices of \bar{S} is that the indices that form the pair cannot be interchanged (condition 1), giving $m!/2$ possible permutations of the indices on \bar{S} . For C_i^m — where S and \bar{S} contain i pairs with the same indices — the number of permutations is $\prod_{j=0}^{i-1} (m-j)/(2^i i!)$ for S and $m!(2^i i!)$ for \bar{S} . The denominators ensure that the first occurrences of an index from a pair are ordered in ascending order (following from condition 2) by dividing by $i!$ and excludes interchanging two indices that form one pair (following from condition 1) by dividing by 2^i .

Our scheme thus allows rotational averaging of multiphoton absorption tensors of arbitrary order. The coefficients for the different contractions up to 7PA (computed using Eqs. (29) and (30)) are given in Table II.

Combining the values from Table II with the corresponding prefactors obtained from Eq. (28), we obtain the following expressions for the rotational average of the first seven m -photon absorption cross sections:

$$\langle \delta^{\text{OPA}} \rangle = \frac{1}{3} \sum_a S_a \bar{S}_a, \quad (31)$$

$$\langle \delta^{\text{TPA}} \rangle = \frac{1}{15} \sum_{ab} (2S_{ab} \bar{S}_{ab} + S_{aa} \bar{S}_{bb}), \quad (32)$$

$$\langle \delta^{\text{3PA}} \rangle = \frac{1}{35} \sum_{abc} (2S_{abc} \bar{S}_{abc} + 3S_{aab} \bar{S}_{bcc}), \quad (33)$$

TABLE II. Contraction coefficients C_i^m for different levels of multiphoton absorption with m the number of absorbed photons and i the number of pairs of equal indices on S and \bar{S} .

C_i^m	m						
	1	2	3	4	5	6	7
C_0^m	1	2	6	24	120	720	5040
C_1^m	-	1	9	72	600	5400	52920
C_2^m	-	-	-	9	225	4050	66150
C_3^m	-	-	-	-	-	225	11025

$$\langle \delta^{4\text{PA}} \rangle = \frac{1}{315} \sum_{abcd} (8S_{abcd} \bar{S}_{abcd} + 24S_{aabc} \bar{S}_{bcdd} + 3S_{aabb} \bar{S}_{ccdd}), \quad (34)$$

$$\langle \delta^{5\text{PA}} \rangle = \frac{1}{693} \sum_{abcde} (8S_{abcde} \bar{S}_{abcde} + 40S_{aabcd} \bar{S}_{bcdee} + 15S_{aabbc} \bar{S}_{cdeee}), \quad (35)$$

$$\langle \delta^{6\text{PA}} \rangle = \frac{1}{3003} \sum_{abcdef} (16S_{abcdef} \bar{S}_{abcdef} + 120S_{aabcde} \bar{S}_{bcdeff} + 90S_{aabbcd} \bar{S}_{cdeeff} + 5S_{aabbcc} \bar{S}_{ddeeff}), \quad (36)$$

$$\langle \delta^{7\text{PA}} \rangle = \frac{1}{6435} \sum_{abcdefg} (16S_{abcdefg} \bar{S}_{abcdefg} + 168S_{aabcdef} \bar{S}_{bcdefgg} + 210S_{aabbcd} \bar{S}_{cdeffgg} + 35S_{aabbcc} \bar{S}_{deeffgg}). \quad (37)$$

In these equations, the coefficients of the contractions have been ordered such that C_0^m comes first and the other coefficients follow in ascending order. Additionally, for 3PA and higher, the greatest common factor of all coefficients has been factorized out and combined with the denominator of ζ_n , namely, 3 for 3PA and 4PA, 15 for 5PA, 45 for 6PA, and 315 for 7PA. The expressions for the rotational average of five-, six-, and seven-photon absorption cross sections are here reported for the first time. Indeed, their derivation is made significantly easier by the general scheme introduced in this work.

VII. CONCLUDING REMARKS

We have presented a scheme for rotational averaging of multiphoton absorption cross sections of arbitrary order. Moreover, we have derived the first explicit expressions for the rotational average of five-, six-, and seven-photon absorption cross sections. All necessary expressions can be derived using only the number of involved photons as input. Our scheme can be implemented straightforwardly to allow for rotational averaging of any even-rank tensor provided linearly polarized light is used. The outcome of this work is required for the calculation of higher-order multiphoton absorption properties of isotropic samples.

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APPENDIX: INTERMEDIATES FOR SIXTH-RANK TENSORS

In this appendix, we repeat the expressions for $\mathbf{f}^{(6)}$, $\mathbf{g}^{(6)}$, and $\mathbf{M}^{(6)}$ from Ref. 24 for the rotational averaging of

sixth-rank tensors.

$$\mathbf{f}^{(6)} = \begin{pmatrix} \delta_{i_1, i_2} \delta_{i_3, i_4} \delta_{i_5, i_6} \\ \delta_{i_1, i_2} \delta_{i_3, i_5} \delta_{i_4, i_6} \\ \delta_{i_1, i_2} \delta_{i_3, i_6} \delta_{i_4, i_5} \\ \delta_{i_1, i_3} \delta_{i_2, i_4} \delta_{i_5, i_6} \\ \delta_{i_1, i_3} \delta_{i_2, i_5} \delta_{i_4, i_6} \\ \delta_{i_1, i_3} \delta_{i_2, i_6} \delta_{i_4, i_5} \\ \delta_{i_1, i_4} \delta_{i_2, i_3} \delta_{i_5, i_6} \\ \delta_{i_1, i_4} \delta_{i_2, i_5} \delta_{i_3, i_6} \\ \delta_{i_1, i_4} \delta_{i_2, i_6} \delta_{i_3, i_5} \\ \delta_{i_1, i_5} \delta_{i_2, i_3} \delta_{i_4, i_6} \\ \delta_{i_1, i_5} \delta_{i_2, i_4} \delta_{i_3, i_6} \\ \delta_{i_1, i_5} \delta_{i_2, i_6} \delta_{i_3, i_4} \\ \delta_{i_1, i_6} \delta_{i_2, i_3} \delta_{i_4, i_5} \\ \delta_{i_1, i_6} \delta_{i_2, i_4} \delta_{i_3, i_5} \\ \delta_{i_1, i_6} \delta_{i_2, i_5} \delta_{i_3, i_4} \end{pmatrix} \quad (\text{A1})$$

$$\mathbf{g}^{(6)} = \begin{pmatrix} \delta_{\lambda_1, \lambda_2} \delta_{\lambda_3, \lambda_4} \delta_{\lambda_5, \lambda_6} \\ \delta_{\lambda_1, \lambda_2} \delta_{\lambda_3, \lambda_5} \delta_{\lambda_4, \lambda_6} \\ \delta_{\lambda_1, \lambda_2} \delta_{\lambda_3, \lambda_6} \delta_{\lambda_4, \lambda_5} \\ \delta_{\lambda_1, \lambda_3} \delta_{\lambda_2, \lambda_4} \delta_{\lambda_5, \lambda_6} \\ \delta_{\lambda_1, \lambda_3} \delta_{\lambda_2, \lambda_5} \delta_{\lambda_4, \lambda_6} \\ \delta_{\lambda_1, \lambda_3} \delta_{\lambda_2, \lambda_6} \delta_{\lambda_4, \lambda_5} \\ \delta_{\lambda_1, \lambda_4} \delta_{\lambda_2, \lambda_3} \delta_{\lambda_5, \lambda_6} \\ \delta_{\lambda_1, \lambda_4} \delta_{\lambda_2, \lambda_5} \delta_{\lambda_3, \lambda_6} \\ \delta_{\lambda_1, \lambda_4} \delta_{\lambda_2, \lambda_6} \delta_{\lambda_3, \lambda_5} \\ \delta_{\lambda_1, \lambda_5} \delta_{\lambda_2, \lambda_3} \delta_{\lambda_4, \lambda_6} \\ \delta_{\lambda_1, \lambda_5} \delta_{\lambda_2, \lambda_4} \delta_{\lambda_3, \lambda_6} \\ \delta_{\lambda_1, \lambda_5} \delta_{\lambda_2, \lambda_6} \delta_{\lambda_3, \lambda_4} \\ \delta_{\lambda_1, \lambda_6} \delta_{\lambda_2, \lambda_3} \delta_{\lambda_4, \lambda_5} \\ \delta_{\lambda_1, \lambda_6} \delta_{\lambda_2, \lambda_4} \delta_{\lambda_3, \lambda_5} \\ \delta_{\lambda_1, \lambda_6} \delta_{\lambda_2, \lambda_5} \delta_{\lambda_3, \lambda_4} \end{pmatrix} \quad (\text{A2})$$

$$\mathbf{M}^{(6)} = \frac{1}{210} \begin{pmatrix} 16 & -5 & -5 & -5 & 2 & 2 & -5 & 2 & 2 & 2 & 2 & -5 & 2 & 2 & -5 \\ -5 & 16 & -5 & 2 & -5 & 2 & 2 & 2 & -5 & -5 & 2 & 2 & 2 & -5 & 2 \\ -5 & -5 & 16 & 2 & 2 & -5 & 2 & -5 & 2 & 2 & -5 & 2 & -5 & 2 & 2 \\ -5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & 2 \\ 2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 & -5 & 2 & 2 & 2 & 2 & -5 \\ 2 & 2 & -5 & -5 & -5 & 16 & 2 & 2 & -5 & 2 & 2 & -5 & -5 & 2 & 2 \\ -5 & 2 & 2 & -5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 & -5 & 2 & 2 \\ 2 & 2 & -5 & 2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 & 2 & 2 & -5 \\ 2 & -5 & 2 & 2 & 2 & -5 & -5 & -5 & 16 & 2 & 2 & -5 & 2 & -5 & 2 \\ 2 & -5 & 2 & 2 & -5 & 2 & -5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 \\ 2 & 2 & -5 & -5 & 2 & 2 & 2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 \\ -5 & 2 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & -5 & 16 & 2 & 2 & -5 & -5 \\ 2 & 2 & -5 & 2 & 2 & -5 & -5 & 2 & 2 & -5 & 2 & 2 & 16 & -5 & -5 \\ 2 & -5 & 2 & -5 & 2 & 2 & 2 & 2 & -5 & 2 & -5 & 2 & -5 & 16 & -5 \\ -5 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & 2 & 2 & -5 & -5 & -5 & 16 & -5 \end{pmatrix} \quad (\text{A3})$$

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