Aspects of Chirality in Light and Matter

Neel Mackinnon

M.A. M.Sc.

Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

School of Physics and Astronomy

College of Science and Engineering

University of Glasgow

Acknowledgements

Physics is a collaborative activity, and so there are many to whom this document owes its existence. Particular thanks go to my supervisors – Robert Cameron, Jörg Götte and Stephen Barnett – for their enthusiasm, expertise and generous guidance. I also wish to thank everyone (past and present) in the Quantum Theory group at Glasgow whose membership I've been fortunate enough to overlap with, for making my time here so enjoyable.

Abstract

This thesis presents a series of complementary pieces of work, each related to chirality and handedness in light-matter interactions. There is a particular focus on the electromagnetic helicity – especially when viewed as a pseudoscalar density constructed from the electromagnetic vector potentials which obeys a local continuity equation. A central theme is the ways in which matter (both chiral and achiral) can act as "sources" of helicity, and the circumstances under which helicity is locally conserved. This feature is connected by Noether's theorem to the duality symmetry of the free-space Maxwell equations – the invariance of the equations under an interchange between electric and magnetic fields.

We begin by discussing free fields, and as the thesis progresses introduce various treatments of matter involving both microscopic and macroscopic electrodynamics. The five chapters focusing on original work (3, 5, 6, 7 and 9) are preceded by chapters introducing the necessary background material and concepts.

The first piece of work is an examination of the difference between electromagnetic helicity and electromagnetic chirality in polychromatic fields. The two quantities are proportional to one another in monochromatic fields, but not in general. We explicitly calculate the two quantities for some simple field configurations, and the origin and nature of the differences is discussed.

This is followed by a discussion of helicity and angular momentum radiated from elementary multipole sources. We examine radiation from the simplest chiral source that can be constructed from point multipoles, consisting of co-located oscillating electric and magnetic dipoles. This is contrasted with the radiation from a rotating dipole, which is an achiral source of circularly polarised light. The former is a net source of helicity, but not of angular momentum, and the latter a net source of angular momentum, but not helicity.

We then move on to macroscopic electrodynamics, and consider the generation of helicity at a dielectric interface. We provide and discuss expressions for the helicity fluxes when light is incident on chiral dielectric interfaces, obtained from the Fresnel coefficients for chiral media.

Following this, we propose an extension to the definition of the helicity density within chiral media. The standard definition of helicity within a dielectric is found to be unsatisfactory when the medium is chiral – it produces an incorrect helicity-per-photon for left- and right-handed circularly polarised light in the medium, and also is not locally conserved even when the medium is macroscopically dual-symmetric. We present a modification to the definition of the density which yields the correct helicity per circularly polarised photon within the medium, and find by inspection that the new density is indeed locally conserved in a dual-symmetric chiral medium. Our definition is

then formally justified by using Noether's theorem in order to derive the locally conserved quantity associated with macroscopic duality symmetry in chiral media.

Finally, we conclude with an extension of a standard semiclassical treatment of molecular light scattering to include higher-order multipole terms. These represent a higher-order correction to the standard results, which should become appreciable when the ratio of scatterer size to the wavelength of the incident light is around 1/10. Expressions for the scattered light from an arbitrary scatterer are presented in terms of its polarisability tensors, with appropriate orientational averaging to describe scattering from an isotropic fluid sample. The transformation of the results under a change in multipolar origin is also examined, and they are found to behave acceptably.

List of Publications

Some of the novel work which is described in this thesis has appeared in various published articles, produced during the course of my PhD work. A full list of publications is provided here, with a brief indication of how the content of each relates to the relevant chapter. The articles are also referred to in directly in the thesis.

Chapter 3

The calculations presented in Chapter 3 are reported in:

Mackinnon N. 2019 On the Differences between Helicity and Chirality *Journal of Optics* **21** 125402

Chapter 5

The results for the helicity radiated from a "chiral" dipole appear in section 3.2 of:

Crimin F., Mackinnon N., Götte J. B. and Barnett S. M. 2019 Optical Helicity and Chirality: Conservation and Sources *Applied Sciences* **9** 828

Chapter 7

The modification to the helicity density in a chiral medium, which is the subject of Chapter 7, appears in:

Crimin F., Mackinnon N., Götte J. B. and Barnett S. M. 2019 On the Conservation of Helicity in a Chiral Medium *Journal of Optics* **21** 094003

Additionally, an alternative derivation of this modification – which applies Noether's theorem to a dual-symmetric Lagrangian and varies over both $\boldsymbol{A}$ and $\boldsymbol{C}$ – is reported in:

F. Crimin, Mackinnon N., Götte J. B. and Barnett S. M. 2020 Continuous Symmetries and Conservation Laws in Chiral Media *SPIE OPTO Proceedings Volume 11297 Complex Light and Optical Forces* XIV112970J

Chapter 9

Finally, the results of the molecular light scattering calculations discussed in Chapter 9 are found in:

Cameron R. P. and Mackinnon N. 2018 Linear Rayleigh and Raman Scattering to the Second order: Analytical Results for Light Scattering by any Scatterer of Size $k_0 d \leq 1/10$ *Physical Review A* **98** 013814

Table of Contents

1. Introduction 1
    1.1 Chirality in Light and Matter 1
    1.2 Electromagnetic Helicity 3
    1.3 Helicity and the Angular Momentum of Light 4
    1.4 Quantum Mechanical Form 4
    1.5 The Use of the Potentials in Defining Electromagnetic Helicity 5
    1.6 Electromagnetic Chirality 6
    1.7 Conclusion 7

2. Symmetries and Conservation 9
    2.1 Local Conservation of Helicity and Chirality in Free Space 9
    2.2 Electromagnetic Duality and the Conservation of Helicity 10
    2.3 Duality Transformations and the Rotation of Polarisation 16
    2.4 Local Continuity of Helicity in the Presence of Charges and Currents 17
    2.5 Continuity of Helicity in Media 18
    2.6 Duality Symmetry in Bulk Media 19
    2.7 Conclusion 20

3. Helicity and Chirality in Polychromatic Fields 22
    3.1 Helicity and Chirality in the Superposition of Two Plane Waves 22
    3.2 Helicity and Chirality in a Chirped Pulse of Circularly Polarised Light 25
    3.3 Approximate Potentials for a Chirped Pulse 29
    3.4 Helicity and Chirality in an Optical Centrifuge 31
    3.5 Conclusion 33

4. Multipolar Electrodynamics 35
    4.1 Electric Multipole Moments 35
    4.2 Magnetic Multipole Moments 36
    4.3 Multipole Moments and Parity Symmetry 37
    4.4 Radiation from Oscillating Multipole Moments 37
    4.5 The Near-Zone and Intermediate Fields 41
    4.6 Angular Momentum in a Circularly Polarised Plane Wave 42
    4.7 The Overall Field Radiated by an Oscillating Charge Distribution 43

5. Elementary Models of Helicity Sources 45
    5.1 Multipole Moments and Parity Symmetry 45
    5.2 Helicity Radiated from a “Chiral” Dipole 46
    5.3 Helicity Flux from Rotating Dipoles 49
    5.4 Angular Momentum Radiated by the “Chiral” Dipole and Rotating Dipole 51
    5.5 Conclusions 54

6. The Generation of Helicity at a Dielectric Interface 55
6.1 Reflection at Vacuum-Chiral Boundaries... 56
6.2 The Helicity Flux at Reflection and Transmission 59
6.3 Linear Incident Polarisation.. 61
6.4 Achiral and Dual-Symmetric Interfaces.. 61
6.5 Chiral Negative Refraction.. 62
6.6 Conclusions.. 64

7. Helicity within Chiral Media.. 66
7.1 Electromagnetic Wave Propagation in Chiral Media 67
7.2 Illustrating the Problem – Helicity per Photon and Group Velocity.............. 68
7.3 Helicity Conservation at a Dual-Symmetric Interface 70
7.4 Modifying the Helicity Density 71
7.5 Noether's Theorem in a Dual-Symmetric Chiral Medium 72
7.6 Conclusions.. 76

8. Semiclassical Electrodynamics... 78
8.1 From the Minimal Coupling to the Multipolar Hamiltonian 78
8.2 proving that the Polarisation Density is Acceptable 80
8.3 Applying the Transformation to the Hamiltonian 81
8.4 The Barron-Gray Potentials 85
8.5 Perturbation Theory for a Molecule in a Radiation Field 86
8.6 Expectation Values of Induced Electric Moments... 90
8.7 Magnetic Moments 93
8.8 Complex Polarisabilities and Complex Multipole Moments 96
8.9 Extension to Regions of Absorption 96
8.10 Raman Scattering 97
8.11 Final Expressions 99
8.12 Stokes Parameters of the Scattered Light 101
8.13 The Polarisability Tensors and Changes of Molecular origin..................... 102
8.14 Symmetries of Tenors and Molecules 109

9. Second-Order Scattering... 113
9.1 Second-Order Scattering 113
9.2 Scattering from an Isotropic Sample 116
9.3 Results and Discussion... 118
9.4 General Origin-Independence of the Procedure... 120
9.5 Transformation of the Induced Moments.. 121
9.6 The Scattered Light under a Change of Origin 123
9.7 Conclusions.. 125

Conclusion.. 127

Appendix A – The Helicity Operator as the Generator of the Duality Transform...... 129

Appendix B – The Maxwell Equations within a Chiral Medium from a Lagrangian... 131

Appendix C – Noether's Theorem for a Lagrangian with 2nd Derivatives 133

Appendix D – Rotational Averaging of High Rank Tensors 135

Appendix E – Full Second-Order Scattering Results.. 139

Appendix F – Transformations of the Induced Moments under a Change of Origin. 146

Chapter 1 – Introduction

The fundamental theme running through this thesis is chirality. The work presented here encompasses a variety of results related to the chirality of light and matter, and particularly to the electromagnetic helicity – with special attention paid to the local continuity of helicity in free space, and the ways in which this is modified by the presence of matter. The various pieces of original work discuss different aspects of chiral light-matter interactions, and treat the matter in different ways: the work in chapter 3 discusses electromagnetic helicity and chirality in free space, that of chapter 5 discusses radiation from point multipole sources, chapters 6 and 7 deal with macroscopic fields in dielectric media, and finally chapter 9 involves a full semiclassical treatment of light scattering from individual molecules. Because of this variety of situations and treatments, each section is preceded by chapters which present the background material necessary to follow the subsequent work.

This chapter introduces some of the relevant concepts which serve as a starting point for all the work mentioned above. Chirality (in the broad sense) is defined, and some elementary aspects of chiroptical effects are discussed. We then turn to various aspects of chirality in electromagnetic fields, presenting definitions of the electromagnetic helicity and chirality densities – which feature heavily in the work reported in this thesis – as well as the angular momentum density. A few features are highlighted which will play a role in subsequent the discussion: the ways in which helicity and chirality densities relate to circular polarisation and spin-angular momentum of photons, the issue of gauge-dependence in the helicity, and and the necessity of the $\boldsymbol{C}$ potential to ensure that the helicity density is locally conserved.

1.1 Chirality in Light and in Matter

We begin with a definition of chirality, and a brief discussion of some common chiroptical effects. An object is said to be *chiral* if it cannot be brought into coincidence with its mirror image by some combination of rotations and translations, and the two distinct mirror-image forms of a chiral object are called *enantiomers*. Left and right hands are a familiar pair of enantiomers – in fact, the word “chiral” originates from the Greek word meaning “hand”. The two enantiomeric configurations are often referred to as left- and right-handed.

Because reflection interconverts between the two enantiomers, any odd number of reflections applied to a chiral object will result in the opposite enantiomer. Spatial inversion is simply a reflection in each of the Cartesian axes, and so (in three dimensions) inversion also interconverts enantiomers. In other words, enantiomers are interconverted by *parity transformations* (i.e. transformations that send $\boldsymbol{x}$ to $-\boldsymbol{x}$).

Furthermore, we may note that Maxwell's equations are invariant under parity transformations – as indeed is all of classical physics[1]. In the absence of parity-violating effects, the only way that the chirality of a physical system can be important is if it interacts with another chiral system. In this case, the relative handedness of the two generally leads to distinct behaviour. This is of crucial importance in biology, as chiral molecules in biological systems are usually found in only one enantiomeric form. This means, for example, that the left- and right-handed forms of chiral drugs can have substantially different effects.

In addition to their differing interactions with other chiral molecules, the two enantiomers of a chiral molecule interact differently with chiral electromagnetic fields. The most obvious manifestation of chirality in light is circular polarisation, and the different interactions between molecules and left/right-circular polarisations forms the basis of most chiroptical techniques. The first such chiroptical effect to be observed was "optical rotation" – rotation of the plane of polarisation of linearly polarised light after passage through a chiral sample [3, §1.2]. Linearly polarised light can be viewed as an equal superposition of left- and right-circularly polarised light, with the plane of polarisation specified by the phase difference between the two circular components. A chiral sample will generally have a different refractive index for the two circular components – so when linearly polarised light is incident, the phase difference between the circular components is changed by an amount proportional to the path length through the sample. This causes the plane of polarisation of the light to be rotated by an angle proportional this length. The sense of rotation changes depending on which of the two enantiomers is predominant in the sample – and the rotation vanishes entirely in a *racemic mixture* (a mixture containing equal proportions of the two enantiomers).

The different refractive indices also lead to other chiroptical phenomena. *Circular dichroism* refers to the differential absorption of left- and right-handed circular polarised light, with the effect that incident linearly polarised light emerges from a chiral sample with some ellipticity. The other side of the coin is differential scattering of the two circular components – which may either by observed by comparing intensities of scattered left- and right- circular polarisations, or by detecting a small amount of ellipticity in the scattering from incident linearly polarised light [3, §1.3].

[1] The laws of physics are not generally invariant under parity transformations; parity violation in the weak nuclear force was famously demonstrated by Wu *et al.* in 1957 [1]. Because of electroweak unification, the violation in principle also affects the electromagnetic forces that hold together atoms and molecules. This has led to the prediction of very slight differences (femto to picojoules per mole) in the energy level spacing, and hence the spectra, of opposite molecular enantiomers [2].

All such effects have their ultimate origin in the differential scattering from left- and right-handed chiral molecules. Molecular light scattering is discussed in detail in chapter 8, and this provides background for the work and results reported in chapter 9.

1.2 Electromagnetic Helicity

Much of this thesis involves the discussion of various quantities connected with "chirality" in electromagnetic fields. A natural form for such a quantity is a pseudoscalar density – *i.e.* a scalar density that changes sign under spatial inversion (and therefore is oppositely signed for any two mirror-image field configurations). It is always possible to construct a pseudoscalar quantity from a given vector field by taking the dot product of the vector field and its curl. Such quantities have found application in many branches of physics, as they are related to topological properties of fluid flows. For example, in fluid mechanics, the dot product of the flow velocity with its curl is related to the knottedness of vortex lines [4].

In electromagnetism, one such pseudoscalar is the *electromagnetic helicity*, which forms a central part of this thesis. Throughout this thesis, we define the helicity density of the free electromagnetic field by

$$h = \frac{1}{2}\left[\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{A}\cdot\boldsymbol{\nabla}\times\boldsymbol{A} + \sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{C}\cdot\boldsymbol{\nabla}\times\boldsymbol{C}\right] = \frac{1}{2}\left[\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{A}\cdot\boldsymbol{B} - \sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{C}\cdot\boldsymbol{D}\right], \qquad 1.2.1$$

where $\boldsymbol{B}$ is the magnetic field vector, and $\boldsymbol{D}$ the displacement field. The vector $\boldsymbol{A}$ is the usual magnetic vector potential, defined by $\boldsymbol{\nabla}\times\boldsymbol{A} = \boldsymbol{B}$, and $\boldsymbol{C}$ is the "electric" vector potential, defined by[2] $\boldsymbol{\nabla}\times\boldsymbol{C} = -\boldsymbol{D}$ [5,6]. The helicity density is a Lorentz invariant pseudoscalar, which is locally conserved in the free field. We also define the helicity flux density (the components of which give the flux of h through an infinitesimal surface oriented in a given direction), by

$$\boldsymbol{v} = \frac{1}{2}\left[\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{E}\times\boldsymbol{A} + \sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{H}\times\boldsymbol{C}\right], \qquad 1.2.2$$

where $\boldsymbol{E}$ is the electric field vector, and $\boldsymbol{H}$ the auxiliary magnetic field vector. Together, h and $\boldsymbol{v}$ obey a local continuity equation

$$\frac{\partial h}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{v} = 0, \qquad 1.2.3$$

which is further discussed in the next chapter. For the moment, we go on to consider the physical interpretation of h.

---

[2] This second vector potential is also sometimes defined as $\nabla\times\boldsymbol{C} = -\boldsymbol{E}$. We choose to define $\boldsymbol{C}$ in terms of the displacement vector, as we will find this more convenient when extending the discussion of helicity from free space into dielectric media. In free space, the two definitions merely differ by a factor of ϵ_0.

1.3 Helicity and the Angular Momentum of Light

In particle physics, the helicity of a particle refers to the component of its spin angular momentum in the direction of propagation. The electromagnetic helicity defined above is closely related to this idea, even in classical physics. In order to see this, we examine the total angular momentum density in an electromagnetic field, which is given by [7, §7]

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} = \frac{1}{c^2} \boldsymbol{r} \times (\boldsymbol{E} \times \boldsymbol{H}). \qquad 1.3.1$$

This quantity is often separated into "spin" and "orbital" parts, given by[3]

$$\boldsymbol{L}_{orbital} = \frac{1}{2}(\epsilon_0 E_i (\boldsymbol{r} \times \boldsymbol{\nabla}) A_i + c B_i (\boldsymbol{r} \times \boldsymbol{\nabla}) C_i), \qquad 1.3.2$$

$$\boldsymbol{S} = \frac{1}{2}(\epsilon_0 \boldsymbol{E} \times \boldsymbol{A} + c\boldsymbol{B} \times \boldsymbol{C}). \qquad 1.3.3$$

This separation is motivated by the fact that the form of (1.3.2) closely resembles an orbital angular momentum operator. Following this analogy, the quantity is identified with the orbital part of the angular momentum, and the remaining part of (1.3.1) with the spin angular momentum. However, we note that the spin and orbital "parts" of the angular momentum, as defined above, are not "true" angular momenta, as their quantum-mechanical forms do not obey the usual angular momentum commutation relations [8].

Since the existence of orbital angular momentum in Laguerre Gaussian beams was pointed out by Allen et. al in 1993 [9], a large body of work has grown up studying the properties of optical orbital angular momentum [10].

It is mainly the spin part which concerns us in this work – we note that the spin angular momentum density (1.3.3) is identical to the helicity flux density (1.2.2) [11]**.** A similar correspondence is found with linear momentum density and the Poynting vector (i.e. the energy flux density) [7, §6.7].

This isolation of a "spin" part of the total angular momentum holds even when, as above, the fields considered are purely classical. If the fields are treated quantum mechanically, the connection between helicity in the particle physics sense and the definition (1.2.1) becomes even clearer.

1.4 Quantum Mechanical Form

The interpretation of the electromagnetic helicity can be further examined by considering its quantum mechanical form, where the classical fields of (1.2.1) are replaced by quantum mechanical field operators. The operators for the two potentials and fields are given by [12, §4.4]

---

[3] Summation is implied over the repeated index *i*, which runs over the three cartesian components. Throughout this thesis, Roman indices run over the three spatial dimensions.

$$\hat{\boldsymbol{A}}(\boldsymbol{r},t) = \sum_{\boldsymbol{k},\lambda} \left(\frac{\hbar}{2\epsilon_0 V \omega_k}\right)^{\frac{1}{2}} \boldsymbol{e}_{\boldsymbol{k},\lambda} \hat{a}_{\boldsymbol{k}\lambda} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)} + \mathrm{h.c.}, \quad 1.4.1$$

$$\hat{\boldsymbol{C}}(\boldsymbol{r},t) = \sum_{\boldsymbol{k},\lambda} \left(\frac{\hbar\epsilon_0 c}{2Vk^3}\right)^{\frac{1}{2}} \left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},\lambda}\right) \hat{a}_{\boldsymbol{k}\lambda} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)} + \mathrm{h.c.}, \quad 1.4.2$$

$$\hat{\boldsymbol{E}}^T = \sum_{\boldsymbol{k},\lambda} \boldsymbol{e}_{\boldsymbol{k},\lambda} \left(\frac{\hbar\omega_k}{2\epsilon_0 V}\right)^{\frac{1}{2}} i\hat{a}_{\boldsymbol{k}\lambda} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)} + \mathrm{h.c.}, \quad 1.4.3$$

$$\hat{\boldsymbol{B}} = \sum_{\boldsymbol{k},\lambda} \left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},\lambda}\right) \left(\frac{\hbar}{2\epsilon_0 V \omega_k}\right)^{\frac{1}{2}} i\hat{a}_{\boldsymbol{k}\lambda} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)} + \mathrm{h.c.} \quad 1.4.4$$

where λ labels two orthogonal polarisations, $\boldsymbol{e}_{\boldsymbol{k},\lambda}$ and $\hat{a}_{\boldsymbol{k}\lambda}$ are, respectively, the polarisation vector and annihilation operator of each mode, and V is the quantisation volume. The abbreviation $\mathrm{h.c.}$ stands for the Hermitian conjugate of the previous term. Substituting these definitions into (1.2.1), and explicitly using circular polarised basis vectors, it can be shown that the total helicity over all space for a localised field is [13]

$$\hat{h}_{total} = \frac{1}{2}\int \left[\sqrt{\frac{\epsilon_0}{\mu_0}}\hat{\boldsymbol{A}}\cdot\boldsymbol{\nabla}\times\hat{\boldsymbol{A}} + \sqrt{\frac{\mu_0}{\epsilon_0}}\hat{\boldsymbol{C}}\cdot\boldsymbol{\nabla}\times\hat{\boldsymbol{C}}\,dV\right] = \hbar\left(\hat{N}_{\boldsymbol{k},+} - \hat{N}_{\boldsymbol{k},-}\right), \quad 1.4.5$$

where $\hat{N}_{\boldsymbol{k},+/-} \equiv \hat{a}^{\dagger}_{\boldsymbol{k},+/-}\hat{a}_{\boldsymbol{k},+/-}$ are the number operators for the two modes. In other words, the total helicity is equal to $\hbar$ times the difference in photon number in the two circular polarisations. This assignment of $\pm\hbar$ helicity to each of the polarisations shows the electromagnetic definition (1.2.1)'s connection to the concept of helicity in particle physics, where the helicity of a particle refers to the component of its spin angular momentum in the propagation direction.

1.5 The Use of the Potentials in Defining Electromagnetic Helicity

One striking feature of the definitions (1.2.1-2) is the explicit appearance of the potentials, which means that the helicity density and flux at a point are gauge-dependent. The total helicity (1.4.5), however, is clearly independent of gauge. The integral over all space of the product of a longitudinal and a transverse vector field is zero [12, p. 147], and the curl of a vector field is always purely transverse. The volume integral in (1.4.5) therefore serves to pick out only the transverse parts of the potentials – and these are gauge-independent. In light of this, a gauge invariant local density can be constructed by using only the transverse parts of the potentials in (1.2.1-2) [11].

Another prominent feature of the definition (1.2.1) is the presence of the $\boldsymbol{C}$ potential, in addition to the more familiar $\boldsymbol{A}$. This can be contrasted with a purely magnetic version introduced by Woltjer in the study of “force-free” magnetic fields [14],

$$h_{magnetic} = \sqrt{\frac{\epsilon_0}{\mu_0}} \boldsymbol{A} \cdot \boldsymbol{\nabla} \times \boldsymbol{A}. \tag{1.5.1}$$

If we replace the classical field $\boldsymbol{A}$ with the operator (1.4.1), we still find that for localised fields [15]

$$\int \hat{h}_{magnetic} \, dV = \hbar\big(\widehat{N}_{\boldsymbol{k},+} - \widehat{N}_{\boldsymbol{k},-}\big). \tag{1.5.2}$$

We have just emphasised that the total helicity is the gauge-independent quantity, and so it might be thought that the two definitions (1.2.1) and (1.5.1) are equivalent. The key difference between them is that the inclusion of the $\boldsymbol{C}$ potential allows the quantity h to be obtained from the duality symmetry of Maxell's equations. This is discussed in detail in the following chapter. Related to this, it is only possible to write down a local continuity equation for *h* if the full definition (1.2.1) is used. The situation is in some ways analogous to that of the electric and magnetic parts of the energy density, $w = \frac{1}{2}(\epsilon_0 \boldsymbol{E}^2 + \mu_0 \boldsymbol{H}^2)$ – the correct total energy in an oscillating field can be obtained by integrating either the electric or magnetic halves and cycle-averaging, but only the full density obeys a local continuity equation.

1.6 Electromagnetic Chirality

As well as the helicity, we will consider another locally conserved pseudoscalar density called the *optical chirality*. Its form is similar to the helicity density, but it is defined in terms of the fields rather than the potentials – the chirality density and flux density are defined by

$$\chi = \frac{\epsilon_0}{2}(\boldsymbol{E} \cdot \boldsymbol{\nabla} \times \boldsymbol{E} + c^2 \boldsymbol{B} \cdot \boldsymbol{\nabla} \times \boldsymbol{B}), \tag{1.6.1}$$

$$\boldsymbol{f} = \frac{\epsilon_0 c^2}{2}[\boldsymbol{E} \times (\boldsymbol{\nabla} \times \boldsymbol{B}) - \boldsymbol{B} \times (\boldsymbol{\nabla} \times \boldsymbol{E})]. \tag{1.6.2}$$

The existence of this conserved quantity was originally pointed out by Lipkin in 1964 [16], although Lipkin remarked that it appeared physically insignificant. It was reintroduced in 2010 by Tang and Cohen, who proposed that it could be interpreted as a measure of local "chirality" in an optical field [17]. They dubbed the quantity the optical chirality, and showed that the differential excitation rate between two enantiomers of a chiral molecule in a monochromatic field is proportional to the chirality density of the field in which they are immersed.

The electromagnetic chirality and helicity are very similar in form – in fact, one could obtain the chirality density by forming a helicity density from the *curl* of the fields, rather than the fields themselves [18]. This correspondence supplies intuition to the observation that, in monochromatic fields, the chirality and helicity densities differ only by the constant c/ω^2 [19]. In polychromatic fields the situation is not so simple – the examination of this issue in more detail is the main subject of chapter 3.

1.7 Conclusion

This chapter has introduced the concept of chirality, and briefly discussed some of the main chiroptical effects. We have also given definitions for the helicity, chirality, spin and orbital angular momentum densities of the electromagnetic field, all of which are distinct quantities that capture different elements of "handedness" and rotation in electromagnetic fields. In the following chapter, we go on to consider the electromagnetic helicity in greater detail – examining its local continuity, and its relation to symmetry transformations of the fields.

References

[1] Wu C. S., Ambler E., Hayward R. W., Hoppes D. D. and Hudson R. P. 1957 Experimental Test of Parity Conservation in Beta Decay *Physical Review* **105** 1413

[2] Quack M. 2002 How Important is Party Violation to Biochemistry? *Angewandte Chemie International Edition* **42** 4618

[3] Barron L. D. 2004 Molecular Light Scattering and Optical Activity (2nd Edition) Cambridge University Press

[4] Moffat H. K. 1969 The Degree of Knottedness of Tangles Vortex Lines *Journal of Fluid Mechanics* **35** 117

[5] Stratton J. A. 1941 *Electromagnetic Theory* McGraw-Hill

[6] Cameron R. P. 2014 On the 'Second Potential' in Electrodynamics *Journal of Optics* **16** 015708

[7] Jackson J. D. 1999 *Classical Electrodynamics* (3rd edition) Wiley

[8] van Enk S. J. and Nienhuis G. 1994 Spin and Orbital Angular Momentum of Photons *European Physics Letters* **25** 497

[9] Allen L., Beijersbergen M. W., Spreeuw R. J. C. and Woerdman J. P. 1992 Orbital Angular Momentum of Light and the Transformation of Laguerre-Gaussian Laser Modes *Physical Review A* **45** 8185

[10] Barnett S. M., Babiker M. and Padgett M. J. 2017 Optical Orbital Angular Momentum *Philosophical Transactions of the Royal Society A* **375** 20150444

[11] Barnett S. M., Cameron R. P. and Yao A. M. 2012 Duplex Symmetry and its Relation to the Conservation of Optical Helicity *Physical Review A* **86** 013845

[12] Loudon R. *The Quantum Theory of Light* (2nd edition) Oxford University Press

[13] Tureba J. L. and Rañada A. F. 1996 The Electromagnetic Helicity *European Journal of Physics* **17** 141

[14] Woltjer L. 1958 A Theorem on Force-Free Magnetic Fields *Proceedings of the National Academy of Sciences* **44** 489

[15] Rañada A. F. 1992 On the Magnetic Helicity *European Journal of Physics* **13** 70

[16] Lipkin D. M. 1964 Existence of a New Conservation Law in Electromagnetic Theory *Journal of Mathematical Physics* **5** 696

[17] Tang Y. and Cohen A. E. 2010 Optical Chirality and its Interaction with Matter *Physical Review Letters* **104** 163901

[18] Cameron R. P., Barnett S. M. and Yao A. M. 2012 Optical Helicity, Optical Spin and Related Quantities in Electromagnetic Theory *New Journal of Physics* **14** 053050

[19] Nienhuis G. 2016 *Physical Review A* Conservation Laws and Symmetry Transformations of the Electromagnetic Field with Sources **93** 023840

Chapter 2 – Symmetries and Conservation

This chapter discusses the conservation of helicity and chirality. We begin with a straightforward derivation of the continuity equations for the two quantities in free space, starting from the definitions that were presented in the previous chapter. We then focus on helicity: having established the local conservation of helicity, we re-examine this in the light of Noether's theorem, and draw attention to its connection with electromagnetic duality symmetry.

We then move on to consider the behaviour of helicity in the presence of charges and currents. This breaks the duality symmetry, and helicity is not generally conserved – the continuity equation acquires a source term related to the current density. Finally, we consider how the definition of the helicity density is modified when describing the macroscopic fields in bulk media.

2.1 Local Conservation of Helicity and Chirality in Free Space

The previous chapter introduced the electromagnetic helicity (1.2.1-2). Helicity is locally conserved in free space, and this fact is expressed mathematically by the continuity equation

$$\frac{\partial h}{\partial t} + \nabla \cdot \boldsymbol{v} = 0, \tag{2.1.1}$$

where h is the helicity density, and $\boldsymbol{v}$ the helicity flux density. This continuity equation can be derived from the free-space Maxwell equations directly. These are given by

$$\nabla \cdot \boldsymbol{E} = 0, \tag{2.1.2}$$

$$\nabla \cdot \boldsymbol{B} = 0, \tag{2.1.3}$$

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}, \tag{2.1.4}$$

$$\nabla \times \boldsymbol{B} = \mu_0 \epsilon_0 \frac{\partial \boldsymbol{E}}{\partial t}. \tag{2.1.5}$$

Starting with the definition of the helicity density (1.2.1), we take the time derivative to obtain

$$\begin{aligned}\frac{\partial h}{\partial t} &= \frac{1}{2}\frac{\partial}{\partial t}\left[\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{A}^T \cdot \boldsymbol{B} - \sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{C} \cdot \boldsymbol{D}\right] \\ &= \frac{1}{2}\left[-\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{E} \cdot \boldsymbol{B} - \sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{A}^T \cdot \nabla \times \boldsymbol{E} + \sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{H} \cdot \boldsymbol{D} - \sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{C} \cdot \nabla \times \boldsymbol{H}\right],\end{aligned} \tag{2.1.6}$$

where use has been made of $\frac{\partial \boldsymbol{A}^T}{\partial t} = -\boldsymbol{E}$ and $\frac{\partial \boldsymbol{B}}{\partial t} = -\nabla \times \boldsymbol{E}$ in the first term, and $\frac{\partial \boldsymbol{C}}{\partial t} = -\boldsymbol{H}$ and $\frac{\partial \boldsymbol{D}^T}{\partial t} = \nabla \times \boldsymbol{H}$ in the second. Similarly, we can take the divergence of the helicity flux density, using the vector calculus identity $\nabla \cdot (\boldsymbol{E} \times \boldsymbol{A}) = \boldsymbol{A} \cdot (\nabla \times \boldsymbol{E}) - \boldsymbol{E} \cdot (\nabla \times \boldsymbol{A})$

$$\frac{1}{2}\nabla\cdot\left(\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{E}\times\boldsymbol{A}+\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{H}\times\boldsymbol{C}\right)$$

$$=\frac{1}{2}\sqrt{\frac{\epsilon_0}{\mu_0}}\big(\boldsymbol{A}\cdot(\nabla\times\boldsymbol{E})-\boldsymbol{E}\cdot(\nabla\times\boldsymbol{A})\big)+\frac{1}{2}\sqrt{\frac{\mu_0}{\epsilon_0}}\big(\boldsymbol{C}\cdot(\nabla\times\boldsymbol{H})-\boldsymbol{H}\cdot(\nabla\times\boldsymbol{C})\big). \quad 2.1.7$$

Adding the time derivative and the divergence together gives

$$\frac{\partial h}{\partial t}+\nabla\cdot\boldsymbol{v}=-\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{E}\cdot\boldsymbol{B}+\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{H}\cdot\boldsymbol{D}. \quad 2.1.8$$

Finally, in free space $\boldsymbol{B}=\mu_0\boldsymbol{H}$ and $\boldsymbol{D}=\epsilon_0\boldsymbol{E}$, so we have

$$\frac{\partial h}{\partial t}+\nabla\cdot\boldsymbol{v}=0. \quad 2.1.9$$

The local conservation of chirality can be similarly demonstrated, taking as a starting point the chirality density and flux density [1]. Making use of the Maxwell equations to rewrite the curls of $\boldsymbol{B}$ and $\boldsymbol{E}$, we see that the time derivative of the chirality density is equal to

$$\frac{\partial}{\partial t}\frac{\epsilon_0}{2}\left[\boldsymbol{E}\cdot\nabla\times\boldsymbol{E}+c^2\boldsymbol{B}\cdot\nabla\times\boldsymbol{B}\right]$$

$$=\frac{\epsilon_0}{2}\left[\frac{\partial\boldsymbol{E}}{\partial t}\cdot\nabla\times\boldsymbol{E}+\boldsymbol{E}\cdot\frac{\partial}{\partial t}\nabla\times\boldsymbol{E}+c^2\frac{\partial\boldsymbol{B}}{\partial t}\cdot\nabla\times\boldsymbol{B}+c^2\boldsymbol{B}\cdot\frac{\partial}{\partial t}\nabla\times\boldsymbol{B}\right]$$

$$=\frac{\epsilon_0}{2}\left[-\frac{\partial\boldsymbol{E}}{\partial t}\cdot\frac{\partial\boldsymbol{B}}{\partial t}-\boldsymbol{E}\cdot\frac{\partial^2\boldsymbol{B}}{\partial t^2}+\frac{\partial\boldsymbol{B}}{\partial t}\cdot\frac{\partial\boldsymbol{E}}{\partial t}+\boldsymbol{B}\cdot\frac{\partial^2\boldsymbol{E}}{\partial t^2}\right]=\frac{\epsilon_0}{2}\left[-\boldsymbol{E}\cdot\frac{\partial^2\boldsymbol{B}}{\partial t^2}+\boldsymbol{B}\cdot\frac{\partial^2\boldsymbol{E}}{\partial t^2}\right], \quad 2.1.10$$

and the divergence of the chirality flux-density is given by

$$\nabla\cdot\frac{\epsilon_0 c^2}{2}\left[\boldsymbol{E}\times(\nabla\times\boldsymbol{B})-\boldsymbol{B}\times(\nabla\times\boldsymbol{E})\right]$$

$$=\frac{\epsilon_0 c^2}{2}\big[(\nabla\times\boldsymbol{B})\cdot(\nabla\times\boldsymbol{E})-\boldsymbol{E}\cdot\nabla\times(\nabla\times\boldsymbol{B})-(\nabla\times\boldsymbol{E})\cdot(\nabla\times\boldsymbol{B})$$

$$+\big(\boldsymbol{B}\cdot\nabla\times(\nabla\times\boldsymbol{E})\big)\big]$$

$$=\frac{\epsilon_0 c^2}{2}\left[\frac{1}{c^2}\boldsymbol{E}\cdot\frac{\partial^2\boldsymbol{B}}{\partial t}-\frac{1}{c^2}\boldsymbol{B}\cdot\frac{\partial^2\boldsymbol{E}}{\partial t}\right]=-\frac{\partial\chi}{\partial t}, \quad 2.1.11$$

from which the continuity equation immediately follows.

2.2 Electromagnetic Duality and the Conservation of Helicity

Whenever a physical system possesses a continuous symmetry, a locally conserved quantity can be constructed by the application of Noether's theorem. Conversely, when a conserved quantity is recognised in a system it can be of interest to ask which symmetry the conservation is connected to.

The symmetry from which the local conservation of helicity may be derived is a symmetry between electric and magnetic fields known as the *duality symmetry*[1]. The essential idea is that in free space, Maxwell's equations treat electric and magnetic fields "on equal footing". More precisely, the form of the equations is invariant under the following transformation, which mixes electric and magnetic fields:

$$\boldsymbol{E}' = \boldsymbol{E}\cos\theta + c\boldsymbol{B}\sin\theta\,, \qquad 2.2.1$$

$$\boldsymbol{B}' = \boldsymbol{B}\cos\theta - \frac{1}{c}\boldsymbol{E}\sin\theta\,, \qquad 2.2.2$$

where θ is any real (pseudoscalar) angle [2, §6.11]. There is, therefore, a certain arbitrariness in what is labelled as an electric field and what as a magnetic field. Similarly, it is in a sense a matter of convention to speak of matter as consisting of electric monopoles – the most we can say is that every particle has the same *ratio* of electric to magnetic charge. A change of this ratio for all particles would leave all observational predictions unchanged [2, p.274].

The conservation of helicity can be derived by considering an infinitesimal version of the duality transformation [3]. When θ is small, the transformation becomes

$$\boldsymbol{E}' = \boldsymbol{E} + c\theta\boldsymbol{B}, \qquad 2.2.3$$

$$\boldsymbol{B}' = \boldsymbol{B} - \frac{1}{c}\theta\boldsymbol{E}. \qquad 2.2.4$$

The fields themselves, however, are not usually taken as the dynamical variables when electromagnetism is derived from an action principle, and so we require an expression for the duality transformation in terms of the potentials.

One approach would be to include both the electric and magnetic vector potentials as separate generalised coordinates at the outset, and consider an appropriate dual-symmetric Lagrangian that contains both sets of potentials. This is the approach taken by Cameron and Barnett in [4]. Written in terms of both potentials, the duality transformation is simply a mixing of the electric and magnetic vector potentials, similar to the mixing of the electric and magnetic fields. In infinitesimal form, it reads:

$$\boldsymbol{A}' = \boldsymbol{A} + \sqrt{\frac{\mu}{\epsilon}}\theta\boldsymbol{C}, \qquad 2.2.5$$

$$\boldsymbol{C}' = \boldsymbol{C} - \sqrt{\frac{\epsilon}{\mu}}\theta\boldsymbol{A}. \qquad 2.2.6$$

It is also possible to work with the more usual Lagrangian, with only the scalar and magnetic vector potentials as generalised coordinates, even though this is not itself strictly dual-symmetric.

[1] This symmetry goes by many names in the literature – amongst others, the Heaviside-Larmor symmetry, duplex symmetry and electromagnetic democracy. In this thesis it will be referred to as duality symmetry, and the associated transformation as the duality transformation.

Nevertheless, we may express the duality transformation in terms of these alone – this is the approach taken by Calkin [3], and the one we shall present here. By applying the duality transformation to the definitions of the potentials, $\boldsymbol{\nabla}\times\boldsymbol{A}=\boldsymbol{B}$ and $-\frac{\partial\boldsymbol{A}}{\partial t}-\boldsymbol{\nabla}\phi=\boldsymbol{E}$, we find that the following equations must be satisfied for the changes in the potentials, $\delta\boldsymbol{A}$ and $\delta\phi$, under the duality transformation:

$$\boldsymbol{\nabla}\times\delta\boldsymbol{A}=-\frac{1}{c}\theta\boldsymbol{E}=\frac{1}{c}\theta\left(\frac{\partial\boldsymbol{A}}{\partial t}+\boldsymbol{\nabla}\phi\right), \qquad 2.2.7$$

$$-\frac{\partial(\delta\boldsymbol{A})}{\partial t}-\boldsymbol{\nabla}(\delta\phi)=c\theta\boldsymbol{B}=c\theta\boldsymbol{\nabla}\times\boldsymbol{A}. \qquad 2.2.8$$

The general solution to these two equations can be written

$$\delta\phi=-\theta\frac{\partial\chi}{\partial t}, \qquad 2.2.9$$

$$\delta\boldsymbol{A}=\theta\boldsymbol{\nabla}\chi-\theta c\boldsymbol{\nabla}\times\boldsymbol{Z}, \qquad 2.2.10$$

where χ is any scalar field, and $\boldsymbol{Z}$ is any vector field which satisfies

$$\frac{\partial\boldsymbol{Z}}{\partial t}=\boldsymbol{A}-\boldsymbol{\nabla}\lambda, \qquad 2.2.11$$

$$\boldsymbol{\nabla}\times(\boldsymbol{\nabla}\times\boldsymbol{Z})=-\frac{\boldsymbol{\nabla}\phi}{c^2}-\frac{1}{c^2}\frac{\partial}{\partial t}\left[\frac{\partial}{\partial t}\boldsymbol{Z}+\boldsymbol{\nabla}\lambda\right]. \qquad 2.2.12$$

Here, λ is another arbitrary scalar field – it arises because the change in $\boldsymbol{A}$ under the duality transformation involves only the curl of $\boldsymbol{Z}$, and so we are free to add any irrotational field $\boldsymbol{\nabla}\lambda$ to our definition of $\boldsymbol{Z}$.

Note that we have written down the most general transformation of the potentials that gives the duality-transformed fields. This means that the solution includes the possibility of a gauge transformation of the potentials, and this is given by the scalar field χ in the usual way. For the remainder of this discussion we set $\chi=0$, and focus on the changes to the potentials specific to the duality transformation. Note also that, because of the relations above, we can identify $\boldsymbol{\nabla}\times\boldsymbol{Z}=-\mu_0\boldsymbol{C}$.

To proceed further, we require the Lagrangian density in terms of the vector and scalar potential. A suitable Lagrangian density for the free electromagnetic field is given by [5, §2.4]

$$\mathcal{L}=\frac{1}{2}\left(\epsilon_0\boldsymbol{E}\cdot\boldsymbol{E}-\frac{1}{\mu_0}\boldsymbol{B}\cdot\boldsymbol{B}\right). \qquad 2.2.13$$

Application of the duality transformation (2.2.3-4) does not leave this Lagrangian unchanged – though it changes it only by a four-divergence, which does not affect the equations of motion. Substituting (2.2.5-6) into (2.2.13), we find [3]

$$\mathcal{L}'-\mathcal{L}=2\epsilon_0 c\theta\boldsymbol{E}\cdot\boldsymbol{B}, \qquad 2.2.14$$

where terms second order in the infinitesimal parameter θ have been ignored. This may be written as a four-divergence as follows [3]:

$$\mathcal{L}' - \mathcal{L} = 2\epsilon_0 c\theta\left(-\frac{\partial \boldsymbol{A}}{\partial t} - \boldsymbol{\nabla}\phi\right)\cdot(\boldsymbol{\nabla}\times\boldsymbol{A}) = \epsilon_0 c\theta\left[\frac{\partial}{\partial t}(-\boldsymbol{A}\cdot\boldsymbol{\nabla}\times\boldsymbol{A}) - \boldsymbol{\nabla}\cdot\big(\boldsymbol{E}\times\boldsymbol{A} + \phi(\boldsymbol{\nabla}\times\boldsymbol{A})\big)\right]. \quad 2.2.15$$

The quantity differentiated with respect to time is equal to negative of the magnetic half of the helicity density, and the quantity in the divergence is the negative of the magnetic half of the helicity flux density[2].

We have shown that the duality transformation changes $\mathcal{L}$ only by a four-divergence, but we have not yet established a local continuity equation. In order to do this, we now make use of the following form of Noether's theorem: for a system described by R different scalar fields that transform according to $\phi_r' = \phi_r + \delta\phi_r$, the resulting change in the Lagrangian is given by

$$\mathcal{L}' - \mathcal{L} = \frac{\partial}{\partial x^\alpha}\left(\frac{\partial \mathcal{L}}{\partial \phi_{r,\alpha}}\delta\phi_r\right), \quad 2.2.16$$

where 4-vector notation has been used: α runs from 0 to 3 to label the four spacetime coordinates, the comma denotes partial differentiation ($\phi_{r,\alpha} \equiv \partial\phi/\partial x^\alpha$), and summation over both α and r is implied [6, §2.2]. If the transformation leaves the Lagrangian unchanged – or causes it to differ only by a 4-divergence – this immediately results in a local continuity equation, and defines an associated conserved quantity. We shall find that the right hand side of (2.2.16) provides us with the *electric* half of the helicity continuity equation, and that equating (2.2.15) with (2.2.16) produces the final result.

Returning to our 3-vector notation, for the electromagnetic field Lagrangian (2.2.16) becomes

$$\begin{aligned}\mathcal{L}' - \mathcal{L} = {} & \frac{\partial}{\partial t}\left(\frac{\partial \mathcal{L}}{\partial \dot{\phi}}\delta\phi + \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{A}}}\cdot\delta\boldsymbol{A}\right) + \frac{\partial}{\partial x}\left(\frac{\partial \mathcal{L}}{\partial(\partial_x\phi)}\delta\phi + \frac{\partial \mathcal{L}}{\partial(\partial_x\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right) \\ & + \frac{\partial}{\partial y}\left(\frac{\partial \mathcal{L}}{\partial(\partial_y\phi)}\delta\phi + \frac{\partial \mathcal{L}}{\partial(\partial_y\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right) + \frac{\partial}{\partial z}\left(\frac{\partial \mathcal{L}}{\partial(\partial_z\phi)}\delta\phi + \frac{\partial \mathcal{L}}{\partial(\partial_z\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right),\end{aligned} \quad 2.2.17$$

A locally conserved current density can be immediately read off by incorporating the four-divergence $\mathcal{L}' - \mathcal{L}$ (2.2.15) into the right-hand side of (2.2.17) to give a local continuity equation. We now show, by explicit evaluation of the derivatives of $\mathcal{L}$, that the terms in the time and space derivatives of the right hand side of (2.2.17) correspond to the electric half of the helicity density and flux density.

In terms of the potentials, the Lagrangian reads

[2] We note the presence of the additional term $\phi(\boldsymbol{\nabla}\times\boldsymbol{A})$, which did not appear in the definitions of spin-angular momentum density or helicity flux density presented in the previous chapter. This term does not contribute to the change in the Lagrangian density when integrated over all space, as $\boldsymbol{\nabla}\cdot\phi(\boldsymbol{\nabla}\times\boldsymbol{A}) = \phi\boldsymbol{\nabla}\cdot(\boldsymbol{\nabla}\times\boldsymbol{A}) + (\boldsymbol{\nabla}\times\boldsymbol{A})\cdot\boldsymbol{\nabla}\phi$. The first term is identically zero, while the second is the product of a transverse and a longitudinal field, and therefore vanishes upon integration. Furthermore, when discussing local densities, we always work in the Coulomb gauge, where the vector potential is transverse and the scalar potential vanishes in free space, so this term does not appear. The term will be dropped in the remainder of this section.

$$\mathcal{L} = \frac{1}{2}\left(\epsilon_0\left(-\boldsymbol{\nabla}\phi - \frac{\partial \boldsymbol{A}}{\partial t}\right)^2 - \frac{1}{\mu_0}(\boldsymbol{\nabla}\times\boldsymbol{A})^2\right)$$
$$= \frac{1}{2}\left(\epsilon_0\left((\boldsymbol{\nabla}\phi)^2 + 2\frac{\partial \boldsymbol{A}}{\partial t}\cdot\boldsymbol{\nabla}\phi + \left(\frac{\partial \boldsymbol{A}}{\partial t}\right)^2\right) - \frac{1}{\mu_0}(\boldsymbol{\nabla}\times\boldsymbol{A})^2\right), \qquad 2.2.18$$

and so the relevant derivatives are

$$\frac{\partial\mathcal{L}}{\partial\dot{\phi}} = 0, \qquad 2.2.19$$

$$\frac{\partial\mathcal{L}}{\partial\dot{\boldsymbol{A}}} = \epsilon_0\left(\frac{\partial \boldsymbol{A}}{\partial t} + \boldsymbol{\nabla}\phi\right), \qquad 2.2.20$$

$$\frac{\partial\mathcal{L}}{\partial(\boldsymbol{\nabla}\phi)} = \epsilon_0\left(\frac{\partial \boldsymbol{A}}{\partial t} + \boldsymbol{\nabla}\phi\right), \qquad 2.2.21$$

$$\frac{\partial\mathcal{L}}{\partial(\partial_a\boldsymbol{A})} = -\frac{1}{2\mu_0}\frac{\partial}{\partial(\partial_a\boldsymbol{A})}(\boldsymbol{\nabla}\times\boldsymbol{A})^2 = \frac{1}{\mu_0}\boldsymbol{n}_a\times(\nabla\times\boldsymbol{A}), \qquad 2.2.22$$

where $\boldsymbol{n}_a$ is a unit vector in the a direction. The change in the Lagrangian density can therefore be written as

$$\mathcal{L}' - \mathcal{L} = \frac{\partial}{\partial t}\left(\frac{\partial\mathcal{L}}{\partial\dot{\boldsymbol{A}}}\cdot\delta\boldsymbol{A}\right) + \frac{\partial}{\partial x}\left(\frac{\partial\mathcal{L}}{\partial(\partial_x\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right) + \frac{\partial}{\partial y}\left(\frac{\partial\mathcal{L}}{\partial(\partial_y\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right) + \frac{\partial}{\partial z}\left(\frac{\partial\mathcal{L}}{\partial(\partial_z\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right)$$
$$= \frac{\partial}{\partial t}\left(-\theta c\epsilon_0\left(\frac{\partial \boldsymbol{A}}{\partial t} + \boldsymbol{\nabla}\phi\right)\cdot\boldsymbol{\nabla}\times\boldsymbol{Z}\right) + \frac{\partial}{\partial x}\left(\frac{\partial\mathcal{L}}{\partial(\partial_x\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right) + \frac{\partial}{\partial y}\left(\frac{\partial\mathcal{L}}{\partial(\partial_y\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right) + \frac{\partial}{\partial z}\left(\frac{\partial\mathcal{L}}{\partial(\partial_z\boldsymbol{A})}\cdot\delta\boldsymbol{A}\right). \qquad 2.2.23$$

Noting that

$$\frac{\partial\mathcal{L}}{\partial\dot{\boldsymbol{A}}}\cdot\delta\boldsymbol{A} = \epsilon_0\left(\frac{\partial \boldsymbol{A}}{\partial t} + \boldsymbol{\nabla}\phi\right)\cdot(-\theta c\boldsymbol{\nabla}\times\boldsymbol{Z}) = -\theta\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{D}\cdot\boldsymbol{C}, \qquad 2.2.24$$

we see that the first term is the time derivative of the electric half of the helicity density. That the other three terms correspond to the (negative of the) divergence of the flux density can be seen from

$$\frac{\partial\mathcal{L}}{\partial(\partial_a\boldsymbol{A})}\cdot\delta\boldsymbol{A} = \theta\sqrt{\frac{\mu_0}{\epsilon_0}}\frac{1}{\mu_0}\boldsymbol{n}_a\times(\nabla\times\boldsymbol{A})\cdot\mathbf{C} = \theta c(\nabla\times\boldsymbol{A})\times\boldsymbol{C}\cdot\boldsymbol{n}_a = \theta c(\boldsymbol{B}\times\boldsymbol{C})_a$$
$$= \theta\sqrt{\frac{\mu_0}{\epsilon_0}}(\boldsymbol{H}\times\boldsymbol{C})_a. \qquad 2.2.25$$

The change in the Lagrangian from Noether's theorem can therefore be written

$$\mathcal{L}' - \mathcal{L} = \theta\sqrt{\frac{\mu_0}{\epsilon_0}}\left(-\frac{\partial}{\partial t}\boldsymbol{C}\cdot\boldsymbol{D} + \boldsymbol{\nabla}\cdot(\boldsymbol{H}\times\boldsymbol{C})\right). \qquad 2.2.26$$

Equating this with the change given directly from the duality transformation gives

$$\theta\sqrt{\frac{\epsilon_0}{\mu_0}}\left(\frac{\partial}{\partial t}(\boldsymbol{A}\cdot\boldsymbol{B}) + \boldsymbol{\nabla}\cdot(\boldsymbol{E}\times\boldsymbol{A})\right) + \theta\sqrt{\frac{\mu_0}{\epsilon_0}}\left(-\frac{\partial}{\partial t}(\boldsymbol{C}\cdot\boldsymbol{D}) + \boldsymbol{\nabla}\cdot(\boldsymbol{H}\times\boldsymbol{C})\right) = 0, \qquad 2.2.27$$

which is the local conservation of electromagnetic helicity.

The above discussion relates to classical field theory – the connection between helicity conservation and duality symmetry can also be exposed succinctly using the quantum mechanical formalism, as follows.

Operators corresponding to conserved quantities commute with the system's Hamiltonian. Any Hermitian operator, $\hat{h}$, can also be used to generate a unitary transformation by

$$\hat{U} = e^{i\theta\hat{h}}, \tag{2.2.28}$$

parameterised by some θ. If such a unitary transformation leaves the Hamiltonian unchanged, then it follows directly that the operator used to generate the transformation commutes with the Hamiltonian [6, p. 31]. So to complement the discussion above, which began with the symmetry and examined the conserved quantity associated with it, we may approach the issue the other way around, as it were – using the helicity operator as the generator of an infinitesimal transformation of the fields, and then examining the effect of the resulting transformation.

Generating an infinitesimal unitary transformation using the helicity operator, and applying this to the electric and magnetic field operators, yields

$$e^{i\hat{h}_{total}\theta}\hat{\boldsymbol{E}}e^{-i\hat{h}_{total}\theta} = \hat{\boldsymbol{E}} + c\theta\hat{\boldsymbol{B}} \tag{2.2.29}$$

$$e^{i\hat{h}_{total}\theta}\hat{\boldsymbol{B}}e^{-i\hat{h}_{total}\theta} = \hat{\boldsymbol{B}} - \frac{1}{c}\theta\hat{\boldsymbol{E}} \tag{2.2.30}$$

with $\hat{h}_{total}$ the helicity density operator, integrated over all space [7]. This is nothing other than the infinitesimal duality transformation. The result is obtained by substituting the definitions of the helicity, $\hat{\boldsymbol{E}}$ and $\hat{\boldsymbol{B}}$ operators (1.2.1, 1.4.3-4), taking the Taylor expansion of the exponentials to first-order in θ, and applying the commutation relations for the creation and annihilation operators. The full calculation is presented in appendix A.

An important benefit of recognising the relationship between helicity and duality symmetry is that it provides some intuition of why helicity is generally not conserved in the presence of matter, and under what special circumstances the conservation will continue to hold. Matter is made of electric charges, not magnetic ones, and so the presence of matter breaks the duality symmetry. However, as we shall see later, there are circumstances where a form of the duality symmetry survives for the macroscopic fields even in the presence of a medium, and under these the helicity of the macroscopic fields is conserved[3].

[3] We remarked earlier that it is, in a sense, a matter of convention to treat the charges in matter as purely electric – the physically important condition being that all particles have the same ratio of electric to magnetic charge. It is worthwhile to note here that the breaking of duality symmetry by matter would not be affected by a more symmetrical choice of convention – for example, taking all charged particles to have half electric and half magnetic charge. In this case, the asymmetry comes about because all charges have (say) positive electric and positive magnetic parts, or negative electric and negative magnetic parts – and *none* have positive electric and negative magnetic, or *vice versa*. It is the introduction of the fixed ratio which breaks the symmetry.

2.3 Duality Transformations and the Rotation of Polarisation

Before turning to the continuity of helicity in the presence of matter, we make a brief digression to discuss the physical effect of the abstract "rotation" between electric and magnetic fields presented above. The conservation of angular momentum is connected by Noether's theorem to rotations. Helicity is closely connected to angular momentum, and also to rotations – though the duality transformation presented above appears at first glance quite unlike a rotation.
To see an intuitive connection between this transformation and helicity, one can consider its effect on a plane-wave. For a transverse plane wave, where the electric and magnetic fields are always perpendicular to one another, the angle θ in the transformation (2.2.3-4) – which parameterises the mixing between electric and magnetic fields – corresponds to a physical rotation of the direction of the electric and magnetic fields about the propagation direction by an angle θ. It is clear, then, how the resulting quantity is related to the component of the angular momentum which is connected with photon polarisation – that is, the spin angular momentum – in the direction of propagation.

We may mention also that the conservations of the spin and orbital parts of the free-field angular momentum – as defined by $\boldsymbol{L} = \frac{1}{2}(\epsilon_0 E_i(\boldsymbol{r} \times \boldsymbol{\nabla})A_i + cB_i(\boldsymbol{r} \times \boldsymbol{\nabla})C_i)$ and $\boldsymbol{S} = \frac{1}{2}(\epsilon_0 \boldsymbol{E} \times \boldsymbol{A} + c\boldsymbol{B} \times \boldsymbol{C})$ – are related to rotations of a sort. One might expect that the decomposition of total angular momentum into spin and orbital parts would be related to a decomposition of the generating rotation into separate transformations: the orbital angular momentum would be connected with rotations of the positions field vectors (rotating the system while "parallel-transporting" the field vectors), and the spin part with rotation of only the direction of the field vectors. While the composition of these two transformations leads to an ordinary rotation (corresponding to the conservation of total angular momentum), these separate rotations are not symmetries of the free-space Maxwell equations, and they can be shown to violate the transversality of the free fields. The infinitesimal transformations which do generate these quantities correspond to performing the aforementioned "rotations", and taking the transverse parts of the result [8]. In this sense, they are the "closest approximation" to these rotations allowed by the free-space Maxwell equations. As pointed out in [8], the fact that spin and orbital momentum conservation are not related to exact rotations may not be entirely surprising, as neither the spin nor the orbital parts are "true" angular momenta, in the sense that their components do not obey the usual angular momentum commutation relations [9].

2.4 Local Continuity of Helicity in the Presence of Charges and Currents

We now turn to the question of defining helicity in the presence of matter. As mentioned earlier, the presence of matter breaks duality symmetry, so we will not expect the helicity to remain a conserved quantity.

To begin with, we will examine the situation from the point of view of microscopic electrodynamics, with all charges and currents written explicitly. We repeat the calculation presented in the first section of this chapter, but employ the Maxwell equations with a charge density $\rho(\boldsymbol{r},t)$ and current density $\boldsymbol{J}(\boldsymbol{r},t)$. In other words, in place of (2.1.2) and (2.1.5) we have

$$\boldsymbol{\nabla}\cdot\boldsymbol{E}=\frac{\rho}{\epsilon_0}, \qquad 2.4.1$$

$$\boldsymbol{\nabla}\times\boldsymbol{B}=\mu_0\boldsymbol{J}+\mu_0\epsilon_0\frac{\partial\boldsymbol{E}}{\partial t}, \qquad 2.4.2$$

while (2.1.3) and (2.1.4) remain unchanged.

Two of the identities used during the derivation in section 2.1 are modified by the presence of matter. First, if we treat the current density as consisting entirely of free current[4], we have $\frac{\partial\boldsymbol{D}^T}{\partial t}=\boldsymbol{\nabla}\times\boldsymbol{H}-\boldsymbol{J}^T$ in place of $\frac{\partial\boldsymbol{D}^T}{\partial t}=\boldsymbol{\nabla}\times\boldsymbol{H}$. The corresponding identity for the $\boldsymbol{C}$ potential also requires modification, and becomes $\frac{\partial\boldsymbol{C}}{\partial t}=-\boldsymbol{H}+\boldsymbol{g}$ in place of $\frac{\partial\boldsymbol{C}}{\partial t}=-\boldsymbol{H}$. To express this latter identity, we have introduced a new vector field $\boldsymbol{g}$, which may be taken as any vector field which satisfies $\boldsymbol{\nabla}\times\boldsymbol{g}=\boldsymbol{J}^T$. Note that in free space the distinction between $\boldsymbol{D}$ and $\boldsymbol{D}^T$ was unimportant, whereas in the presence of charges it is significant.

Using these identities, the time derivative of the helicity density then becomes

$$\frac{\partial h}{\partial t}=\frac{1}{2}\frac{\partial}{\partial t}\left[\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{A}^T\cdot\boldsymbol{B}-\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{C}^T\cdot\boldsymbol{D}^T\right]$$

$$=\frac{1}{2}\left[-\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{E}^T\cdot\boldsymbol{B}-\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{A}^T\cdot\boldsymbol{\nabla}\times\boldsymbol{E}+\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{H}\cdot\boldsymbol{D}^T-\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{g}\cdot\boldsymbol{D}^T-\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{C}^T\cdot\boldsymbol{\nabla}\times\boldsymbol{H}+\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{C}^T\cdot\boldsymbol{J}^T\right]. \qquad 2.4.3$$

The expression for the divergence of the flux density remains unchanged:

$$\frac{1}{2}\boldsymbol{\nabla}\cdot\left(\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{E}^T\times\boldsymbol{A}^T+\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{H}\times\boldsymbol{C}\right)$$

$$=\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{A}^T\cdot(\boldsymbol{\nabla}\times\boldsymbol{E}^T)-\sqrt{\frac{\epsilon_0}{\mu_0}}\boldsymbol{E}^T\cdot(\boldsymbol{\nabla}\times\boldsymbol{A}^T)+\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{C}\cdot(\boldsymbol{\nabla}\times\boldsymbol{H})-\sqrt{\frac{\mu_0}{\epsilon_0}}\boldsymbol{H}\cdot(\boldsymbol{\nabla}\times\boldsymbol{C}). \qquad 2.4.4$$

This means that when we construct the continuity equation, we are left with the source term [1]

[4] In this section we will treat all charges and currents as free, and so $\boldsymbol{D}$ and $\boldsymbol{E}$ will only ever differ by a factor of ϵ_0. $\boldsymbol{B}$ and $\boldsymbol{H}$ differ likewise by a factor of μ_0.

$$\frac{\partial h}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{v} = \frac{1}{2}\sqrt{\frac{\mu_0}{\epsilon_0}}\left(\boldsymbol{C}^T\cdot\boldsymbol{J}^T - \boldsymbol{g}\cdot\boldsymbol{D}^T\right) = \frac{1}{2}\sqrt{\frac{\mu_0}{\epsilon_0}}\big(\boldsymbol{C}\cdot(\boldsymbol{\nabla}\times\boldsymbol{g}) + \boldsymbol{g}\cdot(\boldsymbol{\nabla}\times\boldsymbol{C})\big). \qquad 2.4.5$$

This term shows how matter can act as a source or sink of helicity. A word of caution must be supplied in connection with the terms “source” and “sink”, as – unlike in the case of energy continuity (for example) – there is not a sense in which the matter “gains” or “loses” helicity to compensate for changes in the field. A similar calculation shows that the corresponding equation for the continuity of chirality in the presence of matter is [1]

$$\frac{\partial \chi}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{f} = -\frac{1}{2}\big(\boldsymbol{J}\cdot(\boldsymbol{\nabla}\times\boldsymbol{E}) + \boldsymbol{E}\cdot(\boldsymbol{\nabla}\times\boldsymbol{J})\big). \qquad 2.4.6$$

2.5 Continuity of Helicity in Media

To conclude this chapter, we consider the definition and behaviour of helicity within bulk media, working in the context of macroscopic electrodynamics. We consider linear, lossless, non-dispersive media, but allow the permittivity and permeability to vary in space. We also now assume that there are *no* free charges or currents. Maxwell’s equations then read

$$\boldsymbol{\nabla}\cdot\boldsymbol{D} = 0, \qquad 2.5.1$$

$$\boldsymbol{\nabla}\cdot\boldsymbol{B} = 0, \qquad 2.5.2$$

$$\boldsymbol{\nabla}\times\boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}, \qquad 2.5.3$$

$$\boldsymbol{\nabla}\times\boldsymbol{H} = \frac{\partial \boldsymbol{D}}{\partial t}, \qquad 2.5.4$$

with the constitutive relations

$$\boldsymbol{D} = \epsilon(\boldsymbol{r})\boldsymbol{E}, \qquad 2.5.5$$

$$\boldsymbol{B} = \mu(\boldsymbol{r})\boldsymbol{H}. \qquad 2.5.6$$

When writing the above, we have explicitly indicated the spatial dependence of $\epsilon(\boldsymbol{r})$ and $\mu(\boldsymbol{r})$; this will be left implicit below for notational brevity.

We now again repeat the derivation of the continuity equation. Because we have no free currents or charges, the form of the time derivative of the helicity density is unchanged from the free-space case. However, the spatial variation of the permittivity and permeability adds extra terms when the divergence of the flux density is taken. Using $\boldsymbol{\nabla}\cdot\left(\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}\times\boldsymbol{A}\right) = \boldsymbol{\nabla}\left(\sqrt{\frac{\epsilon}{\mu}}\right)\cdot\boldsymbol{E}\times\boldsymbol{A} + \sqrt{\frac{\epsilon}{\mu}}\boldsymbol{\nabla}\cdot(\boldsymbol{E}\times\boldsymbol{A})$, *etc.*, we obtain

$$\frac{1}{2}\boldsymbol{\nabla}\cdot\left(\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}\times\boldsymbol{A}+\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{H}\times\boldsymbol{C}\right)$$

$$=\frac{1}{2}\sqrt{\frac{\epsilon}{\mu}}\big(\boldsymbol{A}\cdot(\boldsymbol{\nabla}\times\boldsymbol{E})-\boldsymbol{E}\cdot(\boldsymbol{\nabla}\times\boldsymbol{A})\big)+\frac{1}{2}\sqrt{\frac{\mu}{\epsilon}}\big(\boldsymbol{C}\cdot(\boldsymbol{\nabla}\times\boldsymbol{H})-\boldsymbol{H}\cdot(\boldsymbol{\nabla}\times\boldsymbol{C})\big)$$

$$+\frac{1}{2}\nabla\left(\sqrt{\frac{\epsilon}{\mu}}\right)\boldsymbol{E}\times\boldsymbol{A}+\frac{1}{2}\nabla\left(\sqrt{\frac{\mu}{\epsilon}}\right)\boldsymbol{H}\times\boldsymbol{C}. \tag{2.5.7}$$

This means that the helicity continuity equation acquires the source term

$$\frac{\partial h}{\partial t}+\boldsymbol{\nabla}\cdot\boldsymbol{v}=\frac{1}{2}\boldsymbol{\nabla}\left(\sqrt{\frac{\epsilon}{\mu}}\right)\boldsymbol{E}\times\boldsymbol{A}+\frac{1}{2}\boldsymbol{\nabla}\left(\sqrt{\frac{\mu}{\epsilon}}\right)\boldsymbol{H}\times\boldsymbol{C}. \tag{2.5.8}$$

We see that the generation or loss of helicity is directly related to changes in the ratio of the permittivity and permeability. The situation can be clarified by consideration of a generalisation of the duality transformation which applies to the macroscopic fields.

2.6. Duality Symmetry in Bulk Media

It was mentioned earlier that the presence of matter breaks the duality symmetry of Maxwell's equations. However, the absence of free charge gives (2.5.1-4) the same form as the free-space Maxwell equations (2.1.2-5). One can therefore define a generalised duality transformation in terms of the macroscopic fields [10]

$$\boldsymbol{D}'=\boldsymbol{D}\cos\theta+\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{B}\sin\theta\,, \tag{2.6.1}$$

$$\boldsymbol{B}'=\boldsymbol{B}\cos\theta-\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{D}\sin\theta\,, \tag{2.6.2}$$

which leaves the forms of (2.5.1-4) unchanged. Because the permittivity and permeability can vary in space, if the form of Maxwell's equations is to remain unchanged we also have the requirement that the gradient of $\frac{\epsilon}{\mu}$ is zero. We can show this explicitly by applying the transformation to the right-hand sides of the Maxwell equations. For the first equation we have

$$\boldsymbol{\nabla}\cdot\boldsymbol{D}'=\boldsymbol{\nabla}\cdot\left(\boldsymbol{D}\cos\theta+\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{B}\sin\theta\right)=\boldsymbol{\nabla}\left(\sqrt{\frac{\epsilon}{\mu}}\right)\cdot\boldsymbol{B}\sin\theta\,. \tag{2.6.3}$$

For the second, we similarly have

$$\boldsymbol{\nabla}\cdot\boldsymbol{B}'=\boldsymbol{\nabla}\cdot\left(\boldsymbol{B}\cos\theta-\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{D}\sin\theta\right)=-\boldsymbol{\nabla}\left(\sqrt{\frac{\mu}{\epsilon}}\right)\cdot\boldsymbol{D}\sin\theta\,. \tag{2.6.4}$$

For the third, we obtain

$$\nabla \times \boldsymbol{E}' = \nabla \times \left(\boldsymbol{E} \cos\theta + \sqrt{\frac{1}{\epsilon\mu}} \boldsymbol{B} \sin\theta \right) = \nabla \times \left(\boldsymbol{E} \cos\theta + \sqrt{\frac{\mu}{\epsilon}} \boldsymbol{H} \sin\theta \right)$$

$$= -\frac{\partial \boldsymbol{B}}{\partial t} \cos\theta + \sqrt{\frac{\mu}{\epsilon}} \frac{\partial \boldsymbol{D}}{\partial t} \sin\theta + \left(\nabla \sqrt{\frac{\mu}{\epsilon}} \right) \times \boldsymbol{H} \sin\theta = -\frac{\partial \boldsymbol{B}'}{\partial t} + \left(\nabla \sqrt{\frac{\mu}{\epsilon}} \right) \times \boldsymbol{H} \sin\theta \qquad 2.6.5$$

Finally, the fourth Maxwell equation becomes

$$\nabla \times \boldsymbol{H}' = \nabla \times \left(\boldsymbol{H} \cos\theta - \sqrt{\frac{\epsilon}{\mu}} \boldsymbol{E} \sin\theta \right) = \frac{\partial \boldsymbol{D}}{\partial t} \cos\theta + \sqrt{\frac{\epsilon}{\mu}} \frac{\partial \boldsymbol{B}}{\partial t} \sin\theta + \nabla \left(\sqrt{\frac{\epsilon}{\mu}} \right) \times \boldsymbol{E} \sin\theta$$

$$= \frac{\partial \boldsymbol{D}'}{\partial t} + \nabla \left(\sqrt{\frac{\epsilon}{\mu}} \right) \times \boldsymbol{E} \sin\theta \, . \qquad 2.6.6$$

We therefore see that we expect the helicity to be conserved whenever the ratio $\sqrt{\frac{\epsilon}{\mu}}$ remains constant. We shall return to this point in chapter 7, when we examine the definition of helicity within a chiral medium – the idea that helicity should be conserved if the medium exhibits macroscopic duality symmetry is used to motivate an extension to the definition which retains these properties even in a chiral medium.

2.9 Conclusion

This chapter has examined the conservation of helicity, presenting a local conservation law in free space, and showing how this is modified to become a local continuity equation in the presence of matter. The conservation of helicity is related by Noether's theorem to the invariance of Maxwell's equations under duality transformations that interchange electric and magnetic fields.

Even when the presence of matter breaks the duality symmetry, helicity can be locally conserved when defined using the macroscopic fields within a medium – provided the "dual symmetry" condition $\nabla \left(\sqrt{\frac{\epsilon}{\mu}} \right) = 0$ holds.

The idea that matter acts as a source or sink of helicity will be made use of in chapters 5, 6 and 7. In the following chapter, we restrict our attention to free space, and discuss the differences between helicity and electromagnetic chirality in polychromatic fields.

References

[1] Nienhuis G. 2016 *Physical Review A* Conservation Laws and Symmetry Transformations of the Electromagnetic Field with Sources **93** 023840

[2] Jackson J. D. 1999 *Classical Electrodynamics* (3rd edition) Wiley

[3] Calkin M. G. 1965 *American Journal of Physics* An Invariance Property of the Free Electromagnetic Field **33** 958

[4] Cameron R. P. and Barnett S. M. 2012 *New Journal of Physics* Electric-magnetic Symmetry and Noether's Theorem **14** 123019

[5] Craig D. P. and Thirunamachandran T. 1984 *Molecular Quantum Electrodynamics* Dover

[6] Mandl F. and Shaw G. 2010 *Quantum Field Theory* (2nd edition) Wiley

[7] Cameron R. P., Barnett S. M. and Yao A. M. 2012 *New Journal of Physics* Optical Helicity, Optical Spin and Related Quantities in Electromagnetic Theory **14** 053050

[8] Barnett S. M. 2010 *Journal of Modern Optics* Rotation of Electromagnetic Fields and the Nature of Optical Angular Momentum **57** 1339

[9] van Enk S. J. and Nienhuis G. 1994 *European Physics Letters* Spin and Orbital Angular Momentum of Photons **25** 497

[10] van Kruining K. and Götte J. B. 2016 *Journal of Optics* The Conditions for the Preservation of Duality Symmetry in a Linear Medium **18** 085601

Chapter 3 – Helicity and Chirality in Polychromatic Fields

The previous chapters have introduced the electromagnetic helicity and electromagnetic chirality as conserved quantities of the free electromagnetic field. It was noted that in monochromatic fields both quantities differ only by a constant – both being proportional to the difference between the number of right- and left-circularly polarised photons in the field. However, the constant of proportionality differs between the two – in particular, the chirality of a photon depends on the photon's frequency (it is proportional to the square of the photon frequency), while the helicity does not.

This different frequency scaling is the reason that a simple proportionality between helicity and chirality only holds in the monochromatic case, and it has important consequences when evaluating and interpreting the two densities in polychromatic fields. In this chapter, we examine the helicity and chirality densities in some simple polychromatic fields, and show how the presence of multiple frequency components leads to differences between the two quantities. We treat three examples of increasing complexity, beginning with the superposition of two circularly polarised plane waves of different frequencies. We then move on to consider chirped pulses of circularly polarised light, before finally discussing helicity and chirality in an "optical centrifuge" – a superposition of two pulses of circularly polarised light of opposite handedness, one chirped up and the other chirped down. The work presented in this chapter was published in [1], and this chapter follows the paper.

3.1 Helicity and Chirality in the Superposition of two Plane Waves

The superposition of two plane waves of different frequencies is perhaps the simplest example of a polychromatic field, but it is sufficient to illustrate the way that polychromaticity affects the behaviour of the two densities. Consider two co-propagating circularly polarised plane waves of opposite handedness, with frequencies ω_1 and ω_2. Taking the waves to be propagating in the z direction, the complex electric and magnetic fields can be written

$$\boldsymbol{E} = E_0 e^{-i\omega_1\eta}(\boldsymbol{x} + i\boldsymbol{y}) + E_0 e^{-i\omega_2\eta}(\boldsymbol{x} - i\boldsymbol{y}), \tag{3.1.1}$$

$$\boldsymbol{B} = \frac{E_0}{c} e^{-i\omega_1\eta}(-i\boldsymbol{x} + \boldsymbol{y}) + \frac{E_0}{c} e^{-i\omega_2\eta}(i\boldsymbol{x} + \boldsymbol{y}), \tag{3.1.2}$$

with E_0 the peak electric field strength of each plane wave, $\boldsymbol{x}$ and $\boldsymbol{y}$ are unit vectors in the x and y directions, and $\eta \equiv t - z/c$. If the frequency difference is fairly small, then the superposition appears like a linearly polarised plane wave of frequency $\frac{\omega_1+\omega_2}{2}$, with a plane of polarisation that rotates at frequency $\frac{\omega_1-\omega_2}{2}$. This configuration is similar to the "optical centrifuge", which will be discussed later – in an optical centrifuge, frequency chirps of the two waves cause the speed of the polarisation plane's rotation to increase with time.

In order to calculate the helicity density, we require expressions for the vector potentials $\boldsymbol{A}$ and $\boldsymbol{C}$. As we are considering the free field, we may choose a gauge where the scalar potential is zero, and obtain transverse choices for the $\boldsymbol{A}$ and $\boldsymbol{C}$ potentials from the relationships $\boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t}$ and $\boldsymbol{B} = -\frac{1}{\epsilon_0 c^2}\frac{\partial \boldsymbol{C}}{\partial t}$. Integrating the $\boldsymbol{E}$ and $\boldsymbol{B}$ fields with respect to time leads to the potentials

$$\boldsymbol{A} = \frac{E_0}{\omega_1} e^{-i\omega_1\eta}(i\boldsymbol{x} - \boldsymbol{y}) + \frac{E_0}{\omega_2} e^{-i\omega_2\eta}(i\boldsymbol{x} + \boldsymbol{y}), \tag{3.1.3}$$

$$\boldsymbol{C} = -\sqrt{\frac{\epsilon_0}{\mu_0}}\frac{E_0}{\omega_1} e^{-i\omega_1\eta}(\boldsymbol{x} + i\boldsymbol{y}) - \sqrt{\frac{\epsilon_0}{\mu_0}}\frac{E_0}{\omega_2} e^{-i\omega_2\eta}(-\boldsymbol{x} + i\boldsymbol{y}). \tag{3.1.4}$$

This results in a helicity density of

$$h = \epsilon_0 E_0^2\left(\frac{1}{\omega_1} - \frac{1}{\omega_2}\right)(1 + \cos\eta(\omega_1 + \omega_2)), \tag{3.1.5}$$

and a chirality density of

$$\chi = \frac{\epsilon_0 E_0^2}{c}(\omega_1 - \omega_2)(1 + \cos\eta(\omega_1 + \omega_2)). \tag{3.1.6}$$

The most immediately striking feature of this result is that the helicity and chirality densities have opposite signs: if the frequency of the left-handed wave is higher than that of the right-, then the helicity is negative and the chirality positive, and *vice versa* when $\omega_2 > \omega_1$.
The reason for this can be seen intuitively by considering the relationship between the helicity density, chirality density and energy density in a circularly polarised plane wave. The ratio of helicity density to energy density in a circularly polarised wave of frequency ω is given by [2]

$$\frac{h}{w} = \pm\frac{1}{\omega}, \tag{3.1.7}$$

where h is the helicity density, w is the energy density and the positive and negative signs refer to left- and right-handed waves respectively. This relationship is clearly compatible with the notion that a circularly polarised photon carries a helicity of $\pm\hbar$. By contrast, the ratio of chirality density to energy density is

$$\frac{\chi}{w} = \pm\omega, \tag{3.1.8}$$

which corresponds to a chirality of $\pm\hbar\omega^2$ per photon.

The origin of the difference in sign between the measures lies in this different frequency scaling – increasing the frequency, while keeping the energy density constant, decreases the helicity but increases the chirality density of a circularly polarised wave, and so the wave which makes the dominant contribution in the two-wave superposition is different for the two measures. Another way of putting this is that plane-waves of fixed energy density contain more photons if they are of lower frequency – and the helicity-per-photon is independent of frequency, while the chirality-per-photon is not.

In writing (3.1.1) and (3.1.2), we stipulated that each of the two plane waves had the same energy. If we had instead stipulated that each had the same the *photon number* (i.e. $E_1^2/\omega_1 = E_2^2/\omega_2$), then the cycle-averaged helicity density would be zero. In general, modifying the relative intensities of the two plane waves will result in a field resembling an elliptically polarised wave with a rotating major axis. The resulting helicity and chirality densities are

$$h = \epsilon_0 \left(\frac{E_1^2}{\omega_1} - \frac{E_2^2}{\omega_2} + E_1 E_2 \left(\frac{1}{\omega_1} - \frac{1}{\omega_2} \right) \cos(\eta(\omega_1 + \omega_2)) \right), \qquad 3.1.9$$

$$\chi = \frac{\epsilon_0}{c} (E_1^2 \omega_1 - E_2^2 \omega_2 + E_1 E_2 (\omega_1 - \omega_2) \cos(\eta(\omega_1 + \omega_2)), \qquad 3.1.10$$

where E_1 and E_2 are the peak electric field amplitudes of the right- and left-handed waves respectively.

This allows one to construct superpositions where the helicity and chirality have the same sign, or where one is zero and the other is not. For example, we see that the average helicity is equal to zero if

$$\frac{E_1^2}{\omega_1} = \frac{E_2^2}{\omega_2}, \qquad 3.1.11$$

and the average chirality is equal to zero if

$$E_1^2 \omega_1 = E_2^2 \omega_2. \qquad 3.1.12$$

There are two intuitive ways in which the field might be thought to possess a sense of rotation – the handedness of the “elliptical polarisation”, and the sense of rotation of the major axis. We note that the conditions for changes in sign of helicity and chirality are not the same as those for which the handedness of the “elliptical polarisation” changes (this is governed by which is larger of E_1 and E_2), nor do they correspond to changes of the sense of rotation of the major axis (which is governed by which is larger of ω_1 and ω_2). We also note that while certain amplitude scalings can make either the average helicity or chirality separately 0, the only way to have both simultaneously zero is to have both $\omega_1 = \omega_2$ and $E_1 = E_2$, for which the superposition corresponds to ordinary linear polarisation. The path traced by the electric field vector in three cases is illustrated in *figure 3.1* below.

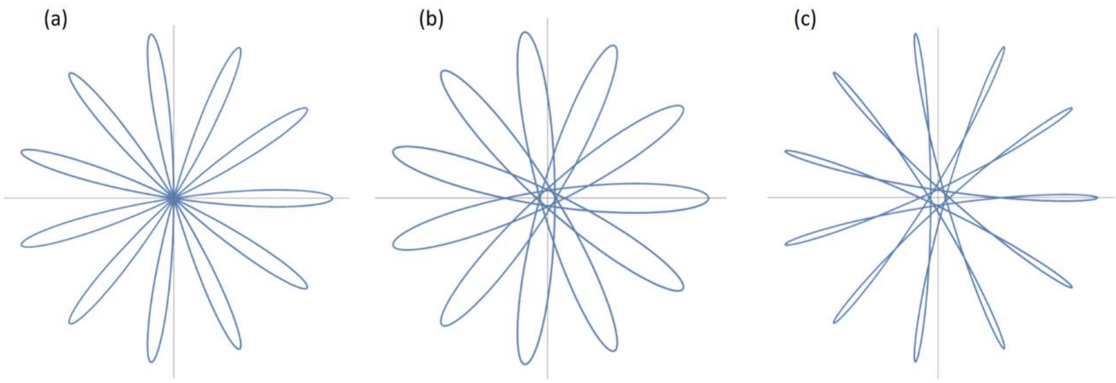

Figure 3.1. *Illustrative plots showing the path traced by the electric field vector in the x–y plane at a point of fixed z, when two plane-waves are coherently superposed as described in the text. Plot (a) shows the field given in (3.1.1), where both plane waves are of equal strength. Plot (b) shows an example scaling where the average helicity is zero, and (c) where the average chirality is zero. For each of the plots, we use the somewhat impractical frequency relationship* $\omega_1 = \frac{5}{6}\omega_2$*, so that the rotation is fast enough that the path can clearly be seen.*

3.2 Helicity and Chirality in a Chirped Pulse of Circularly Polarised Light

We now move on to consider helicity and chirality in a chirped pulse. A chirped pulse is a pulse in which the frequency increases or decreases as the wave progresses – the two situations are referred to as an “up-chirp” and a “down-chirp”, respectively. A negative frequency chirp is illustrated in *figure 3.2.*

A circularly polarised pulse with a linear frequency chirp can be represented by the fields [3]

$$\boldsymbol{E} = E_0(\boldsymbol{x} + i\boldsymbol{y})f(\eta)e^{-i(\omega_0\eta + b\eta^2)}, \qquad 3.2.1$$

$$\boldsymbol{B} = \frac{E_0}{c}(-i\boldsymbol{x} + \boldsymbol{y})f(\eta)e^{-i(\omega_0\eta + b\eta^2)}, \qquad 3.2.2$$

where ω_0 is the initial frequency, b is the chirp parameter (which governs the rate of the frequency change), and $f(\eta)$ is some envelope function which determines the shape of the pulse. For convenience we consider a Gaussian envelope, and set $f(\eta) = e^{-\frac{(\eta-a)^2}{\sigma^2}}$, with a and σ the initial central position and standard deviation of the envelope. The instantaneous frequency (which is defined as the time derivative of the phase) is given by $2b\eta + \omega_0$.

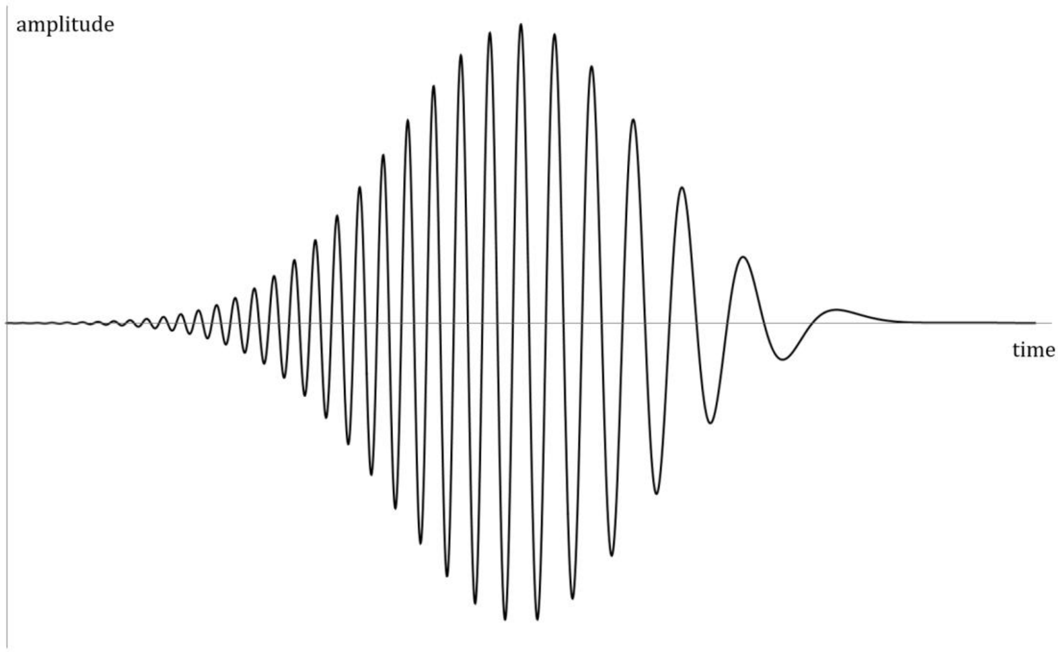

Figure 3.2. *A sine wave with a Gaussian envelope and a negative frequency chirp. The "chirp" means that the instantaneous frequency of the pulse decreases as time passes.*

It should be mentioned at this stage that the fields above are somewhat artificial, as they describe an unbounded linear frequency chirp. In reality, chirped pulses are produced by delaying the different frequency components of a source by different amounts [3], and so the chirp will extend over only a relatively narrow spectral range, fixed by the bandwidth of the laser that produces the pulse. For these fields to be physically reasonable, a and σ will be such that the region of the pulse with appreciable field strengths is appropriately narrow – and, importantly, far from the point at which the instantaneous frequency becomes negative. This unphysical region of negative frequency in the above expressions poses little problem for the calculation of the chirality density – the chirality density at a point is local in the fields – but the issue becomes more subtle in the calculation of the helicity, and the approximations built into (3.2.1-3.2.2) must be handled with care.

Calculating the chirality density using (1.6.1) and the fields above gives

$$\chi = \frac{E_0^2 \epsilon_0}{c} e^{-\frac{(\eta-a)^2}{\sigma^2}} (2b\eta + \omega_0). \qquad 3.2.3$$

Rather than being proportional to the frequency, as in the case of an unchirped plane wave, we see that χ is proportional to the instantaneous frequency. By differentiating with respect to η, we find that the maximum chirality density occurs at

$$\eta_{\chi max} = \frac{2ba - \omega_0 + \sqrt{(2ba + \omega_0)^2 + 8b^2\sigma^2}}{4b}. \qquad 3.2.4$$

Note that the quadratic which results from differentiating the chirality density has two roots, but we choose the higher one, as the lower root corresponds to a local minimum in the unphysical region of negative instantaneous frequency. We can compare this with the position of maximum energy density in the pulse, which occurs at the maximum of the envelope, $\eta = a$. The difference between the two is equal to

$$\eta_{\chi max} - a = \frac{-(2ba+\omega_0) + \sqrt{(2ba+\omega_0)^2 + 8b^2\sigma^2}}{4b}. \qquad 3.2.5$$

We thus see that, for an up-chirped pulse, the maximum of chirality occurs after the maximum of energy. This makes intuitive sense, as the instantaneous frequency of the chirped pulse is higher at later times. This displacement is small: as typical examples of the frequency, pulse envelope and strength of the chirp, we can consider a pulse lasting around 50 ps, with an initial wavelength of 800 nm and a final wavelength of 780 nm (these values are chosen to be of comparable magnitude to those used in existing optical centrifuge experiments, such as [4]). This would correspond to $\sigma \approx 25\text{ps}$, $b \approx 6 \times 10^{23}\text{s}^{-2}$, and $2ba + \omega_0 \approx 2.36 \times 10^{15}\text{s}^{-1}$, making the time between maxima 0.16ps.

A corresponding result is found for the helicity density: in an up-chirped pulse, the maximum of helicity occurs slightly before the maximum energy – fitting with the observation in section 1 that the helicity density for a given energy is higher at low frequencies. However, the explicit calculation of the helicity density is more involved than the chirality density.

To begin, we require expressions for the vector potentials. Proceeding as in section 1, we can evaluate the integrals $\boldsymbol{A} = -\int \boldsymbol{E}dt$ and $\boldsymbol{C} = -\epsilon_0 c^2 \int \boldsymbol{B}dt$. This can be accomplished using the standard integral [5]

$$\int e^{-(\alpha x^2 + 2\beta x + \gamma)}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}\,e^{\frac{\beta^2-\alpha\gamma}{\alpha}}\,\mathrm{erf}\left(\sqrt{\alpha}x + \frac{\beta}{\sqrt{\alpha}}\right), \qquad 3.2.6$$

with the "error function" defined by $\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}dt$. The result remains valid for complex exponentials – in this case, the definition of the error function is extended to complex variables by analytic continuation. We are therefore free to make the identifications $\alpha = \frac{1}{2\sigma^2} + ib$, $\beta = \frac{1}{2}(-\frac{a}{\sigma^2} + i\omega_0)$ and $\gamma = \frac{a^2}{2\sigma^2}$, in order to obtain

$$\boldsymbol{A} = -E_0(\boldsymbol{x} + i\boldsymbol{y})\int e^{-\frac{(\eta-a)^2}{2\sigma^2}} e^{-i(\omega_0\eta + b\eta^2)}d\eta = -\frac{1}{2}E_0(\boldsymbol{x} + i\boldsymbol{y})\sqrt{\frac{\pi}{\alpha}}\,e^{\frac{\beta^2-\alpha\gamma}{\alpha}}\,\mathrm{erf}\left(\sqrt{\alpha}\eta + \frac{\beta}{\sqrt{\alpha}}\right), \qquad 3.2.7$$

$$\boldsymbol{C} = -\epsilon_0 c E_0(-i\boldsymbol{x} + \boldsymbol{y})\int e^{-\frac{(\eta-a)^2}{2\sigma^2}} e^{-i(\omega_0\eta + b\eta^2)}d\eta$$

$$= -\frac{1}{2}\epsilon_0 c E_0(-i\boldsymbol{x} + \boldsymbol{y})\sqrt{\frac{\pi}{\alpha}}\,e^{\frac{\beta^2-\alpha\gamma}{\alpha}}\,\mathrm{erf}\left(\sqrt{\alpha}\eta + \frac{\beta}{\sqrt{\alpha}}\right). \qquad 3.2.8$$

These error functions can in principle be evaluated numerically – for example, by using the power series expansion [5]

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \sum_{k=0}^{\infty} (-1)^k \frac{x^{2k+1}}{k!\,(2k+1)}, \tag{3.2.9}$$

and then the real parts of the potentials may be used to calculate the helicity. However, this approach leads to problems connected with the unphysical nature of the fields (3.2.1-2). As mentioned earlier, the helicity at a point does not only depend on the fields and field derivatives at that point, and this means that the values of (3.2.1-2) at negative η (which do not represent the physical system under consideration) still contribute to the helicity density at positive η.
The error functions were evaluated numerically using *Wolfram Mathematica*, and the helicity density obtained was found to exhibit rapid oscillations on top of a broader distribution (see *figure 3.3*). These oscillations reduce in prominence when the envelope is narrowed, or the centres of the pulses are moved further from the regions of negative instantaneous frequency. Such oscillations give the impression of an oscillatory function being added on top of the expected helicity distribution – and they can in fact be removed entirely by subtracting an appropriate constant from the potentials before the helicity is calculated.

One is always free to add or subtract a constant to the vector potentials – this is, in effect, the simplest gauge transformation. While one may choose any constant without affecting the physical fields, or the total helicity density, the choice can substantially affect the local density. This can be clearly illustrated if one considers calculating the helicity density of a circularly polarised plane wave, but adding a constant to the usually chosen $\boldsymbol{A}$ potential: one would find rapid oscillation in the $\boldsymbol{A} \cdot \boldsymbol{\nabla} \times \boldsymbol{A}$ term, caused by the product of the oscillatory $\boldsymbol{\nabla} \times \boldsymbol{A}$ and the added constant in $\boldsymbol{A}$. However, this freedom is rarely important, as when the fields are localised it is standard to choose a gauge where the potentials approach zero at large distances.

Despite the fact that the $\boldsymbol{E}$ and $\boldsymbol{B}$ fields are localised, the potentials (3.2.7-8) do not approach zero at large distances, as $\lim_{x \to \pm\infty} \mathrm{erf}(x) = \pm 1$[1]. Furthermore, because the limit has opposite sign when η approaches positive or negative infinity, no choice of constant will make the potentials vanish at both $\eta \to \infty$ and $\eta \to -\infty$. This behaviour is again connected with the unphysical nature of an infinite linear frequency chirp. However, it is possible to choose a constant that makes the potential vanish in one of the two limits. The appropriate choices of constants to remove the rapid oscillation are found to be those that make the potentials of the up-chirped pulse vanish at large positive times, and the potentials of the down-chirped pulse vanish at large negative times. It

[1] Provided that the argument of x is always strictly greater than $\frac{\pi}{2}$, which is always the case for (3.2.7) with large $|\eta|$.

must be remembered that these are the large η limits in which the expressions for the respective chirps are still physically sensible, so it seems reasonable to be concerned with the behaviour of the potentials in these limits rather than the complementary ones.

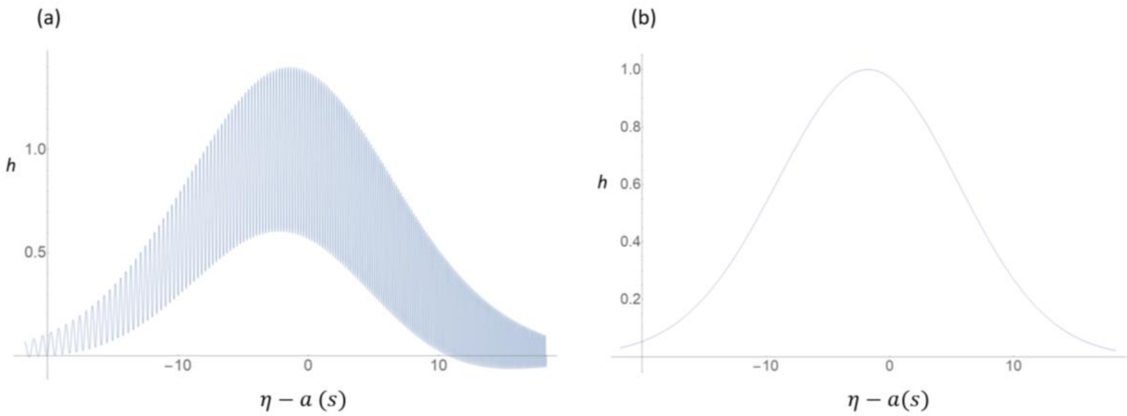

Figure 3.3. *The helicity density in an up-chirped pulse, calculated (a) using the potentials (3.2.7) and (3.2.8), and (b) subtracting the $\eta \to \infty$ limit from each of the potentials as described in the text. Plot (a) exhibits rapid oscillations, which are removed by the choice of potentials in (b). The parameters used in this illustration are standard deviation $\sigma = 10$s, central frequency $\omega_0 + 2ba = 30$ rad s^{-1}, and chirp strength $b = 0.5$ s^{-2}, and both densities have been normalised so that (b) has a maximum of 1. For more realistic pulse parameters, the oscillations (which are of the order of the frequency) are too rapid to be clearly resolved in a plot.*

3.3 Approximate Potentials for a Chirped Pulse

Instead of using numerical methods to analyse the exact solutions given above, our analysis can equally well proceed by making the following approximations for the potentials:

$$\boldsymbol{A} \approx \frac{(-i\boldsymbol{x} + \boldsymbol{y})E_0 e^{-\frac{(\eta-a)^2}{2\sigma^2}} e^{-i(\omega_0\eta + b\eta^2)}}{\omega_0 + 2b\eta}, \qquad 3.3.1$$

$$\boldsymbol{C} \approx \sqrt{\frac{\epsilon_0}{\mu_0}} \frac{(-\boldsymbol{x} - i\boldsymbol{y})E_0 c e^{-\frac{(\eta-a)^2}{2\sigma^2}} e^{-i(\omega_0\eta + b\eta^2)}}{\omega_0 + 2b\eta} \qquad 3.3.2$$

These are simply the vector potentials of a circularly polarised plane-wave, but with the frequency in the denominator replaced by the instantaneous frequency, and with the inclusion of the appropriate frequency chirp and Gaussian envelope.

To check that these are reasonable approximations, we may examine the electric and magnetic fields derived from these potentials:

$$\boldsymbol{E}' = -\frac{\partial \boldsymbol{A}}{\partial t} = E_0(\boldsymbol{x} + i\boldsymbol{y})e^{-\frac{(\eta-a)^2}{2\sigma^2}}e^{-i(\omega_0\eta+b\eta^2)}\left[-\frac{i(\eta-a)}{\sigma^2(\omega_0+2b\eta)} - \frac{2bi}{(\omega_0+2b\eta)^2} + 1\right], \quad 3.3.3$$

$$\boldsymbol{B}' = -\frac{1}{\epsilon_0 c^2}\frac{\partial \boldsymbol{C}}{\partial t} = \frac{E_0}{c}(-i\boldsymbol{x} + \boldsymbol{y})e^{-\frac{(\eta-a)^2}{2\sigma^2}}e^{-i(\omega_0\eta+b\eta^2)}\left[-\frac{i(\eta-a)}{\sigma^2(\omega_0+2b\eta)} - \frac{2bi}{(\omega_0+2b\eta)^2} + 1\right]. \quad 3.3.4$$

The first two terms in the square brackets are always much less than 1, because of the optical frequencies in the denominators, showing that these potentials are indeed good approximations to the exact vector potentials.

The helicity calculated from the approximate vector potentials is equal to

$$h = \epsilon_0 E_0^2 e^{-\frac{(\eta-a)^2}{\sigma^2}}\frac{1}{2b\eta + \omega_0} \quad 3.3.5$$

and so the maximum helicity occurs at

$$\eta_{hmax} = \frac{2ba - \omega_0 + \sqrt{(2ba+\omega_0)^2 - 8b\sigma^2}}{4b}, \quad 3.3.6$$

where again, we have taken the higher root, as the lower one corresponds to a region of negative instantaneous frequency. The difference between the maxima of helicity and energy density is then given by

$$\eta_{hmax} - a = \frac{-(2ba+\omega_0) + \sqrt{(2ba+\omega_0)^2 - 8b^2\sigma^2}}{4b}, \quad 3.3.7$$

confirming that the maximum of helicity occurs slightly before the maximum of energy.

The results of this discussion are summarised in *figure 3.4*, which shows the helicity, chirality and energy density in a right-handed, up-chirped pulse, with parameters chosen to clearly illustrate the different positions of the maxima.

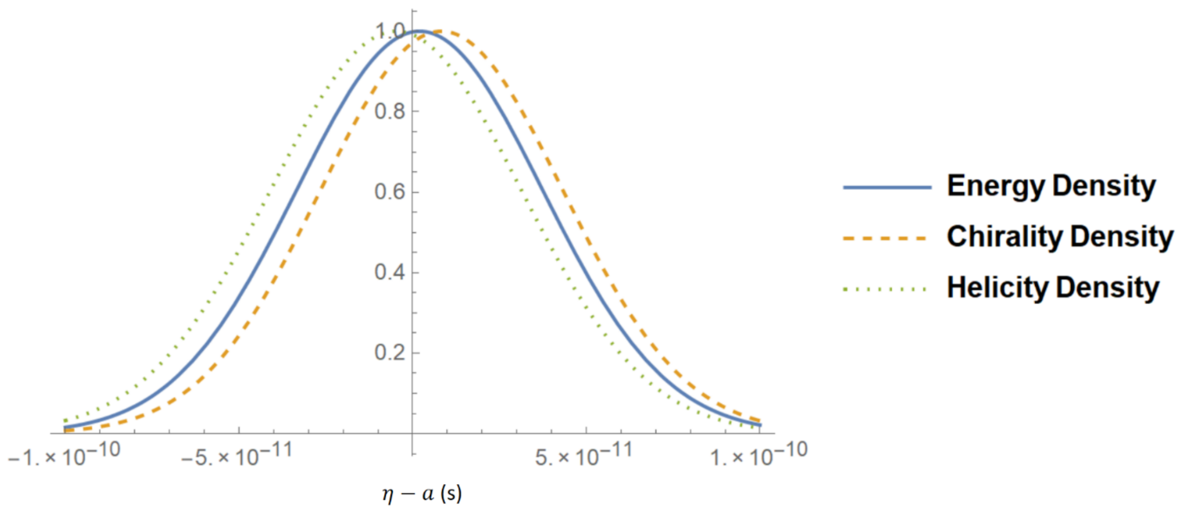

***Figure 3.4**. Calculated energy, chirality and helicity densities for a positive-helicity circularly polarised plane wave pulse, normalised so that each has a maximum of 1. The parameters used are a standard deviation of $\sigma = 0.2$ns, a central frequency of $\omega_0 + 2ba = 2.15 \times 10^{15}$rad s^{-1}, and a chirp strength of $b = 5.6 \times 10^{24}$ s^{-2}. These parameters describe a pulse significantly longer and broader in frequency than the more realistic ones discussed in the text, but are chosen to illustrate the behaviour.*

3.4 Helicity and Chirality in an Optical Centrifuge

An optical centrifuge is a superposition of a left- and a right-handed circularly polarised plane wave, as in section 1, but with each wave linearly chirped—one chirped up and the other down. This means that the frequency difference between the two waves increases linearly with time—and so if the resulting superposition is viewed as linear polarisation with a rotating plane of polarisation, the angular speed of this rotation increases at a constant rate. These fields can be used to excite molecules to very high rotational states, and even dissociate heavy molecules. The action of an optical centrifuge in inducing molecular rotation can be analysed classically, as in the original paper of Karczmarek *et al* [6], or viewed quantum-mechanically as driving the molecules up a successive ladder of rotational transitions [7,8].

We can straightforwardly extend the reasoning of the previous sections to consider the fields of an optical centrifuge. The fields are given by the real parts of

$$\boldsymbol{E} = E_0 f(\eta)\left[(\boldsymbol{x} + i\boldsymbol{y})e^{-i(\omega_0\eta + b\eta^2)} + (\boldsymbol{x} - i\boldsymbol{y})e^{-i(\omega_0\eta - b\eta^2)}\right], \qquad 3.4.1$$

$$\boldsymbol{B} = \frac{E_0}{c} f(\eta)\left[(-i\boldsymbol{x} + \boldsymbol{y})e^{-i(\omega_0\eta + b\eta^2)} + (i\boldsymbol{x} + \boldsymbol{y})e^{-i(\omega_0\eta + b\eta^2)}\right]. \qquad 3.4.2$$

From these, it is straightforward to find the chirality density

$$\chi = \frac{8\epsilon_0 E_0^2}{c^2} e^{-\frac{(\eta-a)^2}{\sigma^2}} b\eta \cos^2(\omega_0\eta)\,. \qquad 3.4.3$$

To find the helicity density, it is most straightforward to use the following approximations to the potentials, similar to the approximations made in section 2.

$$\boldsymbol{A} \approx \boldsymbol{A}' \equiv E_0 e^{-\frac{(\eta-a)^2}{2\sigma^2}} \left[\frac{(-i\boldsymbol{x}+\boldsymbol{y})e^{-i(\omega_0\eta+b\eta^2)}}{\omega_0+2b\eta} + \frac{(-i\boldsymbol{x}-\boldsymbol{y})e^{-i(\omega_0\eta-b\eta^2)}}{\omega_0-2b\eta}\right] \qquad 3.4.4$$

$$\boldsymbol{C} \approx \boldsymbol{C}' \equiv \sqrt{\frac{\epsilon_0}{\mu_0}} E_0 c e^{-\frac{(\eta-a)^2}{2\sigma^2}} \left[\frac{(-\boldsymbol{x}-i\boldsymbol{y})e^{-i(\omega_0\eta+b\eta^2)}}{\omega_0+2b\eta} + \frac{(\boldsymbol{x}-i\boldsymbol{y})e^{-i(\omega_0\eta-b\eta^2)}}{\omega_0-2b\eta}\right] \qquad 3.4.5$$

We then find[2], using $h = \frac{1}{2}\left(\sqrt{\frac{\epsilon_0}{\mu_0}} Re[\boldsymbol{A}'] \cdot Re[\boldsymbol{B}] - \sqrt{\mu_0\epsilon_0} Re[\boldsymbol{C}'] \cdot Re[\boldsymbol{E}]\right)$,

$$h = \frac{-8\epsilon_0 c E_0^2 e^{-\frac{(\eta-a)^2}{\sigma^2}}}{(\omega_0+2b\eta)(\omega_0-2b\eta)} [b\eta \cos^2(\omega_0\eta)]. \qquad 3.4.6$$

The energy density in the centrifuge is given by

$$w = 4E_0^2 \epsilon_0 e^{-\frac{(\eta-a)^2}{\sigma^2}} \cos^2(\omega_0\eta)\,, \qquad 3.4.7$$

so we again have the result that the helicity and the chirality have opposite signs, with the chirality dominated by the higher frequency wave and the helicity by the lower frequency one. Due to the time-varying frequencies, the helicity and chirality densities are no longer proportional to the energy density – the ratios are

$$\frac{h}{w} = \frac{-2cb\eta}{(\omega_0+2b\eta)(\omega_0-2b\eta)}, \qquad 3.4.8$$

$$\frac{\chi}{w} = \frac{2b\eta}{c^2}. \qquad 3.4.9$$

Taking the ratio with the energy density in this way removes the effect of the pulse envelope and the rapid oscillations at ω_0. This makes clear the main qualitative difference between the

---

[2] It would also be possible to use $h = \frac{1}{2}\left(\sqrt{\frac{\epsilon_0}{\mu_0}} Re[\boldsymbol{A}'] \cdot Re[\boldsymbol{\nabla} \times \boldsymbol{A}'] + \sqrt{\frac{\mu_0}{\epsilon_0}} Re[\boldsymbol{C}'] \cdot Re[\boldsymbol{\nabla} \times \boldsymbol{C}']\right)$. One might argue that this is more self-consistent, as here we consistently use the approximate potentials, rather than mixing between exact fields and approximate potentials. If we do this, we obtain

$$h = \frac{-8\epsilon_0 c E_0^2 e^{-\frac{(\eta-a)^2}{\sigma^2}}}{(\omega_0+2b\eta)(\omega_0-2b\eta)} [b\eta \cos^2(\omega_0\eta)] + \frac{8\epsilon_0 c E_0^2 e^{-\frac{(\eta-a)^2}{\sigma^2}}}{2(\omega_0+2b\eta)^2(\omega_0-2b\eta)^2} [b\omega_0 \sin(2\omega_0\eta)].$$

The first term is the same as before, and the second is much smaller, as it contains the squares of the instantaneous frequencies in the denominator. This question does not arise for the single chirped pulse considered in section 3: both procedures lead identically to (3.3.5).

measures—they have opposite signs, and different dependences on the instantaneous frequencies of the two beams.

3.5 Conclusion

This chapter has examined the helicity and chirality densities in various polychromatic fields, and shown how the polychromaticity leads to significant differences between the two measures. It is striking that the quantities, which both in a sense indicate the 'handedness' of the field, may differ in sign in even simple cases. The easiest way to understand this is that the frequency dependence of the two quantities can be a decisive factor when multiple frequency components are present, while in the monochromatic case it leads only to each quantity being multiplied by a different constant. This behaviour seems counter-intuitive if the helicity or chirality densities are thought of, in some sense, as measures of the 'amount' of handedness in an electromagnetic field. However, there can be no single property that captures this idea of handedness – it is impossible in general to define a quantitative measure of chirality which applies to all geometrical systems and assigns opposite signs to opposite enantiomers. To be precise, for any particular pseudoscalar measure that might be supposed to indicate the 'amount' of chirality associated with a configuration of points, there will exist chiral configurations for which the measure is zero. This can be seen by considering that (in three dimensions) it is always possible to smoothly deform a configuration of points into its enantiomer without passing through an achiral configuration on the way [9,10]. If the measure is a continuous function of the positions of the points, it must pass through a zero during this deformation, and therefore assign a zero to a chiral configuration.

In the absence of globally satisfactory criteria, any quantification of chirality—of the electromagnetic field, or otherwise—must be performed with a view towards context and applications. In connection with this, we may note that the helicity is more transparently connected to physical quantities of the field, such as the spin angular momentum and photon number, than the chirality [2].

Ultimately, interest in the measures discussed here is often connected to their usefulness in describing the interaction of the field with matter. In the following chapter we pursue this line of enquiry, presenting the results from multipolar electrodynamics that will be needed to discuss the generation of helicity and chirality by charges and currents.

References

[1] Mackinnon N. 2019 On the Differences between Helicity and Chirality *Journal of Optics* **21** 125402

[2] Barnett S. M., Cameron R. P. and Yao A. M. 2012 Duplex Symmetry and the Conservation of Optical Helicity *Physical Review A* **86** 013845

[3] Milonni P. W. and Eberly J. H. 2010 *Laser Physics* Wiley

[4] Villeneuve D. M., Aseyev S. A., Dietrich P., Spanner M., Ivanov M. Y. and Corkum P. B. 2000 Forced Molecular Rotation in an Optical Centrifuge *Physical Review Letters* **85** 542

[5] Gradshteyn I. S. and Rzyhik I. M. 2007 *Table of Integrals, Series and Products* ed. A. Jeffrey and D. Zwillinger, 7th Edition Academic

[6] Karczmarek J., Wright J., Corkum P. and Ivanov M. 1998 Optical Centrifuge for Molecules *Physical Review Letters* **82** 3420

[7] Armon A. and Friedland L. 2017 Quantum versus Classical Dynamics in the Optical Centrifuge *Physical Review A* **96** 033411

[8] Owens A., Yachmenenv A., Yurchenko S. N. and Küpper J. 2018 Climbing the Rotational Ladder to Chirality *Physical Review Letters* **121** 193201

[9] Harris A. B., Kamien R. D. and Lubensky T. C. 1999 Molecular Chirality and Chiral Parameters *Reviews of Modern* Physics **71** 1745

[10] Weinberg N. and Mislow K. 2000 On Chirality Measures and Chirality Properties *Canadian Journal of Chemistry* **78** 41

Chapter 4 – Multipolar Electrodynamics

It is often convenient to describe localised distributions of charges and currents in terms of their electric and magnetic multipole moments. In this chapter, we review the definitions of the various multipole moments. We then discuss the radiation pattern from harmonically oscillating multipole moments, which will be crucial for our later treatment of molecular light scattering in chapter 9.

4.1 Electric Multipole Moments

In the following, we consider a distribution of α discrete charges, each located at position $\boldsymbol{r}_\alpha$, with charge q_α. The charge and current densities are therefore given by

$$\rho(\boldsymbol{r}) = \sum_\alpha \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha) q_\alpha \qquad 4.1.1$$

$$\boldsymbol{J}(\boldsymbol{r}) = \sum_\alpha \delta(\boldsymbol{r} - \boldsymbol{r}_\alpha) q_\alpha \dot{\boldsymbol{r}}_\alpha \qquad 4.1.2$$

The electric monopole moment is simply the total charge, $\sum_\alpha q_\alpha$.

The electric dipole moment is the first moment of the charge distribution, defined by

$$\mu_a = \sum_\alpha q_\alpha r_{\alpha_a}. \qquad 4.1.3$$

Note that if the system of charges is not neutral overall, then the electric dipole moment depends on the origin from which the positions $\boldsymbol{r}_\alpha$ are measured – so ions (for example) do not have a uniquely defined dipole moment. For general charge distributions, all multipole moments can vary under a change of the molecular origin about which they are calculated, and in chapter 8 we will examine these transformations in detail. This is important, as when predictions are made on the basis of multipolar expansions, the associated behaviour of the predicted observables – which should not vary with the arbitrary choice of molecular origin – can form an important check that the formalism has been used consistently.

The "primitive" electric quadrupole moment is the second moment of the charge distribution

$$\Theta_{ab}^{tr} = \sum_\alpha q_\alpha r_{\alpha_a} r_{\alpha_b} \qquad 4.1.4$$

We use the superscript "tr" to indicate that the expression 4.1.4 possesses a non-zero trace. The electric quadrupole moment enters into the expression for the energy of a charge distribution in an external field though the term $\nabla_a E_b \Theta_{ab}$. Because the free electric field is divergence-free, the trace of this tensor does not contribute to this expression (and many others). For this reason, it is often convenient to define the traceless electric quadrupole moment [1, §9.3],

$$\Theta_{ab} = \frac{1}{2}\sum_{\alpha}\left[3q_\alpha r_{\alpha_a} r_{\alpha_b} - \delta_{ab} q_\alpha r_\alpha^2\right]. \tag{4.1.5}$$

Finally, the electric octupole moment is the third moment of the distribution,

$$Q_{abc} = \sum_{\alpha} q_\alpha r_{\alpha_a} r_{\alpha_b} r_{\alpha_c}. \tag{4.1.6}$$

It is possible to define an analogous "traceless" electric octupole moment, which vanishes on contraction between any pair of suffixes, as [2]

$$\Omega_{abc} = \frac{1}{2}\sum_{\alpha}\left[5q_\alpha r_{\alpha_a} r_{\alpha_b} r_{\alpha_c} - \delta_{ab} q_\alpha r_{\alpha_c} r^2 - \delta_{ac} q_\alpha r_{\alpha_b} r^2 - \delta_{bc} q_\alpha r_{\alpha_a} r^2\right]. \tag{4.1.7}$$

However, it has been pointed out by Raab [3] that this replacement is valid only in electrostatic situations (in contrast to the traceless quadrupole moment, which is valid even for dynamic fields). To give an example that illustrates why this is so, following Raab [3]**,** the energy of an electric octupole moment in an external electric field is proportional to $\nabla_c \nabla_b E_a Q_{abc}$. The transversality of the ***E*** field means that this vanishes on contraction between *a* and *b*, or *a* and *c*, but *not* necessarily on contraction between *b* and *c*. An important case in which $\nabla_b \nabla_b E_a$ is always 0 is, of course, the electrostatic case – where $\nabla \times \boldsymbol{E} = 0 \leftrightarrow \nabla_b E_a = \nabla_a E_b$, so $\nabla_b \nabla_b E_a = \nabla_b \nabla_a E_b = 0$.

4.2 Magnetic Multipole Moments

Just as static electric multipole moments are constructed from localised static distributions of charge, static magnetic multipole moments arise from localised steady distributions of current. We define the magnetic dipole moment by

$$m_a = \sum_{\alpha} \frac{q_\alpha}{2m_\alpha}(\boldsymbol{r}_\alpha \times \boldsymbol{p}_\alpha)_a, \tag{4.2.1}$$

where $\boldsymbol{p}_\alpha$ is the linear momentum of the α^{th} charge. The magnetic quadrupole moment is defined [3]

$$m_{ab} = \sum_{\alpha} \frac{q_\alpha}{3m_\alpha}\left[r_{\alpha_b}(\boldsymbol{r}_\alpha \times \boldsymbol{p}_\alpha)_a + (\boldsymbol{r}_\alpha \times \boldsymbol{p}_\alpha)_a r_{\alpha_b}\right]. \tag{4.2.2}$$

In a classical context, this definition may appear needlessly cumbersome, as the order of multiplication is unimportant in the classical case. However, it becomes important if $\boldsymbol{r}_\alpha$ and $\boldsymbol{p}_\alpha$ are treated as quantum-mechanical operators, as the position and momentum of the α^{th} charge do not commute.

4.3 Multipole Moments and Parity Symmetry

The different multipole moments can be categorised by their behaviour under spatial inversion, and time reversal. Time-reversal leaves all electric multipoles unaltered, but reverses the sign of all magnetic multipoles – as it reverses the direction of motion of all charges, and with this the sign of $\boldsymbol{J}$.

Spatial inversion changes the sign of moments that contain an odd number of factors of position and momentum, but leaves unchanged those with an even number of factors. It therefore changes the sign of the electric dipole, electric octupole and magnetic quadrupole moments, but not of the magnetic dipole or electric quadrupole moments. The higher-order multipoles follow the same pattern, and so all can be classified as either parity-even or parity-odd.

The behaviour of the various multipole moments under parity transformations has implications for the description of chiral radiators and scatterers. A chiral radiator must be neither parity-even nor parity-odd – if it were described by only parity-even oscillating moments it would be unaffected by spatial inversion, and if the moments were only parity-odd spatial inversion would simply change the phase of all the oscillations by π. A chiral radiator must therefore be described by a combination of even and odd multipole moments – spatial inversion changes the sign of one group but not the other, and so changes the relative phase between the two. Another use for the classification of multipole moments by parity is that it allows for the symmetry classification of multipole polarisability tensors, and a molecule may only support non-zero components of polarisability tensors whose symmetries the molecule shares.

4.4 Radiation from Oscillating Multipole Moments

If the charge and current densities vary harmonically in time, then the distribution will act as a source of radiation. The radiation from an arbitrary oscillatory distribution of charges can be decomposed into the contributions from its electric and magnetic multipole moments.
Outside a localised distribution of charge and current, the scalar and vector potentials for a harmonically varying source (in the Lorentz gauge) are given by [1, §9.1]

$$\phi(\boldsymbol{r},t) = \frac{\mu_0}{4\pi}\int \rho(\boldsymbol{r}')\frac{e^{i(k|\boldsymbol{r}-\boldsymbol{r}'|-\omega t)}}{|\boldsymbol{r}-\boldsymbol{r}'|}d^3r' \qquad 4.4.1$$

$$\boldsymbol{A}(\boldsymbol{r},t) = \frac{\mu_0}{4\pi}\int \boldsymbol{J}(\boldsymbol{r}')\frac{e^{i(k|\boldsymbol{r}-\boldsymbol{r}'|-\omega t)}}{|\boldsymbol{r}-\boldsymbol{r}'|}d^3r' \qquad 4.4.2$$

where the “retardation” has been written in the spatial part of the exponential in order to emphasise the harmonic time-dependence of the potentials. Far from the source ($R \gg d$), we can approximate

$$|\boldsymbol{r}-\boldsymbol{r}'| = \sqrt{r^2 - 2\boldsymbol{r}\cdot\boldsymbol{r}' + r'^2} \approx r - \boldsymbol{n}\cdot\boldsymbol{r}', \qquad 4.4.3$$

where $\boldsymbol{n}$ is a unit vector in the $\boldsymbol{r}$ direction, and $r = |\boldsymbol{r}|$. To first order in kr, we also have

$$\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \approx \frac{1}{r}. \tag{4.4.4}$$

These approximations lead to the vector potential

$$\boldsymbol{A}(\boldsymbol{r},t) \approx \frac{\mu_0}{4\pi}\frac{e^{ikr}}{r}\int \boldsymbol{J}(\boldsymbol{r}')e^{-ik\boldsymbol{n}\cdot\boldsymbol{r}'-i\omega t}\ d^3x'. \tag{4.4.5}$$

Finally, if the dimensions of the source are small compared to a wavelength, then $k|\boldsymbol{r}'|$ will be small for the whole range of integration over the source, and the Taylor series

$$e^{-ik\boldsymbol{n}\cdot\boldsymbol{r}'} = 1 + \frac{-ik\boldsymbol{n}\cdot\boldsymbol{r}'}{1} + \frac{(-ik\boldsymbol{n}\cdot\boldsymbol{r}')^2}{2!} + \cdots \tag{4.4.6}$$

will converge rapidly. We therefore write

$$\boldsymbol{A}(\boldsymbol{r},t) \approx \frac{\mu_0}{4\pi}\frac{e^{i(kr-\omega t)}}{r}\sum_{n=0}\frac{(-ik)^n}{n!}\int \boldsymbol{J}(\boldsymbol{r}')(\boldsymbol{n}\cdot\boldsymbol{r}')^n\ d^3r'. \tag{4.4.7}$$

Carrying on the expansion gives the different multipole fields: $n = 0$ gives the fields of an oscillating electric dipole, $n = 1$ the fields of an electric quadrupole and a magnetic dipole, $n = 2$ those of an electric octupole and magnetic quadrupole, and so on.

The vector potential of an oscillating electric dipole is therefore

$$\boldsymbol{A}(\boldsymbol{r},t) = \frac{\mu_0}{4\pi}\frac{e^{i(kr-\omega t)}}{r}\int \boldsymbol{J}(\boldsymbol{r}')\ d^3r'. \tag{4.4.8}$$

We can use integration by parts to explicitly write $\int \boldsymbol{J}(\boldsymbol{r}')\ d^3r'$ in terms of the electric dipole moment, and we obtain [1, p. 410]

$$\int \boldsymbol{J}(\boldsymbol{r}')\ d^3r' = -\int \boldsymbol{r}'(\boldsymbol{\nabla}'\cdot\boldsymbol{J})\,d^3r' = -i\omega\int \boldsymbol{r}'\rho(\boldsymbol{r}')\,d^3r'. \tag{4.4.9}$$

For the final equality above, we have used the continuity equation $\boldsymbol{\nabla}'\cdot\boldsymbol{J} = -\frac{\partial\rho}{\partial t}$, and additionally the fact that for a harmonically varying charge distribution $\frac{\partial\rho}{\partial t} = -i\omega\rho$[1]. We recognise that the integral is simply the electric dipole moment. Calling the dipole moment vector $\boldsymbol{\mu}$, we have

$$\boldsymbol{A}(\boldsymbol{r},t) = -\frac{\mu_0}{4\pi}\frac{i\omega e^{i(kr-\omega t)}}{r}\boldsymbol{\mu}. \tag{4.4.10}$$

The electric and magnetic fields can then be found from

$$\boldsymbol{B}(\boldsymbol{r},t) = \boldsymbol{\nabla}\times\boldsymbol{A}(\boldsymbol{r},t), \tag{4.4.11}$$

$$\boldsymbol{E}(\boldsymbol{r},t) = \frac{ic}{k}\boldsymbol{\nabla}\times\boldsymbol{B}(\boldsymbol{r},t), \tag{4.4.12}$$

[1] This type of time-dependence may appear to be quite a special case. In particular, we can note that making this substitution and then integrating the continuity equation over the charge distribution shows that, if the distribution is localised, it must also be neutral [4, p.75]. However, the treatment can still be made general, as any time-varying charge density can always be Fourier analysed into components with time-dependence of this form [1 §9.1]. $\rho(\omega)$ will no longer be the charge density, but the Fourier transform of the charge density.

which give the well-known results

$$\boldsymbol{B}(\boldsymbol{r},t) = -\frac{i\mu_0 c}{4\pi} e^{i(kr-\omega t)} \left(\frac{ik^2}{r} - \frac{k}{r^2}\right) \boldsymbol{n} \times \boldsymbol{\mu}, \tag{4.4.13}$$

$$\boldsymbol{E}(\boldsymbol{r},t) = \frac{1}{4\pi\epsilon_0} e^{i(kr-\omega t)} \left[\frac{k^2}{r}(\boldsymbol{n} \times \boldsymbol{\mu}) \times \boldsymbol{n} + \left(\frac{ik}{r^2} - \frac{1}{r^3}\right)\big(\boldsymbol{\mu} - 3\boldsymbol{n}(\boldsymbol{n}\cdot\boldsymbol{\mu})\big)\right]. \tag{4.4.14}$$

Note that while the field above is transverse ($\nabla \cdot \boldsymbol{E}(\boldsymbol{r},t) = 0$ everywhere), it contains near-field components parallel (as well as perpendicular) to the direction of observation. Its derivation from ($\boldsymbol{E}(\boldsymbol{r},t) = \frac{ic}{k}\boldsymbol{\nabla} \times \boldsymbol{B}(\boldsymbol{r},t)$) means that it is only valid outside the source, where the current density is zero. So even though the expression is valid for $|r|$ smaller than a wavelength, we still require that $|r|$ is larger than the dimensions of the source.

The next term in the expansion of the vector potential is

$$\boldsymbol{A}(\boldsymbol{r},t) \approx \cdots + \frac{\mu_0}{4\pi}\frac{e^{i(kr-\omega t)}}{r}(-ik)\int \boldsymbol{J}(\boldsymbol{r}')(\boldsymbol{n}\cdot\boldsymbol{r}')\ d^3r' + \cdots. \tag{4.4.15}$$

The integrand can be separated into a magnetic dipole contribution and an electric quadrupole contribution using the vector triple product $\big(\boldsymbol{r}' \times \boldsymbol{J}(\boldsymbol{r}')\big) \times \boldsymbol{n}$ [1, p. 414]:

$$\int \boldsymbol{J}(\boldsymbol{r}')(\boldsymbol{n}\cdot\boldsymbol{r}')\ d^3r' = \int \frac{1}{2}\big(\boldsymbol{r}' \times \boldsymbol{J}(\boldsymbol{r}')\big) \times \boldsymbol{n} + \frac{1}{2}\big[\boldsymbol{J}(\boldsymbol{r}')(\boldsymbol{n}\cdot\boldsymbol{r}') + \big(\boldsymbol{n}\cdot\boldsymbol{J}(\boldsymbol{r}')\big)\boldsymbol{r}'\big]\, d^3r' \tag{4.4.16}$$

The first term is equal to

$$\int \frac{1}{2}\boldsymbol{M}(\boldsymbol{r}') \times \boldsymbol{n}\, d^3r', \tag{4.4.17}$$

with $\boldsymbol{M}(\boldsymbol{r}')$ the magnetisation. For a point magnetic dipole located at the origin, with dipole moment $\boldsymbol{m}$, this "magnetic-dipole" part of the vector potential leads to the radiation fields

$$\boldsymbol{B}(\boldsymbol{r},t) = \frac{\mu_0}{4\pi} e^{i(kr-\omega t)} \left[\frac{k^2}{r}(\boldsymbol{n} \times \boldsymbol{m}) \times \boldsymbol{n}\right], \tag{4.4.18}$$

$$\boldsymbol{E}(\boldsymbol{r},t) = \frac{ic\mu_0}{4\pi} e^{i(kr-\omega t)} \left(\frac{ik^2}{r}\right) \boldsymbol{n} \times \boldsymbol{m}. \tag{4.4.19}$$

The second term in (4.4.16) can be re-written using integration by parts as

$$\int \frac{1}{2}\big[\boldsymbol{J}(\boldsymbol{r}')(\boldsymbol{n}\cdot\boldsymbol{r}') + \big(\boldsymbol{n}\cdot\boldsymbol{J}(\boldsymbol{r}')\big)\boldsymbol{r}'\big] d^3r' = -\frac{i\omega}{2}\int \boldsymbol{r}'(\boldsymbol{n}\cdot\boldsymbol{r}')\rho(\boldsymbol{r}')d^3r'. \tag{4.4.20}$$

The electric quadrupole part gives the fields:

$$\boldsymbol{B}(\boldsymbol{r},t) = -\frac{ick^3\mu_0}{8\pi}\frac{e^{i(kr-\omega t)}}{r}\int (\boldsymbol{n} \times \boldsymbol{r}')(\boldsymbol{n}\cdot\boldsymbol{r}')\rho(\boldsymbol{r}')d^3r'. \tag{4.4.21}$$

The integral over the charge distribution can be written in terms of its electric quadrupole moment as

$$B_{\boldsymbol{a}}(\boldsymbol{r},t) = -\frac{ick^3\mu_0}{8\pi}\frac{e^{i(kr-\omega t)}}{r}\epsilon_{abc}\Theta_{cd}^{tr} n_b n_d. \tag{4.4.22}$$

The electric fields are given by (keeping only terms 1st order in 1/r)

$$E_a = \frac{ic}{k}\nabla \times \boldsymbol{B}(\boldsymbol{r},t)_a = \frac{c^2 k^2 \mu_0 i e^{i(kr-\omega t)}}{8\pi r}[\Theta^{tr}_{bc} n_a n_c k_b - \Theta^{tr}_{ab} n_b k] \qquad 4.4.23$$

Finally, we consider magnetic quadrupole and electric octupole radiation. This arises from the third term in the expansion of the vector potential,

$$\boldsymbol{A}(\boldsymbol{r},t) \approx \cdots + \frac{\mu_0}{4\pi}\frac{e^{i(kr-\omega t)}}{r}\frac{(-ik)^2}{2}\int \boldsymbol{J}(\boldsymbol{r}')(\boldsymbol{n}\cdot\boldsymbol{r}')^2 \; d^3r' + \cdots. \qquad 4.4.24$$

Similarly to (4.4.15), we find this time that the volume integral can be split into terms related to an electric and a magnetic multipole moment – this time the electric octupole and magnetic quadrupole moments.

Following the treatment used in [4, p.75] for the electric quadrupole/magnetic dipole term, we begin with the continuity equation

$$\nabla\cdot\boldsymbol{J} + \frac{\partial\rho}{\partial t} = 0, \qquad 4.4.25$$

or, for our harmonically varying distribution,

$$\nabla\cdot\boldsymbol{J} = i\omega\rho. \qquad 4.4.26$$

We then multiply by the tensor function of position $r'_b r'_c r'_d$, and integrate over space, to obtain

$$\int r'_{\mathrm{b}} r'_{\mathrm{c}} r'_{\mathrm{d}} \nabla'_a J(\boldsymbol{r}')_a \, d^3r' = i\omega \int r'_b r'_c r'_d \rho(\boldsymbol{r}') \, d^3r' \qquad 4.4.27$$

Using integration by parts, the left hand side can be re-written as

$$\int r'_{\mathrm{b}} r'_{\mathrm{c}} r'_{\mathrm{d}} \nabla'_a J(\boldsymbol{r}')_a \, d^3r' = \int \nabla'_a (r'_{\mathrm{b}} r'_{\mathrm{c}} r'_{\mathrm{d}} J(\boldsymbol{r}')_a) d^3r' - \int J(\boldsymbol{r}')_a \nabla'_a (r'_{\mathrm{b}} r'_{\mathrm{c}} r'_{\mathrm{d}}) \, d^3r'. \qquad 4.4.28$$

The first term on the right hand side of (4.4.28) can be converted into a surface integral by Gauss' theorem, and this will vanish if there is no current at the surface. Evaluating the derivatives in the second term, by using $\nabla_a r'_b = \delta_{ab}$, allows (4.4.27) to be rewritten as

$$\int J(\boldsymbol{r}')_b r'_c r'_d + J(\boldsymbol{r}')_c r'_b r'_d + J(\boldsymbol{r}')_d r'_b r'_c \; d^3r' = -i\omega \int r'_b r'_c r'_d \rho(\boldsymbol{r}') \, d^3r'. \qquad 4.4.29$$

The volume integral on the left hand side is equal to the electric octupole moment of the charge distribution, and we will shortly relate the right hand side to the integrand in (4.4.24). First, in order to bring out the magnetic quadrupole part, we make use of the fact that

$$\int J(\boldsymbol{r}')_b r'_c r'_d - J(\boldsymbol{r}')_c r'_b r'_d \; d^3r' = \int r'_d \epsilon_{abc}\epsilon_{aef} J(\boldsymbol{r}')_e r'_f \; d^3r' = -\frac{3}{2m}\epsilon_{abc} M_{ad} \qquad 4.4.30$$

and similarly,

$$\int J(\boldsymbol{r}')_b r'_c r'_d - J(\boldsymbol{r}')_d r'_b r'_c \; d^3r' = -\frac{3}{2m}\epsilon_{abd} M_{ac}. \qquad 4.4.31$$

(if all charges have the same mass, *m*). We can combine now the three results (4.4.29), (4.4.30) and (4.4.31) in order to re-write the integral in the vector potential expansion (4.2.24). We begin by adding them together:

$$\int J(\boldsymbol{r}')_b r'_c r'_d \, d^3r'$$
$$= \frac{1}{3}\int J(\boldsymbol{r}')_b r'_c r'_d + J(\boldsymbol{r}')_c r'_b r'_d + J(\boldsymbol{r}')_d r'_b r'_c + (J(\boldsymbol{r}')_b r'_c r'_d - J(\boldsymbol{r}')_c r'_b r'_d)$$
$$+ (J(\boldsymbol{r}')_b r'_c r'_d - J(\boldsymbol{r}')_d r'_b r'_c) d^3r'$$
$$= -i\omega\frac{1}{3}Q_{bcd} - \frac{1}{2m}\epsilon_{abc}M_{ad} - \frac{1}{2m}\epsilon_{abd}M_{ac} \qquad 4.4.32$$

We can then see that the integral in (4.2.24) is equal to

$$\int J_a(\boldsymbol{r}')n_b r'_b n_c r'_c \;\; d^3r' = -i\omega\frac{1}{3}Q_{abc}n_b n_c - \frac{1}{2m}\epsilon_{dab}M_{dc}n_b n_c - \frac{1}{2m}\epsilon_{dac}M_{db}n_b n_c$$
$$= -i\omega\frac{1}{3}Q_{abc}n_b n_c - \frac{1}{m}\epsilon_{dab}M_{dc}n_b n_c \qquad 4.4.33$$

From this, we obtain the following form for the radiated magnetic field:

$$B_e(\boldsymbol{r},t) = (\nabla\times\mathbf{A})_\mathrm{e} = \frac{\mu_0 k^2}{4\pi}\frac{1}{2}\left[\frac{i\omega}{3}Q_{abc}n_b n_c + \frac{1}{m}\epsilon_{dab}M_{dc}n_b n_c\right]\epsilon_{efa}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}\left(\frac{ik_f}{r} - \frac{r_f}{r^3}\right). \qquad 4.4.34$$

As we are working in the far-field, we drop the $\frac{r_f}{r^3}$ term, leaving us with the following radiated magnetic and electric fields:

$$B_a(\boldsymbol{r},t) = e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}\frac{\mu_0 i k^3}{8\pi r}\epsilon_{abc}n_b\left[\frac{i\omega}{3}Q_{cde}n_d n_e + \frac{1}{m}\epsilon_{cdf}M_{fe}n_d n_e\right] \qquad 4.4.35$$

$$E_a(\boldsymbol{r},t) = \frac{ic}{k}\boldsymbol{\nabla}\times\boldsymbol{B}(\boldsymbol{r},t)_a$$
$$= -\frac{i\mu_0 ck^3}{8\pi}\frac{e^{i(kr-\omega t)}}{r}\left[\frac{i\omega}{3}Q_{bcd}n_a n_b n_c n_d + \frac{1}{m}\epsilon_{ebc}M_{ed}n_a n_b n_c n_d\right]$$
$$+ \frac{i\mu_0 ck^3}{8\pi}\frac{e^{i(kr-\omega t)}}{r}\left[\frac{i\omega}{3}Q_{abc}n_b n_c + \frac{1}{m}\epsilon_{abd}M_{dc}n_b n_c\right]$$
$$= -\frac{\mu_0 ck^3}{8\pi}\frac{e^{i(kr-\omega t)}}{r}\left[\frac{\omega}{3}Q_{abc}n_b n_c - \frac{i}{m}\epsilon_{abd}M_{dc}n_b n_c - \frac{\omega}{3}Q_{bcd}n_a n_b n_c n_d\right.$$
$$\left. + \frac{i}{m}\epsilon_{ebc}M_{ed}n_a n_b n_c n_d\right]$$
$$= \frac{\mu_0 ck^3}{8\pi}\frac{e^{i(kr-\omega t)}}{r}(\delta_{ab} - n_a n_b)\left[-\frac{\omega}{3}Q_{bcd}n_c n_d + \frac{i}{m}\epsilon_{bce}M_{ed}n_c n_d\right]. \qquad 4.4.36$$

4.5 The Near-Zone and Intermediate Fields

The above derivations focused on the fields far from the source compared to the wavelength. This meant that the only terms retained in the field strengths were those that fall off with distance no more rapidly than $\frac{1}{r}$. Such fields are transverse plane waves – they are often referred to as the "radiation" fields, for this reason.

We now briefly examine expressions for the fields of electric and magnetic multipole moments that are valid everywhere outside the source, even at short distances.

The vector potential of the electric dipole (4.4.10) is in fact already valid at all distances [1], and so in order to obtain the full fields we need simply retain all terms in (4.4.11) and (4.4.12). From this, we obtain the well-known expressions

$$\boldsymbol{B}(\boldsymbol{r},t) = -\frac{i\omega\mu_0}{4\pi} e^{i(kr-\omega t)} \left(\frac{ik^2}{r} - \frac{k}{r^2}\right) \boldsymbol{n} \times \boldsymbol{\mu}, \tag{4.5.1}$$

$$\boldsymbol{E}(\boldsymbol{r},t) = \frac{1}{4\pi\epsilon_0} e^{i(kr-\omega t)} \left[\frac{k^2}{r}(\boldsymbol{n}\times\boldsymbol{\mu})\times\boldsymbol{n} + \left(\frac{ik}{r^2} - \frac{1}{r^3}\right)\left(\boldsymbol{\mu} - 3\boldsymbol{n}(\boldsymbol{n}\cdot\boldsymbol{\mu})\right)\right]. \tag{4.5.2}$$

For the next term in the expansion of the vector potential, we use

$$\boldsymbol{A}(\boldsymbol{r},t) \approx \cdots + \frac{\mu_0}{4\pi}\frac{e^{i(kr-\omega t)}}{r}\left(\frac{1}{r} - ik\right)\int \boldsymbol{J}(\boldsymbol{r}')(\boldsymbol{n}\cdot\boldsymbol{r}')\ d^3r' + \cdots. \tag{4.5.3}$$

In order to describe the near-field, we must not make use of approximations (4.4.3) and (4.4.4). Because of this, we see that in addition to the term $\left(-\frac{ik}{r}\right)$ present in (4.4.15), the near-field expression contains another term. The added term, which goes as $\frac{1}{r^2}$, can be shown to emerge from (4.4.2) by a fuller treatment which involves expanding $\boldsymbol{E}$ and $\boldsymbol{B}$ in terms of spherical harmonics [1, §9.3]. The details of this are not presented here, but we note that it does not rely on the assumptions (4.4.3) and (4.4.4), and so (4.5.3) is valid even close to the source. This vector potential leads to the magnetic dipole fields:

$$\boldsymbol{B}(\boldsymbol{r},t) = \frac{\mu_0}{4\pi} e^{i(kr-\omega t)} \left[\frac{k^2}{r}(\boldsymbol{n}\times\boldsymbol{m})\times\boldsymbol{n} + \left(\frac{ik}{r^2} - \frac{1}{r^3}\right)\left(\boldsymbol{m} - 3\boldsymbol{n}(\boldsymbol{n}\cdot\boldsymbol{m})\right)\right], \tag{4.5.4}$$

$$\boldsymbol{E}(\boldsymbol{r},t) = \frac{ic\mu_0}{4\pi} e^{i(kr-\omega t)} \left(\frac{ik^2}{r} - \frac{k}{r^2}\right) \boldsymbol{n} \times \boldsymbol{m}, \tag{4.5.5}$$

and electric quadrupole fields

$$B_{\boldsymbol{a}}(\boldsymbol{r},t) = -\frac{ick^3\mu_0}{8\pi}\frac{e^{i(kr-\omega t)}}{r}\epsilon_{abc}\Theta_{cd}^{tr}n_b n_d. \tag{4.5.6}$$

$$E_a = \frac{ic}{k}\boldsymbol{\nabla}\times\boldsymbol{B}(\boldsymbol{r},t)_a. \tag{4.5.7}$$

4.6 Angular Momentum in a Circularly Polarised Plane-Wave

We now make a small digression to discuss an important situation where the intermediate-zone fields cannot be entirely neglected, regardless of distance. This is the case with calculations involving the angular momentum of light.

The angular momentum density of an electromagnetic field is given by

$$\boldsymbol{j} = \frac{1}{c^2}\boldsymbol{r}\times\boldsymbol{p} = \frac{1}{c^2}\boldsymbol{r}\times(\boldsymbol{E}\times\boldsymbol{H}), \tag{4.6.1}$$

and it is clear that the component of this in the propagation direction is zero for any plane-wave, as $(\boldsymbol{E}\times\boldsymbol{H})$ points in the direction of propagation, while $\boldsymbol{r}$ is perpendicular to it. However, it is well known that circularly polarised plane-waves carry angular momentum in the direction of propagation, and that this is associated with photon spin.

This apparent paradox is related to the unphysical nature of a plane-wave of infinite extent, coupled with the use of a local angular momentum density which is defined so as to give the correct total angular momentum after integration over the entire field.

There are many ways of resolving it. One is to explicitly acknowledge that the field is localised. For a wave propagating in the *z* direction, one can introduce an envelope to localise it in the *x*-*y* plane. It can be shown that any envelope which keeps the $\boldsymbol{E}$ and $\boldsymbol{B}$ fields divergence-free necessarily introduces components that do not propagate in the z-direction. These give rise to the expected angular momentum content [1, p.350]. Note that no such problems occur when calculating the energy or helicity densities of a circularly polarised plane-wave, despite the fact that these densities also do not have well-defined total values when integrated over an infinite plane wave.

The difference between angular momentum and energy/helicity is that calculation of the angular momentum flux from a radiating object (that is, the angular momentum flux to order $\frac{1}{r^2}$) requires consideration of more than just the $\frac{1}{r}$ "radiation" components of the fields – the $\frac{1}{r^2}$ terms of the fields must be considered as well [5]. This can be seen by a simple scaling argument: because the angular momentum has an extra factor of r compared to the linear momentum, $\frac{1}{r^2}$ terms in the angular momentum can arise from multiplying the $\frac{1}{r^2}$ terms of $\boldsymbol{E}$ by the $\frac{1}{r}$ terms of $\boldsymbol{H}$ (and vice-versa), and these will not fall off fast enough to be neglected in the far-field limit. A $\frac{1}{r^2}$ term in the Poynting vector (for instance) can only arise from the multiplication of two $\frac{1}{r}$ terms, one from the $\boldsymbol{E}$ field and one from the $\boldsymbol{H}$ field, and so it is only the $\frac{1}{r}$ "radiation field" components which are necessary to find the radiated energy flux.

4.7 The Overall Field Radiated by an Oscillating Charge Distribution

We now draw the above results together to write down the fields far from an arbitrary, harmonically oscillating charge distribution. If the distribution is resolved into a collection of point multipole moments, then the total electric field radiated is equal to [4, p. 77]

$$E(\boldsymbol{r},t)_a = \frac{\mu_0 \omega^2 e^{ikr-\omega t}}{4\pi r}(\delta_{ab} - n_a n_b)\left[\tilde{\mu}_b^0 + \frac{1}{c}\epsilon_{bcd}\tilde{m}_c^{0^{kin.}} n_d - \frac{ik}{3}\tilde{\Theta}_{bc}^0 n_c - \frac{ik}{2c}\epsilon_{bcd}\tilde{m}_{ce}^{0^{kin.}} n_e n_d \right.$$
$$\left. - \frac{k^2}{6}\tilde{Q}_{bcd}^0 n_c n_d + \cdots \right],$$

where terms have been shown up to electric octupole/magnetic quadrupole order. $\tilde{\mu}^0$ is the electric dipole moment, $\tilde{m}_c^{0^{kin}}$ the magnetic dipole moment, $\tilde{\Theta}_{bc}^0$ the traceless electric quadrupole moment,

$\tilde{Q}^{0}_{bcd}$ the electric octupole moment and $\tilde{m}^{0^{kin.}}_{ce}$ the magnetic quadrupole moment. The tildes indicate that the moments may be complex (allowing for fixed phase differences between them), and the superscript 0's indicate that the time-dependence is excluded from the moments. This notation will become important in chapter 8, where we will find it necessary to distinguish between the induced multipole moments in 4.7.1, and multipole moment operators. The magnetic fields can be obtained from

$$B_a = \frac{1}{c}\epsilon_{abc} n_b E_c. \qquad 4.7.2$$

References

[1] Jackson J. D. 1999 *Classical Electrodynamics* (3rd edition) Wiley

[2] Buckingham A. D. 1959 Molecular Quadrupole Moments *Chemical Society Quarterly Reviews* **3** 183

[3] Raab R. E. 1975 Magnetic Multipole Moments *Molecular Physics* **29** 1323

[4] Barron L. D. 2004 Molecular Light Scattering and Optical Activity (2nd Edition) Cambridge University Press

[5] Barnett S. M. 2002 Optical Angular Momentum Flux *Journal of Optics B* **4** S7

Chapter 5 – Elementary Models of Helicity Sources

The previous chapter reviewed multipole radiation generally. We now use some of these results to examine the helicity and angular momentum radiated by simple point multipole sources. From symmetry considerations, it is clear that only a chiral radiator can be a net source of helicity. Chiral sources can be constructed from combinations of point multipole moments because the different multipole moments have varying behaviour under parity transformations. We begin by discussing the simplest example – the combination of an electric and a magnetic dipole aligned along a common axis – and in section 5.2 we go on to calculate the helicity radiated from such a source. In section 5.3 we contrast the helicity distribution with that of a closely related achiral source: a rotating electric dipole. Finally, in 5.4 we consider the angular momentum radiated by the two sources, and contrast this with the helicity. The "chiral" dipole, which lacks inversion symmetry, is a net source of helicity but not of angular momentum – while the rotating dipole is a net source of angular momentum but not of helicity.

5.1 Multipole Moments and Parity Symmetry

The different multipole moments have distinct behaviours under parity transformations. It is clear from the definitions given in the previous chapter that under a parity transformation (i.e. a transformation sending the positions of all charges from $\boldsymbol{x}_\alpha$ to $-\boldsymbol{x}_\alpha$), the electric dipole, electric octupole, and magnetic quadrupole moments of a charge distribution change sign. The electric quadrupole and magnetic dipole moments, however, remain unchanged.

The simplest model of a chiral radiator described by point multipoles is given by a combination of an electric and a magnetic dipole, both driven at the same frequency. If we restrict ourselves to the case where the two dipoles are aligned, then the electric and magnetic dipole moments may be parallel, anti-parallel, or may have some other phase difference between them. A parity transformation has the effect of changing the sign of the electric, but not the magnetic, dipole moment, and therefore transforms the radiator into its distinct "enantiomer". We can see, then, that the difference between the two enantiomers here lies in the phase difference between the moments: changing enantiomers changes the relative phase of the electric and magnetic moments by π.

A model physical system that gives rise to this sort of behaviour is a small helical coil of wire. Applying an electric field clearly induces an electric dipole moment in the coil, by driving charges up the coil. In addition, the associated motion of the charges causes a current to flow around the wire, giving rise to a magnetic dipole moment. An oscillating electric field will therefore induce both oscillating electric and magnetic dipoles in the coil. Furthermore, as the electric dipole moment depends on charge positions and the magnetic dipole moment on charge velocities, the two moments will be $\pm\frac{\pi}{2}$ out of phase depending on the handedness of the coil. This sort of chiral response was observed in the 1920s by Lindman, using coils of wire in the microwave regime [1] – in hindsight, these experiments can perhaps be seen as an early (crude) construction of what would now be called a metamaterial. The ability of this simple induced-dipoles model to accurately describe the response of such a system has been investigated more recently, using short terahertz pulses to investigate its time-dynamics [2].

A similar structure is found naturally in the optically active molecule hexahelicene, consisting of six connected benzine rings that form a helix. In chapter 8 we will discuss how the ability of an electric field to induce both an electric and a magnetic dipole moment – with associated phase difference – is important in the description of optical activity in many cases, even when it is not associated with such an intuitive geometrical explanation.

In this chapter, we explicitly examine and contrast the helicity and the angular momentum radiated from such sources. We find that they are a net source of helicity, but not of angular momentum. By contrast, a rotating electric dipole (which can be thought of as a superposition of two orthogonal electric dipole moments with a $\pm\frac{\pi}{2}$ phase difference) is a net source of angular momentum, but not of helicity. These properties are related to the inversion and rotational symmetries of the sources. The calculations on the helicity radiated by such a compound dipole have been reported in [3].

5.2 Helicity Radiated from a "Chiral" Dipole

To examine the helicity flux radiated by such chiral sources, we begin with some general remarks on the fields radiated by oscillating electric and magnetic dipoles. The angular distribution of the radiated power is the same for both electric and magnetic dipoles – what differs between the two is the polarisation pattern. In chapter 3, we saw that the electric field vectors in the far-field for the two types of oscillating dipole are given by

$$\boldsymbol{E}_{electric}(\boldsymbol{r},t) = \frac{1}{4\pi\epsilon_0} e^{i(kr-\omega t)} \left[\frac{k^2}{r}(\hat{\boldsymbol{r}}\times\boldsymbol{\mu})\times\hat{\boldsymbol{r}}\right], \qquad 5.2.1$$

$$\boldsymbol{E}_{magnetic}(\boldsymbol{r},t) = \frac{-\mu_0 c}{4\pi} e^{i(kr-\omega t)} \left(\frac{k^2}{r}\right)\hat{\boldsymbol{r}}\times\boldsymbol{m}, \qquad 5.2.2$$

where $\boldsymbol{\mu}$ and $\boldsymbol{m}$ are the electric and magnetic dipole moments at $t = 0$, and $\hat{\boldsymbol{r}}$ is a unit vector in the $\boldsymbol{r}$ direction. If the dipoles both lie along the same direction, then the polarisations of the two radiation fields will be perpendicular, and it is then clear how a phase difference between the two can introduce ellipticity when they are summed to give the overall scattered field.

If the two dipoles are in phase (or anti-phase), then the far-field light will have a linear polarisation. The polarisation direction will be oriented at plus or minus 45 degrees to the dipoles' axis, depending on which of the two "enantiomeric" configurations the source takes – in other words, on whether the dipoles are in phase or anti-phase. Despite this *geometric* chirality, the scattered light has linear polarisation everywhere, and there is no far-field optical helicity. If there is a $\pi/2$ phase difference between the dipoles, however, then the polarisation will be circular everywhere, and there will be a net flux of helicity.

We will now calculate this helicity flux explicitly. For definiteness, let us take the dipoles to be aligned along the z axis, with a phase difference of α between them. Then we may take $\boldsymbol{\mu} = |\mu|\hat{\boldsymbol{z}}$ and $\boldsymbol{m} = |m|\hat{\boldsymbol{z}}e^{i\alpha}$, and the electric and magnetic fields in the far-field are given by

$$\boldsymbol{E}(\boldsymbol{r},t) = \frac{1}{4\pi\epsilon_0} e^{i(kr-\omega t)} \frac{k^2}{r} sin\theta \left[-\widehat{\boldsymbol{\theta}}|\mu| + \frac{\widehat{\boldsymbol{\phi}}|m|}{c} e^{i\alpha}\right] \quad 5.2.3$$

$$\boldsymbol{B}(\boldsymbol{r},t) = \frac{\mu_0 c}{4\pi} e^{i(kr-\omega t)} \frac{k^2}{r} sin\theta \left[-\widehat{\boldsymbol{\phi}}|\mu| - \frac{\widehat{\boldsymbol{\theta}}|m|}{c} e^{i\alpha}\right], \quad 5.2.4$$

where $\widehat{\boldsymbol{\theta}}$ and $\widehat{\boldsymbol{\phi}}$ are unit vectors in the θ and ϕ directions. The far-field parts of the $\boldsymbol{A}$ and $\boldsymbol{C}$ potentials can be found from the fields by inverting

$$\boldsymbol{E}^T = -\frac{\partial \boldsymbol{A}^T}{\partial t}, \quad 5.2.5$$

$$\boldsymbol{B} = -\frac{1}{\epsilon_0 c^2}\frac{\partial \boldsymbol{C}}{\partial t}. \quad 5.2.6$$

Making use of the harmonic time-dependence of the fields, we have

$$\boldsymbol{A}^T = -\frac{i}{\omega}\boldsymbol{E}^T, \quad 5.2.7$$

$$\boldsymbol{C} = -\frac{i\epsilon_0 c^2}{\omega}\boldsymbol{B}. \quad 5.2.8$$

As we are here only interested in the radiated helicity, we may use the far-field expressions (5.2.3) and (5.2.4). These result in the (far-field) vector potentials[1]

$$\boldsymbol{A}^T = \frac{i}{4\pi\epsilon_0 c} e^{i(kr-\omega t)} \frac{k}{r} sin\theta\left[\widehat{\boldsymbol{\theta}}|\mu| - \widehat{\boldsymbol{\phi}}|m|/c\, e^{i\alpha}\right], \quad 5.2.9$$

$$\boldsymbol{C} = \frac{i}{4\pi} e^{i(kr-\omega t)} \frac{k}{r} sin\theta\left[\widehat{\boldsymbol{\phi}}|\mu| + \widehat{\boldsymbol{\theta}}|m|/c\, e^{i\alpha}\right]. \quad 5.2.10$$

[1] Note that despite the notation, these expressions are not divergence-free at all points. The full potentials $\boldsymbol{A}^T$ and $\boldsymbol{C}$ are transverse, but in (5.2.9-10) only the 1/r terms are retained. The same is true of the radiative $\boldsymbol{E}$ and $\boldsymbol{B}$ fields (5.2.3-4). The far-field parts of the transverse fields and potentials (taken alone) are not transverse themselves.

Finally, we can calculate the helicity density and helicity flux densities using these potentials. The helicity density is given by

$$h = \frac{1}{2}\sqrt{\frac{\epsilon_0}{\mu_0}} Re[\boldsymbol{A}] \cdot Re[\boldsymbol{\nabla} \times \boldsymbol{A}] + \frac{1}{2}\sqrt{\frac{\mu_0}{\epsilon_0}} Re[\boldsymbol{C}] \cdot Re[\boldsymbol{\nabla} \times \boldsymbol{C}]$$

$$= -\frac{k^3 \mu_0}{16\pi^2 r^2} \sin\alpha \, |\mu||m| \sin^2\theta \,, \qquad 5.2.11$$

and the flux density is given by

$$\boldsymbol{v} = \frac{1}{2}\sqrt{\frac{\epsilon_0}{\mu_0}} Re[\boldsymbol{E}] \times Re[\boldsymbol{A}] + \frac{1}{2}\sqrt{\frac{\mu_0}{\epsilon_0}} Re[\boldsymbol{H}] \times Re[\boldsymbol{C}]$$

$$= -\frac{k^3 \mu_0 c}{16\pi^2 r^2} \sin\alpha \, |\mu||m| \sin^2\theta \, \hat{\boldsymbol{r}}. \qquad 5.2.12$$

Note that no cycle-averaging is necessary here – the density and flux density are both time-independent for all values of α in this system. Furthermore, both the electric and magnetic parts give the same contribution to the helicity density and flux.

We therefore see that the total radiated helicity through a spherical surface of radius r, centred on the dipole, is equal to

$$\iint_S \boldsymbol{v} \cdot d\boldsymbol{S} = \int_0^{\pi} -\frac{k^3 \mu_0 c}{16\pi^2 r^2} \sin\alpha \, |\mu||m| \sin^2\theta \, r^2 sin\theta d\theta \int_0^{2\pi} d\phi$$

$$= -\frac{k^3 \mu_0 c}{8\pi} \sin\alpha \, |\mu||m| \int_0^{\pi} \sin^3\theta \, d\theta$$

$$= -\frac{c k^3 \mu_0}{6\pi} \sin\alpha \, |\mu||m| \qquad 5.2.13$$

We can also calculate the power radiated by the “chiral” dipole. The cycle-averaged Poynting vector is equal to

$$\overline{\boldsymbol{S}} = Re\left[\frac{1}{2}\boldsymbol{E} \times \boldsymbol{H}^*\right] = \frac{c k^4}{32\pi^2 \epsilon_0 r^2}\left(|\mu|^2 + \frac{|m|^2}{c^2}\right) \sin^2\theta \, \hat{\boldsymbol{r}} \qquad 5.2.14$$

This is simply equal to the sum of the power radiated by the electric and magnetic dipoles individually, and is independent of the phase difference between them.

If $\frac{|m|}{c} = |\mu|$, the fields radiated by the electric and magnetic dipoles are of equal amplitude, and a $\pi/2$ phase difference between the dipoles will cause the polarisation of the radiated light to be circular everywhere. This is reflected in the ratio of helicity flux to energy flux densities, which is given by

$$\frac{v}{\overline{S}} = -\frac{\sin\alpha}{\omega}. \qquad 5.2.15$$

When $\alpha = \pm\frac{\pi}{2}$, the ratio is equal to $\mp\frac{1}{\omega}$, consistent with a helicity of $\mp\hbar$ per photon. The power distribution and polarisation pattern are illustrated in *figure 5.1.*

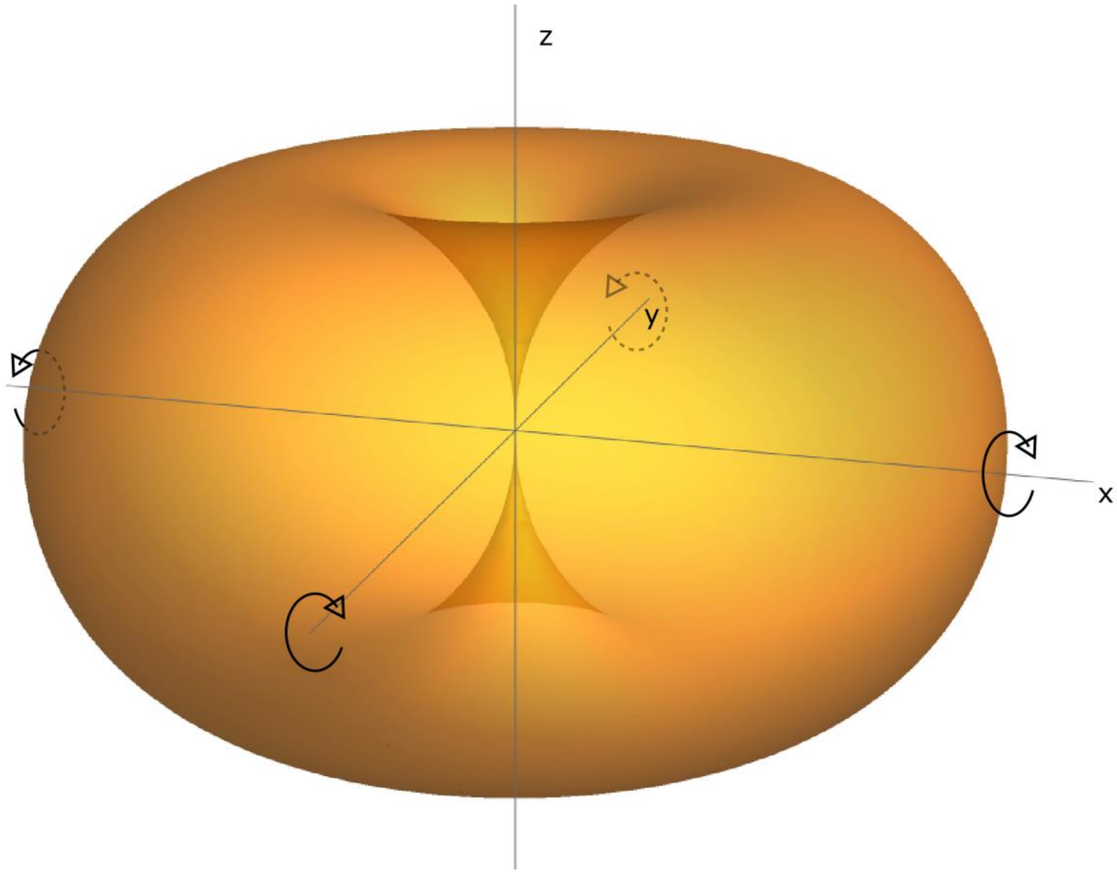

Figure 5.1. *Illustration showing a surface of constant intensity radiated by a "chiral" dipole, as described in the text, with arrows indicating the polarisation of the radiated light. The radiation is circularly polarised everywhere (including in directions which do not lie in the x-y plane), and always has the same sign of helicity. The figure uses $\alpha = \frac{\pi}{2}$; a choice of $\alpha = -\frac{\pi}{2}$ would reverse the sense of the circular polarisation.*

5.3 Helicity Flux from Rotating Dipoles

The situation can be contrasted with that of a rotating electric dipole, which can be conveniently modelled by two oscillating, perpendicular electric dipoles with a $\pi/2$ phase difference. In this case, circularly polarised light is radiated, but there is no net flux of helicity, as the light radiated in opposite directions has opposite helicity [4]. However, this time there is a net flux of angular momentum from the source.

Explicitly, if we take the dipoles to lie along the x and y axes, then we can write down the radiated electric field using (5.2.1-2) and the complex dipole moment

$$\boldsymbol{\mu} = |\mu|(\hat{\boldsymbol{x}} + \sigma i\hat{\boldsymbol{y}})e^{-i\omega t}, \tag{5.3.1}$$

where $\sigma = \pm 1$ is a parameter determining the sense of rotation of the dipole. The total radiated electric and magnetic fields are then given by

$$\boldsymbol{E}_{rotating}(\boldsymbol{r},t) = \frac{k^2|\mu|}{4\pi\epsilon_0 r} e^{i(kr-\omega t)}\left(\widehat{\boldsymbol{\theta}}[\cos\theta\cos\phi + \sigma i\cos\theta\sin\phi] + \widehat{\boldsymbol{\phi}}[-\sin\phi + \sigma i\cos\phi]\right), \quad 5.3.2$$

$$\boldsymbol{B}_{rotating}(\boldsymbol{r},t) = \frac{k^2\mu_0 c|\mu|}{4\pi r} e^{i(kr-\omega t)}\left(\widehat{\boldsymbol{\theta}}[\sin\phi - \sigma i\cos\phi] + \widehat{\boldsymbol{\phi}}[\cos\theta\cos\phi + \sigma i\cos\theta\sin\phi]\right). \quad 5.3.3$$

As in the previous section, these far-field forms are sufficient in order to determine the radiated helicity. The two associated vector potentials are given by

$$\boldsymbol{A}^T_{rotating} = -\frac{i}{\omega}\boldsymbol{E}^T_{rotating}$$

$$= \frac{k|\mu|}{4\pi\epsilon_0 cr} e^{i(kr-\omega t)}\left(\widehat{\boldsymbol{\theta}}[-i\cos\theta\cos\phi + \sigma\cos\theta\sin\phi] + \widehat{\boldsymbol{\phi}}[i\sin\phi + \sigma\cos\phi]\right) \quad 5.3.4$$

$$\boldsymbol{C}_{rotating} = -\frac{i\epsilon_0 c^2}{\omega}\boldsymbol{B}_{rotating}$$

$$= \frac{k|\mu|}{4\pi r} e^{i(kr-\omega t)}\left(\widehat{\boldsymbol{\theta}}[-i\sin\phi - \sigma\cos\phi] + \widehat{\boldsymbol{\phi}}[-i\cos\theta\cos\phi + \sigma\cos\theta\sin\phi]\right) \quad 5.3.5$$

The helicity density is therefore equal to

$$\frac{1}{2}\left(\sqrt{\frac{\epsilon_0}{\mu_0}}Re\left[\boldsymbol{A}^T_{rotating}\right]\cdot Re\left[\boldsymbol{B}_{\mathrm{rotating}}\right] - \sqrt{\frac{\mu_0}{\epsilon_0}}Re\left[\boldsymbol{C}_{rotating}\right]\cdot Re\left[\epsilon_0\boldsymbol{E}_{\mathrm{rotating}}\right]\right)$$

$$= \frac{ck^3\mu_0|\mu|^2\sigma\cos\theta}{16\pi^2 r^2}, \quad 5.3.6$$

and the flux is

$$\frac{1}{2}\left(\sqrt{\frac{\epsilon_0}{\mu_0}}Re[\boldsymbol{E}]\times Re[\boldsymbol{A}] + \sqrt{\frac{\mu_0}{\epsilon_0}}Re[\boldsymbol{H}]\times Re[\boldsymbol{C}]\right) = \frac{c^2k^3\mu_0|\mu|^2\sigma\cos\theta}{16\pi^2 r^2}\widehat{\boldsymbol{r}}. \quad 5.3.7$$

We see that the radiated helicity has opposite sign for $\theta < \frac{\pi}{2}$ and $\theta > \frac{\pi}{2}$. We obtain a helicity density of $\sigma\hbar$ per photon at the "north pole", and $-\sigma\hbar$ per photon at the south pole, with zero helicity radiated along the equator [4]. The situation is illustrated in *figure 5.2*, which indicates the polarisation in various directions alongside a surface of constant intensity.

That there is no net helicity flux is to be expected purely from the symmetry of the source: the rotating electric dipole is achiral, and cannot be a net source of helicity. However, unlike the chiral dipole, it lacks rotational symmetry, and indeed we will see it radiates angular momentum.

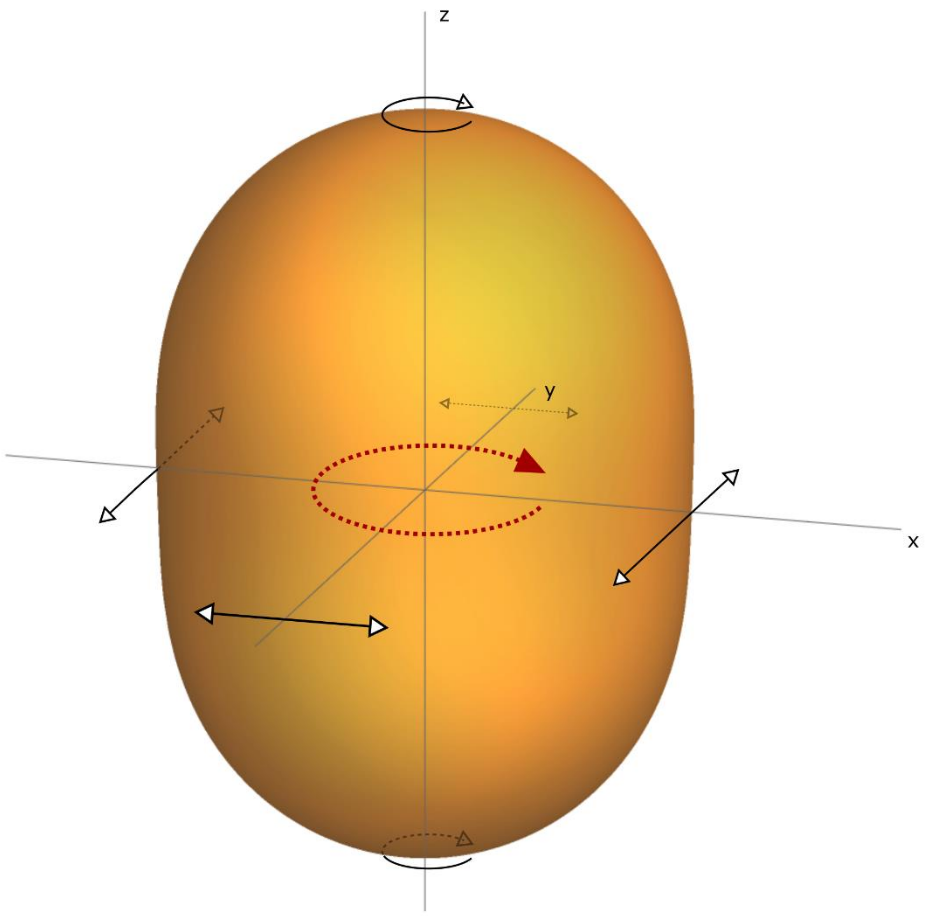

Figure 5.2. *Illustration showing a surface of constant intensity radiated by a rotating electric dipole, as described in the text, with arrows indicating the polarisation of the radiated light, and the central arrow the sense of rotation of the dipole. The radiated light has opposite helicities in the positive and negative z-directions, and is linearly polarised in the x-y plane. In all other directions it has an elliptical polarisation (not shown).*

5.4 Angular Momentum Radiated by the "Chiral" Dipole and Rotating Electric Dipole

As well as considering the helicity radiated from "chiral" and rotating electric dipoles, we can consider the total angular momentum of the radiated light. In the far-field, both of these sources produce fields locally resembling circularly polarised plane waves, and so all of the radiated angular momentum can be attributed to the spin-angular momentum of these waves. The helicity is related to the component of spin angular momentum in the direction of propagation, and so if the helicity flux is calculated in two different positions, the direction about which the angular momentum is measured changes. By contrast, if the flux of a *given component* of angular momentum is calculated, the direction about which the angular momentum is measured does not change as the point of observation is moved. For example, if a radiation pattern has a positive helicity flux in both the x and $-x$ directions, then the flux of x-component-of-angular-momentum will have opposite signs in the two directions. By this and similar reasoning, we might expect that suitably symmetric configurations which radiate a net helicity will radiate a net zero angular momentum, and *vice versa*.

As well as arguing based on the propagation direction and angular momentum content of the plane waves in the far-field, we can calculate the radiated angular momentum from the radiation fields directly. The angular momentum density and flux density is given by [5]

$$\boldsymbol{l} = \epsilon_0 \boldsymbol{r} \times (\boldsymbol{E} \times \boldsymbol{B}), \tag{5.4.1}$$

$$M_{ab} = \epsilon_{bcd} r_c \left(\frac{1}{2} \delta_{da} \left(\epsilon_0 E^2 + \frac{1}{\mu_0} B^2 \right) - \epsilon_0 E_d E_a - \frac{1}{\mu_0} B_d B_a \right). \tag{5.4.2}$$

Note that as angular momentum is a vector quantity, its flux density is a tensor: the component M_{ab} represents the flux of the b component of angular momentum passing through an infinitesimal surface element oriented in the a direction.

For the fields (5.2.3-4) and (5.3.2-3), $\boldsymbol{E}, \boldsymbol{B}$ and $\boldsymbol{r}$ are always mutually perpendicular, and so we can see that the quantity $\boldsymbol{l}$ is always zero. This is because we have so far only considered the radiation fields – it is another manifestation of the complications associated with the angular momentum of plane-waves, discussed in chapter 4. We conclude that in order to calculate the angular momentum and its flux, it is necessary to consider the near-field components as well. Using the relevant expressions from chapter 4 (4.5.1-2, 4.5.4-5), the full electric and magnetic fields of oscillating, co-located electric and magnetic dipoles are given by

$$\boldsymbol{E}(\boldsymbol{x},t) = \frac{1}{4\pi\epsilon_0} e^{i(kr-\omega t)} \left[\frac{k^2}{r} (\boldsymbol{n} \times \boldsymbol{\mu}) \times \boldsymbol{n} + \left(\frac{ik}{r^2} - \frac{1}{r^3} \right) \big(\boldsymbol{\mu} - 3\boldsymbol{n}(\boldsymbol{n} \cdot \boldsymbol{\mu}) \big) + \left(\frac{-k^2}{r} - \frac{ik}{r^2} \right) \frac{1}{c}\, \boldsymbol{n} \times \boldsymbol{m} \right], \tag{5.4.3}$$

$$\boldsymbol{B}(\boldsymbol{x},t) = \frac{\mu_0}{4\pi} e^{i(kr-\omega t)} \left[c \left(\frac{k^2}{r} + \frac{ik}{r^2} \right) \boldsymbol{n} \times \boldsymbol{\mu} + \frac{k^2}{r} (\boldsymbol{n} \times \boldsymbol{m}) \times \boldsymbol{n} + \left(\frac{ik}{r^2} - \frac{1}{r^3} \right) \big(\boldsymbol{m} - 3\boldsymbol{n}(\boldsymbol{n} \cdot \boldsymbol{m}) \big) \right]. \tag{5.4.4}$$

We can now complement our earlier analysis of the helicity by considering the Cartesian components of angular momentum radiated in various directions by the compound dipole. The electric and magnetic fields, including near-field components, are found by substituting $\boldsymbol{\mu} = |\mu| \hat{\boldsymbol{z}}$ and $\boldsymbol{m} = |m| e^{i\alpha} \hat{\boldsymbol{z}}$ into (5.4.3-4), and from this it is straightforward to explicitly evaluate components of M_{ab}.

Rather than reporting these components directly, it is more informative to examine the fluxes of the *x*, *y* and *z* components of angular momentum radiated in the *r* direction. These may be obtained from the Cartesian components of $\boldsymbol{M}$ by

$$\begin{aligned} M_{rx} &= M_{xx} \sin\theta \cos\phi + M_{yx} \sin\theta \sin\phi + M_{zx} \cos\theta \\ M_{ry} &= M_{xy} \sin\theta \cos\phi + M_{yy} \sin\theta \sin\phi + M_{zy} \cos\theta \\ M_{rz} &= M_{xz} \sin\theta \cos\phi + M_{yz} \sin\theta \sin\phi + M_{zz} \cos\theta\,. \end{aligned} \tag{5.4.5}$$

The cycle-averaged M_{rx} is equal to

$$M_{rx} = -\frac{|m||\mu|(k + k^3r^2)\sin\alpha\cos^2\theta\sin\theta\cos\phi}{8\pi^2\epsilon_0 c\, r^4} + \frac{\left(\frac{1}{c^2}|m|^2 + |\mu|^2\right)\cos\theta\sin\theta\sin\phi}{16\pi^2\epsilon_0\, r^5}, \quad 5.4.6$$

and so the radiated flux of x-component of angular momentum is

$$M_{rx}^{rad} = -\frac{k^3|m||\mu|\sin\alpha\cos^2\theta\sin\theta\cos\phi}{8\pi^2\epsilon_0 c\, r^2}. \quad 5.4.7$$

From the $\cos\phi$ dependence, we see that opposite angular momentum fluxes are observed in the positive and negative *x* directions, and so no net angular momentum about the x axis is radiated from the source. The problem is azimuthally symmetric, and so similar expressions are obtained for the *y* component.

For the *z* component, we find

$$M_{rz} = \frac{|m||\mu|(k + k^3r^2)\sin\alpha\sin^2\theta\cos\theta}{8\pi^2\epsilon_0 c\, r^4}, \quad 5.4.8$$

(with no cycle averaging necessary this time). The radiated component of this flux is given by

$$M_{rz}^{rad} = \frac{k^3|m||\mu|\sin\alpha\sin^2\theta\cos\theta}{8\pi^2\epsilon_0 c\, r^2}, \quad 5.4.9$$

We see that this time the angular momentum has opposite signs in the upper and lower hemispheres, and again that no net angular momentum is radiated by the dipole.

We now turn to the rotating dipole (a problem considered in [5]). The angular momentum radiated from a rotating dipole can be calculated by again substituting the fields (5.4.3-4) into (5.4.2), but this time with the complex electric dipole moment (5.2.1), and the magnetic dipole moment set to zero.

As the source rotates about the *z* axis, it is the *z* component of angular momentum that is of interest. Using 5.4.9, the radial flux of angular momentum in the z direction is given by

$$M_{rz} = \frac{|\mu|^2\sin^2\theta\,(k^3r^3 + (2kr - k^3r^3)\cos 2(kr + \phi - \omega t) + (2k^3r^3 - 1)\sin 2(kr + \phi - \omega t))}{16\epsilon_0\pi^2 r^5}. \quad 5.4.10$$

After cycle-averaging, this reduces to

$$M_{rz} = \frac{|\mu|^2\sin^2\theta\, k^3}{16\pi^2\epsilon_0 r^2}, \quad 5.4.11$$

Integrating this over a sphere centred on the dipole shows the radiated angular momentum to be

$$\int_0^{2\pi} d\phi \int_0^{\pi} \frac{|\mu|^2\sin^2\theta\, k^3}{16\pi^2\epsilon_0 r^2} r^2 \sin\theta\, d\theta = \frac{|\mu|^2 k^3}{6\pi\epsilon_0}, \quad 5.4.12$$

with equal fluxes radiated into the two hemispheres above and below the dipole. In contrast, we saw that the helicity flux has opposite sign in each hemisphere, and no net helicity is radiated.

Conclusions

This chapter examined the fields emitted from a chiral source of circularly polarised light – an electric and magnetic dipole with a $\pm\pi/2$ phase difference – and contrasted these with an achiral source of circularly polarised light – a rotating electric dipole. Both the helicity and angular momentum radiated by the sources was considered: the former was shown to be a net source of helicity, but not angular momentum, while the latter was a net source of angular momentum, but not helicity. One point emphasised by this is that helicity is a chiral observable, whereas angular momentum is not. In order for a source to be a net emitter of helicity it is necessary (but not sufficient) that it lacks inversion symmetry.

It is also notable that, as discussed in chapter 4**,** calculating the radiated helicity required only the $\frac{1}{r}$ field and potential components, whereas the radiated angular momentum required near-field contributions, and thus involved much greater complexity. The explicit dependence of the angular momentum on the $\frac{1}{r^3}$ radial components of the field mean that care must be taken in the use of far-field and quasi-plane-wave approximations. The two examples given here show another context in which the difficulties of localising electromagnetic angular momentum become apparent.

References

[1] Lindman K. F. 1920 Über eine durch ein isotropes System von spiralförmigen Resonatoren erzeugte Rotationspolarization der elektromagnetische Wellen *Annalen der Physik* **63** 621

[2] Elezzabi A.Y. and Sederberg S. 2009 Optical Activity in an Artificial Chiral Media: A terahertz Time-domain Investigation of Karl F Lindman's 1920 Pioneering Experiment *Optics Express* **17** 6600

[3] Crimin F., Mackinnon N., Götte J. B. and Barnett S. M. 2019 Optical Helicity and Chirality: Conservation and Sources *Applied Sciences* **9** 828

[4] Barnett S. M., Cameron R. P. and Yao A. M. 2012 Duplex Symmetry and its Relation to the Conservation of Optical Helicity *Physical Review A* **86** 013845

[5] Barnett S. M. 2002 Optical Angular Momentum Flux *Journal of Optics B: Quantum and Semiclassical Optics* **4** (Special issue: Atoms and Angular Momentum of Light) 7

6. The Generation of Helicity at a Dielectric Interface

This chapter discusses the generation of helicity during reflection and transmission at the surface of a dielectric. It was noted in chapter 2 that if a system is not dual-symmetric then the total helicity is generally not conserved. We can see the helicity non-conserving properties of dielectric interfaces intuitively: left-circular polarised light is turned into right-circular polarised light by reflection in a mirror. From the point of view of the local continuity equation for helicity, spatial variation of the ratio ϵ/μ is a necessary condition for the "source" side to be non-zero; it is the variation of this ratio which breaks the system's macroscopic duality symmetry.

In this chapter we explicitly derive expressions for the helicity flux across various interfaces for incident light of arbitrary polarisation and incidence angle. We initially consider the boundary between vacuum and a chiral medium, with the corresponding results for an achiral surface easily obtained by setting the chirality parameter to zero. The presence or absence of material chirality leads to qualitatively different reflection and transmission effects, and a comparison between the different cases is presented. Results for the transmission and reflection Fresnel coefficients at a chiral interface have been reported previously in the literature [1,2]. The novel work in this chapter is to cast the known results which follow from these transmission and reflection coefficients explicitly in terms of the helicity fluxes from chiral interfaces, and to analyse the situation with reference to the local continuity of helicity.

6.1 Reflection at Vacuum-Chiral Boundaries

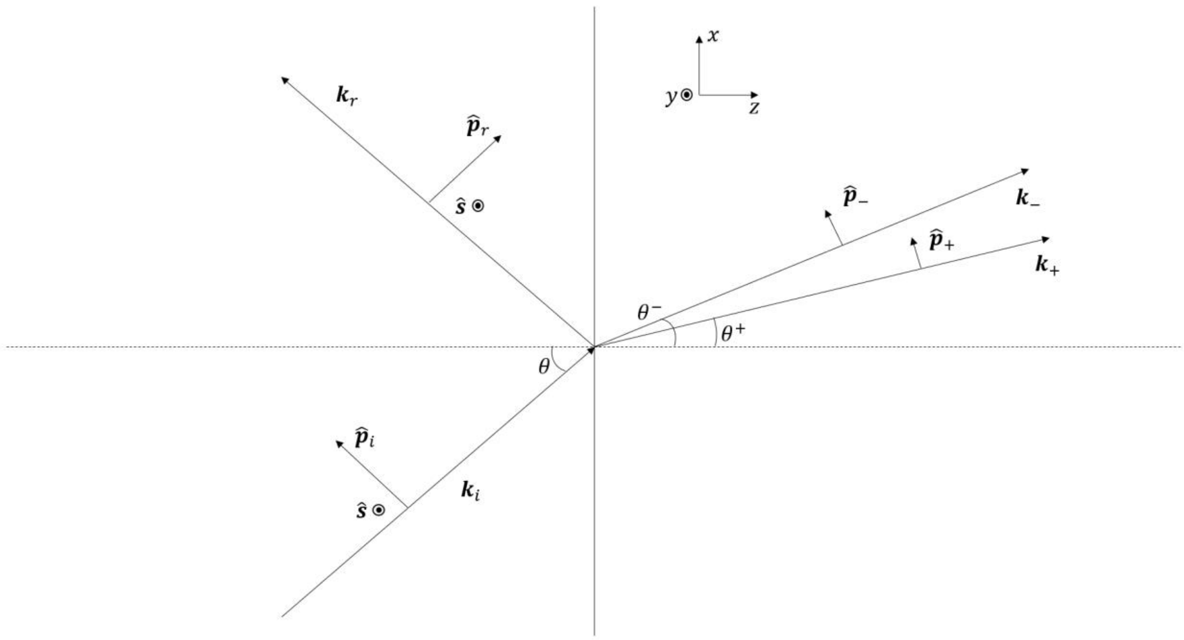

Figure 1 *Reflection and refraction at a vacuum-chiral interface. The* ***p, s*** *and* ***k*** *directions are marked for the incident, reflected and transmitted waves. The diagram shows a material with a positive chirality parameter, so that the positive helicity transmitted wave is refracted more than the negative helicity wave.*

Consider an interface between the vacuum and a lossless isotropic chiral medium, as shown in *Figure 1*. Reflection and transmission at an achiral interface is most often described by decomposing the incident, reflected and transmitted waves into components polarised parallel and perpendicular to the plane of incidence (referred to as "*p*" and "*s*" polarisations). The reflected and transmitted field amplitudes for each polarisation are related to the incident amplitudes by Fresnel coefficients, derived from the boundary conditions on the fields at the interface [3, §7.3].

For the analysis of helicity generated at reflection and transmission, it is more convenient to work in a circular basis, and rather than writing coefficients for the *p* and *s* polarisations we work with transmission and reflection coefficients for the two circular polarisations. The circular polarisations with positive and negative helicity are represented by the complex polarisation vectors $\frac{1}{\sqrt{2}}(\widehat{\boldsymbol{p}}_i + i\widehat{\boldsymbol{s}})$ and $\frac{1}{\sqrt{2}}(\widehat{\boldsymbol{p}}_i - i\widehat{\boldsymbol{s}})$ for the incident wave, and $\frac{1}{\sqrt{2}}(\widehat{\boldsymbol{p}}_r - i\widehat{\boldsymbol{s}})$ and $\frac{1}{\sqrt{2}}(\widehat{\boldsymbol{p}}_r + i\widehat{\boldsymbol{s}})$ for the reflected wave.

This basis is particularly useful when considering chiral media, as they generally rotate the polarisation of the light that they reflect and transmit. This means that an *s* polarised incident wave can give rise to *p* polarised transmitted and reflected waves, and *vice versa* – so the *p-s* basis does not bring the same simplifications that it does for isotropic achiral interfaces.

Furthermore, when linearly polarised light travels through a chiral medium, its plane of polarisation rotates. Only circularly polarised waves propagate unchanged (albeit with different refractive indices for the two polarisations), giving a compelling reason to decompose the light on the chiral side of the boundary into left- and right- circular polarised components rather than *s* and *p* components. Derivations of the Fresnel coefficients for chiral media are presented in [1], and they are also reported in [2].

Because the refractive indices differ for the two polarisations, they will generally have different angles of refraction and $\boldsymbol{k}$ vectors – we designate the two angles of refraction $\theta^{\pm}$, and wavevectors $\boldsymbol{k}_{\pm}$. The generic situation – with an incident wave, a reflected wave and two transmitted waves of opposite helicity – is sketched in *figure 1*. We choose a coordinate system such that the interface's normal lies in the *z*-direction, and the incident wave travels in the positive *z*-direction. Further choosing the *x*-z plane to be the scattering plane, we see that if the $\boldsymbol{k}$ vectors of the incident and transmitted waves make angles θ, θ^{+} and θ^{-} with the surface normal, then the unit vectors in the *p* and *s* directions for each wave are

$$\widehat{\boldsymbol{p}}_i = \cos\theta\,\widehat{\boldsymbol{x}} - \sin\theta\,\widehat{\boldsymbol{z}}, \qquad \widehat{\boldsymbol{p}}_{\pm} = \cos\theta^{\pm}\,\widehat{\boldsymbol{x}} - \sin\theta^{\pm}\,\widehat{\boldsymbol{z}},$$
$$\widehat{\boldsymbol{s}} = \widehat{\boldsymbol{y}}. \tag{6.1.1}$$

For the reflected wave (which travels in the opposite direction) the *p* and *s* directions are given by

$$\widehat{\boldsymbol{p}}_r = \cos\theta\,\widehat{\boldsymbol{x}} + \sin\theta\,\widehat{\boldsymbol{z}},$$
$$\widehat{\boldsymbol{s}} = \widehat{\boldsymbol{y}}. \tag{6.1.2}$$

This convention is chosen so that $\widehat{\boldsymbol{p}}_i$ and $\widehat{\boldsymbol{p}}_r$ coincide at normal incidence – but note that for the incident wave $\widehat{\boldsymbol{p}}_i \times \widehat{\boldsymbol{s}} = \widehat{\boldsymbol{k}}_i$, while for the reflected wave $\widehat{\boldsymbol{s}} \times \widehat{\boldsymbol{p}}_r = \widehat{\boldsymbol{k}}_r$. The $\boldsymbol{k}$ vectors are, accordingly,

$$\boldsymbol{k}_i = k_0(\sin\theta\,\widehat{\boldsymbol{x}} + \cos\theta\,\widehat{\boldsymbol{z}}), \tag{6.1.3}$$

$$\boldsymbol{k}_r = k_0(\sin\theta\,\widehat{\boldsymbol{x}} - \cos\theta\,\widehat{\boldsymbol{z}}), \tag{6.1.4}$$

$$\boldsymbol{k}_{\pm} = k_{\pm}(\sin\theta^{\pm}\,\widehat{\boldsymbol{x}} + \cos\theta^{\pm}\,\widehat{\boldsymbol{z}},) \tag{6.1.5}$$

Using these definitions, the (complex) electric fields may be written

$$\boldsymbol{E}^i = \frac{1}{\sqrt{2}}\left(E_+^i(\widehat{\boldsymbol{p}}_i + i\widehat{\boldsymbol{s}}) + E_-^i(\widehat{\boldsymbol{p}}_i - i\widehat{\boldsymbol{s}})\right)e^{i(\boldsymbol{k}_i\cdot\boldsymbol{r}-\omega t)}, \tag{6.1.6}$$

$$\boldsymbol{E}^r = \frac{1}{\sqrt{2}}\left(E_+^r(\widehat{\boldsymbol{p}}_r - i\widehat{\boldsymbol{s}}) + E_-^r(\widehat{\boldsymbol{p}}_r + i\widehat{\boldsymbol{s}})\right)e^{i(\boldsymbol{k}_r\cdot\boldsymbol{r}-\omega t)}, \tag{6.1.7}$$

$$\boldsymbol{E}^t = \frac{E_+^t}{\sqrt{2}}(\widehat{\boldsymbol{p}}_+ + i\widehat{\boldsymbol{s}})e^{i(\boldsymbol{k}_+\cdot\boldsymbol{r}-\omega t)} + \frac{E_-^t}{\sqrt{2}}(\widehat{\boldsymbol{p}}_- - i\widehat{\boldsymbol{s}})e^{i(\boldsymbol{k}_-\cdot\boldsymbol{r}-\omega t)}. \tag{6.1.8}$$

where $E_+^{i/r/t}$ and $E_-^{i/r/t}$ are the complex amplitudes of the incident/reflected/transmitted field in the positive and negative helicity polarisations. The corresponding $\boldsymbol{H}$ fields for each plane wave are given by $\boldsymbol{H} = \sqrt{\frac{\epsilon}{\mu}}\hat{\boldsymbol{k}} \times \boldsymbol{E}$,

$$\boldsymbol{H}^i = \frac{1}{\sqrt{2}}\sqrt{\frac{\epsilon}{\mu}}\left(E_+^i(\hat{\boldsymbol{s}} - i\hat{\boldsymbol{p}}_i) + E_-^i(\hat{\boldsymbol{s}} + i\hat{\boldsymbol{p}}_i)\right)e^{i(\boldsymbol{k}_i\cdot\boldsymbol{r}-\omega t)}, \quad 6.1.9$$

$$\boldsymbol{H}^r = \frac{1}{\sqrt{2}}\sqrt{\frac{\epsilon}{\mu}}\left(E_+^r(-\hat{\boldsymbol{s}} - i\hat{\boldsymbol{p}}_r) + E_-^r(-\hat{\boldsymbol{s}} + i\hat{\boldsymbol{p}}_r)\right)e^{i(-\boldsymbol{k}_r\cdot\boldsymbol{r}-\omega t)}, \quad 6.1.10$$

$$\boldsymbol{H}^t = \frac{1}{\sqrt{2}}\sqrt{\frac{\epsilon}{\mu}}E_+^t(\hat{\boldsymbol{s}} - i\hat{\boldsymbol{p}}_+)e^{i(\boldsymbol{k}_+\cdot\boldsymbol{r}-\omega t)} + \sqrt{\frac{\epsilon}{\mu}}E_-^t(\hat{\boldsymbol{s}} + i\hat{\boldsymbol{p}}_-)e^{i(\boldsymbol{k}_-\cdot\boldsymbol{r}-\omega t)}. \quad 6.1.11$$

Calculating the helicity flux also requires expressions for the vector potentials. As in chapter 6, we find these by inverting $\boldsymbol{E} = -\frac{\partial \boldsymbol{A}}{\partial t}$ and $\boldsymbol{H} = -\frac{\partial \boldsymbol{C}}{\partial t}$, using the harmonic time dependence of the fields and potentials to obtain

$$\boldsymbol{A} = -\frac{i}{\omega}\boldsymbol{E}, \quad 6.1.12$$

$$\boldsymbol{C} = -\frac{i}{\omega}\boldsymbol{H}. \quad 6.1.13$$

Finally, the reflected and transmitted electric field amplitudes are related to the incident by the following Fresnel coefficients [2][1]

$$r_{+-} = r_{-+} = \frac{(1 - Z_r{}^2)(\alpha^+ + \alpha^-)}{(\alpha^+ + Z_r)(1 + Z_r\alpha^-) + (\alpha^- + Z_r)(1 + Z_r\alpha^+)}, \quad 6.1.14$$

$$r_{++} = \frac{2Z_r(\alpha^+ - 1)(\alpha^- + 1)}{(\alpha^+ + Z_r)(1 + Z_r\alpha^-) + (\alpha^- + Z_r)(1 + Z_r\alpha^+)}, \quad 6.1.15$$

$$r_{--} = \frac{2Z_r(\alpha^+ + 1)(\alpha^- - 1)}{(\alpha^+ + Z_r)(1 + Z_r\alpha^-) + (\alpha^- + Z_r)(1 + Z_r\alpha^+)}, \quad 6.1.16$$

$$t_{++} = \frac{2(Z_r + 1)(\alpha^- + 1)}{(\alpha^+ + Z_r)(1 + Z_r\alpha^-) + (\alpha^- + Z_r)(1 + Z_r\alpha^+)}, \quad 6.1.17$$

$$t_{--} = \frac{2(Z_r + 1)(\alpha^+ + 1)}{(\alpha^+ + Z_r)(1 + Z_r\alpha^-) + (\alpha^- + Z_r)(1 + Z_r\alpha^+)}, \quad 6.1.18$$

$$t_{+-} = \frac{2(Z_r - 1)(\alpha^- - 1)}{(\alpha^+ + Z_r)(1 + Z_r\alpha^-) + (\alpha^- + Z_r)(1 + Z_r\alpha^+)}, \quad 6.1.19$$

$$t_{-+} = \frac{2(Z_r - 1)(\alpha^+ - 1)}{(\alpha^+ + Z_r)(1 + Z_r\alpha^-) + (\alpha^- + Z_r)(1 + Z_r\alpha^+)}, \quad 6.1.20$$

[1] Note that in [2], Chern labels the +/- polarisations by the sense of rotation of the electric field, not by the helicity, and so the labels for the reflected waves are assigned oppositely to those in this chapter. This means that his r_{++} is equal to our r_{-+} and our r_{++} his r_{-+}, etc.

where we have made use of a shorthand notation $\alpha^{\pm} = \frac{\cos\theta^{\pm}}{\cos\theta}$, and Z_r is the ratio of the impedances on the different sides of the interface, $Z_r \equiv \frac{\sqrt{\frac{\mu_0}{\epsilon_0}}}{\sqrt{\frac{\mu}{\epsilon}}}$. The reflected and transmitted amplitudes are related to the incident by the matrices

$$\begin{bmatrix} E_+^r \\ E_-^r \end{bmatrix} = \begin{bmatrix} r_{++} & r_{+-} \\ r_{-+} & r_{--} \end{bmatrix} \begin{bmatrix} E_+^i \\ E_-^i \end{bmatrix} \quad 6.1.21$$

$$\begin{bmatrix} E_+^t \\ E_-^t \end{bmatrix} = \begin{bmatrix} t_{++} & t_{+-} \\ t_{-+} & t_{--} \end{bmatrix} \begin{bmatrix} E_+^i \\ E_-^i \end{bmatrix} \quad 6.1.22$$

6.2 The Helicity Flux at Reflection and Transmission

We now have gathered together explicit expressions for the incident, reflected and transmitted electric and magnetic fields at a vacuum-chiral interface, for arbitrary incident polarisations and angles, so we may straightforwardly calculate the helicity flux from the interface. The cycle-averaged helicity flux density is given by

$$\boldsymbol{v} = \frac{1}{2} Re\left[\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E} \times \boldsymbol{A}^* + \sqrt{\frac{\mu}{\epsilon}}\boldsymbol{H} \times \boldsymbol{C}^*\right], \quad 6.2.1$$

which is valid in both chiral and achiral media. To calculate the net flux of helicity through a surface enclosing the interface, it is sufficient to consider only the *z*-component of $\boldsymbol{v}$: we may (for example) take our surface to be a cuboid, and the fluxes in the *x* and *y* directions will cancel on opposite faces. Using the fields on the vacuum side of the interface, the *z*-component of (6.2.1) is simply

$$v_z^{vac} = \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}\left(\left|E_+^i\right|^2 - \left|E_-^i\right|^2 - |E_+^r|^2 + |E_-^r|^2\right)\cos\theta\,. \quad 6.2.2$$

This is, of course, just the appropriate projection of the intensities of the different circular polarised components onto the z direction (the reflected intensities enter with opposite sign, as the reflected positive/negative helicity waves travel in the negative *z* direction). Note that both the electric and magnetic parts of (6.2.1) must be included in order to obtain this result: the cross-terms between the incident and reflected fields in one half cancel with those of the other. We may use the Fresnel coefficients (6.1.14-6.1.20) to write this explicitly in terms of the incident amplitude,

$$v_z^{vac} = \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}\left(\left|E_+^i\right|^2 - \left|E_-^i\right|^2 - \left|r_{++}E_+^i + r_{+-}E_-^i\right|^2 + \left|r_{-+}E_+^i + r_{--}E_-^i\right|^2\right)\cos\theta \qquad 6.2.3$$

$$= \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}\Big(\left|E_+^i\right|^2(1 - r_{++}^2 + r_{+-}^2) + \left|E_-^i\right|^2(-1 - r_{-+}^2 + r_{--}^2)$$

$$+ \left(E_+^i E_-^{i\,*} + E_+^{i\,*} E_-^i\right)(r_{-+}r_{--} - r_{++}r_{+-})\Big)\cos\theta.$$

On the medium side, we similarly obtain

$$v_z^{med} = \frac{1}{\omega}\sqrt{\frac{\epsilon}{\mu}}(|E_+^t|^2\cos\theta^+ - |E_-^t|^2\cos\theta^-), \qquad 6.2.4$$

where again both parts of (6.2.1) must be used. Using (6.1.22) to write the transmitted amplitudes in terms of the incident gives

$$v_z^{med} = \frac{1}{\omega}\sqrt{\frac{\epsilon}{\mu}}\left(\left|t_{++}E_+^i + t_{+-}E_-^i\right|^2\cos\theta^+ - \left|t_{-+}E_+^i + t_{--}E_-^i\right|^2\cos\theta^-\right) \qquad 6.2.5$$

$$= \frac{1}{\omega}\sqrt{\frac{\epsilon}{\mu}}\Big(\left|E_+^i\right|^2(t_{++}^2\cos\theta^+ - t_{-+}^2\cos\theta^-) + \left|E_-^i\right|^2(t_{+-}^2\cos\theta^+ - t_{--}^2\cos\theta^-)$$

$$+ \left(E_+^i E_-^{i\,*} + E_+^{i\,*} E_-^i\right)(t_{++}t_{+-}\cos\theta^+ - t_{--}t_{-+}\cos\theta^-)\Big).$$

The net flux of helicity from the interface is given by $v_z^{med} - v_z^{vac}$.

The final remark necessary to relate these expressions to properties of the medium is an expression for the two angles of refraction in terms of medium properties. In the following chapter, it will be demonstrated that the phase refractive index for the two polarisations in a chiral medium is given by

$$n_\pm = \sqrt{\frac{\mu\epsilon}{\mu_0\epsilon_0}}(1 \pm \beta k), \qquad 6.2.6$$

where β is the chirality parameter (see section 7.1). With this, we may relate the incident and transmitted angles by using Snell's law. For the vacuum-chiral interface, we have

$$\sin\theta = n_\pm \sin\theta^\pm, \qquad 6.2.7$$

$$\theta^\pm = \arcsin\frac{\sin\theta}{n_\pm}, \qquad 6.2.8$$

$$\cos\theta^\pm = \sqrt{1 - \frac{\sin^2\theta}{n_\pm^2}} = \sqrt{1 - \frac{\mu_0\epsilon_0\sin^2\theta}{\mu\epsilon(1 \pm \beta k)^2}}, \qquad 6.2.9$$

showing explicitly how the chirality of the medium enters into the above formulae.

6.3 Linear Incident Polarisation

When the incident light is linearly polarised $|E^i_+| = |E^i_-|$, and the expressions for the helicity flux on either side reduce to

$$v_z^{vac} = \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}\Big(|E^i_+|^2(r_{--}^2 - r_{++}^2) + (E^i_+ {E^i_-}^* + {E^i_+}^* E^i_-)(r_{-+}r_{--} - r_{++}r_{+-})\Big)\cos\theta \,. \qquad 6.3.1$$

The polarisation of the incident light is governed by the relative phase between E^i_+ and E^i_-. Without loss of generality, we may take E^i_+ to be real and write $E^i_- = E^i_+ e^{i\phi}$, for some constant phase ϕ. We then obtain

$$v_z^{vac} = \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}{E^i_+}^2\big(r_{--}^2 - r_{++}^2 + 2\cos\phi\, r_{-+}(r_{--} - r_{++})\big)\cos\theta \,, \qquad 6.3.2$$

where $\phi = 0$ and $\phi = \pi$ correspond to incident *p* and *s* polarised light, respectively.

When the incident light is linearly polarised, any transmitted or reflected helicity must be due to the chirality of the medium. We see from the coefficients (6.1.15-6.1.16) that in an achiral medium $r_{++} = r_{--}$, and so the above flux is zero.

The flux on the medium side reduces to

$$v_z^{med} = \frac{1}{\omega}\sqrt{\frac{\epsilon}{\mu}}{E^i_+}^2\big((t_{++}^2 + t_{+-}^2 + 2\cos\phi\, t_{++}t_{+-})\cos\theta^+ - (t_{--}^2 + t_{-+}^2 + 2\cos\phi\, t_{--}t_{-+})\cos\theta^-\big), \qquad 6.3.3$$

which similarly vanishes in achiral media.

6.4 Achiral and Dual Symmetric Interfaces

In achiral media $n_+ = n_-$ and $\theta^+ = \theta^-$, so many of the Fresnel coefficients (6.1.14-6.1.20) are greatly simplified. In particular, we see that $r_{++} = r_{--}$, $t_{++} = t_{--}$ and $t_{+-} = t_{-+}$ (as they must, because an achiral medium does not distinguish between the two circular polarisations). The fluxes therefore reduce to

$$v_z^{vac} = \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}\left(|E^i_+|^2 - |E^i_-|^2\right)(1 - r_{++}^2 + r_{+-}^2)\cos\theta \,, \qquad 6.4.1$$

$$v_z^{med} = \frac{1}{\omega}\sqrt{\frac{\epsilon}{\mu}}\left(|E^i_+|^2 - |E^i_-|^2\right)(t_{++}^2 - t_{-+}^2)\cos\theta^+ \,. \qquad 6.4.2$$

In this case a net radiated helicity evidently requires an imbalance between positive and negative helicity incident waves.

The conservation of helicity at dual-symmetric interfaces is also apparent from the Fresnel coefficients (6.1.14-6.1.20). If the vacuum-chiral interface is dual-symmetric, then $\sqrt{\frac{\epsilon_0}{\mu_0}} = \sqrt{\frac{\epsilon}{\mu}}$, and so $Z_r = 1$. We then have $r_{+-} = r_{-+} = t_{+-} = t_{-+} = 0$, and

$$v_z^{vac} = \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}\left(\left|E_+^i\right|^2(1 - r_{++}^2) - \left|E_-^i\right|^2(1 - r_{--}^2)\right)\cos\theta\,, \qquad 6.4.3$$

$$v_z^{med} = \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}\left(\left|E_+^i\right|^2(t_{++}^2\cos\theta^+) - \left|E_-^i\right|^2(t_{--}^2\cos\theta^-)\right). \qquad 6.4.4$$

The total flux of helicity from the interface is equal to

$$v_z^{med} - v_z^{vac} = \frac{1}{\omega}\sqrt{\frac{\epsilon_0}{\mu_0}}\left\{\left|E_+^i\right|^2\left((1 - r_{++}^2)\cos\theta - t_{++}^2\cos\theta^+\right) - \left|E_-^i\right|^2\left((1 - r_{--}^2)\cos\theta - t_{--}^2\cos\theta^-\right)\right\}. \qquad 6.4.5$$

Consideration of the Fresnel coefficients shows that this is identically zero. When $Z_r = 1$, the positive helicity reflection and transmission coefficients reduce to

$$r_{++} = \frac{\alpha^+ - 1}{\alpha^+ + 1}, \qquad t_{++} = \frac{2}{\alpha^+ + 1}. \qquad 6.4.6$$

We can examine the term multiplying $\left|E_+^i\right|^2$, noting that

$$(1 - r_{++}^2)\cos\theta = \frac{4\alpha^+}{(\alpha^+ + 1)^2}\cos\theta\,, \qquad 6.4.7$$

$$t_{++}^2\cos\theta^+ = \frac{4}{(\alpha^+ + 1)^2}\cos\theta^+ = \frac{4\alpha^+}{(\alpha^+ + 1)^2}\cos\theta\,, \qquad 6.4.8$$

where in the last step we have used the definition $\alpha^+ \equiv \frac{\cos\theta^+}{\cos\theta}$. The term therefore vanishes, and a corresponding result is obtained for the coefficient of $\left|E_-^i\right|^2$ from the expressions for r_{--}^2 and t_{--}^2. We therefore see that when $\sqrt{\frac{\epsilon_0}{\mu_0}} = \sqrt{\frac{\epsilon}{\mu}}$ the net helicity flux is identically zero.

6.5 Chiral Negative Refraction

The expression (6.2.6) for the refractive index in a chiral medium carries the implication that if $|\beta k| > 1$, the refractive index will become negative for one of the circular polarisations [4]. As will be discussed in chapter 7, the chirality parameter is extremely small for even highly optically active substances. The realisation of such chiral negative refraction is currently confined to carefully engineered metamaterials, and in the GHz or THz region of the spectrum (see for [5], or [6]). A negative refractive index leads to a variety of novel propagation effects – the “negatively refracted” wave remains on the same side of the normal as the incident wave, and its phase velocity and *k*-vector are anti-parallel rather than parallel [4].

It has been a tacit assumption in the calculations above that this situation does not arise. The presence of negative refraction does not fundamentally change the situation, but alters the geometry somewhat, and this requires some modifications to the definitions of the $\boldsymbol{s}$ and $\boldsymbol{p}$ unit vectors (6.1.1). We sketch briefly below how the above calculations would be altered if one of the waves were negatively refracted.

We shall consider the case where the chirality parameter β is positive. Then, when $|\beta k| > 1$, the wavevector $\boldsymbol{k}_-$ will point in the opposite direction. If we continue to define θ^- as the angle that $\boldsymbol{k}_-$ makes with the *positive z* direction, then the definitions (6.1.3) remain valid, but we now have

$$\hat{\boldsymbol{p}}_- = -\cos\theta^-\,\hat{\boldsymbol{x}} + \sin\theta^-\,\hat{\boldsymbol{z}}, \qquad 6.5.1$$

and normal incidence corresponds to $\theta = \theta^+ = 0, \theta^- = \pi$. The situation is shown schematically in *figure 2*.

This redefinition of $\hat{\boldsymbol{p}}_-$ affects the fields $\boldsymbol{E}^t$, and the corresponding $\boldsymbol{A}$ potential. Furthermore, for a plane wave passing through a negative-index material we have[2] $\boldsymbol{H} = \sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}\times\hat{\boldsymbol{k}}$. The transmitted $\boldsymbol{H}$-field therefore becomes

$$\boldsymbol{H}^t = \frac{1}{\sqrt{2}}\sqrt{\frac{\epsilon}{\mu}}\left[E_+^t(\hat{\boldsymbol{s}} - i\hat{\boldsymbol{p}}_+)e^{i(\boldsymbol{k}_+\cdot\boldsymbol{r}-\omega t)} - E_-^t(\hat{\boldsymbol{s}} + i\hat{\boldsymbol{p}}_-)e^{i(\boldsymbol{k}_-\cdot\boldsymbol{r}-\omega t)}\right], \qquad 6.5.2$$

where, compared with (6.1.9), the sign of the second term has been reversed. The helicity flux on the medium side becomes

$$v_z^{med} = \frac{1}{\omega}\sqrt{\frac{\epsilon}{\mu}}\left(|E_+^t|^2\cos\theta^+ + |E_-^t|^2\cos\theta^-\right), \qquad 6.5.3$$

but it should be stressed that the change of sign in the second term (compared to (6.2.4)) is merely because of the change of meaning of θ^- when the wave is negatively refracted. The projection onto the positive Z-direction is now given by $-\cos\theta^-$ instead of $\cos\theta^-$, so $\cos\theta^-$ enters the expression with opposite sign. The negatively refracted wave still contributes negatively to the helicity flux.

Finally, the Fresnel coefficients (6.1.14-6.1.20) are derived from the continuity of the tangential components of $\boldsymbol{E}$ and $\boldsymbol{H}$, and the resolution of the fields into normal and tangential components encounters the same issue of the redefined θ^-. Because θ^- is now the obtuse angle shown in *figure 2*, the appropriate resolutions of $\boldsymbol{E}$ and $\boldsymbol{H}$ into normal and tangential parts now use $\cos(\pi - \theta^-)$ in place of $\cos(\theta^-)$. In (6.1.14-6.1.20) we must therefore also replace each occurrence

[2]For plane waves in an ordinary dielectric ***E***, ***H*** and ***k*** form the three basis vectors of a right-handed coordinate system. In a material with a negative refractive index, however, the opposition of *k*-vector and Poynting vector means that they form a left-handed one. For this reason, materials with a negative index of refraction are sometimes referred to as “left-handed” materials. This terminology has not been used here to avoid confusion, as this use of the term “left-handed” has nothing to do with material chirality.

of α^- with $-\alpha^-$. These various changes do not fundamentally affect the arguments or conclusions of the other parts of this chapter, which apply equally well for positive and negative refraction.

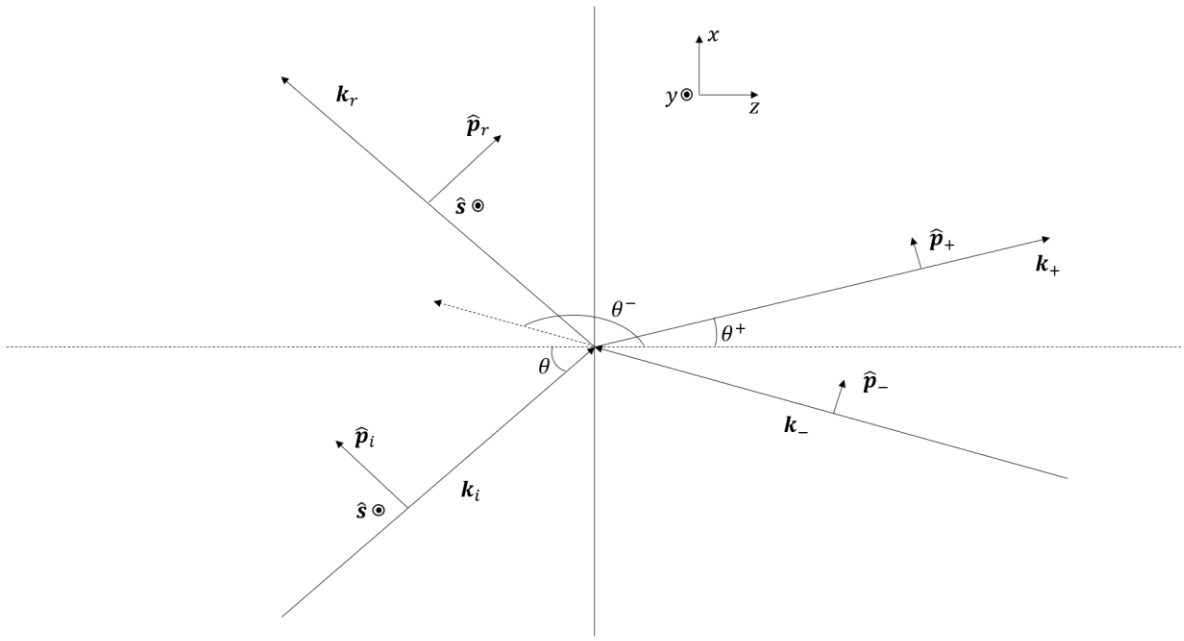

Figure 2 *Negative refraction at a vacuum-chiral interface with a positive chirality parameter. The wavevector of the negatively refracted wave points towards the interface, and so makes an obtuse angle with the positive z direction.*

6.6 Conclusions

In this chapter we have demonstrated how the local continuity of helicity applies at a dielectric interface, and how the Fresnel coefficients for chiral and achiral interfaces provide specific examples of the more general observations about helicity and duality symmetry made in chapter 2. This chapter has exclusively been concerned with helicity fluxes, and we have seen that applying the flux definition (6.2.1) within a chiral medium has presented no obvious problems. In the following chapter, we go on to examine the helicity *density* within a chiral medium in greater detail, and find that here the extension to chiral media is not so straightforward – we will see that it requires modification from the form presented in chapter 2 if it is to be conserved at dual-symmetric interfaces.

References

[1] Lekner J. 1996 Optical Properties of Isotropic Chiral Media *Pure and Applied Optics: Journal of the European Optical Society A* **5** 417

[2] Chern R. 2013 Wave Propagation in Chiral Media: Composite Fresnel Equations *Journal of Optics* **15** 075702

[3] Jackson J. D. 2001 *Classical Electrodynamics* (3rd edition) Wiley

[4] Pendry J. B. 2004 A Chiral Route to Negative Refraction *Science* vol. 306 Issue 5700 p. 1353

[5] Plum E., Zhou J., Dong J., Fedotov V. A., Koschny T., Soukoulis C. M. and Zheludev N. I. 2009 Metamaterial with Negative Index due to Chirality *Physical Review B* **79** 035407

[6] Zhang S., Park Y. Li J., Lu X., Zhang W. and Zhang X. 2009 Negative Refractive Index in Chiral Metamaterials *Physical Review Letters* **102** 023901

Chapter 7 – Helicity within Chiral Media

In chapter 2, we took the definitions of the helicity density, h, and flux density, $\boldsymbol{v}$, within a dielectric medium to be

$$h = \frac{1}{2}\left(\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{A}^T \cdot \boldsymbol{B} - \sqrt{\frac{\mu}{\epsilon}}\boldsymbol{C} \cdot \boldsymbol{D}\right), \quad 7.0.1$$

$$\boldsymbol{v} = \frac{1}{2}\left(\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E} \times \boldsymbol{A} + \sqrt{\frac{\mu}{\epsilon}}\boldsymbol{H} \times \boldsymbol{C}\right). \quad 7.0.2$$

It might be wondered why, when generalising the definitions to apply within a medium, the auxiliary fields enter in the combinations that they do. From a certain point of view, the ultimate reason is that – just as the vacuum helicity density is connected to the dual-symmetry of the free-space Maxwell equations – the quantity defined above is connected by Noether's theorem to a generalised "duality transformation" of the macroscopic fields within the medium, which (for certain material parameters) leaves the macroscopic Maxwell equations invariant. In this chapter, we will examine the helicity within a chiral medium, and argue that in this case the definition of the helicity density given above requires modification. An examination of the consequences of the definition (7.0.1) in chiral media has not been undertaken before – and we show that, in chiral media, it does not possess many properties we would expect of the helicity density. In particular, we find that the helicity per circularly-polarised photon within the chiral medium is not $\pm\hbar$, that the helicity does not travel at the group velocity of the light, and – perhaps most tellingly – that helicity is not generally conserved at a dual-symmetric interface if the media concerned are also chiral. The first two observations strongly imply that something is wrong with the above definition, and the last confirms that the quantity h above is indeed not the locally conserved density connected by Noether's theorem to macroscopic duality symmetry in a chiral medium.

The issues identified above can be remedied by introducing into h a term which is proportional to the electromagnetic energy density and the chirality parameter of the medium. We motivate this modification by showing how it corrects the first two unsatisfactory observations, and then formally justify it through the application of Noether's theorem. The main arguments presented here, and the proposed modification, are reported in [1]. But before describing these in detail, we begin with a few words on the description of chiral media within the framework of macroscopic electrodynamics.

7.1 Electromagnetic Wave Propagation in Chiral Media

Chiral media exhibit different refractive indices for left- and right-handed circularly polarised light. When dealing with the macroscopic fields within a chiral medium, this difference can be described by a modification of the constitutive relations within the medium, introducing a pseudoscalar “chirality parameter” which is connected with the strength of the chiral response. There is not complete agreement as to how exactly the relations should be modified, though the different proposed forms lead to equivalent results for small chirality parameters.

In this chapter, we use the Drude-Born-Federov (*DBF*) constitutive relations[1],

$$\boldsymbol{D} = \epsilon(\boldsymbol{E} + \beta\boldsymbol{\nabla} \times \boldsymbol{E}), \quad 7.1.1$$

$$\boldsymbol{B} = \mu(\boldsymbol{H} + \beta\boldsymbol{\nabla} \times \boldsymbol{H}), \quad 7.1.2$$

with the chirality parameter β, which has the dimensions of length. To see how this modification leads to the description of a chiral material, we can consider the wave equation for the ***E*** field obtained with these constitutive relations. Taking the curl of the electric field, we find

$$(\boldsymbol{\nabla} \times \boldsymbol{E}) = -\frac{\partial \boldsymbol{B}}{\partial t} = -\mu\left(\frac{\partial \boldsymbol{H}}{\partial t} + \beta\boldsymbol{\nabla} \times \frac{\partial \boldsymbol{H}}{\partial t}\right). \quad 7.1.3$$

Taking the curl again, and using Maxwell’s equations (2.5.4) to express the curls of $\boldsymbol{H}$ in terms of $\boldsymbol{D}$,

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \boldsymbol{E}) = -\mu\left(\boldsymbol{\nabla} \times \frac{\partial \boldsymbol{H}}{\partial t} + \beta\boldsymbol{\nabla} \times \left(\boldsymbol{\nabla} \times \frac{\partial \boldsymbol{H}}{\partial t}\right)\right) = -\mu\left(\frac{\partial^2 \boldsymbol{D}}{\partial t^2} + \beta\boldsymbol{\nabla} \times \frac{\partial^2 \boldsymbol{D}}{\partial t^2}\right). \quad 7.1.4$$

Substituting the constitutive relation (7.1.1) into $\boldsymbol{\nabla} \cdot \boldsymbol{D} = 0$ shows that, in the absence of free charge, the ***E*** field is still transverse within the chiral medium. Therefore, we also have

$$\boldsymbol{\nabla} \times (\boldsymbol{\nabla} \times \boldsymbol{E}) = \boldsymbol{\nabla}(\boldsymbol{\nabla} \cdot \boldsymbol{E}) - \boldsymbol{\nabla}^2\boldsymbol{E} = -\boldsymbol{\nabla}^2\boldsymbol{E}. \quad 7.1.5$$

Putting this together with (7.1.4) gives

$$-\boldsymbol{\nabla}^2\boldsymbol{E} = -\mu\left(\frac{\partial^2 \boldsymbol{D}}{\partial t^2} + \beta\boldsymbol{\nabla} \times \frac{\partial^2 \boldsymbol{D}}{\partial t^2}\right). \quad 7.1.6$$

Finally, we use (7.1.1) once more to express (7.1.6) entirely in terms of the ***E*** field, leading to the wave equation

$$\boldsymbol{\nabla}^2\boldsymbol{E} = \mu\epsilon\left(\frac{\partial^2(\boldsymbol{E} + \beta\boldsymbol{\nabla} \times \boldsymbol{E})}{\partial t^2} + \beta\boldsymbol{\nabla} \times \frac{\partial^2(\boldsymbol{E} + \beta\boldsymbol{\nabla} \times \boldsymbol{E})}{\partial t^2}\right)$$

[1] In addition to the Drude-Born-Federov relations, there is an alternative set – the symmetrised Condon relations – given by $\boldsymbol{D} = \epsilon\boldsymbol{E} - g\frac{\partial \boldsymbol{H}}{\partial t}$, $\boldsymbol{B} = \mu\boldsymbol{H} + g\frac{\partial \boldsymbol{E}}{\partial t}$. For monochromatic fields, these can be shown to be equivalent to the *DBF* relations with appropriate redefinitions of the constants ϵ, μ and g [2]. A third set has been advocated by Bassiri et al. [3], $\boldsymbol{D} = \epsilon\boldsymbol{E} + i\xi\boldsymbol{B}$, $\boldsymbol{B} = \mu\boldsymbol{H} - i\xi\mu\boldsymbol{E}$. These do not lead to precisely equivalent predictions, but the differences in observable quantities (for example, the reflectance at an achiral-chiral interface) depend only on terms second order in the chirality parameter [2]. Small chirality parameters are typical in organic chemistry – even a large specific rotation of $\sim 1000^{\circ}\mathrm{mm}^{-1}$ (as is found in solutions of $AgGaS_2$) corresponds to a β of the order $10^{-10}\mathrm{m}$ [2].

$$= \mu\epsilon\left(\frac{\partial^2 \boldsymbol{E}}{\partial t^2} + 2\beta\boldsymbol{\nabla}\times\frac{\partial^2 \boldsymbol{E}}{\partial t^2} + \beta^2\boldsymbol{\nabla}\times\boldsymbol{\nabla}\times\frac{\partial^2 \boldsymbol{E}}{\partial t^2}\right)$$

$$= \mu\epsilon\left(\frac{\partial^2 \boldsymbol{E}}{\partial t^2} + 2\beta\boldsymbol{\nabla}\times\frac{\partial^2 \boldsymbol{E}}{\partial t^2} - \beta^2\boldsymbol{\nabla}^2\frac{\partial^2 \boldsymbol{E}}{\partial t^2}\right). \qquad 7.1.7$$

The β dependent terms lead to different propagation for left- and right-handed circularly polarised waves. Substituting

$$\boldsymbol{E} = \frac{E_0}{\sqrt{2}}(\hat{\boldsymbol{x}} \pm i\hat{\boldsymbol{y}})e^{i(kz-\omega t)}, \qquad 7.1.8$$

we obtain

$$-k^2\boldsymbol{E} = \mu\epsilon(-\omega^2\boldsymbol{E} \mp 2\beta\omega^2 k\boldsymbol{E} - \beta^2\omega^2k^2\boldsymbol{E}),$$

$$\rightarrow k^2 = \mu\epsilon(\omega^2 \pm 2\beta\omega^2 k + \beta^2\omega^2k^2), \qquad 7.1.9$$

leading to the dispersion relation

$$\omega = \frac{k}{\sqrt{\mu\epsilon}(1 \pm \beta k)}, \qquad 7.1.10$$

and a phase refractive index

$$n_{p\pm} = \sqrt{\mu_r\epsilon_r}(1 \pm \beta k), \qquad 7.1.11$$

where the relative permittivities and permeabilities are defined $\epsilon_r \equiv \epsilon/\epsilon_0$ and $\mu_r \equiv \mu/\mu_0$. The group refractive index for the two polarisations can similarly be found – calling the group velocities $v_{g\pm}$ and the group indices $n_{g\pm}$, we obtain

$$v_{g\pm} \equiv \frac{\partial\omega}{\partial k} = \frac{1}{\sqrt{\mu\epsilon}(1 \pm \beta k)^2}, \qquad 7.1.12$$

$$n_{g\pm} \equiv \frac{c}{v_{g\pm}} = \sqrt{\mu_r\epsilon_r}(1 \pm \beta k)^2. \qquad 7.1.13$$

So the constitutive relations (7.1.1-2) lead to the behaviours one would expect in a chiral medium: left- and right-handed plane waves have different phase and group velocities, and the difference is determined by the chirality parameter β.

7.2 Illustrating the Problem – Helicity per Photon and Group Velocity of Circularly Polarised Light

The first problem with the "naïve" definition of h is revealed if we examine the relationship between helicity density and energy density for circularly polarised plane waves propagating within a chiral medium. The energy density within a chiral medium is given by [4]

$$w = \frac{1}{2}\left(\frac{1}{\epsilon}\boldsymbol{D}\cdot\boldsymbol{D} + \frac{1}{\mu}\boldsymbol{B}\cdot\boldsymbol{B}\right). \qquad 7.2.1$$

For the left- and right-handed plane waves,

$$\boldsymbol{E} = \frac{E_0}{\sqrt{2}}(\hat{\boldsymbol{x}} \pm i\hat{\boldsymbol{y}})e^{i(kz-\omega t)}, \qquad 7.2.2$$

$$\boldsymbol{H} = \frac{E_0}{\sqrt{2}}\sqrt{\frac{\epsilon}{\mu}}(\hat{\boldsymbol{y}} \mp i\hat{\boldsymbol{x}})e^{i(kz-\omega t)}, \qquad 7.2.3$$

$$\boldsymbol{D} = \epsilon\frac{E_0}{\sqrt{2}}\big((1 \pm \beta k)\hat{\boldsymbol{x}} + i\hat{\boldsymbol{y}}(\beta k \pm 1)\big)e^{i(kz-\omega t)}, \qquad 7.2.4$$

$$\boldsymbol{B} = \frac{E_0}{\sqrt{2}}\sqrt{\epsilon\mu}\big((1 \pm \beta k)\hat{\boldsymbol{y}} - (\beta k \pm 1)i\hat{\boldsymbol{x}}\big)e^{i(kz-\omega t)}, \qquad 7.2.5$$

$$\boldsymbol{A} = -\int \boldsymbol{E}\,dt = \frac{E_0}{\sqrt{2}}\frac{1}{\omega}(-i\hat{\boldsymbol{x}} \pm \hat{\boldsymbol{y}})e^{i(kz-\omega t)} = \frac{E_0}{\sqrt{2}}\frac{\sqrt{\epsilon\mu}(1 \pm \beta k)}{k}(-i\hat{\boldsymbol{x}} \pm \hat{\boldsymbol{y}})e^{i(kz-\omega t)}$$

$$= \frac{E_0}{\sqrt{2}}\frac{\sqrt{\epsilon\mu}}{k}\big((\beta k \pm 1)\hat{\boldsymbol{y}} - (1 \pm \beta k)i\hat{\boldsymbol{x}}\big)e^{i(kz-\omega t)} \qquad 7.2.6$$

$$\boldsymbol{C} = -\int \boldsymbol{H}\,dt = \frac{E_0}{\sqrt{2}}\frac{1}{\omega}\sqrt{\frac{\epsilon}{\mu}}(-i\hat{\boldsymbol{y}} \mp \hat{\boldsymbol{x}})e^{i(kz-\omega t)} = \frac{E_0}{\sqrt{2}}\frac{\epsilon}{k}(-(1 \pm \beta k)i\hat{\boldsymbol{y}} - (\beta k \pm 1)\hat{\boldsymbol{x}})e^{i(kz-\omega t)} \quad 7.2.7$$

where the expressions for $\boldsymbol{D}$ and $\boldsymbol{B}$ follow from the constitutive relations. (Note that $\boldsymbol{\nabla} \times \boldsymbol{A} = \pm k\boldsymbol{A} = \boldsymbol{B}$, $\boldsymbol{\nabla} \times \boldsymbol{C} = \pm k\boldsymbol{C} = -\boldsymbol{D}$). The (cycle-averaged) energy density is therefore equal to

$$w_{\pm} = Re\left[\frac{1}{2}\left(\frac{1}{\epsilon}\boldsymbol{D}\cdot\boldsymbol{D}^* + \frac{1}{\mu}\boldsymbol{B}\cdot\boldsymbol{B}^*\right)\right] = \frac{1}{2}\left(\frac{\epsilon E_0^2}{2}[(1 \pm \beta k)^2 + (\beta k \pm 1)^2] + \frac{1}{\mu}\boldsymbol{B}\cdot\boldsymbol{B}^*\right)$$

$$= \frac{1}{2}(\epsilon E_0^2[1 \pm 2\beta k + \beta^2 k^2] + \epsilon E_0^2[1 \pm 2\beta k + \beta^2 k^2]) = \epsilon E_0^2(1 \pm \beta k)^2, \qquad 7.2.8$$

while the helicity density from definition (7.0.1) is equal to

$$h_{\pm} = Re\left[\frac{1}{2}\left(\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{A}^T\cdot\boldsymbol{B}^* - \sqrt{\frac{\mu}{\epsilon}}\boldsymbol{C}\cdot\boldsymbol{D}^*\right)\right] = \frac{1}{2}Re\left[\frac{E_0^2}{2}\frac{\epsilon}{\omega}(2\beta k \pm 2) + \frac{E_0}{2}\frac{\epsilon}{\omega}(2\beta k \pm 2)\right]$$

$$= E_0^2\frac{\epsilon}{\omega}(\beta k \pm 1) \qquad 7.2.9$$

Taking the ratio of energy density to helicity density gives

$$\frac{h^{\pm}}{w^{\pm}} = \frac{1}{\omega(\beta k \pm 1)}, \qquad 7.2.10$$

which is not equal to the expected $\pm\frac{1}{\omega}$.

By contrast, the ratio of the helicity and energy flux densities *is* consistent with a helicity of $\pm\hbar$ per photon. The energy flux density is given by the usual Poynting vector $\boldsymbol{S} = \boldsymbol{E} \times \boldsymbol{H}$. The cycle-averaged energy flux density is therefore

$$\boldsymbol{S} = Re[\boldsymbol{E} \times \boldsymbol{H}^*] = E_0^2\sqrt{\frac{\epsilon}{\mu}}\hat{\boldsymbol{z}}, \qquad 7.2.11$$

while the average helicity flux density is

$$\boldsymbol{v} = Re\left[\frac{1}{2}\left(\sqrt{\frac{\epsilon}{\mu}}\,\boldsymbol{E} \times \boldsymbol{A}^* + \sqrt{\frac{\mu}{\epsilon}}\boldsymbol{H} \times \boldsymbol{C}^*\right)\right] = \pm\frac{1}{\omega}E_0^2\sqrt{\frac{\epsilon}{\mu}}\hat{\boldsymbol{z}}. \qquad 7.2.12$$

Taking the ratio of energy and helicity flux densities for the circularly polarised waves gives

$$\frac{v_z^{\pm}}{S_z^{\pm}} = \pm\frac{1}{\omega}, \tag{7.2.13}$$

as would be expected for a helicity of $\pm\hbar$ per circularly polarised photon. This appears to indicate that it is the helicity density, and not the flux density, which requires modification within a chiral medium.

Finally, we may observe that the helicity as defined by (7.0.1-2) does not travel at the group velocity of the light within a chiral medium. To see this, one can evaluate the speed of travel of helicity by dividing the helicity flux density by the helicity density.

$$\frac{\boldsymbol{v}^{\pm}}{h^{\pm}} = \pm\frac{1}{\sqrt{\epsilon\mu}(\beta k \pm 1)}\hat{\boldsymbol{z}} = \frac{1}{\sqrt{\epsilon\mu}(1 \pm \beta k)}\hat{\boldsymbol{z}}, \tag{7.2.14}$$

which is not equal to the group velocity $v_{g\pm} = \frac{1}{\sqrt{\epsilon\mu}(1\pm\beta k)^2}$.

7.3 Helicity Conservation at a Dual-Symmetric Interface

In chapter 2, §2.6**,** it was shown that Maxwell's equations within a dielectric medium are invariant under a generalised duality transform, provided that $\boldsymbol{\nabla}\left(\sqrt{\frac{\epsilon}{\mu}}\right) = \boldsymbol{\nabla}\left(\sqrt{\frac{\mu}{\epsilon}}\right) = 0$ throughout the region under consideration [5]. The modified constitutive relations (7.1.1-2) do not affect this argument, and so the same conclusion holds within a chiral medium.

In chapter 2, we also showed – by starting with the expressions (7.0.1-2) – how the local continuity of helicity in an achiral dielectric medium can be expressed by the equation

$$\frac{\partial h}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{v} = \frac{1}{2}\boldsymbol{\nabla}\left(\sqrt{\frac{\epsilon}{\mu}}\right)\boldsymbol{E}\times\boldsymbol{A} + \frac{1}{2}\boldsymbol{\nabla}\left(\sqrt{\frac{\mu}{\epsilon}}\right)\boldsymbol{H}\times\boldsymbol{C}. \tag{7.3.1}$$

This is consistent with the connection between helicity conservation and the generalised duality symmetry, as the right hand side vanishes when $\boldsymbol{\nabla}\left(\sqrt{\frac{\epsilon}{\mu}}\right) = \boldsymbol{\nabla}\left(\sqrt{\frac{\mu}{\epsilon}}\right) = 0$, turning the continuity equation into a local conservation law.

However, repeating the derivation of chapter 2 with the Drude-Born-Federov constitutive relations (7.1.1-2), while keeping the helicity density and flux definitions (7.0.1-2)**,** gives

$$\frac{\partial h}{\partial t} + \boldsymbol{\nabla}\cdot\boldsymbol{v} = -\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}\cdot\boldsymbol{B} + \sqrt{\frac{\mu}{\epsilon}}\boldsymbol{H}\cdot\boldsymbol{D} + \frac{1}{2}\boldsymbol{\nabla}\left(\sqrt{\frac{\epsilon}{\mu}}\right)\boldsymbol{E}\times\boldsymbol{A} + \frac{1}{2}\boldsymbol{\nabla}\left(\sqrt{\frac{\mu}{\epsilon}}\right)\boldsymbol{H}\times\boldsymbol{C}. \tag{7.3.2}$$

Under the achiral constitutive relations, the first two terms (which arise from the time derivative of the helicity density) are equal and opposite. However, under the Drude-Born-Federov relations they instead reduce to

$$-\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}\cdot\boldsymbol{B}+\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{H}\cdot\boldsymbol{D}=\sqrt{\epsilon\mu}\beta(\boldsymbol{H}\cdot\nabla\times\boldsymbol{E}-\boldsymbol{E}\cdot\nabla\times\boldsymbol{H}), \qquad 7.3.3$$

which is in general non-zero. This contribution to the "source" side of the continuity equation (7.3.2) persists even when the $\nabla\left(\sqrt{\frac{\epsilon}{\mu}}\right)=\nabla\left(\sqrt{\frac{\mu}{\epsilon}}\right)=0$, leading to the conclusion that – if the definition (7.0.1) is adopted – helicity is not generally conserved in a chiral medium even if the medium is dual-symmetric. This indicates that the density defined by (7.0.1) is not related by Noether's theorem to macroscopic duality symmetry in a chiral medium.

7.4 Modifying the Helicity Density

The considerations above suggest modifying the helicity density to

$$h'=\frac{1}{2}\left(\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{A}^T\cdot\boldsymbol{B}-\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{C}\cdot\boldsymbol{D}\right)+\sqrt{\epsilon\mu}\beta w. \qquad 7.4.1$$

This modification, by construction, will remove the unwanted "source" term $\sqrt{\epsilon\mu}\beta(\boldsymbol{H}\cdot\nabla\times\boldsymbol{E}-\boldsymbol{E}\cdot\nabla\times\boldsymbol{H})$ from the continuity equation in a dual-symmetric interface. This is because it is precisely opposite to the time derivative of the additional term $\sqrt{\epsilon\mu}\beta w$. We can use the *DBF* constitutive relations to show

$$\begin{aligned}\sqrt{\epsilon\mu}\beta\frac{\partial}{\partial t}w&=\sqrt{\epsilon\mu}\beta\frac{\partial}{\partial t}\frac{1}{2}\left(\frac{1}{\epsilon}\boldsymbol{D}\cdot\boldsymbol{D}+\frac{1}{\mu}\boldsymbol{B}\cdot\boldsymbol{B}\right)=\sqrt{\epsilon\mu}\beta\left(\frac{1}{\epsilon}\boldsymbol{D}\cdot\dot{\boldsymbol{D}}+\frac{1}{\mu}\boldsymbol{B}\cdot\dot{\boldsymbol{B}}\right)\\&=\sqrt{\epsilon\mu}\beta\left(\frac{1}{\epsilon}\boldsymbol{D}\cdot\nabla\times\boldsymbol{H}-\frac{1}{\mu}\boldsymbol{B}\cdot\nabla\times\boldsymbol{E}\right)\\&=\sqrt{\epsilon\mu}\beta\big((\boldsymbol{E}+\beta\nabla\times\boldsymbol{E})\cdot\nabla\times\boldsymbol{H}-(\boldsymbol{H}+\beta\nabla\times\boldsymbol{H})\cdot\nabla\times\boldsymbol{E}\big)\\&=\sqrt{\epsilon\mu}\beta(\boldsymbol{E}\cdot\nabla\times\boldsymbol{H}-\boldsymbol{H}\cdot\nabla\times\boldsymbol{E}).\end{aligned} \qquad 7.4.2$$

The modification also produces the correct ratio of helicity to energy density for circularly polarised plane waves. Using the energy density (7.2.1), we find that the helicity density for a circularly polarised wave becomes

$$\begin{aligned}h'^{\pm}&=E_0^2\frac{\epsilon}{\omega}(\beta k\pm 1)+\sqrt{\epsilon\mu}\beta\epsilon E_0^2(1\pm\beta k)^2=E_0^2\frac{\epsilon}{\omega}(\beta k\pm 1)+\beta\epsilon E_0^2(1\pm\beta k)\frac{k}{\omega}\\&=E_0^2\frac{\epsilon}{\omega}(\beta k\pm 1)+\beta kE_0^2(1\pm\beta k)\frac{\epsilon}{\omega}=E_0^2\frac{\epsilon}{\omega}(2\beta k\pm 1\pm\beta^2k^2)\\&=\pm E_0^2\frac{\epsilon}{\omega}(\pm 2\beta k+1+\beta^2k^2)=\pm E_0^2\frac{\epsilon}{\omega}(1\pm\beta k)^2.\end{aligned} \qquad 7.4.3$$

We therefore find that

$$\frac{h'^{\pm}}{w^{\pm}}=\frac{\left[\pm E_0^2\frac{\epsilon}{\omega}(1\pm\beta k)^2\right]}{\epsilon E_0^2(1\pm\beta k)^2}=\pm\frac{1}{\omega}, \qquad 7.4.4$$

as expected. We similarly arrive at the expected group velocity,

$$\frac{\boldsymbol{v}^{\pm}}{h'^{\pm}} = \frac{\pm\frac{1}{\omega}E_0^2\sqrt{\frac{\epsilon}{\mu}}\hat{\boldsymbol{z}}}{\pm E_0^2\frac{\epsilon}{\omega}(1\pm\beta k)^2} = \frac{1}{\sqrt{\epsilon\mu}(1\pm\beta k)^2}\hat{\boldsymbol{z}}. \qquad 7.4.5$$

7.5 Noether's Theorem in a Dual-Symmetric Chiral Medium

The motivating arguments above can be given formal justification by applying Noether's theorem to the Lagrangian describing a system in which ϵ, μ and β are functions of position, but the dual-symmetry condition $\boldsymbol{\nabla}\left(\sqrt{\frac{\epsilon}{\mu}}\right) = \boldsymbol{\nabla}\left(\sqrt{\frac{\mu}{\epsilon}}\right) = 0$ holds everywhere. In the absence of free currents and charges the generalised duality symmetry holds, and we use Noether's theorem to identify the conserved quantity which corresponds to this. We note that $\epsilon(\boldsymbol{r})$, $\mu(\boldsymbol{r})$ or $\beta(\boldsymbol{r})$ may vary in space as rapidly as desired, and so our treatment applies equally well to interfaces between different media, provided that the ratio $\sqrt{\frac{\epsilon}{\mu}}$ always remains constant. We also assume that dispersion and loss can always be neglected (that is, the functions $\epsilon(\boldsymbol{r})$ and $\mu(\boldsymbol{r})$ are real and frequency independent). For notational clarity, we will leave the position dependence of ϵ, μ and β implicit in the calculations below.

Guided by the form of the energy density (7.2.1), we write the Lagrangian density of our system (in the absence of free currents and charges) as

$$\mathcal{L} = \frac{1}{2}\left(\frac{1}{\epsilon}\boldsymbol{D}\cdot\boldsymbol{D} - \frac{1}{\mu}\boldsymbol{B}\cdot\boldsymbol{B}\right). \qquad 7.5.1$$

The choice of Lagrangian is justified in appendix B where it is shown, in conjunction with the *DBF* constitutive relations, to lead to the correct field equations in a chiral medium. As discussed in chapter 2, the infinitesimal duality transformation in a medium is given by

$$\boldsymbol{D}' = \boldsymbol{D} + \theta\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{B}, \qquad 7.5.2$$

$$\boldsymbol{B}' = \boldsymbol{B} - \theta\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{D}, \qquad 7.5.3$$

with θ an infinitesimal parameter. Substituting the duality transformation into the Lagrangian density, we find the change in $\mathcal{L}$ to be

$$\mathcal{L}' - \mathcal{L} = \frac{2\theta}{\sqrt{\epsilon\mu}}\boldsymbol{D}\cdot\boldsymbol{B}, \qquad 7.5.4$$

with terms of 2nd order and higher in θ neglected. While the duality transformation does not leave the Lagrangian (7.5.1) unchanged, we find – as in chapter 2 – that the change in the Lagrangian can be written as a 4-divergence,

$$\mathcal{L}' - \mathcal{L} = \frac{2\theta}{\sqrt{\epsilon\mu}}\boldsymbol{D}\cdot(\boldsymbol{\nabla}\times\boldsymbol{A}) = 2\theta\sqrt{\frac{\epsilon}{\mu}}\left(-\frac{\partial\boldsymbol{A}}{\partial t} - \boldsymbol{\nabla}\phi - \beta\boldsymbol{\nabla}\times\frac{\partial\boldsymbol{A}}{\partial t}\right)\cdot(\boldsymbol{\nabla}\times\boldsymbol{A})$$

$$= \theta\sqrt{\frac{\epsilon}{\mu}}\left[\frac{\partial}{\partial t}\left(-\boldsymbol{A}\cdot\boldsymbol{\nabla}\times\boldsymbol{A} - \beta(\boldsymbol{\nabla}\times\boldsymbol{A})^2\right) - \boldsymbol{\nabla}\cdot\left(\boldsymbol{E}\times\boldsymbol{A} + \phi(\boldsymbol{\nabla}\times\boldsymbol{A})\right)\right]. \qquad 7.5.5$$

This is similar to the 4-divergence from chapter 2 (2.2.15), and it was there noted that the terms in the time and space derivatives corresponded to the magnetic parts of the helicity density and flux density. Here, because of the *DBF* constitutive relations, we find the extra term $-\beta(\boldsymbol{\nabla}\times\boldsymbol{A})^2$ in the time derivative. Recognising that $\nabla\times\boldsymbol{A}\equiv\boldsymbol{B}$, we see that this term is proportional to the magnetic half of the energy density. Indeed, it is the magnetic half of the additional term $\sqrt{\epsilon\mu}\beta w$ which we have suggested is added to the helicity density in a chiral medium.

As in the free-space case, we find the term $\phi(\boldsymbol{\nabla}\times\boldsymbol{A})$ in the flux density, which we omit from here on as it does not contribute to the total change in the Lagrangian (for further discussion, see chapter 2). We also note that the right-hand side of (7.5.5) is only a four-divergence if $\sqrt{\frac{\epsilon}{\mu}}$ is position independent – this is, of course, the condition for macroscopic duality symmetry.

To proceed further, we make use of Noether's theorem. We express the change in the Lagrangian as

$$\mathcal{L}' - \mathcal{L} = \frac{\partial}{\partial x_\alpha}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\delta\varphi_r + \sum_{\beta>\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\delta\varphi_{r,\beta} - \sum_{\beta<\alpha}\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r\right]. \qquad 7.5.6$$

and then by subtracting the 4-divergence (7.5.5) from both sides, we may read off a local continuity equation[2].

In three-vector notation, keeping only the derivatives that are not trivially zero, (7.5.6) becomes

$$\mathcal{L}' - \mathcal{L} = \frac{\partial}{\partial t}\left(\frac{\partial\mathcal{L}}{\partial\dot{\boldsymbol{A}}}\cdot\delta\boldsymbol{A} + \frac{\partial\mathcal{L}}{\partial(\partial_a\dot{\boldsymbol{A}})}\cdot\delta(\partial_a\boldsymbol{A})\right) + \frac{\partial}{\partial x}\left(\frac{\partial\mathcal{L}}{\partial(\partial_x\boldsymbol{A})}\cdot\delta\boldsymbol{A} - \frac{\partial}{\partial t}\left[\frac{\partial\mathcal{L}}{\partial(\partial_x\dot{\boldsymbol{A}})}\right]\cdot\delta\boldsymbol{A}\right)$$

$$+\frac{\partial}{\partial y}\left(\frac{\partial\mathcal{L}}{\partial(\partial_y\boldsymbol{A})}\cdot\delta\boldsymbol{A} - \frac{\partial}{\partial t}\left[\frac{\partial\mathcal{L}}{\partial(\partial_y\dot{\boldsymbol{A}})}\right]\cdot\delta\boldsymbol{A}\right) + \frac{\partial}{\partial z}\left(\frac{\partial\mathcal{L}}{\partial(\partial_z\boldsymbol{A})}\cdot\delta\boldsymbol{A} - \frac{\partial}{\partial t}\left[\frac{\partial\mathcal{L}}{\partial(\partial_z\dot{\boldsymbol{A}})}\right]\cdot\delta\boldsymbol{A}\right). \qquad 7.5.7$$

[2] The expression for the change in the Lagrangian is more complicated here than that given in chapter 2. This is because, by virtue of the curls of the fields which appear in the *DBF* constitutive relations, the Lagrangian (7.5.1) contains second derivatives of the potentials (these are shown explicitly in (7.5.14) below). This modifies the form of the Euler-Lagrange equations (which are usually presented assuming the Lagrangian contains only first derivatives of the coordinates), and therefore also the expression for the conserved current. A fuller discussion and derivation of the result is presented in appendix C.

To evaluate this, we require explicit expressions for the changes in the potentials under the duality transformation, $\delta\phi$ and $\delta\boldsymbol{A}$, as well as the relevant derivatives of the Lagrangian with respect to the potentials. We obtain these by following a similar approach as was presented in chapter 2. To begin with, we see from the duality transformation equations (7.5.2-7.5.3) that the following must be satisfied by $\delta\phi$ and $\delta\boldsymbol{A}$

$$\boldsymbol{B}' = \boldsymbol{B} - \theta\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{D} \Rightarrow \nabla\times\delta\boldsymbol{A} = -\theta\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{D} = \theta\sqrt{\frac{\mu}{\epsilon}}\left(\frac{\partial\boldsymbol{A}}{\partial t} + \nabla\phi + \beta\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right), \quad 7.5.8$$

$$\boldsymbol{D}' = \boldsymbol{D} + \theta\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{B} \Rightarrow \epsilon\left(-\frac{\partial(\delta\boldsymbol{A})}{\partial t} - \nabla(\delta\phi) - \beta\nabla\times\frac{\partial(\delta\boldsymbol{A})}{\partial t}\right) = \theta\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{B} = \theta\sqrt{\frac{\epsilon}{\mu}}\nabla\times\boldsymbol{A}. \quad 7.5.9$$

The general solution to these two equations can be written

$$\delta\phi = -\theta\frac{\partial\chi}{\partial t}, \quad 7.5.10$$

$$\delta\boldsymbol{A} = \theta\nabla\chi + \theta\sqrt{\frac{\mu}{\epsilon}}\,\mathbf{C}, \quad 7.5.11$$

where χ is any scalar field, and $\boldsymbol{C}$ is any vector field which satisfies

$$\frac{\partial\boldsymbol{C}}{\partial t} = -\frac{1}{\mu}\nabla\times\boldsymbol{A} - \beta\epsilon\left(\frac{\partial}{\partial t}\nabla\phi + \frac{\partial^2\boldsymbol{A}}{\partial t^2} + \beta\nabla\times\frac{\partial^2\boldsymbol{A}}{\partial t^2}\right), \quad 7.5.12$$

$$\nabla\times\mathbf{C} = \epsilon\left(\nabla\phi + \frac{\partial\boldsymbol{A}}{\partial t} + \beta\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right). \quad 7.5.13$$

As in chapter 2, we see that χ is associated with an ordinary gauge transformation, and that the vector potential $\boldsymbol{C}$ is associated with the duality transformation. As we are only interested in the duality transformation, we set χ to 0 for the remainder of this derivation.

In order to write down the required derivatives of the Lagrangian, we express the Lagrangian in terms of the potentials $\boldsymbol{A}$ and ϕ,

$$\mathcal{L} = \frac{1}{2}\left(\epsilon\left(-\nabla\phi - \frac{\partial\boldsymbol{A}}{\partial t} - \beta\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right)^2 - \frac{1}{\mu}(\nabla\times\boldsymbol{A})^2\right) \quad 7.5.14$$

$$= \frac{1}{2}\left(\epsilon\left((\nabla\phi)^2 + 2\frac{\partial\boldsymbol{A}}{\partial t}\cdot\nabla\phi + \left(\frac{\partial\boldsymbol{A}}{\partial t}\right)^2 + 2\beta\left(\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right)\cdot\nabla\phi + 2\beta\left(\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right)\cdot\frac{\partial\boldsymbol{A}}{\partial t} + \beta^2\left(\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right)^2\right)\right.$$
$$\left. - \frac{1}{\mu}(\nabla\times\boldsymbol{A})^2\right).$$

The relevant derivatives are therefore

$$\frac{\partial\mathcal{L}}{\partial\dot{\phi}} = 0, \quad 7.5.15$$

$$\frac{\partial\mathcal{L}}{\partial\dot{\boldsymbol{A}}} = \epsilon\left(\frac{\partial\boldsymbol{A}}{\partial t} + \nabla\phi + \beta\left(\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right)\right), \quad 7.5.16$$

$$\frac{\partial\mathcal{L}}{\partial(\nabla\phi)} = \epsilon\left(\frac{\partial\boldsymbol{A}}{\partial t} + \nabla\phi + \beta\left(\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right)\right), \quad 7.5.17$$

$$\frac{\partial\mathcal{L}}{\partial(\partial_a\boldsymbol{A})} = -\frac{1}{2\mu}\frac{\partial}{\partial(\partial_a\boldsymbol{A})}(\boldsymbol{\nabla}\times\boldsymbol{A})^2 = \frac{1}{\mu}\boldsymbol{n}_a\times(\nabla\times\boldsymbol{A}), \quad 7.5.18$$

$$\frac{\partial\mathcal{L}}{\partial(\partial_a\dot{\boldsymbol{A}})} = \frac{\partial}{\partial(\partial_a\dot{\boldsymbol{A}})}\left[\frac{1}{2}\epsilon\beta^2\left(\boldsymbol{\nabla}\times\frac{\partial\boldsymbol{A}}{\partial t}\right)^2 + \beta\epsilon\left(\boldsymbol{\nabla}\times\frac{\partial\boldsymbol{A}}{\partial t}\right)\cdot\boldsymbol{\nabla}\phi + \beta\epsilon\left(\boldsymbol{\nabla}\times\frac{\partial\boldsymbol{A}}{\partial t}\right)\cdot\frac{\partial\boldsymbol{A}}{\partial t}\right]$$

$$= -\epsilon\beta^2\boldsymbol{n}_a\times\left(\boldsymbol{\nabla}\times\frac{\partial\boldsymbol{A}}{\partial t}\right) - \beta\epsilon\boldsymbol{n}_a\times\boldsymbol{\nabla}\phi - \beta\epsilon\boldsymbol{n}_a\times\frac{\partial\boldsymbol{A}}{\partial t} = -\epsilon\beta\boldsymbol{n}_a\times\left[\beta\left(\nabla\times\frac{\partial\boldsymbol{A}}{\partial t}\right) + \boldsymbol{\nabla}\phi + \frac{\partial\boldsymbol{A}}{\partial t}\right] \quad 7.5.19$$

where $\boldsymbol{n}_a$ is a unit vector in the a direction. The results (7.5.15-7.5.18) may be compared to (2.2.19-22), from which they differ only by the two β dependent terms in (7.5.16) and (7.5.17), and by the replacement of ϵ_0 and μ_0 by $\epsilon(\boldsymbol{r})$ and $\mu(\boldsymbol{r})$. We also require expressions for the derivatives of $\delta\boldsymbol{A}$,

$$\delta\dot{\boldsymbol{A}} = \theta\sqrt{\frac{\mu}{\epsilon}}\frac{\partial\boldsymbol{C}}{\partial t}, \quad 7.5.20$$

$$\delta(\partial_a\boldsymbol{A}) = \theta\sqrt{\frac{\mu}{\epsilon}}\,\partial_a\mathbf{C}, \quad 7.5.21$$

where we have made use of the dual symmetry condition $\boldsymbol{\nabla}\sqrt{\frac{\mu}{\epsilon}} = 0$ in writing the final line.

We obtain the components of the helicity density and flux density by examining each term of (7.5.7) in turn. Examination of the time derivative shows

$$\frac{\partial\mathcal{L}}{\partial\dot{\boldsymbol{A}}}\cdot\delta\boldsymbol{A} + \frac{\partial\mathcal{L}}{\partial(\partial_a\dot{\boldsymbol{A}})}\cdot\delta(\partial_a\boldsymbol{A})$$

$$= \theta\sqrt{\epsilon\mu}\left(\frac{\partial\boldsymbol{A}}{\partial t} + \boldsymbol{\nabla}\phi + \beta\left(\boldsymbol{\nabla}\times\frac{\partial\boldsymbol{A}}{\partial t}\right)\right)\cdot\boldsymbol{C} - \theta\sqrt{\epsilon\mu}\beta\boldsymbol{n}_a\times\left[\beta(\nabla\times\dot{\boldsymbol{A}}) + \boldsymbol{\nabla}\phi + \frac{\partial\boldsymbol{A}}{\partial t}\right]\cdot\,\partial_a\boldsymbol{C}$$

$$= -\theta\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{D}\cdot\boldsymbol{C} + \theta\sqrt{\epsilon\mu}\beta\frac{1}{\epsilon}\;\boldsymbol{D}\cdot\boldsymbol{D}, \quad 7.5.22$$

as

$$-\theta\sqrt{\epsilon\mu}\beta\boldsymbol{n}_a\times\left[\beta(\nabla\times\dot{\boldsymbol{A}}) + \boldsymbol{\nabla}\phi + \frac{\partial\boldsymbol{A}}{\partial t}\right]\cdot\,\partial_a\boldsymbol{C} = \theta\sqrt{\epsilon\mu}\beta\frac{1}{\epsilon}\,\boldsymbol{n}_a\times[\boldsymbol{D}]\cdot\,\partial_a\boldsymbol{C}$$

$$= -\theta\sqrt{\epsilon\mu}\beta\frac{1}{\epsilon}\,\boldsymbol{n}_a\times\partial_a\boldsymbol{C}\cdot\;\boldsymbol{D} = -\theta\sqrt{\epsilon\mu}\beta\;\frac{1}{\epsilon}\;(\boldsymbol{\nabla}\times\boldsymbol{C})\cdot\;\boldsymbol{D} \quad 7.5.23$$

This is equal to the electric half of the helicity density, with an added term proportional to the electric half of the energy density.

For the flux density, we examine the space derivatives,

$$\frac{\partial\mathcal{L}}{\partial(\partial_a\boldsymbol{A})}\cdot\delta\boldsymbol{A} - \frac{\partial}{\partial t}\left[\frac{\partial\mathcal{L}}{\partial(\partial_a\dot{\boldsymbol{A}})}\right]\cdot\delta\boldsymbol{A}$$

$$= \theta\frac{1}{\sqrt{\epsilon\mu}}\boldsymbol{n}_a\times(\boldsymbol{\nabla}\times\boldsymbol{A})\cdot\boldsymbol{C} + \theta\sqrt{\frac{\mu}{\epsilon}}\frac{\partial}{\partial t}\left[\epsilon\beta\boldsymbol{n}_a\times\left[\beta(\nabla\times\dot{\boldsymbol{A}}) + \boldsymbol{\nabla}\phi + \frac{\partial\boldsymbol{A}}{\partial t}\right]\right]\cdot\;\boldsymbol{C}. \quad 7.5.24$$

As the scalar triple product $(\boldsymbol{A}\times\boldsymbol{B})\cdot\boldsymbol{C}$ is invariant under cyclic permutations of the arguments, we can re-write this as

$$\theta\frac{1}{\sqrt{\epsilon\mu}}(\boldsymbol{B}\times\mathbf{C})_a+\theta\sqrt{\epsilon\mu}\left(\frac{\partial}{\partial t}\left[\beta^2\big(\boldsymbol{\nabla}\times\dot{\boldsymbol{A}}\big)+\beta\boldsymbol{\nabla}\phi+\beta\frac{\partial\boldsymbol{A}}{\partial t}\right]\times\boldsymbol{C}\right)_a$$

$$=\theta\sqrt{\frac{\mu}{\epsilon}}\left(\left(\frac{1}{\mu}\boldsymbol{B}-\beta\dot{\boldsymbol{D}}\right)\times\boldsymbol{C}\right)_a$$

$$=\theta\sqrt{\frac{\mu}{\epsilon}}\left(\left(\frac{1}{\mu}\boldsymbol{B}-\beta\boldsymbol{\nabla}\times\boldsymbol{H}\right)\times\boldsymbol{C}\right)_a$$

$$=\theta\sqrt{\frac{\mu}{\epsilon}}(\boldsymbol{H}\times\boldsymbol{C})_a, \qquad 7.5.25$$

where Maxwell's equations have been used to write $\dot{\boldsymbol{D}}=\boldsymbol{\nabla}\times\boldsymbol{H}$, and the constitutive relations have been used in the final step.

We finally put the two expressions for $\mathcal{L}'-\mathcal{L}$, (7.5.5) and (7.5.7), together to obtain

$$\sqrt{\frac{\epsilon}{\mu}}\left[\frac{\partial}{\partial t}(-\boldsymbol{A}\cdot\boldsymbol{B}-\beta\boldsymbol{B}^2)-\boldsymbol{\nabla}\cdot(\boldsymbol{E}\times\boldsymbol{A}+\phi\boldsymbol{B})\right]=\sqrt{\frac{\mu}{\epsilon}}\left[\frac{\partial}{\partial t}(-\boldsymbol{D}\cdot\boldsymbol{C}+\beta\ \boldsymbol{D}\cdot\boldsymbol{D})+\boldsymbol{\nabla}\cdot(\boldsymbol{H}\times\boldsymbol{C})\right], \qquad 7.5.26$$

which can be rearranged to form the local conservation law

$$\frac{\partial}{\partial t}\left[\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{A}\cdot\boldsymbol{B}-\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{C}\cdot\boldsymbol{D}+\beta\sqrt{\epsilon\mu}\left(\frac{1}{\epsilon}\boldsymbol{D}^2+\frac{1}{\mu}\boldsymbol{B}^2\right)\right]+\boldsymbol{\nabla}\cdot\left(\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}\times\boldsymbol{A}+\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{H}\times\boldsymbol{C}\right)=0. \qquad 7.5.27$$

This proves that the helicity density is indeed modified in the manner suggested in section 7.4. We see that the flux density is unchanged from (7.0.2), but the density is modified according to (7.4.1). An alternative derivation of this result, which varies a dual-symmetric Lagrangian density over both $\boldsymbol{A}$ and $\boldsymbol{C}$, is presented in [6].

7.6 Conclusions

This chapter has examined the helicity density within a chiral medium, and has argued that the presence of material chirality requires that the definition is modified to include a term proportional to the energy density and the chirality parameter of the medium. In terms of the fields in the medium, the full definition is given by

$$h=\frac{1}{2}\left[\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{A}\cdot\boldsymbol{B}-\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{C}\cdot\boldsymbol{D}+\beta\sqrt{\epsilon\mu}\left(\frac{1}{\epsilon}\boldsymbol{D}^2+\frac{1}{\mu}\boldsymbol{B}^2\right)\right]. \qquad 7.6.1$$

This differs from the standard definition of helicity within an achiral dielectric medium, (7.0.1), by the addition of the chirality-dependent term $\frac{1}{2}\beta\sqrt{\epsilon\mu}\left(\frac{1}{\epsilon}\boldsymbol{D}^2+\frac{1}{\mu}\boldsymbol{B}^2\right)$. The flux density, by contrast, remains unchanged from its achiral value, and is given by

$$\boldsymbol{v}=\frac{1}{2}\left(\sqrt{\frac{\epsilon}{\mu}}\boldsymbol{E}\times\boldsymbol{A}+\sqrt{\frac{\mu}{\epsilon}}\boldsymbol{H}\times\boldsymbol{C}\right). \qquad 7.6.2$$

This conclusion is suggested by the requirement that the helicity-per-photon for circularly polarised light within a chiral medium remains $\pm\hbar$, and the requirement that the total helicity is conserved in dual-symmetric conditions – neither of which are satisfied by (7.0.1). It may be ultimately justified because the quantities (7.6.1) and (7.6.2) form the conserved current corresponding to macroscopic duality symmetry within a chiral medium.

References

[1] Crimin F., Mackinnon N., Götte J. B. and Barnett S. M. 2019 On the Conservation of Helicity in a Chiral medium *Journal of Optics* **21** 094003

[2] Lekner J. 1996 Optical Properties of Isotropic Chiral Media *Pure and Applied Optics: Journal of the European Optical Society A* **5** 417

[3] Bassiri S., Papas C. H. and Engheta N. 1988 Electromagnetic Wave Propagation Through a Dielectric-chiral Interface and Through a Chiral Slab *Journal of the Optical Society of America A* **5** 1450–9

[4] Proskurin I., Ovchinnikov A. S., Nosov P. and Kishine J. 2017 Optical Chirality in Gyrotropic Media: Symmetry Approach *New Journal of Physics* **19** 063021

[5] Van Kruining K. and Gotte J. B. 2016 The Conditions for the Preservation of Duality Symmetry in a Linear Medium *Journal of Optics* **18** 085601

[6] Crimin F., Mackinnon N., Götte J. B. and Barnett S. M. 2020 Continuous Symmetries and Conservation Laws in Chiral Media *SPIE OPTO Proceedings Volume 11297 Complex Light and Optical Forces XIV112970J*

Chapter 8 – Semiclassical Electrodynamics

The remainder of this thesis focuses on molecular light scattering, and this chapter presents some of the key background necessary to follow the subsequent chapter's work. We present the apparatus used for a semiclassical treatment of molecular light scattering in terms of molecular polarisability tensors which describe the scatterer.

We begin with a derivation of the multipolar Hamiltonian from the minimal coupling form by means of the Power-Zienau-Wooley transformation. This multipolar Hamiltonian then forms the starting point for a perturbation-theory treatment of linear light scattering, which leads to explicit quantum-mechanical expressions for a series of molecular polarisability tensors. We then examine how these results may be refined and extended to cover scattering in regions of absorption through the inclusion of complex frequencies, and also Raman scattering through the use of the appropriate transition matrix elements. The final, general results for the polarisability tensors are summarised in section 8.10. In section 8.11 we go on to introduce the Stokes parameters as a convenient way to describe the scattered light and its polarisation.

We then examine the behaviour of the polarisability tensors under a change of the origin about which the multipole expansion is taken – the tensors are not invariant under such a transformation, although predictions of observable effects will be. Finally, we briefly discuss some ways in which the property tensor components are constrained by the symmetries of the scatterers which they describe, and how inference of polarisability tensor components therefore provides information about molecular structure.

8.1 From the Minimal Coupling to the Multipolar Hamiltonian – The PZW Transformation

For a system of α charges, the minimal-coupling Hamiltonian is written

$$\hat{H}^{min.\ coup.} = \sum_{\alpha} \frac{\left(\hat{\boldsymbol{p}}_{\alpha} - q_{\alpha}\hat{\boldsymbol{A}}(\boldsymbol{x}_{\alpha})\right)^2}{2m_{\alpha}} + \frac{1}{2}\int \hat{\phi}(\boldsymbol{r}')\hat{\rho}(\boldsymbol{r}')\, d^3\boldsymbol{r}' + \frac{1}{2}\int \left[\epsilon_0 {\hat{\boldsymbol{E}}^{T}}{}^{2}(\boldsymbol{r}') + \frac{1}{\mu_0}\hat{\boldsymbol{B}}^2(\boldsymbol{r}')\right] d^3\boldsymbol{r}' \quad 8.1.1$$

where $\hat{\boldsymbol{p}}_{\alpha}$ is the canonical momentum of the α^{th} charge, q_{α} is the charge of the α^{th} charge and $\boldsymbol{x}_{\alpha}$ its position, $\hat{\boldsymbol{A}}$ is the vector potential, $\hat{\phi}$ the scalar potential, $\hat{\rho}$ the charge density and $\hat{\boldsymbol{E}}^{T}$ and $\hat{\boldsymbol{B}}$ the transverse electric and magnetic field operators[1]. The first term, therefore, represents the kinetic energy of the charges, the second term their potential energy and the third term the energy of the field. Note that this expression presupposes the Coulomb gauge. Note also the infinite self-energies in the Coulomb term, and the lack of retardation.

[1] Throughout this chapter we will use Greek letters to label charges, and Roman letters to label vector or tensor components. Repeated Roman indices are to be understood as implicit sums in the usual way.

When describing the interaction of light with molecules, a key simplifying feature is that the dimensions of the molecules are almost always small compared to the wavelength of the incident light. This mismatch of length scales invites the use of the multipolar series discussed in chapter 4. One might hope that if the charge distribution can be described by a multipolar series, the total energy of the system could be written in terms of the energy of the electric dipole moment in an external field, the energy of the magnetic dipole, and so on – and that for a sufficiently compact distribution of charge, an accurate description would require only the first few terms to be retained. In a static field this would be straightforward – but the complication in a dynamic field, of course, is that the field and the molecule can interact. This makes the separation into "external field" and molecule difficult, and strictly speaking the two must be treated together as one quantum-mechanical system [1]. How, then, could such simplifications be brought into the above Hamiltonian?

It is possible to cast the above Hamiltonian into a form that explicitly brings out the multipole moments by means of a unitary transformation known as the Power-Zienau-Wooley transformation [2]. The transformed Hamiltonian is defined by

$$\widehat{H}^{mult.} = \widehat{U}^{-1}\widehat{H}^{min.coup.}\,\widehat{U}, \tag{8.1.2}$$

with

$$\widehat{U} = \exp\left[\frac{i}{\hbar}\int \widehat{\boldsymbol{P}}(\boldsymbol{r}')\cdot\widehat{\boldsymbol{A}}(\boldsymbol{r}')\,d^{3}\boldsymbol{r}'\right] \tag{8.1.3}$$

where $\widehat{\boldsymbol{P}}$ is the electric polarisation field. Explicitly, for an overall neutral collection of point charges at positions $\boldsymbol{r}_\alpha$, we take

$$\widehat{\boldsymbol{P}}(\boldsymbol{r}) = \sum_{\alpha}\widehat{\boldsymbol{r}}_\alpha q_\alpha \int_0^1 \delta(\boldsymbol{r} - u\widehat{\boldsymbol{r}}_\alpha)du\,. \tag{8.1.4}$$

For each charge, the contribution to the polarisation field is uniformly located on the line connecting that charge to the origin, and is directed along this line with a magnitude proportional to the charge and its distance from the origin. We can visualise this way of describing a point charge at $\boldsymbol{r}_\alpha$ by considering the continuous limit of a line of electric dipoles along the line connecting the charge to the origin. In the limit of a very large number of equally spaced dipoles, the positive and negative charges of the adjacent dipoles cancel, and all that is left are the charges q_α at $\boldsymbol{r}_\alpha$ and -q_α at the origin[2].

---

[2] This is like an electric version of the "Dirac string", which represents a magnetic monopole as one end of a long chain of magnetic dipoles. There is one important difference – the Dirac string is half-infinite, and leads to a magnetic monopole [3 §6.12], whereas the polarisation density given here lies along a finite line segment. So for each charge at $\boldsymbol{r}_\alpha$, there is a corresponding charge of opposite sign at the origin. This leads to no problems for a collection of charges which is neutral overall. In fact, this treatment can also accommodate systems which are not neutral overall – a polarisation

8.2. Proving the Polarisation Density is Acceptable

We can also show explicitly that this is an acceptable choice for the polarisation density with the equations

$$\hat{\rho}_{bound}(\boldsymbol{r},t) = -\nabla \cdot \widehat{\boldsymbol{P}}(\boldsymbol{r},t) \qquad 8.2.1$$

and

$$\hat{\boldsymbol{J}}(\boldsymbol{r},t) = \frac{\partial \widehat{\boldsymbol{P}}}{\partial t} + \nabla \times \widehat{\boldsymbol{M}}. \qquad 8.2.2$$

A formal solution for $\widehat{\boldsymbol{P}}$ can be constructed the via a Fourier transformation. If the charge density is taken to consist of a collection of point charges each at position $\boldsymbol{r}_\alpha(t)$, and we choose to account for all of the charge density as "bound" charge, then we have

$$\hat{\rho}_{bound}(\boldsymbol{r},t) = \sum_\alpha q_\alpha \delta\big(\boldsymbol{r} - \hat{\boldsymbol{r}}_\alpha(t)\big) \qquad 8.2.3$$

The Fourier transform of this charge distribution is given by

$$\begin{aligned}\tilde{\rho}(\boldsymbol{k},t) &= \frac{1}{2\pi^{3/2}} \iiint e^{-i\boldsymbol{k}.\boldsymbol{r}} \sum_\alpha q_\alpha \delta(\boldsymbol{r} - \hat{\boldsymbol{r}}_\alpha(t))\, d^3\boldsymbol{r} \\ &= \frac{1}{2\pi^{3/2}} \sum_\alpha q_\alpha e^{-i\boldsymbol{k}.\boldsymbol{r}_\alpha(t)} \qquad 8.2.4\end{aligned}$$

Writing the exponential as a power series gives

$$\tilde{\rho}(\boldsymbol{k},t) = \frac{1}{2\pi^{3/2}} \sum_\alpha q_\alpha \left(1 - i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t) + \frac{\big(-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t)\big)^2}{2!} + \cdots\right) \qquad 8.2.5$$

We consider only atoms or molecules which are electrically neutral, and the first term – which involves a sum over all the charges in the atom – is therefore equal to zero. Removing it, and taking out a factor of $-i\boldsymbol{k}.\boldsymbol{r}_\alpha(t)$ from the remaining terms, gives

$$\tilde{\rho}(\boldsymbol{k},t) = \sum_\alpha \frac{-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t)}{2\pi^{\frac{3}{2}}} q_\alpha \left(1 + \frac{\big(-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t)\big)}{2!} + \frac{\big(-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t)\big)^2}{3!} + \cdots\right) \qquad 8.2.6$$

The sum in brackets can be re-written as an integra over an auxiliary parameter u,

$$\begin{aligned}\tilde{\rho}(\boldsymbol{k},t) &= \sum_\alpha \frac{-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t)}{2\pi^{3/2}} q_\alpha \int_0^1 \left(1 + (-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t))u + \frac{(-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t)\,u)^2}{2!} + \cdots\right) du \\ &= \sum_\alpha \frac{-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t)}{2\pi^{3/2}} q_\alpha \int_0^1 e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_\alpha(t)u} du\,. \qquad 8.2.7\end{aligned}$$

field is always defined with respect to a reference charge distribution, usually taken to be zero everywhere. Charged systems are described simply by altering this reference charge distribution to place the negative of the net charge at the origin [4, p.281].

When the u integration above is performed, each term is divided by its power of u, restoring the original denominators. The upper limit of integration gives the previous line, and the lower limit evaluates to 0, as after integration each term contains at least one factor of u.

If the inverse Fourier transformation is now be performed, it is seen that the result can be written as the divergence of some quantity – which we may identify with the polarisation field, $\boldsymbol{P}$. The inverse transformation is

$$\rho(\boldsymbol{r}) = \frac{1}{2\pi^{3/2}} \iiint \sum_{\alpha} \frac{-i\boldsymbol{k} \cdot \boldsymbol{r}_{\alpha}}{2\pi^{\frac{3}{2}}} q_{\alpha} \int_{0}^{1} e^{-i\boldsymbol{k}.\boldsymbol{r}_{\alpha} u} du \, e^{i\boldsymbol{k}.\boldsymbol{r}} d^{3}\boldsymbol{k}. \quad 8.2.8$$

To write this as a divergence, we note that the only part of this expression which depends on $\boldsymbol{r}$ is the exponential in the inverse transform. Differentiating the expression with respect to r_i will therefore only have the effect of introducing a factor of ik_i. The factor ik in the dot product $i\boldsymbol{k} \cdot \boldsymbol{r}$ can therefore be re-written by simply differentiating the whole expression with respect to $\boldsymbol{r}$. Writing in terms of components

$$\rho(\boldsymbol{r}) = \sum_{i} -\frac{d}{dr_i} \left[\frac{1}{2\pi^{\frac{3}{2}}} \iiint \sum_{\alpha} \frac{\boldsymbol{r}_{\alpha_i}}{2\pi^{\frac{3}{2}}} q_{\alpha} \int_{0}^{1} e^{-i\boldsymbol{k}.\boldsymbol{r}_{\alpha} u} du \, e^{i\boldsymbol{k}.\boldsymbol{r}} d^{3}\boldsymbol{k} \right] \quad 8.2.9$$

Evaluating the inverse Fourier transform gives

$$\rho(\boldsymbol{r}) = \sum_{i} -\frac{d}{dr_i} \left[\sum_{\alpha} r_{\alpha_i} q_{\alpha} \int_{0}^{1} \delta(\boldsymbol{r} - u\boldsymbol{r}_{\alpha}) du \right]$$

$$= -\boldsymbol{\nabla} \cdot \left[\sum_{\alpha} \boldsymbol{r}_{a} q_{\alpha} \int_{0}^{1} \delta(\boldsymbol{r} - u\boldsymbol{r}_{\alpha}) du \right], \quad 8.2.10$$

so the term in square brackets is the polarisation.

8.3. Applying the Transformation to the Hamiltonian

Having obtained an explicit form for the unitary operator (8.1.3), we can proceed to apply it to the Hamiltonian (8.1.1) In order to do this, we make use of the identity

$$e^{\hat{A}} \hat{B} e^{-\hat{A}} = \hat{B} + [\hat{A}, \hat{B}] + \frac{1}{2!} \left[\hat{A}, [\hat{A}, \hat{B}] \right] + \frac{1}{3!} \left[\hat{A}, \left[\hat{A}, [\hat{A}, \hat{B}] \right] \right] + \cdots, \quad 8.3.1$$

which holds for any operators $\hat{A}$ and $\hat{B}$ [5, p.308]. We will consider the terms of (8.1.1) one at time, starting with the $\hat{\boldsymbol{p}}_{a}^{2}$ term. To begin with, we evaluate $\hat{U}^{-1} \hat{\boldsymbol{p}}_{a} \hat{U}$. using (8.3.1) The second term of (8.3.1) is the commutator

$$\left[\frac{i}{\hbar} \int \hat{\boldsymbol{P}}(\boldsymbol{r}') \cdot \hat{\boldsymbol{A}}(\boldsymbol{r}') \, d^{3}\boldsymbol{r}', \hat{p}_{a_i} \right] = \left[\frac{i}{\hbar} \int \left(\sum_{\alpha} \boldsymbol{r}_{a} q_{\alpha} \int_{0}^{1} \delta(\boldsymbol{r}' - u\boldsymbol{r}_{\alpha}) du \right) \cdot \hat{\boldsymbol{A}}(\boldsymbol{r}') \, d^{3}\boldsymbol{r}', \hat{p}_{a_i} \right]. \quad 8.3.2$$

This commutator will be non-zero, as the canonical electron momenta $\hat{\boldsymbol{p}}_{\alpha}$ do not commute with the charge positions $\hat{\boldsymbol{r}}_{\alpha}$. The commutator between $\hat{\boldsymbol{p}}_{\alpha}$ and $\hat{\boldsymbol{r}}_{\alpha}$ is given by

$$\left[\hat{p}_{\alpha_i}, \hat{r}_{\beta_j}\right] = -i\hbar\delta_{\alpha\beta}\delta_{ij}, \qquad 8.3.3$$

and, more generally the commutator between the momentum and a function of the position is given by [5 p.279]

$$\left[\hat{p}_{\alpha_i}, f(\hat{r}_{\alpha_i})\right] = -i\hbar\frac{\partial}{\partial r_{\alpha_i}} f(\hat{r}_{\alpha_i}), \qquad 8.3.4$$

where there is no sum over i implied on the right hand side.

We may remove the sum in (8.3.2), writing

$$\left[\frac{i}{\hbar}\int\left(\sum_{\alpha} r_{\alpha_j} q_\alpha \int_0^1 \delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\right)\hat{A}_j(\boldsymbol{r}')\, d^3\boldsymbol{r}', \hat{p}_{\alpha_i}\right]$$
$$= \left[\frac{i}{\hbar}\int r_{\alpha_i} q_\alpha \int_0^1 \delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, \hat{A}_i(\boldsymbol{r}')\, d^3\boldsymbol{r}', \hat{p}_{\alpha_i}\right], \qquad 8.3.5$$

where again there is no sum over i in the last line. We have restricted the sum over j in the dot product $r_{\alpha_j}\hat{A}_{\boldsymbol{j}}(\boldsymbol{r}')$ to only the case $i = j$, as the different components of $\hat{\boldsymbol{r}}$ and $\hat{\boldsymbol{p}}$ commute. We drop the sum over α for the same reason – the positions and momenta of the different particles commute. Evaluating (8.3.5) using (8.3.4) gives

$$-\frac{\partial}{\partial r_{\alpha_i}}\left\{\int r_{\alpha_i} q_\alpha \int_0^1 \delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, \hat{A}_i(\boldsymbol{r}')\, d^3\boldsymbol{r}'\right\}$$
$$= -q_\alpha \int\int_0^1 \delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, \hat{A}_i(\boldsymbol{r}')\, d^3\boldsymbol{r}' - \int r_{\alpha_i} q_\alpha \int_0^1 \frac{\partial}{\partial r_{\alpha_i}}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, \hat{A}_i(\boldsymbol{r}')\, d^3\boldsymbol{r}' \qquad 8.3.6$$

Note that this commutes with $\hat{U}$, and so all higher order terms in the expansion (8.3.1) of the transformed momentum are 0. We therefore have

$$U^{-1}P_{\alpha_i}U$$
$$= P_{\alpha_i} - \int\int_0^1 q_\alpha \delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}' - \int r_{\alpha_i} q_\alpha \int_0^1 \frac{\partial}{\partial r_{\alpha_i}}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}' \qquad 8.3.7$$

In order to perform the second integral, we can change the variable that the delta function is differentiated with respect to. This can be done by making use of the fact that

$$r_{\alpha_i}\frac{\partial}{\partial r_{\alpha_i}}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha) = u\frac{\partial}{\partial u}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha), \qquad 8.3.8$$

and

$$\frac{\partial}{\partial r_{\alpha_j}}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha) = -u\frac{\partial}{\partial r_j'}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha). \qquad 8.3.9$$

We first add and subtract

$$\int r_{\alpha_j} q_\alpha \int_0^1 \frac{\partial}{\partial r_{\alpha_j}}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}' \qquad 8.3.10$$

to get

$$U^{-1}P_{\alpha_i}U = P_{\alpha_i} + \delta_{ij}q_\alpha \int\int_0^1 \delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_j(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$+r_{\alpha_j}q_\alpha \int\int_0^1 \frac{\partial}{\partial r_{\alpha_j}}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$+r_{\alpha_j}q_\alpha \int\int_0^1 \frac{\partial}{\partial r_{\alpha_i}}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_j(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$-r_{\alpha_j}q_\alpha \int\int_0^1 \frac{\partial}{\partial r_{\alpha_j}}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}' \qquad 8.3.11$$

Now, we apply (8.3.8) to term 2 of (8.3.11), and (8.3.9) to terms 3 and 4 to get

$$U^{-1}P_{\alpha_i}U = P_{\alpha_i} + q_\alpha \int\int_0^1 \delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$+q_\alpha \int\int_0^1 u\frac{d}{du}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$-r_{\alpha_j}q_\alpha \int\int_0^1 u\frac{\partial}{\partial r_i'}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_j(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$+r_{\alpha_j}q_\alpha \int\int_0^1 u\frac{\partial}{\partial r_j'}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}' \qquad 8.3.12$$

We can now perform the integrals on the first term, and perform the **r**' integrals on the final 2 terms:

$$U^{-1}P_{\alpha_i}U = P_{\alpha_i} + q_\alpha A_i(\boldsymbol{r}_\alpha) + r_{\alpha_j}q_\alpha \int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\frac{\partial}{\partial r_i'}A_j(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$- r_{\alpha_j}q_\alpha \int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\frac{\partial}{\partial r_j'}A_i(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$= P_{\alpha_i} + q_\alpha A_i(\boldsymbol{r}_\alpha) - r_{\alpha_j}q_\alpha \int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\left(\frac{\partial}{\partial r_j'}A_i(\boldsymbol{r}') - \frac{\partial}{\partial r_j'}A_j(\boldsymbol{r}')\right)d^3\boldsymbol{r}'$$
$$= q_\alpha \int\int_0^1 \frac{d}{du}\big(u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)\big)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$-r_{\alpha_j}q_\alpha \int\int_0^1 u\frac{\partial}{\partial r_i'}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_j(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$+r_{\alpha_j}q_\alpha \int\int_0^1 u\frac{\partial}{\partial r_j'}\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\, A_i(\boldsymbol{r}')d^3\boldsymbol{r}'\,. \qquad 8.3.13$$

Now, note that

$$\frac{\partial}{\partial r_j'}A_i(\boldsymbol{r}') - \frac{\partial}{\partial r_j'}A_j(\boldsymbol{r}') = -\varepsilon_{ijk}(\nabla x\boldsymbol{A})_k = -\varepsilon_{ijk}\boldsymbol{B_k}(\boldsymbol{r}'), \qquad 8.3.14$$

so we finally obtain

$$U^{-1}P_{\alpha_i}U = P_{\alpha_i} + q_\alpha A_i(\boldsymbol{r}_\alpha) + r_{\alpha_j}q_\alpha \int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\,\varepsilon_{ijk}\boldsymbol{B_k}(\boldsymbol{r}')d^3\boldsymbol{r}'\,. \qquad 8.3.15$$

Going back to vector notation,

$$U^{-1}\boldsymbol{P}_\alpha U = \boldsymbol{P}_\alpha + q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha) + q_\alpha \int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\,\big(\mathbf{r}_\alpha \times \boldsymbol{B}(\boldsymbol{r}')\big)d^3\boldsymbol{r}'\,. \qquad 8.3.16$$

Using this result, and the fact that the unitary transformation (8.1.3) commutes with $\widehat{\boldsymbol{A}}(\boldsymbol{r}_\alpha)$, the first term in the minimal coupling Hamiltonian then becomes

$$U^{-1}\frac{\left(\boldsymbol{P}_\alpha - q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha)\right)^2}{2m}U = \frac{\left(U^{-1}\left(\boldsymbol{P}_\alpha - q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha)\right)U\right)^2}{2m}$$

$$= \frac{1}{2m}\left(\boldsymbol{P}_\alpha + q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha) + q_\alpha \int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\left(\mathrm{r}_\alpha \times \boldsymbol{B}(\boldsymbol{r}')\right)d^3\boldsymbol{r}' - q_\alpha \boldsymbol{A}(\boldsymbol{r}_\alpha)\right)^2$$

$$= \frac{\boldsymbol{P}_\alpha^2}{2m} + \frac{q_\alpha}{2m}\int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\left(\boldsymbol{P}_\alpha \cdot \left(\mathrm{r}_\alpha \times \boldsymbol{B}(\boldsymbol{r}')\right) + \left(\mathrm{r}_\alpha \times \boldsymbol{B}(\boldsymbol{r}')\right)\cdot \boldsymbol{P}_\alpha\right)d^3\boldsymbol{r}'$$

$$+ \frac{1}{2m}\left(q_\alpha \int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\left(\mathrm{r}_\alpha \times \boldsymbol{B}(\boldsymbol{r}')\right)d^3\boldsymbol{r}'\right)^2$$

$$= \frac{\boldsymbol{P}_\alpha^2}{2m} - \int \boldsymbol{B}(\boldsymbol{r}').\boldsymbol{M}(\boldsymbol{r}').d^3\boldsymbol{r}' + \frac{1}{2m}\left(q_\alpha \int\int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\left(\mathrm{r}_\alpha \times \boldsymbol{B}(\boldsymbol{r}')\right)d^3\boldsymbol{r}'\right)^2,$$

We next move onto the second term of the minimal coupling Hamiltonian, which gives the Coulomb energies of the charges. This commutes with the transformation (as the scalar potential and charge density both commute with the polarisation and vector potential), and so is not modified. Finally, we turn to the third term, which gives the free-field energy. The magnetic field also commutes with the vector potential, so is unmodified, but the electric field does not – the relevant commutator is given by [6, p 145]

$$\left[A(\boldsymbol{r},t)_i, E^T(\boldsymbol{r}',t)_j\right] = -\frac{1}{\varepsilon_0} i\hbar\delta_{ij}^T(\boldsymbol{r} - \boldsymbol{r}') \qquad 8.3.17$$

where δ_{ij}^T is the transverse delta function. This is defined such that, for any vector field $\boldsymbol{F}$,

$$\int F_i(\boldsymbol{r})\delta_{ij}^T(\boldsymbol{r} - \boldsymbol{r}')d^3\boldsymbol{r} = F_j^T(\boldsymbol{r}'), \qquad 8.3.18$$

where $\boldsymbol{F}^T$ is the transverse part of $\boldsymbol{F}$. Using this identity with the transformation U gives

$$U^{-1}E_i^T(\boldsymbol{r})U = e^{-i/\hbar\int \boldsymbol{P}(\boldsymbol{r}').\boldsymbol{A}(\boldsymbol{r}')d^3\boldsymbol{r}'}E_i^T(\boldsymbol{r})e^{i/\hbar\int \boldsymbol{P}(\boldsymbol{r}').\boldsymbol{A}(\boldsymbol{r}')\,d^3\boldsymbol{r}'}$$

$$= E_i^T(\boldsymbol{r}) - \frac{i}{\hbar}\int P(\boldsymbol{r}')_j\left[A_j(\boldsymbol{r}'), E_i^T(\boldsymbol{r})\right]d^3\boldsymbol{r}' + \cdots \qquad 8.3.19$$

Note that all further terms are zero, as the commutator between $\boldsymbol{A}$ and $\boldsymbol{E}$ commutes with $\boldsymbol{A}$. Evaluating the expression using the commutator gives

$$E_i^T(\boldsymbol{r}) - \frac{1}{\varepsilon_0}\int P(\boldsymbol{r}')_j\delta_{ij}^T(\boldsymbol{r}' - \boldsymbol{r})\,d^3\boldsymbol{r}'$$

$$= E_i^T(\boldsymbol{r}) - \frac{1}{\varepsilon_0}P^T(\boldsymbol{r})_i \qquad 8.3.20$$

What we actually require is

$$U^{-1}\boldsymbol{E^T}^2U = (U^{-1}\boldsymbol{E}^TU)^2$$

$$= \boldsymbol{E}^{T^2} - \frac{2}{\epsilon_0}\boldsymbol{E}^T.\boldsymbol{P}^T + \frac{1}{\varepsilon_0^2}\boldsymbol{P}^{T^2}. \qquad 8.3.21$$

The first term is the same as in the minimal coupling Hamiltonian. The second gives the potential energy of the charges in the transverse $\boldsymbol{E}$ field, and the $\boldsymbol{E}$ field can be Taylor-expanded to yield the multipole expansion. The third does not affect the atom-light interaction, as it only contains terms associated with the electron positions – it gives a change to the atomic energy levels [6].

Finally, the complete multipolar Hamiltonian is

$$\frac{\boldsymbol{P}_\alpha^2}{2m} - \int \boldsymbol{B}(\boldsymbol{r}').\boldsymbol{M}(\boldsymbol{r}')d^3\boldsymbol{r}' + \frac{1}{2}\int \rho(\boldsymbol{r}')\phi(\boldsymbol{r}')d^3\boldsymbol{r}' + \frac{1}{2}\int \varepsilon_0 \widehat{\boldsymbol{E}}^T(\boldsymbol{r})^2 + \frac{1}{\mu_0}\widehat{\boldsymbol{B}}(\boldsymbol{r})^2 d^3\boldsymbol{r}$$
$$- \int \boldsymbol{E}^T(\boldsymbol{r}').\boldsymbol{P}^T(\boldsymbol{r}')d^2\boldsymbol{r}' + \frac{1}{2\varepsilon_0}\int \boldsymbol{P}^{T^2} d^3\boldsymbol{r}'$$
$$+ \frac{1}{2m}\left(q_\alpha \int \int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\left(\mathbf{r}_\alpha \times \boldsymbol{B}(\boldsymbol{r}')\right)d^3\boldsymbol{r}'\right)^2.$$

This can be partitioned into [5, p. 269]

$$\widehat{H}_{multipolar} = \widehat{H}_{mol.} + \widehat{H}_{rad.} + \widehat{H}_{inter.} + \frac{1}{2\varepsilon_0}\int \boldsymbol{P}^{T^2} d^3\boldsymbol{r}',$$

with

$$\widehat{H}_{mol.} = \frac{\boldsymbol{P}_\alpha^2}{2m} + \frac{1}{2}\int \rho(\boldsymbol{r}')\phi(\boldsymbol{r}')d^3\boldsymbol{r}',$$
$$\widehat{H}_{rad.} = \frac{1}{2}\int \varepsilon_0 \widehat{\boldsymbol{E}}^T(\boldsymbol{r})^2 + \frac{1}{\mu_0}\widehat{\boldsymbol{B}}(\boldsymbol{r})^2 d^3\boldsymbol{r},$$
$$\widehat{H}_{inter.} = - \int \boldsymbol{E}^T(\boldsymbol{r}').\boldsymbol{P}^T(\boldsymbol{r}')d^2\boldsymbol{r}' - \int \boldsymbol{B}(\boldsymbol{r}').\boldsymbol{M}(\boldsymbol{r}')d^3\boldsymbol{r}'$$
$$+ \frac{1}{2m}\left(q_\alpha \int \int_0^1 u\delta(\boldsymbol{r}' - u\boldsymbol{r}_\alpha)du\left(\mathbf{r}_\alpha \times \boldsymbol{B}(\boldsymbol{r}')\right)d^3\boldsymbol{r}'\right)^2.$$

The first two terms give the energies of a free molecule and free field, while the third term can be cast into a multipole series by writing the appropriate multipolar expansion of the $\boldsymbol{P}^T$ and $\boldsymbol{M}$ fields [6 p. 157].

8.4. The Barron-Gray Potentials

If the electromagnetic field is treated as a classical field, rather than a quantum mechanical operator, then there exists a much faster way to recast the minimal coupling Hamiltonian into a multipolar form, due to Barron and Gray. By making a suitable choice of gauge, it is possible to immediately arrive at the multipolar form (8.3.22) [7]. We choose the potentials

$$\phi(\boldsymbol{r}) = \phi_0 - r_a E_a(0) - \frac{1}{2}r_a r_b \nabla_b E_a(0) - \frac{1}{6}r_a r_b r_c \nabla_b \nabla_c E_a(0) + \cdots, \qquad 8.4.1$$

$$A_a(\boldsymbol{r}) = -\frac{1}{2}\epsilon_{abc} r_b B_c(0) - \frac{1}{3}\epsilon_{abc} r_b r_d \nabla_d B_c(0) + \cdots. \qquad 8.4.2$$

If the $\boldsymbol{E}$ and $\boldsymbol{B}$ fields can be Taylor-expanded, then these potentials lead to the correct $\boldsymbol{E}$ and $\boldsymbol{B}$ fields by construction, as

$$-\nabla_a \phi(\boldsymbol{r}) - \frac{\partial A_a}{\partial t} = E_a(0) + r_b \nabla_b E_a(0) + \frac{1}{2} r_b r_c \nabla_b \nabla_c E_a(0) + \cdots, \qquad 8.4.3$$

$$\nabla \times A_a(\boldsymbol{r}) = B_a(0) + r_b \nabla_b B_a(0) + \frac{1}{2} r_b r_c \nabla_b \nabla_c B_a(0) + \cdots \qquad 8.4.4$$

[8, p. 84]. (Note that to arrive at (8.4.3) we have had to make use of the Maxwell equation $\nabla \times \boldsymbol{E} = -\partial \boldsymbol{B}/\partial t$). Substituting the definitions (8.4.1-8.4.2) into the minimal-coupling Hamiltonian (8.1.1) immediately produces the multipolar Hamiltonian [7],

$$H_{multipolar} = \sum_a \frac{\widehat{\boldsymbol{p}}_a{}^2}{2m_a} + \sum_\alpha q_\alpha\, \phi(\boldsymbol{x}_\alpha) + \frac{1}{2}\int \epsilon_0 {\boldsymbol{E}^T}^2(\boldsymbol{r}') + \frac{1}{\mu_0}\boldsymbol{B}^2(\boldsymbol{r}')\, d^3\boldsymbol{r}' + \sum_\alpha q_\alpha\, \phi_0 - \hat{\mu}_a E_a(0)$$
$$- \widehat{m}_a B_a(0) - \frac{1}{3}\widehat{\Theta}_{ab} \nabla_a E_b(0) \; - \frac{1}{2}\widehat{m}_{ab} \nabla_b B_a(0)$$
$$- \frac{1}{6}\hat{Q}_{abc} \nabla_c \nabla_b E_a(0) - \cdots - \frac{1}{2}\hat{\chi}_{ab}^{(d)} B_a(0) B_b(0) - \cdots. \qquad 8.4.5$$

When comparing this result to (8.3.22), it will be noted that the Hamiltonian above is missing the term $\frac{1}{\varepsilon_0^2}{\boldsymbol{P}^T}^2$. Strictly speaking, one should make the gauge transformation not to the Hamiltonian, but in the *Lagrangian* from which the Hamiltonian is derived [9]. Obtaining a Hamiltonian from this new Lagrangian, with the *old gauge function taken as the canonical coordinates*, produces the correct multipolar Hamiltonian (8.3.22). The origin of this subtlety is that changing gauge changes the definition of the canonical momentum. We may also note that the $\frac{1}{\varepsilon_0^2}{\boldsymbol{P}^T}^2$ term is similarly absent if the derivation of section 8.3 is repeated with the fields treated classically, rather than quantum mechanically – and it is a semi-classical approach we adopt for the present work.

8.5. Perturbation Theory for a Molecule in a Radiation Field

Having cast the Hamiltonian into multipolar form, we can proceed to calculate the scattering of light by a molecule in a radiation field. We will adopt a semi-classical approach, where the atom is treated quantum mechanically, but the light is treated classically. This is reasonable if the energy of the incident light is small compared to the binding energy of the electrons in the atom – the external light field can then be treated as a small perturbation to the free molecular Hamiltonian. The expectation values for the various multipole moment operators can then be evaluated for the perturbed states. Finally, the radiation from the molecule is calculated by treating these expectation values as though they describe the multipole moments of a genuine classical oscillating distribution of charge, and then applying the methods of chapter 2. The presentation below mainly follows Barron's book on molecular light scattering [8].

The molecular wave functions are the solutions of the Schrödinger equation

$$\left(H_{free} + V\right)\psi = i\hbar\frac{\partial}{\partial t}\psi, \tag{8.5.1}$$

with the unperturbed Hamiltonian

$$H_{free} = -\frac{\hbar^2}{2m}\nabla^2 + \sum_{\alpha} q_{\alpha}\,\phi(\boldsymbol{x}_{\alpha}), \tag{8.5.2}$$

and the perturbation

$$V = -\hat{\mu}_a E_a(0) - \widehat{m}_a B_a(0) - \frac{1}{3}\widehat{\Theta}_{ab}\nabla_a E_b(0) - \frac{1}{2}\widehat{m}_{ab}\nabla_b B_a(0) - \frac{1}{6}\hat{Q}_{abc}\nabla_c\nabla_b E_a(0) - \cdots$$

$$-\frac{1}{2}\hat{\chi}_{ab}^{(d)} B_a(0)B_b(0) - \cdots \tag{8.5.3}$$

This perturbation expresses the interaction energy as a series of electric multipole moments multiplying electric fields and field gradients, a series of magnetic multipole moments multiplying magnetic fields and field gradients, and finally a series of diamagnetic terms which are second order in the magnetic field or field gradients. Explicitly, the Coulomb term of the free Hamiltonian is equal to

$$\sum_{\alpha} q_{\alpha}\,\phi(\boldsymbol{x}_{\alpha}) = \frac{1}{2}\sum_{\alpha}\sum_{\beta\neq\alpha}\frac{q_{\alpha}q_{\beta}}{4\pi\epsilon_0\left|\boldsymbol{x}_{\alpha} - \boldsymbol{x}_{\beta}\right|}, \tag{8.5.4}$$

where the sum extends over all electrons and nuclei. Note that the exclusion in the second sum explicitly removes the self-energies, and the factor of a half compensates for the double-counting of each pair of charges.

Suppose that we know the complete set of unperturbed molecular energy eigenfunctions, which we shall denote ψ_n^0, and that each has an energy eigenvalue $\hbar\omega_n$. A general solution of the Schrödinger equation for the free molecule can then be written in terms of this basis as

$$\psi = \sum_{n} c_n \psi_n^0 e^{-i\omega_n t}, \tag{8.5.5}$$

for some (possibly complex) coefficients c_n. When the perturbation is applied, the ψ_n^0 will no longer be eigenfunctions. The solutions of the time-dependent Schrödinger equation with the perturbed Hamiltonian can still be written in the form above, but the coefficients c_n will now be time-dependent. As the perturbation is small, we write each new energy eigenfunction as the corresponding old eigenfunction, with the addition of some (time-dependent) contributions from the other old eigenfunctions,

$$\psi_n' = \left\{\psi_n^0 + \sum_{m} c_m(t)\psi_m^0\right\} e^{-i\omega_n t}. \tag{8.5.6}$$

To proceed further, we assume that these time-dependent terms will all be *first order* in the perturbing fields, or their derivatives. This gives us the following ansatz for the eigenfunctions of the perturbed Hamiltonian:

$$\psi_n' = \Big\{\psi_n^0 + \sum_{m\neq n} \psi_m^0 \big[a_{mn_a}\tilde{E}_a(0) + b_{mn_a}\tilde{E}_a^*(0) + c_{mn_a}\tilde{B}_a(0) + d_{mn_a}\tilde{B}_a^*(0) + e_{mn_{ab}}\nabla_a\tilde{E}_b(0) + f_{mn_{ab}}\nabla_a\tilde{E}_b^*(0) + \cdots\big]\Big\} e^{-i\omega_n t} \qquad 8.5.7$$

and our task is now to determine the coefficients a, b, etc. In writing the above, we have used complex electric and magnetic fields, defined by $\tilde{E} = \tilde{E}^0 e^{-i\omega t}$ and $E = Re[\tilde{E}]$, etc. In the following development we will sometimes need to distinguish between real and complex forms of certain quantities; for the remainder of this chapter and the next we will denote complex fields, multipole moments and polarisability tensors using a tilde.

Substituting the above expression into the Schrödinger equation with the perturbed Hamiltonian, and rearranging to place the perturbation on the left-hand side, gives

$$i\hbar\frac{\partial}{\partial t}\psi'_n - H_{free}\psi'_n = V\psi'_n. \qquad 8.5.8$$

Using the fact that the fields have time-dependence $e^{-i\omega t}$, and their conjugates have dependence $e^{i\omega t}$, we have

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi'_n = \hbar\omega_n \Big\{&\psi_n^0 \\ &+ \sum_{m\neq n} \psi_m^0 \big[a_{mn_a}\tilde{E}_a(0) + b_{mn_a}\tilde{E}_a^*(0) + c_{mn_a}\tilde{B}_a(0) + d_{mn_a}\tilde{B}_a^*(0) + e_{mn_{ab}}\nabla_a\tilde{E}_b(0) \\ &+ f_{mn_{ab}}\nabla_a\tilde{E}_b^*(0) + \cdots\big]\Big\} e^{-i\omega_n t} \\ &+ \hbar\omega \sum_{m\neq n} \psi_m^0 \big[a_{mn_a}\tilde{E}_a(0) - b_{mn_a}\tilde{E}_a^*(0) + c_{mn_a}\tilde{B}_a(0) - d_{mn_a}\tilde{B}_a^*(0) \\ &+ e_{mn_{ab}}\nabla_a\tilde{E}_b(0) - f_{mn_{ab}}\nabla_a\tilde{E}_b^*(0) + \cdots\big] e^{-i\omega_n t} \end{aligned} \qquad 8.5.9$$

The second term of (8.5.8) becomes, using the Schrödinger equation for the free molecule, $H_{free}\psi_n^0 = \hbar\omega_n\psi_n^0$,

$$\begin{aligned} H_{free}\psi'_n = \Big\{&\hbar\omega_n\psi_n^0 \\ &+ \sum_{m\neq n} \hbar\omega_m\psi_m^0 \big[a_{mn_a}\tilde{E}_a(0) + b_{mn_a}\tilde{E}_a^*(0) + c_{mn_a}\tilde{B}_a(0) + d_{mn_a}\tilde{B}_a^*(0) \\ &+ e_{mn_{ab}}\nabla_a\tilde{E}_b(0) + f_{mn_{ab}}\nabla_a\tilde{E}_b^*(0) + \cdots\big]\Big\} e^{-i\omega_n t} \end{aligned} \qquad 8.5.10$$

So the left-hand side of the perturbed equation is equal to

$$i\hbar\frac{\partial}{\partial t}\psi'_n - H_{free}\psi'_n$$

$$= \Big\{\hbar\sum_{m\neq n}\psi_m^0\big[(\omega_{nm}+\omega)a_{mn_a}\tilde{E}_a(0) + (\omega_{nm}-\omega)b_{mn_a}\tilde{E}_a^*(0) + (\omega_{nm} + \omega)c_{mn_a}\tilde{B}_a(0) + (\omega_{nm}-\omega)d_{mn_a}\tilde{B}_a^*(0) + (\omega_{nm}+\omega)e_{mn_{ab}}\nabla_a\tilde{E}_b(0) + (\omega_{nm} - \omega)f_{mn_{ab}}\nabla_a\tilde{E}_b^*(0) + \cdots\big]\Big\}e^{-i\omega_n t} \quad 8.5.11$$

where $\omega_{nm} \equiv \omega_n - \omega_m$. The right-hand-side is equal to

$$V\psi'_n = \Big(-\hat{\mu}_a E_a(0) - \widehat{m}_a B_a(0) - \frac{1}{3}\Theta_{ab}\nabla_a E_b(0) - \frac{1}{2}\widehat{m}_{ab}\nabla_b B_a(0) - \frac{1}{6}\hat{Q}_{abc}\nabla_c\nabla_b E_a(0) - \cdots\Big)\Big\{\psi_n^0 + \sum_{m\neq n}\psi_m^0\big[a_{mn_a}\tilde{E}_a(0) + b_{mn_a}\tilde{E}_a^*(0) + c_{mn_a}\tilde{B}_a(0) + d_{mn_a}\tilde{B}_a^*(0) + e_{mn_{ab}}\nabla_a\tilde{E}_b(0) + f_{mn_{ab}}\nabla_a\tilde{E}_b^*(0) + \cdots\big]\Big\}e^{-i\omega_n t} \quad 8.5.12$$

If we keep only terms linear in the fields, we lose all the terms in curly brackets except the first[3]. Then, writing the real fields in terms of the complex ones, we obtain

$$V\psi'_n = \frac{1}{2}\Big(-\hat{\mu}_a\big(\tilde{E}_a(0) + \tilde{E}^*{}_a(0)\big) - \widehat{m}_a\big(\tilde{B}_a(0) + B^*{}_a(0)\big) - \frac{1}{3}\Theta_{ab}\big(\nabla_a\tilde{E}_b(0) + \nabla_a\tilde{E}_b^*(0)\big) - \frac{1}{2}\widehat{m}_{ab}\big(\nabla_b\tilde{B}_a(0) + \nabla_b\tilde{B}_a^*(0)\big) - \frac{1}{6}\hat{Q}_{abc}\big(\nabla_c\nabla_b\tilde{E}_a(0) + \nabla_c\nabla_b\tilde{E}_a^*(0)\big) - \cdots\Big)\psi_0^n e^{-i\omega_n t} \quad 8.5.13$$

Putting the left- and right-hand-sides together, we finally have

$$\Big\{\hbar\sum_{m\neq n}\psi_m^0\big[(\omega_{nm}+\omega)a_{mn_a}\tilde{E}_a(0) + (\omega_{nm}-\omega)b_{mn_a}\tilde{E}_a^*(0) + (\omega_{nm}+\omega)c_{mn_a}\tilde{B}_a(0) + (\omega_{nm} - \omega)d_{mn_a}\tilde{B}_a^*(0) + (\omega_{nm}+\omega)e_{mn_{ab}}\nabla_a\tilde{E}_b(0) + (\omega_{nm}-\omega)f_{mn_{ab}}\nabla_a\tilde{E}_b^*(0) + \cdots\big]\Big\}e^{-i\omega_n t}$$

$$= \frac{1}{2}\Big(-\hat{\mu}_a\big(\tilde{E}_a(0) + \tilde{E}^*{}_a(0)\big) - \widehat{m}_a\big(\tilde{B}_a(0) + \tilde{B}^*{}_a(0)\big) - \frac{1}{3}\widehat{\Theta}_{ab}\big(\nabla_a\tilde{E}_b(0) + \nabla_a\tilde{E}_b^*(0)\big) - \frac{1}{2}\widehat{m}_{ab}\big(\nabla_b\tilde{B}_a(0) + \nabla_b\tilde{B}_a^*(0)\big) - \frac{1}{6}\hat{Q}_{abc}\big(\nabla_c\nabla_b\tilde{E}_a(0) + \nabla_c\nabla_b\tilde{E}_a^*(0)\big) - \cdots\Big)\psi_0^n e^{-i\omega_n t} \quad 8.5.14$$

[3] Note that by keeping only terms linear in the fields, we have gotten rid of all the "diamagnetic" terms in V – we shall return to this point later.

If we multiply by $\psi_j^{0^*}$ and integrate, the orthogonality of the ψ_n^0 removes the sum over m, and we are left with

$$\hbar\big[(\omega_{nj}+\omega)a_{jn_a}\tilde{E}_a(0)+(\omega_{nj}-\omega)b_{jn_a}\tilde{E}_a^*(0)+(\omega_{nj}+\omega)c_{jn_a}\tilde{B}_a(0)+(\omega_{nj}-\omega)d_{jn_a}\tilde{B}_a^*(0)$$
$$+(\omega_{nj}+\omega)e_{jn_{ab}}\nabla_a\tilde{E}_b(0)+(\omega_{nj}-\omega)f_{jn_{ab}}\nabla_a\tilde{E}_b^*(0)+\cdots\big]e^{-i\omega_n t}$$
$$=\frac{1}{2}\langle j|\left(-\hat{\mu}_a\left(\tilde{E}_a(0)+\tilde{E}^*{}_a(0)\right)-\widehat{m}_a\left(\tilde{B}_a(0)+\tilde{B}^*{}_a(0)\right)\right.$$
$$-\frac{1}{3}\widehat{\Theta}_{ab}\left(\nabla_a\tilde{E}_b(0)+\nabla_a\tilde{E}_b^*(0)\right)-\frac{1}{2}\widehat{m}_{ab}\left(\nabla_b\tilde{B}_a(0)+\nabla_b\tilde{B}_a^*(0)\right)$$
$$\left.-\frac{1}{6}\hat{Q}_{abc}\left(\nabla_c\nabla_b\tilde{E}_a(0)+\nabla_c\nabla_b\tilde{E}_a^*(0)\right)-\cdots\right)|n\rangle e^{-i\omega_n t} \qquad 8.5.15$$

By equating the coefficients of the different field and field-derivative terms, we arrive at the following expressions for *a*, *b*, etc.

$$a_{jn_a}=\frac{\langle j|\hat{\mu}_a|n\rangle}{2\hbar(\omega_{jn}-\omega)}, \qquad 8.5.16$$

$$b_{jn_a}=\frac{\langle j|\hat{\mu}_a|n\rangle}{2\hbar(\omega_{jn}+\omega)}, \qquad 8.5.17$$

$$c_{jn_a}=\frac{\langle j|\widehat{m}_a|n\rangle}{2\hbar(\omega_{jn}-\omega)}, \qquad 8.5.18$$

$$d_{jn_a}=\frac{\langle j|\widehat{m}_a|n\rangle}{2\hbar(\omega_{jn}+\omega)}, \qquad 8.5.19$$

$$e_{jn_{ab}}=\frac{\langle j|\widehat{\Theta}_{ab}|n\rangle}{6\hbar(\omega_{jn}-\omega)}, \qquad 8.5.20$$

$$f_{jn_{ab}}=\frac{\langle j|\widehat{\Theta}_{ab}|n\rangle}{6\hbar(\omega_{jn}+\omega)}, \qquad 8.5.21$$

and so on. With these, we are finally in a position to write down the expectation values of the various multipole moment operators with the perturbed eigenfunctions. It is these expectation values which we will use to calculate the radiated fields.

8.6. Expectation Values of Induced Electric Moments

When expectation values of the multipole moment operators are taken using the above perturbed wavefunction, the result may be expressed as a sum of molecular polarisability tensors, each multiplying the fields or field derivatives at the molecular origin. As an example of how these emerge, we shall go through the steps leading to the extraction of the electric-dipole-electric-dipole polarisability tensor in detail. The expectation value of the electric dipole moment is equal to

$$\bar{\mu}_a = \langle n'|\hat{\mu}_a|n'\rangle = \Big(\langle n| + \sum_{j\neq n}\tfrac{\langle n|\hat{\mu}_b|j\rangle}{2\hbar(\omega_{jn}-\omega)}\tilde{E}_b^*(0)\langle j| + \tfrac{<n|\hat{\mu}_b|j>}{2\hbar(\omega_{jn}+\omega)}\tilde{E}_b(0)\langle j| + \cdots\Big)e^{i\omega_n t}\hat{\mu}_a\Big(|n\rangle + \sum_{m\neq n}\tfrac{\langle m|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{mn}-\omega)}\tilde{E}_b(0)|m\rangle + \tfrac{\langle m|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{mn}+\omega)}\tilde{E}_b^*(0)|m\rangle + \cdots\Big)e^{-i\omega_n t}$$

$$= \langle n|\hat{\mu}_a|n\rangle + \sum_{m\neq n}\frac{\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{mn}-\omega)}\tilde{E}_b(0) + \sum_{m\neq n}\frac{\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{mn}+\omega)}\tilde{E}_b^*(0) + \cdots$$

$$+\sum_{j\neq n}\frac{\langle n|\hat{\mu}_b|j\rangle\langle j|\hat{\mu}_a|n\rangle}{2\hbar(\omega_{jn}-\omega)}\tilde{E}_b^*(0) + \sum_{j\neq n}\frac{\langle n|\hat{\mu}_b|j\rangle\langle j|\hat{\mu}_a|n\rangle}{2\hbar(\omega_{jn}+\omega)}\tilde{E}_b(0) + \cdots$$

$$+\sum_{j\neq n,m\neq n}\frac{\langle n|\hat{\mu}_b|j\rangle\langle m|\hat{\mu}_c|n\rangle\langle j|\hat{\mu}_a|m\rangle}{4\hbar^2(\omega_{jn}-\omega)(\omega_{mn}-\omega)}\tilde{E}_b^*(0)\tilde{E}_c(0) + \sum_{j\neq n,m\neq n}\frac{\langle n|\hat{\mu}_b|j\rangle\langle m|\hat{\mu}_c|n\rangle\langle j|\hat{\mu}_a|m\rangle}{4\hbar^2(\omega_{jn}-\omega)(\omega_{mn}+\omega)}\tilde{E}_b^*(0)\tilde{E}_c^*(0)$$

$$+\sum_{j\neq n,m\neq n}\frac{\langle n|\hat{\mu}_b|j\rangle\langle m|\hat{\mu}_c|n\rangle\langle j|\hat{\mu}_a|m\rangle}{4\hbar^2(\omega_{jn}+\omega)(\omega_{mn}-\omega)}\tilde{E}_b(0)\tilde{E}_c(0) + \sum_{j\neq n,m\neq n}\frac{\langle n|\hat{\mu}_b|j\rangle\langle m|\hat{\mu}_c|n\rangle\langle j|\hat{\mu}_a|m\rangle}{4\hbar^2(\omega_{jn}+\omega)(\omega_{mn}+\omega)}\tilde{E}_b(0)\tilde{E}_c^*(0)$$

$$+\cdots \qquad 8.6.1$$

The first line shows the terms obtained from multiplication of $\langle n|$ in the first bracket by the second, and the second line the terms from $|n\rangle$ in the second bracket by the first. The remaining terms are second-order in the fields, and if we disregard these, then we may use the fact that $\langle n|\hat{\mu}_b|j\rangle\langle j|\hat{\mu}_a|n\rangle = \langle j|\hat{\mu}_b|n\rangle^*\langle n|\hat{\mu}_a|j\rangle^*$ to write the first two lines as

$$\langle n|\hat{\mu}_a|n\rangle + \sum_{m\neq n}\frac{\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{mn}-\omega)}\tilde{E}_b(0) + \sum_{m\neq n}\frac{\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{mn}+\omega)}\tilde{E}_b^*(0) + \cdots$$

$$+\sum_{j\neq n}\frac{\langle n|\hat{\mu}_a|j\rangle^*\langle j|\hat{\mu}_b|n\rangle^*}{2\hbar(\omega_{jn}-\omega)}\tilde{E}_b^*(0) + \sum_{j\neq n}\frac{\langle n|\hat{\mu}_a|j\rangle^*\langle j|\hat{\mu}_b|n\rangle^*}{2\hbar(\omega_{jn}+\omega)}\tilde{E}_b(0) + \cdots \qquad 8.6.2$$

Relabelling j to m in the second line and cross-multiplying to collect terms in $\tilde{E}_b(0)$ and $\tilde{E}_b^*(0)$ gives

$$\langle n|\hat{\mu}_a|n\rangle + \sum_{m\neq n}\frac{\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle(\omega_{mn}+\omega) + \langle n|\hat{\mu}_a|m\rangle^*\langle m|\hat{\mu}_b|n\rangle^*(\omega_{mn}-\omega)}{2\hbar(\omega_{mn}^2-\omega^2)}\tilde{E}_b(0)$$

$$+\sum_{m\neq n}\frac{\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle(\omega_{mn}-\omega) + \langle n|\hat{\mu}_a|j\rangle^*\langle j|\hat{\mu}_b|n\rangle^*(\omega_{mn}+\omega)}{2\hbar(\omega_{mn}^2-\omega^2)}\tilde{E}_b^*(0), \qquad 8.6.3$$

which can be written in terms of the real and imaginary parts of the transition multipole moment products as

$$\langle n|\hat{\mu}_a|n\rangle + \sum_{m\neq n}\frac{\omega_{mn}Re[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle] + i\omega Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]}{\hbar(\omega_{mn}^2-\omega^2)}\tilde{E}_b(0)$$

$$+\sum_{m\neq n}\frac{\omega_{mn}Re[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle] - i\omega Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]}{\hbar(\omega_{mn}^2-\omega^2)}\tilde{E}_b^*(0) \qquad 8.6.4$$

Finally, we may use the relationships $\tilde{E}_b(0) + \tilde{E}_b^*(0) = 2E_b$ and $\frac{i}{\omega}\frac{\partial\tilde{\boldsymbol{E}}}{\partial t} = \boldsymbol{E}$ to obtain an expression purely in terms of real quantities:

$$\langle n|\hat{\mu}_a|n\rangle + \sum_{m\neq n} \frac{2\omega_{mn} Re[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]}{\hbar(\omega_{mn}^2 - \omega^2)} E_b(0)$$

$$+ \sum_{m\neq n} \frac{-Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]\dot{\tilde{E}}_b(0) - Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]\dot{\tilde{E}}_b^*(0)}{\hbar(\omega_{mn}^2 - \omega^2)}$$

$$= \langle n|\hat{\mu}_a|m\rangle + \sum_{m\neq n} \frac{2\omega_{mn} Re[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]}{\hbar(\omega_{mn}^2 - \omega^2)} E_b(0) - \sum_{m\neq n} \frac{2\omega Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]}{\hbar(\omega_{mn}^2 - \omega^2)} \frac{1}{\omega} \dot{E}_b(0) \quad 8.6.5$$

Note that the factors of ω and $\frac{1}{\omega}$ have been placed in the second term in order to ensure that the two prefactors have the same dimension. These prefactors are, respectively, the *symmetric* and the *anti-symmetric real electric-dipole-electric-dipole polarisability tensors*,

$$\alpha_{ab} = \frac{2}{\hbar} \sum_{m\neq n} \frac{\omega_{mn} Re[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]}{(\omega_{mn}^2 - \omega^2)}, \quad 8.6.6$$

$$\alpha'_{ab} = -\frac{2}{\hbar} \sum_{m\neq n} \frac{\omega Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_b|n\rangle]}{(\omega_{mn}^2 - \omega^2)}. \quad 8.6.7$$

If more terms are included in the series 8.6.1, then coefficients *a*,*b*,*c* etc. involving higher multipole moments enter in an exactly analogous way, and the induced electric dipole moment can be written as a series in these polarisability tensors:

$$\bar{\mu}_a = \alpha_{ab} E_b(0) + \alpha'_{ab} \frac{1}{\omega} \dot{E}_b(0) + G_{ab} B_b(0) + G'_{ab} \frac{1}{\omega} \dot{B}_b(0) + \frac{1}{3} A_{a,bc} \nabla_b E_c(0) + A'_{a,bc} \frac{1}{3\omega} \nabla_b \dot{E}_c(0) + \cdots \quad 8.6.8$$

with the polarisability tensors

$$G_{ab} = \frac{2}{\hbar} \sum_{m\neq n} \frac{\omega_{mn} Re[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{m}_b|n\rangle]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.9$$

$$G'_{ab} = -\frac{2}{\hbar} \sum_{m\neq n} \frac{\omega Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{m}_b|n\rangle]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.10$$

$$A_{a,bc} = \frac{2}{\hbar} \sum_{m\neq n} \frac{\omega_{mn} Re\left[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\Theta}_{bc}|n\rangle\right]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.11$$

$$A'_{a,bc} = -\frac{2}{\hbar} \sum_{m\neq n} \frac{\omega Im\left[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\Theta}_{bc}|n\rangle\right]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.12$$

Note that the factors of 1/3 have appeared with the electric-dipole-electric-quadrupole polarisabilities, because of our definition of the traceless quadrupole moment. We have also omitted the permanent dipole moment $\langle n|\hat{\mu}_a|n\rangle$ from the expression for $\bar{\mu}_a$, as this will not contribute to the radiation.

Repeating the same procedure, similar expressions can be obtained for the higher multipole moments:

$$\langle n'|\widehat{\Theta}_{ab}|n'\rangle = \left(\langle n| + \sum_{j\neq n} \frac{\langle n|\hat{\mu}_c|j\rangle}{2\hbar(\omega_{jn}-\omega)} \tilde{E}_c^*(0)\langle j| + \frac{\langle n|\hat{\mu}_c|j\rangle}{2\hbar(\omega_{jn}+\omega)} \tilde{E}_c(0)\langle j| + \cdots\right)\widehat{\Theta}_{ab}\left(|n\rangle\right.$$

$$\left. + \sum_{m\neq n} \frac{\langle m|\hat{\mu}_c|n\rangle}{2\hbar(\omega_{mn}-\omega)} \tilde{E}_c(0)|m\rangle + \frac{\langle m|\hat{\mu}_c|n\rangle}{2\hbar(\omega_{mn}+\omega)} \tilde{E}_c^*(0)|m\rangle + \cdots\right)$$

$$= A_{c,ab}E_c(0) - A'_{c,ab}\frac{1}{\omega}\dot{E}_c(0) + D_{c,ab}B_c(0) - D'_{c,ab}\frac{1}{\omega}\dot{B}_c(0) + C_{ab,cd}\nabla_c E_d(0) + C'_{ab,cd}\frac{1}{\omega}\nabla_c \dot{E}_d(0) + \cdots \quad 8.6.13$$

where we have defined the additional tensors $C_{ab,cd}$ and $D_{a,bc}$ in the obvious way:

$$C_{ab,cd} = \frac{2}{\hbar}\sum_{m\neq n} \frac{\omega_{mn} Re\left[\langle n|\widehat{\Theta}_{ab}|m\rangle\langle m|\widehat{\Theta}_{cd}|n\rangle\right]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.14$$

$$C'_{ab,cd} = -\frac{2}{\hbar}\sum_{m\neq n} \frac{\omega Im\left[\langle n|\widehat{\Theta}_{ab}|m\rangle\langle m|\widehat{\Theta}_{cd}|n\rangle\right]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.15$$

$$D_{a,bc} = \frac{2}{\hbar}\sum_{m\neq n} \frac{\omega_{mn} Re\left[\langle n|\widehat{m}_a|m\rangle\langle m|\widehat{\Theta}_{bc}|n\rangle\right]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.16$$

$$D'_{a,bc} = -\frac{2}{\hbar}\sum_{m\neq n} \frac{\omega Im\left[\langle n|\widehat{m}_a|m\rangle\langle m|\widehat{\Theta}_{bc}|n\rangle\right]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.17$$

Note that here the property tensors involving mixed moments and the time derivatives of fields enter with minus signs. This is because the A tensors are defined with the electric dipole moment operator first, and if we wish to write our final polarisability in that form, the step equivalent to (8.6.2) will involve taking the complex conjugate of the *first* line, not the second, which causes the primed property tensor to enter with the opposite sign. The same thing happens with $D'_{a,bc}$: because the magnetic dipole moment is conventionally written first in the D tensors, it is the first rather than the second line in the equivalent of (8.6.2) that must be conjugated.

Later we shall also require the electric octupole moment, which is given by

$$\langle n'|\hat{Q}_{abc}|n'\rangle = B_{d,abc}E_d(0) - B'_{d,abc}\frac{1}{\omega}\dot{E}_d(0) \quad 8.6.18$$

with

$$B_{a,bcd} = \frac{2}{\hbar}\sum_{m\neq n} \frac{\omega_{mn} Re\left[\langle n|\hat{\mu}_a|m\rangle\langle m|\widehat{Q}_{bcd}|n\rangle\right]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.19$$

$$B'_{a,bcd} = -\frac{2}{\hbar}\sum_{m\neq n} \frac{\omega Im\left[\langle n|\hat{\mu}_a|m\rangle\langle m|\widehat{Q}_{bcd}|n\rangle\right]}{(\omega_{mn}^2 - \omega^2)} \quad 8.6.20$$

8.7. Magnetic Moments

The induced magnetic dipole and quadrupole moments follow similarly, though there is a slight subtlety regarding the appearance of the diamagnetic susceptibility tensors.

It might appear that these contributions, which in the multipolar Hamiltonian are second-order in the magnetic field or its derivatives, were abandoned by our insistence on only retaining terms first-order in the fields in equation (8.5.7). However, the magnetic multipole operators appearing in the Hamiltonian are not the ones we require to calculate the radiated fields, as they are defined using canonical momentum. To give an example, the magnetic dipole moment of a collection of α classical point charges is defined by

$$m_a = \sum_\alpha \frac{q_\alpha}{2m_\alpha}\epsilon_{abc} r_{\alpha_b} p_{\alpha_c}. \quad 8.7.1$$

When we wish to apply this in our present context, and "promote" $\boldsymbol{m}$, $\boldsymbol{r}$ and $\boldsymbol{p}$ to quantum mechanical operators, the question arises of whether the $\hat{\boldsymbol{p}}$ in this definition refers to the kinetic or the canonical momentum of the charges. As the purpose of our dipole moment operator is that its expectation values will be used as a stand-in for the classical dipole moment when calculating the radiated field, it seems clear that it is the kinetic momenta of the charges which should enter. However, as mentioned earlier, the magnetic moment operators which appear in the multipolar Hamiltonian contain the canonical momenta.

Moving from canonical to kinetic has the effect of reintroducing the diamagnetic susceptibilities, as we will now show. The "kinetic" magnetic dipole moment operator, for example, can be obtained from the "canonical" dipole moment,

$$\widehat{m}_a^{canon.} = \sum_\alpha \frac{q_\alpha}{2m_\alpha}\epsilon_{abc} \hat{r}_{\alpha_b} \hat{p}_{\alpha_c}, \quad 8.7.2$$

by replacing the momentum with the kinetic momentum as follows:

$$\widehat{m}_a^{kin.} = \sum_\alpha \frac{q_\alpha}{2m_\alpha}\epsilon_{abc} \hat{r}_{\alpha_b}\left(\hat{p}_{\alpha_c} - q_\alpha A(\boldsymbol{r}_\alpha)_c\right). \quad 8.7.3$$

In order to interpret this, note that in the Barron-Grey gauge (which we used to derive the multipolar Hamiltonian), the vector potential $\boldsymbol{A}$ is given by

$$A(\boldsymbol{r}_\alpha)_c = -\frac{1}{2}\epsilon_{cde} r_{\alpha_d} B_e(0) - \frac{1}{3}\epsilon_{cde} r_{\alpha_d} r_{\alpha_f} \nabla_f B_e(0) - \frac{1}{8}\epsilon_{cde} r_{\alpha_d} r_{\alpha_f} r_{\alpha_g} \nabla_f \nabla_g B_e(0) - \cdots \quad 8.7.4$$

We therefore have

$$\widehat{m}_a{}^{kin.} = \widehat{m}_a^{canon.} - \sum_\alpha \frac{q_\alpha}{2m_\alpha}\epsilon_{abc}\hat{r}_{\alpha_b}(-q_\alpha A(\boldsymbol{r}_\alpha)_c)$$

$$= \widehat{m}_a^{canon.} + \sum_\alpha \frac{q_\alpha^2}{2m_\alpha}\epsilon_{abc}\hat{r}_{\alpha_b}\left(-\frac{1}{2}\epsilon_{cde} r_{\alpha_d} B_e(0) - \frac{1}{3}\epsilon_{cde} r_{\alpha_d} r_{\alpha_f}\nabla_f B_e(0)\right.$$

$$\left. - \frac{1}{8}\epsilon_{cde} r_{\alpha_d} r_{\alpha_f} r_{\alpha_g}\nabla_f\nabla_g B_e(0) + \cdots\right) \quad 8.7.5$$

Which can be re-written, using the identity $\epsilon_{abc}\epsilon_{cde} = \delta_{ad}\delta_{be} - \delta_{ae}\delta_{bd}$, as

$$\widehat{m}_a^{canon.} + \chi_{ab}^{(d)} B_b(0) + \chi_{ab,c}^{(d)} \nabla_c B_b(0) - \cdots \quad 8.7.6$$

with the diamagnetic susceptibility tensors

$$\chi_{ab}^{(d)} = \sum_{\alpha} \frac{q_\alpha^2}{4m_\alpha}\left(r_{\alpha_a} r_{\alpha_b} - \boldsymbol{r}_\alpha^2 \delta_{ab}\right), \qquad 8.7.7$$

$$\chi_{ab,c}^{(d)} = \sum_{\alpha} \frac{q_\alpha^2}{6m_\alpha}\left(r_{\alpha_a} r_{\alpha_b} - \boldsymbol{r}_\alpha^2 \delta_{ab}\right) r_{\alpha_c}, \qquad 8.7.8$$

and so on. This means that the expectation value of the magnetic dipole moment which must be used to calculate the radiated fields is

$$\langle n' | \widehat{m}_a^{kin.} | n' \rangle = \left(\langle n| + \sum_{j\neq n} \frac{\langle n|\hat{\mu}_b|j\rangle}{2\hbar(\omega_{jn} - \omega)} \tilde{E}_c^*(0)\langle j| + \frac{\langle n|\hat{\mu}_b|j\rangle}{2\hbar(\omega_{jn} + \omega)} \tilde{E}_c(0)\langle j| + \cdots \right) \widehat{m}_a^{canon.} \left(|n\rangle \right.$$

$$\left. + \sum_{m\neq n} \frac{\langle m|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{mn} - \omega)} \tilde{E}_c(0)|m\rangle + \frac{\langle m|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{mn} + \omega)} \tilde{E}_c^*(0)|m\rangle + \cdots \right) + \langle n| \chi_{ab}^{(d)} B_b(0)$$

$$+ \chi_{ab,c}^{(d)} \nabla_c B_b(0) + \cdots |n\rangle \qquad 8.7.9$$

where only terms first-order in the fields have been retained – with this approximation, we have $\langle n'|\chi_{ab}^{(d)} B_b(0)|n'\rangle = \langle n|\chi_{ab}^{(d)} B_b(0)|n\rangle$, etc. The development then proceeds exactly as in the electric case, but the polarisability tensors which multiply magnetic fields or field derivatives will contain – in addition to the sums over matrix elements of the (canonical) magnetic multipole operators – an additional diamagnetic contribution. The induced magnetic dipole moment is therefore given by

$$\langle n' | \widehat{m}_a^{kin.} | n' \rangle = G_{ba} E_b(0) - \frac{1}{\omega} G'_{ba} \dot{E}_b(0) + \chi_{ab} B_b + \frac{1}{\omega} \chi'_{ab} \dot{B}_b(0) + \frac{1}{3} D_{a,bc} \nabla_b E_c(0)$$

$$+ \frac{1}{3\omega} D'_{a,bc} \nabla_b \dot{E}_c(0) + \cdots \qquad 8.7.10$$

where we have defined the symmetric and anti-symmetric magnetic susceptibility tensors

$$\chi_{ab} = \frac{2}{\hbar} \sum_{m\neq n} \frac{\omega_{mn} Re[\langle n|\widehat{m}_a|m\rangle\langle m|\widehat{m}_b|n\rangle]}{(\omega_{mn}^2 - \omega^2)} + \sum_{\alpha} \frac{q_\alpha^2}{4m_\alpha} \langle n| \left(r_{\alpha_a} r_{\alpha_b} - \boldsymbol{r}_\alpha^2 \delta_{ab} \right) |n\rangle \qquad 8.7.11$$

$$\chi'_{ab} = -\frac{2}{\hbar} \sum_{m\neq n} \frac{\omega Im[\langle n|\widehat{m}_a|m\rangle\langle m|\widehat{m}_b|n\rangle]}{(\omega_{mn}^2 - \omega^2)} \qquad 8.7.12$$

A similar calculation can be performed for the magnetic quadrupole moment. However, the lowest order analogous "diamagnetic" contribution to $\widehat{m}_{ab}^{kin.}$ depends on $\chi_{ca,b}^{(d)} B_c(0)$ [10, p. 47, eq. 2.104]. Because of the three factors of r_α in $\chi_{ca,b}^{(d)}$, each of the order of the molecular dimensions, the contribution will be small enough that it can be neglected in the next chapter's work. A more systematic discussion of the relative sizes of different multipolar contributions to the scattered light is given in section (8.12).

8.8. Complex Polarisabilities and Complex Multipole Moments

We have taken special care in the preceding section to express our final results purely in terms of real fields and field derivatives, multiplied by real polarisability tensors. However, for the calculation of the radiated fields from a collection of oscillating multipole moments, it is often useful to express the moments and fields in complex form, as was done in chapter 2. In order to do this, we seek *complex polarisability tensors*, which are to multiply the complex electric and magnetic fields in order to produce the expression for a complex multipole moment – the physical multipole moment being given by the real part of this.

As the induced moments are all linear in the fields, this rewriting can be accomplished straightforwardly – all that is required is to replace the real $\boldsymbol{E}$ and $\boldsymbol{B}$ fields in expressions such as (8.6.8) with their complex equivalents. By inspecting the result, we are immediately led to the definitions of the complex polarisability tensors

$$\tilde{\alpha}_{ab} = \alpha_{ab} - i\alpha'_{ab} \tag{8.8.1}$$

$$\tilde{A}_{a,bc} = A_{a,bc} - iA'_{a,bc} \tag{8.8.2}$$

$$\tilde{G}_{ab} = G_{ab} - iG'_{ab} \tag{8.8.3}$$

etc. The expressions for the induced complex moments then become

$$\tilde{\mu}_a = \tilde{\alpha}_{ab}\tilde{E}_b(0) + \tilde{G}_{ab}\tilde{B}_b(0) + \frac{1}{3}\tilde{A}_{a,bc}\nabla_b\tilde{E}_c(0) + \cdots \tag{8.8.4}$$

$$\tilde{\Theta}_{ab} = \tilde{A}^*_{c,ab}\tilde{E}_c(0) + \tilde{D}^*_{c,ab}\tilde{B}_c(0) + \tilde{C}_{ab,cd}\nabla_c\tilde{E}_d(0) + \cdots \tag{8.8.5}$$

Note that where minus signs appeared with the primed property tensors, the corresponding complex tensors are complex-conjugated.

8.9. Extension to Regions of Absorption

So far, the treatment has assumed that no light is absorbed by the sample. This assumption is tacitly made at the outset by the semi-classical description, as can be seen by the evident absence of spontaneous emission: when there is no field, there is no perturbation, and all energy eigenstates will simply evolve under the free Hamiltonian, and will therefore be stable.

Of course, this can only be valid if the frequency of the incident light is far from any of the transition frequencies in the molecule. A rigorous treatment of the behaviour near resonance would require a quantum-mechanical description of the light field, but spontaneous emission (and also absorption) can be introduced into the semiclassical model in a slightly *ad hoc* manner by the use of *complex frequencies* (see [8, §2.6.3]).

We restrict our attention to the case where decays between different excited states are not appreciable: the states decay only to a ground state of infinite lifetime. We can then associate with each state $|n\rangle$ one decay rate, Γ_n. The procedure is then to insert – by hand, as it were – a damping term that causes the excited state populations to decay exponentially at this rate. In other words, we require that the amplitude of the state $|n\rangle$ must fall off as $e^{-\frac{1}{2}\Gamma_n t}$. As the time dependence of each state vector is given by $\mathrm{e}^{-i\omega_n t}$, this requirement can be met simply by introducing complex frequencies, defined by

$$\widetilde{\omega}_n \equiv \omega_n - \frac{1}{2} i\Gamma_n. \qquad 8.9.1$$

The introduction of such complex frequencies into the above polarisability tensors requires a little care, as complex conjugates were taken of the complex polarisability tensors in expressions (8.8.4-8.8.5), solely in order to ensure the correct signs of the real property tensors when multiplied by the real fields. Accordingly, after we have substituted $\omega_n = \widetilde{\omega}_n$, we do not wish for the conjugate of $\widetilde{\omega}_n$ to be taken in these expressions. We therefore define a further set of property tensors, for use with complex frequencies:

$$\tilde{\mathcal{A}}_{a,bc} = A_{a,bc} + iA'_{a,bc} \qquad 8.9.2$$

$$\tilde{\mathcal{G}}_{ab} = G_{ba} + iG'_{ba} \qquad 8.9.3$$

etc.[4] We then have

$$\tilde{\mu}_a = \tilde{\alpha}_{ab}\tilde{E}_b(0) + \tilde{G}_{ab}\tilde{B}_b(0) + \frac{1}{3}\tilde{A}_{a,bc}\nabla_b\tilde{E}_c(0) + \cdots \qquad 8.9.4$$

$$\widetilde{\Theta}_{ab} = \tilde{\mathcal{A}}_{c,ab}\tilde{E}_c(0) + \tilde{\mathcal{D}}_{c,ab}\tilde{B}_c(0) + \tilde{C}_{ab,cd}\nabla_c\tilde{E}_d(0) + \cdots \qquad 8.9.5$$

and so on, where the complex conjugates in (8.8.4-8.8.5) have been replaced with scripted property tensors.

Note that in the complex property tensors of the previous section, the real parts were associated with the symmetric (or for mixed moments, symmetric-type) polarisability tensors, and the imaginary parts with the antisymmetric-type tensors. The treatment of near-resonance phenomena involves the addition of complex frequencies to each part, so the separation of these new property tensors into symmetric-type and anti-symmetric-type parts no longer coincides with their separation into real and imaginary parts.

8.10. Raman Scattering

The present formalism can be slightly modified to also describe Raman scattering – that is, the case where the final state of the molecule is not equal to the initial state, and the scattered light is not of the same frequency as the incident.

To deal with Raman scattering, we replace the expectation values that we have been considering with transition dipole moments such as

---

[4] The labelling of the indices in the definition of $\tilde{\mathcal{G}}_{ab}$ may appear counterintuitive. This convention exists to give an intuitive order of indices in the expression for $\widetilde{m}^{0\,kin.}_{a}$. Equation (8.11.4) reads $\widetilde{m}^{0\,kin.}_{a} = \tilde{\mathcal{G}}_{ab}\tilde{E}^0_b(0) + \cdots$

$$\langle m'|\hat{\mu}_a|n'\rangle + \langle m'|\hat{\mu}_a|n'\rangle^*$$
$$= \left(\langle m| + \sum_{j\neq m} \frac{\langle m|\hat{\mu}_b|j\rangle}{2\hbar(\omega_{jm}-\omega)}\tilde{E}_b^*(0)\langle j| + \frac{\langle m|\hat{\mu}_b|j\rangle}{2\hbar(\omega_{jm}+\omega)}\tilde{E}_b(0)\langle j| + \cdots\right)\hat{\mu}_a\left(|n\rangle\right.$$
$$\left. + \sum_{k\neq n} \frac{\langle k|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{kn}-\omega)}\tilde{E}_b(0)|k\rangle + \frac{\langle k|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{kn}+\omega)}\tilde{E}_b^*(0)|k\rangle + \cdots\right)e^{-i\omega_{nm}t} + c.c. \qquad 8.10.1$$

The first term is independent of the applied fields and oscillates with time-dependence $e^{-i\omega_{nm}t}$, and its conjugate oscillates with $e^{-i\omega_{mn}t}$. Together, they can therefore be interpreted as describing the emission associated with spontaneous decays from the higher to the lower of the two states [11, p. 202].

The other terms can be divided into two categories: those with time-dependence $e^{-i(\omega-\omega_{mn})t}$, and those with dependence $e^{-i(-\omega-\omega_{mn})t} = e^{i(\omega-\omega_{nm})t}$ (along with their complex conjugates). The former describe transitions from state n to state m, while the latter describe transitions from state n to state m [11]. If we restrict our attention to transitions with n as the initial state, and m as the final, we are left with

$$\mu_a^{mn} = \left(\sum_{k\neq n} \frac{\langle m|\mu_a|k\rangle\langle k|\hat{\mu}_b|n\rangle}{2\hbar(\omega_{kn}-\omega)}\tilde{E}_b(0) + \sum_{j\neq m} \frac{\langle m|\hat{\mu}_b|j\rangle\langle j|\mu_a|n\rangle}{2\hbar(\omega_{jm}+\omega)}\tilde{E}_b(0) + \cdots \ldots\right)e^{-i(-\omega_{mn})t} + c.c. \, 8.10.2$$

We can also form a complex polarisability tensor appropriate for Raman scattering, analogous to (8.8.1). To do this we consider, instead of the $n \to m$ part of $\langle m'|\hat{\mu}_a|n'\rangle + \langle m'|\hat{\mu}_a|n'\rangle^*$, twice the $n \to m$ part of just $\langle m'|\hat{\mu}_a|n'\rangle$. This means we drop the complex conjugate in (8.9.2) and multiply by 2, which leaves us with

$$\tilde{\mu}_a^{mn} = \left(\sum_{k\neq n} \frac{\langle m|\mu_a|k\rangle\langle k|\hat{\mu}_b|n\rangle}{\hbar(\omega_{kn}-\omega)}\tilde{E}_b(0) + \sum_{j\neq m} \frac{\langle m|\hat{\mu}_b|j\rangle\langle j|\mu_a|n\rangle}{\hbar(\omega_{jm}+\omega)}\tilde{E}_b(0) + \cdots\right)e^{-i(-\omega_{mn})t}. \qquad 8.10.3$$

This allows us to define the polarisability tensor,

$$\tilde{\alpha}_{ab}^{mn} = \sum_{j\neq m,n} \frac{\langle m|\mu_a|j\rangle\langle j|\hat{\mu}_b|n\rangle}{\hbar(\omega_{jn}-\omega)} + \frac{\langle m|\hat{\mu}_b|j\rangle\langle j|\mu_a|n\rangle}{\hbar(\omega_{jm}+\omega)}\,, \qquad 8.10.4$$

for which

$$\tilde{\mu}_a^{mn} = \left(\tilde{\alpha}_{ab}^{mn}\tilde{E}_b(0) + \cdots\right)e^{-i(-\omega_{mn})t}. \qquad 8.10.5$$

The complex transition moment defined here oscillates with time-dependence $e^{-i(\omega-\omega_{mn})t}$, and reduces to the Rayleigh case for m=n. Note that in going from (8.10.3) to (8.10.4), we have dropped the $k = m$ term from the first sum and the $j = n$ term from the second. This is a good approximation, as the discarded quantity,

$$\frac{(\langle m|\mu_a|m\rangle - \langle n|\mu_a|n\rangle)\langle m|\mu_b|n\rangle}{\hbar(\omega_{mn}-\omega)}\tilde{E}_b(0)e^{-i(-\omega_{mn})t}, \qquad 8.10.6$$

is proportional to the difference between the permanent dipole moments of the two states [8, p. 109].

As in the Rayleigh case, the Raman transition polarisabilities can be extended to regions of absorption by the introduction of complex frequencies, the imaginary parts of which contain the damping rates. However, the requirement that a real electric field produces a real multipole moment implies the condition

$$\tilde{\alpha}_{ab}(\omega) = \tilde{\alpha}^*_{ab}(-\omega), \qquad 8.10.7$$

sometimes referred to as the "crossing relation". This implies that both the complex frequency and its complex conjugate must enter the polarisability tensors, resulting in expression such as

$$\tilde{\alpha}^{mn}_{ab} = \sum_{j\neq m,n} \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{\mu}_b|n\rangle}{\hbar\left(\widetilde{\omega}_{jn} - \omega\right)} + \frac{\langle m|\hat{\mu}_b|j\rangle\langle j|\mu_a|n\rangle}{\hbar\left(\widetilde{\omega}^*_{jm} + \omega\right)} \,. \qquad 8.10.8$$

Further discussion of this point can be found in [13].

8.11. Final Expressions

Drawing all of the preceding discussion together, we can write down very general expressions for the induced multipole moments, which can describe Rayleigh or Raman scattering from plane-wave illumination at transparent or absorbing frequencies. The scattered light is expressed in terms of the induced multipole moments, as in chapter 2. Each moment is given by a series of polarisability tensors which multiply the incident fields or field derivatives, and we give a quantum-mechanical expression for each tensor in terms of sums over transition matrix elements of the multipole moment operators.

The complex scattered fields, at a distance $\boldsymbol{R}$ far from a collection of multipole moments oscillating with frequency ω, are

$$\tilde{E}^{scattered}_a = \frac{\mu_0\omega^2 e^{ikR}}{4\pi R}\left(\delta_{ab} - \hat{R}_a\hat{R}_b\right)\Big[\tilde{\mu}_b + \frac{1}{c}\epsilon_{bcd}\widetilde{m}^{kin.}_c\hat{R}_d - \frac{ik}{3}\widetilde{\Theta}_{bc}\hat{R}_c - \frac{ik}{2c}\epsilon_{bcd}\widetilde{m}^{kin.}_{ce}\hat{R}_e\hat{R}_d - \frac{k^2}{6}\tilde{Q}_{bcd}\hat{R}_c\hat{R}_d + \cdots\Big] \qquad 8.11.1$$

and

$$\tilde{B}^{scattered}_a = \frac{1}{c}\epsilon_{abc}\hat{R}_b\tilde{E}^{scattererd}_a. \qquad 8.11.2$$

with $k = \frac{\omega}{c}$, and $\widehat{\boldsymbol{R}}$ a unit vector in the $\boldsymbol{R}$ direction. The multipole moments are given in terms of the incident fields at the molecule by

$$\tilde{\mu}^0_a = \tilde{\alpha}_{ab}\tilde{E}^0_b(0) + \tilde{G}_{ab}\tilde{B}^0_b(0) + \frac{1}{3}\tilde{A}_{a,bc}\nabla_b\tilde{E}^0_c(0) + \frac{1}{6}\tilde{B}_{a,bcd}\nabla_d\nabla_c\tilde{E}^0_b(0) + \frac{1}{2}\tilde{D}^{(m)}_{a,bc}\nabla_c\tilde{B}^0_b(0) + \cdots \qquad 8.11.3$$

$$\widetilde{m}^{0\,kin.}_{a} = \tilde{\mathcal{G}}_{ab}\tilde{E}^0_b(0) + \frac{1}{3}\tilde{D}_{a,bc}\nabla_c\tilde{E}^0_b(0) + \tilde{\chi}_{ab}\tilde{B}^0_b(0) + \cdots \qquad 8.11.4$$

$$\tilde{\Theta}^0_{ab} = \tilde{\mathcal{A}}_{c,ab}\tilde{E}^0_c(0) + \tilde{C}_{ab,cd}\nabla_d\tilde{E}^0_c(0) + \tilde{\mathcal{D}}_{c,ab}\tilde{B}^0_c(0) + \cdots \quad 8.11.5$$

$$\tilde{m}^{0\,kin.}_{ab} = \tilde{\mathcal{D}}^{(m)}_{c,ab}\tilde{E}^0_c(0) + \cdots \quad 8.11.6$$

$$\tilde{Q}^0_{abc} = \tilde{\mathcal{B}}_{d,abc}\tilde{E}^0_d(0) + \cdots. \quad 8.11.7$$

The superscript 0 indicates that the time-dependence is excluded from the quantity: we have $\tilde{\mu}_a = \tilde{\mu}^0_a e^{-i\omega t}$, $\tilde{E}_a = \tilde{E}^0_a e^{-i\omega_0 t}$, etc. For Raman scattering, $\omega = \omega_0$.

The relevant polarisability tensors are defined

$$\tilde{\alpha}_{ab} = \sum_{j\neq m,n} \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{\mu}_b|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{\mu}_b|j\rangle\langle j|\hat{\mu}_a|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.8$$

$$\tilde{A}_{a,bc} = \sum_{j\neq m,n} \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{\Theta}_{bc}|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{\Theta}_{bc}|j\rangle\langle j|\hat{\mu}_a|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.9$$

$$\tilde{\mathcal{A}}_{a,bc} = \sum_{j\neq m,n} \frac{\langle m|\hat{\Theta}_{bc}|j\rangle\langle j|\hat{\mu}_a|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{\Theta}_{bc}|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.10$$

$$\tilde{G}_{ab} = \sum_{j\neq m,n} \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{m}_b|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{m}_b|j\rangle\langle j|\hat{\mu}_a|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.11$$

$$\tilde{\mathcal{G}}_{ab} = \sum_{j\neq m,n} \frac{\langle m|\hat{m}_a|j\rangle\langle j|\hat{\mu}_b|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{\mu}_b|j\rangle\langle j|\hat{m}_a|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.12$$

$$\tilde{B}_{a,bcd} = \sum_{j\neq m,n} \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{Q}_{bcd}|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{Q}_{bcd}|j\rangle\langle j|\hat{\mu}_a|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.13$$

$$\tilde{\mathcal{B}}_{a,bcd} = \sum_{j\neq m,n} \frac{\langle m|\hat{Q}_{bcd}|j\rangle\langle j|\hat{\mu}_a|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{Q}_{bcd}|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.14$$

$$\tilde{C}_{ab,cd} = \frac{1}{3}\sum_{j\neq m,n} \frac{\langle m|\hat{\Theta}_{ab}|j\rangle\langle j|\hat{\Theta}_{cd}|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{\Theta}_{cd}|j\rangle\langle j|\hat{\Theta}_{ab}|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.15$$

$$\tilde{D}_{a,bc} = \sum_{j\neq m,n} \frac{\langle m|\hat{m}_a|j\rangle\langle j|\hat{\Theta}_{bc}|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{\Theta}_{bc}|j\rangle\langle j|\hat{m}_a|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.16$$

$$\tilde{\mathcal{D}}_{a,bc} = \sum_{j\neq m,n} \frac{\langle m|\hat{\Theta}_{bc}|j\rangle\langle j|\hat{m}_a|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{m}_a|j\rangle\langle j|\hat{\Theta}_{bc}|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.17$$

$$\tilde{D}^{(m)}_{a,bc} = \sum_{j\neq m,n} \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{m}_{bc}|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{m}_{bc}|j\rangle\langle j|\hat{\mu}_a|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.18$$

$$\tilde{\mathcal{D}}^{(m)}_{a,bc} = \sum_{j\neq m,n} \frac{\langle m|\hat{m}_{bc}|j\rangle\langle j|\hat{\mu}_a|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{\mu}_a|j\rangle\langle j|\hat{m}_{bc}|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)}, \quad 8.11.19$$

$$\tilde{\chi}_{ab} = \sum_{j\neq m,n} \frac{\langle m|\hat{m}_a|j\rangle\langle j|\hat{m}_b|n\rangle}{\hbar(\tilde{\omega}_{jn}-\omega)} + \frac{\langle m|\hat{m}_b|j\rangle\langle j|\hat{m}_a|n\rangle}{\hbar(\tilde{\omega}^*_{jm}+\omega)} + \sum_\alpha \frac{q_\alpha^2}{4m_\alpha}\langle m|r_{\alpha_a}r_{\alpha_b} - \delta_{ab}r_\alpha^2|n\rangle. \quad 8.11.20$$

8.12. Stokes Parameters of the Scattered Light

We complete the above treatment by considering how to construct explicit expressions that describe the scattered light field. In the far field of the scatterer, this will be a plane-wave propagating in the radial direction, with polarisation and intensity varying as a function of scattering angle.

There are a number of ways to mathematically specify the polarisation state of a monochromatic plane-wave. One convenient description is in terms of *Stokes parameters*, which are differences between the intensities of various polarisation components. For a wave traveling in the z direction, we define the Stokes parameters[5]

$$S_0 = E_x E_x^* + E_y E_y^*, \qquad 8.12.1$$

$$S_1 = E_x E_x^* - E_y E_y^*, \qquad 8.12.2$$

$$S_2 = -E_x E_y^* - E_y E_x^*, \qquad 8.12.3$$

$$S_3 = -i\left(E_x E_y^* - E_y E_x^*\right). \qquad 8.12.4$$

S_0 is equal to the total intensity, while S_1 is equal to the difference in intensities that would be transmitted through horizontally and vertically oriented polarisers. S_2 is the corresponding difference for diagonal and anti-diagonal polarisers, and finally S_3 is the difference for opposite circular polarisers [8, §2.3]. Together, these specify any pure state of polarisation, and are of practical convenience as their determination requires only intensity measurements.

The different Stokes parameters can be straightforwardly obtained from the definitions above and equation (8.11.1). As the intensities depend on products of the field strengths, the result will be a series of terms each containing a product of two polarisability tensors.

The relative size of these terms can be estimated by the fact that the multipole moment operators each contain factors of the molecular dimensions, and the derivatives of the electric field bring down factors of k. The terms can therefore be grouped into a hierarchy of sizes, each approximately a factor of $k_0 r$ smaller than the last, where r is the size of the molecule. The largest terms, "zeroth-order" in $k_0 r$, will depend on products of components of the $\tilde{\alpha}$ tensor: we will refer to these as the α^2 terms. The next largest, of first-order in $k_0 r$, will depend on products of $\tilde{\alpha}$ and $\tilde{A}$, or $\tilde{\alpha}$ and $\tilde{G}$. The fact that the "αA" terms enter at the same order as the "αG" terms can be seen immediately from the fact that the electric quadrupole and magnetic dipole moments enter into a multipolar expansion at the same order: the αA terms effectively contain the product of three electric dipole moments and an electric quadrupole moment, while the αG terms contain three electric dipole moments and a magnetic dipole moment.

[5] Some conventions use different numbering, or define some parameters with different signs.

This level of multipolar accuracy is where most standard treatments of optical activity end, and it is the next order of terms that will concern us in the following chapter. The "second-order" scattering contains terms involving the products of the tensors normally associated with optical activity: A^2, G^2 and GA. It will also contain products of the α tensor with property tensors associated with electric-dipole-electric-octupole and electric-dipole-magnetic-quadrupole polarisabilities: αB and $\alpha D^{(m)}$. Finally, at the same order as the electric-dipole-magnetic-quadrupole product are the products of two magnetic dipole moments, or a magnetic dipole and an electric quadrupole, so we must also consider contributions from $\alpha\chi$ and αD.

For self-consistency, all of the terms that enter at a given multipolar order must be examined together. One reason for this requirement is that the predictions of scattering intensities should be independent of the point within the molecule about which the multipolar expansions are taken – though the individual polarisability tensors themselves are not. In light of this, we will next review how the various multipole moment operators, and the associated polarisability tensors, behave under a change of molecular origin.

8.13. The Polarisability Tensors and Changes of Molecular Origin

It is obvious from the definitions of the multipole moments that, in general, their values depend on the point about which the multipole expansion is taken. Multipolar expansions are usually made about some convenient point – be it the centre of mass, centre of charge, or some other point selected by the symmetries of the charge distribution. However, this choice is arbitrary, and any physical predictions made from a multipolar treatment should not depend on it. We will explicitly check that the scattering predictions made in the subsequent chapter are independent of the choice of molecular origin about which the multipolar expansions are taken, and in order to do this we must first examine how the various multipole moments behave under a change of molecular origin.

The electric dipole moment is defined by

$$\mu_a = \sum_\alpha q_\alpha r_{\alpha_a}, \qquad 8.13.1$$

with r_α and q_α the position and charge of the α^{th} charge. If the molecular origin is shifted from 0 to a new position, $\boldsymbol{d}$, then the electric dipole moment calculated with this new centre is found by replacing r_{α_a} with $r_{\alpha_a} - d_a$, leading to

$$\mu'_a = \sum_\alpha q_\alpha \left(r_{\alpha_a} - d_a\right) = \mu_a - d_a \sum_\alpha q_\alpha\,. \qquad 8.13.2$$

We see that, unless the system is electrically neutral, the dipole moment changes when the molecular origin is changed. The change in the other moments is found the same way. Now specialising to a neutral system for simplicity, the origin-shifted electric quadrupole moment is given by

$$\Theta'_{ab} = \frac{1}{2}\sum_{\alpha} q_\alpha\left[3\left(r_{\alpha_a} - d_a\right)\left(r_{\alpha_b} - d_b\right) - \delta_{ab}\left(r_{\alpha_c} - d_c\right)\left(r_{\alpha_c} - d_c\right)\right]$$

$$= \Theta_{ab} - \frac{3}{2}\mu_a d_b - \frac{3}{2}\mu_b d_a + \delta_{ab}\mu_c d_c. \qquad 8.13.3$$

Finally, we have the octupole moment,

$$Q'_{abc} = \sum_{\alpha} q_\alpha\left(r_{\alpha_a} - d_a\right)\left(r_{\alpha_b} - d_b\right)\left(r_{\alpha_c} - d_c\right)$$

$$= Q_{abc} + d_a d_b \mu_c + d_a d_c \mu_b + d_b d_c \mu_a - d_a Q_{bc} - d_b Q_{ac} - d_c Q_{ab}, \qquad 8.13.4$$

where Q_{ab} is the *primitive electric quadrupole moment*,

$$Q_{ab} \equiv \sum_{\alpha} q_\alpha r_{\alpha_a} r_{\alpha_b}, \qquad 8.13.5$$

which appears because of the primitive (by which we mean "not-traceless") definition we are using for the electric octupole moment (see chapter 4, §4.1).

In general, for the electric series, the lowest non-vanishing moment is origin-independent: the monopole moment (i.e. the total charge) is always origin independent, the electric dipole moment is origin independent for any neutral system, the electric quadrupole moment is origin independent for any system with no electric dipole moment, and so on.

The magnetic moments are similar, with transformations given by

$$m'_a = \sum_{\alpha} \frac{q_\alpha}{2m_\alpha}\epsilon_{abc}\left(\hat{r}_{\alpha_b} - d_b\right)p_{\alpha_c} \qquad 8.13.6$$

$$= m_a - \sum_{\alpha} \frac{q_\alpha}{2m_\alpha}\epsilon_{abc} d_b p_{\alpha_c}. \qquad 8.13.7$$

The kinetic magnetic dipole moment operator is modified slightly by the addition of the diamagnetic susceptibility, and transforms as

$$m_a^{kin.\prime} = \sum_{\alpha} \frac{q_\alpha}{2m_\alpha}\epsilon_{abc}\left(\hat{r}_{\alpha_b} - d_b\right)p_{\alpha_c} + \sum_{\alpha} \frac{q_\alpha^2}{4m_\alpha}\Big(\left(r_{\alpha_a} - d_a\right)\left(r_{\alpha_b} - d_b\right) - (\boldsymbol{r}_\alpha - \boldsymbol{d})^2\delta_{ab}\Big) B_b(\boldsymbol{d})$$

$$= m_a^{kin.} - \sum_{\alpha} \frac{q_\alpha}{2m_\alpha}\epsilon_{abc} d_b p_{\alpha_c} + \Delta\chi_{ab}^{(d)} B_b(\boldsymbol{d}), \qquad 8.13.8$$

where $\Delta\chi_{ab}^{(d)} \equiv \chi_{ab}^{(d)^t} - \chi_{ab}^{(d)}$. For the magnetic quadrupole moment operator, we have

$$m'_{ab} = \sum_{\alpha} \frac{q_\alpha}{3m_\alpha}\epsilon_{acd}\left[\left(\hat{r}_{\alpha_b} - d_b\right)\left(\hat{r}_{\alpha_c} - d_c\right)\hat{p}_{\alpha_d} + \left(\hat{r}_{\alpha_c} - d_c\right)\hat{p}_{\alpha_d}\left(\hat{r}_{\alpha_b} - d_b\right)\right]$$

$$= m_{ab} + \sum_{\alpha} \frac{q_\alpha}{3m_\alpha}\epsilon_{acd}\left(2d_b d_c p_{\alpha_d} - d_c\left(r_{\alpha_b} p_{\alpha_d} + p_{\alpha_d} r_{\alpha_b}\right) - 2d_b r_{\alpha_c} p_{\alpha_d}\right)$$

$$= m_{ab} - \frac{4}{3}d_b m_a + \sum_{\alpha} \frac{q_\alpha}{3m_\alpha}\epsilon_{acd}\Big(2d_b d_c p_{\alpha_d} - d_c\left(r_{\alpha_b} p_{\alpha_d} + p_{\alpha_d} r_{\alpha_b}\right)\Big)$$

$$= m_{ab} - 2d_b m_a + \sum_\alpha \frac{q_\alpha}{3m_\alpha} \epsilon_{acd} \left(2d_b d_c p_{\alpha_d} - d_c \left(r_{\alpha_b} p_{\alpha_d} + p_{\alpha_d} r_{\alpha_b} \right) + d_b r_{\alpha_c} p_{\alpha_d} \right) \qquad 8.13.9$$

and corresponding expressions for the kinetic moments obtainable by replacing $\hat{\boldsymbol{p}}$ with $m\hat{\boldsymbol{v}}$. This replacement allows us to write some of the terms of (8.13.9) in terms of time derivatives of the electric moments: the kinetic magnetic quadrupole transformation can also be written [13]

$$m_{ab}^{kin.\prime} = m_{ab}^{kin.} - 2d_b m_a^{kin.} + \sum_\alpha \frac{2}{3} \epsilon_{acd} d_b d_c q_\alpha \hat{v}_{\alpha_d} - \frac{1}{3} \epsilon_{acd} d_c \frac{\mathrm{d}}{\mathrm{d}t} \hat{Q}_{bd} + \frac{1}{3} \delta_{ab} d_c \epsilon_{dec} \sum_\alpha q_\alpha \hat{r}_{\alpha_d} \hat{v}_{\alpha_e} \qquad 8.13.10$$

In principle there is also a diamagnetic term that will contribute to $m_{ab}^{kin.\prime}$, but this does not concern us at the order to which we will be working in the next chapter.

Using these expressions, we can straightforwardly derive the changes in the molecular polarisability tensors when the molecular origin is shifted. Just as we have written the changes in the multipole moments in terms of the unshifted multipole moments, we can write the changes in the property tensors in terms of unshifted property tensors. The electric property tensors transform as follows (we use a superscript t to denote the "transformed" property tensors calculated with the molecular origin shifted to $\boldsymbol{d}$, as a prime could cause confusion with with the primes denoting the symmetric-type real polarisability tensors in expressions such as (8.6.6-7)):

$$\tilde{\alpha}_{ab}^t = \tilde{\alpha}_{ab} \qquad 8.13.11$$

$$\tilde{A}_{a,bc}^t = \tilde{A}_{a,bc} - \frac{3}{2} d_b \tilde{\alpha}_{ac} - \frac{3}{2} d_c \tilde{\alpha}_{ab} + \delta_{bc} d_d \tilde{\alpha}_{ad} \qquad 8.13.12$$

$$\tilde{\mathcal{A}}_{a,bc}^t = \tilde{\mathcal{A}}_{a,bc} - \frac{3}{2} d_b \tilde{\alpha}_{ca} - \frac{3}{2} d_c \tilde{\alpha}_{ba} + \delta_{bc} d_d \tilde{\alpha}_{da} \qquad 8.13.13$$

$$\begin{aligned} \tilde{C}_{ab,cd}^t = \tilde{C}_{ab,cd} &- \frac{1}{2} d_d \tilde{\mathcal{A}}_{c,ab} - \frac{1}{2} d_c \tilde{\mathcal{A}}_{d,ab} + \frac{1}{3} \delta_{cd} d_e \tilde{\mathcal{A}}_{e,ab} \\ &- \frac{1}{2} d_b \tilde{A}_{a,cd} - \frac{1}{2} d_a \tilde{A}_{b,cd} + \frac{3}{4} d_b d_d \tilde{\alpha}_{ac} + \frac{3}{4} d_b d_c \tilde{\alpha}_{ad} + \frac{3}{4} d_a d_d \tilde{\alpha}_{bc} + \frac{3}{4} d_a d_c \tilde{\alpha}_{bd} \\ &- \frac{1}{2} \delta_{cd} d_b d_e \tilde{\alpha}_{ae} - \frac{1}{2} \delta_{cd} d_a d_e \tilde{\alpha}_{be} - \frac{1}{2} \delta_{ab} d_d d_e \tilde{\alpha}_{ec} - \frac{1}{2} \delta_{ab} d_c d_e \tilde{\alpha}_{ed} \\ &+ \frac{1}{3} \delta_{ab} d_e \tilde{A}_{e,cd} + \delta_{ab} \delta_{cd} d_e d_f \tilde{\alpha}_{ef} \end{aligned} \qquad 8.13.14$$

$$\tilde{B}_{a,bcd}^t = \tilde{B}_{a,bcd} - d_b \tilde{A}_{a,cd}^{(tr)} - d_c \tilde{A}_{a,bd}^{(tr)} - d_d \tilde{A}_{a,bc}^{(tr)} + d_c d_d \tilde{\alpha}_{ab} + d_b d_d \tilde{\alpha}_{ac} + d_b d_c \tilde{\alpha}_{ad} \qquad 8.13.15$$

The derivations of these expressions depend only on the transformation properties of the electric multipole moment operators, so they are valid for both Rayleigh and Raman polarisabilities, whether real or complex, at transparent or at absorbing frequencies.

Corresponding expressions for the property tensors which depend upon magnetic moments are a little more complicated to derive, and we restrict our attention to Rayleigh scattering at transparent frequencies for simplicity. In order to transform these, we will need to make use of the equality, referred to by Barron as the *velocity-dipole transformation* [8, p. 93]

$$\langle m|\hat{p}_a|n\rangle = im\omega_{mn}\langle m|\hat{r}_a|n\rangle. \tag{8.13.16}$$

This follows from the commutation relation $\hat{r}_a\hat{H}_{free} - \hat{H}_{free}\hat{r}_a = \frac{i\hbar}{m}\hat{p}_a$, when both sides are multiplied by $\langle m|$ on the left and $|n\rangle$ on the right. This allows the terms in the transformation of $\hat{m}_a$ that depend on the canonical momentum to be rewritten in terms of the position, and so the changes in the shifted magnetic property tensors can be expressed in terms of the unshifted electric ones. For example, we can use the transformation to write the transformation of the real unprimed G_{ab} (8.6.9)

$$\begin{aligned}
G^t_{ab} &= \frac{2}{\hbar}\sum_{m\neq n}\frac{\omega_{mn}Re\left[\langle n|\hat{\mu}_a|m\rangle\left\langle m\left|\hat{m}_b - \sum_\alpha \frac{q_\alpha}{2m_\alpha}\epsilon_{bcd}d_c\hat{p}_{\alpha_d}\right|n\right\rangle\right]}{(\omega^2_{mn}-\omega^2)} \\
&= G_{ab} - \frac{2}{\hbar}\sum_{m\neq n}\frac{\omega_{mn}Re\left[\langle n|\hat{\mu}_a|m\rangle\left\langle m\left|\sum_\alpha \frac{q_\alpha}{2m_\alpha}\epsilon_{bcd}d_c\hat{p}_{\alpha_d}\right|n\right\rangle\right]}{(\omega^2_{mn}-\omega^2)} \\
&= G_{ab} - \frac{2}{\hbar}\sum_{m\neq n}\frac{\omega^2_{mn}Re\left[i\langle n|\hat{\mu}_a|m\rangle\left\langle m\left|\sum_\alpha \frac{1}{2}q_\alpha\epsilon_{bcd}d_c\hat{r}_{\alpha_d}\right|n\right\rangle\right]}{(\omega^2_{mn}-\omega^2)} \\
&= G_{ab} - \frac{1}{2}\epsilon_{bcd}d_c\frac{2}{\hbar}\sum_{m\neq n}\frac{\omega^2_{mn}Re[i\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_d|n\rangle]}{(\omega^2_{mn}-\omega^2)} \\
&= G_{ab} + \frac{1}{2}\epsilon_{bcd}d_c\frac{2}{\hbar}\sum_{m\neq n}\frac{\omega^2_{mn}Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_d|n\rangle]}{(\omega^2_{mn}-\omega^2)}.
\end{aligned} \tag{8.13.17}$$

We can re-write the second term as

$$\begin{aligned}
&\frac{1}{2}\epsilon_{bcd}d_c\frac{2}{\hbar}\sum_{m\neq n}\frac{(\omega^2_{mn}-\omega^2+\omega^2)Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_d|n\rangle]}{(\omega^2_{mn}-\omega^2)} \\
&= \frac{1}{2}\epsilon_{bcd}d_c\frac{2}{\hbar}\sum_{m\neq n}Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_d|n\rangle] - \frac{1}{2}\epsilon_{bcd}d_c\omega\alpha'_{ad}.
\end{aligned} \tag{8.13.18}$$

Making use of the completeness relation[6] gives $\sum_{m\neq n} Im[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_d|n\rangle] = \sum_{m\neq n} Im[\langle n|\hat{\mu}_a\hat{\mu}_d|n\rangle]$, which vanishes as $\langle n|\hat{\mu}_a\hat{\mu}_d|n\rangle$ must be real. We therefore have

$$G^t_{ab} = G_{ab} - \frac{1}{2}\epsilon_{bcd}d_c\omega\alpha'_{ad}. \tag{8.13.19}$$

The imaginary part similarly transforms as

$$\begin{aligned}
G'^{\,t}_{ab} &= G'_{ab} - \frac{2}{\hbar}\sum_{m\neq n}\frac{\omega Im\left[\langle n|\hat{\mu}_a|m\rangle\left\langle m\left|-\sum_\alpha \frac{q_\alpha}{2m_\alpha}\epsilon_{bcd}d_c\hat{p}_{\alpha_d}\right|n\right\rangle\right]}{(\omega^2_{mn}-\omega^2)} \\
&= G'_{ab} + \frac{1}{2}\epsilon_{bcd}d_c\frac{2}{\hbar}\sum_{m\neq n}\frac{\omega\omega_{mn}Im[i\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_d|n\rangle]}{(\omega^2_{mn}-\omega^2)}
\end{aligned}$$

[6] In this context we may use the completeness relation despite the exclusion of *n* from the sum, as the term $\langle n|\hat{\mu}_a|n\rangle\langle n|\hat{\mu}_d|n\rangle$ will be purely real, and will not contribute to the expression.

$$= G'_{ab} + \frac{1}{2}\epsilon_{bcd}d_c \frac{2}{\hbar}\sum_{m\neq n} \frac{\omega\omega_{mn} Re[\langle n|\hat{\mu}_a|m\rangle\langle m|\hat{\mu}_d|n\rangle]}{(\omega_{mn}^2 - \omega^2)}$$

$$= G'_{ab} + \frac{1}{2}\epsilon_{bcd}d_c\omega\alpha_{ad}. \qquad 8.13.20$$

Finally, using the definitions $\tilde{G}_{ab} = G_{ab} - iG'_{ab}$ and $\tilde{\alpha}_{ab} = \alpha_{ab} - i\alpha'_{ab}$, we readily see that the result can be written in terms of the complex polarisability tensors

$$\tilde{G}^t_{ab} = \tilde{G}_{ab} - \frac{1}{2} i\omega\epsilon_{bcd}d_c\tilde{\alpha}_{ad}. \qquad 8.13.21$$

For the scripted tensor, $\tilde{\mathcal{G}}_{ab} = G_{ba} + iG'_{ba}$, we have

$$\tilde{G}^t_{ab} = \tilde{\mathcal{G}}_{ab} + \frac{1}{2} i\omega\epsilon_{acd}d_c(\alpha_{bd} + i\alpha'_{bd}) = \tilde{\mathcal{G}}_{ab} + \frac{1}{2} i\omega\epsilon_{acd}d_c\tilde{\alpha}_{db}, \qquad 8.13.22$$

where the final step follows from the symmetry of $\alpha_{bd}$and the antisymmetry of α'_{bd}.

For $D_{a,bc}$ we similarly obtain

$$D^t_{a,bc} = D_{a,bc} - \frac{3}{2}d_cG_{ba} - \frac{3}{2}d_bG_{ca} + \delta_{bc}d_fG_{fa}$$
$$-\frac{1}{2}\omega\epsilon_{ade}d_d\left(-A'_{e,bc} + \frac{3}{2}d_c\alpha'_{eb} + \frac{3}{2}d_b\alpha'_{ec} - \delta_{bc}d_f\alpha'_{ef}\right). \qquad 8.13.23$$

We similarly have

$$D'^t_{a,bc} = -\frac{2}{\hbar}\sum_{m\neq n}\frac{\omega Im\left[\left\langle n\left|m_a - \sum_\alpha \frac{q_\alpha}{2m_\alpha}\epsilon_{ade}d_dp_{\alpha_e}\right|m\right\rangle\left\langle m\left|\Theta_{bc} - \frac{3}{2}\mu_bd_c - \frac{3}{2}\mu_cd_b + \delta_{bc}\mu_fd_f\right|n\right\rangle\right]}{(\omega_{mn}^2 - \omega^2)}$$

$$= D'_{a,bc} + \frac{3}{2}d_cG'_{ba} + \frac{3}{2}d_bG'_{ca} - \delta_{bc}d_fG'_{fa} - \frac{1}{2}\epsilon_{ade}d_d\omega\left(A_{e,bc} - \frac{3}{2}d_c\alpha_{eb} - \frac{3}{2}d_b\alpha_{ec} + \delta_{bc}d_f\alpha_{ef}\right) 8.13.24$$

We therefore find that (using $\widetilde{D}_{a,bc} = D_{a,bc} - iD'_{a,bc}$, etc.),

$$\widetilde{D}^t{}_{a,bc} = \widetilde{D}_{a,bc} - \frac{3}{2}d_c\tilde{\mathcal{G}}_{ab} - \frac{3}{2}d_b\tilde{\mathcal{G}}_{ac} + \delta_{bc}d_f\tilde{\mathcal{G}}_{af}$$
$$+\frac{1}{2}\epsilon_{ade}d_di\omega\left(\tilde{A}_{e,bc} - \frac{3}{2}d_c\tilde{\alpha}_{eb} - \frac{3}{2}d_b\tilde{\alpha}_{ec} + \delta_{bc}d_f\tilde{\alpha}_{ef}\right), \qquad 8.13.25$$

and

$$\widetilde{\mathcal{D}}^t{}_{a,bc} = \widetilde{\mathcal{D}}_{a,bc} - \frac{3}{2}d_c\tilde{G}_{ba} - \frac{3}{2}d_b\tilde{G}_{ca} + \delta_{bc}d_f\tilde{G}_{fa}$$
$$+\frac{1}{2}\epsilon_{ade}d_di\omega\left(-\mathcal{A}_{e,bc} + \frac{3}{2}d_c\tilde{\alpha}_{be} + \frac{3}{2}d_b\tilde{\alpha}_{ce} - \delta_{bc}d_f\tilde{\alpha}_{fe}\right) \qquad 8.13.26$$

Finally, the magnetic susceptibility tensor gives

$$\chi^t_{ab} = \frac{2}{\hbar}\sum_{m\neq n}\frac{\omega_{mn}Re\left[\left\langle n\left|m_a - \sum_\alpha\frac{q_\alpha}{2m_\alpha}\epsilon_{acd}d_cp_{\alpha_d}\right|m\right\rangle\left\langle m\left|m_b - \sum_\alpha\frac{q_\alpha}{2m_\alpha}\epsilon_{bef}d_ep_{\alpha_f}\right|n\right\rangle\right]}{(\omega_{mn}^2 - \omega^2)} + \chi^{(m)}{}^t_{ab}. 8.13.27$$

Applying the velocity dipole transformation, and a little manipulation, gives

$$\chi^t_{ab} = \chi_{ab} + \frac{2}{\hbar}\sum_{m\neq n}\frac{\omega_{mn}}{(\omega_{mn}^2-\omega^2)}Re\left[-i\omega_{mn}\frac{1}{2}\,\epsilon_{bef}d_e\langle n|\widehat{m}_a|m\rangle\langle m|\hat{\mu}_f|n\rangle\right.$$
$$-\,i\omega_{nm}\frac{1}{2}\,\epsilon_{acd}d_c\langle n|\hat{\mu}_d|m\rangle\langle m|\widehat{m}_b|n\rangle$$
$$\left.-\,\omega_{nm}\omega_{mn}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right] + {\chi^{(m)}}^t_{ab}$$
$$= \chi_{ab} + \frac{2}{\hbar}\sum_{m\neq n}\frac{\omega_{mn}^2}{(\omega_{mn}^2-\omega^2)}Im\left[\frac{1}{2}\,\epsilon_{bef}d_e\langle n|\widehat{m}_a|m\rangle\langle m|\hat{\mu}_f|n\rangle - \frac{1}{2}\,\epsilon_{acd}d_c\langle n|\hat{\mu}_d|m\rangle\langle m|\widehat{m}_b|n\rangle\right]$$
$$+\frac{\omega_{mn}^3}{(\omega_{mn}^2-\omega^2)}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right] + {\chi^{(m)}}^t_{ab}$$
$$= \chi_{ab} - \frac{1}{2}\frac{2}{\hbar}\sum_{m\neq n}\frac{\omega^2}{(\omega_{mn}^2-\omega^2)}Im\left[\,\epsilon_{bef}d_e\langle n|\hat{\mu}_f|m\rangle\langle m|\widehat{m}_a|n\rangle + \epsilon_{acd}d_c\langle n|\hat{\mu}_d|m\rangle\langle m|\widehat{m}_b|n\rangle\right]$$
$$-\frac{\omega_{mn}^3}{(\omega_{mn}^2-\omega^2)}Re\left[\frac{1}{2}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right] + {\chi^{(m)}}^t_{ab}$$
$$= \chi_{ab} + \frac{1}{2}\omega\left(\epsilon_{bef}d_eG'_{fa} + \epsilon_{acd}d_cG'_{db}\right)$$
$$+\frac{2}{\hbar}\sum_{m\neq n}\frac{\omega_{mn}^3}{(\omega_{mn}^2-\omega^2)}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right] + {\chi^{(m)}}^t_{ab}. \quad 8.13.28$$

The remaining sum may be expressed in terms of α_{df} as follows:

$$\frac{2}{\hbar}\sum_{m\neq n}\frac{\omega_{mn}^3}{(\omega_{mn}^2-\omega^2)}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right]$$
$$= \frac{2}{\hbar}\sum_{m\neq n}\omega_{mn}\frac{\omega_{mn}^2-\omega^2+\omega^2}{(\omega_{mn}^2-\omega^2)}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right]$$
$$= \frac{2}{\hbar}\sum_{m\neq n}\omega_{mn}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right] + \frac{1}{4}\,\omega^2\epsilon_{acd}\epsilon_{bef}d_cd_e\alpha_{df} \qquad 8.13.29$$

We can see that the first term is in fact equal to 0 by reversing the velocity-dipole transformation, and making use of the closure of the molecular states:

$$\frac{2}{\hbar}\sum_{m\neq n}\omega_{mn}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right]$$
$$= \frac{2}{\hbar}\sum_{m\neq n}\omega_{mn}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\left\langle m\left|\sum_\alpha q_\alpha\hat{r}_{\alpha f}\right|n\right\rangle\right]$$
$$= \frac{2}{\hbar}\sum_{m\neq n}Re\left[-\frac{i}{m}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\langle n|\hat{\mu}_d|m\rangle\left\langle m\left|\sum_\alpha q_\alpha\hat{p}_f\right|n\right\rangle\right]$$
$$= \frac{2}{\hbar}Re\left[-\frac{i}{m}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_cd_e\left\langle n\left|\hat{\mu}_d\sum_\alpha q_\alpha\hat{p}_f\right|n\right\rangle\right] \qquad 8.13.30$$

But we may also reverse the transformation on the first matrix element,

$$\frac{2}{\hbar}\sum_{m\neq n}\omega_{mn}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right]$$

$$= -\frac{2}{\hbar}\sum_{m\neq n}\omega_{nm}Re\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right]$$

$$= \frac{2}{\hbar}Re\left[\frac{i}{m}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\left\langle n\left|\sum_\alpha q_\alpha \hat{p}_{\alpha_d}\right|m\right\rangle\langle m|\hat{\mu}_f|n\rangle\right]$$

$$= \frac{2}{\hbar}Re\left[\frac{i}{m}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\left\langle n\left|\sum_\alpha q_\alpha \hat{p}_{\alpha_d}\,\hat{\mu}_f\right|n\right\rangle\right] \qquad 8.13.31$$

Adding half of (8.13.30) and (8.13.31) together gives

$$\frac{1}{\hbar}Re\left[\frac{i}{m}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\left\langle n\left|\sum_\alpha q_\alpha \hat{p}_{\alpha_d}\,\hat{\mu}_f - \hat{\mu}_d\sum_\alpha q_\alpha \hat{p}_f\right|n\right\rangle\right]$$

$$= \frac{1}{\hbar}Re\left[\frac{i}{m}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\left(-i\hbar\delta_{df}\Sigma_\alpha q_\alpha\right)\right] = Re\left[\frac{1}{m}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bed}d_c d_e\Sigma_\alpha q_\alpha\right], \qquad 8.13.32$$

and $\Sigma_\alpha q_\alpha = 0$ if the molecule is neutral. We therefore finally have

$$\chi_{ab}^t = \chi_{ab} + \frac{1}{2}\omega\left(\epsilon_{bef}d_e G'_{fa} + \epsilon_{acd}d_c G'_{db}\right) + \frac{1}{4}\,\omega^2\epsilon_{acd}\epsilon_{bef}d_c d_e\alpha_{df} + {\chi^{(m)}}_{ab}^{t} \qquad 8.13.33$$

Similarly, the antisymmetric part gives

$${\chi'_{ab}}^t = -\frac{2}{\hbar}\sum_{m\neq n}\frac{\omega Im\left[\left\langle n\left|m_a - \Sigma_\alpha\frac{q_\alpha}{2m_\alpha}\epsilon_{acd}d_c p_{\alpha_d}\right|m\right\rangle\left\langle m\left|m_b - \Sigma_\alpha\frac{q_\alpha}{2m_\alpha}\epsilon_{bef}d_e p_{\alpha_f}\right|n\right\rangle\right]}{(\omega_{mn}^2-\omega^2)}$$

$$= \chi'_{ab} - \frac{2}{\hbar}\sum_{m\neq n}\frac{\omega}{(\omega_{mn}^2-\omega^2)}Im\Big[-i\omega_{mn}\frac{1}{2}\,\epsilon_{bef}d_e\langle n|\widehat{m}_a|m\rangle\langle m|\hat{\mu}_f|n\rangle$$

$$- i\omega_{nm}\frac{1}{2}\,\epsilon_{acd}d_c\langle n|\hat{\mu}_d|m\rangle\langle m|\widehat{m}_b|n\rangle$$

$$- \omega_{nm}\omega_{mn}\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\Big]$$

$$= \chi'_{ab} + \frac{1}{2}\omega\epsilon_{bef}d_e G_{fa} - \frac{1}{2}\omega\epsilon_{acd}d_c G_{db}$$

$$+ \frac{2}{\hbar}\sum_{m\neq n} - \frac{\omega\omega_{mn}^2}{(\omega_{mn}^2-\omega^2)}Im\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right] \qquad 8.13.34$$

This time we can relate the remaining sum to α'_{df},

$$\frac{2}{\hbar}\sum_{m\neq n} - \frac{\omega\omega_{mn}^2}{(\omega_{mn}^2-\omega^2)}Im\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right]$$

$$= \frac{2}{\hbar}\sum_{m\neq n} - \omega\frac{\omega_{mn}^2 - \omega^2 + \omega^2}{(\omega_{mn}^2-\omega^2)}Im\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right]$$

$$= \omega\frac{2}{\hbar}\sum_{m\neq n}Im\left[\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\langle n|\hat{\mu}_d|m\rangle\langle m|\hat{\mu}_f|n\rangle\right] + \omega^2\frac{1}{4}\,\epsilon_{acd}\epsilon_{bef}d_c d_e\alpha'_{df} \qquad 8.13.35$$

Applying the closure of the molecular states and the hermiticity of the dipole moment operator, we find that the expression in square brackets is entirely real, and therefore vanishes. The overall transformation is therefore

$$\chi'^{\,t}_{ab} = \chi'_{ab} + \frac{1}{2}\omega\epsilon_{bef}d_e G_{fa} - \frac{1}{2}\omega\epsilon_{acd}d_c G_{db} + \frac{1}{4}\ \omega^2\epsilon_{acd}\epsilon_{bef}d_c d_e \alpha'_{df} \qquad 8.13.36$$

Finally, we may express the result in terms of the complex tensor $\tilde{\chi}_{ab} = \chi_{ab} - i\chi'_{ab}$,

$$\tilde{\chi}^t_{ab} = \tilde{\chi}_{ab} + \frac{1}{2}i\omega\left(-\epsilon_{bef}d_e\tilde{\mathcal{G}}_{af} + \epsilon_{acd}d_c\tilde{G}_{db}\right) + \frac{1}{4}\omega^2\epsilon_{acd}\epsilon_{bef}d_c d_e\tilde{\alpha}_{df} + {\chi^{(m)}}^t_{ab} \qquad 8.13.37$$

In summary, and with analogous derivations for the other property tensors, we have [10, §3.7]

$$\tilde{G}^t_{ab} = \tilde{G}_{ab} - \frac{i\omega}{2}\epsilon_{bcd}d_c\tilde{\alpha}_{ad} \qquad 8.13.38$$

$$\tilde{\mathcal{G}}'_{ab} = \tilde{\mathcal{G}}_{ab} + \frac{i\omega}{2}\epsilon_{acd}d_c\tilde{\alpha}_{db} \qquad 8.13.39$$

$$\begin{aligned}\widetilde{D}^t_{a,bc} &= \widetilde{D}_{a,bc} - \frac{3}{2}d_c\tilde{\mathcal{G}}_{ab} - \frac{3}{2}d_b\tilde{\mathcal{G}}_{ac} + \delta_{bc}d_f\tilde{\mathcal{G}}_{af} \\ &+ \frac{1}{2}\epsilon_{ade}d_d i\omega\left(\tilde{A}_{e,bc} - \frac{3}{2}d_c\tilde{\alpha}_{eb} - \frac{3}{2}d_b\tilde{\alpha}_{ec} + \delta_{bc}d_f\tilde{\alpha}_{ef}\right)\end{aligned} \qquad 8.13.40$$

$$\begin{aligned}\widetilde{\mathcal{D}}^t_{a,bc} &= \widetilde{\mathcal{D}}_{a,bc} - \frac{3}{2}d_c\tilde{G}_{ba} - \frac{3}{2}d_b G_{ca} + \delta_{bc}d_f G_{fa} \\ &- \frac{1}{2}\epsilon_{ade}d_d i\omega\left(\mathcal{A}_{e,bc} - \frac{3}{2}d_c\tilde{\alpha}_{be} - \frac{3}{2}d_b\tilde{\alpha}_{ce} + \delta_{bc}d_f\tilde{\alpha}_{fe}\right)\end{aligned} \qquad 8.13.41$$

$${\widetilde{D}^{(m)}_{a,bc}}^{\,t} = \widetilde{D}^{(m)}{}_{a,bc} + \frac{2i\omega}{3}\epsilon_{bde}d_c d_d\tilde{\alpha}_{ae} - \frac{i\omega}{3}\epsilon_{bde}d_d\tilde{A}^{(tr)}_{a,ce} - 2d_c\tilde{G}_{ab} + \frac{2}{3}\delta_{bc}d_d\tilde{G}_{ad} \qquad 8.13.42$$

$${\widetilde{\mathcal{D}}^{(m)}_{a,bc}}^{\,t} = \widetilde{\mathcal{D}}^{(m)}{}_{a,bc} - \frac{2i\omega}{3}\epsilon_{bde}d_c d_d\tilde{\alpha}_{ea} + \frac{i\omega}{3}\epsilon_{bde}d_d\tilde{\mathcal{A}}^{(tr)}_{a,ce} - 2d_c\tilde{\mathcal{G}}_{ba} + \frac{2}{3}\delta_{bc}d_d\tilde{\mathcal{G}}_{da} \qquad 8.13.43$$

$$\tilde{\chi}^t_{ab} = \tilde{\chi}_{ab} + \frac{i\omega}{2}\left(\epsilon_{acd}d_c\tilde{G}_{db} - \epsilon_{bcd}d_c\tilde{\mathcal{G}}_{ad}\right) + \frac{1}{4}\omega^2\epsilon_{acd}\epsilon_{bef}d_c d_e\tilde{\alpha}_{df} + \Delta\tilde{\chi}^{diamagnetic}_{ab} \qquad 8.13.44$$

with

$$\begin{aligned}\Delta\tilde{\chi}^{diamagnetic}_{ab} &\equiv \sum_\alpha \frac{q_\alpha^2}{4m_\alpha}\left\langle m\left|(r_{\alpha_a} - d_a)(r_{\alpha_b} - d_b) - \delta_{ab}\left(r_{\alpha_c} - d_c\right)^2\right|n\right\rangle \\ &- \sum_\alpha \frac{q_\alpha^2}{4m_\alpha}\langle m|r_{\alpha_a}r_{\alpha_b} - \delta_{ab}r_\alpha^2|n\rangle.\end{aligned} \qquad 8.13.45$$

8.14 Symmetries of Tensors and Molecules

Different molecular symmetries can preclude or permit different scattering effects. This is immediately apparent from the above formalism: because the various polarisability tensors depend on the sums of multipole moment operators, any symmetries in the charge distribution of the molecule (and therefore in the wavefunctions describing the different molecular states) directly set limits on which polarisability tensor components a molecule with such symmetries can in principle support.

A particularly clear application of these ideas is the fact that an isotropic fluid of achiral molecules cannot support scattering which depends on property tensor products that change sign under spatial inversion. Because spatial inversion is a symmetry of the sample, it follows that any physical properties or effects cannot change under spatial inversion of the sample. Any terms that depended on (say) the product αG would be replaced by $-\alpha G$, and the requirement that the scattering remains unchanged would mean $\alpha G = -\alpha G$, ie. $\alpha G = 0$.

Not every achiral molecule is symmetric under spatial inversion – some are symmetric under spatial inversion followed by some proper rotation – and it may seem as though the above argument would not preclude non-zero contributions from αG in this case. Indeed it does not, provided that the molecules are oriented. If, however, the molecules are distributed with random orientations in an isotropic fluid, the bulk system will be symmetric under spatial inversion, and the above argument holds. In this case, the restrictions fall on the orientational average of the fourth-rank tensor formed by the direct product of α and G.

More generally, if a rotation (proper or improper) is a symmetry operation for a molecule, then it follows that the components of any molecular response tensors must be unchanged under a coordinate transformation corresponding to this rotation. Tables showing the restrictions on various tensor components in different symmetry groups have been compiled by Birss [14, adapted by Barron in 8]. It can be shown, for example, that only molecules belonging to chiral point groups can support a non-zero trace $G_{\alpha\alpha}$.

Finally, we note that we can categorise the primed and unprimed property tensors by their behaviour under time reversal [8, p. 218]. Noting that $\boldsymbol{B}$, $\dot{\boldsymbol{E}}$ and the magnetic multipole moments all change sign under time-reversal, while $\boldsymbol{E}$, $\dot{\boldsymbol{B}}$ and the electric ones do not, we can infer the time-reversal behaviour of the property tensors from expressions such as (8.8.4). Because the unprimed and primed property tensors multiply the fields and their time derivatives respectively, they will each have opposite properties under time reversal: α_{ab} is even under time reversal while α'_{ab} is odd, G_{ab} is odd while G'_{ab} is even, and so on. The situation is summarised in *table 8.1*.

Property Tensor	**Multipole Operators**	**Space Inversion**	**Time Reversal**
α_{ab}	$\hat{\mu}$, $\hat{\mu}$	Even	Even
G_{ab}	$\hat{\mu}$, $\hat{m}$	Odd	Odd
$A_{a,bc}$	$\hat{\mu}$, $\hat{\Theta}$	Odd	Even
$C_{ab,cd}$	$\hat{\Theta}$, $\hat{\Theta}$	Even	Even
$D_{ab,c}$	$\hat{\Theta}$, $\hat{m}$	Even	Odd
χ_{ab}	$\hat{m}$, $\hat{m}$	Even	Even
$B_{a,bcd}$	$\hat{\mu}$, $\hat{Q}$	Even	Even
$D^{(m)}_{a,bc}$	$\hat{\mu}$, $\hat{M}$	Even	Odd

Table 8.1. Summary of the unprimed real property tensors, showing their behaviour under spatial inversion and time reversal, as well as the multipole moment operators on which they depend. The primed tensors have the same properties under spatial inversion, but transform oppositely under time reversal.

Conclusion

This chapter has been a relatively detailed exposition of the semi-classical theory of linear molecular light scattering, treating Raleigh and Raman scattering with or without absorption. The central results are the forms of the molecular polarisability tensors (8.10.8-20), and the expressions for the changes in the polarisability tensors under a change of multipolar centre (8.12.11-15) and (8.12.38-45). These results form the starting point for the following chapter, which presents the next-multipole-order correction to the standard expressions used to analyse optically active molecular light scattering.

References

[1] Power E. A. 1965 *Introductory Quantum Electrodynamics* Elsevier

[2] Power E. A. and Zienau D. 1959 Coulomb Gauge in Non-relativistic Quantum Electrodynamics and the Shape of Spectral Lines *Philosophical Transactions of the Royal Society of London A: Mathematical and Physical Sciences* **251** 427

[3] Jackson J. D. 1998 *Classical Electrodynamics* (3rd edition) Wiley

[4] Cohen-Tannoudji C., Dupont-Roc J. and Grynberg G. 1997 *Photons and Atoms: Introduction to Quantum Electrodynamics* Wiley

[5] Craig D. P. and Thirunamachandran T. 1984 *Molecular Quantum Electrodynamics* Dover

[6] Loudon R. 2000 *The Quantum Theory of Light* (3rd edition) Oxford University Press

[7] Barron L. D. and Gray C. G. The Multipole Interaction Hamiltonian for Time-Dependent Fields J*ournal of Physics A* **6** 59

[8] Barron L. D. 2004 *Molecular Light Scattering and optical Activity* (2nd Edition) Cambridge University Press

[9] Babiker M. and Loudon R. 1982 Derivation of the Power-Zienau-Wooley Hamiltonian in Quantum Electrodynamics by Gauge Transformation *Proceedings of the Royal Society of London A* **385** 439

[10] Raab R. E. and de Lange O. L. 2004 *Multipole Theory in Electromagnetism: Classical, Quantum and Symmetry Aspects, with Applications* Oxford University Press

[11] Born M. and Huang K. 1954 *Dynamical Theory of Crystal Lattices* Oxford University Press

[12] Miloni P. W., Loudon R., Berman P. R. and Barnett S. M. 2008 Linear Polarisabilities of Two and Three Level Atoms *Physical Review A* **77** 043835

[13] Cameron R. and Mackinnon N. 2018 Linear Rayleigh and Raman Scattering to the Second Order: Analytical Results for Light Scattering by any Scatterer of Size $k_0d \leq 1/10$ *Physical Review A* **98** 013814

[14] Briss R. R. 1966 *Symmetry and Magnetism* (2nd edition) North-Holland

Chapter 9 – Second-Order Scattering

The previous chapter presented a semi-classical treatment of molecular light scattering, where the scattered fields are given in terms of a series of tensor polarisabilities that describe the oscillating multipole moments induced in the molecule. The property tensors (8.11.8-20) contain matrix elements of the molecular multipole moment operators, and so the tensors appear in a hierarchy of sizes corresponding to the moments on which they depend.

Various levels of approximation can therefore be obtained by truncating the series of property tensors at an appropriate point. The simplest is to keep only the electric dipole-electric dipole polarisability, $\tilde{\alpha}_{ab}$ (this is equivalent to keeping only the electric dipole term in the Multipolar Hamiltonian (8.4.5)). We will refer to the resulting electric field intensity, which depends on the product α^2, as the "zeroth-order" component of the scattered light.

Extending this one order further requires keeping terms in the scattered intensity that depend on the products αG and αA. These "first-order" terms are responsible for natural optical activity [1].

In this chapter we examine the second-order correction to these results. This involves the retention of a number of additional terms in the intensity – the products G^2 and A^2, as well as products of α and higher property tensors. Unlike the first-order correction, these terms are independent of the chirality of the molecules, but still give information about their structure. It is this extension of the treatment to second-order which is the novel contribution of the present work.

We present the second-order contribution to the Stokes parameters of the scattered light from an isotropic sample. Making use of the rather general property tensors (8.11.8-20) allows the treatment to cover both Rayleigh and Raman scattering, in transparent or absorbing regions. We also examine the special case of Rayleigh scattering without absorption.

Finally, we confirm that the results are independent of the origin about which the multipolar expansions are taken, as a check of the validity of the general procedure. It is demonstrated that truncation of the full multipolar series to second-order should not affect the origin independence of the results, provided that all contributions at second-order and below are considered together.
The results and calculations of this chapter are presented in [2].

9.1. Second-order Scattering

The central result of the previous chapter's labours was an expression for the scattered electric field from an arbitrary molecule in terms of its multipole polarisability tensors. We saw in

Chapter 3 that the scattered electric field from a collection of oscillating multipole moments in the far-field is given by

$$\tilde{E}_a^{0^{scattered}} = \frac{\mu_0 \omega^2 e^{ikR}}{4\pi R}\left(\delta_{ab} - \hat{R}_a\hat{R}_b\right)\left[\tilde{\mu}_b^0 + \frac{1}{c}\epsilon_{bcd}\tilde{m}_c^{0^{kin.}}\hat{R}_d - \frac{ik}{3}\tilde{\Theta}_{bc}^0\hat{R}_c - \frac{ik}{2c}\epsilon_{bcd}\tilde{m}_{ce}^{0^{kin.}}\hat{R}_e\hat{R}_d - \frac{k^2}{6}\tilde{Q}_{bcd}^0\hat{R}_c\hat{R}_d + \cdots\right], \quad 9.1.1$$

where

$$\tilde{E}_a^{scattered} = \tilde{E}_a^{0^{scattered}} e^{-i\omega t}, \quad 9.1.2$$

$$\tilde{\mu}_a = \tilde{\mu}_a^0 e^{-i\omega t}, \quad 9.1.3$$

etc. Here $\boldsymbol{R}$ is the position vector of the point of observation, $\hat{\boldsymbol{R}}$ is the corresponding unit vector, $\tilde{\mu}_a$, $\tilde{m}_a^{0^{kin.}}$ etc. are the complex induced moments, and k and ω are the wavenumber and frequency of the scattered light. In the case of Rayleigh scattering, these are equal to the those of the incident light, k_0 and ω_0. For Raman scattering between molecular states $|f\rangle$ and $|i\rangle$, we have $\omega = \omega_0 - \omega_{fi}$. The induced multipole moments may in turn be written in terms of the incident fields and the molecular property tensors as

$$\tilde{\mu}_a^0 = \tilde{\alpha}_{ab}\tilde{E}_b^0(0) + \tilde{G}_{ab}\tilde{B}_b^0(0) + \frac{1}{3}\tilde{A}_{a,bc}\nabla_b\tilde{E}_c^0(0) + \frac{1}{6}\tilde{B}_{a,bcd}\nabla_d\nabla_c\tilde{E}_b^0(0) + \frac{1}{2}\tilde{D}_{a,bc}^{(m)}\nabla_c\tilde{B}_b^0(0) + \cdots \quad 9.1.4$$

$$\tilde{m}_a^{0^{kin.}} = \tilde{\mathcal{G}}_{ab}\tilde{E}_b^0(0) + \frac{1}{3}\tilde{D}_{a,bc}\nabla_c\tilde{E}_b^0(0) + \tilde{\chi}_{ab}\tilde{B}_b^0(0) + \cdots \quad 9.1.5$$

$$\tilde{\Theta}_{ab}^0 = \tilde{\mathcal{A}}_{c,ab}\tilde{E}_c^0(0) + \tilde{C}_{ab,cd}\nabla_d\tilde{E}_c^0(0) + \tilde{\mathcal{D}}_{c,ab}\tilde{B}_c^0(0) + \cdots \quad 9.1.6$$

$$\tilde{m}_{ab}^{0^{kin.}} = \tilde{\mathcal{D}}_{c,ab}^{(m)}\tilde{E}_c^0(0) + \cdots \quad 9.1.7$$

$$\tilde{Q}_{abc}^0 = \tilde{\mathcal{B}}_{d,abc}\tilde{E}_d^0(0) + \cdots, \quad 9.1.8$$

leading to an explicit expression for the scattered light in terms of the incident light and the properties of the scatterer.

In order to apply these formulae both the series of terms in (9.1.1), and those in (9.1.4-8) must be truncated. Some care must be taken over this: if an expression for one of the Stokes parameters of the scattered light is required, this will involve a product of two components of $\tilde{\boldsymbol{E}}^{0^{scattered}}$, and it is the series of terms in this expression that must be truncated at a given size – not those of the individual expressions for $\tilde{\mu}_a^0$, $\tilde{\Theta}_{ab}^0$, and so on. In order to keep track of the sizes of the different contributions, it is helpful to introduce a dimensionless parameter λ, and write (9.1.4-8) as

$$\tilde{\mu}_a^0 = \lambda^0\tilde{\alpha}_{ab}\tilde{E}_b^0(0) + \lambda^1\tilde{G}_{ab}\tilde{B}_b^0(0) + \frac{1}{3}\lambda^1\tilde{A}_{a,bc}\nabla_b\tilde{E}_c^0(0) + \frac{1}{6}\lambda^2\tilde{B}_{a,bcd}\nabla_d\nabla_c\tilde{E}_b^0(0) + \frac{1}{2}\lambda^2\tilde{D}_{a,bc}^{(m)}\nabla_c\tilde{B}_b^0(0) + \cdots \quad 9.1.9$$

$$\tilde{m}_a^{0^{kin.}} = \lambda^1\tilde{\mathcal{G}}_{ab}\tilde{E}_b^0(0) + \frac{1}{3}\lambda^2\tilde{D}_{a,bc}\nabla_c\tilde{E}_b^0(0) + \lambda^2\tilde{\chi}_{ab}\tilde{B}_b^0(0) + \cdots \quad 9.1.10$$

$$\tilde{\Theta}_{ab}^0 = \lambda^1\tilde{\mathcal{A}}_{c,ab}\tilde{E}_c^0(0) + \lambda^2\tilde{C}_{ab,cd}\nabla_d\tilde{E}_c^0(0) + \lambda^2\tilde{\mathcal{D}}_{c,ab}\tilde{B}_c^0(0) + \cdots \quad 9.1.11$$

$$\widetilde{m}_{ab}^{0^{kin.}} = \lambda^2 \widetilde{\mathcal{D}}_{c,ab}^{(m)} \tilde{E}_c^0(0) + \cdots \qquad 9.1.12$$

$$\tilde{Q}_{abc}^0 = \lambda^2 \widetilde{\mathcal{B}}_{d,abc} \tilde{E}_d^0(0) + \cdots. \qquad 9.1.13$$

If the molecules are of size d, then each successive power of λ approximately indicates an extra factor of $\sim k_0 d$, as – relative to the term before it – each has an extra spatial derivative of an incident field vector (which brings down the factor k), along with an extra factor of charge position in the transition multipole moments that define the relevant property tensor (which will be of the order of some characteristic molecular length scale d).

If only terms of order λ^0 are retained, this is equivalent to making the electric dipole approximation. Retaining terms of order λ^1 produces the standard description of optical activity, where the optically active response is related to the additional terms involving the products αA and αG [1, §3.5.4]. As noted in the previous chapter, proceeding to order λ^2 requires retaining G^2 and A^2 terms, as well as the products αB, $\alpha\chi$, αD, $\alpha D^{(m)}$ and αC.

In order to write the terms required in a succinct way, we write the Stokes parameters in the far field as

$$s_\xi = f_{\xi_{ab}} \tilde{E}_a \tilde{E}_b^* \qquad 9.1.14$$

with ξ running from 0 to 3 for the four parameters. $f_{\xi_{ab}}$ is given by

$$f_{0_{ab}} = \hat{\theta}_a \hat{\theta}_b + \hat{\phi}_a \hat{\phi}_b \qquad 9.1.15$$

$$f_{1_{ab}} = \hat{\theta}_a \hat{\theta}_b - \hat{\phi}_a \hat{\phi}_b \qquad 9.1.16$$

$$f_{2_{ab}} = -\hat{\theta}_a \hat{\phi}_b - \hat{\phi}_a \hat{\theta}_b \qquad 9.1.17$$

$$f_{3_{ab}} = -i\hat{\theta}_a \hat{\phi}_b + i\hat{\phi}_a \hat{\theta}_b, \qquad 9.1.18$$

where $\hat{\theta}$ and $\hat{\phi}$ are unit vectors in the θ and ϕ directions. (9.1.15-18) and (9.1.1) can be substituted into (9.1.14) to explicitly give the contributions to the Stokes parameters, which can then be grouped according to the property tensors on which they depend. This results in the following expression for the "zeroth-order" contribution,

$$s_\xi^{\alpha-\alpha} = K\mathrm{Re}\left[\frac{1}{2} \tilde{\alpha}_{ab} \tilde{\alpha}_{cd}^* f_{\xi ac} \tilde{E}_b \tilde{E}_d^*\right], \qquad 9.1.19$$

where we have defined the constant $K \equiv \frac{\mu_0^2 \omega^2}{8\pi^2 R^2}$. We similarly find the "first-order" contributions,

$$s_\xi^{\alpha-A} = K\mathrm{Re}\left[\frac{1}{3} \tilde{\alpha}_{ab} \tilde{A}_{c,de}^* f_{\xi ac} \tilde{E}_b \nabla_d \tilde{E}_e^* + \frac{ik}{3} \tilde{\alpha}_{ab} \tilde{\mathcal{A}}_{c,de}^* f_{\xi ad} \tilde{E}_b \tilde{E}_c^* \hat{r}_e\right], \qquad 9.1.20$$

$$s_\xi^{\alpha-G} = K\mathrm{Re}\left[\tilde{\alpha}_{ab} \tilde{G}_{cd}^* f_{\xi ac} \tilde{E}_b \tilde{B}_d^* + \frac{1}{c} \tilde{\alpha}_{ab} \tilde{\mathcal{G}}_{cd}^* \epsilon_{ecf} f_{\xi ae} \tilde{E}_b \tilde{E}_d^* \hat{R}_f\right], \qquad 9.1.21$$

familiar from the usual description of optical activity. Finally, we have the "second-order" contributions – which include products of the usual optical activity tensors

$$s_\xi^{A-A} = K\mathrm{Re}\left[\frac{1}{18}\tilde{A}_{a,bc}\tilde{A}^*_{d,ef}f_{\xi ad}\nabla_b\tilde{E}_c\nabla_e\tilde{E}^*_f + \frac{ik}{9}\tilde{A}_{a,bc}\tilde{\mathcal{A}}^*_{d,ef}f_{\xi ae}\nabla_b\tilde{E}_c\tilde{E}^*_d\hat{R}_f \right.$$
$$\left. + \frac{k^2}{18}\tilde{\mathcal{A}}_{a,bc}\tilde{\mathcal{A}}^*_{d,ef}\tilde{E}_a f_{\xi be}\hat{R}_c\tilde{E}^*_d\hat{R}_f\right],$$

$$s_\xi^{G-A} = K\mathrm{Re}\left[\frac{1}{3}G_{ab}\tilde{A}^*_{c,de}f_{\xi ac}\tilde{B}_d\nabla_d\tilde{E}^*_e + \frac{1}{3}\tilde{\mathcal{G}}_{ab}\tilde{A}^*_{c,de}\epsilon_{fag}\hat{R}_g f_{\xi fc}\tilde{E}_b\nabla_d\tilde{E}^*_e + \frac{ik}{3}\tilde{G}_{ab}\tilde{\mathcal{A}}^*_{c,de}f_{\xi ad}\tilde{B}_b\tilde{E}^*_c\hat{R}_e \right.$$
$$\left. + \frac{ik}{3c}\tilde{\mathcal{G}}_{ab}\tilde{\mathcal{A}}^*_{c,de}\epsilon_{fag}\hat{R}_g f_{\xi fd}\tilde{E}_b\tilde{E}^*_c\hat{R}_e\right],$$

$$s_\xi^{G-G} = K\mathrm{Re}\left[\frac{1}{2}\tilde{G}_{ab}\tilde{G}^*_{cd}f_{\xi ac}\tilde{B}_b\tilde{B}^*_d + \frac{1}{c}\tilde{G}_{ab}\mathcal{G}^*_{cd}f_{\xi ae}\epsilon_{ecf}\tilde{B}_b\tilde{E}^*_d\hat{R}_f \right.$$
$$\left. + \frac{1}{2c^2}\tilde{\mathcal{G}}_{ab}\tilde{\mathcal{G}}^*_{cd}\epsilon_{aef}\epsilon_{cgh}f_{\xi eg}\tilde{E}_b\tilde{E}^*_d\hat{R}_f\hat{R}_h\right], \qquad 9.1.24$$

as well products of the higher-order tensors and the electric-dipole electric-dipole polarisability,

$$s_\xi^{\alpha-B} = K\mathrm{Re}\left[\frac{1}{6}\tilde{\alpha}_{ab}\tilde{B}^*_{c,def}f_{\xi ac}\tilde{E}_b\nabla_d\nabla_e\tilde{E}^*_f - \frac{k^2}{6}\tilde{\alpha}_{ab}\tilde{\mathcal{B}}^*_{c,def}f_{\xi ad}\tilde{E}_b\tilde{E}^*_c\hat{R}_e\hat{R}_f\right], \qquad 9.1.25$$

$$s_\xi^{\alpha-C} = K\mathrm{Re}\left[\frac{ik}{3}\tilde{\alpha}_{ab}\tilde{C}^*_{cd,ef}f_{\xi ac}\tilde{E}_b\hat{R}_d\nabla_e\tilde{E}^*_f\right], \qquad 9.1.26$$

$$s_\xi^{\alpha-D} = K\mathrm{Re}\left[\frac{ik}{3}\tilde{\alpha}_{ab}\tilde{\mathcal{D}}^*_{c,de}f_{\xi ad}\tilde{E}_b\tilde{B}^*_c\hat{R}_e + \frac{1}{3}\tilde{\alpha}_{ab}\tilde{D}^*_{c,de}f_{\xi af}\tilde{E}_b\nabla_d\tilde{E}^*_e\epsilon_{cfg}\hat{R}_g\right], \qquad 9.1.27$$

$$s_\xi^{\alpha-D^{(m)}} = K\mathrm{Re}\left[\frac{1}{2}\tilde{\alpha}_{ab}\tilde{D}^{(m)^*}_{c,de}f_{\xi ac}\tilde{E}_b\nabla_e\tilde{B}^*_d + \frac{ik}{2c}\tilde{\alpha}_{ab}\mathcal{D}^*_{c,de}f_{\xi af}\tilde{E}_b\tilde{E}^*_c\epsilon_{fdg}\hat{R}_e\hat{R}_g\right], \qquad 9.1.28$$

$$s_\xi^{\alpha-\chi} = K\mathrm{Re}\left[\frac{1}{c}\tilde{\alpha}_{ab}\tilde{\chi}^*_{cd}f_{\chi ae}\tilde{E}_b\tilde{B}^*_d\epsilon_{ecf}\hat{R}_f\right]. \qquad 9.1.29$$

These expressions give the Stokes parameters if the scattered light at an arbitrary angle from an oriented sample. We now go on to consider the more usual case of scattering from an isotropic sample of randomly oriented molecules.

9.2. Scattering from an Isotropic Sample

If a sample is sufficiently dilute, then interference effects can be ignored and the total scattered intensity can be taken a simply the sum over the contribution from each scatterer. If the sample is also isotropic, then summing over the contribution from each scatterer simply involves averaging the expressions (9.1.19-29) over all possible molecular orientations.

First, we note that for an isotropic sample the only relevant angle is the angle between the incident and scattered light, as the problem is symmetric under rotations around the incident beam direction. This means that, if we take the incident light as traveling along the z-direction, we can fix the angle ϕ without loss of generality, and only consider variations in θ. We choose $\phi = \frac{\pi}{2}$, restricting us to the $y > 0$ region of the $y - z$ plane. The arrangement is shown in *figure 9.1*.

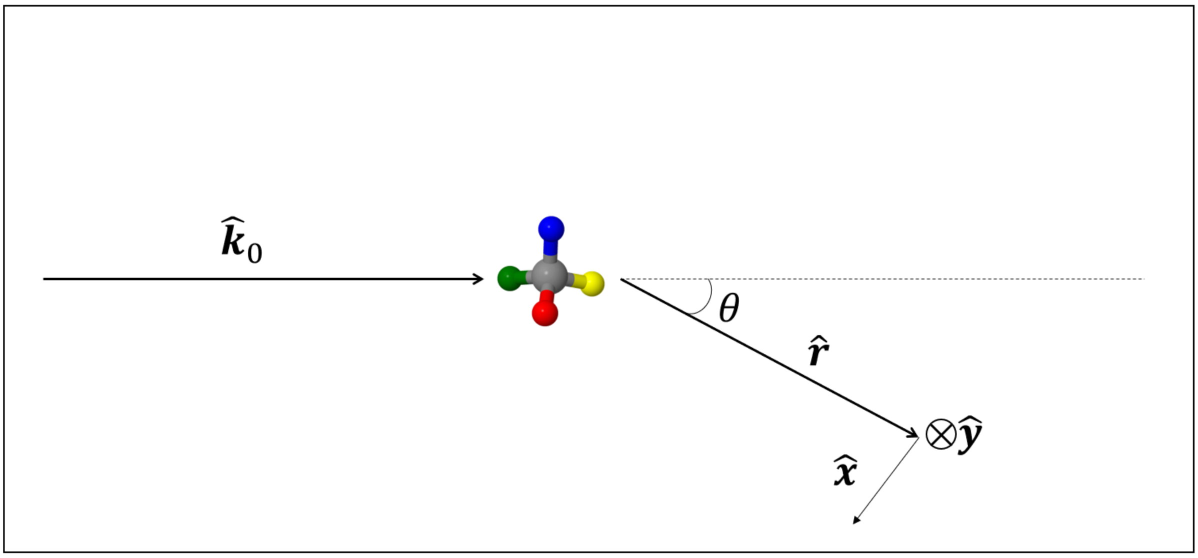

Figure 9.1. The scattering plane, with coordinates as described in the text. Unit vectors in the x, y and r directions are marked, as is the scattering angle θ.

Considering an isotropic sample requires taking the rotational averages of the products of polarisability tensors found in the above expressions. The required averages can be written as a sum of rotationally invariant combinations of the tensor components,

$$\langle T_{abc\dots} \rangle = I_{abc\dots\alpha\beta\gamma\dots} T_{\alpha\beta\gamma\dots}, \qquad 9.2.1$$

where $\langle T_{abc\dots} \rangle$ denotes the rotational average of a tensor T, and $I_{abc\dots\alpha\beta\gamma\dots}$ is constructed so that the contraction on the right hand side gives the appropriate sum of rotational invariants [3]. Further details are given in appendix D, along with expressions for $I_{abc\dots\alpha\beta\gamma\dots}$ for tensors up to rank 6. The resulting expressions are fairly cumbersome, and were evaluated by computer-assisted algebra. This was performed with *Mathematica* in conjunction with *VEST* (*Vector Einstein Summation Tools*), a symbolic tensor algebra package which allows for the easy implementation of user-defined replacement rules (described in [4]). This functionality was used to simplify the expressions, implementing rules derived from Maxwell's equations and the plane-wave forms of the incident light. The curls of $\boldsymbol{E}$ and $\boldsymbol{B}$ were evaluated by $\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}$ and $\nabla \times \boldsymbol{B} = \mu_0\epsilon_0\frac{\partial \boldsymbol{E}}{\partial t}$, with the plane-wave forms of $\boldsymbol{E}$ and $\boldsymbol{B}$ used to evaluate the time derivatives and to express $\boldsymbol{B}$ in terms of $\boldsymbol{E}$. The spatial derivatives of the fields were similarly removed by replacement rules implementing equalities such as $\nabla_i E_j = \delta_{iz}\frac{i\omega}{c}E_j$. The property tensor components themselves were grouped into rotational invariants, defined with reference to the set of rotational invariants used to define the $I_{abc\dots\alpha\beta\gamma\dots}$. This procedure results in a large sum terms, each consisting of the product of a pair of incident electric field components and a rotational invariant (along with trigonometric functions of the scattering angle). The field products were expressed in terms of the incident Stokes parameters by the relations

$$E_x E_x^* = \frac{1}{2}(S_0 + S_1), \quad 9.2.2$$

$$E_y E_y^* = \frac{1}{2}(S_0 - S_1), \quad 9.2.3$$

$$E_x E_y^* = -\frac{1}{2}(S_2 - iS_3), \quad 9.2.4$$

$$E_y E_x^* = -\frac{1}{2}(S_2 + iS_3). \quad 9.2.5$$

This provides the desired expressions for the scattered Stokes parameters (9.1.14) in terms of the incident parameters (9.2.2-5), the scattering angle, and (rotationally invariant combinations of) the molecular property tensor components.

9.3. Results and Discussion

The general expressions for the contributions to each Stokes parameter from each property tensor product, written in terms of rotationally invariant combinations of the tensor components, are given in appendix E (adapted from [2]). Here we explicitly examine the overall form of the contributions for Rayleigh scattering from a non-magnetic scatterer. The restriction to Rayleigh scattering means that the scripted property tensors are simply equal to the complex conjugates of the unscripted ones. Furthermore, if the scatterer is non-magnetic, then it will be symmetrical under time reversal, and we may conclude that all time-odd property tensors vanish (See Chapter 8 §11). Putting these facts together, the complex property tensors are simplified to:

$$\tilde{\alpha}_{ab} = \alpha_{ab}$$

$$\tilde{A}_{a,bc} = A_{a,bc}$$

$$\tilde{\mathcal{A}}_{a,bc} = A_{a,bc}$$

$$\tilde{G}_{ab} = -iG'_{ab}$$

$$\tilde{\mathcal{G}}_{ab} = iG'_{ba}$$

$$\tilde{C}_{ab,cd} = C_{ab,cd}$$

$$\tilde{B}_{a,bcd} = \tilde{\mathcal{B}}_{a,bcd} = B_{a,bcd}$$

$$\tilde{D}_{a,bc} = -iD'_{a,bc}$$

$$\tilde{\mathcal{D}}_{a,bc} = iD'_{a,bc}$$

$$\tilde{D}^{(m)}_{a,bc} = -iD^{(m)\prime}_{a,bc}$$

$$\tilde{\mathcal{D}}^{(m)}_{a,bc} = iD^{(m)\prime}_{a,bc}$$

$$\tilde{\chi}_{ab} = \chi_{ab} \quad 9.3.1 - 9.3.12$$

With these simplifications, the second-order contribution to the Stokes Parameters can be written

$$S_0 = KS_0[A + B' \cos\theta + C\cos^2\theta + D'' \cos^3\theta] + KS_1 \sin^2\theta\,[E + F'' \cos\theta] \qquad 9.3.13$$

$$S_1 = KS_1[G + H' \cos\theta + I\cos^2\theta + J'' \cos^3\theta] + KS_0 \sin^2\theta\,[K + L'' \cos\theta] \qquad 9.3.14$$

$$S_2 = KS_2[M' + N\cos\theta + O' \cos^2\theta] \qquad 9.3.15$$

$$S_3 = KS_3[P' + Q\cos\theta + R' \cos^2\theta], \qquad 9.3.16$$

where A, B, C, etc. are constants formed from rotationally invariant combinations of property tensor components, and the primes and double-primes indicate a grouping of the coefficients into three categories. Explicit expressions for these constants in terms of the simplified property tensors (9.3.1-12) are given in appendix E.

This grouping into three categories reflects the property tensors on which the coefficients depend. The unprimed coefficients contain contributions involving tensor products A^2, GA, G^2, αB and $\alpha D^{(m)}$. The singly-primed coefficients contain contributions of the form A^2, GA, G^2, αC, αD and $\alpha\chi$. Finally, the doubly-primed coefficients contain contributions A^2 and AC. A knowledge of these 18 coefficients represents the most information that one could obtain from an idealised polarimetry experiment, where the incident polarisation and scattering angle can be arbitrarily varied and the scattered polarisation and intensity measured.

It should be noted that the zeroth-order contribution has the same angular dependence as the second order contribution from the unprimed coefficients. This means that it is not sensible to consider the unprimed second-order coefficients on their own – but also that the zeroth-order scattering can be included in the above expressions by simply making a suitable addition to the definition of the unprimed coefficients. The first-order contribution, on the other hand, depends on different Stokes parameters – the first-order contributions to the scattered S_0 and S_1 depend on the incident S_3, and the contributions to the scattered S_2 and S_3 depend on the incident S_0 and S_1. In a sense, the optically active nature of the first-order contribution makes it different in kind to both the zeroth- and second-order contributions.

That said, the singly primed and doubly primed coefficients both have different angular dependencies to the zeroth-order contribution, and depend on different Stokes parameters to the first-order contribution. This means that they can (in principle) be individually determined by a polarimetry experiment. Of the 18 coefficients only 16 are independent of one another, and between them they depend on 20 different isotropic invariants, so it is not possible to infer the value of each invariant from the coefficients. This is unsurprising, as the invariants themselves are not observable quantities (they depend on the origin about which the multipolar expansions are taken, see below). The coefficients themselves, however, are independent of the origin, and it may be possible to construct a simpler set of origin-independent combinations of the invariants, the values of which could be determined from the coefficients.

Finally, we briefly comment on the expected size of these corrections. As mentioned earlier, each factor of λ corresponds approximately to the incident wavevector times the molecular length scale. The applicability of this extended treatment thus depends on the scatterer falling in an intermediate size, between $k_0 d \ll 1$, where the electric-dipole approximation is sufficient to describe the achiral scattering, and $k_0 d > \sim 1/10$, where it would be more appropriate to use Mie theory for scatterers with simple shapes (see [5], for example), or numerical approaches for more complicated cases.

For scatterers as large as $k_0 d \approx 1/10$, we might expect the additional contributions (9.3.13-16) to be around 1% of the size of the leading electric dipole contribution, with the neglected third and higher-order corrections together contributing additional changes of around 0.1%. The upper end of validity of the treatment presented here therefore likely overlaps with other approaches.

9.4. General Origin-Independence of the Procedure

It was shown in the previous chapter that the multipole moments of a charge distribution generally depend upon the point which is taken as the origin of the multipolar expansion, and that this “origin-dependence” gives rise to a similar dependency in the multipole polarisability tensors. If we want to make use of the formalism developed above, it is clear that the predictions related to observable quantities (such as the scattered electric field strength) should be independent of any arbitrary shift in the molecular origin that is used to calculate the polarisability tensors. Insofar as the full multipolar series is retained, this “origin independence” must be exact. However, if the multipolar expansions are truncated at a given order to obtain an *approximate* expression for (say) the scattered E-field, then there is no reason to expect exact origin independence. If such an approximation is useful, though, one would still expect that any changes caused by a shift in molecular origin will be “small” – more precisely, that they can be ignored at the level of accuracy to which the expressions are truncated.

We will discuss this issue in some detail here, and will demonstrate that the results of the above procedure only meet this condition when all of the “second-order” contributions which we have identified are considered simultaneously.

First we consider the induced multipole moments, and show that these transform in the correct way when the property tensors and incident fields are appropriately transformed[1]. We then

[1] It should perhaps be emphasised that this is not quite a tautology. The induced moments are obtained from expectation values of the multipole moment operators acting on the perturbed wavefunctions (8.5.7). While the multipole moment operators by definition transform correctly, the perturbed states – in our approximation – will also transform (as they have been obtained using our truncated multipolar Hamiltonian). It is therefore worthwhile to explicitly check that the expectation values do not transform in an unacceptable way.

go on to consider the effect of these transformations on the expression for the scattered light (9.1.1).

9.5. Transformation of the Induced Moments

Consider repeating the calculations of the previous chapter which lead to (9.1.4-8), but with the centre about which the multipole expansions are taken moved to the point ***d*** rather than the coordinate origin. The induced electric dipole moment, for example, would be

$$\tilde{\mu}_a^{0\prime} = \lambda^0 \tilde{\alpha}_{ab}^t \tilde{E}_b^0(\boldsymbol{d}) + \lambda^1 \tilde{G}_{ab}^t \tilde{B}_b^0(\boldsymbol{d}) + \frac{1}{3}\lambda^1 \tilde{A}_{a,bc}^t \nabla_b \tilde{E}_c^0(\boldsymbol{d}) + \frac{1}{6}\lambda^2 \tilde{B}_{a,bcd}^t \nabla_d \nabla_c \tilde{E}_b^0(\boldsymbol{d}) + \frac{1}{2}\lambda^2 \tilde{D}_{a,bc}^{(m)\,t} \nabla_c \tilde{B}_b^0(\boldsymbol{d}) + \cdots, \qquad 9.5.1$$

where the primes denote that a property tensor is defined about the new multipolar centre ***d*** (not to be confused with the primes denoting the symmetric and antisymmetric parts of complex polarisability tensors, as in (9.3.1-12)). The effect that this shift has on the multipole moment operators, and the property tensors, is given in the previous chapter, § 8.13. In addition to this, we have adjusted the point at which the incident fields are evaluated – we must consider the field strengths at ***d***, rather than at the coordinate origin.

The effect of this latter change can be most clearly understood by considering a Taylor expansion of the incident fields. The centre displacement ***d*** will be at most of the order of the molecular dimensions, and so will be much smaller than a wavelength. We can therefore write

$$E(\boldsymbol{d})_a = E(0)_a + \lambda d_b \nabla_b E(0)_a + \frac{1}{2}\lambda^2 d_b d_c \nabla_b \nabla_c E(0)_a + \cdots, \qquad 9.5.2$$

where, as before, each factor of λ indicates that a term will be smaller than the last by approximately a factor of k_0 times the characteristic length scale of the molecule. The $\lambda' s$ appearing in this expression can be used in conjunction with those in (9.5.1), and show which terms should be consistently retained under truncation to a given order of λ.

Beginning with the induced electric dipole moment, we substitute the expressions for the shifted property tensors (8.13.11-15, 8.13.38-45) into (9.5.1) to obtain

$$\tilde{\mu}_a^{0\prime} = \lambda^0 \tilde{\alpha}_{ab} \tilde{E}_b^0(\boldsymbol{d}) + \lambda^1 \left(\tilde{G}_{ab} - \frac{i\omega}{2} \epsilon_{bcd} d_c \tilde{\alpha}_{ad}\right) \tilde{B}_b^0(\boldsymbol{d})$$
$$+ \frac{1}{3}\lambda^1 \left(\tilde{A}_{a,bc} - \frac{3}{2} d_b \tilde{\alpha}_{ac} - \frac{3}{2} d_c \tilde{\alpha}_{ab} + \delta_{bc} d_d \tilde{\alpha}_{ad}\right) \nabla_b \tilde{E}_c^0(\boldsymbol{d})$$
$$+ \frac{1}{6}\lambda^2 \left(\tilde{B}_{a,bcd} - d_b \tilde{A}_{a,cd}^{(tr)} - d_c \tilde{A}_{a,bd}^{(tr)} - d_d \tilde{A}_{a,bc}^{(tr)} + d_c d_d \tilde{\alpha}_{ab} + d_b d_d \tilde{\alpha}_{ac}\right.$$
$$\left. + d_b d_c \tilde{\alpha}_{ad}\right) \nabla_d \nabla_c \tilde{E}_b^0(\boldsymbol{d})$$
$$+ \frac{1}{2}\lambda^2 \left(\tilde{D}^{(m)}{}_{a,bc} + \frac{2i\omega}{3} \epsilon_{bde} d_c d_d \tilde{\alpha}_{ae} - \frac{i\omega}{3} \epsilon_{bde} d_d A_{a,ce}^{(tr)} - 2 d_c \tilde{G}_{ab}\right.$$
$$\left. + \frac{2}{3} \delta_{bc} d_d \tilde{G}_{ad}\right) \nabla_c \tilde{B}_b^0(\boldsymbol{d}) + \cdots. \qquad 9.5.3$$

Here $\tilde{A}_{a,bc}^{(tr)}$ is defined identically to $\tilde{A}_{a,bc}$, but with the primitive electric quadrupole moment operator $\hat{Q}_{ab} \equiv \Sigma_\alpha \hat{r}_{\alpha_a} \hat{r}_{\alpha_b} q_\alpha$ in place of the traceless electric quadrupole moment $\hat{\Theta}_{ab}$. We can use the Taylor-expansion above for $E(\boldsymbol{d})_a$, and the corresponding one for $B(\boldsymbol{d})_a$

$$B(\boldsymbol{d})_a = B(0)_a + \lambda d_b \nabla_b B(0)_a + \frac{1}{2}\lambda^2 d_b d_c \nabla_b \nabla_c B(0)_a + \cdots, \qquad 9.5.4$$

in order to write $\tilde{\mu}_a^{0\prime}$ in terms of the unshifted property tensors and the fields at the coordinate origin. This finally allows us to express the transformed induced dipole moment in terms of the untransformed induced dipole moment, and therefore to verify that the transformation matches the origin-transformation expression derived in the previous chapter. In the case of the dipole moment, the transformed and untransformed moments should simply be equal.

Substituting the Taylor expansions into the expression for $\tilde{\mu}_a^{0\prime}$ above, and keeping terms up to λ^2, gives

$$\tilde{\mu}_a^{0\prime} = \lambda^0 \left[\tilde{\alpha}_{ab} \tilde{E}_b^0(0)\right]$$
$$+ \lambda^1 \left[\tilde{\alpha}_{ab} d_c \nabla_c \tilde{E}_b^0(0) + \left(\tilde{G}_{ab} - \frac{i\omega}{2} \epsilon_{bcd} d_c \tilde{\alpha}_{bd}\right) \tilde{B}_b^0(0)\right.$$
$$\left. + \left(A_{a,bc} - \frac{3}{2} d_b \alpha_{ac} - \frac{3}{2} d_c \alpha_{ab} + \delta_{bc} d_d \alpha_{ad}\right) \nabla_b \tilde{E}_c^0(0)\right]$$
$$+ \lambda^2 \left[\left(G_{ab} - \frac{i\omega}{2} \epsilon_{bcd} d_c \alpha_{ad}\right) d_e \nabla_e \tilde{B}_b^0(0)\right.$$
$$+ \frac{1}{3}\left(A_{a.bc} - \frac{3}{2} d_b \alpha_{ac} - \frac{3}{2} d_c \alpha_{ab} + \delta_{bc} d_d \alpha_{ad}\right) d_d \nabla_b \nabla_d \tilde{E}_c^0(0)$$
$$+ \frac{1}{6}\left(B_{a,bcd} - d_b A_{a,cd}^{tr} - d_d A_{a,bc}^{tr} + d_c d_d \alpha_{ab} + d_b d_d \alpha_{ac} + d_b d_c \alpha_{ad}\right) \nabla_d \nabla_c \tilde{E}_b^0(0)$$
$$+ \frac{1}{2}\left(D_{a,bc}^{(m)} \frac{2i\omega}{3} \epsilon_{bde} d_c d_d \alpha_{ae} - \frac{i\omega}{3} \epsilon_{bde} d_d A_{a,ce}^{tr} - 2 d_c G_{ab}\right.$$
$$\left.\left. + \frac{2}{3} \delta_{bc} d_d G_{ad}^{canon.}\right) \nabla_c \tilde{B}_b^0(0)\right]. \qquad 9.5.5$$

The terms involving Kronecker deltas will all be zero, due to the transversality of the $\boldsymbol{E}$ and $\boldsymbol{B}$ fields. Furthermore, by relabelling some indices, and making use of the fact that[2]

$$\nabla_a E_b = \nabla_b E_a + i\omega\epsilon_{abc}B_c, \tag{9.5.6}$$

we can see that all of the extra terms cancel out, and we are left with

$$\tilde{\mu}_a^{0\prime} = \lambda^0\tilde{\alpha}_{ab}\tilde{E}_b^0(0) + \lambda^1\tilde{G}_{ab}\tilde{B}_b^0(0) + \frac{\lambda^1}{3}\tilde{A}_{a,bc}\nabla_b\tilde{E}_c^0(0) + \frac{\lambda^2}{6}\tilde{B}_{a,bcd}\nabla_d\nabla_c\tilde{E}_b^0|_{\boldsymbol{r}=0} + \frac{\lambda^2}{2}\tilde{D}_{a,bc}^{(m)}\nabla_c\tilde{B}_b^0(0) + \cdots = \tilde{\mu}_a^0 \tag{9.5.7}$$

That is to say, the induced electric dipole moment remains unchanged, as would be expected from the transformation expressions derived in the previous chapter.

Similar calculations can be carried out for the other induced multipole moments. We again expect the transformations to match those of the previous chapter: that is, we expect to find that the expressions for the transformation of the induced moments, calculated from (9.1.10-13) and the transformation of the property tensors, match those derived from the transformations of the moments directly. The explicit calculations closely follow the method above, and are presented in appendix F – here we simply present the results

$$\tilde{m}_a^{0^{kin.}\prime} = \tilde{m}_a^{0^{kin.}} + \frac{i\omega}{2}\epsilon_{abc}d_b\lambda^1\tilde{\mu}_c^0, \tag{9.5.8}$$

$$\tilde{\Theta}_{ab}^{0\prime} = \tilde{\Theta}_{ab}^0 + \lambda^1\left(-\frac{3}{2}\tilde{\mu}_a d_b - \frac{3}{2}\tilde{\mu}_b d_a + \delta_{ab}\tilde{\mu}_c d_c\right) \tag{9.5.9}$$

$$\tilde{Q}_{abc}^{0}{}' = \tilde{Q}_{abc} + \lambda^2\left(d_a d_b\tilde{\mu}_c + d_a d_c\tilde{\mu}_b + d_b d_c\tilde{\mu}_a - d_a\tilde{Q}_{bc} - d_b\tilde{Q}_{ac} - d_c\tilde{Q}_{ab}\right), \tag{9.5.10}$$

$$\tilde{m}_{ab}^{kin}{}' = \tilde{m}_{ab}^{kin.} + \lambda^2\left(-\frac{2i\omega}{3}\epsilon_{acd}d_b d_c\tilde{\mu}_d + \frac{i\omega}{3}\epsilon_{acd}d_c\tilde{Q}_{bd} - 2d_b\tilde{m}_a^{kin.} + \frac{2}{3}\delta_{ab}d_c\tilde{m}_c^{kin.}\right). \tag{9.5.11}$$

In these expressions, the induced moments on the right should be understood as standing for the expressions (9.1.10-9.1.13), with terms retained up to λ^2. These transformations indeed match those presented in section 8.13 (with the sums over charge momenta that appear in the transformations of $\tilde{m}_a^{0^{kin.}}$ and $\tilde{m}_{ab}^{kin.}$ expressed as the time derivatives of the induced electric multipole moments). We have therefore explicitly demonstrated that the semi-classical approach preserves these transformations up to second order in λ.

9.6. The Scattered Light under a Change of Origin

We now turn to the scattered electric field. When the origin of the expansion is translated by $\boldsymbol{d}$, we have the following expression for the scattered light in the far-field:

[2] This follows from the Maxwell equation $\epsilon_{abc}\nabla_b E_c = i\omega B_a$, when both sides are multiplied by ϵ_{ade} and use is made of $\epsilon_{abc}\epsilon_{ade} = \delta_{bd}\delta_{ce} - \delta_{be}\delta_{cd}$.

$$\tilde{E}_a^{0^{scattered}\prime} = \frac{\mu_0\omega^2 e^{ik(R-\hat{\boldsymbol{R}}\cdot\boldsymbol{d})}}{4\pi R}(\delta_{ab} - R_aR_b)\Bigg[\lambda^0\tilde{\mu}_b^{0\prime} + \lambda^1\frac{1}{c}\epsilon_{bcd}\tilde{m}_c^{0^{kin.}\prime}R_d - \lambda^1\frac{ik}{3}\tilde{\Theta}_{bc}^{0\prime}R_c - \lambda^2\frac{ik}{2c}\epsilon_{bcd}\tilde{m}_{ce}^{0^{kin.}\prime}R_dR_e - \lambda^2\frac{k^2}{6}\tilde{Q}_{bcd}^{0\prime}R_cR_d + \cdots\Bigg]. \quad 9.6.1$$

Substituting in the transformations of the moments (9.5.8-11) gives

$$\begin{aligned}\tilde{E}_a^{0^{scattered}\prime} = {} & \frac{\mu_0\omega^2 e^{ik(R-\hat{\boldsymbol{R}}\cdot\boldsymbol{d})}}{4\pi R}\left(\delta_{ab} - \hat{R}_a\hat{R}_b\right)\Bigg[\lambda^0\tilde{\mu}_b^0 + \lambda^1\frac{1}{c}\epsilon_{bcd}\left(\tilde{m}_c^{0^{kin.}} + \frac{i\omega}{2}\epsilon_{cef}d_e\tilde{\mu}_f^0\right)\hat{R}_d \\ & - \lambda^1\frac{ik}{3}\left(\tilde{\Theta}_{bc}^0 - \frac{3}{2}\tilde{\mu}_bd_c - \frac{3}{2}\tilde{\mu}_cd_b + \delta_{bc}\tilde{\mu}_dd_d\right)\hat{R}_c \\ & - \lambda^2\frac{ik}{2c}\epsilon_{bcd}\left(\tilde{m}_{ce}^{kin.} - \frac{2i\omega}{3}\epsilon_{cfg}d_ed_f\tilde{\mu}_g + \frac{i\omega}{3}\epsilon_{cfg}d_f\tilde{Q}_{eg} - 2d_e\tilde{m}_c^{kin.} \right. \\ & \left. + \frac{2}{3}\delta_{ce}d_f\tilde{m}_f^{kin.}\right)\hat{R}_d\hat{R}_e \\ & - \lambda^2\frac{k^2}{6}\left(\tilde{Q}_{bcd} + d_bd_c\tilde{\mu}_d + d_bd_d\tilde{\mu}_c + d_cd_d\tilde{\mu}_b - d_b\tilde{Q}_{cd} - d_c\tilde{Q}_{bd} - d_d\tilde{Q}_{bc}\right)\hat{R}_c\hat{R}_d \\ & + \cdots\Bigg]. \end{aligned} \quad 9.6.2$$

If we also Taylor expand the phase factor,

$$e^{ik(R-\hat{\boldsymbol{R}}\cdot\boldsymbol{d})} = e^{ikR}\left(\lambda^0 - \lambda^1 ikd_a\hat{R}_a - \lambda^2\frac{1}{2}k^2d_a\hat{R}_ad_b\hat{R}_b + \cdots\right), \quad 9.6.3$$

then algebraic manipulation reveals that (9.6.2) is identical to the original expression (9.1.1). This is easiest to verify order-by-order in λ. At λ^0, we simply have

$$\frac{\mu_0\omega^2 e^{ikR}}{4\pi R}\left(\delta_{ab} - \hat{R}_a\hat{R}_b\right)\left[\lambda^0\tilde{\mu}_b^0\right], \quad 9.6.4$$

which is just the λ^0 part of (9.1.1). At λ^1, we have

$$\begin{aligned}\frac{\mu_0\omega^2 e^{ikR}}{4\pi R}\left(\delta_{ab} - \hat{R}_a\hat{R}_b\right)\lambda^1\Bigg[&\frac{1}{c}\epsilon_{bcd}\left(\tilde{m}_c^{0^{kin.}} + \frac{i\omega}{2}\epsilon_{cef}d_e\tilde{\mu}_f^0\right)\hat{R}_d \\ & - \frac{ik}{3}\left(\tilde{\Theta}_{bc}^0 - \frac{3}{2}\tilde{\mu}_bd_c - \frac{3}{2}\tilde{\mu}_cd_b + \delta_{bc}\tilde{\mu}_dd_d\right)\hat{R}_c - ikd_cR_c\tilde{\mu}_b^0\Bigg],\end{aligned} \quad 9.6.5$$

where the final term arises from the product of the λ^0 term in square brackets in (9.6.2) and the λ^1 term in the Taylor expansion (9.6.3). First, note that the term involving δ_{bc} vanishes, as $\left(\delta_{ab} - \hat{R}_a\hat{R}_b\right)\delta_{bc}\hat{R}_c$ vanishes for unit vectors $\hat{\boldsymbol{R}}$. Then, expanding the products $\epsilon_{bcd}\epsilon_{cef} = \delta_{de}\delta_{bf} - \delta_{df}\delta_{be}$, writing $k = \omega/c$, and re-labelling dummy indices appropriately, we find most of the terms cancel and we are left only with

$$\frac{\mu_0\omega^2 e^{ikR}}{4\pi R}\left(\delta_{ab} - \hat{R}_a\hat{R}_b\right)\lambda^1\left[\frac{1}{c}\epsilon_{bcd}\tilde{m}_c^{0^{kin.}}\hat{R}_d - \frac{ik}{3}\tilde{\Theta}_{bc}^0\hat{R}_c\right], \quad 9.6.6$$

the λ^1 part of (9.1.1).

Finally, at λ^2 we have

$$\frac{\mu_0\omega^2 e^{ikR}}{4\pi R}\left(\delta_{ab}-\hat{R}_a\hat{R}_b\right)\lambda^2\left[\frac{ik}{2c}\epsilon_{bcd}\left(-\widetilde{m}_{ce}^{kin.}+\frac{2i\omega}{3}\epsilon_{cfg}d_e d_f\widetilde{\mu}_g-\frac{i\omega}{3}\epsilon_{cfg}d_f\widetilde{Q}_{eg}+2d_e\widetilde{m}_c^{kin.}\right.\right.$$
$$\left.-\frac{2}{3}\delta_{ce}d_f\widetilde{m}_f^{kin.}\right)\hat{R}_d\hat{R}_e$$
$$+\frac{k^2}{6}\left(-\tilde{Q}_{bcd}-d_b d_c\tilde{\mu}_d-d_b d_d\tilde{\mu}_c-d_c d_d\tilde{\mu}_b+d_b\tilde{Q}_{cd}+d_c\tilde{Q}_{bd}+d_d\tilde{Q}_{bc}\right)\hat{R}_c\hat{R}_d$$
$$-ikd_g\hat{R}_g\left(\frac{1}{c}\epsilon_{bcd}\left(\widetilde{m}_c^{0^{kin.}}+\frac{i\omega}{2}\epsilon_{cef}d_e\tilde{\mu}_f^0\right)\hat{R}_d\right.$$
$$\left.\left.-\frac{ik}{3}\left(\widetilde{\Theta}_{bc}^0-\frac{3}{2}\tilde{\mu}_b d_c-\frac{3}{2}\tilde{\mu}_c d_b+\delta_{bc}\tilde{\mu}_d d_d\right)\hat{R}_c\right)-\frac{k^2}{2}d_c\hat{R}_c d_d\hat{R}_d\tilde{\mu}_b^0\right]. \qquad 9.6.7$$

Again, expanding the products of Levi-Civita symbols and relabelling dummy indices, as well as using the definition $\widetilde{\Theta}_{bc}^0=\frac{3}{2}\tilde{Q}_{bc}-\frac{1}{2}\delta_{bc}\tilde{Q}_{dd}$ and the symmetry of $\tilde{Q}_{bc}$, we find that most of the terms cancel, leaving

$$\frac{\mu_0\omega^2 e^{ikR}}{4\pi R}\left(\delta_{ab}-\hat{R}_a\hat{R}_b\right)\lambda^2\left[-\frac{ik}{2c}\epsilon_{bcd}\left(\widetilde{m}_{ce}^{kin.}\right)\hat{R}_d\hat{R}_e-\frac{k^2}{6}\left(\tilde{Q}_{bcd}\right)\hat{R}_c\hat{R}_d\right], \qquad 9.6.8$$

the λ^2 part of (9.1.1).

The main point to be noted about this procedure is that, in order to guarantee origin-independence at a given order of λ, it is necessary to include the contributions of *all* multipoles up to that order. This feature is seen both in the treatment leading to (9.5.7-11) – where, for example, cancellation between the transformations of B and of $D^{(m)}$ was required in order to give the correct transformation of $\tilde{\mu}_a^0$ – and also in the calculations of this section, where the cancellation of origin-dependent terms in higher orders relied on the presence of corresponding lower-order terms (that were brought up to higher orders in λ by the Taylor expansion (9.6.3)).

9.7. Conclusions

This chapter has presented the correction to the usual expressions describing light scattering from an isotropic fluid sample when the next order of terms is retained in the multipolar expansion describing the scatterer. While the additional terms are insensitive to the scatterer's chirality, they do provide information about its shape and structure. In order to make use of the multipolar approach in a consistent manner, it is necessary to retain all of the additional contributions that occur at each order. One way in which this is apparent is that the results are invariant to a change in the molecular origin about which the expansions are taken only if all of the "second-order" terms in the Stokes parameters are included.

References

[1] Barron L. D. 2004 Molecular Light Scattering and Optical Activity

[2] Cameron R. P. and Mackinnon N. 2018 Linear Rayleigh and Raman Scattering to the Second Order: Analytical Results for Light Scattering by any Scatterer of Size $k_0 d \leq 1/10$ *Physical Review A* **98** 013814

[3] Craig D. P. and Thirunamachandran T. 1984 *Molecular Quantum Electrodynamics* Dover

[4] Squire J., Burby J. and Qin H. 2014 VEST: Abstract Vector Calculus Simplification in Mathematica *Computer Physics Communications* **185** 128

[5] Stratton J. A. 1941 *Electromagnetic Theory* McGraw-Hill

Conclusion

This thesis has examined a number of problems connected with light-matter interactions, particularly related to their description in terms of electromagnetic helicity. Here we briefly summarise and comment on the main findings from each section.

In chapter 3 we examined the distinction between electromagnetic helicity and electromagnetic chirality in polychromatic fields. In monochromatic fields these differ only by a constant factor, and the distinction is largely unimportant. However, even in the simplest polychromatic case of a superposition of two plane waves we found that these densities can have strikingly different properties: they may have opposite sign, or one may average to zero while the other does not. This behaviour can be understood in terms of the different frequency scaling of the two quantities – monochromatic light has a helicity of $\pm\hbar$ per photon, but a chirality of $\pm\hbar\omega^2$. This difference becomes important when the field is polychromatic, and can be used to understand the quantities' behaviours in more complicated settings such as optical pulses.

In chapter 5 we discussed the helicity and angular momentum radiated from a "chiral" dipole, consisting of a co-located electric and magnetic dipole oscillating out of phase – and we compared these with the fields radiated from a rotating electric dipole, which acts as an achiral source of circularly polarised light. The main point made was that the helicity density is a pseudoscalar, and so a *net* flux of helicity is only possible for a chiral source. We also noted that the angular momentum fluxes require near-field components to be retained, while the helicity can be calculated straightforwardly just from the radiation fields.

In chapter 6 we turned to the helicity flux originating from interfaces between vacuum and chiral media. Using the Fresnel coefficients appropriate for a chiral medium, it is straightforward to demonstrate the conservation of helicity when the medium is dual symmetric by checking the helicity fluxes on either side. The helicity fluxes obtained in non-dual symmetric situations can be related to the properties of the interface – both the change in ϵ and μ at the interface, and the chirality parameter of the medium.

While the expressions used for the helicity flux in chapter 6 were unproblematic, chapter 7 examined more carefully the definition of the helicity *density* within a chiral medium. The constitutive relations necessary to describe a chiral medium modify the energy density by a chirality dependent term, and so it is clear that the helicity-per-photon for circularly polarised light inside a chiral medium will not be $\pm\hbar$ unless the definition of helicity is correspondingly modified. This was put on firm footing by applying Noether's theorem within a chiral medium where the ratio $\epsilon(\boldsymbol{r})/\mu(\boldsymbol{r})$ is constant everywhere. Such a medium is macroscopically dual-symmetric, and we can identify a conserved quantity with this symmetry. The free-space helicity is the conserved quantity associated with duality symmetry of the free-space Maxwell equations, and so we argue that whatever quantity is associated with such duality symmetry in the chiral medium is the correct generalisation. We found that our “modified” helicity density is indeed the associated conserved quantity.

Finally, in chapter 9 we presented the results of a second-order correction to general expressions for molecular light scattering from an isotropic fluid sample. Higher-order corrections to the scattered Stokes parameters were given in terms of rotationally invariant combinations of the molecular property tensors. Unlike the first-order terms, these are insensitive to the chirality of the scatterer – but unlike the leading-order dipole term, their dependence on higher-order multipole moments means that they depend on the finer structure of the scatterer’s shape. We examined in more detail the special case of Rayleigh scattering from a non-absorbing sample, and found that while some of the extra contributions shared the same angular dependence as the leading-order electric dipole scattering, others had distinct dependences. In principle, constraints on these combinations of higher-order polarisabilities is the most that could be extracted from a polarimetry experiment.

The work in this thesis has examined electromagnetic helicity in various contexts. A theme running throughout has been the analysis of helicity as a locally continuous quantity, with associated density, flux and “sources” – and the connection between duality symmetry and helicity conservation. This point of view elucidates a number of the phenomena discussed in the thesis, and provides links between the fundamental description of the electromagnetic field, the electric and magnetic responses of matter, and the concept of chirality more broadly.

Appendix A – The Helicity Operator as the Generator of the Duality Transformation

In this appendix we prove equations 2.2.29 and 2.2.30, which show that the helicity operator generates the duality transformation when applied to the electric and magnetic field operators. The electric and magnetic field operators are given by

$$\widehat{\boldsymbol{E}}^T = \sum_{\boldsymbol{k},\lambda} \boldsymbol{e}_{\boldsymbol{k},\lambda} \left(\frac{\hbar\omega_k}{2\epsilon_0 V}\right)^{\frac{1}{2}} i\hat{a}_{\boldsymbol{k}\lambda} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)} + h.c., \qquad \text{A.1}$$

$$\widehat{\boldsymbol{B}} = \sum_{\boldsymbol{k},\lambda} (\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},\lambda}) \left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{\frac{1}{2}} i\hat{a}_{\boldsymbol{k}\lambda} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)} + h.c. \qquad \text{A.2}$$

The unitary transformation generated by the total helicity operator is given by

$$e^{i\theta\hat{h}_{total}} = 1 + i\theta\hat{h}_{total} + \cdots, \qquad \text{A.3}$$

and for an infinitesimal duality transformation only the term first order in θ need be retained. Applying this transformation to the electric field operator, and again working to first order in θ, gives

$$e^{i\theta\hat{h}_{total}}\widehat{\boldsymbol{E}}^T e^{-i\theta\hat{h}_{total}} = (1 + i\theta\hat{h}_{total})\widehat{\boldsymbol{E}}^T(1 - i\theta\hat{h}_{total}) = \widehat{\boldsymbol{E}}^T + i\theta[\hat{h}_{total}, \widehat{\boldsymbol{E}}^T]. \qquad \text{A.4}$$

The commutator is easiest to evaluate by writing the helicity operator in terms of difference between the number operators for left- and right-handed photons,

$$\hat{h}_{total} = \hbar\sum_{\boldsymbol{k}} \widehat{N}_{\boldsymbol{k},+} - \widehat{N}_{\boldsymbol{k},-} \qquad \text{A.5}$$

$$= \hbar\sum_{\boldsymbol{k}} \hat{a}^\dagger_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k},+} - \hat{a}^\dagger_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k},-}. \qquad \text{A.6}$$

We then make use of the commutation relation for the creation and annihilation operators,

$$[\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}^\dagger{}_{\boldsymbol{k}',\lambda'}] = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\lambda\lambda'}, \qquad \text{A.7}$$

$$[\hat{a}^\dagger{}_{\boldsymbol{k},\lambda}, \hat{a}^\dagger{}_{\boldsymbol{k}',\lambda'}] = [\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}_{\boldsymbol{k}',\lambda'}] = 0. \qquad \text{A.8}$$

Because the mode operators for different $\boldsymbol{k}$ vectors commute, the only terms that contribute to $[\hat{h}_{total}, \widehat{\boldsymbol{E}}^T]$ are those with $\boldsymbol{k} = \boldsymbol{k}'$. Explicitly writing the $\widehat{\boldsymbol{E}}^T$ operator's sum over polarisations in terms of the circular basis, we have

$$[\hat{h}_{total}, \widehat{\boldsymbol{E}}^T] = \left[\hbar\sum_{\boldsymbol{k}}(\hat{a}^\dagger_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k},+} - \hat{a}^\dagger_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k},-}), \sum_{\boldsymbol{k}',\lambda} \boldsymbol{e}_{\boldsymbol{k}',\lambda}\left(\frac{\hbar\omega_{k'}}{2\epsilon_0 V}\right)^{\frac{1}{2}} i\hat{a}_{\boldsymbol{k}',\lambda} e^{i(\boldsymbol{k}'\cdot\boldsymbol{r}-\omega_{k'}t)} + h.c.\right] =$$

$$\sum_{\boldsymbol{k}}\left(\frac{\hbar\omega_k}{2\epsilon_0 V}\right)^{\frac{1}{2}} [\hbar(\hat{a}^\dagger_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k},+} - \hat{a}^\dagger_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k},-}), \boldsymbol{e}_{\boldsymbol{k},+} i\hat{a}_{\boldsymbol{k},+} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)} + \boldsymbol{e}_{\boldsymbol{k},-} i\hat{a}_{\boldsymbol{k},-} e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)} + h.c.]. \qquad \text{A.9}$$

This can be evaluated by further application of the commutation relations, and the identity $[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B}$. (so $[\widehat{N}_{+/-}, \hat{a}_{+/-}] = -\hat{a}_{+/-}$, and $[\widehat{N}_{+/-}, \hat{a}^\dagger_{+/-}] = \hat{a}^\dagger_{+/-}$).

$$\left[\hat{h}_{total},\widehat{\boldsymbol{E}}^T\right]=\sum_{\boldsymbol{k}}\hbar\left(\frac{\hbar\omega_k}{2\epsilon_0 V}\right)^{\frac{1}{2}}\left(-\boldsymbol{e}_{\boldsymbol{k},+}i\hat{a}_{\boldsymbol{k},+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}-\boldsymbol{e}_{\boldsymbol{k},-}i\hat{a}^{\dagger}_{\boldsymbol{k},+}e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}+\boldsymbol{e}_{\boldsymbol{k},-}i\hat{a}_{\boldsymbol{k},-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right.$$
$$\left.+\boldsymbol{e}_{\boldsymbol{k},+}i\hat{a}^{\dagger}_{\boldsymbol{k},-}e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right).$$

Recognising that

$$\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},+}=-i\boldsymbol{e}_{\boldsymbol{k},+}, \qquad \text{A. 11}$$

$$\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},-}=i\boldsymbol{e}_{\boldsymbol{k},-}, \qquad \text{A. 12}$$

we finally have

$$\left[\hat{h}_{total},\widehat{\boldsymbol{E}}^T\right]=\sum_{\boldsymbol{k}}\hbar\left(\frac{\hbar\omega_k}{2\epsilon_0 V}\right)^{\frac{1}{2}}\left(\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},+}\right)\hat{a}_{\boldsymbol{k},+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}-\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},-}\right)\hat{a}^{\dagger}_{\boldsymbol{k},+}e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right.$$
$$\left.+\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},-}\right)\hat{a}_{\boldsymbol{k},-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}-\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},+}\right)\hat{a}^{\dagger}_{\boldsymbol{k},-}e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right)$$

$$=\sum_{\boldsymbol{k}}\hbar\left(\frac{\hbar\omega_k}{2\epsilon_0 V}\right)^{\frac{1}{2}}\left(\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},+}\right)\hat{a}_{\boldsymbol{k},+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}+\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},-}\right)\hat{a}_{\boldsymbol{k},-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right)-h.c. \qquad \text{A. 13}$$

So

$$i\theta\left[\hat{h}_{total},\widehat{\boldsymbol{E}}^T\right]=\theta\sum_{\boldsymbol{k}}\hbar\left(\frac{\hbar\omega_k}{2\epsilon_0 V}\right)^{\frac{1}{2}}\left(i\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},+}\right)\hat{a}_{\boldsymbol{k},+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}i\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},-}\right)\hat{a}_{\boldsymbol{k},-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right)+h.c.$$

$$=\theta c\sum_{\boldsymbol{k},\lambda}\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},\lambda}\right)\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{\frac{1}{2}}i\hat{a}_{\boldsymbol{k}\lambda}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}+h.c.=\theta c\widehat{\boldsymbol{B}} \qquad \text{A. 14}$$

Similar working gives

$$\left[\hat{h}_{total},\widehat{\boldsymbol{B}}\right]=\sum_{\boldsymbol{k}}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{1/2}\left[\hbar\left(\hat{a}^{\dagger}_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k},+}-\hat{a}^{\dagger}_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k},-}\right),\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},+}\right)i\hat{a}_{\boldsymbol{k}+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right.$$
$$\left.+\left(\boldsymbol{k}\times\boldsymbol{e}_{\boldsymbol{k},-}\right)i\hat{a}_{\boldsymbol{k}-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}+h.c.\right]$$
$$=\sum_{\boldsymbol{k}}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{1/2}\left[\hbar\left(\hat{a}^{\dagger}_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k},+}-\hat{a}^{\dagger}_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k},-}\right),\boldsymbol{e}_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k}+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right.$$
$$\left.-\boldsymbol{e}_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k}-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}+h.c.\right]$$
$$=\sum_{\boldsymbol{k}}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{1/2}\left(-\boldsymbol{e}_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k}+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}+\boldsymbol{e}_{\boldsymbol{k},-}\hat{a}^{\dagger}{}_{\boldsymbol{k}+}e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right.$$
$$\left.-\boldsymbol{e}_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k}-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}+\boldsymbol{e}_{\boldsymbol{k},+}\hat{a}^{\dagger}{}_{\boldsymbol{k}-}e^{-i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}\right)$$

$$i\theta\left[\hat{h}_{total},\widehat{\boldsymbol{B}}\right]=i\theta\sum_{\boldsymbol{k}}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{1/2}\left(-\boldsymbol{e}_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k}+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}-\boldsymbol{e}_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k}-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}-h.c.\right)$$

$$=\theta\sum_{\boldsymbol{k}}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{\frac{1}{2}}\left(-i\boldsymbol{e}_{\boldsymbol{k},+}\hat{a}_{\boldsymbol{k}+}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}-i\boldsymbol{e}_{\boldsymbol{k},-}\hat{a}_{\boldsymbol{k}-}e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega_k t)}+h.c.\right)=-\frac{\theta}{c}\widehat{\boldsymbol{E}} \qquad \text{A. 16}$$

Appendix B – Obtaining the Maxwell Equations within a Chiral Medium from a Lagrangian

In the main body of chapter 7, we presented the Lagrangian (7.5.1) as a starting point in order to arrive at an expression the helicity density using Noether's theorem. In this appendix, we justify this choice of Lagrangian by showing that the Euler-Lagrange equations, in conjunction with the constitutive relations (7.1.1-2), correctly give Maxwell's equations in a chiral medium (in the absence of free charges and currents).

Some care must be taken, as the Lagrangian (7.5.14) contains second-order derivatives of the generalised coordinates, and this necessitates a slight modification of the usual Euler-Lagrange equations [1, p. 192]. The Euler-Lagrange equations for a Lagrangian including 2nd derivatives are, for fields φ_r,

$$\frac{\partial \mathcal{L}}{\partial \varphi_r} - \frac{\partial}{\partial x_\alpha}\frac{\partial \mathcal{L}}{\partial \varphi_{r,\alpha}} + \sum_{\beta \geq \alpha} \frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}\frac{\partial \mathcal{L}}{\partial \varphi_{r,\alpha\beta}} = 0, \qquad \text{B.1}$$

where summation over the repeated index α is implied, and the Greek indices α and β run over 0,1,2,3 for t, x, y, z. The sum over β is written explicitly, as the condition $\beta \geq \alpha$ is necessary to avoid double-counting the mixed derivatives in the sum.

The Lagrangian (7.5.14) depends on the scalar potential only through $\boldsymbol{\nabla}\phi$, so the Euler-Lagrange equation associated with the scalar potential reduces to

$$-\frac{\partial}{\partial x_a}\frac{\partial \mathcal{L}}{\partial \nabla_a \phi} = 0. \qquad \text{B.2}$$

Using the expression for $\frac{\partial \mathcal{L}}{\partial \nabla_a \phi}$ (7.5.17), we see that this indeed corresponds to the Maxwell equation for the divergence of $\boldsymbol{D}$:

$$-\boldsymbol{\nabla}\cdot\frac{\partial \mathcal{L}}{\partial \boldsymbol{\nabla}\phi} = -\boldsymbol{\nabla}\cdot\epsilon\left(\frac{\partial \boldsymbol{A}}{\partial t} + \boldsymbol{\nabla}\phi + \beta\left(\boldsymbol{\nabla}\times\frac{\partial \boldsymbol{A}}{\partial t}\right)\right) = \boldsymbol{\nabla}\cdot\boldsymbol{D} = 0. \qquad \text{B.3}$$

For the *r* component of the vector potential, we have the Euler Lagrange equation

$$-\frac{\partial}{\partial x_a}\frac{\partial \mathcal{L}}{\partial(\partial_a A_r)} - \frac{\partial}{\partial t}\frac{\partial \mathcal{L}}{\partial\left(\dot{A}_r\right)} + \frac{\partial}{\partial t}\frac{\partial}{\partial x_a}\frac{\partial \mathcal{L}}{\partial_a \dot{A}_r} = 0. \qquad \text{B.4}$$

Using the expressions for the derivatives of $\mathcal{L}$ (7.5.16, 7.5.18, 7.5.19), we obtain

$$-\frac{\partial}{\partial x_a}\left[\frac{1}{\mu}\boldsymbol{n}_a \times (\nabla\times\boldsymbol{A})\right] - \frac{\partial}{\partial t}\left[\epsilon\left(\frac{\partial \boldsymbol{A}}{\partial t} + \boldsymbol{\nabla}\phi + \beta\left(\boldsymbol{\nabla}\times\frac{\partial \boldsymbol{A}}{\partial t}\right)\right)\right]$$
$$+\frac{\partial}{\partial t}\frac{\partial}{\partial x_a}\left[-\epsilon\beta^2\boldsymbol{n}_a\times\left(\nabla\times\frac{\partial \boldsymbol{A}}{\partial t}\right) - \beta\epsilon\boldsymbol{n}_{\boldsymbol{a}}\times\boldsymbol{\nabla}\phi - \beta\epsilon\boldsymbol{n}_{\boldsymbol{a}}\times\frac{\partial \boldsymbol{A}}{\partial t}\right] = 0. \qquad \text{B.5}$$

The second term is straightforwardly seen to be $\dot{\boldsymbol{D}}$. The first and last terms can be simplified as

$$\frac{\partial}{\partial x_a}\boldsymbol{n}_a \times \left[-\frac{1}{\mu}(\nabla \times \boldsymbol{A}) - \epsilon\beta^2\left(\nabla \times \frac{\partial^2 \boldsymbol{A}}{\partial t^2}\right) - \beta\epsilon\boldsymbol{\nabla}\frac{\partial \phi}{\partial t} - \beta\epsilon\frac{\partial^2 \boldsymbol{A}}{\partial t^2}\right]$$
$$= \boldsymbol{\nabla} \times \left[-\frac{1}{\mu}(\nabla \times \boldsymbol{A}) - \epsilon\beta^2\left(\nabla \times \frac{\partial^2 \boldsymbol{A}}{\partial t^2}\right) - \beta\epsilon\boldsymbol{\nabla}\frac{\partial \phi}{\partial t} - \beta\epsilon\frac{\partial^2 \boldsymbol{A}}{\partial t^2}\right]$$
$$= \boldsymbol{\nabla} \times \left[-\frac{1}{\mu}(\nabla \times \boldsymbol{A}) + \beta\frac{\partial \boldsymbol{D}}{\partial t}\right], \quad \text{B.6}$$

where in the final step we have grouped some of the terms together as $\dot{\boldsymbol{D}}$**.** Moving this to the other side of (B.5), we see that the Euler Lagrange equation is

$$\dot{\boldsymbol{D}} = \boldsymbol{\nabla} \times \left[\frac{1}{\mu}(\nabla \times \boldsymbol{A}) - \beta\dot{\boldsymbol{D}}\right]. \quad \text{B.7}$$

This equation – which should be thought of as an equation of motion for the potentials though the relation $\boldsymbol{D} = \epsilon\left(-\dot{\boldsymbol{A}} - \boldsymbol{\nabla}\phi - \beta\boldsymbol{\nabla} \times \dot{\boldsymbol{A}}\right)$ – is in fact an expression of the Maxwell equation $\boldsymbol{\nabla} \times \boldsymbol{H} = \dot{\boldsymbol{D}}$. This is because the constitutive relations require

$$\boldsymbol{H} = \frac{1}{\mu}\boldsymbol{B} - \frac{1}{\mu}\beta\boldsymbol{\nabla} \times \boldsymbol{H}, \quad \text{B.8}$$

and this is only consistent with (B.7) above if $\boldsymbol{\nabla} \times \boldsymbol{H} = \dot{\boldsymbol{D}}$. As in the free-space case, the remaining two Maxwell equations ($\boldsymbol{\nabla} \cdot \boldsymbol{B} = 0$ and $\boldsymbol{\nabla} \times \boldsymbol{E} = -\dot{\boldsymbol{B}}$) follow as identities from the definitions of the potentials.

References

[1] Courant R. and Hilbert D. 1962 *Methods of Mathematical Physics Volume 1*

Appendix C – Noether's Theorem for a Lagrangian with 2nd Derivatives

As well as altering the Euler-Lagrange equations, the presence of second derivatives in the Lagrangian alters the form of the conserved current in Noether's theorem. If a Lagrangian contains second derivatives of the generalised coordinates, then the change in the Lagrangian under an infinitesimal variation of the coordinates is

$$\delta\mathcal{L} = \frac{\partial\mathcal{L}}{\partial\varphi_r}\delta\varphi_r + \frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\delta\varphi_{r,\alpha} + \sum_{\beta\geq\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\delta\varphi_{r,\alpha\beta}\,, \qquad \text{C.1}$$

where, as in (B.1), the sum over β is written explicitly, and the condition $\beta \geq \alpha$ introduced to avoid double-counting of the mixed derivatives. As in the first derivative case discussed in chapter 2, the Euler Lagrange equations can be used in order to write this as a four-divergence. One obtains

$$\delta\mathcal{L} = \frac{\partial}{\partial x_\alpha}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\delta\varphi_r + \sum_{\beta\geq\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\delta\varphi_{r,\beta} - \sum_{\beta\leq\alpha}\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r\right], \qquad \text{C.2}$$

where the derivatives act only on terms within the subsequent brackets. This can be seen to be equivalent to (C.1) with the application of the Euler-Lagrange equations

$$\frac{\partial\mathcal{L}}{\partial\varphi_r} - \frac{\partial}{\partial x_\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}} + \sum_{\beta\geq\alpha}\frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}} = 0. \qquad \text{C.3}$$

We will consider the three terms of (C.2) in turn. Taking the first, we have

$$\begin{aligned}\frac{\partial}{\partial x_\alpha}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\delta\varphi_r\right] &= \frac{\partial}{\partial x_\alpha}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\right]\delta\varphi_r + \frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\delta\varphi_{r,\alpha} \\ &= \left(\frac{\partial\mathcal{L}}{\partial\varphi_r} + \sum_{\beta\geq\alpha}\frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right)\delta\varphi_r + \frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\delta\varphi_{r,\alpha},\end{aligned} \qquad \text{C.4}$$

where the Euler-Lagrange equations have been used to re-write $\frac{\partial}{\partial x_\alpha}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\right]$. The second term is equal to

$$\frac{\partial}{\partial x_\alpha}\left[\sum_{\beta\geq\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\delta\varphi_{r,\beta}\right] = \frac{\partial}{\partial x_\alpha}\left[\sum_{\beta\geq\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_{r,\beta} + \sum_{\beta\geq\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\delta\varphi_{r,\alpha\beta}\,. \qquad \text{C.5}$$

Finally, the third term becomes

$$\sum_{\beta\leq\alpha}\frac{\partial}{\partial x_\alpha}\left[-\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r\right] = -\sum_{\beta\leq\alpha}\frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r - \sum_{\beta\leq\alpha}\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_{r,\alpha}\,. \qquad \text{C.6}$$

We may swap the labels α and β in the final term of (C.6), and use $\partial\varphi_{r,\alpha\beta} = \partial\varphi_{r,\beta\alpha}$, to obtain

$$\sum_{\beta\leq\alpha}\frac{\partial}{\partial x_\alpha}\left[-\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r\right] = -\sum_{\beta\geq\alpha}\frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r - \sum_{\beta\geq\alpha}\frac{\partial}{\partial x_\alpha}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_{r,\beta}\,. \qquad \text{C.7}$$

Note that interchanging the labels has also interchanged the condition on the sum. We have likewise interchanged the condition on the first term of the right-hand-side of (C.7), as $\sum_{\beta\le\alpha}\frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r = \sum_{\beta\ge\alpha}\frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r$.

It is then clear, from summing (C.4), (C.5) and (C.7), that

$$\frac{\partial}{\partial x_\alpha}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\delta\varphi_r + \sum_{\beta\ge\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\delta\varphi_{r,\beta} - \sum_{\beta\le\alpha}\frac{\partial}{\partial x_\beta}\left[\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\right]\delta\varphi_r\right]$$
$$= \frac{\partial\mathcal{L}}{\partial\varphi_r}\delta\varphi_r + \frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha}}\delta\varphi_{r,\alpha} + \sum_{\beta\ge\alpha}\frac{\partial\mathcal{L}}{\partial\varphi_{r,\alpha\beta}}\delta\varphi_{r,\alpha\beta}\,, \qquad \text{C.8}$$

proving (C.2).

Appendix D – Rotational Averaging of High-Rank Tensors

Here we reproduce the proof leading to the expressions given in chapter 8 for the rotational average of tensors up to rank 6. The discussion presented below follows the proof given [1, §A2]. When given explicitly, the components of molecular property tensors are always specified with respect to some particular coordinate axes. We shall refer to this coordinate system as the "molecule frame". However, measurements on the molecule will usually be described in some other coordinate system. We will refer to this as the "lab frame". Throughout this appendix, we will refer to coordinates in the lab frame by Roman indices, and those in the molecule frame by Greek indices. In general, the lab frame and the molecule frame will be related to one another by some rotation, and so the components of a property tensor T in the two frames will be related by [1]

$$T_{abc\ldots} = R_{a\alpha} R_{b\beta} R_{c\gamma} \ldots T_{\alpha\beta\gamma\ldots} \qquad \text{D. 1.1}$$

where R is a *direction cosine matrix*: the entry $R_{\alpha\beta}$, for example, is defined as the cosine of the angle between the α axis and the β axis.

If we have a sample of randomly oriented molecules, and each molecule contributes to the overall response incoherently[1], then to derive the bulk response of the sample we may simply average equation (D1.1) over all possible molecular orientations. The relationship between the molecule and laboratory systems can specified by the three Euler angles[2] θ, ϕ and χ, and the average over these may be written

$$\langle T_{abc\ldots} \rangle = \frac{1}{8\pi^2} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta \, d\theta \int_0^{2\pi} d\chi \, R_{a\alpha} R_{b\beta} R_{c\gamma} \ldots T_{\alpha\beta\gamma\ldots}$$
$$= \langle R_{a\alpha} R_{b\beta} R_{c\gamma} \ldots \rangle T_{\alpha\beta\gamma\ldots} \qquad \text{D. 1.2}$$

So if we wish to compute the "averaged" response tensor $\langle T_{abc\ldots} \rangle$, we require the average of the product of direction cosines,

$$I_{abc\ldots\alpha\beta\gamma\ldots} = \langle R_{a\alpha} R_{b\beta} R_{c\gamma} \ldots \rangle. \qquad \text{D. 1.3}$$

The result can be computed by explicitly writing the direction cosine matrices in terms of the Euler angles and evaluating the required integrals, although this procedure becomes quite cumbersome for high ranks. Alternatively, the average can be found in a systematic way for tensors of arbitrary rank using a method given by [2]. The quantity $I_{abc\ldots\alpha\beta\gamma\ldots}$ is by construction rotationally

[1] This is always the case in Raman scattering, where the frequency shift means that the scattered light from each individual molecule does not have a consistent phase relationship to the incident. It is also the case in Rayleigh scattering from dilute enough samples, where the average distance between scatterers is large compared to the coherence length of the scattered light.
[2] θ and ϕ are the usual polar and azimuthal angles, which give the relative orientation of the z-axis of the second system to that of the first. χ completes the description of the second system by specifying a right-handed rotation about this new z axis.

invariant, and – according to a result of [3] – may be written as a sum of products of isotropic tensors in the laboratory and molecule systems.

The isotropic tensors of a given rank are of a fairly limited variety. The only isotropic tensor of rank two is δ_{ab}, and the only isotropic tensor of rank 3 is ϵ_{abc}. An isotropic tensor of higher rank can clearly be constructed by taking the direct product of δ and ϵ tensors, and further isotropic tensors can be found by permuting the indices. Matters are simplified by the following result, proved by [3], and also more directly by [4]: for a given rank and dimension, the set of tensors constructed in this way always spans the isotropic tensors of that rank and dimension. That is, *any isotropic tensor can be written as a linear combination of products of δ's and at most one ϵ*. It is clear that only one ϵ is ever required: if more than one ϵ were to appear, the result could always be re-written using

$$\epsilon_{abc}\epsilon_{def} = \delta_{ad}\left(\delta_{be}\delta_{cf} - \delta_{bf}\delta_{ce}\right) - \delta_{ae}\left(\delta_{bd}\delta_{cf} - \delta_{bf}\delta_{cd}\right) + \delta_{af}(\delta_{bd}\delta_{ce} - \delta_{be}\delta_{cd}). \qquad \text{D.}1.4$$

Now, suppose we construct such a set of basic isotropic tensors (which we call "isomers"), and label them $f^1, f^2 \dots f^n$. The theorem by Weyl is the statement

$$\left\langle I_{abc\dots\alpha\beta\gamma\dots}\right\rangle = \sum_{m,n} c^{mn} f^m_{abc\dots} f^n_{\alpha\beta\gamma\dots} \qquad \text{D.}1.5$$

and our task is now to determine the coefficients c^{mn}. As the isomers are (of course) isotropic, $\langle f^r\rangle = f^r$, and we can write

$$f^r_{abc} = \langle f^r_{abc\dots}\rangle = \left\langle I_{abc\dots\alpha\beta\gamma\dots}\right\rangle f^r_{\alpha\beta\gamma\dots} \qquad \text{D.}1.6$$

so

$$f^r_{abc\dots} = \sum_{m,n} c^{mn} f^m_{abc\dots} f^n_{\alpha\beta\gamma\dots} f^r_{\alpha\beta\gamma\dots} \qquad \text{D.}1.7$$

If we contract this with another isomer, f^s_{abc}, we obtain

$$f^r_{abc\dots} f^s_{abc\dots} = \sum_{m,n} c^{mn} f^m_{abc\dots} f^n_{\alpha\beta\gamma\dots} f^r_{\alpha\beta\gamma\dots} f^s_{abc\dots} \qquad \text{D.}1.8$$

Calling the number $f^r_{abc\dots} f^s_{abc\dots} \equiv S^{rs}$ (and noting that $f^r_{abc\dots} f^s_{abc\dots} = f^r_{\alpha\beta\gamma\dots} f^s_{\alpha\beta\gamma\dots}$), we have

$$S^{rs} = \sum_{m,n} c^{mn} S^{ms} S^{nr}. \qquad \text{D.}1.9$$

S can be viewed as a matrix of size equal to the number of isomers. If the c^{mn} are also viewed as a matrix of coefficients, we can write the above in matrix notation simply as

$$S = SCS, \qquad \text{D.}1.10$$

from which we can deduce (provided that S is invertible)

$$S^{-1} = C. \qquad \text{D.}1.11$$

So, if we can construct a suitable S, we can then invert it to obtain C and hence obtain an expression for $\left\langle I_{abc\dots\alpha\beta\gamma\dots}\right\rangle$.

Constructing S is a simple enough matter: it involves writing down all the possible isomers of a given rank, and then performing the various possible pairwise contractions to obtain each element of S. A slight complication is that the isomers obtained by permuting the indices will not always form a linearly independent set: in this case one can obtain a simpler expression for the rotational average by choosing a linearly independent subset. There are in general different ways to make this choice – a systematic method is given in [2], but we will not pursue the details here.
The final results for the averages of the relevant direction cosine products are:

$$\langle I_{abcd\alpha\beta\gamma\delta}\rangle = \begin{pmatrix} \delta_{ab}\delta_{cd} \\ \delta_{ac}\delta_{bd} \\ \delta_{ad}\delta_{bc} \end{pmatrix}^T \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{\alpha\beta}\delta_{\gamma\delta} \\ \delta_{\alpha\gamma}\delta_{\beta\delta} \\ \delta_{\alpha\delta}\delta_{\beta\gamma} \end{pmatrix} \qquad \text{D. 1.12}$$

$$\langle I_{abcd\alpha\beta\gamma\delta}\rangle = \begin{pmatrix} \epsilon_{abc}\delta_{de} \\ \epsilon_{abd}\delta_{ce} \\ \epsilon_{abe}\delta_{cd} \\ \epsilon_{acd}\delta_{be} \\ \epsilon_{ace}\delta_{bd} \\ \epsilon_{ade}\delta_{bc} \end{pmatrix}^T \begin{pmatrix} 3 & -1 & -1 & -1 & 1 & 0 \\ -1 & 3 & -1 & -1 & 0 & 1 \\ -1 & -1 & 3 & 0 & -1 & -1 \\ 1 & -1 & 0 & 3 & -1 & 1 \\ 1 & 0 & -1 & -1 & 3 & -1 \\ 0 & 1 & -1 & 1 & -1 & 3 \end{pmatrix} \begin{pmatrix} \epsilon_{\alpha\beta\gamma}\delta_{\delta\epsilon} \\ \epsilon_{\alpha\beta\delta}\delta_{\gamma\epsilon} \\ \epsilon_{\alpha\beta\epsilon}\delta_{\gamma\delta} \\ \epsilon_{\alpha\gamma\delta}\delta_{\beta\epsilon} \\ \epsilon_{\alpha\gamma\epsilon}\delta_{\beta\delta} \\ \epsilon_{\alpha\delta\epsilon}\delta_{\beta\gamma} \end{pmatrix} \qquad \text{D. 1.13}$$

$\langle I_{abcdef\alpha\beta\gamma\delta\epsilon\zeta}\rangle$ presented overleaf.

References

[1] Craig D. P. and Thirunamachandran T. 1984 *Molecular Quantum Electrodynamics* Dover (corrected/republished 1988)

[2] Andrews D. L. and Thirunamachandran T. 1977 *Journal of Chemical Physics* On Three-Dimensional Rotational Averages **67** 5026

[3] Weyl H. 1946 *The Classical Groups* Princeton University Press

[4] Jeffreys H. 1972 *Mathematical Proceedings of the Cambridge Philosophical Society* On Isotropic Tensors **73** 173

$$\left\langle I_{abcdef\alpha\beta\gamma\delta\epsilon\zeta}\right\rangle = \begin{pmatrix} \delta_{ab}\delta_{cd}\delta_{ef} \\ \delta_{ab}\delta_{ce}\delta_{df} \\ \delta_{ab}\delta_{cf}\delta_{de} \\ \delta_{ac}\delta_{bd}\delta_{ef} \\ \delta_{ac}\delta_{be}\delta_{df} \\ \delta_{ac}\delta_{bf}\delta_{de} \\ \delta_{ad}\delta_{bc}\delta_{ef} \\ \delta_{ad}\delta_{be}\delta_{cf} \\ \delta_{ad}\delta_{bf}\delta_{ce} \\ \delta_{ae}\delta_{bc}\delta_{df} \\ \delta_{ae}\delta_{bd}\delta_{cf} \\ \delta_{ae}\delta_{bf}\delta_{cd} \\ \delta_{af}\delta_{bc}\delta_{de} \\ \delta_{af}\delta_{bd}\delta_{ce} \\ \delta_{af}\delta_{be}\delta_{cd} \end{pmatrix}^{T} \begin{pmatrix} 16 & -5 & -5 & -5 & 2 & 2 & -5 & 2 & 2 & 2 & 2 & -5 & 2 & 2 & -5 \\ -5 & 16 & -5 & 2 & -5 & 2 & 2 & 2 & -5 & -5 & 2 & 2 & 2 & -5 & 2 \\ -5 & -5 & 16 & 2 & 2 & -5 & 2 & -5 & 2 & 2 & -5 & 2 & -5 & 2 & 2 \\ -5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & 2 \\ 2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 & -5 & 2 & 2 & 2 & 2 & -5 \\ 2 & 2 & -5 & -5 & -6 & 16 & 2 & 2 & -5 & 2 & 2 & -5 & -5 & 2 & 2 \\ -5 & 2 & 2 & -5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 & -5 & 2 & 2 \\ 2 & 2 & -5 & 2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 & 2 & 2 & -5 \\ 2 & -5 & 2 & 2 & 2 & -5 & -5 & -5 & 16 & 2 & 2 & -5 & 2 & -5 & 2 \\ 2 & -5 & 2 & 2 & -5 & 2 & -5 & 2 & 2 & 16 & -5 & -5 & -5 & 2 & 2 \\ 2 & 2 & -5 & -5 & 2 & 2 & 2 & -5 & 2 & -5 & 16 & -5 & 2 & -5 & 2 \\ -5 & 2 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & -5 & -5 & 16 & 2 & 2 & -5 \\ 2 & 2 & -5 & 2 & 2 & -5 & -5 & 2 & 2 & -5 & 2 & 2 & 16 & -5 & -5 \\ 2 & -5 & 2 & -5 & 2 & 2 & 2 & 2 & -5 & 2 & -5 & 2 & -5 & 16 & -5 \\ -5 & 2 & 2 & 2 & -5 & 2 & 2 & -5 & 2 & 2 & 2 & -5 & -5 & -5 & 16 \end{pmatrix} \begin{pmatrix} \delta_{\alpha\beta}\delta_{\gamma\delta}\delta_{\epsilon\zeta} \\ \delta_{\alpha\beta}\delta_{\gamma\epsilon}\delta_{\delta\zeta} \\ \delta_{\alpha\beta}\delta_{\gamma\zeta}\delta_{\delta\epsilon} \\ \delta_{\alpha\gamma}\delta_{\beta\delta}\delta_{\epsilon\zeta} \\ \delta_{\alpha\gamma}\delta_{\beta\epsilon}\delta_{\delta\zeta} \\ \delta_{\alpha\gamma}\delta_{\beta\zeta}\delta_{\delta\epsilon} \\ \delta_{\alpha\delta}\delta_{\beta\gamma}\delta_{\epsilon\zeta} \\ \delta_{\alpha\delta}\delta_{\beta\epsilon}\delta_{\gamma\zeta} \\ \delta_{\alpha\delta}\delta_{\beta\zeta}\delta_{\gamma\epsilon} \\ \delta_{\alpha\epsilon}\delta_{\beta\gamma}\delta_{\delta\zeta} \\ \delta_{\alpha\epsilon}\delta_{\beta\delta}\delta_{\gamma\zeta} \\ \delta_{\alpha\epsilon}\delta_{\beta\zeta}\delta_{\gamma\delta} \\ \delta_{\alpha\zeta}\delta_{\beta\gamma}\delta_{\delta\epsilon} \\ \delta_{\alpha\zeta}\delta_{\beta\delta}\delta_{\gamma\epsilon} \\ \delta_{\alpha\zeta}\delta_{\beta\epsilon}\delta_{\gamma\delta} \end{pmatrix} \qquad \text{D. 1.14}$$

APPENDIX E

In this appendix we present the full expressions for the rotationally averaged "second-order" contributions to the stokes parameters s_ξ, as described in Chapter 9. The results are stated in terms of rotationally invariant contractions of tensor components, labeled M_a, whose definitions are given immediately following the expressions. As they are rather long, the contributions are broken up according to their dependence on different polarisability tensors, and further by their dependence on either scripted or unscripted tensors.

The '$\alpha - \alpha$' terms are

$$\langle s_\xi^{\alpha-\alpha} \rangle = K\mathrm{Re}\left(\frac{1}{40}\tilde{A}_\xi^{\alpha-\alpha}\right),$$

with

$$\begin{aligned}
\tilde{A}_0^{\alpha-\alpha} &= S_0\left(-M_1 + 14M_2 - M_3\right) \\
&+ S_0\cos^2\theta\left(3M_1 - 2M_2 + 3M_3\right) \\
&+ S_1\sin^2\theta\left(3M_1 - 2M_2 + 3M_3\right), \\
\tilde{A}_1^{\alpha-\alpha} &= S_1\left(-3M_1 + 2M_2 - 3M_3\right) \\
&+ S_1\cos^2\theta\left(-3M_1 + 2M_2 - 3M_3\right) \\
&+ S_0\sin^2\theta\left(-3M_1 + 2M_2 - 3M_3\right), \\
\tilde{A}_2^{\alpha-\alpha} &= S_2\cos\theta\left(-6M_1 + 4M_2 - 6M_3\right) \\
\tilde{A}_3^{\alpha-\alpha} &= S_3\cos\theta\left(10M_1 - 10M_3\right),
\end{aligned} \tag{E.1}$$

with the rotational invariants defined

$$\begin{aligned}
\tilde{M}_1^{\alpha-\alpha} &= \tilde{\alpha}_{aa}\tilde{\alpha}_{bb}^*, \\
\tilde{M}_2^{\alpha-\alpha} &= \tilde{\alpha}_{ab}\tilde{\alpha}_{ab}^* \\
\tilde{M}_3^{\alpha-\alpha} &= \tilde{\alpha}_{ab}\tilde{\alpha}_{ba}^*.
\end{aligned} \tag{E.2}$$

The '$A - A$' terms are

$$\langle s_\xi^{A-A} \rangle = K\mathrm{Re}\left[\frac{1}{7560}\left(\tilde{A}_\xi^{A-A} + \tilde{B}_\xi^{A-A} + \tilde{C}_\xi^{A-A}\right)\right], \tag{E.3}$$

with

$$\begin{aligned}
\tilde{A}_0^{A-A} &= S_0\left(3M_1 + 3M_2\right) \\
&+ S_0\cos^2\theta\left(-9M_1 - 9M_2\right) \\
&+ S_1\sin^2\theta\left(9M_1 + 9M_2\right), \\
\tilde{A}_1^{A-A} &= S_1\left(-9M_1 - 9M_2\right) \\
&+ S_1\cos^2\theta\left(-9M_1 - 9M_2\right) \\
&+ S_0\sin^2\theta\left(9M_1 + 9M_2\right), \\
\tilde{A}_2^{A-A} &= S_2\cos\theta\left(-18M_1 - 18M_2\right), \\
\tilde{A}_3^{A-A} &= S_3\cos\theta\left(14M_1 - 14M_2\right),
\end{aligned}
\qquad
\begin{aligned}
\tilde{B}_0^{A-A} &= S_0\cos\theta\left(24M_3 - 60M_4\right) \\
&+ S_0\cos^3\theta\left(-40M_3 + 16M_4\right) \\
&+ S_1\sin^2\theta\cos\theta\left(-40M_3 + 16M_4\right), \\
\tilde{B}_1^{A-A} &= S_1\cos\theta\left(-32M_3 - 4M_4\right) \\
&+ S_1\cos^3\theta\left(40M_3 - 16M_4\right) \\
&+ S_0\sin^2\theta\cos\theta\left(40M_3 - 16M_4\right), \\
\tilde{B}_2^{A-A} &= S_2\left(-36M_3 + 6M_4\right) \\
&+ S_2\cos^2\theta\left(44M_3 - 26M_4\right) \\
&+ \mathrm{i}S_3\sin^2\theta\left(28M_3 + 14M_4\right), \\
\tilde{B}_3^{A-A} &= S_3\left(28M_3 + 14M_4\right) \\
&+ S_3\cos^2\theta\left(-84M_3 - 42M_4\right) \\
&+ \mathrm{i}S_2\sin^2\theta\left(-28M_3 - 14M_4\right),
\end{aligned} \tag{E.4}$$

$$
\begin{aligned}
\tilde{C}_0^{A-A} &= S_0\left(3M_5 + 3M_6\right) \\
&\quad + S_0\cos^2\theta\left(-9M_5 - 9M_6\right) \\
&\quad + S_1\sin^2\theta\left(-9M_5 - 9M_6\right), \\
\tilde{C}_1^{A-A} &= S_1\left(-9M_5 - 9M_6\right) \\
&\quad + S_1\cos^2\theta\left(-9M_5 - 9M_6\right) \\
&\quad + S_0\sin^2\theta\left(-9M_5 - 9M_6\right), \\
\tilde{C}_2^{A-A} &= S_2\cos\theta\left(-18M_5 - 18M_6\right) \\
\tilde{C}_3^{A-A} &= S_3\cos\theta\left(14M_5 - 14M_6\right),
\end{aligned}
\tag{E.5}
$$

with the rotational invariants

$$
\begin{aligned}
\tilde{M}_1^{A-A} &= \frac{\omega_0^2}{c^2}\tilde{A}_{a,ab}\tilde{A}^*_{c,bc}, \\
\tilde{M}_2^{A-A} &= \frac{\omega_0^2}{c^2}\tilde{A}_{a,bc}\tilde{A}^*_{b,ac}, \\
\tilde{M}_3^{A-A} &= \frac{\omega_0\omega}{c^2}\tilde{A}_{a,ab}\tilde{\mathscr{A}}^*_{c,bc}, \\
\tilde{M}_4^{A-A} &= \frac{\omega_0\omega}{c^2}\tilde{A}_{a,bc}\tilde{\mathscr{A}}^*_{b,ac}, \\
\tilde{M}_5^{A-A} &= \frac{\omega^2}{c^2}\tilde{\mathscr{A}}_{a,ab}\tilde{\mathscr{A}}^*_{c,bc} \\
\tilde{M}_6^{A-A} &= \frac{\omega^2}{c^2}\tilde{\mathscr{A}}_{a,bc}\tilde{\mathscr{A}}^*_{b,ac}.
\end{aligned}
\tag{E.6}
$$

The '$G-A$' terms are

$$
\langle s_\xi^{G-A}\rangle = K\mathrm{Re}\left[\frac{1}{360}\left(\tilde{A}_\xi^{G-A} + \tilde{B}_\xi^{G-A} + \tilde{C}_\xi^{G-A} + \tilde{D}_\xi^{G-A}\right)\right],
\tag{E.7}
$$

with

$$
\begin{aligned}
\tilde{A}_0^{G-A} &= S_0\left(2M_1 - 4M_2\right) & \tilde{B}_0^{G-A} &= S_0\cos\theta\left(-12M_4\right), \\
&\quad + S_0\cos^2\theta\left(-6M_1 + 12M_2\right) & \tilde{B}_1^{G-A} &= S_1\cos\theta\left(-8M_3 + 4M_4\right), \\
&\quad + S_1\sin^2\theta\left(-2M_1 + 4M_2\right), & \tilde{B}_2^{G-A} &= S_2\left(-4M_3 + 2M_4\right) \\
\tilde{A}_1^{G-A} &= S_1\left(2M_1 - 4M_2\right) & &\quad + S_2\cos^2\theta\left(-4M_3 + 2M_4\right) \\
&\quad + S_1\cos^2\theta\left(2M_1 - 4M_2\right) & &\quad + \mathrm{i}S_3\sin^2\theta\left(-4M_3 + 2M_4\right), \\
&\quad + S_0\sin^2\theta\left(6M_1 - 12M_2\right), & \tilde{B}_3^{G-A} &= S_3\left(-4M_3 + 2M_4\right) \\
\tilde{A}_2^{G-A} &= S_2\cos\theta\left(4M_1 - 8M_2\right), & &\quad + S_3\cos^2\theta\left(12M_3 - 6M_4\right) \\
\tilde{A}_3^{G-A} &= S_3\cos\theta\left(-12M_1\right), & &\quad + \mathrm{i}S_2\sin^2\theta\left(-12M_3 + 6M_4\right),
\end{aligned}
\tag{E.8}
$$

$$
\begin{aligned}
\tilde{C}_0^{G-A} &= S_0\cos\theta\left(12M_5\right), & \tilde{D}_0^{G-A} &= S_0\left(4M_7 - 2M_8\right) \\
\tilde{C}_1^{G-A} &= S_1\cos\theta\left(-4M_5 + 8M_6\right), & &\quad + S_0\cos^2\theta\left(-12M_7 + 6M_8\right) \\
\tilde{C}_2^{G-A} &= S_2\left(-2M_5 + 4M_6\right) & &\quad + S_1\sin^2\theta\left(-12M_7 + 6M_8\right), \\
&\quad + S_2\cos^2\theta\left(-2M_5 + 4M_6\right) & \tilde{D}_1^{G-A} &= S_1\left(4M_7 - 2M_8\right) \\
&\quad + \mathrm{i}S_3\sin^2\theta\left(-6M_5 + 12M_6\right), & &\quad + S_1\cos^2\theta\left(4M_7 - 2M_8\right) \\
\tilde{C}_3^{G-A} &= S_3\left(-2M_5 + 4M_6\right) & &\quad + S_0\sin^2\theta\left(4M_7 - 2M_8\right), \\
&\quad + S_3\cos^2\theta\left(6M_5 - 12M_6\right) & \tilde{D}_2^{G-A} &= S_2\cos\theta\left(8M_7 - 4M_8\right) \\
&\quad + \mathrm{i}S_2\sin^2\theta\left(-2M_5 + 4M_6\right), & \tilde{D}_3^{G-A} &= S_3\cos\theta\left(12M_8\right),
\end{aligned}
\tag{E.9}
$$

with the rotational invariants

$$\begin{aligned}
\tilde{M}_1^{G-A} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{A}^*_{a,bd}\tilde{G}_{cd}, & \tilde{M}_5^{G-A} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{A}^*_{a,bd}\tilde{\mathscr{G}}_{cd},\\
\tilde{M}_2^{G-A} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{A}^*_{a,bd}\tilde{G}_{dc}, & \tilde{M}_6^{G-A} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{A}^*_{a,bd}\tilde{\mathscr{G}}_{dc},\\
\tilde{M}_3^{G-A} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\mathscr{A}}^*_{a,bd}\tilde{G}_{cd}, & \tilde{M}_7^{G-A} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\mathscr{A}}^*_{a,bd}\tilde{\mathscr{G}}_{cd}\\
\tilde{M}_4^{G-A} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\mathscr{A}}^*_{a,bd}\tilde{G}_{dc}, & \tilde{M}_8^{G-A} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\mathscr{A}}^*_{a,bd}\tilde{\mathscr{G}}_{dc}.
\end{aligned} \tag{E.10}$$

The '$G-G$' terms are

$$\langle s_\xi^{G-G}\rangle = K\mathrm{Re}\left[\frac{1}{120}\left(\tilde{A}_\xi^{G-G}+\tilde{B}_\xi^{G-G}+\tilde{C}_\xi^{G-G}\right)\right], \tag{E.11}$$

with

$$\begin{aligned}
\tilde{A}_0^{G-G} &= S_0\left(-M_1+14M_2-M_3\right) & \tilde{B}_0^{G-G} &= S_0\cos\theta\left(-20M_4+20M_6\right),\\
&\quad + S_0\cos^2\theta\left(3M_1-2M_2+3M_3\right) & \tilde{B}_1^{G-G} &= S_1\cos\theta\left(-12M_4+8M_5-12M_6\right),\\
&\quad + S_1\sin^2\theta\left(-3M_1+2M_2-3M_3\right), & \tilde{B}_2^{G-G} &= S_2\left(-6M_4+4M_5-6M_6\right)\\
\tilde{A}_1^{G-G} &= S_1\left(3M_1-2M_2+3M_3\right) & &\quad + S_2\cos^2\theta\left(-6M_4+4M_5-6M_6\right)\\
&\quad + S_1\cos^2\theta\left(3M_1-2M_2+3M_3\right) & &\quad + \mathrm{i}S_3\sin^2\theta\left(-6M_4+4M_5-6M_6\right),\\
&\quad + S_0\sin^2\theta\left(-3M_1+2M_2-3M_3\right), & \tilde{B}_3^{G-G} &= S_3\left(2M_4-28M_5+2M_6\right)\\
\tilde{A}_2^{G-G} &= S_2\cos\theta\left(6M_1-4M_2+6M_3\right), & &\quad + S_3\cos^2\theta\left(-6M_4+4M_5-6M_6\right)\\
\tilde{A}_3^{G-G} &= S_3\cos\theta\left(10M_1-10M_3\right), & &\quad + \mathrm{i}S_2\sin^2\theta\left(6M_4-4M_5+6M_6\right),
\end{aligned} \tag{E.12}$$

$$\begin{aligned}
\tilde{C}_0^{G-G} &= S_0\left(-M_7+14M_8-M_9\right)\\
&\quad + S_0\cos^2\theta\left(3M_7-2M_8+3M_9\right)\\
&\quad + S_1\sin^2\theta\left(3M_7-2M_8+3M_9\right),\\
\tilde{C}_1^{G-G} &= S_1\left(3M_7-2M_8+3M_9\right)\\
&\quad + S_1\cos^2\theta\left(3M_7-2M_8+3M_9\right)\\
&\quad + S_0\sin^2\theta\left(3M_7-2M_8+3M_9\right),\\
\tilde{C}_2^{G-G} &= S_2\cos\theta\left(6M_7-4M_8+6M_9\right)\\
\tilde{C}_3^{G-G} &= S_3\cos\theta\left(10M_7-10M_9\right),
\end{aligned} \tag{E.13}$$

with the rotational invariants

$$\begin{aligned}
\tilde{M}_1^{G-G} &= \frac{1}{c^2}\tilde{G}_{aa}\tilde{G}^*_{bb}, & \tilde{M}_4^{G-G} &= \frac{1}{c^2}\tilde{G}_{aa}\tilde{\mathscr{G}}^*_{bb}, & \tilde{M}_7^{G-G} &= \frac{1}{c^2}\tilde{\mathscr{G}}_{aa}\tilde{\mathscr{G}}^*_{bb},\\
\tilde{M}_2^{G-G} &= \frac{1}{c^2}\tilde{G}_{ab}\tilde{G}^*_{ab}, & \tilde{M}_5^{G-G} &= \frac{1}{c^2}\tilde{G}_{ab}\tilde{\mathscr{G}}^*_{ab}, & \tilde{M}_8^{G-G} &= \frac{1}{c^2}\tilde{\mathscr{G}}_{ab}\tilde{\mathscr{G}}^*_{ab}\\
\tilde{M}_3^{G-G} &= \frac{1}{c^2}\tilde{G}_{ab}\tilde{G}^*_{ba}, & \tilde{M}_6^{G-G} &= \frac{1}{c^2}\tilde{G}_{ab}\tilde{\mathscr{G}}^*_{ba}, & \tilde{M}_9^{G-G} &= \frac{1}{c^2}\tilde{\mathscr{G}}_{ab}\tilde{\mathscr{G}}^*_{ba}.
\end{aligned} \tag{E.14}$$

The '$\alpha-B$' terms are

$$\langle s_\xi^{\alpha-B}\rangle = K\mathrm{Re}\left[\frac{1}{5040}\left(\tilde{A}_\xi^{\alpha-B}+\tilde{B}_\xi^{\alpha-B}\right)\right], \tag{E.15}$$

with

$$\begin{aligned}
\tilde{A}_0^{\alpha-B} &= S_0\left(6M_1 - 36M_2 + 6M_3 - 16M_4\right) & \tilde{B}_0^{\alpha-B} &= S_0\left(6M_5 + 6M_6 - 36M_7 - 16M_8\right)\\
&+ S_0\cos^2\theta\left(-18M_1 - 4M_2 - 18M_3 + 48M_4\right) & &+ S_0\cos^2\theta\left(-18M_5 - 18M_6 - 4M_7 + 48M_8\right)\\
&+ S_1\sin^2\theta\left(-10M_1 + 4M_2 - 10M_3 + 8M_4\right), & &+ S_1\sin^2\theta\left(-18M_5 - 18M_6 - 4M_7 + 48M_8\right),\\
\tilde{A}_1^{\alpha-B} &= S_1\left(10M_1 - 4M_2 + 10M_3 - 8M_4\right) & \tilde{B}_1^{\alpha-B} &= S_1\left(10M_5 + 10M_6 - 4M_7 - 8M_8\right)\\
&+ S_1\cos^2\theta\left(10M_1 - 4M_2 + 10M_3 - 8M_4\right) & &+ S_1\cos^2\theta\left(10M_5 + 10M_6 - 4M_7 - 8M_8\right)\\
&+ S_0\sin^2\theta\left(18M_1 + 4M_2 + 18M_3 - 48M_4\right), & &+ S_0\sin^2\theta\left(10M_5 + 10M_6 - 4M_7 - 8M_8\right),\\
\tilde{A}_2^{\alpha-B} &= S_2\cos\theta\left(20M_1 - 8M_2 + 20M_3 - 16M_4\right), & \tilde{B}_2^{\alpha-B} &= S_2\cos\theta\left(20M_5 + 20M_6 - 8M_7 - 16M_8\right)\\
\tilde{A}_3^{\alpha-B} &= S_3\cos\theta\left(-28M_1 + 28M_3\right), & \tilde{B}_3^{\alpha-B} &= S_3\cos\theta\left(-28M_5 + 28M_6\right),
\end{aligned} \tag{E.16}$$

with the rotational invariants

$$\begin{aligned}
\tilde{M}_1^{\alpha-B} &= \frac{\omega_0}{c^2}\tilde{\alpha}_{aa}\tilde{B}^*_{b,bcc}, & \tilde{M}_5^{\alpha-B} &= \frac{\omega}{c^2}\tilde{\alpha}_{aa}\tilde{\mathscr{B}}^*_{b,bcc},\\
\tilde{M}_2^{\alpha-B} &= \frac{\omega_0}{c^2}\tilde{\alpha}_{ab}\tilde{B}^*_{a,bcc}, & \tilde{M}_6^{\alpha-B} &= \frac{\omega}{c^2}\tilde{\alpha}_{ab}\tilde{\mathscr{B}}^*_{a,bcc},\\
\tilde{M}_3^{\alpha-B} &= \frac{\omega_0}{c^2}\tilde{\alpha}_{ab}\tilde{B}^*_{b,acc}, & \tilde{M}_7^{\alpha-B} &= \frac{\omega}{c^2}\tilde{\alpha}_{ab}\tilde{\mathscr{B}}^*_{b,acc}\\
\tilde{M}_4^{\alpha-B} &= \frac{\omega_0}{c^2}\tilde{\alpha}_{ab}\tilde{B}^*_{c,abc}, & \tilde{M}_8^{\alpha-B} &= \frac{\omega}{c^2}\tilde{\alpha}_{ab}\tilde{\mathscr{B}}^*_{c,abc}.
\end{aligned} \tag{E.17}$$

The '$\alpha - C$' terms are

$$\langle s_\xi^{\alpha-C}\rangle = K\mathrm{Re}\left(\frac{1}{1260}\tilde{A}_\xi^{\alpha-C}\right), \tag{E.18}$$

with

$$\begin{aligned}
\tilde{A}_0^{\alpha-C} &= S_0\cos\theta\left(-6M_1 + 30M_2 - 12M_3\right) & \tilde{A}_2^{\alpha-C} &= S_2\left(2M_1 - 3M_2 + 18M_3\right)\\
&+ S_0\cos^3\theta\left(10M_1 - 8M_2 + 20M_3\right) & &+ S_2\cos^2\theta\left(-18M_1 + 13M_2 - 22M_3\right)\\
&+ S_1\sin^2\theta\cos\theta\left(10M_1 - 8M_2 + 20M_3\right), & &+ \mathrm{i}S_3\sin^2\theta\left(-14M_1 + 7M_2 + 14M_3\right)\\
\tilde{A}_1^{\alpha-C} &= S_1\cos\theta\left(-6M_1 + 2M_2 + 16M_3\right) & \tilde{A}_3^{\alpha-C} &= S_3\left(-14M_1 + 7M_2 + 14M_3\right)\\
&+ S_1\cos^3\theta\left(-10M_1 + 8M_2 - 20M_3\right) & &+ S_3\cos^2\theta\left(42M_1 - 21M_2 - 42M_3\right)\\
&+ S_0\sin^2\theta\cos\theta\left(-10M_1 + 8M_2 - 20M_3\right), & &+ \mathrm{i}S_2\sin^2\theta\left(-14M_1 + 7M_2 + 14M_3\right),
\end{aligned} \tag{E.19}$$

with the rotational invariants

$$\begin{aligned}
\tilde{M}_1^{\alpha-C} &= \frac{\omega\omega_0}{c^2}\tilde{\alpha}_{aa}\tilde{C}^*_{bc,bc},\\
\tilde{M}_2^{\alpha-C} &= \frac{\omega\omega_0}{c^2}\tilde{\alpha}_{ab}\tilde{C}^*_{ac,bc}\\
\tilde{M}_3^{\alpha-C} &= \frac{\omega\omega_0}{c^2}\tilde{\alpha}_{ab}\tilde{C}^*_{bc,ac}.
\end{aligned} \tag{E.20}$$

The '$\alpha - D$' terms are

$$\langle s_\xi^{\alpha-D}\rangle = K\mathrm{Re}\left(\frac{1}{180}\tilde{A}_\xi^{\alpha-D}\right), \tag{E.21}$$

with

$$\begin{aligned}
\tilde{A}_0^{\alpha-D} &= S_0\cos\theta\left(-6M_1 + 6M_2 - 6M_3\right),\\
\tilde{A}_1^{\alpha-D} &= S_1\cos\theta\left(-2M_1 - 2M_2 + 2M_3 - 4M_4\right),\\
\tilde{A}_2^{\alpha-D} &= S_2\left(-M_1 - M_2 + M_3 - 2M_4\right)\\
&+ S_2\cos^2\theta\left(-M_1 - M_2 + M_3 - 2M_4\right)\\
&+ \mathrm{i}S_3\sin^2\theta\left(M_1 + M_2 + 3M_3 - 6M_4\right)\\
\tilde{A}_3^{\alpha-D} &= S_3\left(M_1 + M_2 - M_3 + 2M_4\right)\\
&+ S_3\cos^2\theta\left(-3M_1 - 3M_2 + 3M_3 - 6M_4\right)\\
&+ \mathrm{i}S_2\sin^2\theta\left(-3M_1 - 3M_2 - M_3 + 2M_4\right),
\end{aligned} \tag{E.22}$$

with the rotational invariants

$$\begin{aligned}
\tilde{M}_1^{\alpha-D} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\alpha}_{ab}\tilde{\mathscr{D}}^*_{d,cd},\\
\tilde{M}_2^{\alpha-D} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\alpha}_{ad}\tilde{\mathscr{D}}^*_{b,cd},\\
\tilde{M}_3^{\alpha-D} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{\alpha}_{ad}\tilde{D}^*_{b,cd}\\
\tilde{M}_4^{\alpha-D} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{\alpha}_{ab}\tilde{D}^*_{d,cd}.
\end{aligned} \tag{E.23}$$

The '$\alpha - D^m$' terms are

$$\langle s_\xi^{\alpha-D^m}\rangle = K\mathrm{Re}\left[\frac{1}{120}\left(\tilde{A}_\xi^{\alpha-D^m} + \tilde{B}_\xi^{\alpha-D^m}\right)\right], \tag{E.24}$$

with

$$\begin{aligned}
\tilde{A}_0^{\alpha-D^m} &= S_0\left(M_1 - 8M_2 + 6M_3 + M_4 - 6M_6\right) & \tilde{B}_0^{\alpha-D^m} &= S_0\left(-M_8 - M_{10} + 6M_{12}\right)\\
&+ S_0\cos^2\theta\left(-3M_1 + 4M_2 + 2M_3 - 3M_4 - 2M_6\right) & &+ S_0\cos^2\theta\left(3M_8 + 3M_{10} + 2M_{12}\right)\\
&+ S_1\sin^2\theta\left(M_1 - 2M_3 - M_4 + 2M_5 - 2M_6\right), & &+ S_1\sin^2\theta\left(3M_8 + 3M_{10} + 2M_{12}\right),\\
\tilde{A}_1^{\alpha-D^m} &= S_1\left(-M_1 + 2M_3 + M_4 - 2M_5 + 2M_6\right) & \tilde{B}_1^{\alpha-D^m} &= S_1\left(-M_8 + 2M_9 - M_{10} + 2M_{11} - 2M_{12}\right)\\
&+ S_1\cos^2\theta\left(-M_1 + 2M_3 + M_4 - 2M_5 + 2M_6\right) & &+ S_1\cos^2\theta\left(-M_8 + 2M_9 - M_{10} + 2M_{11} - 2M_{12}\right)\\
&+ S_0\sin^2\theta\left(3M_1 - 4M_2 - 2M_3 + 3M_4 + 2M_6\right), & &+ S_0\sin^2\theta\left(-M_8 + 2M_9 - M_{10} + 2M_{11} - 2M_{12}\right),\\
\tilde{A}_2^{\alpha-D^m} &= S_2\cos\theta\left(-2M_1 + 4M_3 + 2M_4 - 4M_5 + 4M_6\right), & \tilde{B}_2^{\alpha-D^m} &= S_2\cos\theta\left(-2M_8 + 4M_9 - 2M_{10} + 4M_{11} - 4M_{12}\right)\\
\tilde{A}_3^{\alpha-D^m} &= S_3\cos\theta\left(2M_1 - 2M_4 + 8M_5\right), & \tilde{B}_3^{\alpha-D^m} &= S_3\cos\theta\left(-4M_7 - 2M_8 + 8M_9 + 2M_{10} - 8M_{11}\right),
\end{aligned} \tag{E.25}$$

with the rotational invariants

$$\begin{aligned}
\tilde{M}_1^{\alpha-D^m} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{\alpha}_{ab}\tilde{D}^{(m)*}_{c,dd}, & \tilde{M}_7^{\alpha-D^m} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\alpha}_{ab}\tilde{\mathscr{D}}^{(m)*}_{c,dd},\\
\tilde{M}_2^{\alpha-D^m} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{\alpha}_{ab}\tilde{D}^{(m)*}_{d,cd}, & \tilde{M}_8^{\alpha-D^m} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\alpha}_{ab}\tilde{\mathscr{D}}^{(m)*}_{d,cd},\\
\tilde{M}_3^{\alpha-D^m} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{\alpha}_{ab}\tilde{D}^{(m)*}_{d,dc}, & \tilde{M}_9^{\alpha-D^m} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\alpha}_{ab}\tilde{\mathscr{D}}^{(m)*}_{d,dc},\\
\tilde{M}_4^{\alpha-D^m} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{\alpha}_{ad}\tilde{D}^{(m)*}_{b,cd}, & \tilde{M}_{10}^{\alpha-D^m} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\alpha}_{ad}\tilde{\mathscr{D}}^{(m)*}_{b,cd},\\
\tilde{M}_5^{\alpha-D^m} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{\alpha}_{ad}\tilde{D}^{(m)*}_{b,dc}, & \tilde{M}_{11}^{\alpha-D^m} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\alpha}_{ad}\tilde{\mathscr{D}}^{(m)*}_{b,dc}\\
\tilde{M}_6^{\alpha-D^m} &= \frac{\mathrm{i}\omega_0}{c^2}\epsilon_{abc}\tilde{\alpha}_{ad}\tilde{D}^{(m)*}_{d,bc}, & \tilde{M}_{12}^{\alpha-D^m} &= \frac{\mathrm{i}\omega}{c^2}\epsilon_{abc}\tilde{\alpha}_{ad}\tilde{\mathscr{D}}^{(m)*}_{d,bc}.
\end{aligned} \tag{E.26}$$

Finally, the '$\alpha - \chi$' terms are

$$\langle s_\xi^{\alpha-\chi}\rangle = K\mathrm{Re}\left(\frac{1}{60}\tilde{A}_\xi^{\alpha-\chi}\right), \tag{E.27}$$

with

$$\begin{aligned}
\tilde{A}_0^{\alpha-\chi} &= S_0\cos\theta\left(10M_1 - 10M_3\right),\\
\tilde{A}_1^{\alpha-\chi} &= S_1\cos\theta\left(-6M_1 + 4M_2 - 6M_3\right),\\
\tilde{A}_2^{\alpha-\chi} &= S_2\left(-3M_1 + 2M_2 - 3M_3\right)\\
&+ S_2\cos^2\theta\left(-3M_1 + 2M_2 - 3M_3\right)\\
&+ \mathrm{i}S_3\sin^2\theta\left(3M_1 - 2M_2 + 3M_3\right)\\
\tilde{A}_3^{\alpha-\chi} &= S_3\left(-M_1 + 14M_2 - M_3\right)\\
&+ S_3\cos^2\theta\left(3M_1 - 2M_2 + 3M_3\right)\\
&+ \mathrm{i}S_2\sin^2\theta\left(3M_1 - 2M_2 + 3M_3\right),
\end{aligned} \tag{E.28}$$

with the rotational invariants

$$\tilde{M}_1^{\alpha-\chi} = \frac{1}{c^2}\tilde{\alpha}_{aa}\tilde{\chi}_{bb}^*,$$
$$\tilde{M}_2^{\alpha-\chi} = \frac{1}{c^2}\tilde{\alpha}_{ab}\tilde{\chi}_{ab}^* \tag{E.29}$$
$$\tilde{M}_3^{\alpha-\chi} = \frac{1}{c^2}\tilde{\alpha}_{ab}\tilde{\chi}_{ba}^*.$$

We also give the explicit expressions for the coefficients $\mathtt{A}, \ldots, \mathtt{R}'$ which appear in equations (9.3.13-9.3.16). The use of the simplified property tensors (9.3.1-9.3.12) mean that the expressions above are much simplified, and so we do not use a shorthand for the rotational invariants, but write them in full.

The unprimed coefficients are

$$\begin{aligned}\mathtt{A} = &\frac{1}{40}\left(-\alpha_{aa}\alpha_{bb} + 13\alpha_{ab}\alpha_{ab}\right)\\ &+ \frac{k_0^2}{7560}\left(6A_{a,ab}A_{c,bc} + 6A_{a,bc}A_{b,ac}\right)\\ &+ \frac{k_0}{360c}\left(4\epsilon_{abc}A_{a,bd}G'_{cd} - 8\epsilon_{abc}A_{a,bd}G'_{dc}\right)\\ &+ \frac{1}{120c^2}\left(-2G'_{aa}G'_{bb} + 24G'_{ab}G'_{ab} - 2G'_{ab}G'_{ba}\right)\\ &+ \frac{k_0}{5040c}\left(12\alpha_{aa}B_{b,bcc} - 60\alpha_{ab}B_{a,bcc} - 32\alpha_{ab}B_{c,abc}\right)\\ &+ \frac{k_0}{120c}\left(2\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,cd} - 12\epsilon_{abc}\alpha_{ad}D^{(m)'}_{d,bc}\right),\end{aligned}$$

$$\begin{aligned}\mathtt{C} = &\frac{1}{40}\left(3\alpha_{aa}\alpha_{bb} + \alpha_{ab}\alpha_{ab}\right)\\ &+ \frac{k_0^2}{7560}\left(-18A_{a,ab}A_{c,bc} - 18A_{a,bc}A_{b,ac}\right)\\ &+ \frac{k_0}{360c}\left(-12\epsilon_{abc}A_{a,bd}G'_{cd} + 24\epsilon_{abc}A_{a,bd}G'_{dc}\right)\\ &+ \frac{1}{120c^2}\left(6G'_{aa}G'_{bb} - 4G'_{ab}G'_{ab} + 6G'_{ab}G'_{ba}\right)\\ &+ \frac{k_0}{5040c}\left(-36\alpha_{aa}B_{b,bcc} - 44\alpha_{ab}B_{a,bcc} + 96\alpha_{ab}B_{c,abc}\right)\\ &+ \frac{k_0}{120c}\left(-\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,cd} + 8\epsilon_{abc}\alpha_{ad}D^{(m)'}_{d,bc}\right),\end{aligned} \tag{E.30}$$

$$\begin{aligned}\mathtt{E} = -\mathtt{K} = &\frac{1}{40}\left(3\alpha_{aa}\alpha_{bb} + \alpha_{ab}\alpha_{ab}\right)\\ &+ \frac{k_0}{360c}\left(-8\epsilon_{abc}A_{a,bd}G'_{cd} + 16\epsilon_{abc}A_{a,bd}G'_{dc}\right)\\ &+ \frac{k_0}{5040c}\left(-28\alpha_{aa}B_{b,bcc} - 28\alpha_{ab}B_{a,bcc} + 56\alpha_{ab}B_{c,abc}\right)\\ &+ \frac{k_0}{120c}\Big(4\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,cd} + 4\epsilon_{abc}\alpha_{ad}D^{(m)'}_{d,bc}\\ &- 2\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,dc}\Big),\end{aligned}$$

$$\begin{aligned}\mathtt{G} = \mathtt{I} = &\frac{1}{40}\left(-3\alpha_{aa}\alpha_{bb} - \alpha_{ab}\alpha_{ab}\right)\\ &+ \frac{k_0^2}{7560}\left(-18A_{a,ab}A_{c,bc} - 18A_{a,bc}A_{b,ac}\right)\\ &+ \frac{k_0}{360c}\left(4\epsilon_{abc}A_{a,bd}G'_{cd} - 8\epsilon_{abc}A_{a,bd}G'_{dc}\right)\\ &+ \frac{1}{120c^2}\left(6G'_{aa}G'_{bb} - 4G'_{ab}G'_{ab} + 6G'_{ab}G'_{ba}\right)\\ &+ \frac{k_0}{5040c}\left(20\alpha_{aa}B_{b,bcc} + 12\alpha_{ab}B_{a,bcc} - 16\alpha_{ab}B_{c,abc}\right)\\ &+ \frac{k_0}{120c}\Big(-2\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,cd} - 4\epsilon_{abc}\alpha_{ad}D^{(m)'}_{d,bc}\\ &+ 4\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,dc}\Big),\end{aligned} \tag{E.31}$$

$$\begin{aligned}\mathtt{N} = &\frac{1}{40}\left(-6\alpha_{aa}\alpha_{bb} - 2\alpha_{ab}\alpha_{ab}\right)\\ &+ \frac{k_0^2}{7560}\left(-36A_{a,ab}A_{c,bc} - 36A_{a,bc}A_{b,ac}\right)\\ &+ \frac{k_0}{360c}\left(8\epsilon_{abc}A_{a,bd}G'_{cd} - 16\epsilon_{abc}A_{a,bd}G'_{dc}\right)\\ &+ \frac{1}{120c^2}\left(12G'_{aa}G'_{bb} - 8G'_{ab}G'_{ab} + 12G'_{ab}G'_{ba}\right)\\ &+ \frac{k_0}{5040c}\left(40\alpha_{aa}B_{b,bcc} + 24\alpha_{ab}B_{a,bcc} - 32\alpha_{ab}B_{c,abc}\right)\\ &+ \frac{k_0}{120c}\Big(-4\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,cd} - 8\epsilon_{abc}\alpha_{ad}D^{(m)'}_{d,bc}\\ &+ 8\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,dc}\Big)\end{aligned}$$

$$\begin{aligned}\mathtt{Q} = &\frac{1}{40}\left(10\alpha_{aa}\alpha_{bb} - 10\alpha_{ab}\alpha_{ab}\right)\\ &+ \frac{k_0^2}{7560}\left(28A_{a,ab}A_{c,bc} - 28A_{a,bc}A_{b,ac}\right)\\ &+ \frac{k_0}{360c}\left(-24\epsilon_{abc}A_{a,bd}G'_{cd}\right)\\ &+ \frac{1}{120c^2}\left(20G'_{aa}G'_{bb} - 20G'_{ab}G'_{ba}\right)\\ &+ \frac{k_0}{5040c}\left(-56\alpha_{aa}B_{b,bcc} + 56\alpha_{ab}B_{a,bcc} - 32\alpha_{ab}B_{c,abc}\right)\\ &+ \frac{k_0}{120c}\left(4\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,cd} - 16\epsilon_{abc}\alpha_{ad}D^{(m)'}_{b,dc}\right).\end{aligned} \tag{E.32}$$

The singly-primed coefficients are

$$\begin{aligned}
\mathtt{B}' &= \frac{k_0^2}{7560}\left(24A_{a,ab}A_{c,bc} - 60A_{a,bc}A_{b,ac}\right) \\
&+ \frac{k_0}{360c}\left(-24\epsilon_{abc}A_{a,bd}G'_{dc}\right) \\
&+ \frac{1}{120c^2}\left(20G'_{aa}G'_{bb} - 20G'_{ab}G'_{ab}\right) \\
&+ \frac{k_0^2}{1260}\left(-6\alpha_{aa}C_{bc,bc} + 28\alpha_{ab}C_{ac,bc}\right) \\
&+ \frac{\omega_0}{180c^2}\left(-12\epsilon_{abc}\alpha_{ad}D'_{b,cd}\right) \\
&+ \frac{1}{60c^2}\left(10\alpha_{aa}\chi_{bb} - 10\alpha_{ab}\chi_{ab}\right),
\end{aligned}
\qquad
\begin{aligned}
\mathtt{H}' &= \frac{k_0^2}{7560}\left(-3A_{a,ab}A_{c,bc} - 4A_{a,bc}A_{b,ac}\right) \\
&+ \frac{k_0}{360c}\left(-16\epsilon_{abc}A_{a,bd}G'_{cd} + 8\epsilon_{abc}A_{a,bd}G'_{dc}\right) \\
&+ \frac{1}{120c^2}\left(12G'_{aa}G'_{bb} + 12G'_{ab}G'_{ab} - 8G'_{ab}G'_{ba}\right) \\
&+ \frac{k_0^2}{1260}\left(-6\alpha_{aa}C_{bc,bc} + 18\alpha_{ab}C_{ac,bc}\right) \\
&+ \frac{k_0}{180c}\left(-4\epsilon_{abc}\alpha_{ad}D'_{b,cd}\right) \\
&+ \frac{1}{60c^2}\left(-6\alpha_{aa}\chi_{bb} - 2\alpha_{ab}\chi_{ab}\right),
\end{aligned}
\tag{E.33}$$

$$\begin{aligned}
\mathtt{M}' &= \frac{k_0^2}{7560}\left(-36A_{a,ab}A_{c,bc} + 6A_{a,bc}A_{b,ac}\right) \\
&+ \frac{k_0}{360c}\left(-8\epsilon_{abc}A_{a,bd}G'_{cd} + 4\epsilon_{abc}A_{a,bd}G'_{dc}\right) \\
&+ \frac{1}{120c^2}\left(6G'_{aa}G'_{bb} + 6G'_{ab}G'_{ab} - 4G'_{ab}G'_{ba}\right) \\
&+ \frac{k_0^2}{1260}\left(2\alpha_{aa}C_{bc,bc} + 15\alpha_{ab}C_{ac,bc}\right) \\
&+ \frac{k_0}{180c}\left(-2\epsilon_{abc}\alpha_{ad}D'_{b,cd}\right) \\
&+ \frac{1}{60c^2}\left(-3\alpha_{aa}\chi_{bb} - \alpha_{ab}\chi_{ab}\right),
\end{aligned}
\qquad
\begin{aligned}
\mathtt{O}' &= \frac{k_0^2}{7560}\left(44A_{a,ab}A_{c,bc} - 26A_{a,bc}A_{b,ac}\right) \\
&+ \frac{k_0}{360c}\left(-8\epsilon_{abc}A_{a,bd}G'_{cd} + 4\epsilon_{abc}A_{a,bd}G'_{dc}\right) \\
&+ \frac{1}{120c^2}\left(6G'_{aa}G'_{bb} + 6G'_{ab}G'_{ab} - 4G'_{ab}G'_{ba}\right) \\
&+ \frac{k_0^2}{1260}\left(-18\alpha_{aa}C_{bc,bc} - 9\alpha_{ab}C_{ac,bc}\right) \\
&+ \frac{k_0}{180c}\left(-2\epsilon_{abc}\alpha_{ad}D'_{b,cd}\right) \\
&+ \frac{1}{60c^2}\left(-3\alpha_{aa}\chi_{bb} - \alpha_{ab}\chi_{ab}\right),
\end{aligned}
\tag{E.34}$$

$$\begin{aligned}
\mathtt{P}' &= \frac{k_0^2}{7560}\left(28A_{a,ab}A_{c,bc} + 14A_{a,bc}A_{b,ac}\right) \\
&+ \frac{k_0}{360c}\left(-8\epsilon_{abc}A_{a,bd}G'_{cd} + 4\epsilon_{abc}A_{a,bd}G'_{dc}\right) \\
&+ \frac{1}{120c^2}\left(-2G'_{aa}G'_{bb} - 2G'_{ab}G'_{ab} + 28G'_{ab}G'_{ba}\right) \\
&+ \frac{k_0^2}{1260}\left(-14\alpha_{aa}C_{bc,bc} + 21\alpha_{ab}C_{ac,bc}\right) \\
&+ \frac{k_0}{180c}\left(2\epsilon_{abc}\alpha_{ad}D'_{b,cd}\right) \\
&+ \frac{1}{60c^2}\left(-\alpha_{aa}\chi_{bb} + 13\alpha_{ab}\chi_{ab}\right)
\end{aligned}
\qquad
\begin{aligned}
\mathtt{R}' &= \frac{k_0^2}{7560}\left(-84A_{a,ab}A_{c,bc} - 42A_{a,bc}A_{b,ac}\right) \\
&+ \frac{k_0}{360c}\left(24\epsilon_{abc}A_{a,bd}G'_{cd} - 12\epsilon_{abc}A_{a,bd}G'_{dc}\right) \\
&+ \frac{1}{120c^2}\left(6G'_{aa}G'_{bb} + 6G'_{ab}G'_{ab} - 4G'_{ab}G'_{ba}\right) \\
&+ \frac{k_0^2}{1260}\left(42\alpha_{aa}C_{bc,bc} - 63\alpha_{ab}C_{ac,bc}\right) \\
&+ \frac{k_0}{180c}\left(-6\epsilon_{abc}\alpha_{ad}D'_{b,cd}\right) \\
&+ \frac{1}{60c^2}\left(3\alpha_{aa}\chi_{bb} + \alpha_{ab}\chi_{ab}\right).
\end{aligned}
\tag{E.35}$$

Finally, the doubly-primed coefficients are

$$\begin{aligned}
&\mathtt{D}'' = \mathtt{F}'' = -\mathtt{J}'' = -\mathtt{L}'' \\
&\quad = \frac{k_0^2}{7560}\left(-40A_{a,ab}A_{c,bc} + 16A_{a,bc}A_{b,ac}\right) + \frac{k_0^2}{1260}\left(10\alpha_{aa}C_{bc,bc} + 12\alpha_{ab}C_{ac,bc}\right).
\end{aligned}
\tag{E.36}$$

Appendix F – Transformations of the Induced Multipole Moments under a Change of Multipolar Origin

This appendix explicitly shows the algebra leading to the expressions (9.5.8-9.5.11), demonstrating up to order λ^2 that the transformation properties of the polarisability tensors do indeed lead to the correct transformations of the induced multipole moments.

F.1 The Magnetic Dipole Moment

The (kinetic) magnetic dipole moment is given by

$$\widetilde{m}_a^{0^{kin.'}} = \lambda^1 \big(\tilde{\mathcal{G}}_{ab}\big)' \tilde{E}_b^0(\boldsymbol{d}) + \frac{1}{3}\lambda^2 \widetilde{D}'_{a,bc} \nabla_c \tilde{E}_b^0(\boldsymbol{d}) + \lambda^2 \tilde{\chi}'_{ab} \tilde{B}_b^0(\boldsymbol{d}) + \cdots \qquad \text{F.1.1}$$

and should transform according to

$$\widetilde{m}_a^{0^{kin.'}} = \widetilde{m}_a^{0^{kin}} - \sum_\alpha \frac{q_\alpha}{2m_\alpha} \epsilon_{abc} d_b \hat{v}_{\alpha_c} + \lambda^2 \Delta\tilde{\chi}_{ab}^{(d)} \tilde{B}_b^0(\boldsymbol{d}). \qquad \text{F.1.2}$$

Using the expressions for the transformations of the individual property tensors leads to

$$\begin{aligned}
\widetilde{m}_a^{0^{kin.'}} &= \lambda^1 \left(\tilde{\mathcal{G}}_{ab} + \frac{i\omega}{2}\epsilon_{acd} d_c \tilde{\alpha}_{db}\right) \tilde{E}_b^0(\boldsymbol{d}) \\
&+ \frac{1}{3}\lambda^2 \Bigg(\widetilde{D}_{a,bc} - \frac{3}{2} d_c \mathcal{G}_{ab} - \frac{3}{2} d_b \mathcal{G}_{ac} + \delta_{bc} d_f \mathcal{G}_{af} \\
&+ \frac{1}{2}\epsilon_{ade} d_d i\omega \left(\tilde{A}_{e,bc} - \frac{3}{2} d_c \tilde{\alpha}_{eb} - \frac{3}{2} d_b \tilde{\alpha}_{ec} + \delta_{bc} d_f \tilde{\alpha}_{ef}\right)\Bigg) \nabla_c \tilde{E}_b^0|_{\boldsymbol{r}=\boldsymbol{d}} \\
&+ \lambda^2 \Bigg(\tilde{\chi}_{ab} + \frac{i\omega}{2}\big(\epsilon_{acd} d_c \tilde{G}_{db} - \epsilon_{bcd} d_c \tilde{\mathcal{G}}_{ad}\big) + \frac{1}{4}\omega^2 \epsilon_{acd}\epsilon_{bef} d_c d_e \tilde{\alpha}_{df} \\
&+ \Delta\tilde{\chi}_{ab}^{(d)}\Bigg) \tilde{B}_b^0(\boldsymbol{d}) + \cdots \qquad \text{F.1.3}
\end{aligned}$$

Substituting the Taylor expansions for the ***E*** and ***B*** fields and omitting terms of order higher than λ^2 gives

$$\begin{aligned}
\widetilde{m}_a^{0^{kin.'}} &= \lambda^1 \left(\tilde{\mathcal{G}}_{ab} + \frac{i\omega}{2}\epsilon_{acd} d_c \tilde{\alpha}_{db}\right) \big(E(0)_b + \lambda d_e \nabla_e E(0)_b\big) \\
&+ \frac{1}{3}\lambda^2 \Bigg(\widetilde{D}_{a,bc} - \frac{3}{2} d_c \mathcal{G}_{ab} - \frac{3}{2} d_b \mathcal{G}_{ac} + \delta_{bc} d_f \mathcal{G}_{af} \\
&+ \frac{1}{2}\epsilon_{ade} d_d i\omega \left(\tilde{A}_{e,bc} - \frac{3}{2} d_c \tilde{\alpha}_{eb} - \frac{3}{2} d_b \tilde{\alpha}_{ec} + \delta_{bc} d_f \tilde{\alpha}_{ef}\right)\Bigg) \nabla_c \tilde{E}_b^0(0) \\
&+ \lambda^2 \left(\tilde{\chi}_{ab} + \frac{i\omega}{2}\big(\epsilon_{acd} d_c \tilde{G}_{db} - \epsilon_{bcd} d_c \tilde{\mathcal{G}}_{ad}\big) + \frac{1}{4}\omega^2 \epsilon_{acd}\epsilon_{bef} d_c d_e \tilde{\alpha}_{df} + \Delta\tilde{\chi}_{ab}^{(d)}\right) \tilde{B}_b^0(0) \\
&+ \cdots.
\end{aligned}$$

$$= \tilde{m}_a^{0^{kin.}} + \lambda^1 \left(\frac{i\omega}{2}\epsilon_{acd} d_c \tilde{\alpha}_{db}\right) E(0)_b + \lambda^2 \left(\tilde{\mathcal{G}}_{ab} + \frac{i\omega}{2}\epsilon_{acd} d_c \tilde{\alpha}_{db}\right) d_e \nabla_e E(0)_b$$
$$+ \frac{1}{3}\lambda^2 \Bigg(-\frac{3}{2} d_c \mathcal{G}_{ab} - \frac{3}{2} d_b \mathcal{G}_{ac} + \delta_{bc} d_f \mathcal{G}_{af}$$
$$+ \frac{1}{2}\epsilon_{ade} d_d i\omega \left(\tilde{A}_{e,bc} - \frac{3}{2} d_c \tilde{\alpha}_{eb} - \frac{3}{2} d_b \tilde{\alpha}_{ec} + \delta_{bc} d_f \tilde{\alpha}_{ef}\right)\Bigg) \nabla_c \tilde{E}_b^0(0)$$
$$+ \lambda^2 \left(\frac{i\omega}{2}\left(\epsilon_{acd} d_c \tilde{G}_{db} - \epsilon_{bcd} d_c \tilde{\mathcal{G}}_{ad}\right) + \frac{1}{4}\omega^2 \epsilon_{acd}\epsilon_{bef} d_c d_e \tilde{\alpha}_{df} + \Delta\tilde{\chi}_{ab}^{(d)}\right) \tilde{B}_b^0(0) + \cdots. \qquad \text{F.1.4}$$

Re-labeling various indices gives

$$\tilde{m}_a^{0^{kin.}} + \lambda^1 \left(\frac{i\omega}{2}\epsilon_{abc} d_b \tilde{\alpha}_{cd}\right) E(0)_d + \lambda^2 \left(\tilde{\mathcal{G}}_{ab} + \frac{i\omega}{2}\epsilon_{acd} d_c \tilde{\alpha}_{db}\right) d_e \nabla_e E(0)_b$$
$$+ \frac{1}{3}\lambda^2 \Bigg(-\frac{3}{2} d_e \tilde{\mathcal{G}}_{ad} - \frac{3}{2} d_d \tilde{\mathcal{G}}_{ae}$$
$$+ \frac{1}{2}\epsilon_{abc} d_b i\omega \left(\tilde{A}_{c,de} - \frac{3}{2} d_e \tilde{\alpha}_{cd} - \frac{3}{2} d_d \tilde{\alpha}_{ce}\right)\Bigg) \nabla_e \tilde{E}_d^0(0)$$
$$+ \lambda^2 \left(\frac{i\omega}{2}\left(\epsilon_{abc} d_b \tilde{G}_{cd} - \epsilon_{dbc} d_b \tilde{\mathcal{G}}_{ac}\right) + \frac{1}{4}\omega^2 \epsilon_{acb}\epsilon_{def} d_c d_e \tilde{\alpha}_{bf} + \Delta\tilde{\chi}_{ad}^{(d)}\right) \tilde{B}_d^0(0) + \cdots.$$
$$= \tilde{m}_a^{0^{kin.}} + \frac{i\omega}{2}\epsilon_{abc} d_b \lambda^1 \left(\tilde{\alpha}_{cd} \tilde{E}_d^0(0) + \lambda^1 \tilde{G}_{cd} \tilde{B}_d^0(0) + \frac{\lambda^1}{3}\tilde{A}_{c,de} \nabla_d \tilde{E}_e^0|_{\mathbf{r}=0}\right)$$
$$+ \lambda^2 \left(\tilde{\mathcal{G}}_{ab} + \frac{i\omega}{2}\epsilon_{acd} d_c \tilde{\alpha}_{db}\right) d_e \nabla_e E(0)_b$$
$$+ \frac{1}{3}\lambda^2 \left(-\frac{3}{2} d_e \tilde{\mathcal{G}}_{ad} - \frac{3}{2} d_d \tilde{\mathcal{G}}_{ae} + \frac{1}{2}\epsilon_{abc} d_b i\omega \left(-\frac{3}{2} d_e \tilde{\alpha}_{cd} - \frac{3}{2} d_d \tilde{\alpha}_{ce}\right)\right) \nabla_e \tilde{E}_d^0(0)$$
$$+ \lambda^2 \left(\frac{i\omega}{2}\left(-\epsilon_{dbc} d_b \tilde{\mathcal{G}}_{ac}\right) + \frac{1}{4}\omega^2 \epsilon_{acb}\epsilon_{def} d_c d_e \tilde{\alpha}_{bf} + \Delta\tilde{\chi}_{ad}^{(d)}\right) \tilde{B}_d^0(0) + \cdots. \qquad \text{F.1.5}$$

The latter terms all cancel. To demonstrate this, we again make use of $\nabla_a E_b = \nabla_b E_a + i\omega\epsilon_{abc} B_c$ to obtain

$$\left(-\frac{1}{2} d_e \tilde{\mathcal{G}}_{ad} - \frac{1}{2} d_d \tilde{\mathcal{G}}_{ae}\right) \nabla_e \tilde{E}_d^0(0) = -\frac{1}{2} d_e \tilde{\mathcal{G}}_{ad} \nabla_e \tilde{E}_d^0(0) - \frac{1}{2} d_d \tilde{\mathcal{G}}_{ae}\left(\nabla_d E_e(0) + i\omega\epsilon_{edc} B_c(0)\right)$$
$$= -\frac{1}{2} d_e \tilde{\mathcal{G}}_{ad} \nabla_e \tilde{E}_d^0(0) - \frac{1}{2} d_e \tilde{\mathcal{G}}_{ad}\left(\nabla_e E_d(0) + i\omega\epsilon_{dec} B_c(0)\right)$$
$$= -d_e \tilde{\mathcal{G}}_{ad} \nabla_e \tilde{E}_d^0(0) - \frac{i\omega}{2}\epsilon_{dec} d_e \tilde{\mathcal{G}}_{ad} B_c(0)$$
$$= -d_e \tilde{\mathcal{G}}_{ad} \nabla_e \tilde{E}_d^0(0) - \frac{i\omega}{2}\epsilon_{cbd} d_b \tilde{\mathcal{G}}_{ac} B_d(0), \qquad \text{F. 1.6}$$

The first term cancels with the first term of line 2 above, and the second with the first term of line 4. We similarly have

$$\frac{1}{2}\epsilon_{abc} d_b i\omega \left(-\frac{1}{2} d_e \tilde{\alpha}_{cd} - \frac{1}{2} d_d \tilde{\alpha}_{ce}\right) \nabla_e \tilde{E}_d^0(0) = \frac{1}{2}\epsilon_{acd} d_c i\omega \left(-\frac{1}{2} d_e \tilde{\alpha}_{db} - \frac{1}{2} d_b \tilde{\alpha}_{de}\right) \nabla_e \tilde{E}_b^0(0)$$
$$= \frac{1}{2}\epsilon_{acd} d_c i\omega \left(-\frac{1}{2} d_e \tilde{\alpha}_{db}\right) \nabla_e \tilde{E}_b^0(0) + \frac{1}{2}\epsilon_{acd} d_c i\omega \left(-\frac{1}{2} d_b \tilde{\alpha}_{de}\right)\left(\nabla_b E_e + i\omega\epsilon_{ebf} B_f\right)$$

$$= \frac{1}{2}\epsilon_{acd}d_c i\omega\left(-\frac{1}{2}d_e\tilde{\alpha}_{db}\right)\nabla_e\tilde{E}_b^0(0) + \frac{1}{2}\epsilon_{acd}d_c i\omega\left(-\frac{1}{2}d_e\tilde{\alpha}_{db}\right)\left(\nabla_e E_b + i\omega\epsilon_{bef}B_f\right)$$

$$= \epsilon_{acd}d_c i\omega\left(-\frac{1}{2}d_e\tilde{\alpha}_{db}\right)\nabla_e\tilde{E}_b^0(0) + \frac{1}{4}\omega^2\epsilon_{acd}\epsilon_{bef}d_c d_e\tilde{\alpha}_{db}B_f \qquad \text{F. 1.7}$$

The first term cancels with the corresponding term in line 2 of (F.1.5), and relabelling indices reveals the second to be

$$\frac{1}{4}\omega^2\epsilon_{acd}\epsilon_{bef}d_c d_e\tilde{\alpha}_{db}B_f = \frac{1}{4}\omega^2\epsilon_{acb}\epsilon_{fed}d_c d_e\tilde{\alpha}_{bf}B_d = -\frac{1}{4}\omega^2\epsilon_{acb}\epsilon_{def}d_c d_e\tilde{\alpha}_{bf}B_d, \qquad \text{F. 1.8}$$

which cancels with the corresponding contribution from the transformed diamagnetic susceptibility. We therefore finally have

$$= \tilde{m}_a^{0^{kin.}} + \frac{i\omega}{2}\epsilon_{abc}d_b\lambda^1\left(\tilde{\alpha}_{cd}\tilde{E}_d^0(0) + \lambda^1\tilde{G}_{cd}\tilde{B}_d^0(0) + \frac{\lambda^1}{3}\tilde{A}_{c,de}\nabla_d\tilde{E}_e^0(0)\right) + \lambda^2\Delta\tilde{\chi}_{ab}^{(d)}B_b(0)$$

$$= \tilde{m}_a^{0^{kin.}} + \frac{i\omega}{2}\epsilon_{abc}d_b\lambda^1\tilde{\mu}_c^0 + \lambda^2\Delta\tilde{\chi}_{ab}^{(d)}B_b(0), \qquad \text{F. 1.9}$$

where in writing the sum in brackets as $\tilde{\mu}_c^0$ we have neglected terms of order λ^2 and above. (F.1.9) is indeed the correct transformation of the magnetic dipole moment (8.13.7), although with the sums over charge momenta expressed as the time derivative of the oscillating induced dipole moment.

F.2 The Electric Quadrupole Moment

The electric quadrupole moment is given by

$$\tilde{\Theta}_{ab}^0 = \lambda^1\tilde{\mathcal{A}}_{c,ab}\tilde{E}_c^0(0) + \lambda^2\tilde{C}_{ab,cd}\nabla_d\tilde{E}_c^0|_{\boldsymbol{r}=0} + \lambda^2\tilde{\mathcal{D}}_{c,ab}\tilde{B}_c^0(0) + \cdots \qquad \text{F. 2.1}$$

and should transform as

$$\tilde{\Theta}'_{ab} = \tilde{\Theta}_{ab} - \frac{3}{2}\tilde{\mu}_a d_b - \frac{3}{2}\tilde{\mu}_b d_a + \delta_{ab}\tilde{\mu}_c d_c. \qquad \text{F. 2.2}$$

Using the transformations of $\tilde{\mathcal{A}}$, $\tilde{C}$ and $\tilde{\mathcal{D}}$ (8.13.13, 8.13.14, 8.32.41) and the Taylor expansions (9.5.2, 9.5.4), and keeping only terms up to λ^2, gives

$$\widetilde{\Theta}_{ab}^{0\prime} = \lambda^1\left(\tilde{\mathcal{A}}_{c,ab} - \frac{3}{2}d_a\tilde{\alpha}_{bc} - \frac{3}{2}d_b\tilde{\alpha}_{ac} + \delta_{ab}d_d\tilde{\alpha}_{dc}\right)(E(0)_c + \lambda d_e\nabla_e E(0)_c)$$
$$+ \lambda^2\left(\tilde{C}_{ab,cd} - \frac{1}{2}d_d\tilde{\mathcal{A}}_{c,ab} - \frac{1}{2}d_c\tilde{\mathcal{A}}_{d,ab} + \frac{1}{3}\delta_{cd}d_e\tilde{\mathcal{A}}_{e,ab} - \frac{1}{2}d_b\tilde{A}_{a,cd} - \frac{1}{2}d_a\tilde{A}_{b,cd}\right.$$
$$+ \frac{3}{4}d_bd_d\tilde{\alpha}_{ac} + \frac{3}{4}d_bd_c\tilde{\alpha}_{ad} + \frac{3}{4}d_ad_d\tilde{\alpha}_{bc} + \frac{3}{4}d_ad_c\tilde{\alpha}_{bd} - \frac{1}{2}\delta_{cd}d_bd_e\tilde{\alpha}_{ae}$$
$$- \frac{1}{2}\delta_{cd}d_ad_e\tilde{\alpha}_{be} - \frac{1}{2}\delta_{ab}d_dd_e\tilde{\alpha}_{ec} - \frac{1}{2}\delta_{ab}d_cd_e\tilde{\alpha}_{ed} + \frac{1}{3}\delta_{ab}d_e\tilde{A}_{e,cd}$$
$$\left. + \delta_{ab}\delta_{cd}d_ed_f\tilde{\alpha}_{ef}\right)\nabla_d\tilde{E}_c^0(0)$$
$$+ \lambda^2\left(\tilde{\mathcal{D}}_{c,ab} - \frac{3}{2}d_b\tilde{G}_{ac} - \frac{3}{2}d_aG_{bc} + \delta_{ab}d_fG_{fc}\right.$$
$$\left. + \frac{1}{2}\epsilon_{cde}d_di\omega\left(-\mathcal{A}_{e,ab} + \frac{3}{2}d_b\tilde{\alpha}_{ae} + \frac{3}{2}d_a\tilde{\alpha}_{be} - \delta_{ab}d_f\tilde{\alpha}_{fe}\right)\right)\tilde{B}_c^0(0). \qquad \text{F.2.3}$$

Making use of the transversality of the $\boldsymbol{E}$ field to remove some of the delta functions,

$$\widetilde{\Theta}_{ab}^{0\prime} = \lambda^1\left(\tilde{\mathcal{A}}_{c,ab} - \frac{3}{2}d_a\tilde{\alpha}_{bc} - \frac{3}{2}d_b\tilde{\alpha}_{ac} + \delta_{ab}d_d\tilde{\alpha}_{dc}\right)(E(0)_c + \lambda d_e\nabla_e E(0)_c)$$
$$+ \lambda^2\left(\tilde{C}_{ab,cd} - \frac{1}{2}d_d\tilde{\mathcal{A}}_{c,ab} - \frac{1}{2}d_c\tilde{\mathcal{A}}_{d,ab} - \frac{1}{2}d_b\tilde{A}_{a,cd} - \frac{1}{2}d_a\tilde{A}_{b,cd} + \frac{3}{4}d_bd_d\tilde{\alpha}_{ac}\right.$$
$$+ \frac{3}{4}d_bd_c\tilde{\alpha}_{ad} + \frac{3}{4}d_ad_d\tilde{\alpha}_{bc} + \frac{3}{4}d_ad_c\tilde{\alpha}_{bd} - \frac{1}{2}\delta_{ab}d_dd_e\tilde{\alpha}_{ec} - \frac{1}{2}\delta_{ab}d_cd_e\tilde{\alpha}_{ed}$$
$$\left. + \frac{1}{3}\delta_{ab}d_e\tilde{A}_{e,cd}\right)\nabla_d\tilde{E}_c^0(0)$$
$$+ \lambda^2\left(\tilde{\mathcal{D}}_{c,ab} - \frac{3}{2}d_b\tilde{G}_{ac} - \frac{3}{2}d_aG_{bc} + \delta_{ab}d_fG_{fc}\right.$$
$$\left. + \frac{1}{2}\epsilon_{cde}d_di\omega\left(-\mathcal{A}_{e,ab} + \frac{3}{2}d_b\tilde{\alpha}_{ae} + \frac{3}{2}d_a\tilde{\alpha}_{be} - \delta_{ab}d_f\tilde{\alpha}_{fe}\right)\right)\tilde{B}_c^0(0). \qquad \text{F.2.4}$$

We then re-write the above as

$$\widetilde{\Theta}_{ab}^{0\prime} = \widetilde{\Theta}_{ab}^{0} + \lambda^1\left(-\frac{3}{2}d_a\tilde{\alpha}_{bc} - \frac{3}{2}d_b\tilde{\alpha}_{ac} + \delta_{ab}d_d\tilde{\alpha}_{dc}\right)E(0)_c$$
$$+ \lambda^2\left(\tilde{\mathcal{A}}_{c,ab} - \frac{3}{2}d_a\tilde{\alpha}_{bc} - \frac{3}{2}d_b\tilde{\alpha}_{ac} + \delta_{ab}d_d\tilde{\alpha}_{dc}\right)d_e\nabla_e E(0)_c$$
$$+ \lambda^2\left(-\frac{1}{2}d_d\tilde{\mathcal{A}}_{c,ab} - \frac{1}{2}d_c\tilde{\mathcal{A}}_{d,ab} - \frac{1}{2}d_b\tilde{A}_{a,cd} - \frac{1}{2}d_a\tilde{A}_{b,cd} + \frac{3}{4}d_bd_d\tilde{\alpha}_{ac}\right.$$
$$+ \frac{3}{4}d_bd_c\tilde{\alpha}_{ad} + \frac{3}{4}d_ad_d\tilde{\alpha}_{bc} + \frac{3}{4}d_ad_c\tilde{\alpha}_{bd} - \frac{1}{2}\delta_{ab}d_dd_e\tilde{\alpha}_{ec} - \frac{1}{2}\delta_{ab}d_cd_e\tilde{\alpha}_{ed}$$
$$\left. + \frac{1}{3}\delta_{ab}d_e\tilde{A}_{e,cd}\right)\nabla_d\tilde{E}_c^0(0)$$
$$+ \lambda^2\left(-\frac{3}{2}d_b\tilde{G}_{ac} - \frac{3}{2}d_a\tilde{G}_{bc} + \delta_{ab}d_f\tilde{G}_{fc}\right.$$
$$\left. + \frac{1}{2}\epsilon_{cde}d_di\omega\left(-\mathcal{A}_{e,ab} + \frac{3}{2}d_b\tilde{\alpha}_{ae} + \frac{3}{2}d_a\tilde{\alpha}_{be} - \delta_{ab}d_f\tilde{\alpha}_{fe}\right)\right)\tilde{B}_c^0(0), \qquad \text{F.2.5}$$

where $\lambda^1\widetilde{\Theta}^0_{ab}$ includes terms only up to λ^2. Finally, we use $\tilde{\mu}_a = \lambda^0\tilde{\alpha}_{ab}\tilde{E}^0_b(0) + \lambda^1\tilde{G}_{ab}\tilde{B}^0_b(0) + \frac{\lambda^1}{3}\tilde{A}_{a,bc}\nabla_b\tilde{E}^0_c(0)$ to write

$$\widetilde{\Theta}^{0\prime}_{ab} = \widetilde{\Theta}^0_{ab} + \lambda^1\left(-\frac{3}{2}\tilde{\mu}_a d_b - \frac{3}{2}\tilde{\mu}_b d_a + \delta_{ab}\tilde{\mu}_c d_c\right)$$
$$+ \lambda^2\left(\tilde{\mathcal{A}}_{c,ab} - \frac{3}{2}d_a\tilde{\alpha}_{bc} - \frac{3}{2}d_b\tilde{\alpha}_{ac} + \delta_{ab}d_d\tilde{\alpha}_{dc}\right)d_e\nabla_e E(0)_c$$
$$+ \lambda^2\left(-\frac{1}{2}d_d\tilde{\mathcal{A}}_{c,ab} - \frac{1}{2}d_c\tilde{\mathcal{A}}_{d,ab} + \frac{3}{4}d_b d_d\tilde{\alpha}_{ac} + \frac{3}{4}d_b d_c\tilde{\alpha}_{ad} + \frac{3}{4}d_a d_d\tilde{\alpha}_{bc}\right.$$
$$\left.+ \frac{3}{4}d_a d_c\tilde{\alpha}_{bd} - \frac{1}{2}\delta_{ab}d_d d_e\tilde{\alpha}_{ec} - \frac{1}{2}\delta_{ab}d_c d_e\tilde{\alpha}_{ed}\right)\nabla_d\tilde{E}^0_c(0)$$
$$+ \lambda^2\frac{1}{2}\epsilon_{cde}d_d i\omega\left(-\mathcal{A}_{e,ab} + \frac{3}{2}d_b\tilde{\alpha}_{ae} + \frac{3}{2}d_a\tilde{\alpha}_{be} - \delta_{ab}d_f\tilde{\alpha}_{fe}\right)\tilde{B}^0_c(0), \qquad \text{F.2.6}$$

where the expression $\lambda^1\left(-\frac{3}{2}\tilde{\mu}_a d_b - \frac{3}{2}\tilde{\mu}_b d_a + \delta_{ab}\tilde{\mu}_c d_c\right)$ contains terms up to order λ^2. Finally, we may use $i\omega\epsilon_{cde}B_c = \nabla_d E_e - \nabla_e E_d$ in the last line, and we then find that the remaining terms all cancel.

$$\widetilde{\Theta}^{0\prime}_{ab} = \widetilde{\Theta}^0_{ab} + \lambda^1\left(-\frac{3}{2}\tilde{\mu}_a d_b - \frac{3}{2}\tilde{\mu}_b d_a + \delta_{ab}\tilde{\mu}_c d_c\right)$$
$$+ \lambda^2\left(\tilde{\mathcal{A}}_{c,ab} - \frac{3}{2}d_a\tilde{\alpha}_{bc} - \frac{3}{2}d_b\tilde{\alpha}_{ac} + \delta_{ab}d_e\tilde{\alpha}_{ec}\right)d_d\nabla_d E(0)_c$$
$$+ \lambda^2\left(-\frac{1}{2}d_d\tilde{\mathcal{A}}_{c,ab} - \frac{1}{2}d_c\tilde{\mathcal{A}}_{d,ab} + \frac{3}{4}d_b d_d\tilde{\alpha}_{ac} + \frac{3}{4}d_b d_c\tilde{\alpha}_{ad} + \frac{3}{4}d_a d_d\tilde{\alpha}_{bc}\right.$$
$$\left.+ \frac{3}{4}d_a d_c\tilde{\alpha}_{bd} - \frac{1}{2}\delta_{ab}d_d d_e\tilde{\alpha}_{ec} - \frac{1}{2}\delta_{ab}d_c d_e\tilde{\alpha}_{ed}\right)\nabla_d\tilde{E}^0_c(0)$$
$$+ \lambda^2\frac{1}{2}d_d\left(-\mathcal{A}_{e,ab} + \frac{3}{2}d_b\tilde{\alpha}_{ae} + \frac{3}{2}d_a\tilde{\alpha}_{be} - \delta_{ab}d_f\tilde{\alpha}_{fe}\right)(\nabla_d E_e - \nabla_e E_d)$$
$$= \widetilde{\Theta}^0_{ab} + \lambda^1\left(-\frac{3}{2}\tilde{\mu}_a d_b - \frac{3}{2}\tilde{\mu}_b d_a + \delta_{ab}\tilde{\mu}_c d_c\right)$$
$$+ \lambda^2\left(\frac{1}{2}\tilde{\mathcal{A}}_{c,ab} - \frac{3}{4}d_a\tilde{\alpha}_{bc} - \frac{3}{4}d_b\tilde{\alpha}_{ac} + \delta_{ab}d_e\tilde{\alpha}_{ec}\right)d_d\nabla_d E(0)_c$$
$$+ \lambda^2\left(-\frac{1}{2}d_c\tilde{\mathcal{A}}_{d,ab} + \frac{3}{4}d_b d_c\tilde{\alpha}_{ad} + \frac{3}{4}d_a d_c\tilde{\alpha}_{bd} - \frac{1}{2}\delta_{ab}d_d d_e\tilde{\alpha}_{ec}\right.$$
$$\left.- \frac{1}{2}\delta_{ab}d_c d_e\tilde{\alpha}_{ed}\right)\nabla_d\tilde{E}^0_c(0)$$
$$+ \lambda^2\frac{1}{2}d_d\left(-\mathcal{A}_{c,ab} + \frac{3}{2}d_b\tilde{\alpha}_{ac} + \frac{3}{2}d_a\tilde{\alpha}_{bc} - \delta_{ab}d_f\tilde{\alpha}_{fc}\right)\nabla_d E_c$$
$$+ \lambda^2\frac{1}{2}d_c\left(\mathcal{A}_{d,ab} - \frac{3}{2}d_b\tilde{\alpha}_{ad} - \frac{3}{2}d_a\tilde{\alpha}_{bd} + \delta_{ab}d_f\tilde{\alpha}_{fd}\right)\nabla_d E_c$$
$$= \widetilde{\Theta}^0_{ab} + \lambda^1\left(-\frac{3}{2}\tilde{\mu}_a d_b - \frac{3}{2}\tilde{\mu}_b d_a + \delta_{ab}\tilde{\mu}_c d_c\right) + \lambda^2\left(-\frac{1}{2}\delta_{ab}d_d d_e\tilde{\alpha}_{ec} - \frac{1}{2}\delta_{ab}d_c d_e\tilde{\alpha}_{ed}\right)\nabla_d\tilde{E}^0_c(0)$$
$$+ \lambda^2\frac{1}{2}d_c(\delta_{ab}d_e\tilde{\alpha}_{ec} + \delta_{ab}d_e\tilde{\alpha}_{ed})\nabla_d E_c. \qquad \text{F.2.7}$$

We are finally left with

$$\widetilde{\Theta}_{ab}^{0\prime} = \widetilde{\Theta}_{ab}^{0} + \lambda^1 \left(-\frac{3}{2}\tilde{\mu}_a d_b - \frac{3}{2}\tilde{\mu}_b d_a + \delta_{ab}\tilde{\mu}_c d_c \right). \qquad \text{F. 2.8}$$

F.3 The Electric Octupole Moment

We now turn to the electric octuple moment. We have

$$\tilde{Q}_{abc}^{0} = \lambda^2 \widetilde{\mathcal{B}}_{d,abc} \tilde{E}_d^0(0) + \cdots, \qquad \text{F. 3.1}$$

and expect the transformation

$$\tilde{Q}_{abc}^{0}{}' = \tilde{Q}_{abc} + d_a d_b \tilde{\mu}_c + d_a d_c \tilde{\mu}_b + d_b d_c \tilde{\mu}_a - d_a \tilde{Q}_{bc} - d_b \tilde{Q}_{ac} - d_c \tilde{Q}_{ab}, \qquad \text{F. 3.2}$$

This is very easily verified to order λ^2 – substituting the transformation of $\widetilde{\mathcal{B}}_{d,abc}$ (8.13.15) gives

$$\tilde{Q}_{abc}^{0}{}' = \lambda^2 \left(\tilde{B}_{d,abc} - d_a \tilde{A}_{d,bc}^{(tr)} - d_b \tilde{A}_{d,ac}^{(tr)} - d_c \tilde{A}_{d,ab}^{(tr)} + d_b d_c \tilde{\alpha}_{da} + d_a d_c \tilde{\alpha}_{db} + d_a d_b \tilde{\alpha}_{dc} \right) \tilde{E}_d^0(0)$$

$$= \tilde{Q}_{abc} + \lambda^2 \left(d_a d_b \tilde{\mu}_c + d_a d_c \tilde{\mu}_b + d_b d_c \tilde{\mu}_a - d_a \tilde{Q}_{bc} - d_b \tilde{Q}_{ac} - d_c \tilde{Q}_{ab} \right), \qquad \text{F. 3.3}$$

with the last line retaining terms only up to λ^2.

F.4 The Magnetic Quadrupole Moment

Finally, we consider the magnetic quadrupole moment. We have

$$\widetilde{m}_{ab}^{0^{kin.}} = \lambda^2 \widetilde{\mathcal{D}}_{c,ab}^{(m)} \tilde{E}_c^0(0), \qquad \text{F. 4.1}$$

and expect the transformation

$$\widetilde{m}_{ab}^{0^{kin.\prime}} = m_{ab}^{kin.} - 2 d_b m_a^{kin.} + \sum_\alpha \frac{2}{3} \epsilon_{acd} d_b d_c q_\alpha \hat{v}_{\alpha_d} - \frac{1}{3} \epsilon_{acd} d_c \frac{\mathrm{d}}{\mathrm{d}t} \hat{Q}_{bd} + \frac{1}{3} \delta_{ab} d_c \epsilon_{dec} \sum_\alpha q_\alpha \hat{r}_{\alpha_d} \hat{v}_{\alpha_e} \,. \qquad \text{F. 4.2}$$

Substituting the transformation for $\widetilde{\mathcal{D}}_{c,ab}^{(m)}$ (8.13.43) into (F.4.1) gives

$$\widetilde{m}_{ab}^{0^{kin.}} = \lambda^2 \left(\widetilde{\mathcal{D}}^{(m)}{}_{c,ab} - \frac{2i\omega}{3} \epsilon_{ade} d_b d_d \tilde{\alpha}_{ec} + \frac{i\omega}{3} \epsilon_{ade} d_d \tilde{\mathcal{A}}_{c,be}^{(tr)} - 2 d_b \tilde{\mathcal{G}}_{ac} + \frac{2}{3} \delta_{ab} d_d \tilde{\mathcal{G}}_{dc} \right) \tilde{E}_c^0(0)$$

$$= m_{ab}^{kin.} + \lambda^2 \left(-\frac{2i\omega}{3} \epsilon_{ade} d_b d_d \widetilde{\mu}_e + \frac{i\omega}{3} \epsilon_{ade} d_d \widetilde{Q}_{be} - 2 d_b \widetilde{m}_a^{kin.} + \frac{2}{3} \delta_{ab} d_d \widetilde{m}_d^{kin.} \right) \qquad \text{F. 4.3}$$

where the replacement of property tensor-electric field products by induced moments is correct to order λ^2. Relabelling the indices to bring the expression into correspondence with (F.4.2) yields

$$m_{ab}^{kin.} + \lambda^2 \left(-\frac{2i\omega}{3} \epsilon_{acd} d_b d_c \widetilde{\mu}_d + \frac{i\omega}{3} \epsilon_{acd} d_c \widetilde{Q}_{bd} - 2 d_b \widetilde{m}_a^{kin.} + \frac{2}{3} \delta_{ab} d_c \widetilde{m}_c^{kin.} \right). \qquad \text{F. 4.4}$$

We see that we have recovered the transformation (F.4.2), though with the sums over electron momenta expressed as the time derivatives of the induced oscillating multipole moments.