Invariant multipole theory of induced macroscopic fields in homogeneous dielectrics

by

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Abstract

A harmonic plane electromagnetic wave incident on a molecule distorts its charge distribution, thereby producing an infinite series of induced multipole moments expressed in terms of contributions that are due to the electric and magnetic fields $\boldsymbol{E}$ and $\boldsymbol{B}$, and their space and time derivatives. For a linear dependence of an induced moment on a particular field property, as treated in this thesis, the constant of proportionality is essentially the corresponding molecular polarizability. Each polarizability is of a definite multipole order (electric dipole, electric quadrupole–magnetic dipole, electric octopole–magnetic quadrupole, etc.). The contribution of each multipole term to a physical property diminishes rapidly with increasing multipole order. In general, the moments and polarizabilities are dependent on an arbitrary choice of molecular coordinate origin, relative to which the positions of molecular constituents are referred.

Electromagnetic observables are expressible, in part, in terms of contributions of the polarizabilities of the same multipole order. The aim of multipole theory is to explain effects to the lowest relevant multipole order, since higher-order contributions are negligible. A necessary criterion for such a theory is that it be independent of the choice of molecular coordinate origin. Van Vleck [1] introduced this condition, and Buckingham [2] and others [3, 4] have used it as a standard test of the theory.

The macroscopic continuum theory of electromagnetics, as embodied in Maxwell's macroscopic equations, involves molecular properties and electromagnetic fields averaged over a sampling volume of dimensions much smaller than the wavelength of the fields and much larger than molecular dimensions [5]. This averaging entails specifying a set of molecular coordinate origins.

The multipole expressions for the macroscopic induced bound charge and current densities and the propagation equation are origin independent in part due to cancellation of their origin dependences among terms of the same multipole order — the so-called Van Vleck–Buckingham condition [6]. The multipole expressions for the dynamic response fields, $\boldsymbol{D}(\boldsymbol{E},\boldsymbol{B})$ and $\boldsymbol{H}(\boldsymbol{E},\boldsymbol{B})$, above electric dipole order depend on origin, and thus the theory is only partially invariant. To obtain a consistent invariant multipole theory of induced macroscopic fields up to electric octopole–magnetic quadrupole order, origin-independent expressions corresponding to the molecular polarizabilities are determined. When used in place of the molecular polarizabilities, these invariant expressions leave the origin-independent aspects of the theory unchanged, and yield physically acceptable expressions for the macroscopic fields. The resulting theory is fully invariant for both transmission and reflection.

The procedure to determine invariant polarizabilities requires manipulations of expressions involving Cartesian tensors up to rank four, contracted with isotropic tensors up to rank eight, at electric octopole–magnetic quadrupole order. The algebraic software package MATHEMATICA was used to facilitate the evaluation of these expressions.

Declaration

I, Allard Welter, declare that

(i) The research reported in this thesis, except where otherwise indicated, is my original research.

(ii) This thesis has not been submitted for any degree or examination at any other university.

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Signed ....

Contents

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Chapter 1

Introduction

The material presented in this thesis is based on the following three publications:

1. O. L. de Lange, R. E. Raab, and A. Welter. On the transition from microscopic to macroscopic electrodynamics. *J. Math. Phys.*, **53**, 013513 (2012).

2. O. L. de Lange, R. E. Raab, and A. Welter. Translational invariance, the Post constraint and uniqueness in macroscopic electrodynamics. *J. Math. Phys.*, **53**, 073518 (2012).

3. A. Welter, R. E. Raab, and O. L. de Lange. Translationally invariant semi-classical electrodynamics of magnetic media to electric octopole–magnetic quadrupole order. *J. Math. Phys.*, **54**, 023512 (2013).

The presentation given here differs from that in the above articles in a number of respects. Emphasis is given to the derivation of the origin-independent expressions for the molecular polarizabilities. The calculations are presented in more detail, with additional reference to the computational aspects. Especially, the demonstration of linear independence of the invariant molecular polarizabilities is presented in a consistent manner. Several examples of the procedure are given, demonstrating various aspects of the method. The calculations of linear independence do not change the published results presented at electric quadrupole–magnetic dipole order [6], and at electric octopole–magnetic quadrupole order for non-magnetics [7]. The invariant expressions for the time-odd polarizabilities at electric octopole–magnetic quadrupole order, however, contain one unresolved coefficient c_2 not identified in Reference [8] (see Chapter 6). The invariant formulation of the time-odd contributions at electric octopole–magnetic quadrupole order specifies the bound charge and current densities and the propagation equation uniquely, but the dynamic response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ at this order depend on the unknown real coefficient c_2.

Multipole theory, as now formulated, is developed from a Taylor expansion of the vector potential of a charge distribution in vacuum [4]. Early theories pair inconsistent multipoles, for instance, electric dipole with magnetic dipole, electric quadrupole with magnetic quadrupole, etc. [9]. Rosenfeld showed that the magnetic dipole is partnered with the electric quadrupole in the contribution to the current density and Maxwell's equations [10, Chapter 2]. The semi-classical formulation of multipole theory to third order was initiated by Buckingham [11]. The first direct measurement of the electric quadrupole of a molecule was performed by Buckingham [12].

Many texts describe classical multipole theory [3, 4, 13]. An overview of the relevant results from semi-classical multipole theory to electric octopole–magnetic quadrupole order, based on the presentation in Reference 4, is given in Chapter 2. These results provide the starting point for the subsequent calculations in this thesis and serve to establish the notation.

The emergence of the macroscopic Maxwell equations from microscopic counterparts was hinted at by Lorentz, before the discovery of the electron, in his doctoral thesis [14]. Subsequent work by Lorentz in 1878, 1880, 1892 and 1902 laid the foundation for the derivation of the macroscopic Maxwell equations from corresponding microscopic (source free) equations [14]. There is consensus that the transition from microscopic to macroscopic electrodynamics is achieved by an averaging process [9, 10, 15–18]. The particulars of the averaging, however, have been the subject of much debate, and depend on the system under consideration.

The necessary theory of spatial averaging is presented in Chapter 3. The transition to macroscopic electrodynamics exposes the limitations that result from the origin dependences of the molecular polarizabilities, presented in Chapter 2, in the formulation of a consistent macroscopic multipole theory. It is found that the induced macroscopic moment densities depend in general on the arbitrarily chosen molecular coordinate origins to which the molecular polarizabilities are referred. The induced bound source densities $\rho(\boldsymbol{r}, t)$ and $\boldsymbol{J}(\boldsymbol{r}, t)$, and the propagation equation, which are derived from the macroscopic moment densities, are found to be independent of the choice of molecular coordinate origins, whereas the dynamic response fields $\boldsymbol{D}(\boldsymbol{E}, \boldsymbol{B})$ and $\boldsymbol{H}(\boldsymbol{E}, \boldsymbol{B})$, and the material constants, depend on the chosen molecular coordinate origins. Thus the macroscopic multipole theory derived from the origin-independent (non-invariant) molecular polarizabilities is only partially invariant (see Figure 1.1).

In Chapters 4 and 5 an invariant theory for linear, homogeneous, anisotropic dielectrics (media without free charges) is proposed as a preparatory step in the transition from the microscopic to a macroscopic theory. The invariant theory is based on origin-independent expressions for the molecular polarizabilities. The invariant polarizabilities leave origin-independent observables unchanged, and result in physically acceptable origin-independent expressions for the multipole fields (see Figure 1.1).

The calculation of the origin-independent expressions at electric octopole–magnetic quadrupole order requires extensive algebraic treatment of tensor equations up to rank four, some of which are contracted with isotropic tensors of rank eight. The number of terms involved renders manual solution prohibitively time consuming. The calculations have thus benefitted from the use of MATHEMATICA [19]. A MATHEMATICA module to simplify this task was written for the purpose. The code for this module, as well as the MATHEMATICA notebooks for all the calculations, is included on the accompanying CD. A description of the routines and their implementation is given in Appendix B.

Throughout this thesis SI units are used. An overview of the common systems of units employed in electromagnetism is given in the appendix of Reference 5. The choice of units does not affect the results presented in this thesis.

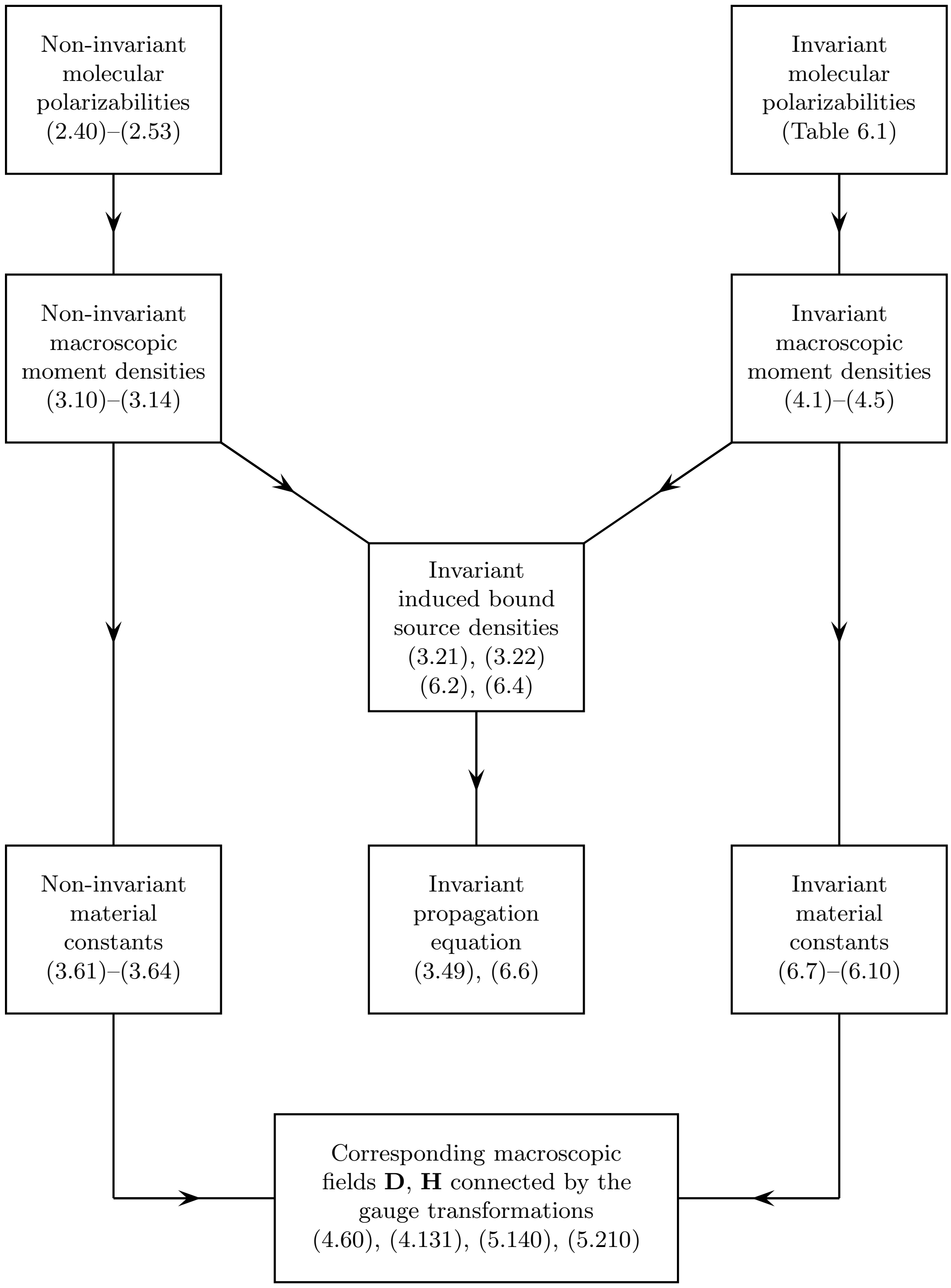

Figure 1.1: A schematic outline of the analysis presented in this thesis [6].

Chapter 2

Multipole theory

In this chapter a brief account of multipole theory is given, based on the presentation of Reference 4. From the expression for the semi-classical Hamiltonian for a system of particles in a vacuum (Section 2.1), and with a suitable choice of gauge for the scalar and vector potentials (Section 2.2), expansions of the Hamiltonian are obtained from which the multipole moment operators are identified (Section 2.3). Expressions for the expectation values of the multipole moment operators, for the interaction with a harmonic plane electromagnetic wave, are then derived using standard perturbation theory (Section 2.4). The expressions for the expectation values of the multipole moment operators are infinite converging series of contributions due to the fields, their gradients and time derivatives. The constants of proportionality between the multipole moments and the field properties are essentially the molecular polarizabilities. Expressions for the polarizabilities are presented up to electric octopole–magnetic quadrupole order. In Section 2.5 the symmetry characteristics of the molecular polarizabilities are discussed. Knowledge of the symmetry can greatly simplify the algebraic analysis when the polarizability tensors occur in expressions describing objects belonging to a particular point group.

The translational behaviour of the molecular multipole moments and polarizabilities is investigated in Section 2.6. It is found that only the polarizabilities at electric dipole order are independent of the choice of molecular coordinate origin. In the absence of spin, and up to electric octopole–magnetic quadrupole order, the origin dependences of the molecular polarizabilities are functions of polarizabilities of lower order. Origin-independent quantities can be obtained by taking linear combinations of the polarizability tensors of a particular order with isotropic tensors. This is possible due to cancellation between the origin dependences of polarizabilities of the same order in these expressions.

2.1 Semi-classical electrodynamics

The semi-classical Hamiltonian for a system of N particles in vacuum is given by [4]

$$H = H^{(0)} + H^{(1)} + H^{(2)}, \tag{2.1}$$

where

$$H^{(0)} = \sum_{\alpha=1}^{N} \left(2m^{(\alpha)}\right)^{-1} \left(\mathbf{\Pi}^{(\alpha)}\right)^{2} + V, \tag{2.2}$$

$$H^{(1)} = \sum_{\alpha=1}^{N} \left\{ -q^{(\alpha)} \left(2m^{(\alpha)}\right)^{-1} \left[2\boldsymbol{A}\left(\boldsymbol{r}^{(\alpha)}, t\right) \cdot \mathbf{\Pi}^{(\alpha)} - i\hbar \boldsymbol{\nabla}^{(\alpha)} \cdot \boldsymbol{A}\left(\boldsymbol{r}^{(\alpha)}, t\right)\right] + q^{(\alpha)} \phi \left(\boldsymbol{r}^{(\alpha)}, t\right) \right\} \tag{2.3}$$

and

$$H^{(2)} = \sum_{\alpha=1}^{N} \left(q^{(\alpha)}\right)^{2} \left(2m^{(\alpha)}\right)^{-1} \boldsymbol{A}^{2} \left(\boldsymbol{r}^{(\alpha)}, t\right). \tag{2.4}$$

Here $m^{(\alpha)}$ and $q^{(\alpha)}$ are the mass and charge of particle α, $\boldsymbol{\Pi}^{(\alpha)}$ is the generalized momentum operator, $\boldsymbol{r}^{(\alpha)}$ is the position operator for an arbitrary choice of origins in the system of particles, $\boldsymbol{A}$ and ϕ are the vector and scalar potentials and V is the potential energy operator.

The Hamiltonian H in (2.1) given by (2.2)–(2.4) does not include a contribution due to spin or spin-orbit coupling. The contribution of spin is not considered in this thesis.

Throughout this thesis, a superscript in round brackets is used as a label. In this chapter, Roman numerals (as in (2.1)) label the perturbation order and α (as in (2.2)–(2.4)) is used to label the particle number. In Section 3.1, n is used to label the molecule number. From Section 3.2 onwards, averaged quantities are considered, hence the particle and molecule labels are no longer needed, and Roman numerals are used to denote the multipole order. The context should make the distinction between the labelling conventions clear.

2.2 The Barron-Gray gauge

The time-dependent fields $\boldsymbol{E}(\boldsymbol{r},t)$ and $\boldsymbol{B}(\boldsymbol{r},t)$ are given in terms of $\boldsymbol{A}(\boldsymbol{r},t)$ and $\phi(\boldsymbol{r},t)$ by

$$\boldsymbol{E}(\boldsymbol{r},t) = -\boldsymbol{\nabla}\phi(\boldsymbol{r},t) - \frac{\partial \boldsymbol{A}(\boldsymbol{r},t)}{\partial t} \tag{2.5}$$

and

$$\boldsymbol{B}(\boldsymbol{r},t) = \boldsymbol{\nabla}\times\boldsymbol{A}(\boldsymbol{r},t), \tag{2.6}$$

with gauge freedom in the choice of $\boldsymbol{A}(\boldsymbol{r},t)$ and $\phi(\boldsymbol{r},t)$. Barron and Gray [20] proposed potentials that produce Taylor expansions of $\boldsymbol{E}(\boldsymbol{r},t)$ and $\boldsymbol{B}(\boldsymbol{r},t)$ about an origin. Thus

$$A_i(\boldsymbol{r},t) = \varepsilon_{ijk}\left\{\tfrac{1}{2}B_j(0,t)r_k + \tfrac{1}{3}\left[\nabla_l B_j(\boldsymbol{r},t)\right]_0 r_k r_l + \tfrac{1}{8}\left[\nabla_m\nabla_l B_j(\boldsymbol{r},t)\right]_0 r_k r_l r_m + \cdots\right\} \tag{2.7}$$

and

$$\phi(\boldsymbol{r},t) = \phi(0,t) - E_i(0,t)r_i - \tfrac{1}{2}\left[\nabla_j E_i(\boldsymbol{r},t)\right]_0 r_i r_j - \tfrac{1}{6}\left[\nabla_k\nabla_j E_i(\boldsymbol{r},t)\right]_0 r_i r_j r_k - \cdots . \tag{2.8}$$

When (2.7) and (2.8) are used in (2.5) and (2.6), with the Maxwell equations

$$\boldsymbol{\nabla}\times\boldsymbol{E} = -\dot{\boldsymbol{B}}, \tag{2.9}$$

$$\boldsymbol{\nabla}\cdot\boldsymbol{B} = 0, \tag{2.10}$$

the fields (2.5) and (2.6) are

$$E_i(\boldsymbol{r},t) = E_i(0,t) + \left[\nabla_j E_i(\boldsymbol{r},t)\right]_0 r_j + \tfrac{1}{2}\left[\nabla_k\nabla_j E_i(\boldsymbol{r},t)\right]_0 r_j r_k + \cdots \tag{2.11}$$

and

$$B_i(\boldsymbol{r},t) = B_i(0,t) + \left[\nabla_j B_i(\boldsymbol{r},t)\right]_0 r_j + \tfrac{1}{2}\left[\nabla_k\nabla_j B_i(\boldsymbol{r},t)\right]_0 r_j r_k + \cdots . \tag{2.12}$$

2.3 Multipole moment operators

The Hamiltonians (2.3) and (2.4) with the potentials (2.7) and (2.8) become

$$\begin{aligned} H^{(1)} = {} & q\phi(\boldsymbol{r},t) - p_i E_i(\boldsymbol{r},t) - \tfrac{1}{2}q_{ij}\nabla_j E_i(\boldsymbol{r},t) - \tfrac{1}{6}q_{ijk}\nabla_j\nabla_k E_i(\boldsymbol{r},t) - \cdots \\ & - m_i B_i(\boldsymbol{r},t) - \tfrac{1}{2}m_{ij}\nabla_j B_i(\boldsymbol{r},t) - \tfrac{1}{6}m_{ijk}\nabla_j\nabla_k B_i(\boldsymbol{r},t) - \cdots \end{aligned} \tag{2.13}$$

and

$$\begin{aligned} H^{(2)} = & -\tfrac{1}{2}\chi_{ij}B_i(\boldsymbol{r},t)B_j(\boldsymbol{r},t) - \tfrac{1}{2}\chi_{ijk}B_i(\boldsymbol{r},t)\nabla_k B_j(\boldsymbol{r},t) - \tfrac{1}{6}\chi_{ijkl}B_i(\boldsymbol{r},t)\nabla_k\nabla_l B_j(\boldsymbol{r},t) - \cdots \\ & - \tfrac{4}{27}\chi_{ijkl}\nabla_k B_i(\boldsymbol{r},t)\nabla_l B_j(\boldsymbol{r},t) - \cdots . \end{aligned} \tag{2.14}$$

The electric and magnetic multipole moment operators in (2.13) are given by [4, 21]

$$q = \sum_{\alpha=1}^{N} q^{(\alpha)}, \qquad p_i = \sum_{\alpha=1}^{N} q^{(\alpha)} r_i^{(\alpha)}, \qquad q_{ij} = \sum_{\alpha=1}^{N} q^{(\alpha)} r_i^{(\alpha)} r_j^{(\alpha)}, \qquad \text{etc.} \tag{2.15}$$

and

$$m_i = \sum_{\alpha=1}^{N} \frac{q^{(\alpha)}}{2m^{(\alpha)}} l_i^{(\alpha)}, \tag{2.16}$$

$$m_{ij} = \sum_{\alpha=1}^{N} \frac{2}{3}\frac{q^{(\alpha)}}{2m^{(\alpha)}} \left(r_j^{(\alpha)} l_i^{(\alpha)} + l_i^{(\alpha)} r_j^{(\alpha)} \right), \tag{2.17}$$

$$m_{ijk} = \sum_{\alpha=1}^{N} \frac{3}{4}\frac{q^{(\alpha)}}{2m^{(\alpha)}} \left(r_k^{(\alpha)} r_j^{(\alpha)} l_i^{(\alpha)} + l_i^{(\alpha)} r_j^{(\alpha)} r_k^{(\alpha)} \right), \tag{2.18}$$

and the magnetic susceptibilities in (2.14) are [4, 21]:

$$\chi_{ij} = \sum_{\alpha=1}^{N} \frac{\left(q^{(\alpha)}\right)^2}{4m^{(\alpha)}} \left(r_i^{(\alpha)} r_j^{(\alpha)} - \left(r^{(\alpha)}\right)^2 \delta_{ij} \right), \tag{2.19}$$

$$\chi_{ijk} = \sum_{\alpha=1}^{N} \frac{\left(q^{(\alpha)}\right)^2}{3m^{(\alpha)}} \left(r_i^{(\alpha)} r_j^{(\alpha)} - \left(r^{(\alpha)}\right)^2 \delta_{ij} \right) r_k^{(\alpha)}, \tag{2.20}$$

$$\chi_{ijkl} = \sum_{\alpha=1}^{N} \frac{3\left(q^{(\alpha)}\right)^2}{8m^{(\alpha)}} \left(r_i^{(\alpha)} r_j^{(\alpha)} - \left(r^{(\alpha)}\right)^2 \delta_{ij} \right) r_k^{(\alpha)} r_l^{(\alpha)}. \tag{2.21}$$

The magnetic moments (2.16)–(2.18) contain $\boldsymbol{\ell} = \boldsymbol{r} \times \boldsymbol{\Pi}$ and must be modified in the presence of a magnetic field, because then the momentum operator is replaced by

$$\boldsymbol{\Pi} \rightarrow \boldsymbol{\Pi} - q\boldsymbol{A}. \tag{2.22}$$

It can be shown that the perturbed magnetic moment operators are [21]

$$m'_i = m_i + \chi_{ij}B_j(t) + \tfrac{1}{2}\chi_{ijk}\nabla_k B_j(t) + \tfrac{1}{6}\chi_{ijkl}\nabla_k\nabla_l B_j(t) + \cdots , \tag{2.23}$$

$$m'_{ij} = m_{ij} + \chi_{kij}B_k(t) + \tfrac{16}{27}\chi_{kijl}\nabla_l B_k(t) + \cdots , \tag{2.24}$$

$$m'_{ijk} = m_{ijk} + \chi_{lijk}B_l(t) + \cdots . \tag{2.25}$$

Generalized expressions for the Hamiltonians (2.13) and (2.14), the multipole moment operators (2.15)–(2.18) and (2.23)–(2.25), and the susceptibilities (2.19)–(2.21) are given in Appendix F.

2.4 Expectation values

Expectation values of the multipole moment operators (2.15) and (2.23)–(2.25) are determined as follows: The first-order perturbation eigenvector is given by [4, 22]

$$|n(t)\rangle = e^{-iW_n^{(0)}t/\hbar} \left| n^{(0)} \right\rangle + \sum_{s \neq n} c_s(t) e^{-iW_s^{(0)}t/\hbar} \left| s^{(0)} \right\rangle, \tag{2.26}$$

where

$$c_s(t) = -\frac{i}{\hbar}\int_0^t e^{-i\omega_{ns}t}\left\langle s^{(0)}\left|H^{(1)}\right|n^{(0)}\right\rangle dt, \tag{2.27}$$

$\left|n^{(0)}\right\rangle$ denotes the unperturbed eigenstate,

$$W_n^{(0)} = \left\langle n^{(0)}\left|H^{(0)}\right|n^{(0)}\right\rangle \tag{2.28}$$

and

$$\hbar\omega_{ns} = W_n^{(0)} - W_s^{(0)}. \tag{2.29}$$

Here, and in what follows, it is assumed that the electric and magnetic fields are represented by harmonic plane waves of angular frequency ω. Thus

$$\boldsymbol{E}(\boldsymbol{r},t) = \boldsymbol{E}_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} \tag{2.30}$$

and

$$\boldsymbol{B}(\boldsymbol{r},t) = \boldsymbol{B}_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}, \tag{2.31}$$

where $\boldsymbol{k}$ is the wave vector and

$$\boldsymbol{B}_0 = \frac{1}{\omega}\boldsymbol{k}\times\boldsymbol{E}_0. \tag{2.32}$$

Then from (2.26) and (2.27), with $H^{(1)}$ given by (2.13), it is straightforward to show that the expectation values of the molecular multipole moments are (see Reference 4, Sec. 2.7)

$$\begin{aligned}
\overline{p}_i &= p_i^{(0)} + \alpha_{ij}E_j + \tfrac{1}{\omega}\alpha'_{ij}\dot{E}_j + \tfrac{1}{2}a_{ijk}\nabla_k E_j + \tfrac{1}{2\omega}a'_{ijk}\nabla_k\dot{E}_j + \tfrac{1}{6}b_{ijkl}\nabla_k\nabla_l E_j + \tfrac{1}{6\omega}b'_{ijkl}\nabla_k\nabla_l\dot{E}_j \\
&\quad + \cdots + G_{ij}B_j + \tfrac{1}{\omega}G'_{ij}\dot{B}_j + \tfrac{1}{2}H_{ijk}\nabla_k B_j + \tfrac{1}{2\omega}H'_{ijk}\nabla_k\dot{B}_j + \cdots, \qquad (2.33)\\
\overline{q}_{ij} &= q_{ij}^{(0)} + a_{kij}E_k - \tfrac{1}{\omega}a'_{kij}\dot{E}_k + \tfrac{1}{2}d_{ijkl}\nabla_l E_k + \tfrac{1}{2\omega}d'_{ijkl}\nabla_l\dot{E}_k \\
&\quad + \cdots + L_{ijk}B_k + \tfrac{1}{\omega}L'_{ijk}\dot{B}_k + \cdots, \qquad (2.34)\\
\overline{q}_{ijk} &= q_{ijk}^{(0)} + b_{lijk}E_l - \tfrac{1}{\omega}b'_{lijk}\dot{E}_l + \cdots, \qquad (2.35)\\
\overline{m}_i &= m_i^{(0)} + G_{ji}E_j - \tfrac{1}{\omega}G'_{ji}\dot{E}_j + \tfrac{1}{2}L_{jki}\nabla_k E_j - \tfrac{1}{2\omega}L'_{jki}\nabla_k\dot{E}_j + \cdots + \chi_{ij}B_j + \tfrac{1}{\omega}\chi'_{ij}\dot{B}_j + \cdots, \qquad (2.36)\\
\overline{m}_{ij} &= m_{ij}^{(0)} + H_{kij}E_k - \tfrac{1}{\omega}H'_{kij}\dot{E}_k + \cdots. \qquad (2.37)
\end{aligned}$$

In these $\overline{p}_i = \langle n(t)|p_i|n(t)\rangle$, etc., $p_i^{(0)}$, $q_{ij\ldots}^{(0)}$, etc. denote the unperturbed (permanent) multipole moments, $E_i = E_i(0,t)$, $\nabla_j E_i = [\nabla_j E_i(\boldsymbol{r},t)]_0$, etc., are values at an arbitrary origin inside or near the molecule, and a prime indicates a contribution due to a time derivative of a field or field gradient [11].

The molecular polarizabilities in (2.33)–(2.37) are given by

$$\alpha_{ij} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} \mathcal{R}e\left\{\langle p_i\rangle_{ns}\langle p_j\rangle_{sn}\right\}, \tag{2.38}$$

$$\alpha'_{ij} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} \mathcal{I}m\left\{\langle p_i\rangle_{ns}\langle p_j\rangle_{sn}\right\}, \tag{2.39}$$

$$a_{ijk} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} \mathcal{R}e\left\{\langle p_i\rangle_{ns}\langle q_{jk}\rangle_{sn}\right\}, \tag{2.40}$$

$$a'_{ijk} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} \mathcal{I}m\left\{\langle p_i\rangle_{ns}\langle q_{jk}\rangle_{sn}\right\}, \tag{2.41}$$

$$G_{ij} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} \mathcal{R}e\left\{\langle p_i\rangle_{ns}\langle m_j\rangle_{sn}\right\}, \tag{2.42}$$

$$G'_{ij} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} \mathcal{I}m\left\{\langle p_i\rangle_{ns}\langle m_j\rangle_{sn}\right\}, \tag{2.43}$$

$$b_{ijkl} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} \mathcal{R}e\left\{\langle p_i\rangle_{ns}\langle q_{jkl}\rangle_{sn}\right\}, \tag{2.44}$$

$$b'_{ijkl} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} \mathcal{I}m\left\{\langle p_i\rangle_{ns}\langle q_{jkl}\rangle_{sn}\right\}, \tag{2.45}$$

$$d_{ijkl} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} \mathcal{R}e\left\{\langle q_{ij}\rangle_{ns}\langle q_{kl}\rangle_{sn}\right\}, \tag{2.46}$$

$$d'_{ijkl} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} \mathcal{I}m\left\{\langle q_{ij}\rangle_{ns}\langle q_{kl}\rangle_{sn}\right\}, \tag{2.47}$$

$$H_{ijk} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} \mathcal{R}e\left\{\langle p_i\rangle_{ns}\langle m_{jk}\rangle_{sn}\right\}, \tag{2.48}$$

$$H'_{ijk} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} \mathcal{I}m\left\{\langle p_i\rangle_{ns}\langle m_{jk}\rangle_{sn}\right\}, \tag{2.49}$$

$$L_{ijk} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} \mathcal{R}e\left\{\langle q_{ij}\rangle_{ns}\langle m_k\rangle_{sn}\right\}, \tag{2.50}$$

$$L'_{ijk} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} \mathcal{I}m\left\{\langle q_{ij}\rangle_{ns}\langle m_k\rangle_{sn}\right\}, \tag{2.51}$$

$$\chi_{ij} = \frac{2}{\hbar}\sum_s \omega_{sn} Z_{sn} \mathcal{R}e\left\{\langle m_i\rangle_{ns}\langle m_j\rangle_{sn}\right\} + \sum_{\alpha=n}^{N}\frac{\left(q^{(\alpha)}\right)^2}{4m^{(\alpha)}}\left\langle r_i^{(\alpha)}r_j^{(\alpha)} - \left(r_k^{(\alpha)}\right)^2\delta_{ij}\right\rangle_{nn}, \tag{2.52}$$

$$\chi'_{ij} = -\frac{2}{\hbar}\sum_s \omega Z_{sn} \mathcal{I}m\left\{\langle m_i\rangle_{ns}\langle m_j\rangle_{sn}\right\}, \tag{2.53}$$

where $\langle p_i\rangle_{ns} = \langle n^{(0)}|p_i|s^{(0)}\rangle$, etc. and, in the absence of absorption,

$$Z_{sn} = \left(\omega_{sn}^2 - \omega^2\right)^{-1}. \tag{2.54}$$

See also Appendix F, where general expressions are presented from which (2.38)–(2.53) can be obtained.

The multipole order of the polarizability tensors (2.38)–(2.53) can be obtained by counting the number of factors of the position vector $\boldsymbol{r}$ in their expressions and subtracting one. For example, the electric quadrupole–electric quadrupole tensors d_{ijkl} and d'_{ijkl}, and the electric dipole–electric octopole tensors b_{ijkl} and b'_{ijkl}, each contain four factors of $\boldsymbol{r}$, see (2.44)–(2.47) and (2.15), and are therefore of third, or electric octopole–magnetic quadrupole, order. The electric dipole–magnetic dipole tensors G'_{ij} and G_{ij} contain three factors of $\boldsymbol{r}$ — one from the matrix element of the electric dipole, see (2.15), and two from the matrix element of the magnetic dipole, see (2.16) which contains $\boldsymbol{\ell} = \boldsymbol{r}\times\boldsymbol{p} = \boldsymbol{r}\times(m\dot{\boldsymbol{r}})$ — and are hence of second, or electric quadrupole–magnetic dipole, order.

Multipole order	Time-even		Time-odd	
	Polar	Axial	Polar	Axial
Electric dipole	$\alpha_{ij} = \alpha_{ji}$		$\alpha'_{ij} = -\alpha'_{ji}$	
Electric quadrupole–magnetic dipole	$a_{ijk} = a_{ikj}$	G'_{ij}	$a'_{ijk} = a'_{ikj}$	G_{ij}
Electric octopole–magnetic quadrupole	$b_{ijkl} = b_{ikjl} = b_{ijlk}$ $d_{ijkl} = d_{jikl} = d_{klij}$ $\chi_{ij} = \chi_{ji}$	$L'_{ijk} = L'_{jik}$ H'_{ijk}	$b'_{ijkl} = b'_{ikjl} = b'_{ijlk}$ $d'_{ijkl} = d'_{jikl} = -d'_{klij}$ $\chi'_{ij} = -\chi'_{ji}$	$L_{ijk} = L_{jik}$ H_{ijk}

Table 2.1: Summary of the symmetries and space and time properties of the molecular polarizabilities in (2.33)–(2.37).

2.5 Symmetry characteristics

The polarizability tensors (2.38)–(2.53) describe the interaction between a physical cause (the fields $\boldsymbol{E}$ and $\boldsymbol{B}$, their gradients and time derivatives), and a physical effect (the molecular multipole moments (2.33)–(2.37)). The polarizability tensors are therefore property tensors. According to Neumann's principle, a property tensor of an object must possess at least the symmetry of that object [23]. Thus a property tensor can possess additional symmetry, besides its intrinsic symmetry, which leads to a reduction of the number of independent components of the tensor, and hence to a simplification of the expressions involving it. The combination of the intrinsic (permutation) symmetry of a property tensor and the point group symmetry of the object it describes (referred to as particularization [23]) can lead to a further reduction in the number of independent components.

Non-magnetic (diamagnetic or paramagnetic) crystals are characterized by one of the classical 32 crystallographic point groups, whereas magnetic (ferromagnetic, ferrimagnetic or antiferromagnetic) crystals include these 32 point groups together with an additional 58 point groups [23–25]. The symmetry operations corresponding to the 32 point groups for non-magnetic crystals are spatial symmetries, and the 90 point groups describing magnetic crystals are combinations of spatial symmetries and time reversal. The property tensors describing non-magnetic molecules are therefore time-even, and those describing magnetic molecules are both time-even and time-odd. By Neumann's principle, a non-magnetic object cannot possess property tensors that are time-odd.

The time-even or time-odd nature of the molecular polarizabilities (2.38)–(2.53) depends on their behaviour under time reversal. The position operator $\boldsymbol{r}$, and hence the electric multipole moment operators p_i, q_{ij}, q_{ijk}, etc. are time-even (see (2.15)). The momentum operator, and hence the angular momentum operator $\boldsymbol{\ell}$, and the magnetic multipole moment operators m_i, m_{ij}, etc. are time-odd (see (2.16)–(2.18)). From their definitions,

$$\boldsymbol{F} = q\boldsymbol{E} \qquad \text{and} \qquad \boldsymbol{F} = q\boldsymbol{v} \times \boldsymbol{B}, \tag{2.55}$$

the electric and magnetic field vectors $\boldsymbol{E}$ and $\boldsymbol{B}$ are time-even and time-odd, respectively; then the behaviour under time reversal of the molecular polarizabilities (2.38)–(2.53) can be obtained by inspection of (2.33)–(2.37).

The polar or axial nature of the molecular polarizabilities is determined from their behaviour under space transformations. A polar vector, like the position vector $\boldsymbol{r}$, changes sign under space inversion, whereas an axial vector, like the angular momentum $\boldsymbol{\ell}$, does not. In general, a tensor of rank N is polar if it acquires a factor $(-1)^N$ under space inversion, and axial if it acquires a factor $(-1)^{N+1}$ [4, Chapter 3]. Thus the electric multipole moments (2.15) are polar and the magnetic multipole moments (2.16)–(2.18) are axial. It can be shown that the product of two polar tensors or two axial tensors is a polar tensor, and the product of a polar tensor and an axial tensor is an axial tensor [4, Chapter 3]. The polar or axial nature of the molecular polarizabilities can therefore be obtained by inspection of their defining relations (2.38)–(2.53).

The relation $(\boldsymbol{\ell})_i = (\boldsymbol{r} \times \boldsymbol{\Pi})_i = \varepsilon_{ijk} r_j \Pi_k$ shows that the Levi-Civita tensor ε_{ijk} (see (C.1)) is a time-even axial tensor, and $r^2 = \delta_{ij} r_i r_j$ shows that the Kronecker delta δ_{ij} (see (C.2)) is a time-even polar tensor [4]. Isotropic tensors of even rank are products of Kronecker deltas, and are therefore time-even polar tensors. Isotropic tensors of odd rank are products of a Levi-Civita tensor and Kronecker deltas, and are therefore time-even axial tensors (see Appendix C).

The permutation symmetry of the tensor subscripts of the molecular polarizabilities is a combination of the symmetries of the multipole moments in the matrix elements in their expressions, the commutation symmetries of the matrix elements, and whether the real or imaginary part of the matrix elements is involved. For instance, $d'_{ijkl} = d'_{jikl} = -d'_{klij}$ follows from the symmetry $q_{ij} = q_{ji}$, and the relation $\langle n|\Omega|s\rangle = \langle s|\Omega|n\rangle^*$ (for Ω Hermitian) since $\mathcal{Im}\{c\} = -\mathcal{Im}\{c^*\}$.

2.6 Origin dependence of molecular polarizabilities

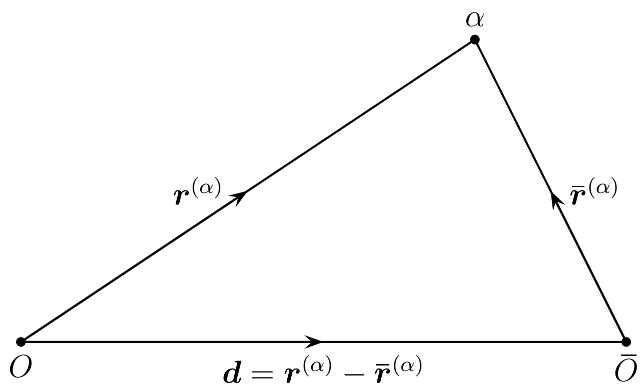

Figure 2.1: Displacement of molecular coordinate origin relative to which the positions of molecular constituents are specified.

The physical properties of a linear medium (such as the charge and current densities (3.18) and (3.19) and the propagation equation (3.49)) are expressed in terms of the molecular polarizabilities (2.38)–(2.53). The origin dependences of these physical properties thus depend on the origin dependences of the molecular polarizabilities, which in turn are functions of the matrix elements of the multipole moment operators (2.15)–(2.18). To determine the origin dependence of the molecular polarizabilities (2.38)–(2.53), one must therefore first determine the origin dependences of the multipole moments. The change due to a shift of the coordinate origin from O to $\bar{O}$ (Figure 2.1) for a multipole moment operator $q_{ij\ldots}$ is given by†

$$\Delta q_{ij\ldots} = \bar{q}_{ij\ldots} - q_{ij\ldots}, \tag{2.56}$$

where $\bar{q}_{ij\ldots}$ denotes the moment operator relative to $\bar{O}$. Substituting $\boldsymbol{r}^{(\alpha)} = \bar{\boldsymbol{r}}^{(\alpha)} + \boldsymbol{d}$ in the expressions

†The use of a bar in $\bar{q}_{ij\ldots}$ should not be confused with its use on page 7 to denote expectation values.

for the multipole moment operators (2.15)–(2.18) and evaluating the differences (2.56) yield [4]:

$$\Delta p_i = -d_i \sum_\alpha^N q^{(\alpha)}, \tag{2.57}$$

$$\Delta q_{ij} = -d_i p_j - d_j p_i + d_i d_j \sum_\alpha^N q^{(\alpha)}, \tag{2.58}$$

$$\Delta q_{ijk} = -d_i q_{jk} - d_j q_{ik} - d_k q_{ij} + d_i d_j p_k + d_j d_k p_i + d_i d_k p_j - d_i d_j d_k \sum_\alpha^N q^{(\alpha)}, \tag{2.59}$$

$$\Delta m_i = -\varepsilon_{ijk} d_j \sum_\alpha^N \frac{q^{(\alpha)}}{2m^{(\alpha)}} \Pi_k^{(\alpha)}, \tag{2.60}$$

$$\Delta m_{ij} = -\varepsilon_{ikl} \sum_\alpha^N \frac{q^{(\alpha)}}{3m^{(\alpha)}} \left(2d_j r_k^{(\alpha)} \Pi_l^{(\alpha)} + d_k r_j^{(\alpha)} \Pi_l^{(\alpha)} + d_k \Pi_l^{(\alpha)} r_j^{(\alpha)} - 2d_j d_k \Pi_l^{(\alpha)}\right). \tag{2.61}$$

To facilitate the calculation of the origin dependences of the molecular polarizabilities, it is convenient to rearrange (2.60) and (2.61) so that the right-hand sides are expressed in terms of multipole moments of lower order. It can be shown that [4] (see Appendix A)

$$\Delta m_i = -\frac{i}{2\hbar} \varepsilon_{ijk} d_j \left[H^{(0)}, p_k\right], \tag{2.62}$$

$$\Delta m_{ij} = -2d_j m_i + \tfrac{2}{3}\delta_{ij} d_k m_k + \frac{i}{3\hbar} \varepsilon_{ikl} d_k \left[H^{(0)}, 2d_j p_l - q_{jl}\right]. \tag{2.63}$$

The origin dependences of the molecular polarizabilities (2.38)–(2.54) can be determined from (2.57)–(2.59), (2.62) and (2.63) [4, 26] (see Appendix A). The results are:

$$\Delta \alpha_{ij} = 0, \tag{2.64}$$

$$\Delta \alpha'_{ij} = 0, \tag{2.65}$$

$$\Delta a_{ijk} = -d_j \alpha_{ik} - d_k \alpha_{ij}, \tag{2.66}$$

$$\Delta a'_{ijk} = -d_j \alpha'_{ik} - d_k \alpha'_{ij}, \tag{2.67}$$

$$\Delta G_{ij} = -\tfrac{1}{2}\omega \varepsilon_{jkl} d_k \alpha'_{il}, \tag{2.68}$$

$$\Delta G'_{ij} = \tfrac{1}{2}\omega \varepsilon_{jkl} d_k \alpha_{il}, \tag{2.69}$$

$$\Delta b_{ijkl} = -d_j a_{ikl} - d_k a_{ijl} - d_l a_{ijk} + d_j d_k \alpha_{il} + d_j d_l \alpha_{ik} + d_k d_l \alpha_{ij}, \tag{2.70}$$

$$\Delta b'_{ijkl} = -d_j a'_{ikl} - d_k a'_{ijl} - d_l a'_{ijk} + d_j d_k \alpha'_{il} + d_j d_l \alpha'_{ik} + d_k d_l \alpha'_{ij}, \tag{2.71}$$

$$\Delta d_{ijkl} = -d_i a_{jkl} - d_j a_{ikl} - d_k a_{lij} - d_l a_{kij} + d_i d_k \alpha_{jl} + d_i d_l \alpha_{jk} + d_j d_k \alpha_{il} + d_j d_l \alpha_{ik}, \tag{2.72}$$

$$\Delta d'_{ijkl} = -d_i a'_{jkl} - d_j a'_{ikl} + d_k a'_{lij} + d_l a'_{kij} + d_i d_k \alpha'_{jl} + d_i d_l \alpha'_{jk} + d_j d_k \alpha'_{il} + d_j d_l \alpha'_{ik}, \tag{2.73}$$

$$\Delta H_{ijk} = -2d_k G_{ij} + \tfrac{2}{3}\delta_{jk} d_l G_{il} - \tfrac{1}{3}\omega \varepsilon_{jlm} d_l \left(a'_{ikm} - 2d_k \alpha'_{im}\right), \tag{2.74}$$

$$\Delta H'_{ijk} = -2d_k G'_{ij} + \tfrac{2}{3}\delta_{jk} d_l G'_{il} + \tfrac{1}{3}\omega \varepsilon_{jlm} d_l \left(a_{ikm} - 2d_k \alpha_{im}\right), \tag{2.75}$$

$$\Delta L_{ijk} = -d_i G_{jk} - d_j G_{ik} + \tfrac{1}{2}\omega \varepsilon_{klm} d_l \left(a'_{mij} + d_i \alpha'_{jm} + d_j \alpha'_{im}\right), \tag{2.76}$$

$$\Delta L'_{ijk} = -d_i G'_{jk} - d_j G'_{ik} + \tfrac{1}{2}\omega \varepsilon_{klm} d_l \left(a_{mij} - d_i \alpha_{jm} - d_j \alpha_{im}\right), \tag{2.77}$$

$$\Delta \chi_{ij} = \tfrac{1}{2}\omega \left(\varepsilon_{ikl} d_k G'_{lj} + \varepsilon_{jkl} d_k G'_{li}\right) + \tfrac{1}{4}\omega^2 \varepsilon_{ikl} \varepsilon_{jmn} d_k d_m \alpha_{ln}, \tag{2.78}$$

$$\Delta \chi'_{ij} = -\tfrac{1}{2}\omega \left(\varepsilon_{ikl} d_k G_{lj} - \varepsilon_{jkl} d_k G_{li}\right) + \tfrac{1}{4}\omega^2 \varepsilon_{ikl} \varepsilon_{jmn} d_k d_m \alpha'_{ln}. \tag{2.79}$$

Generalized expressions for the origin dependences of the molecular polarizabilities which are functions of the electric multipole moments only are presented in Appendix F. An expression for the origin dependence of the magnetic octopole moment (and hence higher magnetic multipole moments), that allows the origin dependences of the molecular polarizabilities that depend on it to be written in terms molecular polarizabilities of lower multipole order, has not been determined. It is therefore not possible at this stage to present generalized expressions for the origin dependences of the molecular polarizabilities which are functions of the magnetic multipole moments.

Chapter 3

The transition to macroscopic electrodynamics

Electromagnetic fields at the microscopic scale are rapidly fluctuating functions of position and time due to the motion of atomic charges. In a crystal, the spatial variations are of the order of the atomic spacing, and the frequencies of nuclear and electronic vibrations are of the order of the infrared and visible to ultraviolet frequencies of the electromagnetic spectrum, respectively. On the macroscopic scale, average values of the microscopic fields are observed. To obtain a macroscopic multipole theory, the microscopic results obtained in Chapter 2 must be subjected to an appropriate averaging. The type of averaging procedure that is employed depends in general on the problem under consideration [17], and usually involves a spatial average followed by an ensemble average [17, 18]. As is shown in Section 3.1, the spatial average is independent of the weight function used [6–8]. The ensemble average depends on the probability distribution function [16, 17, 27], which is a function of the positions and momenta of the particles in the system, and on the internal and external interactions [27, Chapter 10].

The derivation of the origin-independent macroscopic expressions corresponding to the molecular polarizabilities presented in this thesis depends, in part, on the comparison of the macroscopic source densities — a requirement of the invariant formulation is that macroscopic observables are unchanged when the origin-dependent polarizabilities in their expressions are replaced by invariant counterparts (see Sections 4.3.2, 4.4.2, 5.1.7 and 5.2.6). The analysis presented here does not depend on the procedure used to derive the macroscopic source densities, or the macroscopic Maxwell equations. For the purposes of this thesis it suffices therefore to consider a derivation of these results based only on spatial averaging. If required, the results obtained in this thesis can be subjected to additional averaging, depending on the nature of the problem to which the results are to be applied. (See for example Chapter 10 of Gray, Gubbins and Joslin [27, and references therein].)

In Section 3.1 a procedure for performing spatial averages of microscopic quantities is demonstrated. For microscopic quantities that are independent of the choice of molecular origin, it is shown that the corresponding macroscopic expressions can be obtained in a simple manner.

Macroscopic expressions for the induced bound source densities $\rho_b(\boldsymbol{r}, t)$ and $\boldsymbol{J}_b(\boldsymbol{r}, t)$ are derived in terms of the molecular polarizabilities in Section 3.2. Expressions for the dynamic response fields $\boldsymbol{D}(\boldsymbol{E}, \boldsymbol{B})$ and $\boldsymbol{H}(\boldsymbol{E}, \boldsymbol{B})$ and the propagation equation are obtained in Sections 3.4 and 3.3. Section 3.5 introduces a covariant formalism to demonstrate a condition proposed by Post [28] that is relevant to the macroscopic description of electrodynamics.

3.1 Spatial averaging

Induced macroscopic moment densities are obtained from the induced molecular multipole moments (2.33)–(2.37) by spatial averaging [5, 7, 18]. Consider an induced macroscopic moment density

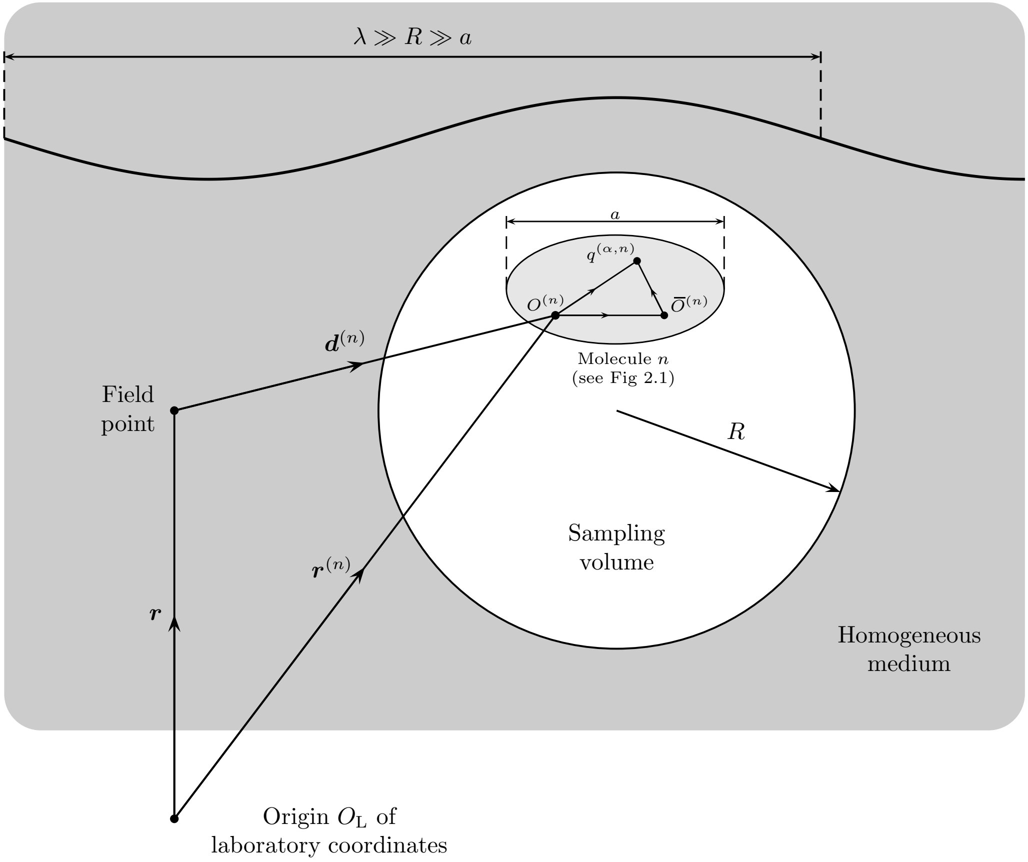

Figure 3.1: The geometry used in spatial averaging. A spherical sampling volume is shown for convenience.

$T_{ij\ldots}(\boldsymbol{r},t)$. Relative to an arbitrary set of molecular coordinate origins $\{O^{(n)}\}$,

$$T_{ij\ldots}(\boldsymbol{r},t) = \left\langle \sum_{n=1}^{N} \bar{t}^{(n)}_{ij\ldots} \left(\boldsymbol{r}^{(n)},t\right) \delta\left(\boldsymbol{r}-\boldsymbol{r}^{(n)}\right) \right\rangle . \tag{3.1}$$

In (3.1), the sum is over all molecules in the medium, $\bar{t}^{(n)}_{ij\ldots}$ is the induced molecular moment of molecule n (see (2.33)–(2.37)), $\boldsymbol{r}$ and $\boldsymbol{r}^{(n)}$ are the position vectors of the field point and the coordinate origin $O^{(n)}$, respectively (relative to laboratory coordinates), and δ is the Dirac delta function. The time dependence of the position vector $\boldsymbol{r}^{(n)}$ of the molecular origin $O^{(n)}$, due to the vibrational and rotational motion of molecule n is implied in (3.1). The angular brackets denote a spatial average with respect to a normalized isotropic weight function W at time t; that is

$$\langle A(\boldsymbol{r},t)\rangle = \int_V A(\boldsymbol{r}-\boldsymbol{r}',t)\, W(\boldsymbol{r}')\, d^3\boldsymbol{r}', \tag{3.2}$$

with

$$\int_V W(\boldsymbol{r}')\, d^3\boldsymbol{r}' = 1, \tag{3.3}$$

and $W(-\boldsymbol{r}) = W(\boldsymbol{r})$. Here V is the volume of the medium. Substitution of (3.1) in (3.2), with use of the isotropy of $W(\boldsymbol{r})$, yields

$$\begin{aligned} T_{ij\ldots}(\boldsymbol{r},t) &= \sum_{n=1}^{N} \bar{t}_{ij\ldots}^{(n)} \int_V W(\boldsymbol{r}')\delta\left(\boldsymbol{r}-\boldsymbol{r}^{(n)}-\boldsymbol{r}'\right) d^3\boldsymbol{r}' \\ &= \sum_{n=1}^{N} \bar{t}_{ij\ldots}^{(n)} W\left(\boldsymbol{d}^{(n)}\right), \end{aligned} \tag{3.4}$$

where

$$\boldsymbol{d}^{(n)} = \boldsymbol{r}^{(n)} - \boldsymbol{r} \tag{3.5}$$

is the position vector of the molecular origin $O^{(n)}$ relative to the field point (see Figure 3.1).

The molecular moments $\bar{t}_{ij\ldots}^{(n)}$ are series that contain terms like (see (2.33)–(2.37))

$$\bar{t}_{ij\ldots}^{(n)} = \cdots + \mathfrak{p}_{ijklm\ldots}^{(n)} \nabla_l^{(n)} \nabla_m^{(n)} \ldots E_k\left(\boldsymbol{r}^{(n)},t\right) + \cdots, \tag{3.6}$$

where $\mathfrak{p}_{ijklm\ldots}^{(n)}$ is a molecular polarizability of molecule n. The fields and their gradients are evaluated at the molecular origin O_n, and it is assumed that the molecules are aligned. With F denoting either E or B in (2.30) and (2.31), the fields and their gradients at the origin of molecule n are related to those at the field point by

$$\begin{aligned} \nabla_j^{(n)}\nabla_k^{(n)}\ldots F_i\left(\boldsymbol{r}^{(n)},t\right) &= \frac{\partial}{\partial r_j^{(n)}}\frac{\partial}{\partial r_k^{(n)}}\ldots F_{0i}e^{i\left(\boldsymbol{k}\cdot\boldsymbol{r}^{(n)}-\omega t\right)} \\ &= (ik_j)(ik_k)\ldots F_{0i}e^{i\left(\boldsymbol{k}\cdot\boldsymbol{r}^{(n)}-\omega t\right)} \\ &= (ik_j)(ik_k)\ldots F_{0i}e^{i\left(\boldsymbol{k}\cdot\boldsymbol{d}^{(n)}+\boldsymbol{k}\cdot\boldsymbol{r}-\omega t\right)} \\ &= e^{i\boldsymbol{k}\cdot\boldsymbol{d}^{(n)}}\nabla_j\nabla_k\ldots F_i(\boldsymbol{r},t). \end{aligned} \tag{3.7}$$

In what follows, it is convenient to define a "weighted transform" [7]

$$\mathcal{T}[\mathfrak{p}_{ij\ldots}] = \sum_{n=1}^{N} \mathfrak{p}_{ij\ldots}^{(n)} e^{i\boldsymbol{k}\cdot\boldsymbol{d}^{(n)}} W\left(\boldsymbol{d}^{(n)}\right) \tag{3.8}$$

of a polarizability tensor $\mathfrak{p}_{ij\ldots}^{(n)}$ of molecule n. For polarizability tensors $\mathfrak{p}_{ij\ldots}$, $\mathfrak{q}_{ij\ldots}$, $\ldots$ of the same rank, and space and time properties, the transform $\mathcal{T}$ in (3.8) is linear. That is,

$$\begin{aligned} \mathcal{T}[\mathfrak{p}_{ij\ldots}+\mathfrak{q}_{ij\ldots}+\cdots] &= \sum_{n=1}^{N}\left(\mathfrak{p}_{ij\ldots}^{(n)}+\mathfrak{q}_{ij\ldots}^{(n)}+\cdots\right)e^{i\boldsymbol{k}\cdot\boldsymbol{d}^{(n)}}W\left(\boldsymbol{d}^{(n)}\right) \\ &= \mathcal{T}[\mathfrak{p}_{ij\ldots}]+\mathcal{T}[\mathfrak{q}_{ij\ldots}]+\cdots. \end{aligned} \tag{3.9}$$

From (3.4) and (3.8), the induced macroscopic moment densities corresponding to the induced molecular moments (2.33)–(2.37) are

$$\begin{aligned} P_i &= P_i^{(0)} + \mathcal{T}[\alpha_{ij}]E_j + \tfrac{1}{\omega}\mathcal{T}[\alpha'_{ij}]\dot{E}_j + \tfrac{1}{2}\mathcal{T}[a_{ijk}]\nabla_k E_j + \tfrac{1}{2\omega}\mathcal{T}[a'_{ijk}]\nabla_k\dot{E}_j \\ &\quad + \tfrac{1}{6}\mathcal{T}[b_{ijkl}]\nabla_k\nabla_l E_j + \tfrac{1}{6\omega}\mathcal{T}[b'_{ijkl}]\nabla_k\nabla_l\dot{E}_j + \cdots \\ &\quad + \mathcal{T}[G_{ij}]B_j + \tfrac{1}{\omega}\mathcal{T}[G'_{ij}]\dot{B}_j + \tfrac{1}{2}\mathcal{T}[H_{ijk}]\nabla_k B_j + \tfrac{1}{2\omega}\mathcal{T}[H'_{ijk}]\nabla_k\dot{B}_j + \cdots, \end{aligned} \tag{3.10}$$

$$\begin{aligned} Q_{ij} &= Q_{ij}^{(0)} + \mathcal{T}[a_{kij}]E_k - \tfrac{1}{\omega}\mathcal{T}[a'_{kij}]\dot{E}_k + \tfrac{1}{2}\mathcal{T}[d_{ijkl}]\nabla_l E_k + \tfrac{1}{2\omega}\mathcal{T}[d'_{ijkl}]\nabla_l\dot{E}_k + \cdots \\ &\quad + \mathcal{T}[L_{ijk}]B_k + \tfrac{1}{\omega}\mathcal{T}[L'_{ijk}]\dot{B}_k + \cdots, \end{aligned} \tag{3.11}$$

$$Q_{ijk} = Q_{ijk}^{(0)} + \mathcal{T}[b_{lijk}]E_l - \tfrac{1}{\omega}\mathcal{T}[b'_{lijk}]\dot{E}_l + \cdots, \tag{3.12}$$

$$\begin{aligned} M_i &= M_i^{(0)} + \mathcal{T}[G_{ji}]E_j - \tfrac{1}{\omega}\mathcal{T}[G'_{ji}]\dot{E}_j + \tfrac{1}{2}\mathcal{T}[L_{jki}]\nabla_k E_j - \tfrac{1}{2\omega}\mathcal{T}[L'_{jki}]\nabla_k\dot{E}_j + \cdots \\ &\quad + \mathcal{T}[\chi_{ij}]B_j + \tfrac{1}{\omega}\mathcal{T}[\chi'_{ij}]\dot{B}_j + \cdots, \end{aligned} \tag{3.13}$$

$$M_{ij} = M_{ij}^{(0)} + \mathcal{T}[H_{kij}]E_k - \tfrac{1}{\omega}\mathcal{T}[H'_{kij}]\dot{E}_k + \cdots, \tag{3.14}$$

where $P_i^{(0)}$, $Q_{ij}^{(0)}$ ... etc. are the permanent multipole moment densities. In (3.10)–(3.14) and what follows, it is understood that the arguments of the macroscopic moment densities and fields are $(\boldsymbol{r}, t)^\dagger$.

Through the transforms $\mathcal{T}$, the induced macroscopic moment densities depend in general on the arbitrarily chosen molecular coordinate origins $O^{(n)}$. If the argument of $\mathcal{T}$ is independent of the choice of molecular origin, as is the case for the electric dipole–electric dipole polarizabilities α_{ij} and α'_{ij}, or if the argument of $\mathcal{T}$ contracts with field gradients to form an origin-independent quantity (see Section 3.2), the superscript on $\mathfrak{p}_{ij...}^{(n)}$ in (3.8) is unnecessary, and

$$\mathcal{T}[\tilde{\mathfrak{p}}_{ij...}] = \tilde{\mathfrak{p}}_{ij...} \sum_n e^{i\boldsymbol{k}\cdot\boldsymbol{d}^{(n)}} W\left(\boldsymbol{d}^{(n)}\right). \tag{3.15}$$

In (3.15), and in what follows, a tilde has been introduced to indicate an origin-independent quantity. For a homogeneous medium the sum in (3.15) can be approximated by an integral according to

$$\sum_n e^{i\boldsymbol{k}\cdot\boldsymbol{d}^{(n)}} W\left(\boldsymbol{d}^{(n)}\right) \to \mathcal{N} \int_V e^{i\boldsymbol{k}\cdot\boldsymbol{d}} W(\boldsymbol{d}) d^3\boldsymbol{d}, \tag{3.16}$$

where $\mathcal{N} = N/V$ is the number density of molecules. The macroscopic theory applies in the limit of long wavelength λ, that is $\lambda \gg R$, where R is the extent of the weight function $W(\boldsymbol{d})$ (see Fig 3.1). In this limit, and because the weight function is normalized to unity, the Fourier transform in (3.16) tends to unity [5, 7], so that $\mathcal{T}$ can be approximated by [7]

$$\mathcal{T}[\tilde{\mathfrak{p}}_{ij...}] = \mathcal{N}\tilde{\mathfrak{p}}_{ij...}, \tag{3.17}$$

which is independent of any particular choice of the weight function.

3.2 Induced bound source densities

The multipole expansions of the macroscopic induced bound charge and current densities are given, to electric octopole–magnetic quadrupole order, by [4]

$$\rho_b = -\nabla_i P_i + \tfrac{1}{2}\nabla_i\nabla_j Q_{ij} - \tfrac{1}{6}\nabla_i\nabla_j\nabla_k Q_{ijk} \tag{3.18}$$

$$J_{bi} = \dot{P}_i - \nabla_j\left(\tfrac{1}{2}\dot{Q}_{ij} - \varepsilon_{ijk}M_k\right) + \nabla_j\nabla_k\left(\tfrac{1}{6}\dot{Q}_{ijk} - \tfrac{1}{2}\varepsilon_{ijl}M_{lk}\right). \tag{3.19}$$

Substitution of (3.10)–(3.14) in (3.18) and (3.19), with the identity

$$B_i = -\tfrac{i}{\omega}\varepsilon_{ijk}\nabla_j E_k, \tag{3.20}$$

based on Faraday's law (2.9), the linear property (3.9) of the transform $\mathcal{T}$, and rearranging, yield:

$$\rho_b = \mathcal{T}\left[\Theta_{ij} + i\Pi_{ij}\right]\nabla_j E_i + \mathcal{T}\left[\Theta_{ijk} + i\Pi_{ijk}\right]\nabla_j\nabla_k E_i + \mathcal{T}\left[\Theta_{ijkl} + i\Pi_{ijkl}\right]\nabla_j\nabla_k\nabla_l E_i, \tag{3.21}$$

$$J_{bi} = \omega\mathcal{T}\left[i\Phi_{ij} + \Omega_{ij}\right]E_j + \omega\mathcal{T}\left[i\Phi_{ijk} + \Omega_{ijk}\right]\nabla_k E_j + \omega\mathcal{T}\left[i\Phi_{ikjl} + \Omega_{ikjl}\right]\nabla_k\nabla_l E_j, \tag{3.22}$$

where, in (3.21),

$$\Theta_{ij} = -\alpha_{ij}, \tag{3.23}$$

$$\Pi_{ij} = -\alpha'_{ij}, \tag{3.24}$$

$$\Theta_{ijk} = -\tfrac{1}{\omega}\varepsilon_{ikl}G'_{jl} + \tfrac{1}{2}\left(a_{ijk} - a_{jik}\right), \tag{3.25}$$

$$\Pi_{ijk} = -\tfrac{1}{\omega}\varepsilon_{ikl}G_{jl} + \tfrac{1}{2}\left(a'_{ijk} + a'_{jik}\right), \tag{3.26}$$

$$\Theta_{ijkl} = -\tfrac{1}{6}\left(b_{ijkl} + b_{jikl}\right) + \tfrac{1}{4}d_{ikjl} + \tfrac{1}{2\omega}\varepsilon_{ikm}\left(L'_{jlm} - H'_{jml}\right), \tag{3.27}$$

$$\Pi_{ijkl} = -\tfrac{1}{6}\left(b'_{ijkl} - b'_{jikl}\right) + \tfrac{1}{4}d'_{ikjl} + \tfrac{1}{2\omega}\varepsilon_{ikm}\left(L_{jlm} - H_{jml}\right), \tag{3.28}$$

†In general, the fields in a medium are superpositions of the external fields and the internal fields, due predominantly to the dipole–dipole interactions, within the medium. The effective field depends on the type of medium, and the nature of the interactions [27]. In many instances, the external fields in (3.10)–(3.14) can be replaced by an effective field equal to the sum of the external and internal fields [10, 27].

and, in (3.22),

$$\Phi_{ij} = -\alpha_{ij}, \tag{3.29}$$

$$\Omega_{ij} = -\alpha'_{ij}, \tag{3.30}$$

$$\Phi_{ijk} = \tfrac{1}{\omega}\varepsilon_{ikl}G'_{jl} - \tfrac{1}{\omega}\varepsilon_{jkl}G'_{il} - \tfrac{1}{2}\left(a_{ijk} - a_{jik}\right), \tag{3.31}$$

$$\Omega_{ijk} = \tfrac{1}{\omega}\varepsilon_{ikl}G_{jl} + \tfrac{1}{\omega}\varepsilon_{jkl}G_{il} - \tfrac{1}{2}\left(a'_{ijk} + a'_{jik}\right), \tag{3.32}$$

$$\Phi_{ikjl} = -\tfrac{1}{6}\left(b_{ijkl} + b_{jikl}\right) + \tfrac{1}{4}d_{ikjl} + \tfrac{1}{2\omega}\left[\varepsilon_{ikm}\left(L'_{jlm} - H'_{jml}\right) + \varepsilon_{jlm}\left(L'_{ikm} - H'_{imk}\right)\right] + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\chi_{mn}, \tag{3.33}$$

$$\Omega_{ikjl} = -\tfrac{1}{6}\left(b'_{ijkl} - b'_{jikl}\right) + \tfrac{1}{4}d'_{ikjl} + \tfrac{1}{2\omega}\left[\varepsilon_{ikm}\left(L_{jlm} - H_{jml}\right) - \varepsilon_{jlm}\left(L_{ikm} - H_{imk}\right)\right] + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\chi'_{mn}. \tag{3.34}$$

The tensors $\Theta_{ij\ldots}$, $\Pi_{ij\ldots}$, $\Phi_{ij\ldots}$ and $\Omega_{ij\ldots}$ relate the fields and their gradients (cause) to the bound charge and current densities (effect), and are therefore property tensors. For non-magnetic media $\Pi_{ij\ldots}$ and $\Omega_{ij\ldots}$ are zero because these contain only time-odd tensors (see Section 2.5).

The expressions for Θ_{ijk}, Π_{ijk}, Θ_{ijkl}, Π_{ijkl}, Φ_{ikjl} and Ω_{ikjl}, in (3.25)–(3.28), (3.33) and (3.34), are not unique, because these are contracted with symmetric products of field gradients in (3.21) and (3.22) — there is ambiguity in how the subscripts are assigned. Consider, for instance, Π_{ijk} in (3.26) which is contracted with the product $\nabla_j\nabla_k$ in (3.21). The alternative forms

$$-\tfrac{1}{\omega}\varepsilon_{ikl}G_{jl} + \tfrac{1}{2}\left(a'_{ijk} + a'_{jik}\right), \tag{3.35}$$

$$-\tfrac{1}{\omega}\varepsilon_{ikl}G_{jl} + \tfrac{1}{2}\left(a'_{ijk} + a'_{kij}\right), \tag{3.36}$$

$$-\tfrac{1}{\omega}\varepsilon_{ijl}G_{kl} + \tfrac{1}{2}\left(a'_{ijk} + a'_{jik}\right), \tag{3.37}$$

$$-\tfrac{1}{\omega}\varepsilon_{ijl}G_{kl} + \tfrac{1}{2}\left(a'_{ijk} + a'_{kij}\right), \tag{3.38}$$

yield identical expressions when these are contracted with $\nabla_j\nabla_k$. For this reason, these property tensors cannot be used to determine origin-independent expressions for the polarizability tensors (see also Section 4.4.2).

By substituting (3.23)–(3.34) in (3.21) and (3.22), and using the results (2.64)–(2.79), it can be shown that the charge and current densities to electric octopole–magnetic quadrupole order are independent of the choice of coordinate origin, even though the property tensors (3.26)–(3.28), (3.33) and (3.34) are not (see (3.43), (3.45)–(3.48) and Chapter 4). Origin independence of the property tensor Θ_{ijk} in (3.25) is achieved through a Van Vleck–Buckingham cancellation [6] between the origin dependences of the molecular polarizabilities in its expression. Origin independence of the tensors Φ_{ijk} and Ω_{ijk} in (3.31) and (3.32) is also achieved through Van Vleck–Buckingham cancellation, whilst these additionally possess the symmetries

$$\Phi_{ijk} = -\Phi_{jik}, \tag{3.39}$$

$$\Omega_{ijk} = \Omega_{jik}. \tag{3.40}$$

Origin independence of the contributions to the charge density, from Π_{ijk} at electric quadrupole–magnetic dipole order, and from Θ_{ijkl} and Π_{ijkl} at electric octopole–magnetic quadrupole order, is achieved because these are contracted with symmetric products of the field gradients $\nabla_j\nabla_k$ and $\nabla_j\nabla_k\nabla_l$. The contributions to the current density, from Φ_{ikjl} and Ω_{ikjl} at electric octopole–magnetic quadrupole order, are contracted with the product $\nabla_k\nabla_l$, and additionally possess the symmetries

$$\Phi_{ikjl} = \Phi_{jlik}, \tag{3.41}$$

$$\Omega_{ikjl} = -\Omega_{jlik}. \tag{3.42}$$

To illustrate the above, first consider the property tensor Π_{ijk}. The origin dependence $\Delta\Pi_{ijk}$ is obtained by using (2.67) and (2.68) in (3.26). Use of the antisymmetry of α'_{ij} (see Table 2.1) gives

$$\Delta\Pi_{ijk} = \tfrac{1}{2}\left(d_k\alpha'_{ij} - d_j\alpha'_{ik}\right). \tag{3.43}$$

When (3.43) is contracted with the symmetric product $\nabla_j\nabla_k$, $\Delta\Pi_{ijk}\nabla_j\nabla_k = 0$ follows. Because of the contraction of Π_{ijk} with $\nabla_j\nabla_k$ in (3.21), the result (3.43) is not unique. If, instead of (3.26), Π_{ijk} is taken as (3.37), then

$$\Delta\Pi_{ijk} = -d_i\alpha'_{jk}, \tag{3.44}$$

which again is zero when contracted with the symmetric product $\nabla_j\nabla_k$.

The origin dependence of Θ_{ijkl} is obtained by substituting (2.70), (2.72), (2.75) and (2.77) in (3.27), and the origin dependence of Π_{ijkl} from (2.71), (2.73), (2.74) and (2.76) in (3.28). After some algebra, one finds

$$\begin{aligned}\Delta\Theta_{ijkl} = {} & \tfrac{1}{6}\left(d_j a_{ikl} - 2d_k a_{ijl} + d_l a_{ijk}\right) + \tfrac{1}{12}\left(4d_k a_{jil} - 3d_j a_{lik} - d_l a_{jik}\right) + \tfrac{1}{6}d_i\left(d_l\alpha_{jk} - d_k\alpha_{jl}\right) \\ & + \tfrac{1}{6}\left(2d_jd_k\alpha_{il} - d_kd_l\alpha_{ij} - d_jd_l\alpha_{ik}\right) - \tfrac{1}{3\omega}\varepsilon_{ikl}d_mG'_{jm} + \tfrac{1}{2\omega}\varepsilon_{ikm}\left(d_lG'_{jm} - d_jG'_{lm}\right)\end{aligned} \tag{3.45}$$

and

$$\begin{aligned}\Delta\Pi_{ijkl} = {} & \tfrac{1}{6}\left(d_j a'_{ikl} - 2d_k a'_{ijl} + d_l a'_{ijk}\right) - \tfrac{1}{12}\left(4d_k a'_{jil} - 3d_j a'_{lik} - d_l a'_{jik}\right) - \tfrac{1}{6}d_i\left(d_l\alpha'_{jk} - d_k\alpha'_{jl}\right) \\ & + \tfrac{1}{6}\left(2d_jd_k\alpha'_{il} - d_kd_l\alpha'_{ij} - d_jd_l\alpha'_{ik}\right) - \tfrac{1}{3\omega}\varepsilon_{ikl}d_mG_{jm} + \tfrac{1}{2\omega}\varepsilon_{ikm}\left(d_lG_{jm} - d_jG_{lm}\right).\end{aligned} \tag{3.46}$$

By inspection, (3.45) and (3.46) yield zero when contracted with the symmetric product $\nabla_j\nabla_k\nabla_l$.

The origin dependences of Φ_{ikjl} and Ω_{ikjl} are obtained by substituting (2.70), (2.72), (2.75), (2.77) and (2.78) in (3.33), and (2.71), (2.73), (2.74), (2.76) and (2.79) in (3.34), respectively. The results are

$$\begin{aligned}\Delta\Phi_{ikjl} = {} & \tfrac{1}{4}d_j\left(a_{kil} - a_{lik}\right) + \tfrac{1}{6}\left(d_l a_{ijk} - d_k a_{ijl}\right) + \tfrac{1}{12}\left(d_k a_{jil} - d_l a_{jik}\right) \\ & + \tfrac{1}{12}d_j\left(d_k\alpha_{il} - d_l\alpha_{ik}\right) + \tfrac{1}{12}d_i\left(d_k\alpha_{jl} - d_l\alpha_{jk}\right) - \tfrac{1}{3\omega}d_m\left(\varepsilon_{ikl}G'_{jm} + \varepsilon_{jkl}G'_{im}\right) \\ & + \tfrac{1}{2\omega}\left(\varepsilon_{jkm}d_l - \varepsilon_{jlm}d_k\right)G'_{im} + \tfrac{1}{2\omega}d_i\left(\varepsilon_{jlm}G'_{km} - \varepsilon_{jkm}G'_{lm}\right)\end{aligned} \tag{3.47}$$

and

$$\begin{aligned}\Delta\Omega_{ikjl} = {} & \tfrac{1}{3}\left(d_l a'_{ijk} - d_k a'_{ijl}\right) - \tfrac{1}{3}\left(d_k a'_{jil} - d_l a'_{jik}\right) \\ & + \tfrac{1}{6}d_j\left(d_k\alpha'_{il} - d_l\alpha'_{ik}\right) + \tfrac{1}{6}d_i\left(d_k\alpha'_{jl} - d_l\alpha'_{jk}\right) - \tfrac{1}{3\omega}d_m\left(\varepsilon_{ikl}G_{jm} + \varepsilon_{jkl}G_{im}\right).\end{aligned} \tag{3.48}$$

Again, it is easy to see that (3.47) and (3.48) yield zero when contracted with the symmetric product $\nabla_k\nabla_l$.

3.3 Propagation equation

The propagation equation for a harmonic plane wave in a dielectric is obtained from the Maxwell equation (3.53) with $\boldsymbol{J}_f = 0$, (3.51) and the current density (3.22):

$$\begin{aligned}\big(\delta_{ij}\nabla^2 - \nabla_i\nabla_j + \mu_0\varepsilon_0\omega^2\delta_{ij} - \mu_0\omega^2\mathcal{T}\left[\Phi_{ij} + \Phi_{ijk}\nabla_k + \Phi_{ikjl}\nabla_k\nabla_l\right] & \\ + i\mu_0\omega^2\mathcal{T}\left[\Omega_{ij} + \Omega_{ijk}\nabla_k + \Omega_{ikjl}\nabla_k\nabla_l\right]\big)E_j = 0. &\end{aligned} \tag{3.49}$$

Since the current density (3.22) is independent of the choice of coordinate origin, the propagation equation (3.49), which is derived from it, is also.

3.4 Response fields and constitutive relations

For a macroscopic system, Maxwell's equations may be written [4]

$$\nabla \cdot \boldsymbol{E} = \varepsilon_0^{-1}(\rho_f + \rho_b), \tag{3.50}$$

$$\nabla \times \boldsymbol{E} + \frac{\partial \boldsymbol{B}}{\partial t} = 0, \tag{3.51}$$

$$\nabla \cdot \boldsymbol{B} = 0, \tag{3.52}$$

$$\nabla \times \boldsymbol{B} - \mu_0\varepsilon_0 \frac{\partial \boldsymbol{E}}{\partial t} = \mu_0 \left(\boldsymbol{J}_f + \boldsymbol{J}_b\right), \tag{3.53}$$

where ε_0 and μ_0 are the vacuum permittivity and permeability, respectively. The bound charge and current densities ρ_b and $\boldsymbol{J}_b$ are given, to electric octopole–magnetic quadrupole order, by (3.18) and (3.19), respectively. The macroscopic response fields are defined, to this order, in terms of the moment densities by [4]

$$D_i = \varepsilon_0 E_i + P_i - \tfrac{1}{2}\nabla_j Q_{ij} + \tfrac{1}{6}\nabla_j \nabla_k Q_{ijk} \tag{3.54}$$

and

$$H_i = \mu_0^{-1} B_i - M_i + \tfrac{1}{2}\nabla_j M_{ij}, \tag{3.55}$$

and they satisfy the inhomogeneous macroscopic Maxwell equations

$$\nabla \cdot \boldsymbol{D} = \rho_f \tag{3.56}$$

and

$$\nabla \times \boldsymbol{H} - \frac{\partial \boldsymbol{D}}{\partial t} = \boldsymbol{J}_f. \tag{3.57}$$

For harmonic plane waves in homogeneous media, linear constitutive relations for $\boldsymbol{D}(\boldsymbol{E}, \boldsymbol{B})$ and $\boldsymbol{H}(\boldsymbol{E}, \boldsymbol{B})$ are obtained by substituting (3.10)–(3.14), with the replacements (see (2.30) and (2.31))

$$\nabla_i \to i k_i \qquad \text{and} \qquad \frac{\partial}{\partial t} \to -i\omega, \tag{3.58}$$

in (3.54) and (3.55). Then

$$\begin{pmatrix} D_i \\ H_i \end{pmatrix} = C \begin{pmatrix} E_j \\ B_j \end{pmatrix}, \tag{3.59}$$

where C is a 6×6 matrix whose elements specify the constitutive tensor (see also Section 3.5)

$$C = \begin{pmatrix} A_{ij} & T_{ij} \\ U_{ij} & X_{ij} \end{pmatrix}. \tag{3.60}$$

To electric octopole–magnetic quadrupole order, the material constants A_{ij} (permittivity), X_{ij} (inverse permeability), T_{ij} and U_{ij} (magnetoelectric coefficients) in (3.60) are given by

$$\begin{aligned} A_{ij} = \varepsilon_0\delta_{ij} + \mathcal{T}\big[&\alpha_{ij} + \tfrac{i}{2}\left(a_{ijk} - a_{jki}\right)k_k + \left\{-\tfrac{1}{6}\left(b_{ijkl} + b_{jikl}\right) + \tfrac{1}{4}d_{ikjl}\right\}k_k k_l \\ &-i\alpha'_{ij} + \tfrac{1}{2}\left(a'_{ijk} + a'_{jki}\right)k_k + \left\{\tfrac{i}{6}\left(b'_{ijkl} - b'_{jikl}\right) - \tfrac{i}{4}d'_{ikjl}\right\}k_k k_l\big], \end{aligned} \tag{3.61}$$

$$T_{ij} = \mathcal{T}\left[-iG'_{ij} + \tfrac{1}{2}\left(H'_{ijk} - L'_{ikj}\right)k_k + G_{ij} + \tfrac{i}{2}\left(H_{ijk} - L_{ikj}\right)k_k\right], \tag{3.62}$$

$$U_{ij} = \mathcal{T}\left[-iG'_{ji} + \tfrac{1}{2}\left(-H'_{jik} + L'_{jki}\right)k_k - G_{ji} + \tfrac{i}{2}\left(H_{jik} - L_{jki}\right)k_k\right], \tag{3.63}$$

$$X_{ij} = \mu_0^{-1}\delta_{ij} - \mathcal{T}\left[\chi_{ij} - i\chi'_{ij}\right], \tag{3.64}$$

where the transform $\mathcal{T}$ is defined in (3.8). The contributions of the permanent multipole moment densities $P_i^{(0)}$, $Q_{ij\ldots}^{(0)}$ and $M_{ij\ldots}^{(0)}$ in (3.10)–(3.14) have been omitted in (3.54) and (3.55) and hence in (3.61)–(3.64). For a homogeneous medium, where the molecules are aligned, there is no variation of the permanent (static) macroscopic moments, so their space derivatives, like their time derivatives, are zero. Hence, these do not contribute to the Maxwell equations (3.56) and (3.57).

In terms of the zeroth-, first-, second- and third-order contributions, corresponding to the vacuum and the electric dipole, electric quadrupole–magnetic dipole and electric octopole–magnetic quadrupole orders, respectively, the constitutive tensor can be written as

$$C = C^{(0)} + C^{(1)} + C^{(2)} + C^{(3)}. \tag{3.65}$$

Here

$$C^{(n)} = \begin{pmatrix} A_{ij}^{(n)} & T_{ij}^{(n)} \\ U_{ij}^{(n)} & X_{ij}^{(n)} \end{pmatrix}, \tag{3.66}$$

where $n = 0, 1, 2, 3$, and

$$A_{ij}^{(0)} = \varepsilon_0 \delta_{ij}, \tag{3.67}$$
$$A_{ij}^{(1)} = \mathcal{N}\left(\alpha_{ij} - i\alpha'_{ij}\right), \tag{3.68}$$
$$A_{ij}^{(2)} = \mathcal{T}\left[\tfrac{i}{2}\left(a_{ijk} - a_{jki}\right) + \tfrac{1}{2}\left(a'_{ijk} + a'_{jki}\right)\right] k_k, \tag{3.69}$$
$$A_{ij}^{(3)} = \mathcal{T}\left[-\tfrac{1}{6}\left(b_{ijkl} + b_{jikl}\right) + \tfrac{1}{4} d_{ikjl} + \tfrac{i}{6}\left(b'_{ijkl} - b'_{jikl}\right) - \tfrac{i}{4} d'_{ikjl}\right] k_k k_l, \tag{3.70}$$
$$T_{ij}^{(0)} = T_{ij}^{(1)} = 0, \tag{3.71}$$
$$T_{ij}^{(2)} = \mathcal{T}\left[-iG'_{ij} + G_{ij}\right], \tag{3.72}$$
$$T_{ij}^{(3)} = \mathcal{T}\left[\tfrac{1}{2}\left(H'_{ijk} - L'_{ikj}\right) + \tfrac{i}{2}\left(H_{ijk} - L_{ikj}\right)\right] k_k, \tag{3.73}$$
$$U_{ij}^{(0)} = U_{ij}^{(1)} = 0, \tag{3.74}$$
$$U_{ij}^{(2)} = \mathcal{T}\left[-iG'_{ji} - G_{ji}\right], \tag{3.75}$$
$$U_{ij}^{(3)} = \mathcal{T}\left[\tfrac{1}{2}\left(-H'_{jik} + L'_{jki}\right) + \tfrac{i}{2}\left(H_{jik} - L_{jki}\right)\right] k_k, \tag{3.76}$$
$$X_{ij}^{(0)} = \mu_0^{-1} \delta_{ij}, \tag{3.77}$$
$$X_{ij}^{(1)} = X_{ij}^{(2)} = 0, \tag{3.78}$$
$$X_{ij}^{(3)} = \mathcal{T}\left[-\chi_{ij} + i\chi'_{ij}\right]. \tag{3.79}$$

The transforms (3.8) are not needed in (3.67) and (3.77), because these describe the vacuum, and in (3.68), because α_{ij} and α'_{ij} are independent of the choice of molecular coordinate origins (see (2.64) and (2.65)). The response fields D_i and H_i are evidently independent of the choice of coordinate origin only at electric dipole order.

The response fields (3.54) and (3.55) are not specified uniquely by the Maxwell equations (3.56) and (3.57). If $\boldsymbol{H}^G$ is a harmonic plane wave like $\boldsymbol{E}$ and $\boldsymbol{B}$ in (2.30) and (2.31), then the "gauge transformations" [4, 29]

$$H_i \to H_i + H_i^G \qquad \text{and} \qquad D_i \to D_i - \tfrac{1}{\omega}\varepsilon_{ijk} k_j H_k^G, \tag{3.80}$$

of the fields $\boldsymbol{D}$ and $\boldsymbol{H}$, leave (3.56) and (3.57) unchanged [4].

3.5 Covariant formulation and the Post constraint

In a covariant (relativistic) formalism, Maxwell's inhomogeneous equations (3.50) and (3.53) take the compact form [4, 5, 13]

$$\partial_\alpha F^{\alpha\beta} = \mu_0 J^\beta, \tag{3.81}$$

where $\partial_\alpha \equiv \dfrac{\partial}{\partial x^\alpha}$ with $x^\alpha = (ct, \boldsymbol{r})$,

$$F^{\alpha\beta} = \begin{pmatrix} 0 & -E_1/c & -E_2/c & -E_3/c \\ E_1/c & 0 & -B_3 & B_2 \\ E_2/c & B_3 & 0 & -B_1 \\ E_3/c & -B_2 & B_1 & 0 \end{pmatrix}, \tag{3.82}$$

$$J^\beta = (c\rho, \boldsymbol{J}). \tag{3.83}$$

In these, ρ and $\boldsymbol{J}$ are the total source densities, and Greek subscripts and superscripts take values from 0 to 3. Similarly, the inhomogeneous equations (3.56) and (3.57) become

$$\partial^\alpha G_{\alpha\beta} = J_\beta, \tag{3.84}$$

where $\partial^\alpha \equiv \dfrac{\partial}{\partial x_\alpha}$,

$$G_{\alpha\beta} = \begin{pmatrix} 0 & cD_1 & cD_2 & cD_3 \\ -cD_1 & 0 & -H_3 & H_2 \\ -cD_2 & H_3 & 0 & -H_1 \\ -cD_3 & -H_2 & H_1 & 0 \end{pmatrix}, \tag{3.85}$$

$$J_\alpha = g_{\alpha\beta} J^\beta = (c\rho, -\boldsymbol{J}) \tag{3.86}$$

and the metric is

$$g_{\alpha\beta} = \begin{cases} 1 & \alpha = \beta = 0 \\ -1 & \alpha = \beta = 1, 2 \text{ or } 3 \\ 0 & \alpha \neq \beta. \end{cases} \tag{3.87}$$

The constitutive relations corresponding to (3.59) can now be written in covariant form

$$G_{\alpha\beta} = \tfrac{1}{2} \chi_{\alpha\beta\gamma\delta} F^{\gamma\delta}. \tag{3.88}$$

The constitutive tensor $\chi_{\alpha\beta\gamma\delta}$ is a fourth-rank tensor with skew symmetry in two index pairs:

$$\begin{aligned} \chi_{\alpha\beta\gamma\delta} &= -\chi_{\beta\alpha\gamma\delta}, \\ \chi_{\alpha\beta\gamma\delta} &= -\chi_{\alpha\beta\delta\gamma}, \end{aligned} \tag{3.89}$$

as can be seen from (3.82) and (3.85). The factor $\frac{1}{2}$ in (3.88) takes care of the duplicate terms arising from (3.89). For non-dissipative media, $\chi_{\alpha\beta\gamma\delta}$ has the additional property [4, 28, 30, 31]

$$\chi_{\alpha\beta\gamma\delta} = \left(\chi_{\gamma\delta\beta\alpha}\right)^*. \tag{3.90}$$

The symmetries (3.89) reduce the number of independent components of the constitutive tensor from $4^4 = 256$ to 36 (the same number of components as the 6×6 constitutive matrix (3.60)), and (3.90) further reduces this to 21. The symmetries (3.89) and (3.90) are reflected in the material constants in (3.60) by [4, 30] (see also Equation (6.21) of Reference 28)

$$A_{ij} = A^*_{ji}, \tag{3.91}$$

$$U_{ij} = -T^*_{ji}, \tag{3.92}$$

$$X_{ij} = X^*_{ji}. \tag{3.93}$$

The relations (3.91)–(3.93) can be derived from the Lagrangian formalism of classical field theory in macroscopic electromagnetism [4, 30]. Inspection of the material constants (3.67)–(3.79) shows that these do satisfy (3.91)–(3.93).

For a uniform medium, Post positted the restriction [28]

$$\begin{aligned}\chi_{[\alpha\beta\gamma\delta]} &= \tfrac{1}{4!}(\chi_{\alpha\beta\gamma\delta} - \chi_{\alpha\beta\delta\gamma} + \chi_{\alpha\gamma\delta\beta} \mp \cdots) \\ &= \tfrac{1}{3!}(\chi_{\alpha\beta\gamma\delta} + \chi_{\alpha\delta\beta\gamma} + \chi_{\beta\gamma\alpha\delta} + \chi_{\beta\delta\gamma\alpha} + \chi_{\gamma\alpha\beta\delta} + \chi_{\gamma\delta\alpha\beta}) = 0\end{aligned} \tag{3.94}$$

on the antisymmetric part [32, Section 2.4] of the constitutive tensor $\chi_{\alpha\beta\gamma\delta}$, on the basis that it does not contribute to the Euler-Lagrange derivative [4, 28]. $\chi_{[\alpha\beta\gamma\delta]}$ therefore has no effect on the Maxwell equations for $\boldsymbol{D}$ and $\boldsymbol{H}$ [4] and carries no electromagnetic energy [31]. In terms of the material constants in (3.60), the condition (3.94) becomes [4, 30] (see also Equation (6.18b) of Reference 28)

$$T_{ii} = U_{ii}. \tag{3.95}$$

For non-dissipative media, where (3.91)–(3.93) hold, (3.92) shows that (3.95) is automatically satisfied when T_{ij} and U_{ij} are imaginary. Thus (3.95) holds for non-magnetic media at electric quadrupole–magnetic dipole order, and for magnetic media at electric octopole–magnetic quadrupole order (see (3.72) and (3.75), and (3.73) and (3.76)). The constraint (3.95) is also satisfied at first-order where $T_{ij}^{(1)} = U_{ij}^{(1)} = 0$. The validity of (3.95), for magnetic media at electric quadrupole–magnetic dipole order and non-magnetic media at electric octopole–magnetic quadrupole order, is addressed in Sections 4.4.4 and 5.1.9, respectively.

The condition (3.94) was dubbed the 'Post constraint' by Lakhtakia [33, and references therein]. An alternative proof of (3.94) based on a 'principle of parsimony' was derived by Lakhtakia and Weiglhofer [34–36]. Both Post [28, Page 129], and Lakhtakia [36, 37], further motivated (3.94) on the grounds that (3.94) was not violated by any known physical media. Their analysis places the origin of the Post constraint in the structure of Maxwell's equations, the non-contribution of (3.94) to Maxwell's equations for the response fields $\boldsymbol{D}$ and $\boldsymbol{H}$ being the prime motivator.

Other authors [30, 38–42] have advocated a more circumspect approach, claiming instead that the Post constraint is a consequence of the structure of the material. The validity of (3.94) would then depend on whether the symmetry of the material does, or does not, allow the violation of (3.94). In particular, with respect to the Tellegen medium [43], an artificial material that violates (3.94), Raab and Sihvola [39] showed that a Tellegen medium is allowed in principle, contradicting earlier claims by Lakhtakia [44, 45]. Tretyakov *et al.* [46] and Gosch *et al.* [47] subsequently reported measurements on an artificial Tellegen particle violating (3.94), the work of the former authors refuted by Lakhtakia [33], and that of the latter authors tentatively welcomed [48].

Hehl *et al.* [31, 49, and references therein] have measured the magnetoelectric effect of Cr_2O_3 as a function of temperature. From their data they have extracted non-zero values for the pseudoscalar

$$\tilde{\alpha} = \tfrac{1}{4!}\varepsilon_{\alpha\beta\gamma\delta}\chi^{\alpha\beta\gamma\delta}, \tag{3.96}$$

where $\varepsilon_{\alpha\beta\gamma\delta} = 0, \pm 1$ is the fourth-rank totally antisymmetric Levi-Civita tensor.

In the light of this experimental evidence, it seems that Post's condition (3.94) cannot be imposed as a general constraint. In multipole theory, in terms of origin-dependent molecular polarizabilities, the Post constraint is violated at electric quadrupole–magnetic dipole order for magnetic media, and at electric octopole–magnetic quadrupole order for non-magnetic media [4], but the invariant theory, to leading order, does satisfy the Post constraint [4, 6]. The extent to which the invariant theory at electric octopole–magnetic quadrupole order is compliant with the Post constraint is discussed in Sections 5.1.9 and 5.2.8, and in Chapter 6.

Chapter 4

Invariant formulation

In the previous chapter it was noted that the induced source densities (3.21), (3.22) and the propagation equation (3.49) are independent of the choice of molecular coordinate origins, whereas the induced macroscopic moment densities, in terms of which they are expressed, are in general origin dependent. Also, the material constants (3.61)–(3.64), and hence the response fields (3.54) and (3.55), depend on the choice of molecular coordinate origins. The origin dependence of the response fields results also in the origin dependence of the time average of the instantaneous Poynting vector $\langle \boldsymbol{S} \rangle = \frac{1}{2}\mathcal{R}e(\boldsymbol{E} \times \boldsymbol{H}^*)$ [50]. Multipole theory of linear, homogeneous, anisotropic media, expressed in terms of origin-dependent molecular polarizabilities, is therefore only partially invariant. A theory that yields an infinite set of response fields corresponding to an arbitrary set of molecular coordinate origins $\{O_n\}$ is physically untenable.

This chapter and Chapter 5 contain the core of the thesis, namely a fully invariant electrodynamics, at both electric quadrupole–magnetic dipole and electric octopole–magnetic quadrupole orders, for both non-magnetic and magnetic, linear homogeneous anisotropic media. To this end, origin-independent expressions corresponding to the molecular polarizabilities in (2.33)–(2.37) are obtained. These expressions leave the bound source densities and the propagation equation unchanged, and produce physically acceptable (invariant) expressions for the material constants.

From the expressions for the induced macroscopic moment densities (3.10)–(3.14), which depend on the choice of coordinate origins, origin-independent expressions are obtained by replacing the polarizability tensors in the arguments of the transforms $\mathcal{T}[\cdots]$ by the corresponding origin-independent quantities. Equations (3.10)–(3.14) with (3.17) then become

$$\begin{aligned}
\tilde{P}_i &= P_i^{(0)} + \mathcal{N}\Big(\tilde{\alpha}_{ij}E_j + \tfrac{1}{\omega}\tilde{\alpha}'_{ij}\dot{E}_j + \tfrac{1}{2}\tilde{a}_{ijk}\nabla_k E_j + \tfrac{1}{2\omega}\tilde{a}'_{ijk}\nabla_k \dot{E}_j \\
&\quad + \tfrac{1}{6}\tilde{b}_{ijkl}\nabla_k\nabla_l E_j + \tfrac{1}{6\omega}\tilde{b}'_{ijkl}\nabla_k\nabla_l E_j + \cdots \\
&\quad + \tilde{G}_{ij}B_j + \tfrac{1}{\omega}\tilde{G}'_{ij}\dot{B}_j + \tfrac{1}{2}\tilde{H}_{ijk}\nabla_k B_j + \tfrac{1}{2\omega}\tilde{H}'_{ijk}\nabla_k \dot{B}_j + \cdots\Big), && (4.1)\\
\tilde{Q}_{ij} &= Q_{ij}^{(0)} + \mathcal{N}\Big(\tilde{a}_{kij}E_k - \tfrac{1}{\omega}\tilde{a}'_{kij}\dot{E}_k + \tfrac{1}{2}\tilde{d}_{ijkl}\nabla_l E_k + \tfrac{1}{2\omega}\tilde{d}'_{ijkl}\nabla_l \dot{E}_k + \cdots \\
&\quad + \tilde{L}_{ijk}B_k + \tfrac{1}{\omega}\tilde{L}'_{ijk}\dot{B}_k + \cdots\Big), && (4.2)\\
\tilde{Q}_{ijk} &= Q_{ijk}^{(0)} + \mathcal{N}\Big(\tilde{b}_{lijk}E_l - \tfrac{1}{\omega}\tilde{b}'_{lijk}\dot{E}_l + \cdots\Big), && (4.3)\\
\tilde{M}_i &= M_i^{(0)} + \mathcal{N}\Big(\tilde{G}_{ji}E_j - \tfrac{1}{\omega}\tilde{G}'_{ji}\dot{E}_j + \tfrac{1}{2}\tilde{L}_{jki}\nabla_k E_j - \tfrac{1}{2\omega}\tilde{L}'_{jki}\nabla_k \dot{E}_j + \cdots \\
&\quad + \tilde{\chi}_{ij}B_j + \tfrac{1}{\omega}\tilde{\chi}'_{ij}\dot{B}_j + \cdots\Big), && (4.4)\\
\tilde{M}_{ij} &= M_{ij}^{(0)} + \mathcal{N}\Big(\tilde{H}_{kij}E_k - \tfrac{1}{\omega}\tilde{H}'_{kij}\dot{E}_k + \cdots\Big), && (4.5)
\end{aligned}$$

where $\tilde{\alpha}_{ij}$, $\tilde{a}_{ijk}$, $\ldots$ denote invariant polarizabilities that are to be determined.

The invariant expressions corresponding to the multipole polarizabilities on the right-hand sides of (4.1)–(4.5) are origin-independent linear combinations of molecular polarizability tensors of the same order contracted, where necessary, with isotropic tensors (see Section D.3). The tensors α_{ij} and

α'_{ij}, at electric dipole order, are origin independent (see (2.64) and (2.65)); thus

$$\tilde{\alpha}_{ij} = \alpha_{ij} \qquad \text{and} \qquad \tilde{\alpha}'_{ij} = \alpha'_{ij}. \tag{4.6}$$

The vacuum and the multipole contributions at electric dipole order, electric quadrupole–magnetic dipole order and electric octopole–magnetic quadrupole order, are treated in Sections 4.1, 4.2, 4.3, 4.4, 5.1 and 5.2, respectively. The contributions of the three multipole orders to the source densities, response fields (and material constants) and the wave equation are distinguished by a superscript notation. For example, the charge density (3.21) to electric octopole–magnetic quadrupole order is written

$$\begin{aligned}\rho &= \mathcal{T}\left[\Theta_{ij} + i\Pi_{ij}\right]\nabla_j E_i + \mathcal{T}\left[\Theta_{ijk} + i\Pi_{ijk}\right]\nabla_j\nabla_k E_i + \mathcal{T}\left[\Theta_{ijkl} + i\Pi_{ijkl}\right]\nabla_j\nabla_k\nabla_l E_i \\ &= \rho^{(1)} + \rho^{(\overline{1})} + \rho^{(2)} + \rho^{(\overline{2})} + \rho^{(3)} + \rho^{(\overline{3})},\end{aligned} \tag{4.7}$$

where a bar is used to indicate time-odd contributions. The vacuum contribution $\rho^{(0)} = 0$.

A brief review of electrodynamics in a vacuum is given in Section 4.1. Various methods to determine the origin-independent expressions corresponding to the molecular polarizability tensors at each order are presented, beginning with electric dipole in Section 4.2. In Section 4.3, the expressions for the origin-independent time-even tensors $\tilde{G}'_{ij}$ and $\tilde{a}_{ijk}$ at electric quadrupole–magnetic dipole order are derived. The method used here is presented for its transparency, but is not suitable for the calculations at higher multipole order, where the number of tensors involved renders the expressions prohibitively complex. A more direct method, suitable for higher multipole orders, is presented at electric quadrupole–magnetic dipole order for magnetic molecules in Section 4.4.

The calculations at electric quadrupole–magnetic dipole order and at electric octopole–magnetic quadrupole order are contained in MATHEMATICA notebooks included on the accompanying CD. The calculations for the time-even and time-odd contributions at each multipole order are contained in separate directories. The directory names consist of a prefix and postfix. The prefix corresponds to the multipole order (`e2m1` and `e3m2` for electric quadrupole–magnetic dipole and electric octopole–magnetic quadrupole order, respectively) and the postfix indicates a time-even (`-nm`) or time-odd (`-m`) contribution. Because the calculations for the time-even and time-odd contributions are similar at a particular order, many of the notebooks have the same name. When referring to a notebook, only the notebook's name, and not the directory in which it is contained, is included in the text. The hyperlinks in the `pdf` version of this thesis automatically launch MATHEMATICA and the corresponding notebook from the correct directory (see the `README` file on the accompanying CD and Appendix B).

4.1 Electrodynamics in a vacuum

Fields in a vacuum are described by the source-free Maxwell equations

$$\boldsymbol{\nabla}\cdot\boldsymbol{E} = 0, \qquad \boldsymbol{\nabla}\cdot\boldsymbol{B} = 0, \tag{4.8}$$

$$\boldsymbol{\nabla}\times\boldsymbol{E} = -\frac{\partial\boldsymbol{B}}{\partial t}, \qquad \boldsymbol{\nabla}\times\boldsymbol{B} = \mu_0\varepsilon_0\frac{\partial\boldsymbol{E}}{\partial t}. \tag{4.9}$$

By taking the curl of Equations (4.9), using the identity $\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\boldsymbol{A}) = \boldsymbol{\nabla}(\boldsymbol{\nabla}\cdot\boldsymbol{A}) - \nabla^2\boldsymbol{A}$, (4.8) and rearranging, one obtains the non-dispersive, three-dimensional wave equations

$$\left(\nabla^2 - \mu_0\varepsilon_0\frac{\partial^2}{\partial t^2}\right)\boldsymbol{E} = 0 \qquad \text{and} \qquad \left(\nabla^2 - \mu_0\varepsilon_0\frac{\partial^2}{\partial t^2}\right)\boldsymbol{B} = 0. \tag{4.10}$$

Thus, all electromagnetic waves in vacuum are non-dispersive, and propagate with speed

$$c = \frac{1}{\sqrt{\mu_0\varepsilon_0}}, \tag{4.11}$$

the speed of light in vacuum.

In particular, (4.10) possesses the harmonic plane wave solutions

$$\boldsymbol{E}(\boldsymbol{r},t)=\boldsymbol{E}_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)} \qquad \text{and} \qquad \boldsymbol{B}(\boldsymbol{r},t)=\boldsymbol{B}_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}, \tag{4.12}$$

where $\omega = |\boldsymbol{k}|c$ and the wave vector $\boldsymbol{k}$ specifies the direction of propagation. It follows from (4.8) and (4.12) that $\boldsymbol{k}\cdot\boldsymbol{E}=0$ and $\boldsymbol{k}\cdot\boldsymbol{B}=0$; therefore $\boldsymbol{E}$ and $\boldsymbol{B}$ are transverse. Also, from (4.9) and (4.12)

$$\boldsymbol{B}=\frac{1}{\omega}\boldsymbol{k}\times\boldsymbol{E}, \tag{4.13}$$

and therefore $\boldsymbol{E}$, $\boldsymbol{B}$ and $\boldsymbol{k}$ are orthogonal.

It is apparent that for a vacuum (3.49) reduces to (4.10) when $\boldsymbol{E}$ is given by (4.12), as required. Also (3.59) reduces to

$$\boldsymbol{D}^{(0)}=\varepsilon_0\boldsymbol{E} \qquad \text{and} \qquad \boldsymbol{H}^{(0)}=\mu_0^{-1}\boldsymbol{B}. \tag{4.14}$$

The product $\mu_0\varepsilon_0$ is of fundamental importance: in inertial space it is the reciprocal of a universal speed squared. Also, the ratio ε_0/μ_0 is a universal quantity (in both inertial and non-inertial space) equal to the square of the vacuum admittance [31].

4.2 Electric dipole order

At electric dipole order, the only non-zero induced multipole moment density is that of the electric dipole. Thus the contributions to the observables for non-magnetic molecules at this order can be expressed in terms of α_{ij}, the only time-even polarizability tensor at this order. Time-odd observables for magnetic molecules are described in terms of the additional polarizability α'_{ij}. According to (2.64) and (2.65), both α_{ij} and α'_{ij} are independent of the choice of coordinate origin. Consequently, macroscopic quantities can be obtained directly from their microscopic counterparts with the replacement $\mathcal{T}[\cdots]\to\mathcal{N}[\cdots]$ (see (3.17)).

From (3.23) and (3.24) in (3.21) and (3.29) and (3.30) in (3.22), and with the replacement (3.17), the contributions to the source densities at electric dipole order are[†]

$$\rho^{(1)}=\mathcal{N}\left[\Theta_{ij}+i\Pi_{ij}\right]\nabla_j E_i=-\mathcal{N}\left[\alpha_{ij}+i\alpha'_{ij}\right]\nabla_j E_i \tag{4.15}$$

and

$$J_i^{(1)}=\omega\mathcal{N}\left[i\Phi_{ij}+\Omega_{ij}\right]E_j=-\omega\mathcal{N}\left[i\alpha_{ij}+\alpha'_{ij}\right]E_j. \tag{4.16}$$

The contributions to the response fields are obtained from (3.59), (3.60), (3.68), (3.71), (3.74) and (3.78), with the replacement (3.17); thus

$$\tilde{D}_i^{(1)}=\mathcal{N}\left(\alpha_{ij}-i\alpha'_{ij}\right)E_j \tag{4.17}$$

and

$$\tilde{H}_i^{(1)}=0. \tag{4.18}$$

Finally, the propagation equation to electric dipole order — obtained from (3.49) with (3.29) and (3.30), and the replacement (3.17) — is

$$\left[\delta_{ij}\nabla^2-\nabla_i\nabla_j+\mu_0\varepsilon_0\omega^2\delta_{ij}+\mu_0\omega^2\mathcal{N}\left(\alpha_{ij}-i\alpha'_{ij}\right)\right]E_j=0. \tag{4.19}$$

[†]Note that, in Reference 6, the subscribts in the expressions for the source densities are assigned first to the gradient operators and then to the electric field. In (3.21) and (3.22), the first subscript is assigned to the electric field so that the same subscript is used on the electric field for all the multipole contributions. This results in a change of sign before the time-odd contributions in (4.15) due to the antisymmetry $\alpha'_{ij}=-\alpha'_{ji}$.

4.3 Electric quadrupole–magnetic dipole order: Non-magnetic molecules

At electric quadrupole–magnetic dipole order for non-magnetic molecules, the contributions to the source densities are obtained from (3.25) in (3.21) and (3.31) in (3.22):

$$\begin{aligned}\rho^{(2)} &= \mathcal{T}[\Theta_{ijk}]\nabla_j\nabla_k E_i \\ &= \mathcal{T}\left[-\tfrac{1}{\omega}\varepsilon_{ikl}\left(G'_{jl}-\tfrac{1}{2}\omega\varepsilon_{lmn}a_{mnj}\right)\right]\nabla_j\nabla_k E_i, \qquad (4.20)\\ J_i^{(2)} &= i\omega\mathcal{T}[\Phi_{ijk}]\nabla_k E_j \\ &= i\mathcal{T}\left[\varepsilon_{ikl}\left(G'_{jl}-\tfrac{1}{2}\omega\varepsilon_{lmn}a_{mnj}\right)-\varepsilon_{jkl}\left(G'_{il}-\tfrac{1}{2}\omega\varepsilon_{lmn}a_{mni}\right)\right]\nabla_k E_j. \qquad (4.21)\end{aligned}$$

The expressions in square brackets in (4.20) and (4.21) have been rearranged using the identity (C.4) for later convenience. The contributions to the response fields are obtained from (3.69), (3.72), (3.75) and (3.78) in (3.60) and (3.59):

$$\begin{aligned}D_i^{(2)} &= A_{ij}^{(2)}E_j + T_{ij}^{(2)}B_j \\ &= i\mathcal{T}\left[\tfrac{1}{2}\left(a_{ijk}-a_{jki}\right)\right]k_kE_j - i\mathcal{T}\left[G'_{ij}\right]B_j, \qquad (4.22)\\ H_i^{(2)} &= U_{ij}^{(2)}E_j + X_{ij}^{(2)}B_j \\ &= -i\mathcal{T}\left[G'_{ji}\right]E_j. \qquad (4.23)\end{aligned}$$

It has previously been noted that the molecular tensor

$$v_{ij} = G'_{ij} - \tfrac{1}{2}\omega\varepsilon_{jkl}a_{kli} \qquad (4.24)$$

is origin independent [4]. Thus, by inspection, $\rho^{(2)}$ and $J_i^{(2)}$ are origin independent and can be written in terms of (4.24), so that from (3.17) [6]

$$\begin{aligned}\rho^{(2)} &= -\tfrac{1}{\omega}\mathcal{N}\varepsilon_{ikl}v_{jl}\nabla_j\nabla_k E_i, \qquad (4.25)\\ J_i^{(2)} &= i\mathcal{N}\left(\varepsilon_{ikl}v_{jl}-\varepsilon_{jkl}v_{il}\right)\nabla_k E_j. \qquad (4.26)\end{aligned}$$

To investigate the origin dependence of $D_i^{(2)}$, (4.22) can be rewritten using (3.20) and the replacements (3.58). Then

$$\begin{aligned}D_i^{(2)} &= i\mathcal{T}\left[\tfrac{1}{2}\left(a_{ijk}-a_{jki}\right)+\tfrac{1}{\omega}\varepsilon_{jkl}G'_{il}\right]k_kE_j \\ &= i\mathcal{T}\left[\tfrac{1}{2}\left(a_{ijk}-a_{kij}\right)+\tfrac{1}{\omega}\varepsilon_{jkl}v_{il}\right]k_kE_j, \qquad (4.27)\end{aligned}$$

where the identity (C.4) was used. Since v_{il} is origin independent and $a_{ijk}-a_{kij}$ is not, $D_i^{(2)}$ is not origin independent. Because $\Delta G'_{ij} \neq 0$, $H_i^{(2)}$ in (4.23) is not origin independent either.

Physically acceptable origin-independent expressions for the response fields $\boldsymbol{D}^{(2)}$ and $\boldsymbol{H}^{(2)}$ are obtained by replacing the origin-dependent polarizability tensors G'_{ij} and a_{ijk} by their origin-independent counterparts $\tilde{G}'_{ij}$ and $\tilde{a}_{ijk}$, determined below.

The calculations described in this section can be found in the MATHEMATICA notebook `01-calculation.nb`, which is located in the directory `mathematica/e2m1-nm` on the accompanying CD.

4.3.1 General invariant expressions

Origin-independent expressions $\tilde{G}'_{ij}$ and $\tilde{a}_{ijk}$, corresponding to G'_{ij} and a_{ijk}, are constructed by taking linear combinations of polarizability tensors of the same order so that the origin-independent physical observables, such as the source densities and the propagation equation, are unchanged [6].

At electric quadrupole–magnetic dipole order, for a non-magnetic molecule, the most general linear combinations with the same rank, and space and time properties (see Table 2.1), as G'_{ij} and a_{ijk} are

$$\tilde{G}'_{ij} = I_{ijkl}G'_{kl} + \omega I_{ijklm}a_{klm} \tag{4.28}$$

and

$$\tilde{a}_{ijk} = \tfrac{1}{\omega}I_{ijklm}G'_{lm} + I_{ijklmn}a_{lmn}. \tag{4.29}$$

The (time-even) tensors $I_{ij\ldots}$ represent general linearly independent combinations, with real coefficients, of the isotropic tensors (see Section 2.5 and Appendix C). For example, the fourth-rank tensor

$$I_{ijkl} = c_1\delta_{ij}\delta_{kl} + c_2\delta_{ik}\delta_{jl} + c_3\delta_{il}\delta_{jk} \tag{4.30}$$

is polar, while the fifth-rank tensor I_{ijklm} given by (C.17) is axial, and the sixth-rank tensor I_{ijklmn} given by (C.18) is polar. Thus $\tilde{G}'_{ij}$ and $\tilde{a}_{ijk}$ have the same space and time properties as G'_{ij} and a_{ijk} (see Section 2.5). The factors ω and $\frac{1}{\omega}$ in (4.28) and (4.29) have been introduced to make the unknown coefficients dimensionless. Here, and elsewhere, ω is the only parameter available in the electrodynamics for this purpose.

Consider first the second-rank tensor (4.28). Since G'_{kl} has no symmetry, the fourth-rank isotropic tensor multiplying G'_{kl} is given by (C.16). Thus

$$\begin{aligned} I_{ijkl}G'_{kl} &= (c_1\delta_{ij}\delta_{kl} + c_2\delta_{ik}\delta_{jl} + c_3\delta_{il}\delta_{jk})G'_{kl} \\ &= c_1\delta_{ij}G'_{kk} + c_2G'_{ij} + c_3G'_{ji}. \end{aligned} \tag{4.31}$$

The polarizability a_{klm} possesses the intrinsic symmetry $a_{klm} = a_{kml}$ (see Table 2.1). This can be taken into account in (4.28) by first removing from I_{ijklm} any terms that are duplicated after interchanging the subscripts l and m (see Section C.7). The result can be obtained by inspection of (C.17):

$$I_{ijklm} = c_1\delta_{jk}\varepsilon_{ilm} + c_2\delta_{jl}\varepsilon_{ikm} + c_4\delta_{kl}\varepsilon_{ijm} + c_6\delta_{lm}\varepsilon_{ijk}. \tag{4.32}$$

To simplify the notation, the symbol I_{ijklm} has been retained in (4.32). The term involving c_1 in (4.32) yields zero in the product $I_{ijklm}a_{klm}$, because of the contraction of the antisymmetric pair of subscripts l and m in ε_{ilm} with the symmetric pair in $a_{klm} = a_{kml}$. Thus the second term in (4.28) becomes

$$\begin{aligned} I_{ijklm}a_{klm} &= (c_6\delta_{jl}\varepsilon_{ikm} + c_5\delta_{kl}\varepsilon_{ijm} + c_4\delta_{lm}\varepsilon_{ijk})a_{klm} \\ &= c_4\varepsilon_{ijk}a_{kll} + c_5\varepsilon_{ijk}a_{lkl} + c_6\varepsilon_{ikl}a_{kjl}, \end{aligned} \tag{4.33}$$

where the coefficients c_i have been renumbered to follow the three unknown c_i in (4.31) and to correspond with the assignment in the notebook `01-calculation.nb`. From (4.31) and (4.33), the general expression (4.28) reduces to

$$\tilde{G}'_{ij} = c_1\delta_{ij}G'_{kk} + c_2G'_{ij} + c_3G'_{ji} + c_4\omega\varepsilon_{ijk}a_{kll} + c_5\omega\varepsilon_{ijk}a_{lkl} + c_6\omega\varepsilon_{ikl}a_{kjl}. \tag{4.34}$$

The condition of origin independence is imposed on $\tilde{G}'_{ij}$ by solving the expression

$$\Delta\tilde{G}'_{ij} = 0,$$

where $\Delta\tilde{G}'_{ij}$ is obtained by replacing each occurrence of G'_{ij} and a_{ijk} on the right-hand side of (4.34) by their respective origin dependences (2.69) and (2.66). The result is

$$\begin{aligned} c_4 &= -\tfrac{1}{2}c_2, \\ c_5 &= \tfrac{1}{2}c_2, \\ c_6 &= -\tfrac{1}{2}(c_2+c_3). \end{aligned} \tag{4.35}$$

Substitution of (4.35) in (4.34), and use of the identity (based on (C.8))

$$\varepsilon_{ikl}a_{kjl} = -\varepsilon_{ijk}a_{kll} + \varepsilon_{ijk}a_{lkl} + \varepsilon_{jkl}a_{kil},$$

simplifies (4.34) to

$$\begin{aligned} \tilde{G}'_{ij} &= c_1\delta_{ij}G'_{kk} + c_2\left(G'_{ij} - \tfrac{1}{2}\omega\varepsilon_{jkl}a_{kli}\right) + c_3\left(G'_{ji} - \tfrac{1}{2}\omega\varepsilon_{ikl}a_{klj}\right) \\ &= c_1\delta_{ij}v_{kk} + c_2v_{ij} + c_3v_{ji}. \end{aligned} \tag{4.36}$$

A similar calculation for $\tilde{a}_{ijk}$, from (4.29), yields

$$\tilde{a}_{ijk} = \tfrac{1}{\omega}\left[c_4\delta_{jk}\varepsilon_{ilm}v_{lm} + c_5\left(\varepsilon_{ijl}v_{kl} + \varepsilon_{ikl}v_{jl}\right) + c_6\left(\varepsilon_{ijl}v_{lk} + \varepsilon_{ikl}v_{lj}\right)\right], \tag{4.37}$$

where the coefficients in (4.37) have been renumbered to follow those in (4.36).

4.3.2 Comparison of source densities

The next step is to replace the polarizability tensors G'_{ij} and a_{ijk} in (4.20) and (4.21) by their origin-independent counterparts $\tilde{G}'_{ij}$ and $\tilde{a}_{ijk}$, and solve the equations

$$\rho^{(2)}\left(G'_{ij}, a_{ijk}\right) = \rho^{(2)}\left(\tilde{G}'_{ij}, \tilde{a}_{ijk}\right), \tag{4.38}$$

$$J_i^{(2)}\left(G'_{ij}, a_{ijk}\right) = J_i^{(2)}\left(\tilde{G}'_{ij}, \tilde{a}_{ijk}\right), \tag{4.39}$$

for the unknown coefficients c_i in (4.36) and (4.37). The comparison (4.38) yields

$$\begin{aligned} c_5 &= -\tfrac{2}{3} + \tfrac{1}{3}(2c_2 - c_4), \\ c_6 &= \tfrac{1}{3}(2c_3 + c_4), \end{aligned} \tag{4.40}$$

and (4.39) the additional relation

$$c_3 = 1 - 3c_1 - c_2. \tag{4.41}$$

The tensors Θ_{ijk} and Φ_{ijk} in (4.20) and (4.21) are property tensors. To constitute physically acceptable expressions for observables, Θ_{ijk} and Φ_{ijk} should therefore be origin independent. By inspection, both Θ_{ijk} and Φ_{ijk} can be expressed in terms of the origin-independent tensor v_{ij}, and are therefore origin independent.

4.3.3 Linear independence

To resolve the remaining three coefficients (c_1, c_2 and c_4 — see (4.40) and (4.41)) one must turn to the properties of the polarizability tensors themselves. The polarizability tensors are constants of proportionality between the expectation values of the multipole moment operators and *different* gradients (and time derivatives) of the electromagnetic fields $\boldsymbol{E}$ and $\boldsymbol{B}$ (see (2.33) and (2.36)). As such, the polarizability tensors are necessarily linearly independent. If they were not, then different field gradients (or time derivatives) would always contribute to the expectation values proportionally. Furthermore, the expressions for the polarizability tensors all contain contributions from transitions between eigenstates due to *different* multipole moments (see (2.38)–(2.53)). A linear dependence between polarizability tensors would imply that the quantum-mechanical transitions due to different multipole moments (which are different functions of position vectors and angular momenta) also contribute proportionally. Therefore the origin-independent polarizability tensors derived above should also be linearly independent.

Because the polarizability tensors have different rank, linear independence can only be established by first constructing tensors of the same rank (see Appendix D). This is achieved by contracting the origin-independent expressions corresponding to each polarizability tensor with isotropic tensors of appropriate rank. Thus, the linear combinations

$$\Lambda_{ij} = I_{ijkl}\tilde{G}'_{kl} + \omega I_{ijklm}\tilde{a}_{klm} \tag{4.42}$$

and

$$\Lambda_{ijk} = \tfrac{1}{\omega}I_{ijklm}\tilde{G}'_{lm} + I_{ijklmn}\tilde{a}_{lmn} \tag{4.43}$$

(after eliminating duplicate terms arising from the required intrinsic symmetry $\tilde{a}_{ijk} = \tilde{a}_{ikj}$) should be zero only for the trivial solutions $k_i = 0$, where k_i are the unknown coefficients† in the isotropic tensors $I_{ij\ldots}$. The factors ω and $\frac{1}{\omega}$ in (4.42) and (4.43) have been introduced to make the k_i dimensionless. The expressions (4.42) and (4.43) are constructed in the same manner described in Section 4.3.1 to obtain (4.34) from (4.28). Here G'_{ij} and a_{ijk} are replaced by $\tilde{G}'_{ij}$ and $\tilde{a}_{ijk}$ given by (4.36) and (4.37) with (4.40) and (4.41), and the coefficients c_i in the isotropic tensors $I_{ij\ldots}$ are replaced by k_i (to distinguish the arbitrary coefficients in I_{ijkl} from the unknown c_i in $\tilde{G}'_{kl}$ and $\tilde{a}_{klm}$).

The solution to $\Lambda_{ij} = 0$ yields three relations (see `01-calculation.nb`). The first,

$$k_1 = \frac{2c_1k_4}{(3c_1 - 1)}, \tag{4.44}$$

shows that unless

$$c_1 = 0, \tag{4.45}$$

there exists a linear dependence between k_1 and k_4. Equation (4.44) can be rearranged as

$$k_4 = \frac{(3c_1 - 1)}{2c_1}k_1. \tag{4.46}$$

In this case, $k_4 = 0$ when $c_1 = \frac{1}{3}$. It is shown in the notebook `01-calculation.nb` that linear independence cannot be achieved with this solution.

With $c_1 = 0$, the second and third relations reduce to (see `01-calculation.nb`)

$$k_2 = -k_3 = \frac{6(1 - c_2)k_4 + (4 - 4c_2 + 5c_4)k_5 - (8 - 8c_2 - 5c_4)k_6}{(3 - 6c_2)}. \tag{4.47}$$

Inspection of (4.47) shows that

$$c_2 = 1 \quad \text{and} \quad c_4 = 0 \tag{4.48}$$

results in $k_2 = k_3 = 0$. Rearranging (4.47) does not lead to other values for c_2 and c_4 that achieve a trivial solution for k_4, k_5 or k_6. For instance, multiplying (4.47) by $(3 - 6c_2)$ and setting $c_2 = \frac{1}{2}$ leaves a dependency between k_4 and k_5, or k_4 and k_6, since the coefficients of k_5 and k_6 with $c_2 = \frac{1}{2}$ cannot

† The symbols k_i for the unknown coefficients in the isotropic tensors are used only in the calculations of linear independence. The expressions in these calculations do not contain the wave vector $\boldsymbol{k}$, so that there should be no confusion between these symbols.

both be zero. Setting $\tilde{a}_{ijk} = 0$ in (4.42) resolves this dependency; however, the relation between k_2 and k_3 remains (see `01-calculation.nb`). Finally, from (4.40), (4.41), (4.45) and (4.48),

$$c_3 = c_5 = c_6 = 0. \tag{4.49}$$

The solutions (4.45), (4.48) and (4.49) are necessary for linear independence of $\tilde{G}'_{ij}$ and $\tilde{a}_{ijk}$ in the second-rank linear combination (4.42), and also result in a linearly independent solution for the third-rank expression (4.43).

Substitution of (4.45), (4.48) and (4.49) into (4.36) and (4.37) yields the unique solutions,

$$\tilde{G}'_{ij} = v_{ij} \tag{4.50}$$

and

$$\tilde{a}_{ijk} = 0, \tag{4.51}$$

for the origin-independent time-even molecular polarizabilities corresponding to G'_{ij} and a_{ijk} at electric quadrupole–magnetic dipole order.

4.3.4 DC limit

In the limit $\omega \to 0$, $G'_{ij} \to 0$ and $\tilde{G}'_{ij} = v_{ij} \to 0$, whereas a_{ijk} and $\frac{1}{\omega}G'_{ij}$, and hence $\frac{1}{\omega}v_{ij}$, are finite (see (2.40), (2.43) and (4.24)). For a harmonic plane wave, the molecular dipole moment (2.33) to electric quadrupole–magnetic dipole order for non-magnetics is

$$\bar{p}_i = p^{(0)} + \alpha_{ij}E_j + \tfrac{1}{2}a_{ijk}\nabla_k E_j + \tfrac{1}{\omega}G'_{ij}\dot{B}_{ij}. \tag{4.52}$$

When $\omega \to 0$, (4.52) reduces to

$$\bar{p}_i = p^{(0)} + \alpha_{ij}E_j, \tag{4.53}$$

since

$$\nabla_k E_j = ik_k E_j = i\tfrac{\omega}{v}\sigma_k E_j \to 0 \tag{4.54}$$

and $\dot{B}_j = -i\omega B_j \to 0$. In (4.54), σ_k is a unit vector in the direction of k_k.

In the DC limit, the electric dipole moment (4.52) to electric quadrupole–magnetic dipole order therefore reduces to the same expression in the invariant and non-invariant theories.

4.3.5 Summary and Discussion

Origin-independent expressions corresponding to the molecular polarizabilities for non-magnetic molecules at electric quadrupole–magnetic dipole order are given by (4.50) and (4.51). Origin-independent property tensors corresponding to (3.25) and (3.31) in terms of (4.50) and (4.51) are

$$\tilde{\Theta}_{ijk} = -\tfrac{1}{\omega}\varepsilon_{ikl}v_{jl} \qquad \text{or} \qquad \tilde{\Theta}_{ijk} = -\tfrac{1}{\omega}\varepsilon_{ijl}v_{kl} \tag{4.55}$$

and

$$\tilde{\Phi}_{ijk} = \tfrac{1}{\omega}(\varepsilon_{ikl}v_{jl} - \varepsilon_{jkl}v_{il}). \tag{4.56}$$

The ambiguity in (4.55) is due to the symmetry of the product of the field gradients $\nabla_j\nabla_k$ in (4.20) (see Section 3.2). The contributions to the source densities are given by (4.25) and (4.26). From (3.49) with the replacement $\Phi_{ijk} \to \tilde{\Phi}_{ijk}$, (3.29), (4.56) and (3.17), the propagation equation, to electric quadrupole–magnetic dipole order in non-magnetics, is

$$\left(\delta_{ij}\nabla^2 - \nabla_i\nabla_j + \mu_0\varepsilon_0\omega^2\delta_{ij} + \mu_0\omega^2\mathcal{N}\left[\alpha_{ij} - \tfrac{1}{\omega}\left\{\varepsilon_{ikl}v_{jl} - \varepsilon_{jkl}v_{il}\right\}\nabla_k\right]\right)E_j = 0. \tag{4.57}$$

The response fields (4.22) and (4.23) are not specified uniquely by the Maxwell equations (3.56) and (3.57) (see Section 3.4). The transition from the non-invariant fields (4.22) and (4.23) to invariant forms (with the replacements $G'_{ij} \to \tilde{G}'_{ij}$ and $a_{ijk} \to \tilde{a}_{ijk}$), namely

$$\tilde{D}_i^{(2)} = -i\mathcal{N}v_{ij}B_j \tag{4.58}$$

and

$$\tilde{H}_i^{(2)} = -i\mathcal{N}v_{ji}E_j, \tag{4.59}$$

corresponds to a "gauge transformation" (3.80) of (4.22) and (4.23) with [6]

$$H_i^G = \tfrac{1}{2}i\omega\mathcal{T}\left[\varepsilon_{ikl}a_{klj}\right]E_j, \tag{4.60}$$

where (3.20) and the linear property (3.9) of the transform $\mathcal{T}$ were used.

Origin-independent contributions to the material constants at electric quadrupole–magnetic dipole order for non-magnetic media are obtained from the time-even parts of (3.69), (3.72), (3.75) and (3.78) with the replacements $G'_{ij} \to \tilde{G}'_{ij}$ and $a_{ijk} \to \tilde{a}_{ijk}$:

$$\tilde{A}_{ij}^{(2)} = 0, \tag{4.61}$$

$$\tilde{T}_{ij}^{(2)} = -i\mathcal{N}v_{ij}, \tag{4.62}$$

$$\tilde{U}_{ij}^{(2)} = -i\mathcal{N}v_{ji}, \tag{4.63}$$

$$\tilde{X}_{ij}^{(2)} = 0. \tag{4.64}$$

From (4.62) and (4.63) it is clear that the Post constraint (3.95) holds at leading order for non-magnetic media.

In the invariant theory, origin-independent expressions for the multipole moment densities at electric quadrupole–magnetic dipole order are obtained by making the replacements $G'_{ij} \to \tilde{G}'_{ij}$ and $a_{ijk} \to \tilde{a}_{ijk}$ in (3.10), (3.11) and (3.13). For instance, the electric dipole moment density (3.10), for non-magnetics to electric quadrupole–magnetic dipole order, becomes

$$\tilde{P}_i = P_i^{(0)} + \mathcal{N}\alpha_{ij}E_j + \tfrac{1}{\omega}\mathcal{N}v_{ij}\dot{B}_j. \tag{4.65}$$

The field gradient term $\frac{1}{2}a_{ijk}\nabla_k E_j$ in the non-invariant dipole moment density (3.10) is now contained in the last term of (4.65). Use of Faraday's law

$$\dot{B}_j = -\varepsilon_{jkl}\nabla_k E_l, \tag{4.66}$$

(4.24) and (C.4), one finds

$$\tilde{P}_i = P_i^{(0)} + \mathcal{N}\alpha_{ij}E_j + \tfrac{1}{2}\mathcal{N}(a_{kij} - a_{jik})\nabla_k E_j + \tfrac{1}{\omega}\mathcal{N}G'_{ij}\dot{B}_j. \tag{4.67}$$

Inspection of (3.10) and (4.67) reveals that the expressions for the macroscopic moments are in general not the same. In Reference 6, the same symbol ($\overline{p}$) was used for both the non-invariant, as well as the invariant, expressions (see (1) and (58) of Reference 6).

4.4 Electric quadrupole–magnetic dipole order: Magnetic molecules

At electric quadrupole–magnetic dipole order for magnetic molecules, the time-odd contributions to the source densities are obtained from (3.26) in (3.21) and (3.32) in (3.22):

$$\begin{aligned}
\rho^{(2)} &= i\mathcal{T}[\Pi_{ijk}]\nabla_j\nabla_k E_i \\
&= i\mathcal{T}\left[-\tfrac{1}{\omega}\varepsilon_{ikl}G_{jl} + \tfrac{1}{2}\left(a'_{ijk} + a'_{jik}\right)\right]\nabla_j\nabla_k E_i, &(4.68)\\
J_i^{(2)} &= \omega\mathcal{T}[\Omega_{ijk}]\nabla_k E_j \\
&= \mathcal{T}\left[\varepsilon_{ikl}G_{jl} + \varepsilon_{jkl}G_{il} - \tfrac{1}{2}\omega\left(a'_{ijk} + a'_{jik}\right)\right]\nabla_k E_j, &(4.69)
\end{aligned}$$

The contributions to the response fields are obtained from (3.69), (3.72), (3.75) and (3.78) in (3.60) and (3.59):

$$\begin{aligned}
D_i^{(2)} &= A_{ij}^{(2)}E_j + T_{ij}^{(2)}B_j \\
&= \mathcal{T}\left[\tfrac{1}{2}\left(a'_{ijk} + a'_{jki}\right)\right]k_k E_j + \mathcal{T}\left[G_{ij}\right]B_j, &(4.70)\\
H_i^{(2)} &= U_{ij}^{(2)}E_j + X_{ij}^{(2)}B_j \\
&= -\mathcal{T}\left[G_{ji}\right]E_j. &(4.71)
\end{aligned}$$

As in the previous section for non-magnetic molecules, the source densities (4.68) and (4.69) are origin independent, whereas the response fields (4.70) and (4.71) are not. In contrast to the case for non-magnetic molecules, the property tensor Π_{ijk} that appears in the contribution to the charge density (4.68) for magnetic molecules depends on the choice of coordinate origin. Origin-independent expressions corresponding to the polarizability tensors G_{ij} and a'_{ijk} can be constructed using the method presented in Section 4.3. In this section the method is modified in anticipation of the increased difficulty encountered in the calculations at electric octopole–magnetic quadrupole order.

The MATHEMATICA notebooks referred to in this section are contained in the directory `mathematica/e2m1-m` on the accompanying CD.

4.4.1 Time-odd basis tensors of electric quadrupole–magnetic dipole order

In the previous section, it was found that all observables for non-magnetic media at electric quadrupole–magnetic dipole order, as well as the invariant polarizabilities and response fields, could be expressed in terms of the single tensor v_{ij}. It is natural to ask whether there exist other origin-independent tensors that are linearly independent of v_{ij} constructed from the same polarizability tensors G'_{ij} and a_{ijk}. In Appendix E it is shown that there is indeed only one origin-independent tensor, at electric quadrupole–magnetic dipole order for non-magnetic molecules, in terms of which all other origin-independent tensors of the same order, linear in the polarizabilities, can be expressed (see `02-basis.nb`). The method to determine tensors like v_{ij} is described in Appendix D, and is applied here to the time-odd tensors at electric quadrupole–magnetic dipole order. These tensors are then used to obtain origin-independent expressions corresponding to the polarizability tensors G_{ij} and a'_{ijk} at electric quadrupole–magnetic dipole order for magnetic molecules.

At this order, the most general linear combinations of rank two and three, corresponding to the ranks of the polarizability tensors G_{ij} and a'_{ijk}, and with the same time and space properties, are

$$\Lambda_{ij} = I_{ijkl}G_{kl} + \omega I_{ijklm}a'_{klm} \tag{4.72}$$

and

$$\Lambda_{ijk} = \tfrac{1}{\omega} I_{ijklm} G_{lm} + I_{ijklmn} a'_{lmn}. \tag{4.73}$$

The tensors I_{ijkl}, I_{ijklm} and I_{ijklmn}, given by (C.16), (C.17) and (C.18), respectively, represent the most general linearly independent combination of isotropic tensors, and the factors ω and $\frac{1}{\omega}$ in (4.72) and (4.73) have been introduced to make the unknown coefficients dimensionless. The expressions (4.72) and (4.73) are made origin independent by replacing each occurrence of a'_{ijk} and G_{ij} in (4.72) and (4.73) by the origin dependences (2.67) and (2.68), equating the resultant expressions to zero, and solving for the unknown coefficients in the $I_{ij\ldots}$ (see Section D.4). The general expression for Λ_{ij}, after eliminating duplicate terms arising from the intrinsic symmetry $a'_{ijk} = a'_{ikj}$ (see Table 2.1), is

$$\Lambda_{ij} = c_1 \delta_{ij} G_{kk} + c_2 G_{ij} + c_3 G_{ji} + \omega \left(c_4 \varepsilon_{ijk} a'_{kll} + c_5 \varepsilon_{ijk} a'_{lkl} + c_6 \varepsilon_{ikl} a'_{kjl} \right). \tag{4.74}$$

The origin dependence $\Delta\Lambda_{ij}$ is obtained by replacing a'_{ijk} and G_{ij} in (4.74) by their origin dependences (2.67) and (2.68). Origin independence is imposed on Λ_{ij} by setting $\Delta\Lambda_{ij} = 0$ and solving for the coefficients c_i in (4.74). The result is (see `01-basis.nb`)

$$\begin{aligned} c_6 &= \tfrac{1}{2} c_1, \\ c_5 &= \tfrac{1}{2}(c_2 + 4c_4), \\ c_3 &= -c_2 - 3c_1. \end{aligned} \tag{4.75}$$

When (4.75) is substituted into (4.74), one obtains an origin-independent second-rank expression $\tilde{\Lambda}_{ij}$, which consists of three arbitrary coefficients, each multiplying an origin-independent expression (see Section D.4):

$$\tilde{\Lambda}_{ij} = c_1 \tilde{T}^{(1)}_{ij} + c_2 \tilde{T}^{(2)}_{ij} + c_4 \tilde{T}^{(3)}_{ij}, \tag{4.76}$$

where

$$\tilde{T}^{(1)}_{ij} = -3 \left(G_{ji} - \tfrac{1}{3} \delta_{ij} G_{kk} - \tfrac{1}{6} \omega \varepsilon_{ikl} a'_{kjl} \right), \tag{4.77}$$

$$\tilde{T}^{(2)}_{ij} = G_{ij} - G_{ji} + \tfrac{1}{2} \omega \varepsilon_{ijk} a'_{lkl}, \tag{4.78}$$

$$\tilde{T}^{(3)}_{ij} = \omega \varepsilon_{ijk} \left(a'_{kll} + 2a'_{lkl} \right). \tag{4.79}$$

Expressions that are origin-independent extensions of the polarizability tensors G_{ij} and a'_{ijk} can now be identified. The expression in brackets in (4.77) is an obvious starting point. Interchanging i and j gives

$$w_{ij} = G_{ij} - \tfrac{1}{3} \delta_{ij} G_{kk} - \tfrac{1}{6} \omega \varepsilon_{jkl} a'_{kli}. \tag{4.80}$$

The next step is to write (4.78) and (4.79) in terms of (4.80). One finds that this is not possible, and that there always remain terms independent of G_{ij}, and involving a trace of a'_{ijk}. There must therefore exist at least one other origin-independent tensor linearly independent of w_{ij}. Since the remainders involve only trace terms of a'_{ijk}, it is expedient to turn next to the third-rank expression.

After taking into account the intrinsic symmetry $a'_{ijk} = a'_{ikj}$ (see Table 2.1), the general expression for Λ_{ijk} is

$$\begin{aligned} \Lambda_{ijk} = {} & \tfrac{1}{\omega} \left(c_1 G_{lm} \delta_{jk} \varepsilon_{ilm} + c_2 G_{jl} \varepsilon_{ikl} + c_3 G_{lj} \varepsilon_{ikl} + c_4 G_{kl} \varepsilon_{ijl} + c_5 G_{lk} \varepsilon_{ijl} + c_6 G_{ll} \varepsilon_{ijk} \right) \\ & + c_7 a'_{ijk} + c_8 a'_{jik} + c_9 a'_{kij} + c_{10} a'_{kll} \delta_{ij} + c_{11} a'_{lkl} \delta_{ij} + c_{12} a'_{jll} \delta_{ik} + c_{13} a'_{ljl} \delta_{ik} \\ & + c_{14} a'_{ill} \delta_{jk} + c_{15} a'_{lil} \delta_{jk}. \end{aligned} \tag{4.81}$$

The factor $\frac{1}{\omega}$ in (4.81) has been introduced to ensure that the coefficients c_i are dimensionless. Origin independence of Λ_{ijk} is imposed by requiring $\Delta\Lambda_{ijk} = 0$. The result is (see `01-basis.nb`)

$$\begin{aligned} c_6 &= \tfrac{1}{3}(c_2 + c_3 - c_4 - c_5), \\ c_7 &= -\tfrac{1}{6}(c_2 + c_3 + 2c_4 + 2c_5 - 6c_8), \\ c_9 &= \tfrac{1}{6}(c_2 + c_3 - c_4 - c_5 + 6c_8), \\ c_{11} &= \tfrac{1}{2}(c_3 + 4c_{10}), \\ c_{13} &= \tfrac{1}{2}(c_5 + 4c_{12}), \\ c_{15} &= \tfrac{1}{2}(c_1 - c_3 - c_5 + 4c_{14}). \end{aligned} \tag{4.82}$$

On substituting (4.82) in (4.81) one obtains

$$\tilde{\Lambda}_{ijk} = c_1\tilde{T}^{(1)}_{ijk} + c_2\tilde{T}^{(2)}_{ijk} + c_3\tilde{T}^{(3)}_{ijk} + c_4\tilde{T}^{(4)}_{ijk} + c_5\tilde{T}^{(5)}_{ijk} + c_8\tilde{T}^{(6)}_{ijk} + c_{10}\tilde{T}^{(7)}_{ijk} + c_{12}\tilde{T}^{(8)}_{ijk} + c_{14}\tilde{T}^{(9)}_{ijk}, \tag{4.83}$$

where

$$\tilde{T}^{(1)}_{ijk} = \tfrac{1}{\omega}\delta_{jk}\varepsilon_{ilm}G_{lm} + \tfrac{1}{2}\delta_{jk}a'_{lil}, \tag{4.84}$$
$$\tilde{T}^{(2)}_{ijk} = \tfrac{1}{\omega}\left(\tfrac{1}{3}\varepsilon_{ijk}G_{ll} + \varepsilon_{ikl}G_{jl}\right) - \tfrac{1}{6}\left(a'_{ijk} - a'_{kij}\right), \tag{4.85}$$
$$\tilde{T}^{(3)}_{ijk} = \tfrac{1}{\omega}\left(\tfrac{1}{3}\varepsilon_{ijk}G_{ll} + \varepsilon_{ikl}G_{lj}\right) - \tfrac{1}{6}\left(a'_{ijk} - a'_{kij} - 3\delta_{ij}a'_{lkl} + 3\delta_{jk}a'_{lil}\right), \tag{4.86}$$
$$\tilde{T}^{(4)}_{ijk} = -\tfrac{1}{\omega}\left(\tfrac{1}{3}\varepsilon_{ijk}G_{ll} - \varepsilon_{ijl}G_{kl}\right) - \tfrac{1}{6}\left(2a'_{ijk} + a'_{kij}\right), \tag{4.87}$$
$$\tilde{T}^{(5)}_{ijk} = -\tfrac{1}{\omega}\left(\tfrac{1}{3}\varepsilon_{ijk}G_{ll} - \varepsilon_{ijl}G_{lk}\right) - \tfrac{1}{6}\left(2a'_{ijk} + a'_{kij} - 3\delta_{ik}a'_{ljl} + 3\delta_{jk}a'_{lil}\right), \tag{4.88}$$
$$\tilde{T}^{(6)}_{ijk} = a'_{ijk} + a'_{jik} + a'_{kij}, \tag{4.89}$$
$$\tilde{T}^{(7)}_{ijk} = \delta_{ij}\left(a'_{kll} + 2a'_{lkl}\right), \tag{4.90}$$
$$\tilde{T}^{(8)}_{ijk} = \delta_{ik}\left(a'_{jll} + 2a'_{ljl}\right), \tag{4.91}$$
$$\tilde{T}^{(9)}_{ijk} = \delta_{jk}\left(a'_{ill} + 2a'_{lil}\right). \tag{4.92}$$

The relation (4.89) is the only origin-independent tensor that is an extension of a'_{ijk}, and which does not involve G_{ij}. This tensor has previously been identified [4, Chapter 8], where a factor $\frac{1}{3}$ was introduced. Thus

$$s_{ijk} = \tfrac{1}{3}\left(a'_{ijk} + a'_{jki} + a'_{kij}\right) \tag{4.93}$$
$$= s_{jik} = s_{ikj}, \tag{4.94}$$

is an origin-independent extension of a'_{ijk}.

For non-magnetic molecules at electric quadrupole–magnetic dipole order, there is no origin-independent extension of the time-even polarizability a_{ijk} (see Appendix E). Whether an origin-independent combination of polarizabilities at a paricular multipole order can be constructed depends on the intrinsic symmetries of the polarizabilities (see Table 2.1), the structure of their origin dependences (see (2.64)–(2.79)), as well as the intrinsic symmetries of the polarizabilities of lower order appearing in the expressions of their origin dependences.

It is straightforward to show that the remaining expressions in (4.76) can be written in terms of (4.80) and (4.93). One finds

$$\tilde{T}^{(2)}_{ij} = w_{ij} - w_{ji} - \tfrac{1}{2}\omega\varepsilon_{ijk}s_{kll}, \tag{4.95}$$
$$\tilde{T}^{(3)}_{ij} = 3\varepsilon_{ijk}s_{kll}. \tag{4.96}$$

Furthermore, each origin-independent expression in (4.83) can also be written in terms of (4.80) and (4.93) (see `01-basis.nb`):

$$\tilde{T}^{(1)}_{ijk} = \delta_{jk}\left(\tfrac{1}{\omega}\varepsilon_{ilm}w_{lm} + \tfrac{1}{2}s_{ill}\right), \tag{4.97}$$

$$\tilde{T}^{(2)}_{ijk} = \tfrac{1}{\omega}\left(\tfrac{1}{3}\varepsilon_{ijk}w_{ll} + \varepsilon_{ikl}w_{jl}\right), \tag{4.98}$$

$$\tilde{T}^{(3)}_{ijk} = \tfrac{1}{\omega}\left(\tfrac{1}{3}\varepsilon_{ijk}w_{ll} + \varepsilon_{ikl}w_{lj}\right) + \tfrac{1}{2}\left(\delta_{ij}s_{kll} - \delta_{jk}s_{ill}\right), \tag{4.99}$$

$$\tilde{T}^{(4)}_{ijk} = -\tfrac{1}{\omega}\left(\tfrac{1}{3}\varepsilon_{ijk}w_{ll} - \varepsilon_{ijl}w_{kl}\right) - \tfrac{1}{2}s_{ijk}, \tag{4.100}$$

$$\tilde{T}^{(5)}_{ijk} = -\tfrac{1}{\omega}\left(\tfrac{1}{3}\varepsilon_{ijk}w_{ll} - \varepsilon_{ijl}w_{lk}\right) - \tfrac{1}{2}\left(s_{ijk} - \delta_{ik}s_{jll} + \delta_{jk}s_{ill}\right), \tag{4.101}$$

$$\tilde{T}^{(6)}_{ijk} = 3s_{ijk}, \tag{4.102}$$

$$\tilde{T}^{(7)}_{ijk} = \tilde{T}^{(8)}_{ikj} = \tilde{T}^{(9)}_{jki} = 3\delta_{ij}s_{kll}. \tag{4.103}$$

At electric quadrupole–magnetic dipole order for magnetic molecules, all origin-independent expressions can therefore be expressed in terms of (4.80) and (4.93). The tensors w_{ij} and s_{ijk} therefore span the set of origin-independent time-odd tensors at electric quadrupole–magnetic dipole order for magnetic molecules. To show that w_{ij} and s_{ijk} are the only tensors, i.e. that they are a basis, it must be proved that they are linearly independent. The procedure is the same as that described in Section 4.3 to establish linear independence between $\tilde{G}'_{ij}$ and $\tilde{a}_{ijk}$, and is demonstrated in the notebook `01-basis.nb`.

4.4.2 General invariant expressions

The procedure to determine origin-independent polarizability tensors corresponding to G_{ij} and a'_{ijk} is now routine. One first constructs general origin-independent expressions, with the same ranks, space and time properties, and symmetry properties as G_{ij} and a'_{ijk} (see Table 2.1). From (4.80), (4.93) and the appropriate general isotropic tensors (C.16), (C.17) and (C.18), one obtains (see `02-source.nb`)

$$\tilde{G}_{ij} = c_1 w_{ij} + c_2 w_{ji} + c_3\omega\varepsilon_{ijk}s_{kll}, \tag{4.104}$$

$$\begin{aligned}\tilde{a}'_{ijk} = {}& \tfrac{1}{\omega}\left[c_4\delta_{jk}\varepsilon_{ilm}w_{lm} + c_5(\varepsilon_{ijl}w_{kl} + \varepsilon_{ikl}w_{jl}) + c_6(\varepsilon_{ijl}w_{lk} + \varepsilon_{ikl}w_{lj})\right] \\ & + c_7 s_{ijk} + c_8(\delta_{ij}s_{kll} + \delta_{ik}s_{jll}) + c_9\delta_{jk}s_{ill},\end{aligned} \tag{4.105}$$

where the factors ω and $\frac{1}{\omega}$ in (4.104) and (4.105) ensure that the unknown coefficients c_i are dimensionless. In (4.104) the term involving $\delta_{ij}w_{kk}$ is absent, since $w_{kk} = 0$ (see (4.123)). Comparison of the charge density $\rho^{(2)}(G_{ij}, a'_{ijk})$ in (4.68) with $\rho^{(2)}(\tilde{G}_{ij}, \tilde{a}'_{ijk})$ gives (see `02-source.nb`)

$$\begin{aligned} c_4 &= 0, \\ c_5 &= 2c_1 - 2, \\ c_6 &= 2c_2, \\ c_7 &= 1, \\ c_8 &= -2c_3, \\ c_9 &= 4c_3. \end{aligned} \tag{4.106}$$

Comparison of the current density $J^{(2)}_i(G_{jk}, a'_{jkl})$ in (4.69) with $J^{(2)}_i(\tilde{G}_{jk}, \tilde{a}'_{jkl})$ yields no additional relations between the unknown coefficients.

Because the property tensor Π_{ijk} in (4.68) is origin dependent (see Section 3.2), equating $\Pi_{ijk}(G_{jk}, a'_{jkl})$ and $\Pi_{ijk}(\tilde{G}_{jk}, \tilde{a}'_{jkl})$ is not meaningful. It is straighforward to obtain an origin-independent expression for Π_{ijk}, in terms of the basis tensors (4.80) and (4.93), that leaves the source densities (4.68) and (4.69) unchanged. For instance, the charge density at electric quadrupole–magnetic dipole order for magnetic molecules can be written

$$\begin{aligned}\rho^{(2)} = i\mathcal{N}\tilde{\Pi}_{ijk}\nabla_j\nabla_k E_i = i\mathcal{N}\left[-\tfrac{1}{\omega}\varepsilon_{ikl}w_{jl} + s_{ijk}\right]\nabla_j\nabla_k E_i \\ = i\mathcal{N}\left[-\tfrac{1}{\omega}\varepsilon_{ikl}G_{jl} + \tfrac{1}{2}\left(a'_{ijk} + a'_{jik}\right)\right]\nabla_j\nabla_k E_i.\end{aligned} \tag{4.107}$$

However, the choice of $\tilde{\Pi}_{ijk}$ in (4.107) is not unique (see Section 3.2) because the addition of a term like $\varepsilon_{jkl}w_{il}$, which is antisymmetric in the subscripts j and k, has no effect on $\rho^{(2)}$. Therefore, because there is ambiguity in obtaining origin-independent expressions for the property tensors (3.26)–(3.28), (3.33) and (3.34), these cannot be used to determine unique invariant expressions corresponding to the molecular polarizability tensors.

4.4.3 Linear independence

To establish uniqueness, the remaining three coefficients c_1, c_2 and c_3 in (4.106) must be determined. The calculation to establish linear independence of the invariant expressions corresponding to the time-odd polarizability tensors is similar to that in Section 4.3.3 for the time-even tensors at electric quadrupole–magnetic dipole order, and is not repeated here (see `03-li.nb`).

There are two sets of linearly independent expressions derived from (4.104) and (4.105) that leave the source densities (4.68) and (4.69) unchanged when the replacements $G_{ij} \to \tilde{G}_{ij}$ and $a'_{ijk} \to \tilde{a}'_{ijk}$ are made. These are

$$\begin{aligned} c_1 &= 1, \\ c_2 = c_3 &= 0, \end{aligned} \tag{4.108}$$

and

$$c_1 = c_2 = c_3 = 0. \tag{4.109}$$

Together with (4.106), (4.108) yields

$$\begin{aligned} c_1 = c_7 &= 1, \\ c_2 = c_3 = c_4 = c_5 = c_6 = c_8 = c_9 &= 0, \end{aligned} \tag{4.110}$$

and (4.106) with (4.109) gives

$$\begin{aligned} c_5 &= -2, \\ c_7 &= 1, \\ c_1 = c_2 = c_3 = c_4 = c_6 = c_8 = c_9 &= 0. \end{aligned} \tag{4.111}$$

Thus (4.104) and (4.105) with (4.110) and (4.111) yield two sets of origin-independent, time-odd polarizability tensors corresponding to G_{ij} and a'_{ijk}:

$$\tilde{G}_{ij} = w_{ij}, \tag{4.112}$$

$$\tilde{a}'_{ijk} = s_{ijk} \tag{4.113}$$

and

$$\tilde{G}_{ij} = 0, \tag{4.114}$$

$$\tilde{a}'_{ijk} = s_{ijk} - 2(\varepsilon_{ijl}w_{kl} + \varepsilon_{ikl}w_{jl}). \tag{4.115}$$

Origin-independent contributions to the material constants at electric quadrupole–magnetic dipole order for magnetic media are obtained from the time-odd parts of (3.69), (3.72), (3.75), and (3.78) with the replacements $G_{ij} \to \tilde{G}_{ij}$ and $a'_{ijk} \to \tilde{a}'_{ijk}$. For the solution (4.110), the material constants are

$$\tilde{A}^{(2)}_{ij} = \mathcal{N} s_{ijk} k_k, \tag{4.116}$$

$$\tilde{T}^{(2)}_{ij} = \mathcal{N} w_{ij}, \tag{4.117}$$

$$\tilde{U}^{(2)}_{ij} = -\mathcal{N} w_{ji}, \tag{4.118}$$

$$\tilde{X}^{(2)}_{ij} = 0, \tag{4.119}$$

and for (4.111) one finds

$$\tilde{A}^{(2)}_{ij} = \mathcal{N}(s_{ijk} - \varepsilon_{ikl} w_{jl} - \varepsilon_{jkl} w_{il}) k_k, \tag{4.120}$$

$$\tilde{T}^{(2)}_{ij} = \tilde{U}^{(2)}_{ij} = 0, \tag{4.121}$$

$$\tilde{X}^{(2)}_{ij} = 0. \tag{4.122}$$

For non-dissipative media, the polarizabilities are real [4], so that the material constants (4.116)–(4.118) and (4.120) are real and respect the symmetries (3.91) and (3.92). The material constants given by (4.116)–(4.119) contain 15 independent components (see Section 3.5) and those given by (4.120)–(4.122) contain 6 independent components.

According to (4.117) and (4.118), the Post constraint (3.95) is respected because the trace

$$w_{ii} = G_{ii} - \tfrac{1}{3}\delta_{ii} G_{kk} - \tfrac{1}{6}\omega \varepsilon_{ikl} a'_{kli} = 0, \tag{4.123}$$

since $\delta_{ii} = 3$ and a'_{kli} is symmetric in the subscripts i and l, whereas ε_{ikl} is antisymmetric in i and l [6]. The material constants given by (4.121) satisfy the Post constraint (3.95) trivially. Thus the Post constraint holds also for the time-odd contributions at this order.

4.4.4 Summary and Discussion

In Section 3.5 it was noted that the constitutive tensor for non-dissipative media has a maximum of 21 independent components. At electric quadrupole–magnetic dipole order, there is no contribution to the inverse permeability X_{ij} (see (3.78)), hence the constitutive tensor at this order has 15 independent components. The solutions (4.112) and (4.113) preserve the maximum number of independent components in the constitutive tensor, whereas the solutions (4.114) and (4.115), with only 6 independent components, place an unphysical restriction on the constitutive tensor. The solutions (4.114) and (4.115) should therefore be rejected (see also Sections 5.1.9 and 5.2.8).

From (4.62), (4.63), (4.117), (4.118) and (4.123), invariant multipole theory, for a linear dependence of the induced moments on the field properties, is compliant with the Post constraint (3.95) to leading order, for both non-magnetic and magnetic media.

Origin-independent tensors corresponding to the time-odd molecular polarizabilities at electric quadrupole–magnetic dipole order are given by (4.112) and (4.113). The origin-independent property tensors corresponding to (3.26) and (3.32) in terms of (4.112) and (4.113) are

$$\tilde{\Pi}_{ijk} = -\tfrac{1}{\omega}\varepsilon_{ikl} w_{jl} + s_{ijk} \qquad \text{or} \qquad \tilde{\Pi}_{ijk} = -\tfrac{1}{\omega}\varepsilon_{ijl} w_{kl} + s_{ijk} \tag{4.124}$$

and

$$\tilde{\Omega}_{ijk} = \tfrac{1}{\omega}(\varepsilon_{ikl} w_{jl} + \varepsilon_{jkl} w_{il}) - s_{ijk}. \tag{4.125}$$

The ambiguity in (4.124) is due to the symmetry of the product of the field gradients $\nabla_j \nabla_k$ in (4.68) (see Section 3.2). The contributions to the source densities for non-magnetic molecules at this order are given by [6]

$$\rho^{(\overline{2})} = i\mathcal{N}(-\tfrac{1}{\omega}\varepsilon_{ikl}w_{jl} + s_{ijk})\nabla_j \nabla_k E_i \tag{4.126}$$

and

$$J_i^{(\overline{2})} = \mathcal{N}(\varepsilon_{ikl}w_{jl} + \varepsilon_{jkl}w_{il} - \omega s_{ijk})\nabla_k E_j. \tag{4.127}$$

The propagation equation to electric quadrupole–magnetic dipole order in magnetic media is obtained from (3.49) with the replacements $\Phi_{ijk} \to \tilde{\Phi}_{ijk}$ and $\Omega_{ijk} \to \tilde{\Omega}_{ijk}$, (3.29), (3.30), (4.56), (4.125) and (3.17); thus

$$\begin{aligned}\big(\delta_{ij}\nabla^2 - \nabla_i \nabla_j + \mu_0\varepsilon_0\omega^2\delta_{ij} + \mu_0\omega^2\mathcal{N}\,\big[\alpha_{ij} - \tfrac{1}{\omega}\left\{\varepsilon_{ikl}v_{jl} - \varepsilon_{jkl}v_{il}\right\}\nabla_k \\ -i\alpha'_{ij} + \tfrac{i}{\omega}\left\{\varepsilon_{ikl}w_{jl} + \varepsilon_{jkl}w_{il} - \omega s_{ijk}\right\}\nabla_k\big]\big)\,E_j = 0.\end{aligned} \tag{4.128}$$

From (4.70) and (4.71) with (4.112) and (4.113), and using (3.17), the invariant time-odd contributions to the response fields at electric quadrupole–magnetic dipole order for magnetic molecules are [6]

$$\tilde{D}_i^{(\overline{2})} = \mathcal{N}s_{ijk}k_k E_j + \mathcal{N}w_{ij}B_j \tag{4.129}$$

and

$$\tilde{H}_i^{(\overline{2})} = -\mathcal{N}w_{ji}E_j. \tag{4.130}$$

The invariant fields (4.129) and (4.130) are related to the origin-dependent fields (4.70) and (4.71) by the transformation (3.80) with the “gauge field”

$$H_i^G = \tfrac{1}{3}\mathcal{T}\left[\delta_{ij}G_{kk} + \tfrac{1}{2}\omega\varepsilon_{ikl}a'_{klj}\right]E_j, \tag{4.131}$$

where (3.20) and the linear property (3.9) of the transform $\mathcal{T}$ were used.

Chapter 5

Invariant formulation: third order

This chapter contains the derivation of origin-independent expressions corresponding to the molecular polarizability tensors at electric octopole–magnetic quadrupole order for non-magnetic molecules (Section 5.1) and magnetic molecules (Section 5.2).

5.1 Electric octopole–magnetic quadrupole order: Non-magnetic molecules

For non-magnetic molecules, the contributions at electric octopole–magnetic quadrupole order to the source densities are obtained from (3.27) in (3.21) and (3.33) in (3.22):

$$\begin{aligned}
\rho^{(3)} &= \mathcal{T}\left[\Theta_{ijkl}\right]\nabla_j\nabla_k\nabla_l E_i \\
&= \mathcal{T}\left[-\tfrac{1}{6}\left(b_{ijkl}+b_{jikl}\right)+\tfrac{1}{4}d_{ikjl}+\tfrac{1}{2\omega}\varepsilon_{ikm}\left(L'_{jlm}-H'_{jml}\right)\right]\nabla_j\nabla_k\nabla_l E_i, &(5.1)\\
J_i^{(3)} &= i\omega\mathcal{T}\left[\Phi_{ikjl}\right]\nabla_k\nabla_l E_j \\
&= i\omega\mathcal{T}\left[-\tfrac{1}{6}\left(b_{ijkl}+b_{jikl}\right)+\tfrac{1}{4}d_{ikjl}+\tfrac{1}{2\omega}\left\{\varepsilon_{ikm}\left(L'_{jlm}-H'_{jml}\right)+\varepsilon_{jlm}\left(L'_{ikm}-H'_{imk}\right)\right\}\right.\\
&\qquad\left.+\tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\chi_{mn}\right]\nabla_k\nabla_l E_j. &(5.2)
\end{aligned}$$

The contributions to the response fields are obtained from (3.70), (3.73), (3.76) and (3.79) in (3.60) and (3.59):

$$\begin{aligned}
D_i^{(3)} &= A_{ij}^{(3)}E_j+T_{ij}^{(3)}B_j \\
&= \mathcal{T}\left[-\tfrac{1}{6}\left(b_{ijkl}+b_{jikl}\right)+\tfrac{1}{4}d_{ikjl}\right]k_k k_l E_j+\mathcal{T}\left[\tfrac{1}{2}\left(H'_{ijk}-L'_{ikj}\right)\right]k_k B_j, &(5.3)\\
H_i^{(3)} &= U_{ij}^{(3)}E_j+X_{ij}^{(3)}B_j \\
&= \mathcal{T}\left[\tfrac{1}{2}\left(-H'_{jik}+L'_{jki}\right)\right]k_k E_j+\mathcal{T}\left[-\chi_{ij}\right]B_j. &(5.4)
\end{aligned}$$

Neither the property tensors Θ_{ijkl} and Φ_{ikjl}, nor the material constants $A_{ij}^{(3)}$, $T_{ij}^{(3)}$, $U_{ij}^{(3)}$ and $X_{ij}^{(3)}$, are origin independent. As noted in Section 3.2, the induced source densities are nevertheless origin independent because $\Delta\Theta_{ijkl}$ and $\Delta\Phi_{ikjl}$ contract to zero with the symmetric products $\nabla_j\nabla_k\nabla_l$ and $\nabla_k\nabla_l$, respectively. In the following sections, origin-independent expressions corresponding to the polarizability tensors χ_{ij}, b_{ijkl}, d_{ijkl}, L'_{ijk} and H'_{ijk} are determined. The origin-independent expressions have at least the symmetry of their origin-dependent counterparts, they leave the induced source densities (5.1) and (5.2) unchanged, yield invariant forms for the property tensors Θ_{ijkl} and Φ_{ikjl}, and the material constants $A_{ij}^{(3)}$, $T_{ij}^{(3)}$, $U_{ij}^{(3)}$ and $X_{ij}^{(3)}$, and hence yield physically acceptable expressions for the response fields (5.3) and (5.4).

The MATHEMATICA notebooks referred to in this section are contained in the directory `mathematica/e3m2-nm` on the accompanying CD.

5.1.1 Time-even basis tensors of electric octopole–magnetic quadrupole order

The aim here is to construct origin-independent basis tensors from molecular polarizabilities of electric octopole–magnetic quadrupole order. The method used is described in Appendix E and Section 4.4.1, although the calculation is considerably longer (see `01-basis.nb`). It is found that there are three linearly independent invariant tensors in terms of which all origin-independent expressions, at electric octopole–magnetic quadrupole order for non-magnetic molecules, can be expressed. These are

$$\begin{aligned} \mathcal{Q}_{ij} &= \chi_{ij} + \tfrac{1}{12}\omega^2(d_{ijkk} - d_{ikjk}) - \tfrac{1}{24}\omega^2\delta_{ij}(d_{kkll} - d_{klkl}) - \tfrac{1}{4}\omega\left(\varepsilon_{ikl}H'_{kjl} + \varepsilon_{jkl}H'_{kil}\right) && (5.5)\\ &= \mathcal{Q}_{ji}, && (5.6)\\ \mathcal{R}'_{ijk} &= L'_{ijk} - \tfrac{1}{4}\left(\delta_{ik}L'_{jll} + \delta_{jk}L'_{ill}\right) - \tfrac{1}{2}\left(H'_{ikj} + H'_{jki}\right) + \tfrac{1}{8}\left(\delta_{ik}H'_{llj} + \delta_{jk}H'_{lli}\right) - \tfrac{1}{6}\omega\varepsilon_{klm}b_{lijm} && (5.7)\\ &= \mathcal{R}'_{jik}, && (5.8)\\ \mathcal{S}_{ijkl} &= d_{ijkl} + d_{ikjl} + d_{iljk} - b_{ijkl} - b_{jikl} - b_{kijl} - b_{lijk} && (5.9)\\ &= \mathcal{S}_{jikl} = \mathcal{S}_{jikl} = \mathcal{S}_{kjil} = \mathcal{S}_{ljki}. && (5.10) \end{aligned}$$

The symmetries (5.6), (5.8) and (5.10) follow from the intrinsic symmetries of χ_{ij}, b_{ijkl}, d_{ijkl}, L'_{ijk} and H'_{ijk} (see Table 2.1).

5.1.2 General invariant expressions

General origin-independent precursor expressions corresponding to the multipole polarizability tensors at electric octopole–magnetic quadrupole order for non-magnetic molecules can now be written down in terms of (5.5), (5.7) and (5.9) and the general isotropic tensors (C.16)–(C.20). Because of the length of the expressions, it is impractical to reproduce them here (see `02-general.nb`).

The precursor expressions

$$\begin{aligned} \tilde{\chi}_{ij} &= I_{ijkl}\mathcal{Q}_{kl} + \omega I_{ijklm}\mathcal{R}'_{klm} + \omega^2 I_{ijklmn}\mathcal{S}_{klmn}, && (5.11)\\ \tilde{b}_{ijkl} &= \omega^{-2}I_{ijklmn}\mathcal{Q}_{mn} + \omega^{-1}I_{ijklmnp}\mathcal{R}'_{mnp} + I_{ijklmnpq}\mathcal{S}_{mnpq}, && (5.12)\\ \tilde{d}_{ijkl} &= \omega^{-2}I_{ijklmn}\mathcal{Q}_{mn} + \omega^{-1}I_{ijklmnp}\mathcal{R}'_{mnp} + I_{ijklmnpq}\mathcal{S}_{mnpq}, && (5.13)\\ \tilde{L}'_{ijk} &= \omega^{-1}I_{ijklm}\mathcal{Q}_{lm} + I_{ijklmn}\mathcal{R}'_{lmn} + \omega I_{ijklmnp}\mathcal{S}_{lmnp}, && (5.14)\\ \tilde{H}'_{ijk} &= \omega^{-1}I_{ijklm}\mathcal{Q}_{lm} + I_{ijklmn}\mathcal{R}'_{lmn} + \omega I_{ijklmnp}\mathcal{S}_{lmnp}, && (5.15) \end{aligned}$$

contain 422 unknown coefficients in the general isotropic tensors $I_{ij\ldots}$. The factors involving ω have been introduced to render these coefficients dimensionless. The process of arranging the terms in (5.11)–(5.15) so that these reflect the symmetries of the corresponding tensors χ_{ij}, b_{ijkl}, d_{ijkl}, L'_{ijk} and H'_{ijk} (see Table 2.1) is a time-consuming and repetitive task. The notebook uses a more direct (and less error-prone) approach. A set of linearly independent building blocks with the correct symmetry for each polarizability tensor is first constructed (see Section H.3). The building blocks are contained in lists, which can then be turned into sums by taking the dot product with another list, containing an appropriate number of unknown coefficients. The resulting expressions are origin independent, their terms are linearly independent, and — by construction — possess the correct symmetry. The number of unknown coefficients is now reduced to 51.

5.1.3 DC limit

In the DC limit ($\omega \to 0$), $\tilde{\chi}_{ij}$ reduces to the static expression $\chi_{ij}(0)$ given by Van Vleck [1]. From (5.5)–(5.7), (5.9) and (C.16), (5.11) reduces at DC to

$$\begin{aligned} \tilde{\chi}_{ij}(0) &= c_1\delta_{ij}\mathcal{Q}_{kk}(0) + (c_2 + c_3)\mathcal{Q}_{ij}(0)\\ &= c_1\chi_{ij}(0) + (c_2 + c_3)\chi_{ij}(0), && (5.16) \end{aligned}$$

where (2.44), (2.46), (2.49) and (2.51) were used. Inspection of (5.16) shows that $c_1 = 0$ and $c_3 = 1 - c_2$. The coefficients in I_{ijklm} and I_{ijklmn} multiplying $\mathcal{R}'_{klm}$ and $\mathcal{S}_{klmn}$ in (5.11) remain undetermined.

In (5.12)–(5.15), χ_{ij} enters only through $\mathcal{Q}_{ij}$ (see (5.5), (5.7) and (5.9)). Thus any occurrence of χ_{ij} in the expressions for $\tilde{b}_{ijkl}$, $\tilde{d}_{ijkl}$, $\tilde{L}'_{ijk}$ and $\tilde{H}'_{ijk}$ becomes singular at DC (see (2.52), (2.54) and (5.12)–(5.15)). Since (5.12)–(5.15) are constructed from linearly independent building blocks, there can be no relations between the unknown coefficients that produce cancellation of these singularities. Hence to produce acceptable expressions in the DC limit, the expressions (5.12)–(5.15) cannot contain χ_{ij} — and hence $\mathcal{Q}_{ij}$. The calculation to make (5.11)–(5.15) compliant in the DC limit is straightforward (see `03-dc-limit.nb`). The resulting expressions now contain 38 unknown coefficients.

5.1.4 The trace of the magnetic quadrupole moment is zero

In the absence of spin, the trace of the magnetic quadrupole moment operator (2.17) is zero [7] because $r_i l_i = \varepsilon_{ijk} r_i r_j \Pi_k = 0$. The quantum-mechanical expression for the electric dipole–magnetic quadrupole polarizability tensor H'_{ijk} in (2.49) contains the magnetic quadrupole moment operator and therefore, in the absence of spin, has a vanishing trace [7]

$$H'_{ijj} = 0. \tag{5.17}$$

Of the general expressions (5.11)–(5.15), only $\tilde{b}_{ijkl}$, $\tilde{L}'_{ijk}$ and $\tilde{H}'_{ijk}$ contain occurrences of H'_{ijj}. (Due to the symmetry of d_{ijkl}, there are no building blocks for d_{ijkl} that give rise to terms involving the trace H'_{ijj} — see (5.19) and Section H.3.3). For instance, the expression for $\tilde{b}_{ijkl}$ contains the building block (H.30)

$$\tilde{b}^{(3)}_{\mathcal{R}'} = \tfrac{1}{\omega}(\delta_{jk}\varepsilon_{ilm} + \delta_{jl}\varepsilon_{ikm} + \delta_{kl}\varepsilon_{ijm})\mathcal{R}'_{mnn}, \tag{5.18}$$

which must be zero because from (5.7), the intrinsic symmetry of $\tilde{b}_{ijkl}$, and (5.17),

$$\mathcal{R}'_{ijj} = -\tfrac{1}{2}H'_{ijj} = 0. \tag{5.19}$$

The relation (5.17) is a property of the polarizability tensor H'_{ijk}; thus the invariant tensor $\tilde{H}'_{ijk}$ should also have this property. The requirement

$$\tilde{H}'_{ijj} = 0 \tag{5.20}$$

results in two relations between the coefficients of $\tilde{H}'_{ijk}$ (see `04-trace-m2.nb`). Eight unknown coefficients are resolved, or multiply expressions that are zero, so leaving 30.

5.1.5 Gauss' law for magnetism

The polarizability tensors originate as constants of proportionality between the expectation values of the molecular multipole moments (2.33)–(2.37) and the electric and magnetic fields, their gradients and time derivatives. In the macroscopic theory, the invariant expressions corresponding to the molecular polarizability tensors will be used in the induced macroscopic moment densities (3.10)–(3.14) to produce physically acceptable macroscopic observables, that are independent of the arbitrary set of molecular coordinate origins $\{O^{(n)}\}$ of the microscopic theory (Section 3.1).

The invariant expressions corresponding to the polarizability tensors are linear combinations of products of the molecular polarizability tensors and isotropic tensors. They thus contain the isotropic tensors δ_{ij} and ε_{ijk}. In the expressions for the induced macroscopic moment densities, some of these contract with gradients of the magnetic field to produce $\delta_{jk}\nabla_k B_j = \boldsymbol{\nabla}\cdot\boldsymbol{B} = 0$. Consider the electric octopole–magnetic quadrupole contribution to the electric dipole moment (4.1). For non-magnetic molecules this contribution is

$$\tfrac{1}{2\omega}\mathcal{N}\tilde{H}'_{ijk}\nabla_k B_j. \tag{5.21}$$

The expression (5.15) for $\tilde{H}'_{ijk}$, after the considerations of Sections 5.1.3 and 5.1.4, becomes

$$\begin{aligned}\tilde{H}'_{ijk} &= c_1\left(\mathcal{R}'_{ijk} - \mathcal{R}'_{ikj}\right) + c_2\left(\delta_{ij}\mathcal{R}'_{llk} - \mathcal{R}'_{jki}\right) + c_3\left(\delta_{ik}\mathcal{R}'_{llj} - \mathcal{R}'_{jki}\right) + c_4\left(\delta_{jk}\mathcal{R}'_{lli} - 3\mathcal{R}'_{jki}\right)\\ &\quad + c_5\omega\varepsilon_{ijl}S_{klmm} + c_6\omega\varepsilon_{ikl}S_{jlmm} + c_7\omega S_{ilmm}\varepsilon_{jkl} \end{aligned} \tag{5.22}$$

(see `05-divB.nb`). As the term $c_4\delta_{jk}\mathcal{R}'_{lli}$ produces zero in (5.21), it may be omitted from (5.22) without affecting the latter's origin independence. When (5.7) and (5.9) are substituted into (5.22), the only tensors that produce δ_{jk} are $\mathcal{R}'_{ijk}$ and $\mathcal{R}'_{ikj}$, multiplying c_1 (see (5.7)). Since the difference $\mathcal{R}'_{ijk} - \mathcal{R}'_{ikj}$ is antisymmetric in j and k, the contributions in the symmetric δ_{jk} cancel. The expression multiplying c_1 therefore contains no occurrences of δ_{jk}, and remains origin independent.

At electric octopole–magnetic quadrupole order, consideration of Gauss' law for magnetism has no effect on the invariance of the origin-independent expressions corresponding to the time-even molecular polarizabilities in the expressions for the induced macroscopic moment densities. However, for the time-odd contributions of magnetic molecules, it will be apparent later that there are terms that vanish as described above, leaving the resulting expression origin dependent (see Section 5.2.5). At higher multipole order there will be additional terms that vanish due to the appearance of multiple gradients of the magnetic field. It is anticipated that these will not only break origin independence of certain molecular polarizabilities, but also their intrinsic symmetry.

5.1.6 Relabelling the coefficients

The considerations in Sections 5.1.2–5.1.5 have been applied to the origin-independent precursor expressions independently of each other. Therefore, no relations between the unknown coefficients of one polarizability with those of any other have been established to this point. Consequently, there has been no need to label the coefficients separately for all five polarizabilities. Instead of starting with 51 consecutively labelled coefficients at the end of Section 5.1.2, the coefficients for $\tilde{\chi}_{ij}$, $\tilde{b}_{ijkl}$, $\tilde{d}_{ijkl}$, $\tilde{L}'_{ijk}$ and $\tilde{H}'_{ijk}$ were labelled from 1 to 5, 1 to 12, 1 to 11, 1 to 8 and 1 to 15, respectively (see `02-general.nb`). At the end of Section 5.1.4 there were 30 coefficients in the corresponding expressions, which were labelled from 1 to 3, 8, 7, 5 and 7, respectively (see for example Equation (5.22) and `04-trace-m2.nb`). The remainder of the calculation involves comparisons of the five polarizabilities in the same expressions. Before continuing, the remaining unknowns in the expressions for the invariant polarizabilities must therefore be separately labelled at this stage. Thus the origin-independent precursor expressions for the polarizabilities, with the relabelled coefficients, for use in the next section are (see `06-source.nb`)

$$\begin{aligned}\tilde{\chi}_{ij} &= \tilde{\chi}^{(1)}_{\mathcal{Q}} + c_1\tilde{\chi}^{(1)}_{\mathcal{R}'} + c_2\tilde{\chi}^{(1)}_{\mathcal{S}} + c_3\tilde{\chi}^{(2)}_{\mathcal{S}}\\ &= \mathcal{Q}_{ij} + c_1\omega(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}) + c_2\omega^2\mathcal{S}_{ijkk} + c_3\omega^2\delta_{ij}\mathcal{S}_{kkll},\end{aligned} \tag{5.23}$$

$$\begin{aligned}\tilde{b}_{ijkl} &= c_4\tilde{b}^{(1)}_{\mathcal{R}'} + c_5\tilde{b}^{(2)}_{\mathcal{R}'} + c_6\tilde{b}^{(5)}_{\mathcal{R}'} + c_7\tilde{b}^{(6)}_{\mathcal{R}'} + c_8\tilde{b}^{(1)}_{\mathcal{S}} + c_9\tilde{b}^{(2)}_{\mathcal{S}} + c_{10}\tilde{b}^{(3)}_{\mathcal{S}} + c_{11}\tilde{b}^{(4)}_{\mathcal{S}}\\ &= c_4\tfrac{1}{\omega}\left[\varepsilon_{ijm}\left(\mathcal{R}'_{kml} + \mathcal{R}'_{lmk}\right) + \varepsilon_{ikm}\left(\mathcal{R}'_{jml} + \mathcal{R}'_{lmj}\right) + \varepsilon_{ilm}\left(\mathcal{R}'_{jmk} + \mathcal{R}'_{kmj}\right)\right]\\ &\quad + c_5\tfrac{1}{\omega}\left(\varepsilon_{ijm}\mathcal{R}'_{klm} + \varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{ilm}\mathcal{R}'_{jkm}\right) + c_6\tfrac{1}{\omega}\varepsilon_{imn}\left(\delta_{jk}\mathcal{R}'_{lmn} + \delta_{jl}\mathcal{R}'_{kmn} + \delta_{kl}\mathcal{R}'_{jmn}\right)\\ &\quad + c_7\tfrac{1}{\omega}\left(\delta_{jk}\varepsilon_{lmn} + \delta_{jl}\varepsilon_{kmn} + \delta_{kl}\varepsilon_{jmn}\right)\mathcal{R}'_{imn} + c_8\mathcal{S}_{ijkl} + c_9(\delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm} + \delta_{kl}\mathcal{S}_{ijmm})\\ &\quad + c_{10}(\delta_{ij}\mathcal{S}_{klmm} + \delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm}) + c_{11}(\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\mathcal{S}_{mmnn},\end{aligned} \tag{5.24}$$

$$\begin{aligned}\tilde{d}_{ijkl} &= c_{12}\tilde{d}^{(1)}_{\mathcal{R}'} + c_{13}\tilde{d}^{(2)}_{\mathcal{R}'} + c_{14}\tilde{d}^{(1)}_{\mathcal{S}} + c_{15}\tilde{d}^{(2)}_{\mathcal{S}} + c_{16}\tilde{d}^{(3)}_{\mathcal{S}} + c_{17}\tilde{d}^{(4)}_{\mathcal{S}} + c_{18}\tilde{d}^{(5)}_{\mathcal{S}}\\ &= c_{12}\tfrac{1}{\omega}\left[\varepsilon_{ikm}(\mathcal{R}'_{jml} - \mathcal{R}'_{lmj}) + \varepsilon_{ilm}(\mathcal{R}'_{jmk} - \mathcal{R}'_{kmj}) + \varepsilon_{jkm}(\mathcal{R}'_{iml} - \mathcal{R}'_{lmi}) + \varepsilon_{jlm}(\mathcal{R}'_{imk} - \mathcal{R}'_{kmi})\right]\\ &\quad + c_{13}\tfrac{1}{\omega}\left[\delta_{ij}\left(\varepsilon_{kmn}\mathcal{R}'_{lmn} + \varepsilon_{lmn}\mathcal{R}'_{kmn}\right) + \delta_{kl}\left(\varepsilon_{imn}\mathcal{R}'_{jmn} + \varepsilon_{jmn}\mathcal{R}'_{imn}\right)\right]\\ &\quad + c_{14}\mathcal{S}_{ijkl} + c_{15}(\delta_{ij}\mathcal{S}_{klmm} + \delta_{kl}\mathcal{S}_{ijmm}) + c_{16}(\delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm} + \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm})\\ &\quad + c_{17}\delta_{ij}\delta_{kl}\mathcal{S}_{mmnn} + c_{18}(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})\mathcal{S}_{mmnn},\end{aligned} \tag{5.25}$$

$$\begin{aligned}
\tilde{L}'_{ijk} &= c_{19}\tilde{L}'^{(1)}_{\mathcal{R}'} + c_{20}\tilde{L}'^{(2)}_{\mathcal{R}'} + c_{21}\tilde{L}'^{(5)}_{\mathcal{R}'} + c_{22}\tilde{L}'^{(6)}_{\mathcal{R}'} + c_{23}\tilde{L}'^{(1)}_{\mathcal{S}} \\
&= c_{19}\mathcal{R}'_{ijk} + c_{20}(\mathcal{R}'_{ikj} + \mathcal{R}'_{jki}) + c_{21}\delta_{ij}\mathcal{R}'_{llk} + c_{22}(\delta_{ik}\mathcal{R}'_{llj} + \delta_{jk}\mathcal{R}'_{lli}) \\
&\quad + c_{23}\omega(\varepsilon_{ikl}\mathcal{S}_{jlmm} + \varepsilon_{jkl}\mathcal{S}_{ilmm}), \qquad (5.26) \\
\tilde{H}'_{ijk} &= c_{24}\left(\tilde{H}'^{(1)}_{\mathcal{R}'} - \tilde{H}'^{(2)}_{\mathcal{R}'}\right) - (c_{25} + c_{26} + 3c_{27})\tilde{H}'^{(3)}_{\mathcal{R}'} + c_{25}\tilde{H}'^{(7)}_{\mathcal{R}'} + c_{26}\tilde{H}'^{(8)}_{\mathcal{R}'} \\
&\quad + c_{27}\tilde{H}'^{(9)}_{\mathcal{R}'} + c_{28}\tilde{H}'^{(1)}_{\mathcal{S}} + c_{29}\tilde{H}'^{(2)}_{\mathcal{S}} + c_{30}\tilde{H}'^{(3)}_{\mathcal{S}} \\
\tilde{H}'_{ijk} &= c_{24}(\mathcal{R}'_{ijk} - \mathcal{R}'_{ikj}) - (c_{25} + c_{26} + 3c_{27})\mathcal{R}'_{jki} + c_{25}\delta_{ij}\mathcal{R}'_{llk} + c_{26}\delta_{ik}\mathcal{R}'_{llj} \\
&\quad + c_{27}\delta_{jk}\mathcal{R}'_{lli} + \omega(c_{28}\varepsilon_{ijl}\mathcal{S}_{klmm} + c_{29}\varepsilon_{ikl}\mathcal{S}_{jlmm} + c_{30}\varepsilon_{jkl}\mathcal{S}_{ilmm}). \qquad (5.27)
\end{aligned}$$

The expressions for the building blocks in the first lines of (5.23)–(5.27) are listed in Appendix H.

5.1.7 Comparison of bound source densities

Based on (5.1) and (5.2), comparison of the bound source densities takes the forms

$$\rho^{(3)}\left(b_{ijkl}, d_{ijkl}, L'_{ijk}, H'_{ijk}\right) = \rho^{(3)}\left(\tilde{b}_{ijkl}, \tilde{d}_{ijkl}, \tilde{L}'_{ijk}, \tilde{H}'_{ijk}\right), \qquad (5.28)$$

$$J^{(3)}_i\left(\chi_{ij}, b_{ijkl}, d_{ijkl}, L'_{ijk}, H'_{ijk}\right) = J^{(3)}_i\left(\tilde{\chi}_{ij}, \tilde{b}_{ijkl}, \tilde{d}_{ijkl}, \tilde{L}'_{ijk}, \tilde{H}'_{ijk}\right). \qquad (5.29)$$

The comparisons (5.28) and (5.29), are performed in the notebook `06-source.nb`. The relations between the 30 unknowns in (5.23)–(5.27) that achieve (5.28) are

$$\begin{aligned}
c_4 &= \tfrac{1}{4}c_{13} + \tfrac{3}{2}c_{20} - \tfrac{3}{4}c_{24} + \tfrac{3}{4}c_{25} + \tfrac{3}{4}c_{26} + \tfrac{9}{4}c_{27}, \\
c_5 &= -\tfrac{1}{2}c_{13} + \tfrac{3}{2}c_{19} + \tfrac{3}{2}c_{24} - \tfrac{3}{2}, \\
c_6 &= 3c_7 = \tfrac{3}{4}c_{13}, \\
c_8 &= \tfrac{3}{4}c_{14} - \tfrac{1}{4}, \\
c_9 &= \tfrac{1}{4}c_{15} + \tfrac{1}{2}c_{16} + 3c_{23} - \tfrac{3}{2}c_{28} + \tfrac{3}{2}c_{30}, \\
c_{10} &= \tfrac{1}{4}c_{15} + \tfrac{1}{2}c_{16} - 3c_{23} + \tfrac{3}{2}c_{28} - \tfrac{3}{2}c_{30}, \\
c_{11} &= \tfrac{1}{4}c_{17} + \tfrac{1}{2}c_{18}, \\
c_{21} &= c_{26}.
\end{aligned} \qquad (5.30)$$

The comparison (5.29) further requires

$$\begin{aligned}
c_1 &= \tfrac{1}{4}c_{12} - \tfrac{1}{12}c_{13} + \tfrac{1}{4}c_{24} + \tfrac{1}{4}c_{25} + \tfrac{1}{4}c_{26} + \tfrac{3}{4}c_{27}, \\
c_2 &= -\tfrac{1}{12}c_{15} + \tfrac{1}{12}c_{16} + \tfrac{1}{2}c_{28} + c_{29} + \tfrac{1}{2}c_{30}, \\
c_3 &= \tfrac{1}{12}c_{15} - \tfrac{1}{12}c_{16} + \tfrac{1}{12}c_{17} - \tfrac{1}{12}c_{18} - \tfrac{1}{2}c_{28} - \tfrac{1}{2}c_{30}.
\end{aligned} \qquad (5.31)$$

After comparison of the source densities, the origin-independent precursor expressions, corresponding to the polarizabilities χ_{ij}, b_{ijkl}, d_{ijkl}, L'_{ijk} and H'_{ijk}, now contain 18 unknown coefficients. The choice of independents and dependents in (5.30) and (5.31) is an artefact of the way in which the MATHEMATICA routines were executed. It is a straightforward matter to relabel the coefficients to suit a specific preference. The most logical, and safest, procedure is to substitute (5.30) and (5.31) in (5.23)–(5.27) and to relabel the 18 coefficients on the right-hand sides of (5.30) and (5.31) according to

$$\begin{gathered}
c_{12} \to c_1,\ c_{13} \to c_2,\ c_{14} \to c_3,\ c_{15} \to c_4,\ c_{16} \to c_5,\ c_{17} \to c_6, \\
c_{18} \to c_7,\ c_{19} \to c_8,\ c_{20} \to c_9,\ c_{22} \to c_{10},\ c_{23} \to c_{11},\ c_{24} \to c_{12}, \\
c_{25} \to c_{13},\ c_{26} \to c_{14},\ c_{27} \to c_{15},\ c_{28} \to c_{16},\ c_{29} \to c_{17},\ c_{30} \to c_{18}.
\end{gathered} \qquad (5.32)$$

Then (5.11)–(5.15) may be expressed in terms of the building blocks listed in Appendix H as

$$\begin{aligned}
\tilde{\chi}_{ij} &= \tilde{\chi}^{(1)}_{\mathcal{Q}} + \tfrac{1}{4}\left(c_1 - \tfrac{1}{3}c_2 + c_{12} + c_{13} + c_{14} + 3c_{15}\right)\tilde{\chi}^{(1)}_{\mathcal{R}'} \\
&\quad - \tfrac{1}{12}\left(c_4 - c_5 - 6c_{16} - 12c_{17} - 6c_{18}\right)\tilde{\chi}^{(1)}_{\mathcal{S}} \\
&\quad + \tfrac{1}{12}\left(c_4 - c_5 + c_6 - c_7 - 6c_{16} - 6c_{18}\right)\tilde{\chi}^{(2)}_{\mathcal{S}} && (5.33)\\
&= \tilde{\chi}_{ji}, && (5.34)\\
\tilde{b}_{ijkl} &= -\tfrac{1}{4}(1 - 3c_3)\tilde{b}^{(1)}_{\mathcal{S}} + \tfrac{1}{4}(c_4 + 2c_5 + 12c_{11} - 6c_{16} + 6c_{18})\tilde{b}^{(2)}_{\mathcal{S}} \\
&\quad + \tfrac{1}{4}(c_4 + 2c_5 - 12c_{11} + 6c_{16} - 6c_{18})\tilde{b}^{(3)}_{\mathcal{S}} + \tfrac{1}{4}(c_6 + 2c_7)\tilde{b}^{(4)}_{\mathcal{S}} \\
&\quad + \tfrac{1}{4}(c_2 + 6c_9 - 3c_{12} + 3c_{13} + 3c_{14} + 4c_{15})\tilde{b}^{(1)}_{\mathcal{R}'} \\
&\quad - \tfrac{3}{2}\left(1 + \tfrac{1}{3}c_2 - c_8 - c_{12}\right)\tilde{b}^{(2)}_{\mathcal{R}'} + \tfrac{1}{4}c_2\left(3\tilde{b}^{(5)}_{\mathcal{R}'} + \tilde{b}^{(6)}_{\mathcal{R}'}\right) && (5.35)\\
&= \tilde{b}_{ikjl} = \tilde{b}_{ilkj}, && (5.36)\\
\tilde{d}_{ijkl} &= c_3\tilde{d}^{(1)}_{\mathcal{S}} + c_4\tilde{d}^{(2)}_{\mathcal{S}} + c_5\tilde{d}^{(3)}_{\mathcal{S}} + c_6\tilde{d}^{(4)}_{\mathcal{S}} + c_7\tilde{d}^{(5)}_{\mathcal{S}} + c_1\tilde{d}^{(1)}_{\mathcal{R}'} + c_2\tilde{d}^{(2)}_{\mathcal{R}'} && (5.37)\\
&= \tilde{d}_{jikl} = \tilde{d}_{klij}, && (5.38)\\
\tilde{L}'_{ijk} &= c_8\tilde{L}'^{(1)}_{\mathcal{R}'} + c_9\tilde{L}'^{(2)}_{\mathcal{R}'} + c_{14}\tilde{L}'^{(5)}_{\mathcal{R}'} + c_{10}\tilde{L}'^{(6)}_{\mathcal{R}'} + c_{11}\tilde{L}'^{(1)}_{\mathcal{S}} && (5.39)\\
&= \tilde{L}'_{jik}, && (5.40)\\
\tilde{H}'_{ijk} &= c_{12}\left(\tilde{H}'^{(1)}_{\mathcal{R}'} - \tilde{H}'^{(2)}_{\mathcal{R}'}\right) - (c_{13} + c_{14} + 3c_{15})\tilde{H}'^{(3)}_{\mathcal{R}'} + c_{13}\tilde{H}'^{(7)}_{\mathcal{R}'} \\
&\quad + c_{14}\tilde{H}'^{(8)}_{\mathcal{R}'} + c_{15}\tilde{H}'^{(9)}_{\mathcal{R}'} + c_{16}\tilde{H}'^{(1)}_{\mathcal{S}} + c_{17}\tilde{H}'^{(2)}_{\mathcal{S}} + c_{18}\tilde{H}'^{(3)}_{\mathcal{S}}. && (5.41)
\end{aligned}$$

5.1.8 Linear independence

Because the basis tensors $\mathcal{Q}_{ij}$, $\mathcal{R}'_{ijk}$ and $\mathcal{S}_{ijkl}$ are linear combinations of the polarizability tensors χ_{ij}, b_{ijkl}, d_{ijkl}, L'_{ijk} and H'_{ijk}, (5.33)–(5.41) are not necessarily linearly independent. In this section the conditions on the origin-independent expressions $\tilde{\chi}_{ij}$, $\tilde{b}_{ijkl}$, $\tilde{d}_{ijkl}$, $\tilde{L}'_{ijk}$ and $\tilde{H}'_{ijk}$ to be linearly independent are determined. A simplification of the analysis can be made by recognizing that, because there are only three basis tensors, at most three of the invariant expressions can be non-zero.

In (5.33)–(5.41), only $\tilde{\chi}_{ij}$ contains $\mathcal{Q}_{ij}$, so $\tilde{\chi}_{ij}$ must be non-zero. Further inspection reveals that both the two fourth-rank tensors $\tilde{b}_{ijkl}$ and $\tilde{d}_{ijkl}$ contain the fourth-rank tensor $\mathcal{S}_{ijkl}$, whereas $\tilde{L}'_{ijk}$ and $\tilde{H}'_{ijk}$ contain only the trace of this tensor. Thus if $\tilde{b}_{ijkl}$ is zero (requiring *inter alia* from (5.35) that $c_3 = \frac{1}{3}$), then $\tilde{d}_{ijkl}$ cannot be zero, and vice versa. There are consequently four possibilities for the remaining origin-independent expressions corresponding to the four polarizability tensors b_{ijkl}, d_{ijkl}, L'_{ijk} and H'_{ijk}; namely

1. $\tilde{H}'_{ijk} = 0$ and $\tilde{b}_{ijkl} = 0$, (5.42)
2. $\tilde{H}'_{ijk} = 0$ and $\tilde{d}_{ijkl} = 0$, (5.43)
3. $\tilde{L}'_{ijk} = 0$ and $\tilde{b}_{ijkl} = 0$, (5.44)
4. $\tilde{L}'_{ijk} = 0$ and $\tilde{d}_{ijkl} = 0$. (5.45)

The calculations to determine the relations between the 18 unknown coefficients in (5.33)–(5.41) that produce (5.42)–(5.45) is contained in the notebook `07-li-cases.nb`. The linearly independent solutions corresponding to (5.42)–(5.45) are discussed below. The calculations are contained in the notebooks `08-li-case1.nb`, `09-li-case2.nb`, `10-li-case3.nb` and `11-li-case4.nb`.

Case 1: $\tilde{H}'_{ijk} = 0$ and $\tilde{b}_{ijkl} = 0$

To achieve $\tilde{H}'_{ijk} = 0$ and $\tilde{b}_{ijkl} = 0$ requires (see `08-li-case1.nb`)

$$\begin{gathered} c_2 = c_9 = c_{11} = c_{12} = c_{13} = c_{14} = c_{15} = c_{16} = c_{17} = c_{18} = 0, \\ c_3 = \tfrac{1}{3}, \\ c_4 = -2c_5, \\ c_6 = -2c_7, \\ c_8 = 1. \end{gathered} \tag{5.46}$$

The invariant expressions corresponding to the polarizabilities χ_{ij}, d_{ijkl} and L'_{ijk} are then

$$\tilde{\chi}_{ij} = \mathcal{Q}_{ij} + \tfrac{1}{4}\omega c_1 \left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}\right) + \tfrac{1}{4}\omega^2 c_5 \mathcal{S}_{ijkk} - \tfrac{1}{4}\omega^2(c_5 + c_7)\delta_{ij}\mathcal{S}_{kkll}, \tag{5.47}$$

$$\begin{aligned} \tilde{d}_{ijkl} = {} & \tfrac{1}{3}\mathcal{S}_{ijkl} + c_5(\delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm} + \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm}) \\ & - 2c_5(\delta_{ij}\mathcal{S}_{klmm} + \delta_{kl}\mathcal{S}_{ijmm}) + c_7(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})\mathcal{S}_{mmnn} - 2c_7\delta_{ij}\delta_{kl}\mathcal{S}_{mmnn} \\ & + \tfrac{1}{\omega}c_1 \left[\varepsilon_{ikm}\left(\mathcal{R}'_{jml} - \mathcal{R}'_{lmj}\right) + \varepsilon_{ilm}\left(\mathcal{R}'_{jmk} - \mathcal{R}'_{kmj}\right)\right. \\ & \quad \left. + \varepsilon_{jkm}\left(\mathcal{R}'_{iml} - \mathcal{R}'_{lmi}\right) + \varepsilon_{jlm}\left(\mathcal{R}'_{imk} - \mathcal{R}'_{kmi}\right)\right], \end{aligned} \tag{5.48}$$

$$\tilde{L}'_{ijk} = \mathcal{R}'_{ijk} + c_{10}\left(\delta_{ik}\mathcal{R}'_{llj} + \delta_{jk}\mathcal{R}'_{lli}\right). \tag{5.49}$$

To establish linear independence, each of the linear relations

$$\Lambda_{ij} = I_{ijkl}\tilde{\chi}_{kl} + \omega I_{ijklm}\tilde{L}'_{klm} + \omega^2 I_{ijklmn}\tilde{d}_{klmn}, \tag{5.50}$$

$$\Lambda_{ijk} = \omega^{-1} I_{ijklm}\tilde{\chi}_{lm} + I_{ijklmn}\tilde{L}'_{lmn} + \omega I_{ijklmnp}\tilde{d}_{lmnp}, \tag{5.51}$$

$$\Lambda_{ijkl} = \omega^{-2} I_{ijklmn}\tilde{\chi}_{mn} + \omega^{-1} I_{ijklmnp}\tilde{L}'_{mnp} + I_{ijklmnpq}\tilde{d}_{mnpq}, \tag{5.52}$$

must equal zero for the trivial solution $k_1 = k_2 = \ldots = k_i = 0$, where the k_i are arbitrary coefficients multiplying the linearly independent isotropic tensors in the $I_{ij\ldots}$. The factors involving ω in (5.50)–(5.52) have been introduced to make the arbitrary coefficients k_i dimensionless. Thus, when c_i is replaced with k_i in (C.16), (C.17) and (C.18), and after taking into account the symmetry of $\tilde{\chi}_{ij}$, $\tilde{L}'_{ijk}$ and $\tilde{d}_{ijkl}$, (5.50) becomes

$$\begin{aligned} \Lambda_{ij} = {} & k_1\tilde{\chi}_{ij} + k_2\delta_{ij}\tilde{\chi}_{kk} + \omega\left(k_3\varepsilon_{ijk}\tilde{L}'_{kll} + k_4\varepsilon_{ijk}\tilde{L}'_{llk} + k_5\varepsilon_{ikl}\tilde{L}'_{jkl}\right) \\ & + \omega^2\left(k_6\tilde{d}_{ijkk} + k_7\tilde{d}_{ikjk} + k_8\delta_{ij}\tilde{d}_{klkl} + k_9\delta_{ij}\tilde{d}_{kkll}\right). \end{aligned} \tag{5.53}$$

Use of (5.47)–(5.49) in (5.53), followed by the substitutions of (5.5), (5.7) and (5.9), yields an expression with 9 arbitrary coefficients k_i, four unknown coefficients (c_1, c_5, c_7 and c_{10}) and consists of 137 terms. In the remainder of this calculation, the substitution of (5.5), (5.7) and (5.9) following use of expressions involving $\mathcal{Q}_{ij}$, $\mathcal{R}'_{ijk}$ and $\mathcal{S}_{ijkl}$ is implied.

The expressions for Case 1 are the 'simplest' of the four cases. This is because the tensors that carry the most information (have the most independent components — see Appendix G) are zero. For instance, the fourth-rank expression (5.52) for Case 1 has 49 arbitrary coefficients k_i, four unknown coefficients c_i and consists of 1171 terms. The largest expression is the fourth-rank relation for Case 4, which contains 4 061 terms, 70 arbitrary k_i and six unknown coefficients c_i. To establish linear independence, it is expedient therefore to start with the second-rank expressions to obtain relations between the unknown c_i of the invariant expressions. Once relations between some of the c_i have been found, the expressions of higher rank become more manageable.

The solution to (5.53) with $\Lambda_{ij} = 0$, for the arbitrary k_i, is

$$k_1 = k_2 = 0, \tag{5.54}$$

$$k_3 = -k_4 = \tfrac{1}{2}k_5 = \frac{c_1}{3(c_5 + 2c_7)}A, \tag{5.55}$$

$$k_6 = \frac{3c_5 + 1}{9(c_5 + 2c_7)}A, \tag{5.56}$$

$$k_7 = \frac{6c_5 - 1}{9(c_5 + 2c_7)}A, \tag{5.57}$$

where

$$A = (1 + 12c_5 + 18c_7)k_8 + (1 - 24c_5 - 36c_7)k_9. \tag{5.58}$$

The solution consists of five dependent coefficients and two independents. The only k_i that are zero are k_1 and k_2, being the two coefficients from the term $I_{ijkl}\tilde{\chi}_{kl}$ in (5.50).

It is not sufficient to solve the simultaneous set of equations $k_i = 0$ for the unknown c_i, because it is possible that the invariant expressions possess more symmetry than the corresponding non-invariant polarizability tensors (see, for example, the calculation for the time-odd tensors at electric quadrupole–magnetic dipole order in Section 4.4, where $\tilde{a}_{ijk} = s_{ijk}$ is totally symmetric). Extra symmetry would result in fewer terms in the expressions (5.50)–(5.52), and hence fewer dependencies between the k_i in (5.55)–(5.57). Equations (5.55)–(5.57) must therefore be examined in turn.

It is tempting to deduce from (5.55) that $c_1 = 0$, and that (5.56) and (5.57) imply there exists an unresolvable linear relation between k_6, k_8 and k_9, or k_7, k_8 and k_9. For example, if $c_1 = 0$, inspection of (5.56), (5.57) and (5.58) suggests that c_5 and c_7 cannot both be zero, and setting either c_5 or c_7 zero would require the other to take on multiple values simultaneously. It should be recognized, however, that the independent k_i are not cast in stone, and eliminating k_3 in favour of k_8 leads to a different conclusion. The systematic way to proceed is to avoid setting any of the c_i to definite values until no other choice exists.

Consider first the relation (5.55) for k_3, which can be rewritten as

$$3(c_5 + 2c_7)k_3 = c_1[(1 + 12c_5 + 18c_7)k_8 + (1 - 24c_5 - 36c_7)k_9]. \tag{5.59}$$

All possibilities that lead to trivial solutions for k_3, k_8 or k_9 should be investigated in turn. One strategy is to substitute the relations obtained for c_1, c_5 and c_7 into (5.47)–(5.49) in turn, and solve $\Lambda_{ij} = 0$ for each solution. Alternatively, the solutions can be substituted in the remaining expressions for the independent k_i until a logical inconsistency is obtained. The former procedure, although computationally more time consuming, and possibly involving calculations that could be avoided by careful logical consideration, is found to be less prone to error due to human prejudice.

The possibility $c_1 = 0$ should be deferred because (5.55)–(5.57) all contain the same factors $(c_5 + 2c_7)$ and (5.58). Hence, if an acceptable combination of c_5 and c_7 produces linear independence, it is possible that c_1 can remain undetermined. Besides $c_1 = 0$, Equation (5.59) contains four trial solutions:

1. $c_7 = -\tfrac{1}{2}c_5,$ (5.60)
2. $c_7 = -\tfrac{2}{3}c_5 - \tfrac{1}{18},$ (5.61)
3. $c_7 = -\tfrac{2}{3}c_5 + \tfrac{1}{36},$ (5.62)
4. $c_5 = c_7 = 0.$ (5.63)

The trial solution (5.63) can be included because it produces symmetric contributions from k_8 and k_9, which is possible if $\tilde{d}_{ijkl}$ is totally symmetric (see (5.53)). It should be considered as a last resort, however, not least because it can be produced by (5.60).

The trial solution (5.60) in (5.47)–(5.49), substituted in the second-rank expression (5.53) with $\Lambda_{ij} = 0$, yields the set of solutions

$$k_1 = k_2 = 0, \tag{5.64}$$

$$k_3 = -k_4 = \tfrac{1}{2}k_5 = \frac{3c_1k_7}{6c_5 - 1}, \tag{5.65}$$

$$k_6 = \frac{3c_5 + 1}{6c_5 - 1}k_7, \tag{5.66}$$

$$k_8 = \frac{6c_5 - 1}{3c_5 + 1}k_9. \tag{5.67}$$

To obtain (5.64)–(5.67) from (5.54)–(5.57) would require that (5.54)–(5.57) be rearranged with k_7 and k_9 as independents, followed by the substitution (5.60). Equations (5.65)–(5.67) allow three more possibilities:

1. $c_5 = \frac{1}{6}$ (and hence $c_7 = -\frac{1}{12}$), (5.68)
2. $c_5 = -\frac{1}{3}$ and $c_1 = 0$ (and hence $c_7 = \frac{1}{6}$), (5.69)
3. $c_1 = 0$ with c_5 determined as a result of the symmetry of $\tilde{d}_{ijkl}$. (5.70)

The argument used in (5.70) is possible because the coefficients k_6, k_7, k_8 and k_9 in (5.66) and (5.67) all multiply contributions due to $\tilde{d}_{ijkl}$ in (5.53), and the expression for $\tilde{d}_{ijkl}$ in (5.48) contains c_5. Note that this argument cannot be used for (5.65) to obtain a relation between c_1 and c_5 say. This is because in (5.53), k_3, k_4 and k_5 are due to contributions from $\tilde{L}'_{ijk}$, and k_7 is due to $\tilde{d}_{ijkl}$. Eliminating k_3, k_4 and k_5 so that $k_7 = 0$ would require $\tilde{L}'_{ijk} = 0$, or $\tilde{L}'_{ijk} = -\tilde{L}'_{ikj}$, neither of which can be achieved from (5.49). Alternately, eliminating the k_7 contribution from (5.53) would require $\tilde{d}_{ijkl} = 0$. Inspection of (5.48) shows that this is not possible either.

The first possibility (5.68) of the trial solution (5.60) in (5.47)–(5.49), substituted into the second-rank expression (5.53) with $\Lambda_{ij} = 0$, yields the revised set of solutions

$$k_1 = k_2 = k_7 = k_8 = 0, \tag{5.71}$$

$$k_3 = -k_4 = \tfrac{1}{2}k_5 = 2c_1k_6. \tag{5.72}$$

Inspection of (5.72) shows that $c_1 = 0$ produces the trivial solution $k_i = 0$ (k_6 becomes zero when the calculation is repeated with $c_1 = 0$). Thus (5.47)–(5.49) with

$$c_1 = 0, \quad c_5 = \tfrac{1}{6} \quad \text{and} \quad c_7 = -\tfrac{1}{12} \tag{5.73}$$

are a linearly independent set of origin-independent tensors for the second-rank expression (5.53). The coefficient c_{10} remains unspecified. Because the three tensors $\tilde{\chi}_{ij}$, $\tilde{L}'_{ijk}$ and $\tilde{d}_{ijkl}$ are second-, third- and fourth-rank tensors, it must now be verified that the solution (5.73) also produces linear independence for the third- and fourth-rank linear combinations (5.51) and (5.52). Equation (5.51) contains 20 arbitrary coefficients k_i. Substitution of (5.47)–(5.49) with (5.73) in the third-rank expression (5.51) and equating the result to zero gives

$$k_1 = k_2 = \cdots = k_{11} = k_{12} = 0, \tag{5.74}$$

$$k_{13} = -\tfrac{1}{2}k_{15} = \tfrac{1}{2}k_{18} = -\tfrac{1}{2}k_{19}, \tag{5.75}$$

the terms involving k_{14}, k_{16}, k_{17} and k_{20} having contracted to zero. The contributions to (5.51) that are non-trivial in (5.75) all originate from the expression $I_{ijklmnp}\tilde{d}_{lmnp}$ in (5.51), which contains terms involving k_{13} to k_{20}. Now $\tilde{d}_{ijkl}$ given by (5.48) with (5.73) is

$$\begin{aligned}\tilde{d}_{ijkl} = {} & \tfrac{1}{3}\mathcal{S}_{ijkl} + \tfrac{1}{6}(\delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm} + \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm}) \\ & - \tfrac{1}{3}(\delta_{ij}\mathcal{S}_{klmm} + \delta_{kl}\mathcal{S}_{ijmm}) - \tfrac{1}{12}(\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})\mathcal{S}_{mmnn} + \tfrac{1}{6}\delta_{ij}\delta_{kl}\mathcal{S}_{mmnn},\end{aligned} \tag{5.76}$$

which has the symmetry of d_{ijkl} (see Table 2.1) and contains no unknown coefficients. Thus there is no way to eliminate the dependency (5.75). Therefore the solution corresponding to (5.73) must be rejected.

The second possibility (5.69) of the trial solution (5.60) in (5.47)–(5.49), substituted into the second-rank expression (5.53) with $\Lambda_{ij} = 0$, leads directly to a linearly independent solution (see `08-li-case1.nb` and Section C.7). The origin-independent expressions (5.47)–(5.49) with (5.69) are

$$\tilde{\chi}_{ij} = \mathcal{Q}_{ij} - \tfrac{1}{12}\omega^2 \mathcal{S}_{ijkk} + \tfrac{1}{24}\omega^2 \delta_{ij}\mathcal{S}_{kkll}, \tag{5.77}$$

$$\tilde{d}_{ijkl} = \tfrac{1}{3}\mathcal{S}_{ijkl} + \tfrac{2}{3}(\delta_{ij}\mathcal{S}_{klmm} + \delta_{kl}\mathcal{S}_{ijmm}) - \tfrac{1}{3}(\delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm} + \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm}) + \tfrac{1}{6}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - 2\delta_{ij}\delta_{kl})\mathcal{S}_{mmnn}, \tag{5.78}$$

$$\tilde{L}'_{ijk} = \mathcal{R}'_{ijk} + c_{10}\left(\delta_{ik}\mathcal{R}'_{llj} + \delta_{jk}\mathcal{R}'_{lli}\right). \tag{5.79}$$

The third possibility (5.70) of the trial solution (5.60) in (5.47)–(5.49), substituted in the second-rank expression (5.53) with $\Lambda_{ij} = 0$, gives

$$k_1 = k_2 = k_3 = k_4 = k_5 = 0, \tag{5.80}$$

$$k_6 = \frac{3c_5 + 1}{6c_5 - 1}k_7, \tag{5.81}$$

$$k_8 = \frac{6c_5 - 1}{3c_5 + 1}k_9. \tag{5.82}$$

Clearly (5.81) and (5.82) contain the solutions of (5.68) and (5.69), which do not lead to an acceptable linearly independent set of invariant tensors. The only recourse left is to examine the expressions multiplying k_6, k_7, k_8 and k_9 in (5.53), and find a relation between these expressions such that those multiplying k_6 and k_7, and k_8 and k_9 are equal (since it has already been noted that $\tilde{d}_{ijkl}$ cannot be zero). Inspection of these terms in (5.53) reveals that if $\tilde{d}_{ijkl}$ is totally symmetric, then

$$k_6\tilde{d}_{ijkk} + k_7\tilde{d}_{ikjk} + k_8\delta_{ij}\tilde{d}_{klkl} + k_9\delta_{ij}\tilde{d}_{kkll} = (k_6 + k_7)\tilde{d}_{ijkk} + (k_8 + k_9)\delta_{ij}\tilde{d}_{kkll}, \tag{5.83}$$

and k_6 or k_7 and k_8 or k_9 would not be present in (5.53), leading to a linearly independent solution for (5.47)–(5.49). It is straightforward to show that a totally symmetric form for $\tilde{d}_{ijkl}$ is possible only for $c_5 = 0$. Furthermore, the complete trial solution

$$c_1 = c_5 = c_7 = 0 \tag{5.84}$$

also results in linear independence of the third- and fourth-rank relations (5.51) and (5.52) (see `08-li-case1.nb`).

The origin-independent expressions (5.47)–(5.49) with (5.84) are

$$\tilde{\chi}_{ij} = \mathcal{Q}_{ij}, \tag{5.85}$$

$$\tilde{d}_{ijkl} = \tfrac{1}{3}\mathcal{S}_{ijkl}, \tag{5.86}$$

$$\tilde{L}'_{ijk} = \mathcal{R}'_{ijk} + c_{10}\left(\delta_{ik}\mathcal{R}'_{llj} + \delta_{jk}\mathcal{R}'_{lli}\right). \tag{5.87}$$

The procedure described above must now be repeated for the trial solutions (5.61) and (5.62), (5.63) being the same as the solution that leads to (5.85)–(5.87). The calculations proceed along the same lines as the calculation described above and are not repeated here. They do not lead to any linearly independent solutions for $\tilde{\chi}_{ij}$, $\tilde{d}_{ijkl}$ and $\tilde{L}'_{ijk}$ (see `08-li-case1.nb`).

For Case 1 (page 44) origin-independent contributions to the material constants at electric octopole–magnetic quadrupole order for non-magnetic media are obtained from the time-even parts of (3.70), (3.73), (3.76), and (3.79) with the replacements $\chi_{ij} \to \tilde{\chi}_{ij}$, $L'_{ijk} \to \tilde{L}'_{ijk}$, $d_{ijkl} \to \tilde{d}_{ijkl}$ and

$\{b_{ijkl}, H'_{ijk}\} \to 0$. The resulting expressions corresponding to (5.77)–(5.79) are

$$\begin{aligned}
\tilde{A}^{(3)}_{ij} &= \tfrac{1}{12}\mathcal{N}\,[\mathcal{S}_{ijkl} - \delta_{kl}\mathcal{S}_{ijmm} + \delta_{jl}\mathcal{S}_{ikmm} + \delta_{il}\mathcal{S}_{jkmm} - \delta_{ij}\mathcal{S}_{klmm} \\
&\quad - \tfrac{1}{2}\delta_{ik}\delta_{jl}\mathcal{S}_{mmnn} + \tfrac{1}{2}\delta_{ij}\delta_{kl}\mathcal{S}_{mmnn}]\, k_k k_l, && (5.88)\\
\tilde{T}^{(3)}_{ij} &= -\tfrac{1}{2}\mathcal{N}\left[\mathcal{R}'_{ikj} + c_{10}\left(\delta_{ij}\mathcal{R}'_{llk} + \delta_{jk}\mathcal{R}'_{lli}\right)\right] k_k, && (5.89)\\
\tilde{U}^{(3)}_{ij} &= -T^{(3)}_{ji}, && (5.90)\\
\tilde{X}^{(3)}_{ij} &= -\mathcal{N}\left[\mathcal{Q}_{ij} - \tfrac{1}{12}\omega^2\mathcal{S}_{ijkk} + \tfrac{1}{24}\omega^2\delta_{ij}\mathcal{S}_{kkll}\right]. && (5.91)
\end{aligned}$$

The permittivity tensor given by (5.88) has the property $\tilde{A}^{(3)}_{ii} = 0$; hence, for non-dissipative media, the material constants given by (5.88)–(5.91) contain 20 independent components instead of 21 (see Section 3.5). The expressions for the material constants corresponding to (5.85)–(5.87) are

$$\begin{aligned}
\tilde{A}^{(3)}_{ij} &= \tfrac{1}{12}\mathcal{N}\mathcal{S}_{ijkl}k_k k_l, && (5.92)\\
\tilde{T}^{(3)}_{ij} &= -\tfrac{1}{2}\mathcal{N}\left[\mathcal{R}'_{ikj} + c_{10}\left(\delta_{ij}\mathcal{R}'_{llk} + \delta_{jk}\mathcal{R}'_{lli}\right)\right] k_k, && (5.93)\\
\tilde{U}^{(3)}_{ij} &= -T^{(3)}_{ji}, && (5.94)\\
\tilde{X}^{(3)}_{ij} &= -\mathcal{N}\mathcal{Q}_{ij}. && (5.95)
\end{aligned}$$

For non-dissipative media, the polarizabilities are real [4], so that the material constants (5.88)–(5.91) and (5.92)–(5.95) are real and respect the symmetries (3.91)–(3.93).

The coefficient c_{10} is undetermined by the analysis presented above. If c_{10} is non-zero, (5.79) and (5.87) give

$$\tilde{L}'_{ijj} = \mathcal{R}'_{ijj} + c_{10}\left(\mathcal{R}'_{jji} + 3\mathcal{R}'_{jji}\right) = 4c_{10}\mathcal{R}'_{jji}. \tag{5.96}$$

Hence (5.89), (5.90) and (5.93), (5.94) are non-zero, and are not compliant with the Post constraint (3.95). Materials that do not violate (3.95) would require $c_{10} = 0$. Materials whose symmetry allows the violation of (3.95), on the other hand, might have a non-zero value of c_{10}.

Case 2: $\tilde{H}'_{ijk} = 0$ and $\tilde{d}_{ijkl} = 0$

The calculations that produce linearly independent solutions for Cases 2–4 ((5.43)–(5.45)) are similar to the calculation for Case 1.

When $\tilde{H}'_{ijk} = 0$ and $\tilde{d}_{ijkl} = 0$, there are two sets of linearly independent origin-independent expressions for $\tilde{\chi}_{ij}$, $\tilde{b}_{ijkl}$ and $\tilde{L}'_{ijk}$ (see `09-li-case2.nb`):

$$\begin{aligned}
\tilde{\chi}_{ij} &= \mathcal{Q}_{ij}, && (5.97)\\
\tilde{b}_{ijkl} &= -\tfrac{1}{4}\mathcal{S}_{ijkl}, && (5.98)\\
\tilde{L}'_{ijk} &= \mathcal{R}'_{ijk} + c_{10}\left(\delta_{ik}\mathcal{R}'_{llj} + \delta_{jk}\mathcal{R}'_{lli}\right) && (5.99)
\end{aligned}$$

and

$$\begin{aligned}
\tilde{\chi}_{ij} &= \mathcal{Q}_{ij}, && (5.100)\\
\tilde{b}_{ijkl} &= -\tfrac{1}{4}\mathcal{S}_{ijkl} - \tfrac{3}{2\omega}\left(\varepsilon_{ijm}\mathcal{R}'_{klm} + \varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{ilm}\mathcal{R}'_{jkm}\right), && (5.101)\\
\tilde{L}'_{ijk} &= 0. && (5.102)
\end{aligned}$$

The solution (5.97)–(5.99) produces the same material constants (5.92)–(5.95) as the solution (5.85)–(5.87), and complies with the Post constraint (3.95) in the same manner. The material constants obtained from the time-even parts of (3.70), (3.73), (3.76), and (3.79) with the replacements $\chi_{ij} \to \tilde{\chi}_{ij}$, $b_{ijkl} \to \tilde{b}_{ijkl}$ and $\{L'_{ijk}, H'_{ijk}, d_{ijkl}\} \to 0$, corresponding to (5.100)–(5.102), are

$$\tilde{A}^{(3)}_{ij} = \mathcal{N}\left[\tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{jkm}\mathcal{R}'_{ilm}\right)\right] k_k k_l, \tag{5.103}$$

$$\tilde{T}^{(3)}_{ij} = U^{(3)}_{ij} = 0, \tag{5.104}$$

$$\tilde{X}^{(3)}_{ij} = -\mathcal{N}\mathcal{Q}_{ij}. \tag{5.105}$$

Because $\tilde{T}^{(3)}_{ij}$ and $\tilde{U}^{(3)}_{ij}$ are both zero, the material constants given by (5.103)–(5.105) contain 12 independent components, and the Post constraint (3.95) is trivially satisfied by (5.100)–(5.102).

Case 3: $\tilde{L}'_{ijk} = 0$ and $\tilde{b}_{ijkl} = 0$

The case when

$$\tilde{L}'_{ijk} = 0 \qquad \text{and} \qquad \tilde{b}_{ijkl} = 0 \tag{5.106}$$

produces two linearly independent solution sets (`10-li-case3.nb`):

$$\tilde{\chi}_{ij} = \mathcal{Q}_{ij} - \tfrac{1}{12}\omega^2\mathcal{S}_{ijkk} + \tfrac{1}{24}\omega^2\delta_{ij}\mathcal{S}_{kkll} + \tfrac{1}{2}\omega\left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}\right), \tag{5.107}$$

$$\begin{aligned}\tilde{d}_{ijkl} = {} & \tfrac{1}{3}\mathcal{S}_{ijkl} + \tfrac{2}{3}(\delta_{ij}\mathcal{S}_{klmm} + \delta_{kl}\mathcal{S}_{ijmm}) - \tfrac{1}{3}(\delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm} + \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm}) \\ & + \tfrac{1}{6}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - 2\delta_{ij}\delta_{kl})\mathcal{S}_{mmnn},\end{aligned} \tag{5.108}$$

$$\tilde{H}'_{ijk} = \mathcal{R}'_{ijk} - \mathcal{R}'_{ikj} - \mathcal{R}'_{jki} + \delta_{ij}\mathcal{R}'_{llk}, \tag{5.109}$$

and

$$\tilde{\chi}_{ij} = \mathcal{Q}_{ij} + \tfrac{1}{2}\omega\left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}\right), \tag{5.110}$$

$$\tilde{d}_{ijkl} = \tfrac{1}{3}\mathcal{S}_{ijkl}, \tag{5.111}$$

$$\tilde{H}'_{ijk} = \mathcal{R}'_{ijk} - \mathcal{R}'_{ikj} - \mathcal{R}'_{jki} + \delta_{ij}\mathcal{R}'_{llk}. \tag{5.112}$$

The material constants obtained from the time-even parts of (3.70), (3.73), (3.76), and (3.79) with the replacements $\chi_{ij} \to \tilde{\chi}_{ij}$, $d_{ijkl} \to \tilde{d}_{ijkl}$, $H'_{ijk} \to \tilde{H}'_{ijk}$ and $\{L'_{ijk}, b_{ijkl}\} \to 0$, corresponding to (5.107)–(5.109), are

$$\begin{aligned}\tilde{A}^{(3)}_{ij} = {} & \tfrac{1}{12}\mathcal{N}\left[\mathcal{S}_{ijkl} - \delta_{kl}\mathcal{S}_{ijmm} + \delta_{jl}\mathcal{S}_{ikmm} + \delta_{il}\mathcal{S}_{jkmm} - \delta_{ij}\mathcal{S}_{klmm}\right. \\ & \left. - \tfrac{1}{2}\delta_{ik}\delta_{jl}\mathcal{S}_{mmnn} + \tfrac{1}{2}\delta_{ij}\delta_{kl}\mathcal{S}_{mmnn}\right] k_k k_l,\end{aligned} \tag{5.113}$$

$$\tilde{T}^{(3)}_{ij} = \tfrac{1}{2}\mathcal{N}\left(\mathcal{R}'_{ijk} - \mathcal{R}'_{ikj} - \mathcal{R}'_{jki} + \delta_{ij}\mathcal{R}'_{llk}\right) k_k = \tilde{T}^{(3)}_{ji}, \tag{5.114}$$

$$\tilde{U}^{(3)}_{ij} = -\tilde{T}^{(3)}_{ij}, \tag{5.115}$$

$$\tilde{X}^{(3)}_{ij} = -\mathcal{N}\left[\mathcal{Q}_{ij} + \tfrac{1}{2}\omega\left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}\right) - \tfrac{1}{12}\omega^2\mathcal{S}_{ijkk} + \tfrac{1}{24}\omega^2\delta_{ij}\mathcal{S}_{kkll}\right]. \tag{5.116}$$

The material constants corresponding to (5.110)–(5.112), are

$$\tilde{A}^{(3)}_{ij} = \tfrac{1}{12}\mathcal{N}\mathcal{S}_{ijkl}k_k k_l, \tag{5.117}$$

$$\tilde{T}^{(3)}_{ij} = \tfrac{1}{2}\mathcal{N}\left(\mathcal{R}'_{ijk} - \mathcal{R}'_{ikj} - \mathcal{R}'_{jki} + \delta_{ij}\mathcal{R}'_{llk}\right) k_k = \tilde{T}^{(3)}_{ji}, \tag{5.118}$$

$$\tilde{U}^{(3)}_{ij} = -\tilde{T}^{(3)}_{ij}, \tag{5.119}$$

$$\tilde{X}^{(3)}_{ij} = -\mathcal{N}\left[\mathcal{Q}_{ij} + \tfrac{1}{2}\omega\left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}\right)\right]. \tag{5.120}$$

The permittivity tensor (5.113) has zero trace, $\tilde{A}^{(3)}_{ii} = 0$, and the magnetoelectric tensors $\tilde{T}^{(3)}_{ij}$ and $\tilde{U}^{(3)}_{ij}$ corresponding to the solutions (5.107)–(5.109) and (5.110)–(5.112) are both symmetric; thus the material constants given by (5.113)–(5.116) contain 17 independent components, and those given by (5.117)–(5.120) contain 18 independent components (see Section 3.5 and (3.92)).

The trace of the magnetoelectric coefficient corresponding to both solutions (5.107)–(5.109) and (5.110)–(5.112) is

$$\begin{aligned}\tilde{T}^{(3)}_{ii} &= \tfrac{1}{2}\mathcal{N}\left(\mathcal{R}'_{iik} - \mathcal{R}'_{iki} - \mathcal{R}'_{iki} + \delta_{ii}\mathcal{R}'_{llk}\right) k_k \\ &= 2\mathcal{N}\mathcal{R}'_{iij} k_j, \end{aligned} \tag{5.121}$$

where (5.19) and the symmetry of $\mathcal{R}'_{ijk}$ in (5.8) were used. From (5.115), (5.119) and (5.121), and since the trace $\mathcal{R}'_{iij}$ is not in general zero, the Post constraint (3.95) is not satisfied by the magnetoelectric coefficients of either solution set (5.107)–(5.109) or (5.110)–(5.112).

Case 4: $\tilde{L}'_{ijk} = 0$ and $\tilde{d}_{ijkl} = 0$

For the case when

$$\tilde{L}'_{ijk} = 0 \qquad \text{and} \qquad \tilde{d}_{ijkl} = 0, \tag{5.122}$$

there are two solutions (`11-li-case4.nb`):

$$\tilde{\chi}_{ij} = \mathcal{Q}_{ij} + \tfrac{1}{2}\omega\left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}\right), \tag{5.123}$$

$$\tilde{b}_{ijkl} = -\tfrac{1}{4}\mathcal{S}_{ijkl}, \tag{5.124}$$

$$\tilde{H}'_{ijk} = \mathcal{R}'_{ijk} - \mathcal{R}'_{ikj} - \mathcal{R}'_{jki} + \delta_{ij}\mathcal{R}'_{llk} \tag{5.125}$$

and

$$\tilde{\chi}_{ij} = \mathcal{Q}_{ij}, \tag{5.126}$$

$$\tilde{b}_{ijkl} = -\tfrac{1}{4}\mathcal{S}_{ijkl} - \tfrac{3}{2\omega}\left(\varepsilon_{ijm}\mathcal{R}'_{klm} + \varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{ilm}\mathcal{R}'_{jkm}\right), \tag{5.127}$$

$$\tilde{H}'_{ijk} = 0. \tag{5.128}$$

The material constants resulting from (5.123)–(5.125) are the same as (5.117)–(5.120) for the solution (5.110)–(5.112), and those from (5.126)–(5.128) correspond with (5.103)–(5.105) for the solution (5.100)–(5.102). As for (5.110)–(5.112), the solution (5.123)–(5.125) is not compliant with the Post constraint (3.95). The solution (5.126)–(5.128), like (5.100)–(5.102), satisfies the Post constraint trivially.

5.1.9 Summary and Discussion

The analysis in Sections 5.1.1–5.1.8 produces eight origin-independent solution sets that satisfy the requirements outlined in Section 5.1. The six solution sets (5.85)–(5.87), (5.97)–(5.99), (5.110)–(5.112), (5.123)–(5.125), (5.100)–(5.102) and (5.126)–(5.128) exhibit a duality between $\tilde{b}_{ijkl}$ and $\tilde{d}_{ijkl}$ [7], and can be combined into three sets of equations

$$\begin{gathered}\tilde{\chi}_{ij} = \mathcal{Q}_{ij}, \\ 3\kappa\tilde{d}_{ijkl} + 4(\kappa-1)\tilde{b}_{ijkl} = \mathcal{S}_{ijkl}, \\ \tilde{L}'_{ijk} = \mathcal{R}'_{ijk} + c_{10}\left(\delta_{ik}\mathcal{R}'_{llj} + \delta_{jk}\mathcal{R}'_{lli}\right), \\ \tilde{H}'_{ijk} = 0, \end{gathered} \tag{5.129}$$

$$\begin{gathered}\tilde{\chi}_{ij} = \mathcal{Q}_{ij} + \tfrac{1}{2}\omega\left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}\right), \\ 3\kappa\tilde{d}_{ijkl} + 4(\kappa-1)\tilde{b}_{ijkl} = \mathcal{S}_{ijkl}, \\ \tilde{L}'_{ijk} = 0, \\ \tilde{H}'_{ijk} = \mathcal{R}'_{ijk} - \mathcal{R}'_{ikj} - \mathcal{R}'_{jki} + \delta_{ij}\mathcal{R}'_{llk}, \end{gathered} \tag{5.130}$$

$$\begin{gathered}\tilde{\chi}_{ij} = \mathcal{Q}_{ij}, \\ 3\kappa \tilde{d}_{ijkl} + 4(\kappa-1)\tilde{b}_{ijkl} = \mathcal{S}_{ijkl} - \tfrac{3}{2\omega}(7\kappa-4)\left(\varepsilon_{ijm}\mathcal{R}'_{klm} + \varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{ilm}\mathcal{R}'_{jkm}\right), \\ \tilde{L}'_{ijk} = \tilde{H}'_{ijk} = 0,\end{gathered} \tag{5.131}$$

where

$$\kappa = 0 \quad \text{or} \quad 1. \tag{5.132}$$

The two solutions sets (5.77)–(5.79) and (5.107)–(5.109) arise because the extra symmetry of $\tilde{d}_{ijkl}$, compared to the symmetry of $\tilde{b}_{ijkl}$ (see Table 2.1 and Section C.7), supports the inclusion of the trace terms of $\mathcal{S}_{ijkl}$ in $\tilde{\chi}_{ij}$ and $\tilde{d}_{ijkl}$ without introducing a linear dependence. These two solution sets can be obtained from (5.129) and (5.130) with $\kappa = 1$ and the addition of

$$-\tfrac{1}{12}\omega^2\mathcal{S}_{ijkk} + \tfrac{1}{24}\omega^2\delta_{ij}\mathcal{S}_{kkll} \tag{5.133}$$

and

$$\begin{gathered}\tfrac{2}{3}(\delta_{ij}\mathcal{S}_{klmm} + \delta_{kl}\mathcal{S}_{ijmm}) - \tfrac{1}{3}(\delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm} + \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm}) \\ +\tfrac{1}{6}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - 2\delta_{ij}\delta_{kl})\mathcal{S}_{mmnn}\end{gathered} \tag{5.134}$$

to $\tilde{\chi}_{ij}$ and $\tilde{d}_{ijkl}$, respectively, in each solution set.

In Section 3.5 it was noted that the constitutive tensor for non-dissipative media has 21 independent components. Materials with structural symmetry may have fewer independent components. The material constants resulting from (5.77)–(5.79) have a permittivity tensor (5.88) with zero trace, $\tilde{A}^{(3)}_{ii} = 0$, which reduces the number of independent components in the constitutive tensor to 20. The material constants resulting from (5.130) and (5.107)–(5.109) have additional symmetry to (3.91)–(3.93), because T_{ij} and U_{ij} are both symmetric for these solutions. This additional symmetry reduces the number of independent components in the constitutive tensor to 18 for the solution (5.130), and to 17 for the solution (5.107)–(5.109), due to the zero trace $\tilde{A}^{(3)}_{ii} = 0$ of (5.113). Solution (5.131) results in $T_{ij} = U_{ij} = 0$, which reduces the number of independent components to only 12. Since there is no basis to assume that *all* non-magnetic materials should be restricted to a symmetric response in $\boldsymbol{D}$ due to $\boldsymbol{B}$, or in $\boldsymbol{H}$ due to $\boldsymbol{E}$ (or no third-order response at all in the case of (5.131)), these solutions should be rejected.

The solutions (5.130) and (5.107)–(5.109) have the additional property that the Post constraint (3.95) is violated. This would imply that all non-magnetic materials exhibiting an electric octopole–magnetic quadrupole response, and whose symmetry does not prohibit (3.95), should necessarily have a measurable property corresponding to (3.96). If a phenomenon is not prohibitted, it may be observed; however, this does not imply that it *must* be observed. Thus the Post constraint also rules out solutions (5.130) and (5.107)–(5.109).

The only pair of solutions, corresponding to the two κ values in (5.132), that is faithful to the symmetries (3.91)–(3.93) of the material constants, and hence allows all 21 independent components in the constitutive tensor, is (5.129), with the corresponding material constants in (5.92)–(5.95). The expression for $\tilde{L}'_{ijk}$ in (5.129) contains the coefficient c_{10} which remains unresolved. If c_{10} is non-zero, (5.129) is not compliant with the Post constraint (3.95). Hence materials that do not violate (3.95) would require $c_{10} = 0$. Materials whose symmetry allows the violation of (3.95), on the other hand, would have a non-zero value of c_{10}. The determination of c_{10} must therefore be postponed to experimental evaluation, or the consideration of additional constraints not recognized here (see also Chapter 6).

The choice whether $\tilde{b}_{ijkl}$ or $\tilde{d}_{ijkl}$ is zero, depending on the value of κ, cannot be resolved from the analysis presented here. The duality of these two tensors is such that the source densities, the property tensors in the source densities, as well as the material constants and hence the response fields, have the same form for either choice [7]. To distinguish between these tensors would also require an experimental verification or additional insight.

Equations (5.129) yield origin-independent expressions for the property tensors Θ_{ijkl} and Φ_{ijkl} when the replacements $\chi_{ij} \to \tilde{\chi}_{ij}$, $b_{ijkl} \to \tilde{b}_{ijkl}$, $d_{ijkl} \to \tilde{d}_{ijkl}$, $L'_{ijk} \to \tilde{L}'_{ijk}$ and $H'_{ijk} \to \tilde{H}'_{ijk}$ are made in (3.27) and (3.33). The same expressions are obtained whether $\kappa = 0$ or $\kappa = 1$. Thus

$$\tilde{\Theta}_{ijkl} = \tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\varepsilon_{ikm}\mathcal{R}'_{jlm} - \tfrac{1}{2\omega}c_{10}\left(\varepsilon_{ijk}\mathcal{R}'_{mml} - \varepsilon_{ikl}\mathcal{R}'_{mmj}\right) \tag{5.135}$$

and

$$\begin{aligned}\tilde{\Phi}_{ikjl} = {} & \tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{jlm}\mathcal{R}'_{ikm}\right) + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}_{mn} \\ & - \tfrac{1}{2\omega}c_{10}\left(\varepsilon_{ijk}\mathcal{R}'_{mml} - \varepsilon_{ijl}\mathcal{R}'_{mmk} - \varepsilon_{ikl}\mathcal{R}'_{mmj} + \varepsilon_{jkl}\mathcal{R}'_{mmi}\right).\end{aligned} \tag{5.136}$$

Because $\tilde{\Theta}_{ijkl}$ and $\tilde{\Phi}_{ikjl}$ contract with the symmetric products $\nabla_j\nabla_k\nabla_l$ and $\nabla_k\nabla_l$, respectively, in the charge and current densities, the order of the subscripts j, k and l in (5.135), and k and l in (5.136) is arbitrary (see Section 3.2).

With the replacements $\chi_{ij} \to \tilde{\chi}_{ij}$, $b_{ijkl} \to \tilde{b}_{ijkl}$, $d_{ijkl} \to \tilde{d}_{ijkl}$, $L'_{ij} \to \tilde{L}'_{ijk}$ and $H'_{ijk} \to \tilde{H}'_{ijk}$ in (5.1) and (5.2), the time-even contributions to the charge and current densities at electric octopole–magnetic quadrupole order for the solution (5.129) are

$$\rho^{(3)} = \mathcal{N}\left(\tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\varepsilon_{ikm}\mathcal{R}'_{jlm}\right)\nabla_j\nabla_k\nabla_l E_i \tag{5.137}$$

and

$$J_i^{(3)} = i\omega\mathcal{N}\left[\tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{jkm}\mathcal{R}'_{ilm}\right) + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}_{mn}\right]\nabla_k\nabla_l E_j. \tag{5.138}$$

The propagation equation to electric octopole–magnetic quadrupole order for non-magnetic media is obtained from (3.49) with the replacements $\Phi_{ijk} \to \tilde{\Phi}_{ijk}$ and $\Phi_{ikjl} \to \tilde{\Phi}_{ikjl}$, (3.29), (4.56), (5.136) and (3.17); thus

$$\begin{aligned}&\Big(\delta_{ij}\nabla^2 - \nabla_i\nabla_j + \mu_0\varepsilon_0\omega^2\delta_{ij} + \mu_0\omega^2\mathcal{N}\Big[\alpha_{ij} - \tfrac{1}{\omega}\left\{\varepsilon_{ikl}v_{jl} - \varepsilon_{jkl}v_{il}\right\}\nabla_k \\ &\qquad - \left\{\tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{jlm}\mathcal{R}'_{ikm}\right) + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}_{mn}\right\}\nabla_k\nabla_l\Big]\Big)E_j = 0.\end{aligned} \tag{5.139}$$

The transition from the non-invariant fields (5.3) and (5.4) to invariant forms, with $\tilde{A}^{(3)}_{ij}$, $\tilde{T}^{(3)}_{ij}$, $\tilde{U}^{(3)}_{ij}$ and $\tilde{X}^{(3)}_{ij}$ given by (5.92)–(5.95), is achieved with the "gauge field"

$$\begin{aligned}H_i^G &= \tfrac{1}{2}\mathcal{T}\left(H'_{jik} - L'_{jki} + \mathcal{R}'_{jki}\right)k_kE_j + \mathcal{T}(\chi_{ij} - \mathcal{Q}_{ij})B_j + \tfrac{1}{2}c_{10}\mathcal{T}(\delta_{ij}\mathcal{R}'_{llk} + \delta_{ik}\mathcal{R}'_{llj})k_kE_j \\ &= \mathcal{T}\left\{\tfrac{1}{4}\left(H'_{jik} - H'_{kij}\right) + \tfrac{1}{16}\left(\delta_{ij}H'_{llk} + \delta_{ik}H'_{llj}\right) - \tfrac{1}{8}\left(\delta_{ij}L'_{kll} + \delta_{ik}L'_{jll}\right) - \tfrac{1}{12}\omega\varepsilon_{ilm}b_{ljkm}\right\}k_kE_j \\ &\quad + \mathcal{T}\left\{\tfrac{1}{4}\omega\left(\varepsilon_{ikl}H'_{kjl} + \varepsilon_{jkl}H'_{kil}\right) + \tfrac{1}{12}\omega^2(d_{ikjk} - d_{ijkk}) + \tfrac{1}{24}\omega^2\delta_{ij}(d_{kkll} - d_{klkl})\right\}B_j \\ &\quad - \tfrac{1}{2}c_{10}\mathcal{T}\left\{\left(\delta_{ij}H'_{lkl} + \delta_{ik}H'_{ljl}\right) - \tfrac{1}{4}\left(\delta_{ij}H'_{llk} + \delta_{ik}H'_{llj}\right) - \left(\delta_{ij}L'_{llk} + \delta_{ik}L'_{llj}\right)\right. \\ &\quad \left. + \tfrac{1}{2}\left(\delta_{ij}L'_{kll} + \delta_{ik}L'_{jll}\right) + \tfrac{1}{6}\omega\left(\delta_{ij}\varepsilon_{klm} + \delta_{ik}\varepsilon_{jlm}\right)b_{lmnn}\right\}k_kE_j,\end{aligned} \tag{5.140}$$

where the linear property (3.9) of the transform $\mathcal{T}$ was used.

The following origin-independent expression corresponding to the AC magnetizability (2.52) has previously been published [51]:

$$\begin{aligned}\alpha^{\mathrm{m}}_{ij} &= \chi_{ij} - \tfrac{1}{2}\omega\left[\varepsilon_{ikl}\left(H'_{jkl} + L'_{jkl}\right) + \varepsilon_{jkl}\left(H'_{ikl} + L'_{ikl}\right)\right] + \omega^2\left[\tfrac{1}{6}\left(b_{ijkk} + b_{jikk}\right) - \tfrac{1}{4}d_{ikjk}\right] \\ &\quad + \tfrac{1}{2}\omega\delta_{ij}\varepsilon_{klm}H'_{klm} - \omega^2\delta_{ij}\left(\tfrac{1}{6}b_{kkll} - \tfrac{1}{8}d_{klkl}\right) \qquad (5.141) \\ &= \mathcal{Q}_{ij} - \tfrac{1}{2}\omega\left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \varepsilon_{jkl}\mathcal{R}'_{ikl}\right) - \tfrac{1}{12}\omega^2\mathcal{S}_{ijkk} + \tfrac{1}{24}\omega^2\delta_{ij}\mathcal{S}_{kkll}, \qquad (5.142)\end{aligned}$$

which differs from the result $\alpha^{\mathrm{m}}_{ij} = \tilde{\chi}_{ij} = \mathcal{Q}_{ij}$ found above (see (5.129)) [7]. The most general origin-independent second-rank expression constructed from $\mathcal{Q}_{ij}$, $\mathcal{R}'_{ijk}$ and $\mathcal{S}_{ijkl}$, and having the symmetry of χ_{ij}, is (see `02-general.nb`)

$$c_1\mathcal{Q}_{ij} + c_2\mathcal{Q}_{kk}\delta_{ij} + c_3\omega\left(\varepsilon_{ikl}\mathcal{R}'_{jkl} + \mathcal{R}'_{ikl}\varepsilon_{jkl}\right) + c_4\omega^2\mathcal{S}_{ijkk} + c_5\omega^2\delta_{ij}\mathcal{S}_{kkll}, \tag{5.143}$$

so that (5.142) corresponds with (5.143) when

$$c_1 = 1, \quad c_2 = 0, \quad c_3 = -\tfrac{1}{2}, \quad c_4 = -\tfrac{1}{12} \quad \text{and} \quad c_5 = \tfrac{1}{24}. \tag{5.144}$$

Equation (5.141) was derived without also considering origin-independent expressions corresponding to b_{ijkl}, d_{ijkl}, L'_{ijk} and H'_{ijk}. Inspection of the eight solutions presented for Cases 1–4 above shows that (5.142) is not a member of a linearly independent set, and is therefore not an acceptable invariant expression for the polarizability χ_{ij} [7]. (The result (5.142) differs from (5.107) only in the sign of the contributions of $\mathcal{R}'_{ijk}$.)

An origin-independent expression for the quadrupole–quadrupole polarizability has also been previously published [52]. In this work it was found that

$$\tilde{d}_{ijkl} = C_1\mathcal{S}_{ijkl} + C_2(\delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm} + \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm}), \tag{5.145}$$

where C_1 and C_2 are arbitrary real numbers. The present work shows that either $C_1 = \frac{1}{3}$ and $C_2 = 0$, or $C_1 = C_2 = 0$ (so that $\tilde{d}_{ijkl} = 0$).

5.2 Electric octopole–magnetic quadrupole order: Magnetic molecules

For magnetic molecules, the contributions at electric octopole–magnetic quadrupole order to the source densities are obtained from (3.27) in (3.21) and (3.33) in (3.22):

$$\begin{aligned}
\rho^{(3)} &= i\mathcal{T}\left[\Pi_{ijkl}\right]\nabla_j\nabla_k\nabla_l E_i \\
&= i\mathcal{T}\left[-\tfrac{1}{6}\left(b'_{ijkl} - b'_{jikl}\right) + \tfrac{1}{4}d'_{ikjl} + \tfrac{1}{2\omega}\varepsilon_{ikm}\left(L_{jlm} - H_{jml}\right)\right]\nabla_j\nabla_k\nabla_l E_i, &(5.146)\\
J^{(3)}_i &= \omega\mathcal{T}\left[\Omega_{ikjl}\right]\nabla_k\nabla_l E_j \\
&= \omega\mathcal{T}\left[-\tfrac{1}{6}\left(b'_{ijkl} - b'_{jikl}\right) + \tfrac{1}{4}d'_{ikjl} + \tfrac{1}{2\omega}\left\{\varepsilon_{ikm}\left(L_{jlm} - H_{jml}\right) - \varepsilon_{jlm}\left(L_{ikm} - H_{imk}\right)\right\}\right. \\
&\qquad \left. + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\chi'_{mn}\right]\nabla_k\nabla_l E_j. &(5.147)
\end{aligned}$$

The contributions to the response fields are obtained from (3.70), (3.73), (3.76) and (3.79) in (3.60) and (3.59):

$$\begin{aligned}
D^{(3)}_i &= A^{(3)}_{ij}E_j + T^{(3)}_{ij}B_j \\
&= i\mathcal{T}\left[\tfrac{1}{6}\left(b'_{ijkl} - b'_{jikl}\right) - \tfrac{1}{4}d'_{ikjl}\right]k_k k_l E_j + i\mathcal{T}\left[\tfrac{1}{2}\left(H_{ijk} - L_{ikj}\right)\right]k_k B_j, &(5.148)\\
H^{(3)}_i &= U^{(3)}_{ij}E_j + X^{(3)}_{ij}B_j \\
&= i\mathcal{T}\left[\tfrac{1}{2}\left(H_{jik} - L_{jki}\right)\right]k_k E_j + i\mathcal{T}\left[\chi'_{ij}\right]B_j. &(5.149)
\end{aligned}$$

Neither the property tensors Π_{ijkl} and Ω_{ikjl}, nor the material constants $A^{(3)}_{ij}$, $T^{(3)}_{ij}$, $U^{(3)}_{ij}$ and $X^{(3)}_{ij}$, are origin independent. As noted in Section 3.2, the induced source densities are origin independent because Π_{ijkl} and Ω_{ikjl} contract with the symmetric products $\nabla_j\nabla_k\nabla_l$ and $\nabla_k\nabla_l$, respectively. In the following sections, origin-independent expressions corresponding to the time-odd molecular polarizability tensors χ'_{ij}, b'_{ijkl}, d'_{ijkl}, L_{ijk} and H_{ijk} are determined. These origin-independent expressions have at least the symmetry of their origin-dependent counterparts, they leave the induced source densities (5.146) and (5.147) unchanged, and yield physically acceptable forms for the response fields (5.148) and (5.149).

The MATHEMATICA notebooks referred to in this section are contained in the directory `mathematica/e3m2-m` on the accompanying CD.

5.2.1 Time-odd basis tensors of electric octopole–magnetic quadrupole order

The calculation to determine the time-odd basis tensors at electric octopole–magnetic quadrupole order for magnetic molecules is performed in the notebook `01-basis.nb`. It is found that there are just two linearly independent invariant tensors, in terms of which all time-odd origin-independent expressions at electric octopole–magnetic quadrupole order can be expressed. These are

$$\begin{aligned}\mathcal{Q}'_{ij} &= \chi'_{ij} - \tfrac{1}{4}\omega\varepsilon_{ijk}L_{kll} + \tfrac{3}{8}\omega\varepsilon_{ijk}H_{llk} && (5.150)\\ &= -\,\mathcal{Q}'_{ji} && (5.151)\end{aligned}$$

and

$$\begin{aligned}\mathcal{R}_{ijk} &= L_{ijk} - \tfrac{1}{4}(\delta_{ik}L_{jll} + \delta_{jk}L_{ill}) - \tfrac{1}{2}(H_{ikj} + H_{jki}) + \tfrac{1}{8}(\delta_{ik}H_{llj} + \delta_{jk}H_{lli})\\ &\quad + \omega\varepsilon_{klm}\left(\tfrac{1}{4}d'_{iljm} - \tfrac{1}{3}b'_{lijm}\right) && (5.152)\\ &= \mathcal{R}_{jik}. && (5.153)\end{aligned}$$

There are no linearly independent, invariant linear extensions of H_{ijk}, b'_{ijkl} or d'_{ijkl}. The symmetries (5.151) and (5.153) follow from the intrinsic symmetries of χ'_{ij}, b'_{ijkl}, d'_{ijkl}, L_{ijk} and H_{ijk} (see Table 2.1).

5.2.2 General invariant expressions

General origin-independent precursor expressions, corresponding to the time-odd molecular polarizability tensors at electric octopole–magnetic quadrupole order, can be written down in terms of (5.150), (5.152) and the general isotropic tensors (C.16)–(C.19). They are:

$$\begin{aligned}\tilde{\chi}'_{ij} &= I_{ijkl}\mathcal{Q}'_{kl} + \omega I_{ijklm}\mathcal{R}_{klm}, && (5.154)\\ \tilde{b}'_{ijkl} &= \omega^{-2}I_{ijklmn}\mathcal{Q}'_{mn} + \omega^{-1}I_{ijklmnp}\mathcal{R}_{mnp}, && (5.155)\\ \tilde{d}'_{ijkl} &= \omega^{-2}I_{ijklmn}\mathcal{Q}'_{mn} + \omega^{-1}I_{ijklmnp}\mathcal{R}_{mnp}, && (5.156)\\ \tilde{L}_{ijk} &= \omega^{-1}I_{ijklm}\mathcal{Q}'_{lm} + I_{ijklmn}\mathcal{R}_{lmn}, && (5.157)\\ \tilde{H}_{ijk} &= \omega^{-1}I_{ijklm}\mathcal{Q}'_{lm} + I_{ijklmn}\mathcal{R}_{lmn}, && (5.158)\end{aligned}$$

where the factors involving ω have been introduced to make the arbitrary coefficients c_i in the isotropic tensors $I_{ij\ldots}$ dimensionless. Again, in practice, it is easier to construct the precursor expressions from the building blocks in Section H.4 (see `02-general.nb`).

5.2.3 DC limit

Inspection of (2.45), (2.47), (2.48), (2.50), (2.53), (2.54), (5.150) and (5.152), shows that each term in (5.155) and (5.156), except those involving b'_{ijkl} or d'_{ijkl}, which are proportional to ω (see (2.45) and (2.47)), is singular when $\omega \to 0$. At electric octopole–magnetic quadrupole order, for the time-odd molecular polarizabilities, no origin-independent combination can be constructed only from b'_{ijkl} or d'_{ijkl}. Thus

$$\begin{aligned}\tilde{b}'_{ijkl} &= 0, && (5.159)\\ \tilde{d}'_{ijkl} &= 0. && (5.160)\end{aligned}$$

After the symmetries of χ'_{ij} and L_{ijk} (see Table 2.1) are enforced on (5.154) and (5.157) — or when these are constructed from the building blocks in Sections H.4 — the three remaining invariant expressions $\tilde{\chi}'_{ij}$, $\tilde{L}_{ijk}$ and $\tilde{H}_{ijk}$ contain 23 unknown coefficients.

5.2.4 The trace of the magnetic quadrupole moment is zero

The quantum-mechanical expression for the time-odd electric dipole–magnetic quadrupole polarizability tensor H_{ijk} in (2.48) contains matrix elements of the magnetic quadrupole moment operator which, in the absence of spin, has a vanishing trace (see also Section 5.1.4). This translates in H_{ijk} to

$$H_{ijj} = 0. \tag{5.161}$$

The precursor expressions $\tilde{\chi}'_{ij}$, $\tilde{L}_{ijk}$ and $\tilde{H}_{ijk}$ all contain terms involving the trace of $\mathcal{R}_{ijk}$. From (5.152), and the symmetries of b'_{ijkl} and d'_{ijkl} (see Table 2.1), it follows that

$$\mathcal{R}_{ijj} = -\tfrac{1}{2}H_{ijj} = 0. \tag{5.162}$$

Thus, the contributions (H.82) in (5.154), (H.111) and (H.112) in (5.157), and (H.129)–(H.131) in (5.158) can be omitted.

The relation (5.161) is a property of the polarizability tensor H_{ijk}; thus the invariant counterpart $\tilde{H}_{ijk}$ should also have this property. The requirement

$$\tilde{H}_{ijj} = 0 \tag{5.163}$$

results in three relations between the coefficients of $\tilde{H}_{ijk}$ (see `03-trace-m2.nb`). The above means that nine unknown coefficients are resolved, or multiply expressions that are zero, so leaving 14.

Note that in Reference 8 it was assumed that for magnetic molecules the trace of the magnetic quadrupole moment is in general not zero, and hence the trace $\tilde{H}_{ijj}$ was included in the analysis.

5.2.5 Gauss' law for magnetism

The expression for the induced electric dipole moment density $\tilde{P}_i$ in (4.1) contains the term $\frac{1}{2}\mathcal{N}\tilde{H}_{ijk}\nabla_k B_j$. Occurrences of δ_{jk} in the expression for $\tilde{H}_{ijk}$ will result in $\delta_{jk}\nabla_k B_j = \boldsymbol{\nabla}\cdot\boldsymbol{B} = 0$. The expression for $\tilde{H}_{ijk}$ after Section 5.2.4 is (see `03-trace-m2.nb`)

$$\begin{aligned}\tilde{H}_{ijk} = {}& c_9\tfrac{1}{\omega}\varepsilon_{jkl}\mathcal{Q}'_{il} - c_{10}\tfrac{1}{\omega}\left(\varepsilon_{ikl}\mathcal{Q}'_{jl} - \delta_{ij}\varepsilon_{klm}\mathcal{Q}'_{lm}\right) - c_{11}(\mathcal{R}_{ijk} - \mathcal{R}_{ikj}) \\ & - (c_{12}+c_{13}+3c_{14})\mathcal{R}_{jki} + c_{12}\delta_{ij}\mathcal{R}_{llk} + c_{13}\delta_{ik}\mathcal{R}_{llj} + c_{14}\delta_{jk}\mathcal{R}_{lli}.\end{aligned} \tag{5.164}$$

Thus the contribution to $\tilde{P}_i$ of the last term in (5.164), with coefficient c_{14}, is zero. Omitting this term from (5.164) does not change the origin independence of $\tilde{H}_{ijk}$, so that c_{14} may still be specified arbitrarily. When (5.150) and (5.152) are substituted into (5.164), the only occurrences of δ_{jk} are in the expression multiplied by c_{10}, namely

$$\begin{aligned}&-\tfrac{1}{\omega}\left(\varepsilon_{ikl}\mathcal{Q}'_{jl} - \delta_{ij}\varepsilon_{klm}\mathcal{Q}'_{lm}\right) = \\ &\qquad -\tfrac{1}{\omega}\left(\varepsilon_{ikl}\chi'_{jl} - \delta_{ij}\varepsilon_{klm}\chi'_{lm}\right) - \tfrac{3}{8}(\delta_{jk}H_{lli} - 3\delta_{ij}H_{llk}) - \tfrac{1}{4}(3\delta_{ij}L_{kll} - \delta_{jk}L_{ill}).\end{aligned} \tag{5.165}$$

The contribution of (5.165) to the induced dipole moment density is

$$\begin{aligned}P_i &= \cdots + \tfrac{1}{2}\mathcal{T}\left[\tilde{H}_{ijk}\right]\nabla_k B_j + \cdots \\ &= \cdots + \tfrac{1}{2}\mathcal{T}\left[\cdots - c_{10}\tfrac{1}{\omega}\left(\varepsilon_{ikl}\mathcal{Q}'_{jl} - \delta_{ij}\varepsilon_{klm}\mathcal{Q}'_{lm}\right)\nabla_k B_j + \cdots\right] + \cdots \\ &= \cdots + \tfrac{1}{2}\mathcal{T}\left[\cdots - c_{10}\left\{\tfrac{1}{\omega}\left(\varepsilon_{ikl}\chi'_{jl} - \delta_{ij}\varepsilon_{klm}\chi'_{lm}\right) + \tfrac{9}{8}\delta_{ij}H_{llk} + \tfrac{3}{4}\delta_{ij}L_{kll}\right\}\nabla_k B_j + \cdots\right] + \cdots.\end{aligned} \tag{5.166}$$

The two terms involving δ_{jk} in (5.165) have been omitted from the last line of (5.166), because they produce $\boldsymbol{\nabla} \cdot \boldsymbol{B}$. Consequently, the expression in curly brackets in (5.166) does not possess the origin independence of (5.165). Thus the weighted transform $\mathcal{T}[\cdots]$ in (5.166) cannot be replaced by (3.17) to obtain an origin-independent expression for the induced dipole moment density P_i. Origin independence of $\tilde{H}_{ijk}$ in the expression for $\tilde{P}_i$, and hence an origin-independent expression for $\tilde{P}_i$, can be obtained by setting (see `04-divB.nb`)

$$c_{10} = 0. \tag{5.167}$$

At electric quadrupole–magnetic dipole order for magnetic molecules (Section 4.4), the term $-\frac{1}{\omega}\delta_{jl}G_{mm}$ is added to the property tensor Π_{ijk}, through its appearance in the invariant basis tensor w_{ij} in (4.80), resulting in the origin-independent property tensor $\tilde{\Pi}_{ijk}$ (see for example (4.107)). When $\tilde{\Pi}_{ijk}$ is used in the charge density (4.68) instead of Π_{ijk}, the same expression for the charge density is obtained. This is because the symmetry of the field gradients $\nabla_k\nabla_l$ in (4.68) allows the subscript j in the addition $-\frac{1}{\omega}\delta_{jl}G_{mm}$ to be replaced by k. Hence the additional term $-\frac{1}{\omega}\delta_{kl}G_{mm}$ contracts to zero with the antisymmetric tensor ε_{ikl}.

One may argue that the consideration of Gauss' law for magnetism in this section is similar to the role that the term $\delta_{ij}G_{kk}$ plays in w_{ij}. However, it should be noted that the charge density (4.126) is identical to (4.68), which is origin independent regardless of whether the term $\delta_{jl}G_{mm}$ is present or not. In the expressions for the induced multipole moments (4.1) and (4.4), the response fields (4.129) and (4.130) and the material constants (4.116)–(4.119), there is no contraction that renders the terms proportional to $\delta_{ij}G_{kk}$ zero.

5.2.6 Comparison of bound source densities

After the considerations of Sections 5.2.3–5.2.5, the origin-independent expressions corresponding to χ'_{ij}, b'_{ijkl}, d'_{ijkl}, L_{ijk} and H_{ijk} are

$$\tilde{\chi}'_{ij} = c_1\mathcal{Q}'_{ij} + c_2\omega\varepsilon_{ijk}\mathcal{R}_{llk}, \tag{5.168}$$

$$\tilde{b}'_{ijkl} = \tilde{d}'_{ijkl} = 0, \tag{5.169}$$

$$\begin{aligned}\tilde{L}_{ijk} &= c_3\tfrac{1}{\omega}\left(\varepsilon_{ikl}\mathcal{Q}'_{jl} + \varepsilon_{jkl}\mathcal{Q}'_{il}\right) + c_4\tfrac{1}{\omega}\delta_{ij}\varepsilon_{klm}\mathcal{Q}'_{lm} \\ &\quad + c_5\mathcal{R}_{ijk} + c_6(\mathcal{R}_{ikj} + \mathcal{R}_{jki}) + c_7\delta_{ij}\mathcal{R}_{llk} + c_8(\delta_{ik}\mathcal{R}_{llj} + \delta_{jk}\mathcal{R}_{lli}),\end{aligned} \tag{5.170}$$

$$\begin{aligned}\tilde{H}_{ijk} &= c_9\tfrac{1}{\omega}\varepsilon_{jkl}\mathcal{Q}'_{il} - c_{10}(\mathcal{R}_{ijk} - \mathcal{R}_{ikj}) - (c_{11} + c_{12} + 3c_{13})\mathcal{R}_{jki} \\ &\quad + c_{11}\delta_{ij}\mathcal{R}_{llk} + c_{12}\delta_{ik}\mathcal{R}_{llj} + c_{13}\delta_{jk}\mathcal{R}_{lli}.\end{aligned} \tag{5.171}$$

In (5.171) the replacements $c_{11} \to c_{10}$, $c_{12} \to c_{11}$, $c_{13} \to c_{12}$ and $c_{14} \to c_{13}$ were made after the substitution of (5.167). Based on (5.146) and (5.147), comparison of the source densities takes the forms

$$\rho^{(3)}\left(b'_{ijkl}, d'_{ijkl}, L_{ijk}, H_{ijk}\right) = \rho^{(3)}\left(\tilde{b}'_{ijkl}, \tilde{d}'_{ijkl}, \tilde{L}_{ijk}, \tilde{H}_{ijk}\right), \tag{5.172}$$

$$J_i^{(3)}\left(\chi'_{ij}, b'_{ijkl}, d'_{ijkl}, L_{ijk}, H_{ijk}\right) = J_i^{(3)}\left(\tilde{\chi}'_{ij}, \tilde{b}'_{ijkl}, \tilde{d}'_{ijkl}, \tilde{L}_{ijk}, \tilde{H}_{ijk}\right). \tag{5.173}$$

First, the replacements $\chi'_{ij} \to \tilde{\chi}'_{ij}$, $L_{ijk} \to \tilde{L}_{ijk}$, $H_{ijk} \to \tilde{H}_{ijk}$ and $\{b'_{ijkl}, d'_{ijkl}\} \to 0$ are made in (5.146) and (5.147), followed by the substitution of (5.150) and (5.152). The resulting expressions contain terms involving various traces of H_{ijk}. Before continuing with the comparisons (5.172) and (5.173), these traces should be eliminated using identities, based on (C.8), such as

$$\varepsilon_{ijk}H_{llk} = \varepsilon_{ijl}H_{lkk} - \varepsilon_{jkl}H_{kil} + \varepsilon_{ikl}H_{kjl}, \tag{5.174}$$

followed by the replacement $H_{lkk} \to 0$ (see Section 5.2.4). This ensures that the zero trace of H_{ijk} (5.163) is not contained in other combinations of terms involving H_{ijk} (see `05-source.nb`, where all the different traces and the identities used to eliminate them are listed). As an alternative to eliminating the traces of H_{ijk} as described above, the replacement $H_{izz} = -(H_{ixx} + H_{iyy})$ can be made after the components in the differences corresponding to (5.172) and (5.173) have been calculated.

The equality (5.172) requires

$$\begin{aligned} c_{13} &= -\tfrac{1}{3}(c_5 + 2c_6 + c_7 + c_{11} - 1), \\ c_{12} &= c_7, \\ c_{10} &= c_5 - 1, \\ c_9 &= 2c_4, \\ c_3 &= 0, \end{aligned} \tag{5.175}$$

and (5.173) requires

$$\begin{aligned} c_{11} &= -\tfrac{1}{2}(2c_2 - c_5 - c_6 - 2c_8 + 1), \\ c_4 &= \tfrac{1}{2}(c_1 - 1). \end{aligned} \tag{5.176}$$

The invariant expressions corresponding to corresponding to χ'_{ij}, b'_{ijjk}, d'_{ijkl}, L_{ijk} and H_{ijk}, obtained from (5.168)–(5.171) with (5.175) and (5.176), are

$$\tilde{\chi}'_{ij} = c_1 \mathcal{Q}'_{ij} + c_2 \omega \varepsilon_{ijk} \mathcal{R}_{llk} \tag{5.177}$$

$$\tilde{b}'_{ijkl} = \tilde{d}'_{ijkl} = 0, \tag{5.178}$$

$$\begin{aligned} \tilde{L}_{ijk} &= c_5 \mathcal{R}_{ijk} + c_6(\mathcal{R}_{ikj} + \mathcal{R}_{jki}) + c_7 \delta_{ij} \mathcal{R}_{llk} + c_8(\delta_{ik} \mathcal{R}_{llj} + \delta_{jk} \mathcal{R}_{lli}) \\ &\quad + (c_1 - 1)\tfrac{1}{2\omega} \delta_{ij} \varepsilon_{klm} \mathcal{Q}'_{lm}, \end{aligned} \tag{5.179}$$

$$\begin{aligned} \tilde{H}_{ijk} &= (c_5 - 1)(\mathcal{R}_{ikj} - \mathcal{R}_{ijk}) + (c_5 + 2c_6 - 1)\mathcal{R}_{jki} \\ &\quad - \tfrac{1}{2}(2c_2 - c_5 - c_6 - 2c_8 + 1)\delta_{ij} \mathcal{R}_{llk} + c_7 \delta_{ik} \mathcal{R}_{llj} \\ &\quad + \tfrac{1}{6}(2c_2 - 3c_5 - 5c_6 - 2c_7 - 2c_8 + 3)\delta_{jk} \mathcal{R}_{lli} + (c_1 - 1)\tfrac{1}{\omega} \varepsilon_{jkl} \mathcal{Q}'_{il}. \end{aligned} \tag{5.180}$$

5.2.7 Linear independence

At electric octopole–magnetic quadrupole order for magnetic molecules, there are only two time-odd basis tensors (5.150) and (5.152). There can therefore be only two linearly independent origin-independent expressions corresponding to the molecular polarizability tensors. The occurrences of $\mathcal{Q}'_{ij}$ in $\tilde{L}_{ijk}$ and $\tilde{H}_{ijk}$ in (5.179) and (5.180) contain at most one free subscript (i). As is evident from (5.177), where $\mathcal{Q}'_{ij}$ occurs with two free subscripts (i and j), it is not possible to obtain $\tilde{\chi}'_{ij}$ from a linear combination of $\tilde{L}_{ijk}$ and $\tilde{H}_{ijk}$. Thus $\tilde{\chi}'_{ij}$ must be non-zero, and either $\tilde{L}_{ijk}$ or $\tilde{H}_{ijk}$ must be zero. By construction, the terms on the right-hand sides of (5.179) and (5.180) are linearly independent. The conditions on the unknown coefficients c_1 to c_8 that result in $\tilde{L}'_{ijk} = 0$ or $\tilde{H}'_{ijk} = 0$ can therefore be determined by inspection of (5.179) and (5.180). The resulting expressions are required in subsequent calculations, so they are nevertheless determined using MATHEMATICA (see `06-li-cases.nb`).

Case 1: $\tilde{H}_{ijk} = 0$

From (5.180),

$$\tilde{H}_{ijk} = 0 \tag{5.181}$$

is attained when

$$\begin{aligned} c_1 = c_5 &= 1, \\ c_6 = c_7 &= 0, \\ c_8 &= c_2. \end{aligned} \tag{5.182}$$

The resulting expressions for $\tilde{\chi}'_{ij}$ and $\tilde{L}_{ijk}$ with (5.182) can be obtained by inspection, and are linearly independent (see `07-li-H-zero.nb`). Thus

$$\tilde{\chi}'_{ij} = \mathcal{Q}'_{ij} + c_2\omega\varepsilon_{ijk}\mathcal{R}_{llk} \tag{5.183}$$

and

$$\tilde{L}_{ijk} = \mathcal{R}_{ijk} + c_2(\delta_{ik}\mathcal{R}_{llj} + \delta_{jk}\mathcal{R}_{lli}). \tag{5.184}$$

Origin-independent contributions to the material constants, at electric octopole–magnetic quadrupole order for magnetic media, are obtained from the time-odd parts of (3.70), (3.73), (3.76) and (3.79), with the replacements $\chi'_{ij} \to \tilde{\chi}'_{ij}$, $L_{ijk} \to \tilde{L}_{ijk}$ and $\{b'_{ijkl}, d'_{ijkl}, H_{ijk}\} \to 0$. The resulting expressions are

$$\tilde{A}^{(3)}_{ij} = 0, \tag{5.185}$$

$$T^{(3)}_{ij} = -\tfrac{1}{2}i\mathcal{N}\left[\mathcal{R}_{ikj} + c_2\left(\delta_{ij}\mathcal{R}_{llk} + \delta_{jk}\mathcal{R}_{lli}\right)\right]k_k, \tag{5.186}$$

$$\tilde{U}^{(3)}_{ij} = \tilde{T}^{(3)}_{ji} = -\left(\tilde{T}^{(3)}_{ji}\right)^*, \tag{5.187}$$

$$\tilde{X}^{(3)}_{ij} = i\mathcal{N}\left[\mathcal{Q}'_{ij} + c_2\omega\varepsilon_{ijk}\mathcal{R}_{llk}\right]. \tag{5.188}$$

Because $\tilde{A}^{(3)}_{ij} = 0$, the time-odd contributions (5.185)–(5.188) at electric octopole–magnetic quadrupole order represent 15 independent components in the constitutive tensor.

By inspection of (5.186) and (5.187) it is evident that the solution (5.184) is compliant with the Post constraint (3.95).

Case 2: $\tilde{L}_{ijk} = 0$

$\tilde{L}_{ijk} = 0$ can be determined by inspection of (5.179). The solution is

$$\begin{aligned} c_1 &= 1, \\ c_5 = c_6 = c_7 = c_8 &= 0. \end{aligned} \tag{5.189}$$

Linear independence of $\tilde{\chi}'_{ij}$ and $\tilde{H}_{ijk}$, when $\tilde{L}_{ijk} = 0$, requires

$$c_2 = -\tfrac{3}{2} \tag{5.190}$$

(see `08-li-L-zero.nb`). Equations (5.177) and (5.180) with (5.189) and (5.190) become

$$\tilde{\chi}'_{ij} = \mathcal{Q}'_{ij} - \tfrac{3}{2}\omega\varepsilon_{ijk}\mathcal{R}_{llk} \tag{5.191}$$

and

$$\tilde{H}_{ijk} = \mathcal{R}_{ijk} - \mathcal{R}_{ikj} - \mathcal{R}_{jki} + \delta_{ij}\mathcal{R}_{kll}. \tag{5.192}$$

Origin-independent contributions to the material constants, at electric octopole–magnetic quadrupole order for magnetic media, are obtained from the time-odd parts of (3.70), (3.73), (3.76), and (3.79), with the replacements $\chi'_{ij} \to \tilde{\chi}'_{ij}$, $H_{ijk} \to \tilde{H}_{ijk}$ and $\{b'_{ijkl}, d'_{ijkl}, L_{ijk}\} \to 0$. The resulting expressions are

$$\tilde{A}_{ij}^{(3)} = 0, \tag{5.193}$$

$$T_{ij}^{(3)} = \tfrac{1}{2} i\mathcal{N} \left[\mathcal{R}_{ijk} - \mathcal{R}_{ikj} - \mathcal{R}_{jki} + \delta_{ij}\mathcal{R}_{llk}\right] k_k = \tilde{T}_{ji}^{(3)}, \tag{5.194}$$

$$\tilde{U}_{ij}^{(3)} = \tilde{T}_{ij}^{(3)} = -\left(\tilde{T}_{ji}^{(3)}\right)^*, \tag{5.195}$$

$$\tilde{X}_{ij}^{(3)} = i\mathcal{N}\left[\mathcal{Q}'_{ij} - \tfrac{3}{2}\omega\varepsilon_{ijk}\mathcal{R}_{llk}\right]. \tag{5.196}$$

Because $\tilde{A}_{ij}^{(3)} = 0$, and $\tilde{T}_{ij}^{(3)}$ and $\tilde{U}_{ij}^{(3)}$ are both symmetric (see (5.194) and (5.195)) for the solutions (5.191) and (5.192), the time-odd contributions (5.193)–(5.196) represent only 12 independent components in the constitutive tensor.

Inspection of (5.194) and (5.195) shows that the solution (5.192) is also compliant with the Post constraint (3.95).

5.2.8 Summary and Discussion

For non-dissipative media, the symmetries (3.91)–(3.93) restrict the maximum number of independent components in the constitutive tensor to 21 (see Section 3.5). At electric octopole–magnetic quadrupole order, the time-odd contribution to the electric permittivity (3.70) is

$$A_{ij}^{(3)} = \mathcal{T}\left[\tfrac{i}{6}\left(b'_{ijkl} - b'_{jikl}\right) - \tfrac{i}{4} d'_{ikjl}\right] k_k k_l. \tag{5.197}$$

Since the origin-independent counterparts of the time-odd tensors b'_{ijkl} and d'_{ijkl} at electric octopole–magnetic quadrupole order are both zero (see Section 5.2.3), the invariant permittivity contribution $\tilde{A}_{ij}^{(3)}$, obtained by making the replacements $b'_{ijkl} \to \tilde{b}'_{ijkl}$ and $d'_{ijkl} \to \tilde{d}'_{ijkl}$ in (5.197), is zero. The contribution to the constitutive tensor, from the time-odd tensors at electric octopole–magnetic quadrupole order, can therefore have at most 15 independent components. The solutions that place the least restriction on the allowed symmetries of macroscopic magnetic media at electric octopole–magnetic quadrupole order, and which allow all 15 possible independent components in the constitutive tensor, are (5.183) and (5.184) of Case 1 above. The solutions (5.191) and (5.192) for Case 2 allow only 12 independent components in the constitutive tensor, and should therefore be rejected.

The Post constraint (3.95) for the time-odd contributions (5.186) and (5.187) at electric octopole–magnetic quadrupole order is automatically satisfied, as discussed in Section 3.5.

From (5.178) and Case 1 above, the origin-independent expressions corresponding to the time-odd molecular polarizabilities at electric octopole–magnetic quadrupole order are

$$\tilde{\chi}'_{ij} = \mathcal{Q}'_{ij} + c_2\omega\varepsilon_{ijk}\mathcal{R}_{llk}, \tag{5.198}$$

$$\tilde{L}_{ijk} = \mathcal{R}_{ijk} + c_2(\delta_{ik}\mathcal{R}_{llj} + \delta_{jk}\mathcal{R}_{lli}), \tag{5.199}$$

$$\tilde{b}'_{ijkl} = \tilde{d}'_{ijkl} = \tilde{H}_{ijk} = 0. \tag{5.200}$$

It is possible to write $\tilde{\chi}'_{ij}$ in terms of the trace of $\tilde{L}_{ijk}$ by combining (5.198) and (5.199); then

$$\tilde{\chi}'_{ij} = \mathcal{Q}'_{ij} + \frac{c_2\omega}{2c_2+1}\varepsilon_{ijk}\tilde{L}_{llk}. \tag{5.201}$$

To eliminate such a functional dependency requires

$$c_2 = 0, \tag{5.202}$$

in which case (5.198) and (5.199) become

$$\tilde{\chi}'_{ij} = \mathcal{Q}'_{ij}, \tag{5.203}$$

$$\tilde{L}_{ijk} = \mathcal{R}_{ijk}. \tag{5.204}$$

The solutions (5.203) and (5.204) correspond with the solutions published in Reference 8, where a trace term involving $\mathcal{R}_{ijj}$, which is zero if spin is not included (see Section 5.2.4), is incorporated in $\mathcal{Q}'_{ij}$.

Equations (5.198)–(5.200) yield origin-independent expressions for the property tensors Π_{ijkl} and Ω_{ikjl} when the replacements $\chi'_{ij} \to \tilde{\chi}'_{ij}$, $L_{ijk} \to \tilde{L}_{ijk}$ and $\{b'_{ijkl}, d'_{ijkl}, H_{ijk}\} \to 0$ are made in (3.28) and (3.34). Thus

$$\tilde{\Pi}_{ijkl} = \tfrac{1}{2\omega}\left[\varepsilon_{ikm}\mathcal{R}_{jlm} + c_2\left(\varepsilon_{ikl}\mathcal{R}_{mmj} - \varepsilon_{ijk}\mathcal{R}_{mml}\right)\right] \tag{5.205}$$

and

$$\tilde{\Omega}_{ikjl} = \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}'_{mn} + \tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}_{jlm} - \varepsilon_{jlm}\mathcal{R}_{ikm}\right) + c_2\tfrac{1}{\omega}\left(\varepsilon_{ikl}\mathcal{R}_{mmj} + \varepsilon_{jkl}\mathcal{R}_{mmi}\right). \tag{5.206}$$

It is easily verified that $\tilde{\Omega}_{ikjl}$ possesses the symmetry (3.42).

The solutions (5.183) and (5.184) of Case 1, and (5.191) and (5.192) of Case 2, in Section 5.2.7, result in the same expressions for the time-odd contributions to the charge and current densities at electric octopole–magnetic quadrupole; namely

$$\rho^{(\bar{3})} = \tfrac{1}{2\omega}i\mathcal{N}\varepsilon_{ikm}\mathcal{R}_{jlm}\nabla_j\nabla_k\nabla_l E_i, \tag{5.207}$$

$$J_i^{(\bar{3})} = \mathcal{N}\left[\tfrac{1}{2}\left(\varepsilon_{ikm}\mathcal{R}_{jlm} - \varepsilon_{jlm}\mathcal{R}_{ikm}\right) + \tfrac{1}{\omega}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}'_{mn}\right]\nabla_k\nabla_l E_j. \tag{5.208}$$

The propagation equation to electric octopole–magnetic quadrupole order in magnetic media is obtained from (3.49) with the replacements $\Phi_{ijk} \to \tilde{\Phi}_{ijk}$, $\Omega_{ijk} \to \tilde{\Omega}_{ijk}$, $\Phi_{ikjl} \to \tilde{\Phi}_{ikjl}$ and $\Omega_{ikjl} \to \tilde{\Omega}_{ikjl}$, (3.29), (3.30), (4.56), (4.125), (5.136), (5.206) and (3.17); thus

$$\begin{aligned}\big(\delta_{ij}\nabla^2 - \nabla_i\nabla_j + \mu_0\varepsilon_0\omega^2\delta_{ij} + \mu_0\omega^2\mathcal{N}\big[\alpha_{ij} - i\alpha'_{ij} \\ - \tfrac{1}{\omega}\left\{\varepsilon_{ikl}v_{jl} - \varepsilon_{jkl}v_{il}\right\}\nabla_k + \tfrac{i}{\omega}\left\{\varepsilon_{ikl}w_{jl} + \varepsilon_{jkl}w_{il} - \omega s_{ijk}\right\}\nabla_k \\ - \left\{\tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{jlm}\mathcal{R}'_{ikm}\right) + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}_{mn}\right\}\nabla_k\nabla_l \\ +i\left\{\tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}_{jlm} - \varepsilon_{jlm}\mathcal{R}_{ikm}\right) + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}'_{mn}\right\}\nabla_k\nabla_l\big]\big)E_j = 0.\end{aligned} \tag{5.209}$$

The transition from the non-invariant fields (5.148) and (5.149) to invariant forms, with $\tilde{A}_{ij}^{(\bar{3})}$, $\tilde{T}_{ij}^{(\bar{3})}$, $\tilde{U}_{ij}^{(\bar{3})}$ and $\tilde{X}_{ij}^{(\bar{3})}$ given by (5.185)–(5.188), is achieved with the "gauge field"

$$\begin{aligned}H_i^G = & -\tfrac{1}{2}\mathcal{T}\left(H_{jik} - L_{jki} + \mathcal{R}_{jki}\right)k_k E_j - \mathcal{T}\left(\chi'_{ij} - \mathcal{Q}'_{ij}\right)B_j \\ & -\tfrac{1}{2}c_2\mathcal{T}\left(\delta_{ij}\mathcal{R}_{llk} + \delta_{ik}\mathcal{R}_{llk}\right)k_k E_j + c_2\omega\mathcal{T}\left(\varepsilon_{ijk}\mathcal{R}_{llk}\right)B_j,\end{aligned} \tag{5.210}$$

where the linear property (3.9) of the transform $\mathcal{T}$ was used. Alternative expressions, where the origin-independent basis tensors $\mathcal{Q}'_{ij}$ and $\mathcal{R}_{ijk}$ are eliminated in favour of χ'_{ij}, b'_{ijkl}, d'_{ijkl}, L_{ijk} and H_{ijk}, or Faraday's law is used to write the magnetic field $\boldsymbol{B}$ in terms of $\boldsymbol{E}$, are presented in the notebook `10-gauge.nb`.

The expressions (5.198)–(5.200) differ from those presented in Reference 8. Firstly, the definition of the origin-independent basis tensor $\mathcal{Q}'_{ij}$ in (5.150) does not include the trace term

$$-\tfrac{1}{4}\omega\varepsilon_{ijk}\mathcal{R}_{kll} = \tfrac{1}{8}\omega\varepsilon_{ijk}H_{kll}, \tag{5.211}$$

which was introduced in Reference 8 to 'simplify the analysis'. This modification has no effect on the final expressions as (5.211) is identically zero in the absence of spin. Secondly, in Reference 8, origin-independent expressions for the property tensors (3.28) and (3.34) were presented without considering additions which contract to zero, with the symmetric products $\nabla_j\nabla_k\nabla_l$ and $\nabla_k\nabla_l$, in the source densities (5.146) and (5.147), respectively. This is reflected in the unknown coefficient c_2

(see (5.205) and (5.206)). Equations (43) and (47) of Reference 8 correspond with (5.198) and (5.199) when

$$c_2 = 0, \tag{5.212}$$

and the trace term (5.211) is set to zero in the absence of spin. The analysis presented here cannot resolve the coefficient c_2. It may be possible to determine a value for c_2 from experimental measurements of the material constants, otherwise additional insight on theoretical constraints, not recognized here, is needed.

Chapter 6

Summary and conclusion

A consistent invariant multipole theory of induced macroscopic fields for a linear, homogeneous, anisotropic dielectric, interacting with harmonic plane electromagnetic waves, has been obtained up to electric octopole–magnetic quadrupole order. The procedure has involved the determination of origin-independent expressions corresponding to the molecular polarizabilities in quantum-mechanical expressions for the multipole moments (2.33)–(2.37), which depend in general on the choice of molecular coordinate origin. These origin-independent expressions are summarised in Table 6.1 in terms of the origin-independent basis tensors listed in Table 6.2.

Multipole order	Origin-independent polarizability tensors	Equation
Electric dipole	$\tilde{\alpha}_{ij} = \alpha_{ij}$	(4.6)
	$\tilde{\alpha}'_{ij} = \alpha'_{ij}$	(4.6)
Electric quadrupole–magnetic dipole	$\tilde{G}'_{ij} = v_{ij}$ $\tilde{a}_{ijk} = 0$	(4.50) (4.51)
	$\tilde{G}_{ij} = w_{ij}$ $\tilde{a}'_{ijk} = s_{ijk}$	(4.112) (4.113)
Electric octopole–magnetic quadrupole	$\tilde{\chi}_{ij} = \mathcal{Q}_{ij}$ $\left.\begin{aligned}\tilde{b}_{ijkl} &= \tfrac{1}{4}(\kappa - 1)\mathcal{S}_{ijkl} \\ \tilde{d}_{ijkl} &= \tfrac{1}{3}\kappa\mathcal{S}_{ijkl}\end{aligned}\right\} \kappa = 0 \text{ or } 1$ $\tilde{L}'_{ijk} = \mathcal{R}'_{ijk} + c_1\left(\delta_{ik}\mathcal{R}'_{llj} + \delta_{jk}\mathcal{R}'_{lli}\right)$ $\tilde{H}'_{ijk} = 0$	(5.85) or (5.97) (5.98) or (5.42) (5.43) or (5.86) (5.87) or (5.99) (5.42) or (5.43)
	$\tilde{\chi}'_{ij} = \mathcal{Q}'_{ij} + c_2\omega\varepsilon_{ijk}\mathcal{R}_{llk}$ $\tilde{b}'_{ijkl} = 0$ $\tilde{d}'_{ijkl} = 0$ $\tilde{L}_{ijk} = \mathcal{R}_{ijk} + c_2(\delta_{ik}\mathcal{R}_{llj} + \delta_{jk}\mathcal{R}_{lli})$ $\tilde{H}_{ijk} = 0$	(5.183) (5.159) (5.160) (5.184) (5.181)

Table 6.1: Origin-independent expressions corresponding to the molecular polarizabilities up to electric octopole–magnetic quadrupole order. c_1 corresponds with c_{10} in (5.87) and (5.99).

Electromagnetic observables like the bound source densities $\rho(\boldsymbol{r}, t)$ and $\boldsymbol{J}(\boldsymbol{r}, t)$ in (3.21) and (3.22), and the propagation equation (3.49), were found to be independent of the choice of molecular coordinate origin. Spatial averages of these quantities can therefore be expressed in terms of the number density of molecules $\mathcal{N}$ (see (3.17)). When the molecular polarizabilities in the expressions for the bound source densities and the propagation equation are replaced by their invariant counterparts, listed in Table 6.1, the bound source densities and propagation equation are unchanged. To electric

Multipole order	Origin-independent basis tensors	Time nature	Equation
Electric dipole	$\alpha_{ij} = \alpha_{ji}$	Time even	(4.6)
	$\alpha'_{ij} = -\alpha'_{ji}$	Time odd	(4.6)
Electric quadrupole–magnetic dipole	$v_{ij} = G'_{ij} - \frac{1}{2}\omega\varepsilon_{jkl}a_{kli}$	Time even	(4.24)
	$w_{ij} = G_{ij} - \frac{1}{3}\delta_{ij}G_{kk} - \frac{1}{6}\omega\varepsilon_{jkl}a'_{kli}$	Time odd	(4.80)
	$s_{ijk} = \frac{1}{3}\left(a'_{ijk} + a'_{jki} + a'_{kij}\right) = s_{jik} = s_{ikj}$		(4.93)
Electric octopole–magnetic quadrupole	$\mathcal{Q}_{ij} = \chi_{ij} + \frac{1}{12}\omega^2(d_{ijkk} - d_{ikjk}) - \frac{1}{24}\omega^2\delta_{ij}(d_{kkll} - d_{klkl}) - \frac{1}{4}\omega\left(\varepsilon_{ikl}H'_{kjl} + \varepsilon_{jkl}H'_{kil}\right) = \mathcal{Q}_{ji}$	Time even	(5.5)
	$\mathcal{R}'_{ijk} = L'_{ijk} - \frac{1}{4}\left(\delta_{ik}L'_{jll} + \delta_{jk}L'_{ill}\right) - \frac{1}{2}\left(H'_{ikj} + H'_{jki}\right) + \frac{1}{8}\left(\delta_{ik}H'_{llj} + \delta_{jk}H'_{lli}\right) - \frac{1}{6}\omega\varepsilon_{klm}b_{lijm} = \mathcal{R}'_{jik}$		(5.7)
	$\mathcal{S}_{ijkl} = d_{ijkl} + d_{ikjl} + d_{iljk} - b_{ijkl} - b_{jikl} - b_{kijl} - b_{lijk} = \mathcal{S}_{jikl} = \mathcal{S}_{kjil} = \mathcal{S}_{ljki}$		(5.9)
	$\mathcal{Q}'_{ij} = \chi'_{ij} - \frac{1}{4}\omega\varepsilon_{ijk}L_{kll} + \frac{3}{8}\omega\varepsilon_{ijk}H_{llk} = -\mathcal{Q}'_{ji}$	Time odd	(5.150)
	$\mathcal{R}_{ijk} = L_{ijk} - \frac{1}{4}(\delta_{ik}L_{jll} + \delta_{jk}L_{ill}) - \frac{1}{2}(H_{ikj} + H_{jki}) + \frac{1}{8}(\delta_{ik}H_{llj} + \delta_{jk}H_{lli}) + \omega\varepsilon_{klm}\left(\frac{1}{4}d'_{iljm} - \frac{1}{3}b'_{lijm}\right) = \mathcal{R}_{jik}$		(5.152)

Table 6.2: Time-even and time-odd origin-independent basis tensors up to electric octopole–magnetic quadrupole order. α_{ij}, α'_{ij}, s_{ijk}, $\mathcal{Q}_{ij}$, $\mathcal{S}_{ijkl}$ and $\mathcal{Q}'_{ij}$ are polar tensors, and v_{ij}, w_{ij}, $\mathcal{R}'_{ijk}$ and $\mathcal{R}_{ijk}$ are axial tensors.

octopole–magnetic quadrupole order the bound charge density is given by

$$\rho_b = \mathcal{N}\Big(\tilde{\Theta}_{ij} + i\tilde{\Pi}_{ij}\Big)\nabla_j E_i + \mathcal{N}\Big(\tilde{\Theta}_{ijk} + i\tilde{\Pi}_{ijk}\Big)\nabla_j\nabla_k E_i + \mathcal{N}\Big(\tilde{\Theta}_{ijkl} + i\tilde{\Pi}_{ijkl}\Big)\nabla_j\nabla_k\nabla_l E_i \qquad (6.1)$$

$$= -\mathcal{N}\left(\alpha_{ij} + i\alpha'_{ij}\right)\nabla_j E_i - \mathcal{N}\left(\tfrac{1}{\omega}\varepsilon_{ikl}v_{jl} + \tfrac{i}{\omega}\left[\varepsilon_{ikl}w_{jl} - \omega s_{ijk}\right]\right)\nabla_j\nabla_k E_i$$
$$+\mathcal{N}\left(\left[\tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\varepsilon_{ikm}\mathcal{R}'_{jlm}\right] + \tfrac{i}{2\omega}\varepsilon_{ikm}\mathcal{R}_{jlm}\right)\nabla_j\nabla_k\nabla_l E_i, \qquad (6.2)$$

and the bound current density by

$$J_{bi} = \omega\mathcal{N}\left(i\tilde{\Phi}_{ij} + \tilde{\Omega}_{ij}\right)E_j + \omega\mathcal{N}\left(i\tilde{\Phi}_{ijk} + \tilde{\Omega}_{ijk}\right)\nabla_k E_j + \omega\mathcal{N}\left(i\tilde{\Phi}_{ikjl} + \tilde{\Omega}_{ikjl}\right)\nabla_k\nabla_l E_j \qquad (6.3)$$

$$= -\omega\mathcal{N}\left(i\alpha_{ij} + \alpha'_{ij}\right)E_j + \omega\mathcal{N}\left(\tfrac{i}{\omega}\left[\varepsilon_{ikl}v_{jl} - \varepsilon_{jkl}v_{il}\right] + \tfrac{1}{\omega}\left[\varepsilon_{ikl}w_{jl} + \varepsilon_{jkl}w_{il} - \omega s_{ijk}\right]\right)\nabla_k E_j$$
$$+\omega\mathcal{N}\left(i\left[\tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\left\{\varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{jkm}\mathcal{R}'_{ilm}\right\} + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}_{mn}\right]\right.$$
$$\left.+\left[\tfrac{1}{2\omega}\left\{\varepsilon_{ikm}\mathcal{R}_{jlm} - \varepsilon_{jlm}\mathcal{R}_{ikm}\right\} + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}'_{mn}\right]\right)\nabla_k\nabla_l E_j. \qquad (6.4)$$

As required, Equations (6.2) and (6.4) reduce to (3.21) and (3.22) when the origin-independent basis tensors are replaced by their expressions listed in Table 6.2. The propagation equation in magnetic media, to electric octopole–magnetic quadrupole order, is given by

$$\Big(\delta_{ij}\nabla^2 - \nabla_i\nabla_j + \mu_0\varepsilon_0\omega^2\delta_{ij} - \mu_0\omega^2\mathcal{N}\Big[\tilde{\Phi}_{ij} + \tilde{\Phi}_{ijk}\nabla_k + \tilde{\Phi}_{ikjl}\nabla_k\nabla_l\Big]$$
$$+i\mu_0\omega^2\mathcal{N}\Big[\tilde{\Omega}_{ij} + \tilde{\Omega}_{ijk}\nabla_k + \tilde{\Omega}_{ikjl}\nabla_k\nabla_l\Big]\Big)E_j = 0. \qquad (6.5)$$

In terms of the invariant basis tensors in Table 6.2, Equation (6.5) is

$$\Big(\delta_{ij}\nabla^2 - \nabla_i\nabla_j + \mu_0\varepsilon_0\omega^2\delta_{ij} + \mu_0\omega^2\mathcal{N}\Big[\alpha_{ij} - i\alpha'_{ij}$$
$$-\tfrac{1}{\omega}\left\{\varepsilon_{ikl}v_{jl} - \varepsilon_{jkl}v_{il}\right\}\nabla_k + \tfrac{i}{\omega}\left\{\varepsilon_{ikl}w_{jl} + \varepsilon_{jkl}w_{il} - \omega s_{ijk}\right\}\nabla_k$$
$$-\left\{\tfrac{1}{12}\mathcal{S}_{ijkl} + \tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{jlm}\mathcal{R}'_{ikm}\right) + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}_{mn}\right\}\nabla_k\nabla_l$$
$$+i\left\{\tfrac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}_{jlm} - \varepsilon_{jlm}\mathcal{R}_{ikm}\right) + \tfrac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}'_{mn}\right\}\nabla_k\nabla_l\Big]\Big)E_j = 0, \qquad (6.6)$$

which reduces to (3.49) when the invariant tensors are replaced by the expressions in Table 6.2.

The invariant property tensors $\tilde{\Theta}_{ij\ldots}$, $\tilde{\Pi}_{ij\ldots}$, $\tilde{\Phi}_{ij\ldots}$ and $\tilde{\Omega}_{ij\ldots}$ in (6.1), (6.3) and (6.5) are summarized in Table 6.3. The assignment of the subscripts in the expressions for $\tilde{\Theta}_{ijk}$, $\tilde{\Pi}_{ijk}$, $\tilde{\Theta}_{ijkl}$, $\tilde{\Pi}_{ijkl}$, $\tilde{\Phi}_{ikjl}$ and $\tilde{\Omega}_{ikjl}$ is not unique, because these tensors are contracted with symmetric products of field gradients in the bound charge and current densities (6.1) and (6.3), and the propagation equation (6.5) (see Section 3.2).

The expressions multiplying c_1 and c_2 in $\tilde{\Theta}_{ijkl}$ and $\tilde{\Pi}_{ijkl}$ contract to zero with the symetric product $\nabla_j\nabla_k\nabla_l$ in (6.1), and the expressions multiplying c_1 and c_2 in $\tilde{\Phi}_{ikjl}$ and $\tilde{\Omega}_{ikjl}$ contract to zero with the symetric product $\nabla_k\nabla_l$ in (6.3) and (6.5). The unknowns c_1 and c_2 therefore do not affect the expressions for the bound charge and current densities, and the propagation equation.

The multipole expressions for the induced multipole moment densities (3.10)–(3.14) and the dynamic response fields $\boldsymbol{D}(\boldsymbol{E},\boldsymbol{B})$ and $\boldsymbol{H}(\boldsymbol{E},\boldsymbol{B})$ (3.54)–(3.55), on the other hand, depend on the choice of molecular coordinate origin, and hence cannot be specified uniquely in a spatial average, thus leading to non-unique macroscopic expressions for these quantities, and hence an unphysical macroscopic theory (see Chapter 3).

When the molecular polarizabilities in the expressions for the material constants (3.61)–(3.64) are replaced by the corresponding expressions listed in Table 6.1, a fully invariant, and hence physically acceptable theory for linear, homogeneous, anisotropic media is obtained. The invariant material

Multipole order	Origin-independent property tensors	Time nature
Electric dipole	$\tilde{\Theta}_{ij} = -\alpha_{ij}$	Time even
	$\tilde{\Phi}_{ij} = -\alpha_{ij}$	
	$\tilde{\Pi}_{ij} = -\alpha'_{ij}$	Time odd
	$\tilde{\Omega}_{ij} = -\alpha'_{ij}$	
Electric quadrupole–magnetic dipole	$\tilde{\Theta}_{ijk} = -\frac{1}{\omega}\varepsilon_{ikl}v_{jl}$	Time even
	$\tilde{\Phi}_{ijk} = \frac{1}{\omega}(\varepsilon_{ikl}v_{jl} - \varepsilon_{jkl}v_{il})$	
	$= -\tilde{\Phi}_{jik}$	
	$\tilde{\Pi}_{ijk} = -\frac{1}{\omega}\varepsilon_{ikl}w_{jl} + s_{ijk}$	Time odd
	$\tilde{\Omega}_{ijk} = \frac{1}{\omega}\varepsilon_{ikl}w_{jl} + \frac{1}{\omega}\varepsilon_{jkl}w_{il} - s_{ijk}$	
	$= \tilde{\Omega}_{jik}$	
Electric octopole–magnetic quadrupole	$\tilde{\Theta}_{ijkl} = \frac{1}{12}\mathcal{S}_{ijkl} + \frac{1}{2\omega}\varepsilon_{ikm}\mathcal{R}'_{jlm} + c_1\frac{1}{2\omega}\left(\varepsilon_{ikl}\mathcal{R}'_{mmj} - \varepsilon_{ijk}\mathcal{R}'_{mml}\right)$	Time even
	$\tilde{\Phi}_{ikjl} = \frac{1}{12}\mathcal{S}_{ijkl} + \frac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{jlm}\mathcal{R}'_{ikm}\right) + \frac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}_{mn}$	
	$- \frac{1}{2\omega}c_1\left(\varepsilon_{ijk}\mathcal{R}'_{mml} - \varepsilon_{ijl}\mathcal{R}'_{mmk} - \varepsilon_{ikl}\mathcal{R}'_{mmj} + \varepsilon_{jkl}\mathcal{R}'_{mmi}\right)$	
	$= \tilde{\Phi}_{jlik}$	
	$\tilde{\Pi}_{ijkl} = \frac{1}{2\omega}\varepsilon_{ikm}\mathcal{R}_{jlm} + c_2\frac{1}{2\omega}\left(\varepsilon_{ikl}\mathcal{R}_{mmj} - \varepsilon_{ijk}\mathcal{R}_{mml}\right)$	Time odd
	$\tilde{\Omega}_{ikjl} = \frac{1}{2\omega}\left(\varepsilon_{ikm}\mathcal{R}_{jlm} - \varepsilon_{jlm}\mathcal{R}_{ikm}\right) + \frac{1}{\omega^2}\varepsilon_{ikm}\varepsilon_{jln}\mathcal{Q}'_{mn}$	
	$+ c_2\frac{1}{\omega}\left(\varepsilon_{ikl}\mathcal{R}_{mmj} + \varepsilon_{jkl}\mathcal{R}_{mmi}\right)$	
	$= -\tilde{\Omega}_{jlik}$	

Table 6.3: Origin-independent expressions for the property tensors appearing in the charge and current densities, and the propagation equation.

constants are given by

$$\tilde{A}_{ij} = \varepsilon_0\delta_{ij} + \mathcal{N}\left(\alpha_{ij} - i\alpha'_{ij} + k_k s_{ijk} + \tfrac{1}{12}k_k k_l \mathcal{S}_{ijkl}\right), \tag{6.7}$$

$$\tilde{T}_{ij} = \mathcal{N}\big(w_{ij} - iv_{ij} - \tfrac{1}{2}k_k\left[\mathcal{R}'_{ikj} + i\mathcal{R}_{ikj} + c_1\{\delta_{ij}\mathcal{R}'_{llk} + \delta_{jk}\mathcal{R}'_{lli}\} + ic_2\{\delta_{ij}\mathcal{R}_{llk} + \delta_{jk}\mathcal{R}_{lli}\}\right]\big), \tag{6.8}$$

$$\tilde{U}_{ij} = -\tilde{T}^*_{ji}, \tag{6.9}$$

$$X_{ij} = \mu_0^{-1}\delta_{ij} - \mathcal{N}\left(\mathcal{Q}_{ij} - i\mathcal{Q}'_{ij} - ic_2\omega\varepsilon_{ijk}\mathcal{R}_{llk}\right). \tag{6.10}$$

The invariant material constants (6.7)–(6.10) yield physically acceptable, invariant expressions for the response fields (3.59). The constitutive tensor in (3.59), to electric octopole–magnetic quadrupole order, is

$$C = C^{(0)} + C^{(1)} + C^{(2)} + C^{(3)}. \tag{6.11}$$

Here, the vacuum contribution is given by

$$C^{(0)} = \begin{pmatrix} \varepsilon_0\delta_{ij} & 0 \\ 0 & \mu_0^{-1}\delta_{ij} \end{pmatrix}, \tag{6.12}$$

and the electric dipole, electric quadrupole–magnetic dipole and electric octopole–magnetic quadrupole order contributions are

$$C^{(1)} = \mathcal{N}\begin{pmatrix}\alpha_{ij} & 0\\ 0 & 0\end{pmatrix} - i\mathcal{N}\begin{pmatrix}\alpha'_{ij} & 0\\ 0 & 0\end{pmatrix}, \tag{6.13}$$

$$C^{(2)} = -i\mathcal{N}\begin{pmatrix}0 & v_{ij}\\ v_{ji} & 0\end{pmatrix} + \mathcal{N}\begin{pmatrix}k_k s_{ijk} & w_{ij}\\ -w_{ji} & 0\end{pmatrix}, \tag{6.14}$$

$$\begin{aligned}C^{(3)} = {} & \mathcal{N}\begin{pmatrix}\frac{1}{12}k_k k_l \mathcal{S}_{ijkl} & -\frac{1}{2}k_k\mathcal{R}'_{ikj}\\ \frac{1}{2}k_k\mathcal{R}'_{jki} & -\mathcal{Q}_{ij}\end{pmatrix} + i\mathcal{N}\begin{pmatrix}0 & -\frac{1}{2}k_k\mathcal{R}_{ikj}\\ -\frac{1}{2}k_k\mathcal{R}_{jki} & \mathcal{Q}'_{ij}\end{pmatrix}\\ & + c_1\mathcal{N}\begin{pmatrix}0 & -\frac{1}{2}k_k(\delta_{ij}\mathcal{R}'_{llk} + \delta_{jk}\mathcal{R}'_{lli})\\ \frac{1}{2}k_k\left(\delta_{ij}\mathcal{R}'_{llk} + \delta_{ik}\mathcal{R}'_{llj}\right) & 0\end{pmatrix}\\ & + ic_2\mathcal{N}\begin{pmatrix}0 & -\frac{1}{2}k_k(\delta_{ij}\mathcal{R}_{llk} + \delta_{jk}\mathcal{R}_{lli})\\ -\frac{1}{2}k_k(\delta_{ij}\mathcal{R}_{llk} + \delta_{ik}\mathcal{R}_{lli}) & \omega\varepsilon_{ijk}\mathcal{R}_{llk}\end{pmatrix}.\end{aligned} \tag{6.15}$$

Equations (6.12)–(6.15) differ from (57)–(60) in Reference [8] only in the last two terms in (6.15), which contain the arbitrary real coefficients c_1 and c_2.

The expressions in Table 6.1 contain one parameter κ, which is either zero or one, resulting from a duality between the invariant expressions corresponding to the electric dipole–electric octopole polarizability b_{ijkl} and the electric quadrupole–electric quadrupole polarizability d_{ijkl} [7]. Either choice, $\kappa = 0$ or $\kappa = 1$, leads to the same bound source densities (3.59) and (6.4), propagation equation (6.6), dynamic response fields and material constants (6.7)–(6.10). The two arbitrary unknown coefficients, c_1 in the invariant expression corresponding to the time-even electric quadrupole–magnetic dipole polarizability L'_{ijk}, and c_2 in the expressions corresponding to the time-odd magnetic dipole–magnetic dipole and the electric quadrupole–magnetic dipole polarizabilities χ'_{ij} and L_{ijk}, respectively, do not affect the bound source densities or the propagation equation, but result in additional terms in the expressions for the magnetoelectric tensors (6.8) and (6.9), and the magnetic susceptibility tensor (6.10), at electric octopole–magnetic quadrupole order.

Because the two arbitrary coefficients c_1 and c_2 appear in the expressions of the material constants and hence the response fields, which in principle are measurable properties of a material, it should be possible to determine a value for these experimentally. The parameter κ, on the other hand, can only be determined experimentally from observations of either the electric dipole–electric octopole polarizability b_{ijkl}, or the electric quadrupole–electric quadrupole polarizability d_{ijkl}.

Appendix A

Sample calculation of origin dependence

The derivation of the origin dependence of the magnetic quadrupole moment Δm_{ij} is given. This is then used to find the origin dependence of the time-even electric dipole–magnetic quadrupole polarizability tensor H'_{ijk}. A possible inconsistency due to the origin dependence of the magnetic octopole is then presented.

To simplify the notation, the summation over all particles in (2.61) is assumed. Then, rewriting (2.61) with the terms grouped for clarity,

$$\Delta m_{ij} = -\frac{4}{3}d_j\left(\frac{q}{2m}\varepsilon_{ikl}r_k\Pi_l\right) - \frac{q}{3m}\varepsilon_{ikl}\left[d_k\left(r_j\Pi_l + \Pi_l r_j\right) - 2d_jd_k\Pi_l\right]. \tag{A.1}$$

The first term in (A.1) is simply $-\frac{4}{3}d_jm_i$ (see (2.16)), and the last term is related to the commutator

$$\left[H^{(0)}, r_l\right] = -\frac{i\hbar}{m}\Pi_l, \tag{A.2}$$

where $H^{(0)}$ is given by (2.2). Pre- and post-multiplying (A.2) by $p_j = qr_j$ and adding gives

$$p_j\left[H^{(0)}, r_l\right] + \left[H^{(0)}, r_l\right]p_j = -\frac{iq\hbar}{m}(r_j\Pi_l + \Pi_l r_j). \tag{A.3}$$

It is straightforward to show that

$$p_j\left[H^{(0)}, r_l\right] = \left[H^{(0)}, q_{jl}\right] - q\left[H^{(0)}, r_j\right]r_l, \tag{A.4}$$

hence use of (A.4) in (A.3), expanding the commutators in $\boldsymbol{r}$, and rearranging gives

$$(r_j\Pi_l + \Pi_l r_j) = \frac{im}{q\hbar}\left(\left[H^{(0)}, q_{jl}\right] - p_lH^{(0)}r_j + p_jH^{(0)}r_l\right). \tag{A.5}$$

The last two terms on the right-hand side of (A.5) can be made to cancel using the identity (C.6), which then brings in a term with two Levi-Civita tensors. Use of (C.6), and multiplying the last two terms on the right-hand side of (A.5) by ε_{ikl}, yields

$$\begin{aligned}\varepsilon_{ikl}\left(-p_lH^{(0)}r_j + p_jH^{(0)}r_l\right) &= \varepsilon_{ikl}\varepsilon_{jlw}\varepsilon_{uvw}p_uH^{(0)}r_v \\ &= (\delta_{iw}\delta_{kj} - \delta_{ij}\delta_{kw})\varepsilon_{uvw}p_uH^{(0)}r_v \\ &= (\delta_{iw}\delta_{kj} - \delta_{ij}\delta_{kw})\varepsilon_{uvw}\left(qr_ur_vH^{(0)} + r_u\left[H^{(0)}, p_v\right]\right),\end{aligned} \tag{A.6}$$

where (C.4) was used. The term $\varepsilon_{uvw}qr_ur_vH^{(0)}$ in (A.6) is zero because ε_{uvw} is antisymmetric in u and v, and the product r_ur_v is symmetric in u and v. Thus (A.6) with (A.2) and using the definition (2.16) yields

$$\varepsilon_{ikl}\left(-p_lH^{(0)}r_j + p_jH^{(0)}r_l\right) = -2i\hbar\left(\delta_{jk}m_i - \delta_{ij}m_k\right). \tag{A.7}$$

Then (A.5) multiplied by ε_{ikl} with (A.7) becomes

$$\varepsilon_{ikl}\left(r_j\Pi_l + \Pi_l r_j\right) = (-i\hbar q/m)^{-1}\varepsilon_{ikl}\left[H^{(0)}, q_{jl}\right] + (2m/q)(\delta_{jk}m_i - \delta_{ij}m_k). \tag{A.8}$$

Finally, (2.16), (A.2) and (A.8) in (A.1) give Equation (2.63).

The origin dependence of H'_{ijk} is obtained from

$$\Delta H'_{ijk} = \bar{H}'_{ijk} - H'_{ijk}. \tag{A.9}$$

The polarizability $\bar{H}'_{ijk}$ involves matrix elements calculated with respect to the new origin $\bar{O}$. Before continuing, it is shown that the state vectors $|n\rangle$ and $|s\rangle$ are unaffected when the molecular origin is shifted from O to $\bar{O}$. Consider the matrix element $\langle f\rangle_{ns}$ of a function $f(\boldsymbol{R}, \boldsymbol{r}^{(\alpha)})$, where $\boldsymbol{R}$ is the position vector of the origin O of a molecule relative to some origin, and $\boldsymbol{r}^{(\alpha)}$ is the position vector of particle α of the molecule with respect to the origin O (see Figure A.1). Then

$$\langle f\rangle_{ns} = \left\langle n\left|f\left(\boldsymbol{R}, \boldsymbol{r}^{(\alpha)}\right)\right|s\right\rangle = \int \psi_n^*(\boldsymbol{R}) f\left(\boldsymbol{R}, \boldsymbol{r}^{(\alpha)}\right)\psi_s(\boldsymbol{R})d\boldsymbol{R}. \tag{A.10}$$

When the molecular coordinate origin is shifted from O to $\bar{O}$ by $\boldsymbol{d}$, the matrix element calculated with respect to the new origin is (see Figure A.1)

$$\overline{\langle f\rangle}_{ns} = \int \psi_n^*(\boldsymbol{R}+\boldsymbol{d}) f\left(\boldsymbol{R}+\boldsymbol{d}, \bar{\boldsymbol{r}}^{(\alpha)}\right)\psi_s(\boldsymbol{R}+\boldsymbol{d})d(\boldsymbol{R}+\boldsymbol{d}). \tag{A.11}$$

By changing the integration variable from $\boldsymbol{R}+\boldsymbol{d}$ to $\boldsymbol{R}$ in (A.11), one obtains

$$\begin{aligned}\overline{\langle f\rangle}_{ns} &= \int \psi_n^*(\boldsymbol{R}) f\left(\boldsymbol{R}, \bar{\boldsymbol{r}}^{(\alpha)}\right)\psi_s(\boldsymbol{R})d\boldsymbol{R} \\ &= \langle \bar{f}\,\rangle_{ns},\end{aligned} \tag{A.12}$$

because $\boldsymbol{d}$ is constant and the states are orthogonal.

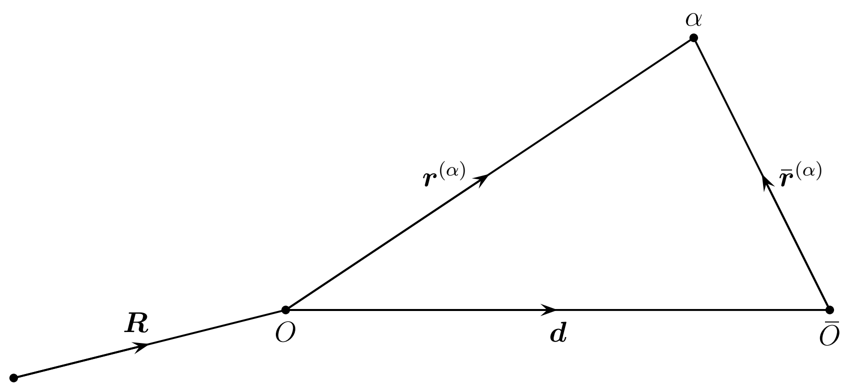

Figure A.1: Displacement of molecular coordinate origin relative to which the positions of molecular constituents are specified.

Use of (2.49) and (A.12) in (A.9) results in

$$\begin{aligned}\Delta H'_{ijk} &= -\frac{2}{\hbar}\sum_s \omega Z_{sn}\mathcal{I}m\left\{\langle\bar{p}_i\rangle_{ns}\langle\bar{m}_{jk}\rangle_{sn} - \langle p_i\rangle_{ns}\langle m_{jk}\rangle_{sn}\right\}, \\ &= -\frac{2}{\hbar}\sum_s \omega Z_{sn}\mathcal{I}m\left\{\langle\Delta p_i + p_i\rangle_{ns}\langle\Delta m_{jk} + m_{jk}\rangle_{sn} - \langle p_i\rangle_{ns}\langle m_{jk}\rangle_{sn}\right\}, \\ &= -\frac{2}{\hbar}\sum_s \omega Z_{sn}\mathcal{I}m\left\{\langle\Delta p_i\rangle_{ns}\langle\Delta m_{jk}\rangle_{sn} + \langle\Delta p_i\rangle_{ns}\langle m_{jk}\rangle_{sn} + \langle p_i\rangle_{ns}\langle\Delta m_{jk}\rangle_{sn}\right\}.\end{aligned} \tag{A.13}$$

From (2.57)

$$\langle\Delta p_i\rangle_{ns} = \langle n\left|-d_i q\right|s\rangle = -d_i q\langle n|s\rangle = 0 \tag{A.14}$$

for orthogonal kets $|n\rangle$ and $|s\rangle$, so the first two terms in (A.13) are zero. Expanding the commutator in (2.63) and substituting the result in (A.13) using (A.14) yields

$$\Delta H'_{ijk} = -\frac{2}{\hbar}\sum_s \omega Z_{sn}\mathcal{Im}\left\{-2d_k \langle p_i\rangle_{ns} \langle m_j\rangle_{sn} + \frac{2}{3}\delta_{jk}d_l \langle p_i\rangle_{ns} \langle m_l\rangle_{sn} \right.$$
$$\left. - \frac{i}{3\hbar}\varepsilon_{jlm}d_l \langle p_i\rangle_{ns} \left(\left\langle H^{(0)}(2d_kp_m - q_{km})\right\rangle_{sn} - \left\langle (2d_kp_m - q_{km})H^{(0)}\right\rangle_{ns}\right)\right\}. \quad \text{(A.15)}$$

The Hamiltonian $H^{(0)}$ in the last two terms of (A.15) operates to the left and right, respectively, to produce eigenvalues

$$\left\langle s \right| H^{(0)} = W_s^{(0)} \langle s| \quad \text{and} \quad H^{(0)}\left| n \right\rangle = W_n^{(0)}\left| n \right\rangle.$$

From $\mathcal{Im}\{ic\} = \mathcal{Re}\{c\}$, (2.38), (2.40), (2.43) and (2.29) in (A.15), and simplifying the result, one obtains (2.75).

The calculation of Δm_{ijk} proceeds in a similar way to the calculation for Δm_{ij} presented above. The result is

$$\Delta m_{ijk} = 3d_jd_km_i - \frac{3}{4}(\delta_{ij}d_k + \delta_{ik}d_j)\, d_lm_l - \frac{9}{8}(d_jm_{ik} + d_km_{ij})$$
$$- \frac{3i}{8\hbar}\varepsilon_{ilm}d_l \left[H^{(0)}, 2d_jd_kp_m - d_jq_{km} - d_kq_{jm} + q_{jkm}\right]$$
$$+ \frac{3i}{8\hbar}\varepsilon_{ilm}d_l \left(r_jr_kH^{(0)}r_m - r_mH^{(0)}r_jr_k\right). \quad \text{(A.16)}$$

The last two terms of (A.16) cannot be written in terms of magnetic multipoles, or as a commutator of $H^{(0)}$ and electric multipoles (so that a factor ω_{sn} is produced in the result). These terms can be written in terms of electric dipole moments as follows:

$$\frac{3i}{8\hbar}\varepsilon_{ilm}d_l \left(r_jr_kH^{(0)}r_m - r_mH^{(0)}r_jr_k\right) = -\frac{3i}{8\hbar}\varepsilon_{ilm}d_l \left[H^{(0)}, q_{jkm}\right] + \frac{3i\hbar}{8m}d_l\left(\varepsilon_{ijl}p_k + \varepsilon_{ikl}p_j\right). \quad \text{(A.17)}$$

The last two terms on the right-hand side of (A.17) do not, however, yield expressions for multipole polarizabilities when used in the calculation of the origin dependence of polarizabilities of higher multipole order (as happens in the calculation for H'_{ijk} above). It is unclear how one would proceed at higher multipole order without an appropriate expression for the origin dependence of the magnetic octopole.

Appendix B

Computer algebra

This appendix contains a description of the MATHEMATICA modules and routines used to perform the simplifications of Cartesian tensor expressions in Chapter 4, Appendix C and Appendix H. All the calculations were performed using MATHEMATICA version 8.0.4, on a dual processor AMD Athlon MP 2400+ personal computer, running a custom-compiled Linux operating system with kernel version 2.6.30.9.

All directory paths and file locations quoted in this appendix are relative to the root directory of the accompanying CD. Running the commands in a MATHEMATICA notebook opened directly from the CD will likely result in an error. The reason is twofold: firstly MATHEMATICA will try to change the file, and the CD is write-protected; secondly, many notebooks use expressions that are loaded from MATHEMATICA definition files, which are machine dependent. A solution would be to copy the entire contents of the CD to some local directory and then regenerate the machine dependent definition files. Detailed instructions are given in the `README` file in the root directory of the CD.

All the software on the CD was tested on the above-mentioned Linux platform. Any unexpected success, as a result of running the software on another operating system, will be purely by chance.

Most of the routines described below were written as the need for them arose. The software was never intended to be released commercially, or used for any other purpose than to facilitate the calculations in this thesis. For these reasons many routines lack generality and adequate protection from users not familiar with their intended use. It is likely that substantial performance gains can be achieved for many of the routines. Particularly, the algorithm that calculates the components of tensor expressions is slow, and does not factor tensors that occur with different coefficients. For instance the components of A_{ijkl} in an expression like

$$c_1 A_{ijkl} + c_2 A_{ijkl}$$

get computed twice. A function that factorizes such expressions was written later (see the description of `FactorizeTensors[ ]` on page 74) and could easily be incorporated in the `Components[ ]` routine. In the calculations, `FactorizeTensors[ ]` is simply executed as a separate call before `Components[ ]`.

To avoid confusion, the code examples, and command input and output, provided in this appendix are reproduced without additional punctuation.

B.1 Cartesian tensor module

The module `cTensor.m` contains the routines that perform algebraic manipulation of Cartesian tensor expressions. Only the routines available to the user are described here. Some comments (often of limited helpfulness) regarding the usage of the private routines are contained in the source file.

After opening MATHEMATICA, and before any variables are defined, the module `cTensor.m` should be loaded with the command

```
<< "mathematica/routines/cTensor.m"
```

The tensor subscripts are protected for obvious reasons, and are contained in the variable

`$PreferredSubscripts`. The MATHEMATICA concept "`Context‘`" was discovered after a substantial amount of code had been written. Placing the subscripts in their own context was not deemed a priority. The only other publicly accessible variable is `$cTensors`, which contains a list of defined tensors.

The available routines are listed in the next section with a brief description of their usage.

B.1.1 Routines in cTensor.m

- `DefCT[A,r,{s}]`
  This defines a tensor `A` of rank `r` and symmetry `s`. The first two arguments are required. The last argument is optional and should consist of a list of the positions of the subscripts that possess symmetry. The symmetry list should list all pairs of subscripts that have symmetry, and should make no assumption about any implied symmetry. Antisymmetric pairs are indicated by a negative sign. The Kronecker delta (δ_{ij}) and the Levi-Civita tensor (ε_{ijk}) are predefined. As an example, the fourth-rank electric dipole–electric octopole tensor for a non-magnetic molecule ($b_{ijkl} = b_{ikjl} = b_{ijlk}$) would be defined as
  ```
  DefCT[b,4,{{2,3},{2,4},{3,4}}]
  ```
  Symmetry of pairs of subscripts is entered as a nested list. Thus, the electric quadrupole–electric quadrupole polarizability tensor for a magnetic molecule ($d'_{ijkl} = d'_{jikl} = -d'_{klij}$) is defined as
  ```
  DefCT[d,4,{{1,2},{3,4},{{-1,2},{3,4}}}]
  ```
  The negative sign indicating antisymmetry can be placed before any of the positions in the last set of braces.

  Tensors that have been defined with `DefCT[ ]` are entered and used with the function notation. For example, the expression $\delta_{lm} b_{ijkm}$ is entered as
  ```
  CT[δ,{l,m}]CT[b,{i,j,k,m}]
  ```
  The choice of tensor symbol is left to the user. Any symbol that can be used in MATHEMATICA as a `Symbol` should work, including protected symbols, since the definition `DefCT[ ]` places the symbol in the protected 'Context' `cTensor‘`. Use of esoteric symbols and operators is, however, discouraged.

- `UndefCT[A]`
  Remove the tensor `A` from the list of definitions. To redefine a tensor, it should first be undefined, before issuing a modified definition with `DefCT[ ]`.

- `SimplifyCT[expression,order,altorder]`
  Simplify a tensor expression. The second and third arguments are optional, and affect the way in which products of Levi-Civita tensors are simplified. If an expression contains more than one Levi-Civita tensor, these are simplified in pairs. The result often depends on the order in which the pairs are evaluated. The `order` argument is a list of the three numbers 0,1 and 2. The default is `{2,1,0}` which instructs `SimplifyCT[ ]` to first evaluate pairs of Levi-Civita tensors that have two common subscripts, then one, and lastly any pairs with no common subscripts. The last argument instructs `SimplifyCT[ ]` to try a different ordering of the pairs. The value of `altorder` is either `True` or `False` (the default). Either `order`, `altorder` or both may be passed. If both are passed, then the list argument must be passed before the `True/False` argument.

  For example,
  ```
  SimplifyCT[CT[δ,{l,m}] CT[b,{i,k,m,j}]]
  ```
  or, equivalently, in the often more convenient postfix form,
  ```
  CT[δ,{l,m}] CT[b,{i,k,m,j}] // SimplifyCT
  ```

produces

```
CT[b,{i,j,k,l}]
```

An example of the use of the optional arguments is given with the discussion of the function `CommuteCT[ ]` below.

- `DisplayCT[expression]`
  Display a tensor expression in a more human-friendly way. A typical example of the use of `DisplayCT[ ]` is

```
temp = CT[δ,{l,m}] CT[b,{i,k,m,j}] // SimplifyCT;
% // DisplayCT
```

  The above command stores the output from the `SimplifyCT[ ]` in the temporary variable `temp` and displays

  b_{ijkl}

  The output from `DisplayCT[ ]` should not be used in subsequent calculations.

- `Components[expression]`
  Evaluates the components of a tensor expression. For a tensor of rank r, the output is a list of length 3^r. Thus the components of the second-rank electric dipole–magnetic dipole tensor G_{ij} can be computed with

```
CT[G,{i,j}] // Components
```

  which produces

```
{CT[G,{1,1}], CT[G,{2,1}], CT[G,{3,1}], CT[G,{1,2}],
   CT[G,{2,2}], CT[G,{3,2}], CT[G,{1,3}], CT[G,{2,3}], CT[G,{3,3}]}
```

  The routines `DisplayCT[ ]` and `SimplifyCT[ ]` are not overloaded to operate on lists. In order to view the output from `Components[ ]`, the next command should therefore be

```
DisplayCT /@ %
```

  to produce

  $\{G_{11}, G_{21}, G_{31}, G_{12}, G_{22}, G_{32}, G_{13}, G_{23}, G_{33}\}$

- `ListComponents[ ]`

  In the example of the second-rank tensor G_{ij} for the `Components[ ]` routine, it is easy to recognize each component. Because the output of `Components[ ]` is a one-dimensional list, this is not always the case, especially when subscripts are contracted. `ListComponents[ ]` shows what components are present at each position in the list. The output of `ListComponents[ ]` will vary according to the rank of the previously computed tensor expression, no matter which function was employed.

- `GetTensorOrder[ ]`
  The symbols of the defined tensors are stored as a list. The symbol of each new definition is appended at the end of this list. The order in which the tensor symbols are listed affects the way in which dummy subscripts are assigned. The dummy subscripts appearing first in the `$preferredSubscripts` list are assigned to the tensor which appears first in the list of tensor symbols. This matters only when aesthetics are important. The next command can be used to change this.

- `SetTensorOrder[{symbols}]`
  Define a new order for the list of tensor symbols. Execute the previous command and copy, paste and edit its output into `SetTensorOrder[ ]` as desired.

- `CommuteCT[tensor,positions]`
  There are two versions of this routine which commutes tensor subscripts. This version, with two arguments, commutes a pair of subscripts, indicated by the list `positions`, of the tensor passed in the first argument.
  ```
  CommuteCT[CT[G,{i,j}],{1,2}]
  ```
  produces
  ```
  CT[G,{j,i}] + CT[G,{u$1,v$1}] CT[ε,{i,j,w$1}] CT[ε,{u$1,v$1,w$1}]
  ```
  When simplified, this version usually reproduces the original input. It can be useful when the tensor multiplies a tensor expression involving Levi-Civita tensors.

- `CommuteCT[expression,symbols,positions]`
  This version of `CommuteCT[ ]` commutes subscripts on different tensors. The expression can consist of any number of tensors. The second argument is a list of the two tensor symbols whose subscripts are to be commuted, and the last argument indicates the position of the subscripts on each tensor. When the resulting expression is simplified, it usually produces the original expression. Here use of the optional arguments to `SimplifyCT[ ]` can give different results. For instance
  ```
  CommuteCT[CT[G,{i,j}] CT[ε,{k,l,m}],{G,ε},{2,1}] // SimplifyCT[#,True]&;
  % // DisplayCT
  ```
  gives
  $G_{im}\varepsilon_{jkl} - G_{il}\varepsilon_{jkm} + G_{ik}\varepsilon_{jlm}$
  and
  ```
  CommuteCT[CT[G,{i,j}] CT[ε,{k,l,m}],{G,ε},{2,1}] // SimplifyCT[#,{0,1,2}]&;
  % // DisplayCT
  ```
  gives
  $G_{ik}\varepsilon_{jlm} - G_{in}\delta_{km}\varepsilon_{jln} + G_{in}\delta_{kl}\varepsilon_{jmn} + G_{in}\delta_{jm}\varepsilon_{kln} - G_{in}\delta_{jl}\varepsilon_{kmn}$

There are several unresolved issues with the module `cTensor.m`. The main issues are briefly listed.

- When a first-rank tensor appears in a product of tensors, the subscripts on each factor are not commuted. For instance, the expression
  $d_i d_j G_{ij} + d_i d_j G_{ji}$
  will not simplify to
  $2d_i d_j G_{ij}$.
  To program the recognition of such symmetries, a product of first-rank tensors can be redefined as an appropriate totally symmetric tensor. Until this has been implemented, a substitution rule like
  ```
  {CT[d,{i_}] CT[d,{j_}] -> CT[d2,{i,j}], CT[d,{i_}]^2 -> CT[d2,{i,i}]}
  ```
  will convert occurrences of two first-rank tensors to a (predefined) symmetric second-rank tensor.

- The routines that order a tensor's subscripts canonically, according to the symmetries of the subscripts, has not been tested thoroughly for tensors of rank higher than four. There is, however, no reason why they should fail. Likewise, symmetries of groups of more than two subscripts have also not been tested.

- There is one known case where a symmetry combination is not simplified. This is an oversight which has not yet been implemented. The expression $\varepsilon_{ijk}d_{iljl}$ should evaluate to zero, because the electric quadrupole–electric quadrupole tensor $d_{iljl} = d_{jlil}$, thus introducing symmetry in i and j. Such occurrences are rare, and can easily be addressed manually. Solving identities that contain such combinations by comparing components does not affect the result.

- When simplifying large expressions it is sometimes necessary to use `SimplifyCT[ ]` twice.

B.2 Miscellaneous functions

The module `functions.m` contains miscellaneous routines that perform operations on tensor expressions. Only a few of the routines in this module are used in the calculations — these are described below. The unused routines date from earlier experimentation and have not been purged for the reason encapsulated in the well-known paradigm: "if it ain't broken, don't fix it".

Some of the routines in `functions.m` depend on the routines in `cTensor.m`, which must therefore be loaded first. After opening MATHEMATICA and loading the module `cTensor.m`, the `functions.m` module can be loaded with the command

```
<< "mathematica/routines/functions.m"
```

The routines from `functions.m` used in the calculations are described in the next section.

B.2.1 Routines in `functions.m`

- `GenerateCoefficients[int,string]`
  A simple macro to generate a list of length `int` of numbered symbols with prefix `string`. The default of the optional argument `string` is `"c"`.
  ```
  GenerateCoefficients[3,"k"]
  ```
  produces
  ```
  {k1, k2, k3}
  ```

- `FactorizeTensors[expression,string]`
  This function returns a list of two values. The first is a sum of all the unique tensor forms in `expression`, each with a single coefficient constructed from `string`, the second is a list of replacements rules that restore the original coefficients. The second argument is optional and defaults to `string="tmp"`. As an example, consider the expression for $\tilde{\chi}_{ij}$ in (5.33). If `expression` is the right-hand side of (5.33), then
  ```
  {expr,rule} = FactorizeTensors[expression];
  expr // DisplayCT
  rule
  ```
  produces
  $\mathrm{tmp1}\,\mathcal{Q}_{ij} + \mathrm{tmp2}\,\mathcal{S}_{ijkl} + \mathrm{tmp3}\,\delta_{ij}\mathcal{S}_{kkll} + \mathrm{tmp4}\,\varepsilon_{ikl}\mathcal{R}'_{jkl} + \mathrm{tmp5}\,\varepsilon_{jkl}\mathcal{R}'_{ikl}$
  $\{\mathrm{tmp1} \to 1, \mathrm{tmp2} \to -\frac{1}{12}\omega^2\,(c_4 - c_5 - 6c_{16} - 12c_{17} - 6c_{18})\,, \mathrm{tmp3} \to \ldots\}$
  The factorization in the list for `rule` in the line above is artificial. MATHEMATICA has its own idea about how humans wish to view the results.

- `ExtractRelations[cc,coeff,list]`
  Returns a matrix, with columns corresponding to the coefficients `coeff`, and rows corresponding to the relations of the components of the tensors listed in `list`, from the matrix of components `cc`. An example should make this a little clearer. Consider the tensor identity

  $$c_1 G_{ij} = c_2 G_{ij} + c_3 \delta_{ij} G_{kk}, \tag{B.1}$$

  which must be solved for the unknown coefficients c_1, c_2 and c_3. (The solution here is obvious. However, when considering expressions with hundreds of terms, involving 5 tensors of different rank in all possible combinations with isotropic tensors, the situation is different: Linear dependencies creep in and a calculation that might take a human weeks to perform can be done in seconds on a computer.) The first step is to determine `cc`, the components of the difference $c_1G_{ij} - (c_2G_{ij} + c_3\delta_{ij}G_{kk})$. This yields a list of nine components

$$\{-c_1G_{11} + c_2G_{11} + c_3G_{11} + c_3G_{22} + c_3G_{33},\ c_2G_{21} - c_1G_{21},\ c_2G_{31} - c_1G_{31},\\ c_2G_{12} - c_1G_{12},\ -c_1G_{22} + c_2G_{22} + c_3G_{11} + c_3G_{22} + c_3G_{33},\ c_2G_{32} - c_1G_{32},\\ c_2G_{13} - c_1G_{13},\ c_2G_{23} - c_1G_{23},\ -c_1G_{33} + c_2G_{33} + c_3G_{11} + c_3G_{22} + c_3G_{33}\}, \tag{B.2}$$

each of which must be equated to zero. In this case the coefficients `coeff` would be `{c1,c2,c3}`, and `list` a list of symbols in the expression, which here would be `{G}`. Since the components of G_{ij} are in general non-zero, the first entry in (B.2) contains two distinct equations, $-c_1+c_2+c_3 = 0$ and $c_3 = 0$, and produces three entries in the returned matrix: $\{-1, 1, 1, 0\}$, $\{0, 0, 1, 0\}$ and $\{0, 0, 1, 0\}$. In the above example, `ExtractRelations[ ]` returns a matrix with 15 rows, three of which are unique. The result of

```
mm = ExtractRelations[cc,coeff,list] // RowReduce // DeleteDuplicates
```

for the above example gives `mm` equal to

```
{{1,-1,0,0},{0,0,1,0},{0,0,0,0}}
```

The next three routines used together translate the output from `ExtractRelations[ ]` to a list of rules suitable for substitution into the original expressions, which usually would be either the left- or right-hand side of (B.1).

- `ListIndependents[mm,coeff]`
  Returns a lists of the *dependent* coefficients from `coeff` corresponding to the first non-zero entries of each row in the row-reduced matrix `mm`. The name of the routine is historical. The dangers of upsetting dependent routines in the code far outweigh the aesthetic advantages gained by renaming it. With the value of `mm` from the example above
  ```
  dcoeff = ListIndependents[mm,coeff]
  ```
  returns `dcoeff` equal to
  ```
  {c1, c3}
  ```

- `MatrixToEquations[mm,coeff]`
  Returns a list of rules corresponding to the relations represented by the non-zero rows of the row-reduced matrix `mm`, with columns corresponding to the coefficients `coeff`. With the value of `mm` from the example above, and `coeff = {c1, c2, c3}`,
  ```
  rules = MatrixToEquations[mm,coeff]
  ```
  returns `rules` equal to
  ```
  {c1-c2->0, c3->0, 0->0}
  ```

- `RearrangeEquations[rules,dcoeff]`
  The output from `MatrixToEquations[ ]` cannot be used to make a substitution. The list of rules returned by `MatrixToEquations[ ]` must first be rearranged with the dependent coefficients `dcoeff` on the left-hand side of each rule. Thus if `rules` is given by the output from the previous example, and `dcoef = {c1, c3}`, then
  ```
  replace = RearrangeEquations[rules,dcoeff]
  ```
  returns
  ```
  replace = {c1->c2, c3->0}
  ```

The routines described in this section are used in the various notebooks whenever tensor identities are solved. A more realistic example is now presented to illustrate how these routines are used in conjunction with each other. The comparison (5.28) is performed in the notebook `06-source.nb`. The essential code from this calculation is:

```
1. coeff = GenerateCoefficients[30];
2. tensorlist = {χ, b, d, H, L};
3. diff = (tildeρ - (charge[i] // SimplifyCT)) // Expand;
4. {expr, rule} = FactorizeTensors[diff];
5. cc = Components[expr] /. rule // Expand;
6. ExtractRelations[cc, coeff, tensorlist];
7. mm = % // DeleteDuplicates // Expand // RowReduce // DeleteDuplicates;
8. rules = MatrixToEquations[mm, coeff];
9. dcoeff = ListIndependents[mm, coeff];
10. chargeRule = RearrangeEquations[rules, dcoeff]
```

For clarity, some of the lines above have been expanded in terms of the symbols used in the example given in the explanations of the routines in this section. Use of the MATHEMATICA object `%` — which represents the output from the previous calculation — has also been avoided. In case the above code is not self-explanatory, comments are provided below.

1. The 30 coefficients corresponding to the 30 unknowns in (5.23)–(5.27) are generated.

2. The symbols of the time-even tensors at electric octopole–magnetic quadrupole order that appear in these expressions are placed in a variable. (This facilitates reusing the code in other calculations).

3. `tildeρ` is the name given to the right-hand side of (5.28) and `charge[i]` is a module containing the expression for the charge density (5.1), corresponding to the left-hand side of (5.28). Note that in the calculations this module is a first-rank tensor. This is because the field E_i plays no role in the comparison, and is therefore not included in the expressions for the charge density. The MATHEMATICA function `Expand[ ]` is used liberally because the expressions often contain substitutions, with the result that the substituted expressions are placed in brackets. Expanding the expression can lead to cancellation of terms.

4. This normally results in a shorter expression that is evaluated orders-of-magnitude times faster by the routine `Components[ ]` in the next step (see the comment at the beginning of this appendix).

5. Construct a matrix corresponding to the components of the difference of the left- and right-hand sides of (5.28).

6. Extract a matrix of the relations that are required for each component in the matrix `cc` calculated in Step 5, corresponding to the difference in Step 3, to be zero.

7. Perform a row reduction on the output from the previous step and delete duplicate entries.

8. Convert the matrix of relations to a set of rules.

9. Make a list of the dependent coefficients that will be substituted out of the initial expressions.

10. Create a substitution rule from the list of relations and the dependent coefficients.

Appendix C

Isotropic tensors

An isotropic tensor is a tensor that is invariant under rotation. It can be shown [53] that the only isotropic tensor of rank two is the Kronecker delta

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j. \end{cases} \tag{C.1}$$

The only isotropic tensor of rank three is the Levi-Civita tensor [53]

$$\varepsilon_{ijk} = \begin{cases} 0 & \text{if any two subscripts are equal} \\ 1 & \text{if } ijk \text{ is a cyclic permutation of 123} \\ -1 & \text{if } ijk \text{ is an anticyclic permutation of 123,} \end{cases} \tag{C.2}$$

where, for Cartesian tensors, i, j and $k = 1, 2$ or 3.

C.1 Identities

The following identities between the Kronecker delta δ_{ij} in (C.1), and the Levi-Civita tensor ε_{ijk} in (C.2) are readily established:

$$\varepsilon_{ijk}\varepsilon_{lmn} = \delta_{il}(\delta_{jm}\delta_{kn} - \delta_{jn}\delta_{km}) + \delta_{im}(\delta_{jn}\delta_{kl} - \delta_{jl}\delta_{kn}) + \delta_{in}(\delta_{jl}\delta_{km} - \delta_{jm}\delta_{kl}), \tag{C.3}$$

$$\varepsilon_{ijm}\varepsilon_{klm} = \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}, \tag{C.4}$$

$$\varepsilon_{ikl}\varepsilon_{jkl} = 2\delta_{ij}. \tag{C.5}$$

To prove (C.3), one first establishes that any repeated subscripts in the sets i, j and k, or l, m and n, yield zero for the right-hand side of (C.3), as is required by the left-hand side, and that both sides are antisymmetric on exchange of any two subscripts in either of these sets. Because the subscripts can be permuted cyclically, it then suffices to consider components for a particular case, $ijk = 123$ say. The identity (C.4) follows from (C.3) by setting $k = n$ in (C.3), and (C.5) follows from (C.4) by setting $j = l$ in (C.4).

The identity (C.4) can be employed to obtain a useful relation that interchanges any two subscripts of a tensor. It is sufficient to consider a non-symmetric second-rank tensor T_{ij}:

$$\begin{aligned} T_{ij} &= T_{ji} + T_{ij} - T_{ji} \\ &= T_{ji} + (\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk})T_{kl} \\ &= T_{ji} + \varepsilon_{ijm}\varepsilon_{klm}T_{kl}. \end{aligned} \tag{C.6}$$

Consider the product $\varepsilon_{ijk}T_l$. If any subscript of the Levi-Civita tensor, k say, is swapped with the subscript of T_l, then (C.6) yields

$$\varepsilon_{ijk}T_l = \varepsilon_{ijl}T_k + \varepsilon_{klw}\varepsilon_{uvw}(\varepsilon_{iju}T_v), \tag{C.7}$$

with similar expressions when i or j are swapped with l. Use of (C.4) with the product $\varepsilon_{uvw}\varepsilon_{iju}$ in (C.7) yields the identity

$$\varepsilon_{ijk}T_l - \varepsilon_{jkl}T_i + \varepsilon_{kli}T_j - \varepsilon_{lij}T_k = 0. \tag{C.8}$$

C.2 The number of isotropic tensors

The isotropic tensors of even rank $N > 2$ are products of $N/2$ Kronecker deltas, each with distinct subscript permutations (after taking into account the symmetry $\delta_{ij} = \delta_{ji}$). A particular subscript can combine in $(N-1)$ ways with the other subscripts on one of the Kronecker deltas in each product. Each such combination leaves $(N-2)$ subscripts to be assigned on the remaining $N/2 - 1$ Kronecker deltas. Repeating this procedure, and using the product rule for combinations, shows that for even N there are

$$(N-1) \times (N-3) \times \cdots \times 3 \times 1 \equiv (N-1)!! \tag{C.9}$$

such permutations. For example, there are three isotropic tensors of rank four

$$\delta_{ij}\delta_{kl}, \quad \delta_{ik}\delta_{jl} \quad \text{and} \quad \delta_{il}\delta_{jk}. \tag{C.10}$$

For rank six there are $5 \times 3 = 15$ combinations and for rank 8 there are 105 combinations. A method to generate these tensors is given in Section C.4.

The number of linearly independent combinations of isotropic tensors of even rank differs from (C.9) for $N \geq 8$. It can be shown that for tensors of even rank $N = 2p$, the number of linearly independent isotropic tensors is [54]

$$1 + \sum_{q=1}^{q=p} \frac{(2p)!(2p-3p+1)}{(2p-2q+1)!q!q!}\,. \tag{C.11}$$

A method to generate a linearly independent set of isotropic tensors of even rank greater than six is outlined in Section C.5.

The isotropic tensors of odd rank $N > 3$ are products of $(N-3)/2$ Kronecker deltas and a Levi-Civita tensor. The subscripts on each Levi-Civita tensor can be selected in

$$\binom{N}{3} = \frac{N!}{(N-3)!3!}$$

ways. Once the subscripts on each Levi-Civita tensor are assigned, there remain $(N-3)$ subscripts which populate the Kronecker deltas. Thus for isotropic tensors of odd rank $N > 3$ there are

$$\frac{N!}{(N-3)!3!} \times (N-3-1)!! = \frac{N!(N-4)!!}{(N-3)!3!} \tag{C.12}$$

combinations with distinct subscript permutations. The combinations obtained in this way are not linearly independent because of the relation (C.8). The number of linearly independent combinations of isotropic tensors of odd rank $N = 2p+1$ is [54]†

$$\sum_{q=0}^{q=p} \frac{(2p+1)!(3q-2p)}{(2p-2q+1)!q!(q+1)!}\,. \tag{C.13}$$

For example, there are 10 isotropic tensors of rank five with distinct subscript permutations, six of which are linearly independent:

$$\varepsilon_{ijk}\delta_{lm}, \quad \varepsilon_{ijl}\delta_{km}, \quad \varepsilon_{ijm}\delta_{kl}, \quad \varepsilon_{ikl}\delta_{jm}, \quad \varepsilon_{ikm}\delta_{jl} \quad \text{and} \quad \varepsilon_{ilm}\delta_{jk}. \tag{C.14}$$

Four equivalent linearly independent sets can be obtained from (C.14) by permuting the subscripts cyclically. A method to generate a linearly independent set of isotropic tensors of odd rank greater than three is outlined in Section C.5.

†The expression for the number of basic tensor products of odd rank in the paper of Boyle and Matthews [54] contains a typographical error and should read $(2p+1)!/[3 \times 2^p(p-1)!]$, instead of $(2p+1)!/[3 \times 2^p!(p-1)!]$. It is straightforward to show that for $N > 3$, $(2p+1)!/[3 \times 2^p(p-1)!] = N!(N-4)!!/[(N-3)!3!]$, where $N = 2p+1$.

C.3 General isotropic tensors

If $\mathcal{I}^{(i)}_{\{r\}}$ is the i^{th} linearly independent isotropic tensor of rank r, then the most general isotropic tensor of rank r is

$$I_{\{r\}} = \sum_{i=1}^{N_r} c_i \mathcal{I}^{(i)}_{\{r\}}, \tag{C.15}$$

where c_i are arbitrary real coefficients and N_r is the number of linearly independent isotropic tensors of rank r. The calculations in Chapter 4 require general isotropic tensors, with linearly independent terms, of rank four to eight. These are (see `iso.nb`):

$$I_{\{4\}} = c_1\delta_{ij}\delta_{kl} + c_2\delta_{ik}\delta_{jl} + c_3\delta_{il}\delta_{jk}, \tag{C.16}$$

$$I_{\{5\}} = c_1\delta_{jk}\varepsilon_{ilm} + c_2\delta_{jl}\varepsilon_{ikm} + c_3\delta_{jm}\varepsilon_{ikl} + c_4\delta_{kl}\varepsilon_{ijm} + c_5\delta_{km}\varepsilon_{ijl} + c_6\delta_{lm}\varepsilon_{ijk}, \tag{C.17}$$

$$\begin{aligned}
I_{\{6\}} = {} & c_1\delta_{ij}\delta_{kl}\delta_{mn} + c_2\delta_{ij}\delta_{km}\delta_{ln} + c_3\delta_{ij}\delta_{kn}\delta_{lm} + c_4\delta_{ik}\delta_{jl}\delta_{mn} + c_5\delta_{ik}\delta_{jm}\delta_{ln} \\
& + c_6\delta_{ik}\delta_{jn}\delta_{lm} + c_7\delta_{il}\delta_{jk}\delta_{mn} + c_8\delta_{il}\delta_{jm}\delta_{kn} + c_9\delta_{il}\delta_{jn}\delta_{km} + c_{10}\delta_{im}\delta_{jk}\delta_{ln} \\
& + c_{11}\delta_{im}\delta_{jl}\delta_{kn} + c_{12}\delta_{im}\delta_{jn}\delta_{kl} + c_{13}\delta_{in}\delta_{jk}\delta_{lm} + c_{14}\delta_{in}\delta_{jl}\delta_{km} + c_{15}\delta_{in}\delta_{jm}\delta_{kl},
\end{aligned} \tag{C.18}$$

$$\begin{aligned}
I_{\{7\}} = {} & c_1\delta_{kn}\delta_{lp}\varepsilon_{ijm} + c_2\delta_{kl}\delta_{np}\varepsilon_{ijm} + c_3\delta_{kp}\delta_{mn}\varepsilon_{ijl} + c_4\delta_{kn}\delta_{mp}\varepsilon_{ijl} + c_5\delta_{km}\delta_{np}\varepsilon_{ijl} + c_6\delta_{lp}\delta_{mn}\varepsilon_{ijk} \\
& + c_7\delta_{ln}\delta_{mp}\varepsilon_{ijk} + c_8\delta_{lm}\delta_{np}\varepsilon_{ijk} + c_9\delta_{jk}\delta_{lm}\varepsilon_{inp} + c_{10}\delta_{jk}\delta_{ln}\varepsilon_{imp} + c_{11}\delta_{jk}\delta_{lp}\varepsilon_{imn} \\
& + c_{12}\delta_{jm}\delta_{kn}\varepsilon_{ilp} + c_{13}\delta_{jk}\delta_{mn}\varepsilon_{ilp} + c_{14}\delta_{jm}\delta_{kp}\varepsilon_{iln} + c_{15}\delta_{jk}\delta_{mp}\varepsilon_{iln} + c_{16}\delta_{jn}\delta_{kp}\varepsilon_{ilm} \\
& + c_{17}\delta_{jk}\delta_{np}\varepsilon_{ilm} + c_{18}\delta_{jn}\delta_{lm}\varepsilon_{ikp} + c_{19}\delta_{jm}\delta_{ln}\varepsilon_{ikp} + c_{20}\delta_{jl}\delta_{mn}\varepsilon_{ikp} + c_{21}\delta_{jp}\delta_{lm}\varepsilon_{ikn} \\
& + c_{22}\delta_{jm}\delta_{lp}\varepsilon_{ikn} + c_{23}\delta_{jl}\delta_{mp}\varepsilon_{ikn} + c_{24}\delta_{jp}\delta_{ln}\varepsilon_{ikm} + c_{25}\delta_{jn}\delta_{lp}\varepsilon_{ikm} + c_{26}\delta_{jl}\delta_{np}\varepsilon_{ikm} \\
& + c_{27}\delta_{jp}\delta_{mn}\varepsilon_{ikl} + c_{28}\delta_{jn}\delta_{mp}\varepsilon_{ikl} + c_{29}\delta_{jm}\delta_{np}\varepsilon_{ikl} + c_{30}\delta_{kn}\delta_{lm}\varepsilon_{ijp} + c_{31}\delta_{km}\delta_{ln}\varepsilon_{ijp} \\
& + c_{32}\delta_{kl}\delta_{mn}\varepsilon_{ijp} + c_{33}\delta_{kp}\delta_{lm}\varepsilon_{ijn} + c_{34}\delta_{km}\delta_{lp}\varepsilon_{ijn} + c_{35}\delta_{kl}\delta_{mp}\varepsilon_{ijn} + c_{36}\delta_{kp}\delta_{ln}\varepsilon_{ijm},
\end{aligned} \tag{C.19}$$

$$\begin{aligned}
I_{\{8\}} = {} & c_1\delta_{iq}\delta_{jm}\delta_{kn}\delta_{lp} + c_2\delta_{iq}\delta_{jm}\delta_{kp}\delta_{ln} + c_3\delta_{iq}\delta_{jn}\delta_{kl}\delta_{mp} + c_4\delta_{iq}\delta_{jn}\delta_{km}\delta_{lp} + c_5\delta_{iq}\delta_{jn}\delta_{kp}\delta_{lm} \\
& + c_6\delta_{iq}\delta_{jp}\delta_{kl}\delta_{mn} + c_7\delta_{iq}\delta_{jp}\delta_{km}\delta_{ln} + c_8\delta_{iq}\delta_{jp}\delta_{kn}\delta_{lm} + c_9\delta_{ij}\delta_{kn}\delta_{lq}\delta_{mp} + c_{10}\delta_{ij}\delta_{kp}\delta_{nq}\delta_{lm} \\
& + c_{11}\delta_{ij}\delta_{kp}\delta_{ln}\delta_{mq} + c_{12}\delta_{ij}\delta_{kp}\delta_{lq}\delta_{mn} + c_{13}\delta_{ij}\delta_{kq}\delta_{np}\delta_{lm} + c_{14}\delta_{ij}\delta_{kq}\delta_{ln}\delta_{mp} + c_{15}\delta_{ij}\delta_{kq}\delta_{lp}\delta_{mn} \\
& + c_{16}\delta_{ik}\delta_{jl}\delta_{mq}\delta_{np} + c_{17}\delta_{ik}\delta_{jm}\delta_{lq}\delta_{np} + c_{18}\delta_{ik}\delta_{jn}\delta_{pq}\delta_{lm} + c_{19}\delta_{ik}\delta_{jn}\delta_{lq}\delta_{mp} + c_{20}\delta_{ik}\delta_{jp}\delta_{nq}\delta_{lm} \\
& + c_{21}\delta_{ik}\delta_{jp}\delta_{ln}\delta_{mq} + c_{22}\delta_{ik}\delta_{jp}\delta_{lq}\delta_{mn} + c_{23}\delta_{ik}\delta_{jq}\delta_{np}\delta_{lm} + c_{24}\delta_{ik}\delta_{jq}\delta_{ln}\delta_{mp} + c_{25}\delta_{ik}\delta_{jq}\delta_{lp}\delta_{mn} \\
& + c_{26}\delta_{il}\delta_{jk}\delta_{mn}\delta_{pq} + c_{27}\delta_{il}\delta_{jk}\delta_{mp}\delta_{nq} + c_{28}\delta_{il}\delta_{jk}\delta_{mq}\delta_{np} + c_{29}\delta_{il}\delta_{jm}\delta_{kq}\delta_{np} + c_{30}\delta_{il}\delta_{jn}\delta_{km}\delta_{pq} \\
& + c_{31}\delta_{il}\delta_{jn}\delta_{kq}\delta_{mp} + c_{32}\delta_{il}\delta_{jp}\delta_{km}\delta_{nq} + c_{33}\delta_{il}\delta_{jp}\delta_{kn}\delta_{mq} + c_{34}\delta_{il}\delta_{jp}\delta_{kq}\delta_{mn} + c_{35}\delta_{il}\delta_{jq}\delta_{km}\delta_{np} \\
& + c_{36}\delta_{il}\delta_{jq}\delta_{kn}\delta_{mp} + c_{37}\delta_{il}\delta_{jq}\delta_{kp}\delta_{mn} + c_{38}\delta_{im}\delta_{jk}\delta_{ln}\delta_{pq} + c_{39}\delta_{im}\delta_{jk}\delta_{lp}\delta_{nq} + c_{40}\delta_{ij}\delta_{kl}\delta_{mq}\delta_{np} \\
& + c_{41}\delta_{im}\delta_{jk}\delta_{lq}\delta_{np} + c_{42}\delta_{im}\delta_{jl}\delta_{kn}\delta_{pq} + c_{43}\delta_{im}\delta_{jl}\delta_{kp}\delta_{nq} + c_{44}\delta_{im}\delta_{jl}\delta_{kq}\delta_{np} + c_{45}\delta_{im}\delta_{jn}\delta_{kl}\delta_{pq} \\
& + c_{46}\delta_{im}\delta_{jn}\delta_{kq}\delta_{lp} + c_{47}\delta_{im}\delta_{jp}\delta_{kl}\delta_{nq} + c_{48}\delta_{im}\delta_{jp}\delta_{kn}\delta_{lq} + c_{49}\delta_{im}\delta_{jp}\delta_{kq}\delta_{ln} + c_{50}\delta_{im}\delta_{jq}\delta_{kl}\delta_{np} \\
& + c_{51}\delta_{im}\delta_{jq}\delta_{kn}\delta_{lp} + c_{52}\delta_{im}\delta_{jq}\delta_{kp}\delta_{ln} + c_{53}\delta_{in}\delta_{jk}\delta_{pq}\delta_{lm} + c_{54}\delta_{in}\delta_{jk}\delta_{lp}\delta_{mq} + c_{55}\delta_{in}\delta_{jk}\delta_{lq}\delta_{mp} \\
& + c_{56}\delta_{in}\delta_{jl}\delta_{km}\delta_{pq} + c_{57}\delta_{in}\delta_{jl}\delta_{kp}\delta_{mq} + c_{58}\delta_{in}\delta_{jl}\delta_{kq}\delta_{mp} + c_{59}\delta_{in}\delta_{jm}\delta_{kl}\delta_{pq} + c_{60}\delta_{in}\delta_{jm}\delta_{kp}\delta_{lq} \\
& + c_{61}\delta_{in}\delta_{jm}\delta_{kq}\delta_{lp} + c_{62}\delta_{in}\delta_{jp}\delta_{kl}\delta_{mq} + c_{63}\delta_{in}\delta_{jp}\delta_{km}\delta_{lq} + c_{64}\delta_{in}\delta_{jp}\delta_{kq}\delta_{lm} + c_{65}\delta_{in}\delta_{jq}\delta_{kl}\delta_{mp} \\
& + c_{66}\delta_{in}\delta_{jq}\delta_{km}\delta_{lp} + c_{67}\delta_{in}\delta_{jq}\delta_{kp}\delta_{lm} + c_{68}\delta_{ip}\delta_{jk}\delta_{nq}\delta_{lm} + c_{69}\delta_{ip}\delta_{jk}\delta_{ln}\delta_{mq} + c_{70}\delta_{ij}\delta_{km}\delta_{lq}\delta_{np} \\
& + c_{71}\delta_{ip}\delta_{jk}\delta_{lq}\delta_{mn} + c_{72}\delta_{ip}\delta_{jl}\delta_{km}\delta_{nq} + c_{73}\delta_{ip}\delta_{jl}\delta_{kn}\delta_{mq} + c_{74}\delta_{ip}\delta_{jl}\delta_{kq}\delta_{mn} + c_{75}\delta_{ip}\delta_{jm}\delta_{kl}\delta_{nq} \\
& + c_{76}\delta_{ip}\delta_{jm}\delta_{kn}\delta_{lq} + c_{77}\delta_{ip}\delta_{jm}\delta_{kq}\delta_{ln} + c_{78}\delta_{ip}\delta_{jn}\delta_{kl}\delta_{mq} + c_{79}\delta_{ip}\delta_{jn}\delta_{km}\delta_{lq} + c_{80}\delta_{ip}\delta_{jn}\delta_{kq}\delta_{lm} \\
& + c_{81}\delta_{ij}\delta_{kn}\delta_{pq}\delta_{lm} + c_{82}\delta_{ip}\delta_{jq}\delta_{kl}\delta_{mn} + c_{83}\delta_{ip}\delta_{jq}\delta_{km}\delta_{ln} + c_{84}\delta_{ip}\delta_{jq}\delta_{kn}\delta_{lm} + c_{85}\delta_{iq}\delta_{jk}\delta_{np}\delta_{lm} \\
& + c_{86}\delta_{iq}\delta_{jk}\delta_{ln}\delta_{mp} + c_{87}\delta_{iq}\delta_{jk}\delta_{lp}\delta_{mn} + c_{88}\delta_{iq}\delta_{jl}\delta_{km}\delta_{np} + c_{89}\delta_{iq}\delta_{jl}\delta_{kn}\delta_{mp} + c_{90}\delta_{iq}\delta_{jl}\delta_{kp}\delta_{mn} \\
& + c_{91}\delta_{iq}\delta_{jm}\delta_{kl}\delta_{np}.
\end{aligned} \tag{C.20}$$

In the next two sections, methods to obtain sets of basic isotropic tensors of rank $r > 3$ are presented. A method to reduce a set of basic isotropic tensors to a linearly independent set is described in Section C.6. The methods employ MATHEMATICA and are contained in the notebook `isotropic.nb`.

C.4 Isotropic tensors of even rank

Isotropic tensors of even rank are linear combinations of products of Kronecker deltas with distinct subscript permutations. The procedure to generate a complete set of isotropic tensors of even rank is equivalent to populating the Kronecker deltas of each product with distinct subscripts. This can be achieved as follows:

1. Generate all the subsets of length two from a set of unique subscripts corresponding to the rank of the tensor required.
2. Generate all the subsets of length $\frac{1}{2}$ rank from the set of pairs generated in the previous step.
3. Remove all the subsets with repeated subscripts from the set generated in Step 2.

The above procedure can be programmed in one line, but is computationally expensive:

```
Select[DeleteDuplicates /@ Flatten /@ Subsets[Subsets[
   Take[$PreferredSubscripts, rank],{2}], {rank/2}], Length[#] == rank&]
```

(To generate isotropic tensors by the method above is impractical for rank greater than 10, because in Step 2 unneeded subsets are generated.)

Avoiding redundant computation makes the algorithm more complicated, but reduces computation time dramatically. The procedure consists of a `while` loop that starts with four subscripts which are incremented by two until the required rank is attained. The procedure is as follows (the output corresponds to that from the generation of the sixth-rank isotropic tensors):

1. Generate the subscripts of the isotropic tensors of rank 4 using the previous method, or input them directly. Store this set in a variable (`previous`) to be used in each subsequent loop.
   ```
   previous = {{i,j,k,l},{i,k,j,l},{i,l,j,k}}
   ```
2. generate an inverse ordering of `previous` using MATHEMATICA's `Ordering[ ]` function.
   ```
   order = {{1,2,3,4},{1,3,2,4},{1,4,2,3}}
   ```
3. Increment the number of subscripts by two and generate a set of subscripts of this length.
   ```
   subs = {i,j,k,l,m,n}
   ```
4. Choose any subscript from the set generated in the previous step. Create a set of pairs of subscripts, each pair containing the selected subscript and one subscript from the rest of the set. (The number of pairs is one less than the number of subscripts.) When the selected subscript is `i`, then
   ```
   subsets = {{i,j},{i,k},{i,l},{i,m},{i,n}}
   ```
5. Loop the subscript pairs from Step 4.
   (a) Apply the ordering of Step 2 to the complement of the subscripts from Step 3 and the pair being looped (only the first complement is reproduced below).
   ```
   complements = {{k,l,m,n},{k,m,l,n},{k,n,l,m}}
   ```
   (b) Distribute the pair into the corresponding set of ordered complements.
   ```
   {{i,j,k,l,m,n},{i,j,k,m,l,n},{i,j,k,n,l,m}}
   ```

(c) Join the output into a single list

```
sublist = Join[sublist,{{i,j,k,l,m,n},{i,j,k,m,l,n},{i,j,k,n,l,m}}]
```

6. Store the resulting set as `previous`.

```
previous = sublist
```

7. Increment the rank by two (if the required rank is greater than six) and continue with Step 2.

The second method is 23 times faster for rank 8 than the first method, and 247 times faster for rank 10. The first method uses all available memory (4 Gb) for rank 12 and higher. The second method generates the 135 135 isotropic tensors of rank 14 in about 20 seconds. There are 2 027 025 rank-16 isotropic tensors: these take about five minutes to generate and use 65% of available memory (see Appendix B).

C.5 Isotropic tensors of odd rank

Obtaining all the permutations of odd rank, by combining a Levi-Civita tensor with a product of Kronecker deltas, is a simple extension of the method used for even rank. Here one generates all the subsets of length three. Each subset is then distributed into the even-rank isotropic tensors obtained from the complement of the set of subscripts and the subset of length three.

C.6 Linearly independent sets of isotropic tensors

The sets of isotropic tensors of even rank greater than six, and of odd rank greater than three, are not linearly independent because of the relation (C.8). Because the odd-rank tensors all contain a Levi-Civita tensor, this is obvious. For even-rank tensors, the reason is less obvious and is easiest illustrated by example. Consider the identically zero combination

$$\begin{aligned}
&-\delta_{iq}\delta_{jp}\delta_{kn}\delta_{lm}+\delta_{ip}\delta_{jq}\delta_{kn}\delta_{lm}+\delta_{iq}\delta_{jn}\delta_{kp}\delta_{lm}-\delta_{in}\delta_{jq}\delta_{kp}\delta_{lm}\\
&-\delta_{ip}\delta_{jn}\delta_{kq}\delta_{lm}+\delta_{in}\delta_{jp}\delta_{kq}\delta_{lm}+\delta_{iq}\delta_{jp}\delta_{km}\delta_{ln}-\delta_{ip}\delta_{jq}\delta_{km}\delta_{ln}\\
&-\delta_{iq}\delta_{jm}\delta_{kp}\delta_{ln}+\delta_{im}\delta_{jq}\delta_{kp}\delta_{ln}+\delta_{ip}\delta_{jm}\delta_{kq}\delta_{ln}-\delta_{im}\delta_{jp}\delta_{kq}\delta_{ln}\\
&-\delta_{iq}\delta_{jn}\delta_{km}\delta_{lp}+\delta_{in}\delta_{jq}\delta_{km}\delta_{lp}+\delta_{iq}\delta_{jm}\delta_{kn}\delta_{lp}-\delta_{im}\delta_{jq}\delta_{kn}\delta_{lp}\\
&-\delta_{in}\delta_{jm}\delta_{kq}\delta_{lp}+\delta_{im}\delta_{jn}\delta_{kq}\delta_{lp}+\delta_{ip}\delta_{jn}\delta_{km}\delta_{lq}-\delta_{in}\delta_{jp}\delta_{km}\delta_{lq}\\
&-\delta_{ip}\delta_{jm}\delta_{kn}\delta_{lq}+\delta_{im}\delta_{jp}\delta_{kn}\delta_{lq}+\delta_{in}\delta_{jm}\delta_{kp}\delta_{lq}-\delta_{im}\delta_{jn}\delta_{kp}\delta_{lq}.
\end{aligned}\tag{C.21}$$

By means of the identity (C.3), (C.21) becomes

$$\varepsilon_{ijk}(\delta_{lm}\varepsilon_{npq}-\delta_{ln}\varepsilon_{mpq}+\delta_{lp}\varepsilon_{mnq}-\delta_{lq}\varepsilon_{mnp}),\tag{C.22}$$

which, from (C.8), is zero.

Recognizing all the relations such as (C.21) to reduce the 105 basic isotropic tensors of rank 8 to a linearly independent set as in (C.20) is a formidable task. The following algorithm describes a method to obtain a linearly independent set of isotropic tensors using MATHEMATICA.

1. Form a matrix of the components of each isotropic tensor in the linearly dependent set. The rows correspond to the isotropic tensors, and the columns are the components. For rank five this is a 10×243 matrix, and for rank seven a 105×729 matrix.

2. Generate a unique symbol for each isotropic tensor in the linearly dependent set and place these on the diagonal of a unit matrix. (Better performance was attained, and less memory used, when prime numbers were used instead of unique symbols.)

3. Form the augmented matrix from the matrix of components obtained in Step 1, and the matrix of symbols obtained in Step 2, and perform a row reduction.

4. The first row, that contains zeroes in the first 3^{rank} columns of the matrix obtained in Step 3, corresponds to the first dependent. For rank five, this is row seven, which has the form
   $\{0,0,\ldots,0,1,0,0,0,-\frac{\$7}{\$3},\frac{\$8}{\$3},-\frac{\$9}{\$3},0,0,0\}$
   The denominator is the symbol corresponding to the first dependent isotropic tensor, the other symbols correspond to independents. Each of the rows, that contain zeroes in the first 3^{rank} columns, therefore represents a relation between one dependent and other independent isotropic tensors. Construct a list of symbols corresponding to the dependents from the denominators.

5. Construct a list of symbols corresponding to the independent isotropic tensors from the complement of the symbols from Step 2 and those from Step 4.

6. The independent isotropic tensors can now be obtained from the symbols corresponding to them.

7. If required, the linearly independent relations between the isotropic tensors can be obtained from the rows with zeroes in the first 3^{rank} columns identified in Step 4.

The major drawback of the above method is that the matrix of components consists of 3^{rank} columns, plus an additional number of columns corresponding to the number of symbols, given by (C.12). MATHEMATICA takes $3\frac{1}{2}$ seconds to row reduce the matrix for rank seven. For rank 9, the matrix consists of 1260 rows and $(19\,683 + 1260)$ columns. The time taken to row reduce the augmented matrix for rank 9 was just over three hours, and the memory used about 2 Gb. The method described above failed for rank 10. The isotropic tensors of rank 10 in the notebook `iso.nb` were determined by making small improvements, like using prime numbers as described in Step 2 above, and using lists for the Kronecker and Levi-Civita tensors instead of defining them as tensors. Sensible use of sparse matrices should make it possible to determine linearly independent sets of higher-rank isotropic tensors if needed. This author is not aware of published results for linearly independent sets of isotropic tensors of rank seven or higher.

C.7 Isotropic tensors contracted with symmetric tensors

In the calculations of linear independence, tensors with different symmetries are considered. When a general linearly independent isotropic tensor is contracted with a tensor that has intrinsic symmetry, some terms yield zero, and some terms acquire the same symmetry. Before linear independence can be established between tensors with intrinsic symmetries, the general isotropic tensors must therefore be modified accordingly.

In general, it is not sufficient to contract a symmetric tensor with a general isotropic tensor and then to remove duplicate terms and those that yield zero. It is possible that the intrinsic symmetry of the tensor introduces linear dependences, which must also be removed. Consider, for example, the electric quadrupole–electric quadrupole tensor d_{ijkl}. In the calculation of linear independence at electric octopole–magnetic quadrupole order for non-magnetics, the corresponding invariant tensor $\tilde{d}_{ijkl}$ is contracted with seventh- and eight-rank isotropic tensors to obtain linear combinations of rank three and four, respectively. The seventh-rank general isotropic tensor consists of 36 terms, and simplification of

$$I_{ijklmnp}d_{lmnp} \tag{C.23}$$

yields

$$c_1\varepsilon_{ijk}d_{lmlm} + c_2\varepsilon_{ijk}d_{llmm} + c_3\varepsilon_{ijl}d_{kmlm} + c_4\varepsilon_{ijl}d_{klmm} + c_5\varepsilon_{ikl}d_{jlmm} + c_6\varepsilon_{ikl}d_{jmlm} + c_7\varepsilon_{ilm}d_{jlkm}. \tag{C.24}$$

The terms in (C.24) are, however, not linearly independent because

$$\varepsilon_{ilm}d_{jlkm} = \tfrac{1}{2}\varepsilon_{ijk}d_{lmlm} - \tfrac{1}{2}\varepsilon_{ijk}d_{llmm} - \varepsilon_{ijl}d_{kmlm} + \varepsilon_{ijl}d_{klmm} - \varepsilon_{ikl}d_{jlmm} + \varepsilon_{ikl}d_{jmlm}. \tag{C.25}$$

To establish linear independence of the invariant tensor $\tilde{d}_{ijkl}$, the relation (C.25) must also be taken into account. The seventh-rank tensor with which $\tilde{d}_{ijkl}$ must be contracted, has only six terms. If the last term is eliminated, then the seventh-rank general isotropic tensor in the calculations of linear independence at electric octopole–magnetic quadrupole order for non-magnetics is

$$c_1\delta_{lp}\delta_{mn}\varepsilon_{ijk} + c_2\delta_{lm}\delta_{np}\varepsilon_{ijk} + c_3\delta_{kn}\delta_{lp}\varepsilon_{ijm} + c_4\delta_{kl}\delta_{np}\varepsilon_{ijm} + c_5\delta_{jn}\delta_{lm}\varepsilon_{ikp} + c_6\delta_{jm}\delta_{ln}\varepsilon_{ikp}. \tag{C.26}$$

Appendix D

Mathematical structure

The theory reviewed in Chapter 2 describes the interaction between a physical cause (the fields, their gradients and time derivatives), and a physical effect (multipole moments, source densities). The relation between cause and effect is described by a property tensor, which is in general origin dependent. The source densities (3.21) and (3.22) are origin independent due to a Van Vleck–Buckingham type cancellation of the origin dependences of tensors of the same multipole order in their expressions [6–8]. However, the property tensors Θ_{ijkl} and Φ_{ikjl} which appear in (3.21) and (3.22) are not origin independent (Chapters 3 and 4). In this appendix a procedure is described to determine the combinations of the polarizability tensors that yield invariant property tensors like Θ_{ijkl} and Φ_{ikjl}, whilst leaving (3.21) and (3.22) unchanged.

In order to find origin-independent combinations of polarizabilities, one needs to solve tensor equations consisting of linear combinations of property tensors (of different rank and contracted with appropriate isotropic tensors — Section D.2). Because tensors are completely described by their components, any identity must hold for each component. Thus a tensor identity of rank r in D dimensions yields D^r simultaneous linear equations. At higher multipole order, the equations involve tensors of higher rank (some of rank four at electric octopole–magnetic quadrupole order). The number of equations and unknowns involved makes manual solution a formidable task. Computer algebra packages are able to simplify this task, at the same time minimizing human error.

It is expedient to adapt the standard tensor notation (Section D.1), to allow generalization of the results from multipole theory (Chapter 2), and to facilitate the computer calculations.

D.1 Notation

In this section, notation is introduced that facilitates generalization of tensor expressions, particularly when these are infinite sums. The notation introduced here was conceived for the purpose of expressing the relations in Sections D.2–D.4, and the results in Appendix F. This author is not aware of similar notation in the literature.

1. Combinations of Cartesian tensors $T_{ijk\ldots}$, where $i, j, k, \ldots = 1, 2$ or 3, are considered.

2. If the tensor subscripts are not explicitly needed, the notation $T_{\{r\}}$ is used for a tensor of rank r. Thus

$$T_{\{4\}} \equiv T_{ijkl}. \tag{D.1}$$

3. When considering a product of tensors, the positions of the free indices and dummy indices are indicated using a list notation. The free subscripts are given by the unmatched entries in the lists of subscripts of the tensors in the product, and contracted subscripts are indicated by equal entries in the same positions. Thus, the outer product of a fifth-rank and a third-rank tensor is written as

$$A_{ijklm}B_{klm} \equiv A_{\{2,3\}}B_{\{0,3\}}. \tag{D.2}$$

The first position in the subscript list of A is unmatched in the list of B, indicating that A has two free subscripts. The number of subscripts in the second positions are matched, indicating that these are contracted. The rank of each tensor is the sum of the entries in its subscript list. As a further example, the vector potential (2.7)

$$A_i(\boldsymbol{r},t) = \varepsilon_{ijk}\left\{\tfrac{1}{2}B_j(0,t)r_k + \tfrac{1}{3}\left[\nabla_l B_j(\boldsymbol{r},t)\right]_0 r_k r_l + \tfrac{1}{8}\left[\nabla_m\nabla_l B_j(\boldsymbol{r},t)\right]_0 r_k r_l r_m + \cdots\right\}$$

can be expressed as

$$A_{\{1\}} = \varepsilon_{\{1,1,1\}}\sum_{\mu=1}\frac{\mu}{(\mu+1)!}B_{\{0,1,0,\mu-1\}}r_{\{0,0,1,\mu-1\}}, \tag{D.3}$$

where

$$\left[\nabla_j\nabla_k\nabla_l\ldots B_i(\boldsymbol{r},t)\right]_0 = B_{ijkl\ldots} \equiv B_{\{\mu\}}, \tag{D.4}$$

$$r_i r_j r_k\ldots = r_{ijk\ldots} \equiv r_{\{\nu\}}. \tag{D.5}$$

All trailing zeroes in the subscript lists can be safely omitted (i.e. $A_{\{1\}} \equiv A_{\{1,0,0,0\}}$).

4. Tensors are labelled with a counter in round brackets: $T^{(i)}_{\{r_i\}}$ is the i^{th} tensor of rank r_i.

5. Isotropic tensors of rank r are denoted $\mathcal{I}_{\{r\}}$. The most general linearly independent combination of isotropic tensors of rank r is (see Appendix C)

$$I_{\{r\}} = \sum_{i=1}^{N_r} c_i\mathcal{I}^{(i)}_{\{r\}}, \tag{D.6}$$

where c_i are arbitrary real coefficients and N_r is the number of linearly independent isotropic tensors of rank r.

6. Origin-independent tensors are indicated by a tilde. If $T_{\{r\}}$ is an origin-dependent tensor of rank r, then $\tilde{T}_{\{r\}}$ is the origin-independent linear extension of $T_{\{r\}}$ (see Section D.3).

D.2 Linear independence

Tensors of different rank can be compared by forming products with other tensors to form tensors of the same rank. In order to preserve the behaviour of the tensors under rotations of the reference frame, these products should be with isotropic tensors. The tensors A_{ij} and B_{ijk} have a linear dependency if, for instance, $\varepsilon_{ijl}A_{kl} = k\delta_{ij}B_{kll}$, where k is a constant. To eliminate all such possibilities, it is necessary to consider contractions of tensors of different rank with the appropriate general sets of linearly independent isotropic tensors as described below.

Consider a set of tensors $\{T^{(i)}_{\{r_i\}}\}$ of different rank with $i = 1,\ 2,\ \ldots,\ N$ and $r_i \geq 2$. If the set $\{r_j\} = \cup\{r_i\}$ represents the set of distinct ranks of the $T^{(i)}_{\{r_i\}}$, the most general linear combinations for each rank r_j, constructed from $\{T^{(i)}_{\{r_i\}}\}$ and isotropic tensors, are given by

$$\Lambda^{(j)}_{\{r_j\}} = \sum_{i=1}^{N} I_{\{r_j,r_i\}}T^{(i)}_{\{0,r_i\}}. \tag{D.7}$$

Equation (D.7) consists of two sets of equations. For each unique tensor rank r_j there is a sum consisting of D^{r_j} simultaneous equations in $c^{(j)}_k$ unknowns, where D is the physical dimension (three for Cartesian tensors), $k = 1,\ \ldots,\ N^{(j)}_k$, and $N^{(j)}_k$ is the sum of the number of linearly independent isotropic tensors of rank $r_i + r_j$ for each i.

Consider, for example, the set of tensors

$$\left\{T^{(1)}_{\{2\}}, T^{(2)}_{\{3\}}\right\} \equiv \{A_{ij}, B_{ijk}\}. \tag{D.8}$$

Here $N = 2$ and the distinct ranks are $\{r_1, r_2\} = \{2, 3\}$. The two linear combinations in (D.7) are

$$\begin{aligned}\Lambda^{(1)}_{\{r_1\}} &= I_{\{r_1,r_1\}} T^{(1)}_{\{0,r_1\}} + I_{\{r_1,r_2\}} T^{(2)}_{\{0,r_2\}} \\ &= I_{\{2,2\}} T^{(1)}_{\{0,2\}} + I_{\{2,3\}} T^{(2)}_{\{0,3\}}\end{aligned} \tag{D.9}$$

and

$$\begin{aligned}\Lambda^{(2)}_{\{r_2\}} &= I_{\{r_2,r_1\}} T^{(1)}_{\{0,r_1\}} + I_{\{r_2,r_2\}} T^{(2)}_{\{0,r_2\}} \\ &= I_{\{3,2\}} T^{(1)}_{\{0,2\}} + I_{\{3,3\}} T^{(2)}_{\{0,3\}},\end{aligned} \tag{D.10}$$

which are equivalent to

$$\Lambda^{(1)}_{ij} = I_{ijkl} A_{kl} + I_{ijklm} B_{klm}, \tag{D.11}$$

and

$$\Lambda^{(2)}_{ijk} = I_{ijklm} A_{lm} + I_{ijklmn} B_{lmn}, \tag{D.12}$$

respectively. Equation (D.11) consists of $3^2 = 9$ equations, each with $N^{(1)}_k = 3 + 6 = 9$ unknowns c_k (see (C.16) and (C.17)). Equation (D.12) consists of $3^3 = 27$ equations, each with $N^{(2)}_k = 6 + 15 = 21$ unknowns c_k (see (C.17) and (C.18)).

The tensors $\{T^{(i)}_{\{r_i\}}\}$ are linearly independent if each $\Lambda^{(j)} = 0$ only for the trivial solutions

$$c^{(j)}_k = 0. \tag{D.13}$$

If $r_{\max}$ is the maximum $\{r_j\}$, the question of whether it is sufficient to consider only the linear combinations $\Lambda_{\{r_{\max}\}}$ has not been considered. In practice, it is easier to first consider the linear combinations of smallest rank, as is done in Chapter 4. Linear independence of the combinations of higher rank then follows in a straightforward way due to the relations required by linear independence of the combinations of lower rank.

D.3 Origin independence

A tensor T^n of multipole order n is translationally invariant if it has the property

$$\Delta T^n = 0, \tag{D.14}$$

where Δ is a substitution operator that replaces T^n by its change $\bar{T}^n - T^n$ due to a shift of the coordinate origin. In general

$$\Delta T^n = f(T^m) \neq 0, \tag{D.15}$$

where $n > m \geq 1$,

$$\Delta T^1 = 0, \tag{D.16}$$

and f is a linear function of tensors (of lower multipole order) contracted with isotropic tensors, and products of the displacement of the origin $\boldsymbol{d}$ (see (2.64)–(2.79)).

At each multipole order, there is a finite set of polarizability tensors $T^{(i)}$ (see (2.38)–(2.53) and Table F.1). Origin-independent extensions of $T^{(i)}_{\{r\}}$ of the form

$$\tilde{T}^{(i)}_{\{r\}} = T^{(i)}_{\{r\}} + g\left(\mathcal{I}_{\{r,r'\}}T^{(j)}_{\{0,r'\}}\right) \tag{D.17}$$

are determined such that the $\tilde{T}^{(i)}_{\{r\}}$ are linearly independent, $T^{(i)}_{\{r\}}$ and $T^{(j)}_{\{r'\}}$ are of the same multipole order and g is a linear function of $\mathcal{I}_{\{r,r'\}}T^{(j)}_{\{0,r'\}}$. Furthermore, the extensions $\tilde{T}^{(i)}_{\{r\}}$ must yield observables that are unchanged when they are used in place of the origin-dependent $T^{(i)}_{\{r\}}$ in expressions for origin-independent observables (the bound source densities, Chapter 4).

D.4 Basis tensors

For a given rank, at a particular multipole order, an infinite set of linear combinations can be constructed from the finite set of the origin-dependent polarizabilities combined with isotropic tensors. In order to determine origin-independent linear extensions of the polarizability tensors of the form (D.17), it is helpful to first determine a set of origin-independent tensors that form a basis for the subset of all origin-independent tensors at a particular multipole order.

In general, there can be more than one polarizability tensor of a certain rank at each multipole order (for example, for a non-magnetic molecule at electric octopole–magnetic quadrupole order there are two fourth-rank tensors b_{ijkl} and d_{ijkl}, two third-rank tensors H'_{ijk} and L'_{ijk} and one second-rank tensor χ_{ij}).

To obtain linearly independent sets of tensors, linear combinations corresponding to each rank from the subset $\{r_j\}$ of the distinct ranks $\cup\{r_i\}$ are constructed according to (D.7). Each linear combination in (D.7) can be made origin independent by making the replacement

$$T^{(i)} \to \Delta T^{(i)} \tag{D.18}$$

and solving the resulting equations,

$$\Delta\Lambda^{(j)}_{\{r_j\}} = 0, \tag{D.19}$$

for the unknowns in the general isotropic tensors $I_{\{r\}}$. Substituting these solutions back into (D.7) one obtains

$$\tilde{\Lambda}^{(j)}_{\{r_j\}} = \sum_{i=1}^{\bar{N}}\left(\bar{c}_i\tilde{T}^{(i)}_{\{r_j\}}\right), \tag{D.20}$$

where each $\bar{c}_i$ multiplies an origin-independent expression $\tilde{T}^{(i)}_{\{r_j\}}$.

By the nature of the construction (D.7), the sets of tensors $\tilde{T}^{(i)}_{\{r_j\}}$ span the set of origin-independent tensors at each multipole order. The process of reducing this spanning set to a set of linearly independent basis tensors is tedious and best performed with algebraic manipulation software such as MATHEMATICA. The calculations at electric quadrupole–magnetic dipole order for non-magnetic and magnetic molecules are presented in Appendix E and Section 4.4.1, respectively.

Appendix E

Sample calculation of basis tensors

At electric quadrupole–magnetic dipole order for a non-magnetic molecule, linear origin-independent expressions are constructed from the polarizability tensors G'_{ij} and a_{ijk} (which depend on the choice of coordinate origin) and combinations of the isotropic tensors δ_{ij} and ε_{ijk}. The obvious way to proceed is to add linear combinations of G'_{ij} and a_{ijk}, formed with δ_{ij} and ε_{ijk}, to each polarizability tensor G'_{ij} and a_{ijk} until an origin-independent expression is found. This approach is not feasible, primarily because it does not provide a systematic way to obtain a span of the set of all origin-independent combinations. Instead, linear combinations of rank two and three are constructed from G'_{ij}, a_{ijk} and general isotropic tensors according to (D.7). The condition of origin independence (D.19) is then imposed on the linear combinations. The resulting expressions (D.20) contain unknown (arbitrary) coefficients $\overline{c}_i$, each multiplying an origin-independent expression. The resulting set of origin-independent expressions spans the set of origin-independent combinations that can be constructed from a linear combination of G'_{ij} and a_{ijk} contracted with isotropic tensors. To determine basis tensors, this set is reduced to a linearly independent set.

E.1 General expression

At electric quadrupole–magnetic dipole order there are two time-even polarizability tensors, G'_{ij} and a_{ijk} (Chapter 2). General expressions of rank two and three constructed from G'_{ij} and a_{ijk}, after taking into account the intrinsic symmetry $a_{ijk} = a_{ikj}$ (see Table 2.1), are given by

$$\begin{aligned}
\Lambda_{ij} &= I_{ijkl}G'_{kl} + \omega I_{ijklm}a_{klm} \\
&= c_1\delta_{ij}G'_{kk} + c_2G'_{ij} + c_3G'_{ji} + \omega(c_4\varepsilon_{ijk}a_{kll} + c_5\varepsilon_{ijk}a_{lkl} + c_6\varepsilon_{ikl}a_{kjl}), \qquad \text{(E.1)}\\
\Lambda_{ijk} &= \tfrac{1}{\omega}I_{ijklm}G'_{lm} + I_{ijklmn}a_{lmn} \\
&= \tfrac{1}{\omega}\left(c_1\delta_{jk}\varepsilon_{ilm}G'_{lm} + c_2\varepsilon_{ikl}G'_{jl} + c_3\varepsilon_{ikl}G'_{lj} + c_4\varepsilon_{ijl}G'_{kl} + c_5\varepsilon_{ijl}G'_{lk} + c_6\varepsilon_{ijk}G'_{ll}\right) \\
&\quad + c_7a_{ijk} + c_8a_{jik} + c_9a_{kij} + c_{10}\delta_{ij}a_{kll} + c_{11}\delta_{ij}a_{lkl} + c_{12}\delta_{ik}a_{jll} \\
&\quad + c_{13}\delta_{ik}a_{ljl} + c_{14}\delta_{jk}a_{ill} + c_{15}\delta_{jk}a_{lil}. \qquad \text{(E.2)}
\end{aligned}$$

The factors ω and $\frac{1}{\omega}$ in (E.1) and (E.2) have been introduced to ensure that the coefficients c_i are dimensionless.

The origin dependences $\Delta\Lambda_{ij}$ and $\Delta\Lambda_{ijk}$ are obtained by replacing a_{ijk} and G'_{ij} in (E.1) and (E.2) by their origin shifts (2.66) and (2.69). Origin independence is now imposed by requiring $\Delta\Lambda_{ij} = 0$ and $\Delta\Lambda_{ijk} = 0$. For the second-rank expression (E.1), this requires (see `02-basis.nb`)

$$\begin{aligned}
c_4 &= -\tfrac{1}{2}c_2,\\
c_5 &= \tfrac{1}{2}c_2, \qquad \text{(E.3)}\\
c_6 &= -\tfrac{1}{2}(c_2 + c_3),
\end{aligned}$$

and hence (E.1) yields

$$\tilde{\Lambda}_{ij} = c_1\tilde{T}^{(1)}_{ij} + c_2\tilde{T}^{(2)}_{ij} + c_3\tilde{T}^{(3)}_{ij}, \qquad \text{(E.4)}$$

where

$$\tilde{T}^{(1)}_{ij} = \delta_{ij} G'_{kk}, \tag{E.5}$$

$$\tilde{T}^{(2)}_{ij} = G'_{ij} - \tfrac{1}{2}\omega(\varepsilon_{ijk} a_{kll} - \varepsilon_{ijk} a_{lkl} + \varepsilon_{ikl} a_{kjl}), \tag{E.6}$$

$$\tilde{T}^{(3)}_{ij} = G'_{ji} - \tfrac{1}{2}\omega \varepsilon_{ikl} a_{kjl}. \tag{E.7}$$

The relation (E.7) is an obvious starting point: it is just v_{ji}, the transpose of the origin-independent tensor v_{ij} defined in (4.24). It is straightforward to show that

$$T^{(1)}_{ij} = \delta_{ij} v_{kk} \tag{E.8}$$

(because $v_{kk} = G'_{kk}$) and

$$T^{(2)}_{ij} = v_{ij}. \tag{E.9}$$

To obtain (E.9), the identity

$$\varepsilon_{jkl} a_{kil} = \varepsilon_{ijk} a_{kll} - \varepsilon_{ijk} a_{lkl} + \varepsilon_{ikl} a_{kjl}, \tag{E.10}$$

based on (C.8), was used.

Similarly, origin independence of (E.2) requires (see `02-basis.nb`)

$$\begin{aligned} c_7 &= -\tfrac{1}{2}(c_2 + c_3 + c_4 + c_5), \\ c_8 &= \tfrac{1}{2}(c_4 + c_5), \\ c_9 &= \tfrac{1}{2}(c_2 + c_3), \\ c_{10} &= -c_{11} = -\tfrac{1}{2}c_3, \\ c_{12} &= -c_{13} = -\tfrac{1}{2}c_5, \\ c_{14} &= -c_{15} = -\tfrac{1}{2}(c_1 - c_3 - c_5). \end{aligned} \tag{E.11}$$

Then, (E.2) yields

$$\tilde{\Lambda}_{ijk} = c_1 \tilde{T}^{(1)}_{ijk} + c_2 \tilde{T}^{(2)}_{ijk} + c_3 \tilde{T}^{(3)}_{ijk} + c_4 \tilde{T}^{(4)}_{ijk} + c_5 \tilde{T}^{(5)}_{ijk} + c_6 \tilde{T}^{(6)}_{ijk}, \tag{E.12}$$

where

$$\tilde{T}^{(1)}_{ijk} = \delta_{jk} \varepsilon_{ilm} G'_{lm}, \tag{E.13}$$

$$\tilde{T}^{(2)}_{ijk} = \varepsilon_{ikl} G'_{jl} - \tfrac{1}{2}\omega(a_{ijk} - a_{kij}), \tag{E.14}$$

$$\tilde{T}^{(3)}_{ijk} = \varepsilon_{ikl} G'_{lj} - \tfrac{1}{2}\omega(a_{ijk} - a_{kij} + \delta_{ij} a_{kll} - \delta_{ij} a_{lkl} - \delta_{jk} a_{ill} + \delta_{jk} a_{lil}), \tag{E.15}$$

$$\tilde{T}^{(4)}_{ijk} = \varepsilon_{ijl} G'_{kl} - \tfrac{1}{2}\omega(a_{ijk} - a_{jik}), \tag{E.16}$$

$$\tilde{T}^{(5)}_{ijk} = \varepsilon_{ijl} G'_{lk} - \tfrac{1}{2}\omega(a_{ijk} - a_{jik} + \delta_{ik} a_{jll} - \delta_{ik} a_{ljl} - \delta_{jk} a_{ill} + \delta_{jk} a_{lil}), \tag{E.17}$$

$$\tilde{T}^{(6)}_{ijk} = \varepsilon_{ijk} G'_{ll}. \tag{E.18}$$

It is straightforward to show that,

$$\tilde{T}^{(1)}_{ijk} = \delta_{jk} \varepsilon_{ilm} v_{lm}, \tag{E.19}$$

$$\tilde{T}^{(2)}_{ijk} = \tilde{T}^{(4)}_{ikj} = \varepsilon_{ikl} v_{jl}, \tag{E.20}$$

$$\tilde{T}^{(3)}_{ijk} = \tilde{T}^{(5)}_{ikj} = \varepsilon_{ikl} v_{lj}, \tag{E.21}$$

$$\tilde{T}^{(6)}_{ijk} = \varepsilon_{ijk} v_{ll}. \tag{E.22}$$

The tensor v_{ij} therefore spans the set of all origin-independent tensors that can be constructed from linear combinations of G'_{ij} and a_{ijk} with the aid of isotropic tensors. Here, linear independence is trivial as there is only one basis tensor; v_{ij} is a basis for the origin-independent tensors constructed from the time-even tensors at electric quadrupole–magnetic dipole order. These apply in linear, homogeneous media: in non-linear, inhomogeneous media, origin independence is achieved in other ways [7, Section XII].

Appendix F

Generalized results

The expressions quoted in the literature, corresponding to the results reviewed in Chapter 2, often obscure the origin of their derivation, since general forms in terms of the perturbation order are not given. In this appendix, generalized results are presented for these results using the notation described in Appendix D. These expressions are useful when they need to be incorporated in computer code, as well as to generalize the results to higher multipole orders.

In this appendix, the symbol q_i is used for the electric dipole moment operator; thus $q_i \equiv p_i$. The short-hand notations

$$r_i r_j r_k \ldots = r_{ijk\ldots} \equiv r_{\{\nu\}}, \tag{F.1}$$

$$[\nabla_j \nabla_k \nabla_l \ldots E_i(\boldsymbol{r}, t)]_0 = E_{ijkl\ldots} \equiv E_{\{\mu\}}, \tag{F.2}$$

$$[\nabla_j \nabla_k \nabla_l \ldots B_i(\boldsymbol{r}, t)]_0 = B_{ijkl\ldots} \equiv B_{\{\mu\}}, \tag{F.3}$$

are implied throughout (see (D.4) and (D.5)).

Use of the potentials (2.7) and (2.8) in the perturbation Hamiltonians (2.3) and (2.4) yields

$$H^{(1)} = q\phi - \sum_{\mu=1} \frac{1}{\mu!} \left[q_{\{\mu\}} E_{\{\mu\}} + m_{\{\mu\}} B_{\{\mu\}} \right] \tag{F.4}$$

and

$$\begin{aligned} H^{(2)} = -2 \sum_{\mu=1} \frac{\mu}{(\mu+1)!} \Bigg[& \frac{\mu^2}{(2\mu-1)(\mu+1)!} \chi_{\{1,1,\mu-1,\mu-1\}} B_{\{1,0,\mu-1,0\}} B_{\{0,1,0,\mu-1\}} \\ & + \sum_{\nu=1} \frac{(2\mu+\nu)(\mu+\nu)}{(2\mu+\nu-1)(\mu+\nu+1)!} \chi_{\{1,1,\mu-1,\mu+\nu-1\}} B_{\{1,0,\mu-1,0\}} B_{\{0,1,0,\mu+\nu-1\}} \Bigg], \end{aligned} \tag{F.5}$$

where the generalized electric multipole moments are given by

$$q_{\{\mu\}} = \sum_{\alpha=1}^{N} q^{(\alpha)} r^{(\alpha)}_{\{\mu\}}. \tag{F.6}$$

Generalized magnetic multipole moments are given by

$$m'_{\{\mu\}} = m_{\{\mu\}} + \frac{2\mu}{\mu+1} \sum_{\nu=1} \frac{\nu(\mu+\nu)}{(\mu+\nu-1)(\nu+1)!} \chi_{\{2,\mu+\nu-2\}} B_{\{0,\nu\}}, \tag{F.7}$$

where

$$m_{\{\mu\}} = \sum_{\alpha=1}^{N} \frac{q^{(\alpha)}}{2m^{(\alpha)}} \frac{\mu}{\mu+1} \left[r^{(\alpha)}_{\{0,\mu-1\}} l^{(\alpha)}_{\{1\}} + l^{(\alpha)}_{\{1\}} r^{(\alpha)}_{\{0,\mu-1\}} \right] \tag{F.8}$$

and

$$\chi_{\{2,\mu\}} = \sum_{\alpha=1}^{N} \frac{\left(q^{(\alpha)}\right)^2}{2m^{(\alpha)}} \frac{\mu+1}{\mu+2} \left[r^{(\alpha)}_{\{2\}} - \delta_{\{2\}} \left(r^{(\alpha)} \right)^2 \right] r^{(\alpha)}_{\{0,\mu\}}. \tag{F.9}$$

F.1 Expectation values

Generalized expectation values for electric multipole moments are

$$\overline{q}_{\{\mu\}} = q^{(0)}_{\{\mu\}} + \sum_{\nu=1} \frac{1}{\nu!} \left[\mathcal{P}^{qq}_{\{\mu,\nu\}} E_{\{0,\nu\}} + \frac{1}{\omega} \mathcal{P}'^{qq}_{\{\mu,\nu\}} \dot{E}_{\{0,\nu\}} + \mathcal{P}^{qm}_{\{\mu,\nu\}} B_{\{0,\nu\}} + \frac{1}{\omega} \mathcal{P}'^{qm}_{\{\mu,\nu\}} \dot{B}_{\{0,\nu\}} \right], \tag{F.10}$$

and for magnetic multipole moments

$$\overline{m}_{\{\mu\}} = m^{(0)}_{\{\mu\}} + \sum_{\nu=1} \frac{1}{\nu!} \left[\mathcal{P}^{mq}_{\{\mu,\nu\}} E_{\{0,\nu\}} + \frac{1}{\omega} \mathcal{P}'^{mq}_{\{\mu,\nu\}} \dot{E}_{\{0,\nu\}} + \mathcal{P}^{mm+}_{\{\mu,\nu\}} B_{\{0,\nu\}} + \frac{1}{\omega} \mathcal{P}'^{mm}_{\{\mu,\nu\}} \dot{B}_{\{0,\nu\}} \right]. \tag{F.11}$$

Here $q^{(0)}_{\{\mu\}}$ and $m^{(0)}_{\{\mu\}}$ are the permanent electric and magnetic 2^μ-pole moments,

$$\mathcal{P}^{qq}_{\{\mu,\nu\}} = \frac{2}{\hbar} \sum_{s\neq n} \omega_{sn} Z_{sn} \mathcal{Re} \left\{ \langle q_{\{\mu\}} \rangle_{ns} \langle q_{\{\nu\}} \rangle_{sn} \right\}, \tag{F.12}$$

$$\mathcal{P}'^{qq}_{\{\mu,\nu\}} = -\frac{2}{\hbar} \sum_{s\neq n} \omega Z_{sn} \mathcal{Im} \left\{ \langle q_{\{\mu\}} \rangle_{ns} \langle q_{\{\nu\}} \rangle_{sn} \right\}, \tag{F.13}$$

$$\mathcal{P}^{qm}_{\{\mu,\nu\}} = \frac{2}{\hbar} \sum_{s\neq n} \omega_{sn} Z_{sn} \mathcal{Re} \left\{ \langle q_{\{\mu\}} \rangle_{ns} \langle m_{\{\nu\}} \rangle_{sn} \right\}, \tag{F.14}$$

$$\mathcal{P}'^{qm}_{\{\mu,\nu\}} = -\frac{2}{\hbar} \sum_{s\neq n} \omega Z_{sn} \mathcal{Im} \left\{ \langle m_{\{\mu\}} \rangle_{ns} \langle q_{\{\nu\}} \rangle_{sn} \right\}, \tag{F.15}$$

$$\mathcal{P}^{mm}_{\{\mu,\nu\}} = \frac{2}{\hbar} \sum_{s\neq n} \omega_{sn} Z_{sn} \mathcal{Re} \left\{ \langle m_{\{\mu\}} \rangle_{ns} \langle m_{\{\nu\}} \rangle_{sn} \right\}, \tag{F.16}$$

$$\mathcal{P}'^{mm}_{\{\mu,\nu\}} = -\frac{2}{\hbar} \sum_{s\neq n} \omega Z_{sn} \mathcal{Im} \left\{ \langle m_{\{\mu\}} \rangle_{ns} \langle m_{\{\nu\}} \rangle_{sn} \right\} \tag{F.17}$$

and

$$\mathcal{P}^{mm+}_{\{\mu,\nu\}} = \mathcal{P}^{mm}_{\{\mu,\nu\}} + \frac{2\mu\nu}{(\mu+1)(\nu+1)} \sum_{\alpha} \frac{\left(q^{(\alpha)}\right)^2}{2m^{(\alpha)}} \left\langle \left[r^{(\alpha)}_{\{2\}} + \delta_{\{2\}} \left(r^{(\alpha)}\right)^2 \right] r^{(\alpha)}_{\{0,\mu+\nu-2\}} \right\rangle_{nn}. \tag{F.18}$$

For example, $\mathcal{P}^{qq}_{\{1,1\}} = \alpha_{ij}$, $\mathcal{P}^{qq}_{\{1,3\}} = b_{ijkl}$ and $\mathcal{P}^{qq}_{\{3,1\}} = b_{lijk}$, etc.

F.2 Origin shifts

Generalized origin shifts for electric 2^μ–electric 2^ν polarizabilities are

$$\Delta\mathcal{P}^{qq}_{\{\mu,\nu\}} = \sum_{\substack{\kappa=1\\ \mu>1}}^{\mu-1} (-1)^\kappa \sum_{\mathscr{P}(\kappa)}^{\binom{\mu}{\kappa}} \mathcal{P}^{qq}_{\{\mu-\kappa,\nu\}} d_{\{\kappa\}} + \sum_{\substack{\lambda=1\\ \nu>1}}^{\nu-1} (-1)^\lambda \sum_{\mathscr{P}(\lambda)}^{\binom{\nu}{\lambda}} \mathcal{P}^{qq}_{\{\mu,\nu-\lambda\}} d_{\{0,\lambda\}} + \sum_{\substack{\kappa=1\\ \mu>1}}^{\mu-1} \sum_{\substack{\lambda=1\\ \nu>1}}^{\nu-1} (-1)^{\kappa+\lambda} \sum_{\mathscr{P}(\kappa)}^{\binom{\mu}{\kappa}} \sum_{\mathscr{P}(\lambda)}^{\binom{\nu}{\lambda}} \mathcal{P}^{qq}_{\{\mu-\kappa,\nu-\lambda\}} d_{\{\kappa,\lambda\}}, \tag{F.19}$$

$$\Delta\mathcal{P}'^{qq}_{\{\mu,\nu\}} = \sum_{\substack{\kappa=1\\ \mu>1}}^{\mu-1} (-1)^\kappa \sum_{\mathscr{P}(\kappa)}^{\binom{\mu}{\kappa}} \mathcal{P}'^{qq}_{\{\mu-\kappa,\nu\}} d_{\{\kappa\}} - \sum_{\substack{\lambda=1\\ \nu>1}}^{\nu-1} (-1)^\lambda \sum_{\mathscr{P}(\lambda)}^{\binom{\nu}{\lambda}} \mathcal{P}'^{qq}_{\{\mu,\nu-\lambda\}} d_{\{0,\lambda\}} + \sum_{\substack{\kappa=1\\ \mu>1}}^{\mu-1} \sum_{\substack{\lambda=1\\ \nu>1}}^{\nu-1} (-1)^{\kappa+\lambda} \sum_{\mathscr{P}(\kappa)}^{\binom{\mu}{\kappa}} \sum_{\mathscr{P}(\lambda)}^{\binom{\nu}{\lambda}} \mathcal{P}'^{qq}_{\{\mu-\kappa,\nu-\lambda\}} d_{\{\kappa,\lambda\}}. \tag{F.20}$$

In (F.19) and (F.20), the sums with the symbol $\mathscr{P}(\lambda)$ in the lower limit denote that the sums are taken over the permutations of λ. The upper limit simply counts the number of permutations and is redundant. Consider for example the time-even electric dipole–electric octopole polarizability tensor b_{ijkl} given by (F.12) with $\mu = 1$ and $\nu = 3$. The origin dependence Δb_{ijkl} is given by (F.19). The first and last sums in (F.19) are zero because $\mu = 1$; thus

$$\begin{aligned}\Delta b_{ijkl} &= \sum_{\lambda=1}^{2}(-1)^{\lambda}\sum_{\mathscr{P}(\lambda)}^{\binom{3}{\lambda}}\mathcal{P}^{qq}_{\{1,3-\lambda\}}d_{\{0,\lambda\}} \\ &= -\sum_{\mathscr{P}(\lambda)}^{3}\mathcal{P}^{qq}_{\{1,2\}}d_{\{0,1\}} + \sum_{\mathscr{P}(\lambda)}^{3}\mathcal{P}^{qq}_{\{1,1\}}d_{\{0,2\}} \\ &= -(a_{ijk}d_l + a_{ijl}d_k + a_{ikl}d_j) + \alpha_{ij}d_kd_l + \alpha_{ik}d_jd_l + \alpha_{il}d_jd_k. \end{aligned} \tag{F.21}$$

The electric quadrupole–electric quadrupole polarizability requires all three sums, and perhaps provides a better example. Consider the origin dependence $\Delta d'_{ijkl}$ of the time-odd tensor; (F.20) with $\mu = \nu = 2$ gives

$$\begin{aligned}\Delta d'_{ijkl} = \Delta\mathcal{P}'^{qq}_{\{2,2\}} &= -\sum_{\mathscr{P}(\kappa)}^{2}\mathcal{P}'^{qq}_{\{1,2\}}d_{\{1\}} + \sum_{\mathscr{P}(\lambda)}^{2}\mathcal{P}'^{qq}_{\{2,1\}}d_{\{0,1\}} + \sum_{\mathscr{P}(\kappa)}^{2}\sum_{\mathscr{P}(\lambda)}^{2}\mathcal{P}'^{qq}_{\{1,1\}}d_{\{1,1\}} \\ &= -(a'_{ikl}d_j + a'_{jkl}d_i) + \mathfrak{a}'_{ijk}d_l + \mathfrak{a}'_{ijl}d_k + \alpha'_{ik}d_jd_l + \alpha'_{jk}d_id_k + \alpha'_{il}d_jd_k + \alpha'_{jl}d_id_k, \end{aligned} \tag{F.22}$$

where $\mathfrak{a}'_{ijk} = a'_{kij}$.

Generalized results for the multipole polarizabilities involving matrix elements of the magnetic multipole moments are not given, as it is unclear what the general form of the origin dependences for the magnetic multipoles are (see Appendix A).

m	Multipole order	Multipole moments	Polarizabilities	N_m
1	Electric dipole	p_i	α_{ij} e_1e_1	1
2	Electric quadrupole– magnetic dipole	$p_i,\ q_{ij},\ m_i$	a_{ijk} G'_{ij} e_1e_2 e_1m_1	2
3	Electric octopole– magnetic quadrupole	p_i q_{ij} q_{ijk} m_i m_{ij}	b_{ijkl} d_{ijkl} H'_{ijk} L'_{ijk} χ_{ij} e_1e_3 e_2e_2 e_1m_2 e_2m_1 m_1m_1	5
4	Electric hexadecapole– magnetic octopole	p_i q_{ij} q_{ijk} q_{ijkl} m_i m_{ij} m_{ijk}	e_1e_4 e_2e_3 e_1m_3 e_2m_2 e_3m_1 m_1m_2	6
5	Electric 2^5 pole – magnetic hexadecapole	p_i q_{ij} q_{ijk} q_{ijkl} q_{ijklm} m_i m_{ij} m_{ijk} m_{ijkl}	e_1e_5 e_2e_4 e_3e_3 e_1m_4 e_2m_3 e_3m_2 e_4m_1 m_1m_3 m_2m_2	9

Table F.1: Multipole moments and polarizabilities for a non-magnetic molecule. The notation in the fourth column refers to the multipole moments occurring in the matrix elements of the molecular polarizabilities (e_1 for electric dipole, e_2 for electric quadrupole, m_1 for magnetic dipole etc. See (2.38)–(2.53)). The last column is a count (N_m) of the number of polarizability tensors at each multipole order.

Note that for even multipole order

$$N_m = \binom{m}{2} + (m-1) + \binom{m-2}{2} = 2m - 2 \tag{F.23}$$

and for odd multipole order

$$N_m = \binom{m+1}{2} + (m-1) + \binom{m-1}{2} = 2m - 1. \tag{F.24}$$

Appendix G

Tensor components

Consider a Cartesian tensor of rank r which has no symmetry. Then the number of components is 3^r. For a totally symmetric tensor, the number of independent components equals the number of combinations of the subscripts with repetitions allowed (order is irrelevant). This is the multiset of size r that can be selected from n elements, given by [55]

$$\begin{pmatrix} r+n-1 \\ r \end{pmatrix}. \tag{G.1}$$

Here n corresponds to the range of values which the subscripts can assume: for a Cartesian tensor, this is always three. The number of independent components of a totally symmetric Cartesian tensor is therefore

$$N_r = \begin{pmatrix} r+3-1 \\ r \end{pmatrix}. \tag{G.2}$$

G.1 Totally symmetric tensors

For a second-rank tensor, which is symmetric in both subscripts, N_2 is equal to the multiset of size two selected from three elements; that is

$$N_2 = \begin{pmatrix} 2+3-1 \\ 2 \end{pmatrix} = \begin{pmatrix} 4 \\ 2 \end{pmatrix} = \frac{4!}{2!(4-2)!} = 6. \tag{G.3}$$

For a third-rank tensor which is symmetric in all three subscripts, N_3 is equal to the multiset of size three selected from three elements; that is

$$N_3 = \begin{pmatrix} 3+3-1 \\ 3 \end{pmatrix} = \begin{pmatrix} 5 \\ 3 \end{pmatrix} = \frac{5!}{3!(5-3)!} = 10. \tag{G.4}$$

For a fourth-rank tensor which is symmetric in all four subscripts, N_4 is equal to the multiset of size four selected from three elements; that is

$$N_4 = \begin{pmatrix} 4+3-1 \\ 4 \end{pmatrix} = \begin{pmatrix} 6 \\ 4 \end{pmatrix} = \frac{6!}{4!(6-4)!} = 15. \tag{G.5}$$

G.2 Tensors with partial symmetries

A third-rank tensor symmetric in two subscripts can be viewed as the product of a first-rank tensor and a second-rank symmetric tensor. The first-rank tensor has three independent components, each of which combines with the six independent components of the second-rank symmetric tensor. A third-rank tensor symmetric in two subscripts therefore has $3N_2 = 3 \times 6 = 18$ independent components.

A fourth-rank tensor symmetric in three subscripts can be viewed as the product of a first-rank tensor and a third-rank totally symmetric tensor. Thus a tensor like the electric dipole–electric octopole molecular polarizability b_{ijkl} has $3N_3 = 3 \times 10 = 30$ independent components.

A tensor like the time-even electric quadrupole–electric quadrupole molecular polarizability d_{ijkl} requires some care. Consider first two *different* second-rank symmetric tensors. Each has six independent components, so their combination would produce $N_2N_2 = 6 \times 6 = 36$ independent components.

Now consider the combination of a second-rank symmetric tensor with itself. One must now subtract from the 36 independent components when the tensors are distinct, the number of (unordered) subsets of length two that are formed from the six independent coefficients of the symmetric second-rank tensor. The number of independent components of a tensor like d_{ijkl} is thus

$$36 - \begin{pmatrix} 6 \\ 2 \end{pmatrix} = 36 - \frac{6!}{2!(6-2)!} = 36 - 15 = 21. \tag{G.6}$$

Alternatively, the 36 components of two different second-rank symmetric tensors can be regarded as the components of a 6×6 matrix. When the two second-rank tensors are the same, the 6×6 matrix is symmetric. A symmetric 6×6 matrix has $\frac{36-6}{2} + 6 = 21$ independent components.

G.3 Antisymmetric tensors

The diagonal components of an antisymmetric second-rank tensor are zero. The number of independent components of a second-rank antisymmetric tensor, like the time-odd electric dipole–electric dipole tensor α'_{ij}, can therefore be obtained from (G.3) minus the number of zero diagonal components. A second-rank antisymmetric tensor thus has $6 - 3 = 3$ independent components.

The time-odd electric quadrupole-electric quadrupole tensor is antisymmetric in a pair of subscripts: $d'_{ijkl} = d'_{jikl} = -d'_{klij}$. From the 21 independent components of the symmetric time-even counterpart d_{ijkl} described above, must therefore be subtracted six, corresponding to the six symmetric diagonal components of d_{ijkl}. The tensor d'_{ijkl} therefore has $21 - 6 = 15$ independent components.

Appendix H

Building blocks

Origin-independent tensors (building blocks), with symmetries corresponding to the time-even and time-odd molecular polarizability tensors at electric quadrupole–magnetic dipole and electric octopole–magnetic quadrupole order, are listed. Where there are linear dependencies between the building blocks, the relations are given. The calculations used to construct the building blocks, and to verify their linear independence, are contained in MATHEMATICA notebooks. The notebooks are named according to the molecular polarizability tensors for which the building blocks are constructed in a consistent, and hopefully obvious, manner. Thus the notebooks containing the calculations used to obtain (H.1)–(H.8) for the building blocks of the time-even tensors at electric quadrupole–magnetic dipole order are in the directory `e2m1-nm`, and are named `bbG.nb` and `bba.nb`.

The building blocks listed in this appendix are used to construct general invariant precursor expressions corresponding to the molecular polarizabilities at electric quadrupole–magnetic dipole order (Sections 4.3 and 4.4) and electric octopole–magnetic quadrupole order (Chapter 5).

H.1 Electric quadrupole–magnetic dipole order: Non-magnetic molecules

H.1.1 Building blocks for $\tilde{G}'_{ij}$

The building blocks for $\tilde{G}'_{ij}$ are constructed in the notebook `bbG.nb`.

$$\tilde{G}'^{(1)}_v = v_{ij}, \tag{H.1}$$
$$\tilde{G}'^{(2)}_v = v_{ji}, \tag{H.2}$$
$$\tilde{G}'^{(3)}_v = \delta_{ij} v_{kk}. \tag{H.3}$$

H.1.2 Building blocks for $\tilde{a}_{ijk}$

The building blocks for $\tilde{a}_{ijk}$ are constructed in the notebook `bba.nb`.

$$\tilde{a}^{(1)}_v = \varepsilon_{ijl} v_{kl} + \varepsilon_{ikl} v_{jl}, \tag{H.4}$$
$$\tilde{a}^{(2)}_v = \varepsilon_{ijl} v_{lk} + \varepsilon_{ikl} v_{lj}, \tag{H.5}$$
$$\tilde{a}^{(3)}_v = \delta_{jk} \varepsilon_{ilm} v_{lm}, \tag{H.6}$$
$$\tilde{a}^{(4)}_v = \delta_{ij} \varepsilon_{klm} v_{lm} + \delta_{ik} \varepsilon_{jlm} v_{lm}, \tag{H.7}$$

where

$$\tilde{a}^{(1)}_v - \tilde{a}^{(2)}_v - 2\tilde{a}^{(3)}_v + \tilde{a}^{(4)}_v = 0. \tag{H.8}$$

H.2 Electric quadrupole–magnetic dipole order: Magnetic molecules

H.2.1 Building blocks for $\tilde{G}_{ij}$

The building blocks for $\tilde{G}_{ij}$ are constructed in the notebook `bbG.nb`.

$$\tilde{G}_w^{(1)} = w_{ij}, \tag{H.9}$$
$$\tilde{G}_w^{(2)} = w_{ji}, \tag{H.10}$$
$$\tilde{G}_w^{(3)} = \delta_{ij} w_{kk}, \tag{H.11}$$
$$\tilde{G}_s^{(4)} = \varepsilon_{ijk} s_{kll}. \tag{H.12}$$

H.2.2 Building blocks for $\tilde{a}'_{ijk}$

The building blocks for $\tilde{a}'_{ijk}$ are constructed in the notebook `bba.nb`.

$$\tilde{a}_w'^{(1)} = \varepsilon_{ijl} w_{kl} + \varepsilon_{ikl} w_{jl}, \tag{H.13}$$
$$\tilde{a}_w'^{(2)} = \varepsilon_{ijl} w_{lk} + \varepsilon_{ikl} w_{lj}, \tag{H.14}$$
$$\tilde{a}_w'^{(3)} = \delta_{jk} \varepsilon_{ilm} w_{lm}, \tag{H.15}$$
$$\tilde{a}_w'^{(4)} = \delta_{ij} \varepsilon_{klm} w_{lm} + \delta_{ik} \varepsilon_{jlm} w_{lm}, \tag{H.16}$$

where

$$\tilde{a}_w'^{(1)} - \tilde{a}_w'^{(2)} - 2\tilde{a}_w'^{(3)} + \tilde{a}_w'^{(4)} = 0. \tag{H.17}$$

$$\tilde{a}_s'^{(1)} = s_{ijk}, \tag{H.18}$$
$$\tilde{a}_s'^{(2)} = \delta_{ij} s_{kll} + \delta_{ik} s_{jll}, \tag{H.19}$$
$$\tilde{a}_s'^{(3)} = \delta_{jk} s_{ill}. \tag{H.20}$$

H.3 Electric octopole–magnetic quadrupole order: Non-magnetic molecules

H.3.1 Building blocks for $\tilde{\chi}_{ij}$

The building blocks for $\tilde{\chi}_{ij}$ are constructed in the notebook `bbx.nb`.

$$\tilde{\chi}_{\mathcal{Q}}^{(1)} = \mathcal{Q}_{ij}, \tag{H.21}$$
$$\tilde{\chi}_{\mathcal{Q}}^{(2)} = \delta_{ij} \mathcal{Q}_{kk}, \tag{H.22}$$
$$\tilde{\chi}_{\mathcal{R}'}^{(1)} = \omega(\varepsilon_{ikl} \mathcal{R}'_{jkl} + \varepsilon_{jkl} \mathcal{R}'_{ikl}), \tag{H.23}$$
$$\tilde{\chi}_{\mathcal{S}}^{(1)} = \omega^2 \mathcal{S}_{ijkk}, \tag{H.24}$$
$$\tilde{\chi}_{\mathcal{S}}^{(2)} = \omega^2 \delta_{ij} \mathcal{S}_{kkll}. \tag{H.25}$$

H.3.2 Building blocks for $\tilde{b}_{ijkl}$

The building blocks for $\tilde{b}_{ijkl}$ are constructed in the notebook `bbb.nb`.

$$\tilde{b}_{\mathcal{Q}}^{(1)} = \tfrac{1}{\omega^2}(\delta_{kl} \mathcal{Q}_{ij} + \delta_{jl} \mathcal{Q}_{ik} + \delta_{jk} \mathcal{Q}_{il}). \tag{H.26}$$
$$\tag{H.27}$$

$$\tilde{b}^{(1)}_{\mathcal{R}'} = \frac{1}{\omega}[\varepsilon_{ijm}(\mathcal{R}'_{kml} + \mathcal{R}'_{lmk}) + \varepsilon_{ikm}(\mathcal{R}'_{jml} + \mathcal{R}'_{jml}) + \varepsilon_{ilm}(\mathcal{R}'_{jmk} + \mathcal{R}'_{kmj})], \tag{H.28}$$
$$\tilde{b}^{(2)}_{\mathcal{R}'} = \frac{1}{\omega}(\varepsilon_{ijm}\mathcal{R}'_{klm} + \varepsilon_{ikm}\mathcal{R}'_{jlm} + \varepsilon_{ilm}\mathcal{R}'_{jkm}), \tag{H.29}$$
$$\tilde{b}^{(3)}_{\mathcal{R}'} = \frac{1}{\omega}(\delta_{jk}\varepsilon_{ilm} + \delta_{jl}\varepsilon_{ikm} + \delta_{kl}\varepsilon_{ijm})\mathcal{R}'_{mnn}, \tag{H.30}$$
$$\tilde{b}^{(4)}_{\mathcal{R}'} = \frac{1}{\omega}(\delta_{jk}\varepsilon_{ilm} + \delta_{jl}\varepsilon_{ikm} + \delta_{kl}\varepsilon_{ijm})\mathcal{R}'_{nnm}, \tag{H.31}$$
$$\tilde{b}^{(5)}_{\mathcal{R}'} = \frac{1}{\omega}\varepsilon_{imn}(\delta_{jk}\mathcal{R}'_{lmn} + \delta_{jl}\mathcal{R}'_{kmn} + \delta_{kl}\mathcal{R}'_{jmn}), \tag{H.32}$$
$$\tilde{b}^{(6)}_{\mathcal{R}'} = \frac{1}{\omega}\mathcal{R}'_{imn}(\delta_{jk}\varepsilon_{lmn} + \delta_{jl}\varepsilon_{kmn} + \delta_{kl}\varepsilon_{jmn}), \tag{H.33}$$
$$\tilde{b}^{(7)}_{\mathcal{R}'} = \frac{1}{\omega}[\varepsilon_{jmn}(\delta_{ik}\mathcal{R}'_{lmn} + \delta_{il}\mathcal{R}'_{kmn}) + \varepsilon_{kmn}(\delta_{ij}\mathcal{R}'_{lmn} + \delta_{il}\mathcal{R}'_{jmn}) + \varepsilon_{lmn}(\delta_{ij}\mathcal{R}'_{kmn} + \delta_{ik}\mathcal{R}'_{jmn})], \tag{H.34}$$

where

$$\tilde{b}^{(1)}_{\mathcal{R}'} - 2\tilde{b}^{(2)}_{\mathcal{R}'} + 2\tilde{b}^{(5)}_{\mathcal{R}'} - \tilde{b}^{(7)}_{\mathcal{R}'} = 0, \tag{H.35}$$
$$\tilde{b}^{(3)}_{\mathcal{R}'} - \tilde{b}^{(4)}_{\mathcal{R}'} + \tilde{b}^{(5)}_{\mathcal{R}'} - \tilde{b}^{(6)}_{\mathcal{R}'} = 0. \tag{H.36}$$

$$\tilde{b}^{(1)}_{\mathcal{S}} = \mathcal{S}_{ijkl}, \tag{H.37}$$
$$\tilde{b}^{(2)}_{\mathcal{S}} = \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm} + \delta_{kl}\mathcal{S}_{ijmm}, \tag{H.38}$$
$$\tilde{b}^{(3)}_{\mathcal{S}} = \delta_{il}\mathcal{S}_{jkmm} + \delta_{ik}\mathcal{S}_{jlmm} + \delta_{ij}\mathcal{S}_{klmm}, \tag{H.39}$$
$$\tilde{b}^{(4)}_{\mathcal{S}} = (\delta_{ij}\delta_{kl} + \delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\mathcal{S}_{mmnn}. \tag{H.40}$$

H.3.3 Building blocks for $\tilde{d}_{ijkl}$

The building blocks for $\tilde{d}_{ijkl}$ are constructed in the notebook `bbd.nb`.

$$\tilde{d}^{(1)}_{\mathcal{Q}} = \frac{1}{\omega^2}(\delta_{ij}\mathcal{Q}_{kl} + \delta_{kl}\mathcal{Q}_{ij}), \tag{H.41}$$
$$\tilde{d}^{(2)}_{\mathcal{Q}} = \frac{1}{\omega^2}(\delta_{ik}\mathcal{Q}_{jl} + \delta_{il}\mathcal{Q}_{jk} + \delta_{jk}\mathcal{Q}_{il} + \delta_{jl}\mathcal{Q}_{ik}), \tag{H.42}$$
$$\tilde{d}^{(3)}_{\mathcal{Q}} = \frac{1}{\omega^2}\delta_{ij}\delta_{kl}\mathcal{Q}_{mm}, \tag{H.43}$$
$$\tilde{d}^{(4)}_{\mathcal{Q}} = \frac{1}{\omega^2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\mathcal{Q}_{mm}. \tag{H.44}$$

$$\begin{aligned}\tilde{d}^{(1)}_{\mathcal{R}'} = \frac{1}{\omega}[&\varepsilon_{ikm}(\mathcal{R}'_{jml} - \mathcal{R}'_{lmj}) + \varepsilon_{ilm}(\mathcal{R}'_{jmk} - \mathcal{R}'_{kmj}) \\ &+ \varepsilon_{jkm}(\mathcal{R}'_{iml} - \mathcal{R}'_{lmi}) + \varepsilon_{jlm}(\mathcal{R}'_{imk} - \mathcal{R}'_{kmi})],\end{aligned} \tag{H.45}$$
$$\tilde{d}^{(2)}_{\mathcal{R}'} = \frac{1}{\omega}[\delta_{ij}(\varepsilon_{kmn}\mathcal{R}'_{lmn} + \varepsilon_{lmn}\mathcal{R}'_{kmn}) + \delta_{kl}(\varepsilon_{imn}\mathcal{R}'_{jmn} + \varepsilon_{jmn}\mathcal{R}'_{imn})], \tag{H.46}$$
$$\begin{aligned}\tilde{d}^{(3)}_{\mathcal{R}'} = \frac{1}{\omega}[&\varepsilon_{imn}(\delta_{jk}\mathcal{R}'_{lmn} + \delta_{jl}\mathcal{R}'_{kmn}) + \varepsilon_{jmn}(\delta_{ik}\mathcal{R}'_{lmn} + \delta_{il}\mathcal{R}'_{kmn}) \\ &+ \varepsilon_{kmn}(\delta_{il}\mathcal{R}'_{jmn} + \delta_{jl}\mathcal{R}'_{imn}) + \varepsilon_{lmn}(\delta_{ik}\mathcal{R}'_{jmn} + \delta_{jk}\mathcal{R}'_{imn})],\end{aligned} \tag{H.47}$$

where

$$\tilde{d}^{(1)}_{\mathcal{R}'} + 2\tilde{d}^{(2)}_{\mathcal{R}'} - \tilde{d}^{(3)}_{\mathcal{R}'} = 0. \tag{H.48}$$

$$\tilde{d}^{(1)}_{\mathcal{S}} = \mathcal{S}_{ijkl}, \tag{H.49}$$
$$\tilde{d}^{(2)}_{\mathcal{S}} = \delta_{ij}\mathcal{S}_{klmm} + \delta_{kl}\mathcal{S}_{ijmm}, \tag{H.50}$$
$$\tilde{d}^{(3)}_{\mathcal{S}} = \delta_{ik}\mathcal{S}_{jlmm} + \delta_{il}\mathcal{S}_{jkmm} + \delta_{jk}\mathcal{S}_{ilmm} + \delta_{jl}\mathcal{S}_{ikmm}, \tag{H.51}$$
$$\tilde{d}^{(4)}_{\mathcal{S}} = \delta_{ij}\delta_{kl}\mathcal{S}_{mmnn}, \tag{H.52}$$
$$\tilde{d}^{(5)}_{\mathcal{S}} = (\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\mathcal{S}_{mmnn}. \tag{H.53}$$

H.3.4 Building blocks for $\tilde{L}'_{ijk}$

The building blocks for $\tilde{L}'_{ijk}$ are constructed in the notebook `bbL.nb`.

$$\tilde{L}'^{(1)}_{\mathcal{Q}} = \frac{1}{\omega}(\varepsilon_{ikl}\mathcal{Q}_{jl} + \varepsilon_{jkl}\mathcal{Q}_{il}). \tag{H.54}$$

$$\tilde{L}'^{(1)}_{\mathcal{R}'} = \mathcal{R}'_{ijk}, \tag{H.55}$$
$$\tilde{L}'^{(2)}_{\mathcal{R}'} = \mathcal{R}'_{ikj} + \mathcal{R}'_{jki}, \tag{H.56}$$
$$\tilde{L}'^{(3)}_{\mathcal{R}'} = \delta_{ij}\mathcal{R}'_{kll}, \tag{H.57}$$
$$\tilde{L}'^{(4)}_{\mathcal{R}'} = \delta_{ik}\mathcal{R}'_{jll} + \delta_{jk}\mathcal{R}'_{ill}, \tag{H.58}$$
$$\tilde{L}'^{(5)}_{\mathcal{R}'} = \delta_{ij}\mathcal{R}'_{llk}, \tag{H.59}$$
$$\tilde{L}'^{(6)}_{\mathcal{R}'} = \delta_{ik}\mathcal{R}'_{llj} + \delta_{jk}\mathcal{R}'_{lli}. \tag{H.60}$$

$$\tilde{L}'^{(1)}_{\mathcal{S}} = \omega(\varepsilon_{ikl}\mathcal{S}_{jlmm} + \varepsilon_{jkl}\mathcal{S}_{ilmm}). \tag{H.61}$$

H.3.5 Building blocks for $\tilde{H}'_{ijk}$

The building blocks for $\tilde{H}'_{ijk}$ are constructed in the notebook `bbH.nb`.

$$\tilde{H}'^{(1)}_{\mathcal{Q}} = \frac{1}{\omega}\varepsilon_{ijl}\mathcal{Q}_{kl}, \tag{H.62}$$
$$\tilde{H}'^{(2)}_{\mathcal{Q}} = \frac{1}{\omega}\varepsilon_{ikl}\mathcal{Q}_{jl}, \tag{H.63}$$
$$\tilde{H}'^{(3)}_{\mathcal{Q}} = \frac{1}{\omega}\varepsilon_{jkl}\mathcal{Q}_{il}, \tag{H.64}$$
$$\tilde{H}'^{(4)}_{\mathcal{Q}} = \frac{1}{\omega}\varepsilon_{ijk}\mathcal{Q}_{ll}, \tag{H.65}$$

where

$$\tilde{H}'^{(1)}_{\mathcal{Q}} - \tilde{H}'^{(2)}_{\mathcal{Q}} + \tilde{H}'^{(3)}_{\mathcal{Q}} - \tilde{H}'^{(4)}_{\mathcal{Q}} = 0. \tag{H.66}$$

$$\tilde{H}'^{(1)}_{\mathcal{R}'} = \mathcal{R}'_{ijk}, \tag{H.67}$$
$$\tilde{H}'^{(2)}_{\mathcal{R}'} = \mathcal{R}'_{ikj}, \tag{H.68}$$
$$\tilde{H}'^{(3)}_{\mathcal{R}'} = \mathcal{R}'_{jki}, \tag{H.69}$$
$$\tilde{H}'^{(4)}_{\mathcal{R}'} = \delta_{ij}\mathcal{R}'_{kll}, \tag{H.70}$$
$$\tilde{H}'^{(5)}_{\mathcal{R}'} = \delta_{ik}\mathcal{R}'_{jll}, \tag{H.71}$$
$$\tilde{H}'^{(6)}_{\mathcal{R}'} = \delta_{jk}\mathcal{R}'_{ill}, \tag{H.72}$$
$$\tilde{H}'^{(7)}_{\mathcal{R}'} = \delta_{ij}\mathcal{R}'_{llk}, \tag{H.73}$$
$$\tilde{H}'^{(8)}_{\mathcal{R}'} = \delta_{ik}\mathcal{R}'_{llj}, \tag{H.74}$$
$$\tilde{H}'^{(9)}_{\mathcal{R}'} = \delta_{jk}\mathcal{R}'_{lli}. \tag{H.75}$$

$$\tilde{H}'^{(1)}_{\mathcal{S}} = \omega\varepsilon_{ijl}\mathcal{S}_{klmm}, \tag{H.76}$$
$$\tilde{H}'^{(2)}_{\mathcal{S}} = \omega\varepsilon_{ikl}\mathcal{S}_{jlmm}, \tag{H.77}$$
$$\tilde{H}'^{(3)}_{\mathcal{S}} = \omega\varepsilon_{jkl}\mathcal{S}_{ilmm}, \tag{H.78}$$
$$\tilde{H}'^{(4)}_{\mathcal{S}} = \omega\varepsilon_{ijk}\mathcal{S}_{llmm}, \tag{H.79}$$

where

$$\tilde{H}'^{(1)}_{\mathcal{S}} - \tilde{H}'^{(2)}_{\mathcal{S}} + \tilde{H}'^{(3)}_{\mathcal{S}} - \tilde{H}'^{(4)}_{\mathcal{S}} = 0. \tag{H.80}$$

H.4 Electric octopole–magnetic quadrupole order: Magnetic molecules

H.4.1 Building blocks for $\tilde{\chi}'_{ij}$

The building blocks for $\tilde{\chi}'_{ij}$ are constructed in the notebook `bbx.nb`.

$$\tilde{\chi}'^{(1)}_{\mathcal{Q}'} = \mathcal{Q}'_{ij}, \tag{H.81}$$

$$\tilde{\chi}'^{(1)}_{\mathcal{R}} = \omega\varepsilon_{ijk}\mathcal{R}_{kll}, \tag{H.82}$$

$$\tilde{\chi}'^{(2)}_{\mathcal{R}} = \omega\varepsilon_{ijk}\mathcal{R}_{llk}, \tag{H.83}$$

$$\tilde{\chi}'^{(3)}_{\mathcal{R}} = \omega(\varepsilon_{ikl}\mathcal{R}_{jkl} - \varepsilon_{jkl}\mathcal{R}_{ikl}), \tag{H.84}$$

where

$$\tilde{\chi}'^{(1)}_{\mathcal{R}} - \tilde{\chi}'^{(2)}_{\mathcal{R}} + \tilde{\chi}'^{(3)}_{\mathcal{R}} = 0. \tag{H.85}$$

H.4.2 Building blocks for $\tilde{b}'_{ijkl}$

The building blocks for $\tilde{b}'_{ijkl}$ are constructed in the notebook `bbb.nb`.

$$\tilde{b}'^{(1)}_{\mathcal{Q}'} = \frac{1}{\omega^2}(\delta_{kl}\mathcal{Q}'_{ij} + \delta_{jl}\mathcal{Q}'_{ik} + \delta_{jk}\mathcal{Q}'_{il}). \tag{H.86}$$

$$\tilde{b}'^{(1)}_{\mathcal{R}} = \frac{1}{\omega}[\varepsilon_{ijm}(\mathcal{R}_{kml} + \mathcal{R}_{lmk}) + \varepsilon_{ikm}(\mathcal{R}_{jml} + \mathcal{R}_{jml}) + \varepsilon_{ilm}(\mathcal{R}_{jmk} + \mathcal{R}_{kmj})], \tag{H.87}$$

$$\tilde{b}'^{(2)}_{\mathcal{R}} = \frac{1}{\omega}(\varepsilon_{ijm}\mathcal{R}_{klm} + \varepsilon_{ikm}\mathcal{R}_{jlm} + \varepsilon_{ilm}\mathcal{R}_{jkm}), \tag{H.88}$$

$$\tilde{b}'^{(3)}_{\mathcal{R}} = \frac{1}{\omega}(\delta_{jk}\varepsilon_{ilm} + \delta_{jl}\varepsilon_{ikm} + \delta_{kl}\varepsilon_{ijm})\mathcal{R}_{mnn}, \tag{H.89}$$

$$\tilde{b}'^{(4)}_{\mathcal{R}} = \frac{1}{\omega}(\delta_{jk}\varepsilon_{ilm} + \delta_{jl}\varepsilon_{ikm} + \delta_{kl}\varepsilon_{ijm})\mathcal{R}_{nnm}, \tag{H.90}$$

$$\tilde{b}'^{(5)}_{\mathcal{R}} = \frac{1}{\omega}\varepsilon_{imn}(\delta_{jk}\mathcal{R}_{lmn} + \delta_{jl}\mathcal{R}_{kmn} + \delta_{kl}\mathcal{R}_{jmn}), \tag{H.91}$$

$$\tilde{b}'^{(6)}_{\mathcal{R}} = \frac{1}{\omega}\mathcal{R}_{imn}(\delta_{jk}\varepsilon_{lmn} + \delta_{jl}\varepsilon_{kmn} + \delta_{kl}\varepsilon_{jmn}), \tag{H.92}$$

$$\tilde{b}'^{(7)}_{\mathcal{R}} = \frac{1}{\omega}[\varepsilon_{jmn}(\delta_{ik}\mathcal{R}_{lmn} + \delta_{il}\mathcal{R}_{kmn}) + \varepsilon_{kmn}(\delta_{ij}\mathcal{R}_{lmn} + \delta_{il}\mathcal{R}_{jmn}) + \varepsilon_{lmn}(\delta_{ij}\mathcal{R}_{kmn} + \delta_{ik}\mathcal{R}_{jmn})], \tag{H.93}$$

where

$$\tilde{b}'^{(1)}_{\mathcal{R}} - 2\tilde{b}'^{(2)}_{\mathcal{R}} + 2\tilde{b}'^{(5)}_{\mathcal{R}} - \tilde{b}'^{(7)}_{\mathcal{R}} = 0, \tag{H.94}$$

$$\tilde{b}'^{(3)}_{\mathcal{R}} - \tilde{b}'^{(4)}_{\mathcal{R}} + \tilde{b}'^{(5)}_{\mathcal{R}} - \tilde{b}'^{(6)}_{\mathcal{R}} = 0. \tag{H.95}$$

H.4.3 Building blocks for $\tilde{d}'_{ijkl}$

The building blocks for $\tilde{d}'_{ijkl}$ are constructed in the notebook `bbd.nb`.

$$\tilde{d}'^{(1)}_{\mathcal{Q}'} = \frac{1}{\omega^2}(\delta_{ik}\mathcal{Q}'_{jl} + \delta_{il}\mathcal{Q}'_{jk} + \delta_{jk}\mathcal{Q}'_{il} + \delta_{jl}\mathcal{Q}'_{ik}). \tag{H.96}$$

$$\begin{aligned}\tilde{d}'^{(1)}_{\mathcal{R}} = \frac{1}{\omega}[&\varepsilon_{ikm}(\mathcal{R}_{jml} + \mathcal{R}_{lmj}) + \varepsilon_{ilm}(\mathcal{R}_{jmk} + \mathcal{R}_{kmj}) \\ &+ \varepsilon_{jkm}(\mathcal{R}_{iml} + \mathcal{R}_{lmi}) + \varepsilon_{jlm}(\mathcal{R}_{imk} + \mathcal{R}_{kmi})],\end{aligned} \tag{H.97}$$

$$\tilde{d}'^{(2)}_{\mathcal{R}} = \frac{1}{\omega}(\varepsilon_{ikm}\mathcal{R}_{jlm} + \varepsilon_{ilm}\mathcal{R}_{jkm} + \varepsilon_{jkm}\mathcal{R}_{ilm} + \varepsilon_{jlm}\mathcal{R}_{ikm}), \tag{H.98}$$

$$\tilde{d}'^{(3)}_{\mathcal{R}} = \frac{1}{\omega}(\delta_{jl}\varepsilon_{ikm} + \delta_{jk}\varepsilon_{ilm} + \delta_{il}\varepsilon_{jkm} + \delta_{ik}\varepsilon_{jlm})\mathcal{R}_{mnn}, \tag{H.99}$$

$$\tilde{d}'^{(4)}_{\mathcal{R}} = \frac{1}{\omega}(\delta_{jl}\varepsilon_{ikm} + \delta_{jk}\varepsilon_{ilm} + \delta_{il}\varepsilon_{jkm} + \delta_{ik}\varepsilon_{jlm})\mathcal{R}_{nnm}, \tag{H.100}$$

$$\tilde{d}'^{(5)}_{\mathcal{R}} = \frac{1}{\omega}[\delta_{ij}(\varepsilon_{kmn}\mathcal{R}_{lmn} + \varepsilon_{lmn}\mathcal{R}_{kmn}) - \delta_{kl}(\varepsilon_{imn}\mathcal{R}_{jmn} + \varepsilon_{jmn}\mathcal{R}_{kmn})], \tag{H.101}$$

$$\begin{aligned}\tilde{d}'^{(6)}_{\mathcal{R}} = \frac{1}{\omega}[&\varepsilon_{imn}(\delta_{jk}\mathcal{R}_{lmn} + \delta_{jl}\mathcal{R}_{kmn}) + \varepsilon_{jmn}(\delta_{ik}\mathcal{R}_{lmn} + \delta_{il}\mathcal{R}_{kmn}) \\ &- \varepsilon_{kmn}(\delta_{il}\mathcal{R}_{jmn} + \delta_{jl}\mathcal{R}_{imn}) - \varepsilon_{lmn}(\delta_{ik}\mathcal{R}_{jmn} + \delta_{jk}\mathcal{R}_{imn})],\end{aligned} \tag{H.102}$$

where

$$\tilde{d}'^{(3)}_{\mathcal{R}} - \tilde{d}'^{(4)}_{\mathcal{R}} + \tilde{d}'^{(6)}_{\mathcal{R}} = 0, \qquad \text{(H.103)}$$
$$\tilde{d}'^{(1)}_{\mathcal{R}} - 2\tilde{d}'^{(2)}_{\mathcal{R}} - 2\tilde{d}'^{(5)}_{\mathcal{R}} + \tilde{d}'^{(6)}_{\mathcal{R}} = 0. \qquad \text{(H.104)}$$

H.4.4 Building blocks for $\tilde{L}_{ijk}$

The building blocks for $\tilde{L}_{ijk}$ are constructed in the notebook `bbL.nb`.

$$\tilde{L}^{(1)}_{\mathcal{Q}'} = \tfrac{1}{\omega}(\varepsilon_{ikl}\mathcal{Q}'_{jl} + \varepsilon_{jkl}\mathcal{Q}'_{il}), \qquad \text{(H.105)}$$
$$\tilde{L}^{(2)}_{\mathcal{Q}'} = \tfrac{1}{\omega}(\delta_{ik}\varepsilon_{jlm} + \delta_{jk}\varepsilon_{ilm})\mathcal{Q}'_{lm}, \qquad \text{(H.106)}$$
$$\tilde{L}^{(3)}_{\mathcal{Q}'} = \tfrac{1}{\omega}\delta_{ij}\varepsilon_{klm}\mathcal{Q}'_{lm}, \qquad \text{(H.107)}$$

where

$$2\tilde{L}^{(1)}_{\mathcal{Q}'} - \tilde{L}^{(2)}_{\mathcal{Q}'} + 2\tilde{L}^{(3)}_{\mathcal{Q}'} = 0. \qquad \text{(H.108)}$$

$$\tilde{L}^{(1)}_{\mathcal{R}} = \mathcal{R}_{ijk}, \qquad \text{(H.109)}$$
$$\tilde{L}^{(2)}_{\mathcal{R}} = \mathcal{R}_{ikj} + \mathcal{R}_{jki}, \qquad \text{(H.110)}$$
$$\tilde{L}^{(3)}_{\mathcal{R}} = \delta_{ij}\mathcal{R}_{kll}, \qquad \text{(H.111)}$$
$$\tilde{L}^{(4)}_{\mathcal{R}} = \delta_{ik}\mathcal{R}_{jll} + \delta_{jk}\mathcal{R}_{ill}, \qquad \text{(H.112)}$$
$$\tilde{L}^{(5)}_{\mathcal{R}} = \delta_{ij}\mathcal{R}_{llk}, \qquad \text{(H.113)}$$
$$\tilde{L}^{(6)}_{\mathcal{R}} = \delta_{ik}\mathcal{R}_{llj} + \delta_{jk}\mathcal{R}_{lli}. \qquad \text{(H.114)}$$

H.4.5 Building blocks for $\tilde{H}_{ijk}$

The building blocks for $\tilde{H}_{ijk}$ are constructed in the notebook `bbH.nb`.

$$\tilde{H}^{(1)}_{\mathcal{Q}'} = \tfrac{1}{\omega}\varepsilon_{ijl}\mathcal{Q}'_{kl}, \qquad \text{(H.115)}$$
$$\tilde{H}^{(2)}_{\mathcal{Q}'} = \tfrac{1}{\omega}\varepsilon_{ikl}\mathcal{Q}'_{jl}, \qquad \text{(H.116)}$$
$$\tilde{H}^{(3)}_{\mathcal{Q}'} = \tfrac{1}{\omega}\varepsilon_{jkl}\mathcal{Q}'_{il}, \qquad \text{(H.117)}$$
$$\tilde{H}^{(4)}_{\mathcal{Q}'} = \tfrac{1}{\omega}\delta_{ij}\varepsilon_{klm}\mathcal{Q}'_{lm}, \qquad \text{(H.118)}$$
$$\tilde{H}^{(5)}_{\mathcal{Q}'} = \tfrac{1}{\omega}\delta_{jk}\varepsilon_{ilm}\mathcal{Q}'_{lm}, \qquad \text{(H.119)}$$
$$\tilde{H}^{(6)}_{\mathcal{Q}'} = \tfrac{1}{\omega}\delta_{ik}\varepsilon_{jlm}\mathcal{Q}'_{lm}. \qquad \text{(H.120)}$$

There are four relations (each between three building blocks) between the building blocks involving $\mathcal{Q}'_{ij}$, of which three are linearly independent.

$$\tilde{H}^{(1)}_{\mathcal{Q}'} - \tilde{H}^{(2)}_{\mathcal{Q}'} + \tilde{H}^{(3)}_{\mathcal{Q}'} = 0, \qquad \text{(H.121)}$$
$$2\tilde{H}^{(1)}_{\mathcal{Q}'} - \tilde{H}^{(5)}_{\mathcal{Q}'} + \tilde{H}^{(6)}_{\mathcal{Q}'} = 0, \qquad \text{(H.122)}$$
$$2\tilde{H}^{(2)}_{\mathcal{Q}'} + \tilde{H}^{(4)}_{\mathcal{Q}'} - \tilde{H}^{(5)}_{\mathcal{Q}'} = 0, \qquad \text{(H.123)}$$
$$2\tilde{H}^{(3)}_{\mathcal{Q}'} + \tilde{H}^{(4)}_{\mathcal{Q}'} - \tilde{H}^{(6)}_{\mathcal{Q}'} = 0, \qquad \text{(H.124)}$$

where

$$2(\text{H.121}) = (\text{H.122}) - (\text{H.123}) + (\text{H.124}). \qquad \text{(H.125)}$$

$$\tilde{H}_{\mathcal{R}}^{(1)} = \mathcal{R}_{ijk}, \tag{H.126}$$

$$\tilde{H}_{\mathcal{R}}^{(2)} = \mathcal{R}_{ikj}, \tag{H.127}$$

$$\tilde{H}_{\mathcal{R}}^{(3)} = \mathcal{R}_{jki}, \tag{H.128}$$

$$\tilde{H}_{\mathcal{R}}^{(4)} = \delta_{ij}\mathcal{R}_{kll}, \tag{H.129}$$

$$\tilde{H}_{\mathcal{R}}^{(5)} = \delta_{ik}\mathcal{R}_{jll}, \tag{H.130}$$

$$\tilde{H}_{\mathcal{R}}^{(6)} = \delta_{jk}\mathcal{R}_{ill}, \tag{H.131}$$

$$\tilde{H}_{\mathcal{R}}^{(7)} = \delta_{ij}\mathcal{R}_{llk}, \tag{H.132}$$

$$\tilde{H}_{\mathcal{R}}^{(8)} = \delta_{ik}\mathcal{R}_{llj}, \tag{H.133}$$

$$\tilde{H}_{\mathcal{R}}^{(9)} = \delta_{jk}\mathcal{R}_{lli}. \tag{H.134}$$

Publications

The publications on which the research presented in this thesis is based are reproduced in this appendix. Details of the contributions to these publications by this author are:

1. O. L. de Lange, R. E. Raab, and A. Welter. On the transition from microscopic to macroscopic electrodynamics. *J. Math. Phys.*, **53**, 013513 (2012).

   The calculations in this publication were jointly carried out by the three authors. The results were checked using the software described in Appendix B. The MATHEMATICA [19] modules that contain the routines used to perform the calculations were conceived, coded, implemented and debugged by this author.

2. O. L. de Lange, R. E. Raab, and A. Welter. Translational invariance, the Post constraint and uniqueness in macroscopic electrodynamics. *J. Math. Phys.*, **53**, 073518 (2012).

   The results presented in this paper are dependent on the origin-independent basis tensors $\mathcal{Q}_{ij}$, $\mathcal{R}'_{ijk}$ and $\mathcal{S}_{ijkl}$. These tensors were conceived by this author, and the method used to derive them was developed and implemented by this author. The calculations of the origin-independent expressions corresponding to the molecular polarizabilities χ_{ij}, b_{ijkl}, d_{ijkl}, L'_{ijk} and H'_{ij} presented in this publication were performed by this author using the method described in Section 5.1, and the software described in Appendix B. Linear independence was first used by this author in the calulation of $\mathcal{Q}_{ij}$, $\mathcal{R}'_{ijk}$ and $\mathcal{S}_{ijkl}$, and was applied to the polarizability tensors without realizing the significance, which had to be pointed out. Subsequently the method to establish linear independence using isotropic tensors, described in Appendix C, was developed and implemented by this author.

3. A. Welter, R. E. Raab, and O. L. de Lange. Translationally invariant semi-classical electrodynamics of magnetic media to electric octopole–magnetic quadrupole order. *J. Math. Phys.*, **54**, 023512 (2013).

   This publication is a sequel to the second publication above and the same comments apply. The basis tensors here are $\mathcal{Q}'_{ij}$ and $\mathcal{R}_{ijk}$.

Signed...

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