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Optical Spin, Optical Helicity, and Light-Matter Interactions

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Abstract

Over the past three decades, a tremendous amount of research has been dedicated to the theoretical analysis and experimental realization of *structured* forms of light—optical fields with complex structures in their phase, polarization, or other degrees of freedom. Beyond their inherent optical properties, which are often interesting and unexpected compared to simpler, unstructured fields, structured light fields also give rise to novel effects when interacting with matter. In this Thesis, I examine some fundamental and practical aspects of the angular momentum and chirality of light, two key topics in modern structured light research. My focus is on the optical spin angular momentum and the optical helicity in monochromatic fields. Regarding the former, I examine the local spin in non-interfering superpositions of plane waves. Amongst other intriguing features, the electric and magnetic spins—which are distinct physical contributions to the total optical spin—show striking differences in these fields, and I discuss the implications of these spin structures on light-matter interactions. In connection with the optical helicity, I develop a theoretical model for the transfer of helicity from a monochromatic optical field to a single atom, shedding greater light on the fundamental role of helicity in light-matter interactions. I also present two derivations—one of the Faraday effect in a gas, the other of the helicity-dependent chiroptical force—within the framework of molecular quantum electrodynamics, opening the door to future explorations of structured light-matter interactions from the fundamental photonic perspective.

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CHAPTER 1

Introduction

My work is primarily concerned with aspects of optical angular momentum, optical chirality, and related light-matter interactions. Here I outline the structure of my Thesis and provide some context for the work which appears in it.

In 1909, Poynting [1] concluded, based on a mechanical analogy, that circularly polarized (CP) light should induce a torque on a birefringent disk, and thus should also possess angular momentum (AM). Poynting's intuition was experimentally confirmed by Beth in 1935 [2, 3], who found that his results could be explained by assigning an AM in the direction of propagation of $+\hbar$ to left-circularly polarized (LCP) photons and $-\hbar$ to right-circularly polarized (RCP) photons. Although it had long been realized that the total AM of an optical field consists of two distinct terms [4–7], only one of which corresponds to the polarization-dependent or 'spin' AM, it was not until the early 1990s that the 'orbital' contribution was brought to the fore, due to the work of Allen et al. [8, 9]. They showed that paraxial 'vortex beams', which can be created with relative ease in the lab, possess a well-defined and theoretically unbounded orbital AM in their direction of propagation. In contrast to the spin AM of Beth and Poynting, this new form of optical AM was shown to be linked not to the polarization of the beam, but to its intensity and phase profiles.

The work of Allen et al. [8] showed that, by moving away from the very simplest optical fields, we can find interesting and surprising results, both in terms of the intrinsic qualities

of the light fields and in the way they interact with matter [10, 11]. This has led, in the last three decades, to a tremendous amount of activity on the topic of 'structured light', which has become one of the most active sub-fields of modern optics. Researchers are now engaged in the analysis and production of light with non-trivial structure in the polarization, phase, intensity, and temporal degrees of freedom [12–14].

The theory of optical AM is reviewed in some detail in Chapter 2, starting in §2.1 with the derivation of the optical AM from Maxwell's theory, and its splitting into intrinsic (spin) and extrinsic (orbital) contributions. In §2.2 I discuss the theory of paraxial light beams and their AM. By comparing the results for a plane wave with the results for a paraxial beam, we see that the features of the spin and orbital contributions in more complex optical fields can rarely be inferred from their behaviours in simpler optical fields. This theme is continued in §2.3, where I discuss the features of the optical spin in more complex, non-paraxial fields, analysing the features of the distinct 'electric' and 'magnetic' spin densities [15, 16] in non-interfering superpositions of plane waves [17]. The spin structures which arise in these optical fields have many interesting properties and have the potential for diverse applications in light-matter interactions.

Chapter 3 is somewhat of an outlier in this Thesis, because it is not directly connected to work on structured light, instead being dedicated to an overview of molecular quantum electrodynamics (QED) [18–20], which is a theory for the interactions between electromagnetic (EM) fields and non-relativistic charged particles. It uses many of the same tools to study light-atom interactions as quantum optics [21–23] but, as I shall discuss in §3.1, is developed more formally starting from the Lagrangian, proceeding to the quantum theory via canonical quantization. In §3.2, I use the molecular QED formalism in a new derivation of the Faraday effect.

Another aspect of structured light research, besides optical AM, which has garnered significant attention is the study of *chiral optical fields* and their role in light-matter interactions. Any object which cannot be superposed onto its mirror image, by means of rotations and translations, is called *chiral* and is said to exhibit *chirality* [24, 25]. This terminology, introduced by Kelvin [26], comes from the Greek word for hand [27], reflective of the fact that human hands are the prototypical example of (approximately) chiral objects. The distinct mirror-image forms of a chiral object are known as *enantiomorphs* in general and *enantiomers* in the case of chiral molecules.

Chirality appears across all of the sciences, perhaps most significantly in biology and pharmacology. In biological systems, chiral molecules appear almost exclusively in single-enantiomer

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forms, amino acids always being left-handed and sugars right-handed, and it is an enduring mystery how the *homochirality* of the world came about [28]. The fact that the human body is composed of chiral chemicals means that the creation of single-enantiomer drugs is of great importance, because the left- and right-handed forms of a drug can interact very differently with our biological framework. This is exemplified by the well-known thalidomide tragedy, in which one enantiomer caused beneficial effects whilst the other led to birth defects [29].

The simplest and most fundamental example of a chiral optical field is a CP wave. The chirality of this field may be appreciated by noting the helical path traced out by its polarization vector [30], a helix being an inherently chiral object [24]. The chirality of light is of interest because generally, in light-matter interactions, it takes a chiral optical influence to distinguish between different molecular enantiomers. These *chiroptical effects* are many and varied, and have played an important role in the study of chiral molecules since their discovery in the 19th Century [18, 24, 25].

There has been renewed interest in the last decade or so in chiral light-matter interactions, due to the realization that their effects can be magnified by using structured optical fields. A major development in this regard was Tang and Cohen's discovery of 'superchiral' light and its enhancement of circular dichroism [31], which led to a flurry of further research activity [32–36]. In the ensuing decade, diverse aspects of the chirality of light and its interactions with matter have been explored [13, 37–49]. One topic which has received considerable interest is the investigation of *enantioselective chiroptical forces*, that is, optical forces whose magnitude and direction are sensitive to measures of the molecular and optical chirality [37–39, 50]. It has been proposed that these forces could provide a new method for sensing and separating molecular enantiomers [38, 50, 51], which is of great importance in the pharmaceutical and many other industries.

The fact that CP light is fundamentally linked to aspects of optical AM and optical chirality hints at close connections between these two seemingly distinct topics, and these connections are firmly established when one considers the *optical helicity* [27, 52, 53], which is the subject of Chapter 4. In Section 4.1 I discuss the concepts of *true* and *false* chirality introduced by Barron [54], which is instructive for my later considerations of optical chirality, and in Section 4.2 I discuss the *dual symmetry* of electromagnetic fields in vacuum, which is intimately connected with optical helicity. These first two Sections allow for an in-depth discussion of some fundamental aspects of the optical helicity, and in particular its links with optical chirality, in §4.3. The optical helicity is also connected with the aforementioned chiroptical forces, and in §4.4 I derive the energy shift which leads to this force using molecular QED. Finally, in Chapter 5, I investigate the transfer of optical helicity to matter, specifically trying to answer the question of whether or not a single atom can faithfully detect the *local* helicity of an optical field. To do this I study a toy model consisting of an arbitrary monochromatic field interacting with a hydrogen-like atom, taking into account both the atom's internal and external degrees of freedom. As I shall show, a suitable measure of *atomic* helicity can be defined, and I explore the correlations between this and the optical helicity in light-atom interactions.

CHAPTER 2

Optical Angular Momentum

In this Chapter I give an overview of the most important features of optical AM. The following review articles have proven useful: [10, 11, 15, 55, 56]. Some useful aspects of classical electrodynamics are discussed in Appendix B.

For the forthcoming discussions, I need to choose a polarization convention. A useful comparison of the different conventions may be found in Appendix III of the book by Simmons and Guttmann [6]. At a particular instant in time, the tips of the electric field vector of a CP plane wave trace out a helix [30]. Throughout this Thesis, I choose a convention such that, if you point the thumb of your left (right) hand in the direction of wave propagation, your fingers curl in the same direction as the helix in a left (right) CP wave. Mathematically, a LCP plane wave travelling in the positive z-direction will be described by a complex electric field of the form

$$\tilde{\boldsymbol{E}} = \mathcal{E}_0 \frac{(\hat{\mathbf{x}} + i\hat{\mathbf{y}})}{\sqrt{2}} e^{i(kz - \omega t + \phi_0)}, \qquad (2.1)$$

where $\hat{\mathbf{x}}$ and $\hat{\mathbf{y}}$ are the unit vectors in the x- and y-directions, respectively, of a right-handed Cartesian coordinate system. A RCP plane wave travelling in the same direction is given by

$$\tilde{\boldsymbol{E}} = \mathcal{E}_0 \frac{(\hat{\mathbf{x}} - i\hat{\mathbf{y}})}{\sqrt{2}} e^{i(kz - \omega t + \phi_0)}.$$
(2.2)

The CP unit vectors are thus

$$\hat{\boldsymbol{\epsilon}}_L \equiv \frac{1}{\sqrt{2}} (\hat{\mathbf{x}} + i\hat{\mathbf{y}}), \qquad (2.3a)$$

$$\hat{\boldsymbol{\epsilon}}_R \equiv \frac{1}{\sqrt{2}} (\hat{\mathbf{x}} - i\hat{\mathbf{y}}).$$
 (2.3b)

In this convention, a LCP photon has helicity $+\hbar$ whilst a RCP photon has helicity $-\hbar$ (this convention was already assumed in my discussion of Beth's results in the Introduction).

2.1 Overview

I shall, unless otherwise stated, suppose that light, with associated fields \boldsymbol{E} and \boldsymbol{B} , is contained in a volume of space V, within which there may also be a charge distribution¹, η , and an associated current density, \boldsymbol{J}_{η} . I assume the charges and currents occupy only a small proportion of V and that otherwise the space is free of electromagnetic material. Then within this volume we can write $\boldsymbol{D} = \varepsilon_0 \boldsymbol{E}$ and $\boldsymbol{H} = \mu_0^{-1} \boldsymbol{B}$ [55], and Maxwell's equations (B.1) become

$$\varepsilon_0 \nabla \cdot \boldsymbol{E} = \eta, \tag{2.4a}$$

$$\mu_0^{-1} \nabla \times \boldsymbol{B} - \varepsilon_0 \dot{\boldsymbol{E}} = \boldsymbol{J}_{\eta}, \qquad (2.4b)$$

$$\nabla \cdot \boldsymbol{B} = 0, \qquad (2.4c)$$

$$\nabla \times \boldsymbol{E} + \boldsymbol{B} = 0. \tag{2.4d}$$

2.1.1 Definition of Optical Angular Momentum

The *linear* momentum density of the EM field is usually taken to be^2 [6, 55, 62]

$$\mathbf{g} \equiv \varepsilon_0 \boldsymbol{E} \times \boldsymbol{B},\tag{2.5}$$

¹Following Jackson's lead [57, §6.6], I use a different letter for the macroscopic charge density (η) and the microscopic charge density (ρ).

²In a medium the identification of the linear momentum is not so simple, see, e.g., [58]. Even in free space, one can distinguish between the linear momentum density I have given here (sometimes called the Poynting form) and the so-called 'canonical' or 'orbital' momentum density [59–61]. I will return to the connections between the two later. Historically, in discussions of optical AM, the Poynting form is the usual starting point [4, 6, 8].

giving the total momentum in the volume V as

$$\boldsymbol{P} = \varepsilon_0 \int_V \mathrm{d}^3 r \, \boldsymbol{E} \times \boldsymbol{B}. \tag{2.6}$$

The optical AM *density* is defined, by analogy with the mechanics of a rigid body, as $\mathbf{j} = (\mathbf{r} - \mathbf{r}_0) \times \mathbf{g}$, with respect to some reference point \mathbf{r}_0 . For simplicity I will always take \mathbf{r}_0 to coincide with the origin. The total optical angular momentum in the volume V is thus [6, 20, 55]

$$\boldsymbol{J} = \varepsilon_0 \int_V \mathrm{d}^3 r \; \boldsymbol{r} \times (\boldsymbol{E} \times \boldsymbol{B}). \tag{2.7}$$

It can be shown that the optical angular momentum obeys a continuity equation akin to Poynting's theorem. Recall that the latter takes the form [6, 62]

$$\frac{\partial w}{\partial t} + \nabla \cdot \boldsymbol{S} = -\boldsymbol{J}_{\eta} \cdot \boldsymbol{E}, \qquad (2.8)$$

where

$$w = \frac{\varepsilon_0}{2} \left(\boldsymbol{E}^2 + c^2 \boldsymbol{B}^2 \right) \tag{2.9}$$

is the electromagnetic energy density and

$$\boldsymbol{S} \equiv \boldsymbol{E} \times \boldsymbol{H} = \varepsilon_0 c^2 \boldsymbol{E} \times \boldsymbol{B} \tag{2.10}$$

is Poynting's vector [62]. The integral

$$\int_{S} \boldsymbol{S} \cdot \mathrm{d}\boldsymbol{a} \tag{2.11}$$

tells us how much electromagnetic energy flows through the surface S per second. In the absence of charges, the source term $(J_{\eta} \cdot E)$ vanishes and Poynting's theorem demonstrates the local conservation of electromagnetic energy. Note that the *flow* of energy and the *density* of momentum are intrinsically linked: $\mathbf{g} = \mathbf{S}/c^2$.

The analogous continuity equation for the optical AM is [55, 63]

$$\partial_t j_i + \partial_l M_{il} = -\epsilon_{ijk} x_j f_k, \qquad (2.12)$$

written using index notation (see §A.3), in which $\partial_t \equiv \partial/\partial t$ and $\partial_l \equiv \partial/\partial x_l$, and repeated

indices are summed over. The symbol

$$\epsilon_{ijk} = \begin{cases} +1, & \text{for } (i, j, k) \in \{(1, 2, 3), (3, 1, 2), (2, 3, 1)\} \\ -1, & \text{for } (i, j, k) \in \{(2, 1, 3), (3, 2, 1), (1, 3, 2)\} \\ 0, & \text{for } i = j, j = k \text{ or } k = i \end{cases}$$
(2.13)

is the Levi-Civita pseudotensor [64, §2.9], j_i is the i^{th} Cartesian component of the angular momentum density, and f_k is the k^{th} component of the Lorentz force density (see Eq. (B.13)). The right-hand side of (2.12) is simply the negative of the *torque density* $\mathbf{r} \times \mathbf{f}$, written in index notation. The quantity

$$M_{il} = \epsilon_{ijk} x_j \left[\delta_{kl} w - \varepsilon_0 E_k E_l - \mu_0^{-1} B_k B_l \right]$$
(2.14)

is the angular-momentum flux density [55, 63], which has the dimensions of angular momentum per unit area per unit time. If we are dealing with a light beam propagating along the z-axis, say, then the amount of optical AM flowing each second through a z = constantsurface S is

$$\int_{S} M_{zz} \,\mathrm{d}x \mathrm{d}y. \tag{2.15}$$

2.1.2 Separation into Spin and Orbital Terms

The total optical AM (2.7) can be written in a variety of alternative forms. First of all, it is customary to replace the magnetic field with $\nabla \times A_{\perp}$. We could write this as the curl of the total vector potential $\mathbf{A} = \mathbf{A}_{\perp} + \mathbf{A}_{\parallel}$, but this would be somewhat artificial, as we know $\mathbf{j} = \mathbf{r} \times (\mathbf{E} \times \mathbf{B})$ is gauge independent (it is defined in terms of the fields), and thus it is more natural to write everything in terms of the gauge-invariant transverse vector potential. The cross products may be expressed in index notation using the Levi-Civita symbol (2.13), and we find after some manipulation that \mathbf{J} can be written in the exact form

$$\boldsymbol{J} = \varepsilon_0 \int_V \mathrm{d}^3 r \left[E_i (\boldsymbol{r} \times \nabla) A_i^{\perp} + \boldsymbol{E} \times \boldsymbol{A}_{\perp} - (\boldsymbol{E} \cdot \nabla) (\boldsymbol{r} \times \boldsymbol{A}_{\perp}) \right].$$
(2.16)

(Note the sum over the repeated indices in the first term.) Assuming that the EM fields vanish at the boundary of V, as is typical in an actual experiment, we can write J in the

form (derivation in Appendix D.1.1)

$$\boldsymbol{J} = \varepsilon_0 \int_V \mathrm{d}^3 r \left[E_i (\boldsymbol{r} \times \nabla) A_i^{\perp} + \boldsymbol{E} \times \boldsymbol{A}_{\perp} + (\boldsymbol{r} \times \boldsymbol{A}_{\perp}) (\nabla \cdot \boldsymbol{E}) \right].$$
(2.17)

It is also convenient to split the electric field into its transverse and longitudinal components (see §B.2), $\boldsymbol{E} = \boldsymbol{E}_{\perp} + \boldsymbol{E}_{\parallel}$, and to write

$$\boldsymbol{J} = \boldsymbol{J}_{\text{trans}} + \boldsymbol{J}_{\text{long}},\tag{2.18}$$

where

$$\boldsymbol{J}_{\text{trans}} \equiv \varepsilon_0 \int_V \mathrm{d}^3 r \ \boldsymbol{r} \times (\boldsymbol{E}_{\perp} \times \boldsymbol{B}), \qquad (2.19a)$$

$$\boldsymbol{J}_{\text{long}} \equiv \varepsilon_0 \int_V \mathrm{d}^3 r \ \boldsymbol{r} \times (\boldsymbol{E}_{\parallel} \times \boldsymbol{B}). \tag{2.19b}$$

Then using (2.17) we have

$$\boldsymbol{J}_{\text{trans}} = \varepsilon_0 \int_V \mathrm{d}^3 r \left[E_i^{\perp} (\boldsymbol{r} \times \nabla) A_i^{\perp} + \boldsymbol{E}_{\perp} \times \boldsymbol{A}_{\perp} \right], \qquad (2.20a)$$

$$\boldsymbol{J}_{\text{long}} = \varepsilon_0 \int_V \mathrm{d}^3 r \left[E_i^{\parallel} (\boldsymbol{r} \times \nabla) A_i^{\perp} + \boldsymbol{E}_{\parallel} \times \boldsymbol{A}_{\perp} + (\boldsymbol{r} \times \boldsymbol{A}_{\perp}) (\nabla \cdot \boldsymbol{E}_{\parallel}) \right],$$
(2.20b)

where I have used $\nabla \cdot \boldsymbol{E}_{\perp} \equiv 0$. The decomposition into transverse and longitudinal components has some physical significance. To see this, note that after some work we can re-write $\boldsymbol{J}_{\text{long}}$ in the form (see derivation in Appendix D.1.2) [20, p. 46]

$$\boldsymbol{J}_{\text{long}} = \int_{V} \mathrm{d}^{3} r \, \eta(\boldsymbol{r} \times \boldsymbol{A}_{\perp}). \tag{2.21}$$

If we are considering microscopic fields and charges, i.e., if η is a sum over delta functions (see Eq. (B.9)), then this becomes

$$\boldsymbol{J}_{\text{long}} = \sum_{\alpha} e_{\alpha} \boldsymbol{q}_{\alpha} \times \boldsymbol{A}_{\perp}(\boldsymbol{q}_{\alpha}).$$
(2.22)

The total AM of the *combined system* of charges and fields can thus be written as

$$\begin{aligned} \boldsymbol{J}_{\text{tot}} &= \boldsymbol{J}_{\text{trans}} + \boldsymbol{J}_{\text{long}} + \sum_{\alpha} \boldsymbol{q}_{\alpha} \times m_{\alpha} \boldsymbol{v}_{\alpha} \\ &= \boldsymbol{J}_{\text{trans}} + \sum_{\alpha} \boldsymbol{q}_{\alpha} \times \left(m_{\alpha} \boldsymbol{v}_{\alpha} + e_{\alpha} \boldsymbol{A}_{\perp}(\boldsymbol{q}_{\alpha}) \right). \end{aligned}$$
(2.23)

The final term in brackets is the *canonical momentum*, p_{α} , of the particles, so not only does J_{long} vanish in the absence of charges, as is clear from (2.22), it can even be thought of as a property of the particles.

Returning our attention to the transverse contribution (2.20a), this may be written as

$$\boldsymbol{J}_{\text{trans}} = \boldsymbol{L} + \boldsymbol{S},\tag{2.24}$$

where

$$\boldsymbol{L} \equiv \varepsilon_0 \int_V \mathrm{d}^3 r \, E_i^{\perp}(\boldsymbol{r} \times \nabla) A_i^{\perp}, \qquad (2.25a)$$

$$\boldsymbol{S} \equiv \varepsilon_0 \int_V \mathrm{d}^3 r \, \boldsymbol{E}_\perp \times \boldsymbol{A}_\perp, \qquad (2.25\mathrm{b})$$

which are often called the optical orbital angular momentum (OAM) and spin angular momentum (SAM), respectively. The decomposition of J_{trans} into a spin and orbital term has a long history, dating back at least as far as Darwin's work in 1932 [4]. Alternative names for S and L are the *intrinsic* and *extrinsic* contributions to the optical AM. These terms are derived from the fact that S is purely defined by the optical field under consideration, whilst L also depends on the reference point r_0 (taken as the origin above). The orbital contribution with respect to the origin and the orbital contribution with respect to an arbitrary point r_0 , are related by [65, 66]

$$\boldsymbol{L}_{\boldsymbol{r}_0} = \boldsymbol{L}_0 - \boldsymbol{r}_0 \times \boldsymbol{P}, \qquad (2.26)$$

where P is the linear optical momentum (2.6). Whilst in some specific (and practically important) examples the components of L_{r_0} and L_0 in the direction of propagation are the same [66], this is not generally the case [67]. The terms intrinsic and extrinsic optical AM are thus quite natural. In quantum mechanics the distinction between spin and orbital AM stems from a similar argument, and this partly justifies the names optical SAM and OAM as well. However, this terminology also comes with some caveats which I shall discuss below.

2.1.3 Angular Momentum of a Plane Wave

To gain some insight into the physical nature of the SAM and OAM, let's consider a simple example: suppose a plane, monochromatic light wave travels in the z-direction with frequency $\omega = ck$. The (transverse) vector potential and electric field may be written as

$$\mathbf{A}_{\perp} = \operatorname{Re}\left\{A_0\hat{\boldsymbol{\epsilon}}e^{i(kz-\omega t)}\right\},\tag{2.27a}$$

$$\boldsymbol{E}_{\perp} = \operatorname{Re}\left\{i\omega A_{0}\hat{\boldsymbol{\epsilon}}e^{i(kz-\omega t)}\right\},\tag{2.27b}$$

where

$$\hat{\boldsymbol{\epsilon}} = \alpha \hat{\mathbf{x}} + \beta \hat{\mathbf{y}}, \qquad (2.28)$$

subject to $|\alpha|^2 + |\beta|^2 = 1$, is an arbitrary unit polarization vector. The integrand of Eq. (2.25b) is the *optical spin density*,

$$\boldsymbol{s} = \varepsilon_0 \boldsymbol{E}_\perp \times \boldsymbol{A}_\perp. \tag{2.29}$$

A straightforward calculation shows that, for the plane wave defined above, this equals

$$\boldsymbol{s} = \frac{\varepsilon_0}{2} \omega \sigma |A_0|^2 \hat{\boldsymbol{z}},\tag{2.30}$$

where

$$\sigma \equiv i(\alpha\beta^* - \alpha^*\beta). \tag{2.31}$$

The intrinsic AM contained in a volume V is thus

$$\boldsymbol{S} = \frac{\varepsilon_0}{2} \omega \sigma |A_0|^2 V \hat{\boldsymbol{z}}.$$
(2.32)

Strictly speaking, a plane wave occupies all of space, so we should take $V = \mathbb{R}^3$. The total SAM of a plane wave thus appears to diverge. I will return to this point later.

Let's compare with the orbital contribution. The integrand of Eq. (2.25a) is the orbital AM density,

$$\boldsymbol{l} = \varepsilon_0 E_i^{\perp} (\boldsymbol{r} \times \nabla) A_i^{\perp}, \qquad (2.33)$$

which for the plane wave becomes

$$\boldsymbol{l} = \frac{\varepsilon_0}{c} (y\hat{\mathbf{x}} - x\hat{\mathbf{y}}) \boldsymbol{E}_{\perp}^2.$$
(2.34)

We can see immediately that, for a plane wave, the spin and orbital AM have very different characteristics. The key features of the spin are that: (a) it is parallel to the direction of propagation and (b) it is dependent on the polarization of the wave. Neither of these are true of the orbital contribution. The polarization dependence of \boldsymbol{S} is entirely contained in σ . By writing (with no loss of generality) $\alpha = a$ and $\beta = be^{i\theta}$, for $a, b, \theta \in \mathbb{R}$, we have $\sigma = 2ab\sin\theta$, and we may recognise $\omega^2 |A_0|^2 \sigma$ as the third Stokes parameter of the wave [6, 30]. It is easy to see that $0 \leq |\sigma| \leq 1$. When the x- and y-components are in phase, i.e., when the wave is linearly polarized, $\sigma = 0$, whilst σ takes the maximum value (+1) for LCP light and the minimum value (-1) for RCP light. Elliptically polarized light sits between these two extremes. Another enlightening result is the ratio of $\boldsymbol{S} \cdot \hat{\boldsymbol{z}} = S_z$ with the time-averaged EM energy, \overline{W} . We find

$$\frac{S_z}{\overline{W}} = \frac{\sigma}{\omega}.$$
(2.35)

This may be, and commonly is, interpreted as the result that every photon in the plane wave carries, in addition to the energy $\hbar\omega$, an AM $\sigma\hbar$ in the direction of propagation. For CP light, this is $\pm\hbar$. These results strongly suggest that \boldsymbol{S} is the contribution to optical AM which was predicted by Poynting and measured by Beth. However, there are a few subtleties we must address.

If we go back to the linear momentum density, Eq. (2.5), then for a plane wave we have $\mathbf{g} = |\mathbf{g}|\hat{\mathbf{z}}$, and $(\mathbf{r} \times \mathbf{g}) \cdot \hat{\mathbf{z}}$ is identically zero. Therefore, a plane wave has no AM in its direction of propagation [6, 68]. But we have just shown that $\mathbf{S} = S_z \hat{\mathbf{z}} \neq 0$. How can this be? We must remember that in deriving $\mathbf{J}_{\text{trans}} = \mathbf{L} + \mathbf{S}$, we assumed that the fields vanish at the surface of V. For a plane wave this is not the case, and therefore $\mathbf{J}_{\text{trans}} \neq \mathbf{L} + \mathbf{S}$. If we return to the exact form, Eq. (2.16), now retaining only the transverse contribution, we have

$$\boldsymbol{J}_{\text{trans}} = \boldsymbol{L} + \boldsymbol{S} - \varepsilon_0 \int_V d^3 r \, (\boldsymbol{E}_{\perp} \cdot \nabla) (\boldsymbol{r} \times \boldsymbol{A}_{\perp}). \tag{2.36}$$

A simple calculation shows that the additional term exactly cancels the spin contribution, which also resolves the issue mentioned above that S appears to diverge. The following two statements are both true and are not contradictory: the spin contribution to the AM of a plane wave is generally non-zero and points in the direction of propagation; the total optical AM of a plane wave has no component in the direction of propagation.

As plane waves only exist mathematically, in a real experiment we are safe to use the decomposition into \boldsymbol{L} and \boldsymbol{S} by choosing a sufficiently large volume (usually $V = \mathbb{R}^3$). The spin contribution in a real quasi-plane wave or paraxial beam does not have the exact form

as given in Eq. (2.32), and it also does not diverge, but the key features of polarization dependence and a dominant component parallel to the direction of propagation remain, as does the ratio of SAM in the direction of propagation to energy [6, 10].

One might conclude from this Section that S is always inherently linked to circularly polarized light and is always parallel to the direction of propagation, but this is not the case. That is to say, these are not *defining* features of optical SAM, and as I shall discuss in §2.3, the spin can exhibit a variety of features in different optical fields. Nonetheless, the features outlined in this Section are those which are most commonly associated with SAM, because they occur in the simplest and most ubiquitous waves.

2.1.4 'True' Angular Momenta?

I summarized earlier how, in a particular sense, S is intrinsic whilst L is extrinsic. Now I wish to address whether we can go so far as to associate S and L with 'true' spin and orbital angular momenta of light, and thus justify the use of the terms SAM and OAM? To answer this we turn to the quantum theory.

The total AM about a particular axis is, by definition, the generator of rotations about that axis [69]. In quantum theory, this is equivalent to saying that the Cartesian components of a total AM operator J satisfy [70, 71]

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k. \tag{2.37}$$

In non-relativistic quantum mechanics (QM) we take this commutation relation as the definition of an AM operator, be it spin, orbital or total.

Lenstra and Mandel [65] showed a long time ago that \hat{J}_{trans} (the operator form of Eq. (2.24)) does obey (2.37). What about the SAM and OAM operators, \hat{S} and \hat{L} ? This question was answered by van Enk and Nienhuis [72, 73]. Their analysis begins with a mode expansion of the (transverse) vector potential operator, \hat{A}_{\perp} ,

$$\hat{A}_{\perp}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\lambda} \mathscr{A}(\boldsymbol{k}) \left[\hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda} + \hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda}^* e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda}^\dagger \right], \qquad (2.38)$$

where the sum is over the wave vectors \mathbf{k} and orthogonal polarization vectors $\hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda}$, for $\lambda = 1, 2$. (I discuss mode expansions of the EM field operators in detail in Chapter 3.) The operators $\hat{a}_{\boldsymbol{k}\lambda}$ and $\hat{a}^{\dagger}_{\boldsymbol{k}\lambda}$ are the annihilation and creation operators of the $(\boldsymbol{k}, \lambda)$ mode, which act upon states of the quantized radiation field and satisfy the commutation relations

$$[\hat{a}_{\boldsymbol{k}\lambda}, \hat{a}^{\dagger}_{\boldsymbol{k}'\lambda'}] = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\lambda\lambda'}.$$
(2.39)

Using (2.38) one can show that [65, 72-74]

$$\hat{\boldsymbol{S}} = \sum_{\boldsymbol{k},\lambda} \sigma_{\lambda} \,\hbar \hat{\boldsymbol{k}} \,\hat{n}_{\boldsymbol{k}\lambda},\tag{2.40}$$

where $\hat{n}_{k\lambda}$ is the *number operator* of mode (\mathbf{k}, λ) , which counts the number of photons in that mode, $\hat{\mathbf{k}} = \mathbf{k}/|\mathbf{k}|$, and σ_{λ} is the value of the polarization parameter (2.31) for the different polarizations λ . As discussed, $\sigma_L = 1$, $\sigma_R = -1$, and we once again arrive at the result that a CP photon carries an intrinsic AM of $\pm \hbar$ in its direction of propagation.

The commutation relations for the components of \hat{S} follow simply from (2.40). We find [73]

$$[\hat{S}_i, \hat{S}_j] = 0, \tag{2.41}$$

which is *not* the desired form of Eq. (2.37). It follows that the components of \hat{L} do not obey the 'correct' commutation relations either. Whilst Van Enk and Nienhuis make clear that the spin and orbital contributions *are* physical observables, because they are represented by gauge-invariant Hermitian operators, it is concluded on the basis of the above result that \hat{S} and \hat{L} are not 'true' AM of light [69, 72, 73]. I think it is worth dissecting this conclusion.

Whilst spin AM operators in non-relativistic QM must obey the commutation relation (2.37), in *relativistic* QM the situation is not so simple. In fact, in relativistic QM we can only define spin operators for particles *at rest* [75]. As photons are inherently relativistic, and can never be at rest, it seems that we should not expect \hat{S} to behave exactly as a spin operator in the non-relativistic theory. The operator which is actually used to define the photon as a spin-1 particle is the *helicity operator*, and the photon's spin quantum number (s = 1) is defined as the magnitude of the helicity quantum number [75]. Another manifestation of the difference between the non-relativistic and relativistic theories is that a massive spin-1 particle must have three distinct spin projection eigenvalues $(-\hbar, 0, +\hbar)$, but this is not the case for a massless particle [74, 76], and it is entirely consistent that the SAM of light only has two eigenvalues $(\pm\hbar)$.

In conclusion, it is important to recognise, as van Enk and Nienhuis [72, 73] and others [69] have, that S and L are not of exactly the same nature as the most familiar spin and orbital AM. However, S and L do possess what I think are the most important features of spin

and orbital AM, respectively, which is the intrinsic and extrinsic properties discussed above. Therefore, I shall adhere to the commonly used terminology, calling S the spin angular momentum of light and L the orbital angular momentum of light.

2.2 Paraxial Beams and Orbital Angular Momentum

In this Section, I show that certain paraxial laser beams possess, in addition to a polarizationdependent SAM, a well-defined and controllable OAM in their direction of propagation. I closely follow the review articles by Allen, Padgett and Babiker [10], and Götte and Barnett [55].

2.2.1 Paraxial Approximation

In geometrical optics a ray which makes a small angle with the optical axis is said to be 'paraxial' [77]. In a well-collimated laser beam, the majority of the plane waves which sum to form the beam will have wave vectors which are approximately parallel to the optical axis (direction of beam propagation), and thus such a beam is also called paraxial.

We consider an optical field in vacuum $(\eta = 0 = J_{\eta})$, in which case Maxwell's equations (2.4) become:

$$\nabla \cdot \boldsymbol{E} = 0, \qquad (2.42a)$$

$$c^2 \nabla \times \boldsymbol{B} = \dot{\boldsymbol{E}},\tag{2.42b}$$

$$\nabla \cdot \boldsymbol{B} = 0, \tag{2.42c}$$

$$\nabla \times \boldsymbol{E} = -\boldsymbol{B}.$$
 (2.42d)

The electric field is now entirely transverse (divergence-free), i.e., $\boldsymbol{E} = \boldsymbol{E}_{\perp}$, and thus $\boldsymbol{J} = \boldsymbol{J}_{\text{trans}} = \boldsymbol{L} + \boldsymbol{S}$. The light is also assumed to be perfectly monochromatic, of frequency ω , and I shall write the fields in the form $\text{Re}\{\boldsymbol{E}(\boldsymbol{r})e^{-i\omega t}\}$, where $\boldsymbol{E}(\boldsymbol{r})$ now denotes the time-independent complex electric field

Working in the Lorenz gauge (B.20), and eliminating the scalar potential Φ using the gauge condition, the complex electric and magnetic fields may be written in terms of the complex

vector potential \boldsymbol{A} as [10, 55]

$$\boldsymbol{B} = \nabla \times \boldsymbol{A},\tag{2.43a}$$

$$\boldsymbol{E} = ick\left(\boldsymbol{A} + \frac{1}{k^2}\nabla(\nabla \cdot \boldsymbol{A})\right), \qquad (2.43b)$$

where $\omega = ck$. The vector potential satisfies the wave equation [18, 55], which for the monochromatic fields I am considering reduces to the vector Helmholtz equation,

$$\nabla^2 \mathbf{A} + k^2 \mathbf{A} = 0. \tag{2.44}$$

In the theory of laser beams, the *paraxial approximation* involves two principal assumptions: first, that the (Lorenz-gauge) vector potential is perpendicular to the beam propagation axis, taken as the z-axis. The second is that the variation of the potential in the z-direction is dominated by an exponential factor e^{ikz} [8, 55, 78]. These assumptions align well with the real properties of a collimated laser beam and make it possible to derive analytical expressions for various laser modes. Following the first assumption we write $\mathbf{A} = \psi(\mathbf{r})\hat{\mathbf{\epsilon}}$, where $\hat{\mathbf{\epsilon}} = \alpha \hat{\mathbf{x}} + \beta \hat{\mathbf{y}}$. It is common to say that \mathbf{A} is 'transverse' [78], in the sense that it is transverse to the propagation axis. However, it is important to distinguish between this notion of transversality and the one I use throughout this Thesis, in which a divergence-free vector field is called transverse (see §B.2). Because we are working in the Lorenz gauge $\mathbf{A} \neq \mathbf{A}_{\perp}$, i.e., \mathbf{A} is not divergence free. Shortly, after developing the theory from the Lorenz gauge, I will discuss some issues which can arise if one naively uses the Coulomb-gauge potential in the theory of paraxial beams.

In general the polarization amplitudes α and β can depend on \boldsymbol{r} , a necessary condition for so-called 'vector beams', for example [12, 79]. Such beams are not of interest here however and I will assume $\nabla^2(\psi \hat{\boldsymbol{\epsilon}}) = \hat{\boldsymbol{\epsilon}} \nabla^2 \psi$. Thus (2.44) reduces to the scalar Helmholtz equation for ψ ,

$$\nabla^2 \psi + k^2 \psi = 0. \tag{2.45}$$

Next we write

$$\psi(\mathbf{r}) = u(\mathbf{r})e^{ikz},\tag{2.46}$$

and invoke the second assumption of the paraxial approximation, that the variation of u in

the z-direction is small compared to the variation of the exponential factor [10, 80],

$$\left|\frac{\partial u}{\partial z}\right| \ll k|u|, \qquad \left|\frac{\partial^2 u}{\partial z^2}\right| \ll k \left|\frac{\partial u}{\partial z}\right|.$$
 (2.47)

The double z-derivative of ψ thus becomes

$$\frac{\partial^2}{\partial z^2} \left(u e^{ikz} \right) = e^{ikz} \left(\frac{\partial^2 u}{\partial z^2} + 2ik \frac{\partial u}{\partial z} - k^2 u \right) \approx e^{ikz} \left(2ik \frac{\partial u}{\partial z} - k^2 u \right), \quad (2.48)$$

which upon inserting into (2.45) leaves us with the (approximate) equation of motion for u [10, 55, 80],

$$\nabla_t^2 u + 2ik\frac{\partial u}{\partial z} = 0, \qquad (2.49)$$

where $\nabla_t^2 \equiv \partial_x^2 + \partial_y^2$ is the 'transverse Laplacian' [55, 80]. Eq. (2.49) is known as the *paraxial* wave equation (PWE) [80].

The exact expressions (in the sense that the inequalities in (2.47) are not yet invoked) for the electric and magnetic fields in terms of u are found from Eqs. (2.43),

$$\boldsymbol{E} = ick \begin{pmatrix} \alpha u + \frac{1}{k^2} (\alpha \frac{\partial^2}{\partial x^2} + \beta \frac{\partial^2}{\partial x \partial y}) u \\ \beta u + \frac{1}{k^2} (\alpha \frac{\partial^2}{\partial x \partial y} + \beta \frac{\partial^2}{\partial y^2}) u \\ \frac{i}{k} (\alpha \frac{\partial}{\partial x} + \beta \frac{\partial}{\partial y}) u + \frac{1}{k^2} \frac{\partial}{\partial z} (\alpha \frac{\partial}{\partial x} + \beta \frac{\partial}{\partial y}) u \end{pmatrix} e^{ikz}, \quad (2.50a)$$
$$\boldsymbol{B} = ik \begin{pmatrix} -\beta u + \frac{i}{k} \beta \frac{\partial}{\partial z} u \\ \alpha u - \frac{i}{k} \alpha \frac{\partial}{\partial z} u \\ -\frac{i}{k} (\beta \frac{\partial}{\partial x} - \alpha \frac{\partial}{\partial y}) u \end{pmatrix} e^{ikz}. \quad (2.50b)$$

Different degrees or orders of the paraxial approximation can now be employed. Most commonly, perhaps, the term paraxial beam is associated with a 'zeroth-order' paraxial approximation, in which only terms of order k are retained in the above expressions [15, 80]. The resulting transverse (in the second sense) or '2D' fields are

$$\boldsymbol{E} \approx \boldsymbol{E}_{t} \equiv ick \begin{pmatrix} \alpha u \\ \beta u \\ 0 \end{pmatrix} e^{ikz}, \qquad (2.51a)$$
$$\boldsymbol{B} \approx \boldsymbol{B}_{t} \equiv ik \begin{pmatrix} -\beta u \\ \alpha u \\ 0 \end{pmatrix} e^{ikz}. \qquad (2.51b)$$

Note that $cB_t = \hat{\mathbf{z}} \times E_t$, which is reminiscent of the relation for a plane wave, although in that case it is the exact fields which satisfy this relationship. These 2D fields do not satisfy the divergence-free conditions imposed by Maxwell's equations (2.42a) and (2.42c), but this is not particularly surprising because in making the zeroth-order approximation we have thrown away the z-components of E and B.

In the next order of approximation, we retain in \boldsymbol{E} and \boldsymbol{B} all terms of order k^0 or higher. From the PWE, the $(1/k)\partial_z u$ terms are equivalent to terms of the order $(1/k^2)|\nabla_t^2 u|$, so we are left with [10]

$$\boldsymbol{E} \approx ick \begin{pmatrix} \alpha u \\ \beta u \\ \frac{i}{k} (\alpha \frac{\partial}{\partial x} + \beta \frac{\partial}{\partial y}) u \end{pmatrix} e^{ikz}$$
(2.52)

and

$$\boldsymbol{B} \approx ik \begin{pmatrix} -\beta u \\ \alpha u \\ -\frac{i}{k} (\beta \frac{\partial}{\partial x} - \alpha \frac{\partial}{\partial y}) u \end{pmatrix} e^{ikz}.$$
 (2.53)

Unlike the 2D fields above, these '3D' paraxial fields satisfy both the paraxiality conditions and Maxwell's divergence equations (within the paraxial approximation), and they are thus a more accurate representation of real paraxial beams. The approach I have taken, using the Lorenz gauge, was first developed by Davis [81]. It is a simple analytical procedure which captures the most important features of paraxial beams, but it does not account for the real behaviour of laser beams as effectively as advanced numerical techniques [82], which should be employed if one is interested in comparing theoretical calculations to experimental results with high accuracy. One particular area in which Davis's approach is lacking is the asymmetry between the produced electric and magnetic fields. For instance, if $\beta = 0$, then from Eqs. (2.50), the electric field will have a dominant x-component but also a small ycomponent, whereas the magnetic field has a dominant y-component but its x-component is identically zero (both fields have small z-components of course). The electric and magnetic fields of a real laser beam are not asymmetric [82] and thus, if greater accuracy is desired, a symmetrization procedure should be used on the above formulae [83].

Let us now see how the preceding development would differ if we used the Coulomb gauge rather than the Lorenz gauge. For this brief interlude, I will call the Coulomb-gauge potential \mathbf{A}^{C} and the Lorenz-gauge potential \mathbf{A}^{L} . The magnetic field is still found from the usual expression (2.43a) regardless of what potential one uses, but the electric field is no longer found from (2.43b), but from the expression $\mathbf{E} = ick\mathbf{A}^{C}$. We assert, as we previously did for \mathbf{A}^{L} , that the electric field (or equivalently \mathbf{A}^{C}) has a constant polarization which is transverse to the beam direction, so $\mathbf{E} = icku(\mathbf{r})e^{ikz}\hat{\boldsymbol{\epsilon}}$, where again $\hat{\boldsymbol{\epsilon}} = \alpha\hat{\mathbf{x}} + \beta\hat{\mathbf{y}}$. The Maxwell equation (2.42a) requires that \mathbf{E} be divergence free, and thus u must satisfy

$$\left(\alpha \frac{\partial}{\partial x} + \beta \frac{\partial}{\partial y}\right) u(\boldsymbol{r}) = 0.$$
(2.54)

As was first pointed out by Lax et al. [84], this condition presents a problem for a light beam. To see this, take the beam to be linearly polarized in the x-direction, $\hat{\boldsymbol{\epsilon}} = \hat{\mathbf{x}}$, so the condition becomes

$$\frac{\partial}{\partial x}u(\boldsymbol{r}) = 0. \tag{2.55}$$

Whilst a plane wave can satisfy this condition, a real light beam's amplitude is not of infinite cross section and must vary in the x-direction. Thus the assumption that \boldsymbol{E} (or \boldsymbol{A}^{C}) is of the above transverse form leads to an impossible condition for a paraxial beam [6, 55, 84]. To remedy this, a common approach when working in the Coulomb gauge is to add a small z-component to the potential which, to fulfil the divergence-free condition, must satisfy [6, 78, 85]

$$\frac{\partial}{\partial z}A_z^C = -\nabla_t \cdot \boldsymbol{A}^C.$$
(2.56)

Now using the paraxiality condition from (2.47), we make the approximation $(\partial/\partial z)A_z^C \approx ikA_z^C$, and thus

$$A_z^C \approx \frac{i}{k} \nabla_t \cdot \mathbf{A}^C = \frac{i}{k} \left(\alpha \frac{\partial}{\partial x} + \beta \frac{\partial}{\partial y} \right) u e^{ikz}.$$
 (2.57)

The resulting electric and magnetic fields are

$$\boldsymbol{E} \approx ick \begin{pmatrix} \alpha u \\ \beta u \\ \frac{i}{k} (\alpha \frac{\partial}{\partial x} + \beta \frac{\partial}{\partial y}) u \end{pmatrix} e^{ikz}$$
(2.58)

and

$$\boldsymbol{B} \approx ik \begin{pmatrix} -\beta u + \frac{i}{k}\beta\frac{\partial}{\partial z}u + \frac{1}{k^2}(\alpha\frac{\partial^2}{\partial x\partial y} + \beta\frac{\partial^2}{\partial y^2})u\\ \alpha u - \frac{i}{k}\alpha\frac{\partial}{\partial z}u - \frac{1}{k^2}(\alpha\frac{\partial^2}{\partial x^2} + \beta\frac{\partial^2}{\partial x\partial y})u\\ -\frac{i}{k}(\beta\frac{\partial}{\partial x} - \alpha\frac{\partial}{\partial y})u \end{pmatrix} e^{ikz}.$$
(2.59)

These fields are not identical to those found using the Lorenz gauge, Eqs. (2.50). This is to be expected because \mathbf{A}^{C} and \mathbf{A}^{L} , as defined above, do not differ by the gradient of a scalar function, and thus should not produce the same fields. However, to order k^{1} and k^{0} , the two approaches do produce the same fields, and it is only when one considers terms of the order k^{-1} that differences appear. These terms may become important in non-paraxial fields, in which case it may be necessary to model the higher-order terms more accurately [82, 83], but for the paraxial beams I am interested in, the first-order expressions are sufficient.

Many well-known solutions of the PWE exist. An elementary solution is a *Gaussian beam* with an intensity profile $(|u|^2)$ proportional to a Gaussian exponential factor, $e^{-2a(x^2+y^2)}$ [80]. The *Laguerre-Gaussian* (LG) modes are solutions of the PWE which are most naturally expressed in cylindrical coordinates (ρ, φ, z) (see Appendix A.2), as they possess cylindrical symmetry [55, 80]. Defined by two parameters p and m, I shall denote the LG mode functions by $u_{pm}^{LG} = LG_p^m$. Their name derives from the fact that LG_p^m is formed from the product of a Gaussian exponential factor and a generalized Laguerre polynomial $L_p^{|m|}$ [10, 55, 56]. The exact form of the modes is not of much interest here, they may be found in the preceding references. Their most important feature, for my discussion, is the aforementioned cylindrical symmetry, which means we can write LG_p^m in the form

$$LG_p^m = v_{pm}(\rho, z)e^{im\varphi}.$$
(2.60)

Modes which can be written in this form are sometimes called vortex beams or 'doughnut' modes, for reasons that I shall now outline.

The mode parameters $p \in \mathbb{N}$ and $m \in \mathbb{Z}$ of an LG mode determine the phase and intensity structures of the beam. The index m, sometimes called the 'topological charge' of the beam [55], is often denoted by ℓ , but m is more in-keeping with the connection (to be discussed) between optical OAM and QM. For p = 0, m = 0 we have a simple Gaussian beam. For |m| > 0 the intensity and phase profiles become much more interesting, with zero intensity and thus a phase singularity on the z-axis, and helical phase fronts [55, 56]. See Figure 2.1 for a visualization of these features for the LG_0^1 mode. The parameter p also drastically alters the phase and intensity of the beam, with p + 1 bright concentric rings forming when $m \neq 0$. The phase and intensity profiles for various LG modes are shown in Figure 2.2.

Having reviewed the basic theory of paraxial beams, let's return to the AM.

2.2.2 Angular Momentum of a Paraxial Beam

For the monochromatic fields of interest, the optical AM will contain both time-independent terms and terms which oscillate at $\pm 2\omega$. When ω is an optical frequency, the latter terms fluctuate far too rapidly to be of any significance in most experiments, and thus the physically relevant quantities are the time-averaged ones, which I denote by an overbar, e.g.,

$$\overline{J_i} \equiv \frac{\omega}{2\pi} \int_0^{\frac{2\pi}{\omega}} \mathrm{d}t \ J_i(t).$$
(2.61)

The time-averaged OAM and SAM are [69, 86]:

$$\overline{\boldsymbol{L}} = \frac{\varepsilon_0}{2i\omega} \int_V \mathrm{d}^3 r \ E_i^{\perp *} (\boldsymbol{r} \times \nabla) E_i^{\perp}, \qquad (2.62a)$$

$$\overline{\boldsymbol{S}} = \frac{\varepsilon_0}{2i\omega} \int_V \mathrm{d}^3 r \; \boldsymbol{E}_{\perp}^* \times \boldsymbol{E}_{\perp}.$$
(2.62b)

Note that, strictly speaking, it is not necessary to take the time-average of the SAM for a purely monochromatic field, because it is already time independent. This follows from the fact that $e^{-2i\omega t} \mathbf{E}_{\perp} \times \mathbf{E}_{\perp} = 0 = e^{2i\omega t} \mathbf{E}_{\perp}^* \times \mathbf{E}_{\perp}^*$, on account of the fundamental property of the cross product.

Following Allen et al. [8, 10], let's ask which fields, if any, are capable of having an OAM in their direction of propagation? Examining (2.62a) we see that $\overline{L} \cdot \hat{z}$ contains the operator

$$\frac{1}{i}\hat{\mathbf{z}}\cdot(\mathbf{r}\times\nabla) = \frac{1}{i}\frac{\partial}{\partial\varphi},\tag{2.63}$$

where φ is the azimuthal angle of the cylindrical coordinates (ρ, φ, z) . This operator is almost identical (except for a factor of \hbar) to the quantum-mechanical operator L_z , and it



(c)

Figure 2.1: Features of the LG_0^1 mode: (a) normalized intensity profile, showing the wellknown 'doughnut' shape; (b) phase profile, which is singular on the propagation axis; (c) wave front, i.e., surface of constant phase, showing the signature helical shape. Examples of how the intensity and phase profiles vary with the mode indices p and m are shown in Figure 2.2.



Figure 2.2: Laguerre-Gaussian modes: the intensity (top row) and phase (bottom row) profiles of several LG modes. Colouring is the same as in Figure 2.1.

tells us that the only fields capable of having a non-zero OAM in the direction of propagation are those for which $\partial E_i/\partial \varphi \neq 0$, for at least one $i \in \{x, y, z\}$. Examining the LG modes defined above, (2.60), we see that

$$\frac{1}{i}\frac{\partial}{\partial\varphi}LG_p^m = mLG_p^m,\tag{2.64}$$

and thus for $m \neq 0$ the LG modes have non-zero OAM in the z-direction.

With $u = v(\rho, z)e^{im\varphi}$ (which could be an LG mode or a Bessel beam [55]) we find that, to lowest order in the paraxial approximation, the time-averaged z-components of the orbital and spin densities are:

$$\overline{l_z} = \frac{\varepsilon_0}{2} \omega m |u|^2, \qquad (2.65a)$$

$$\overline{s_z} = \frac{\varepsilon_0}{2} \omega \sigma |u|^2, \qquad (2.65b)$$

giving the total AM of the beam in the direction of propagation as

$$\overline{J_z} = \omega(m+\sigma)\frac{\varepsilon_0}{2} \int_V \mathrm{d}^3 r \, |u|^2.$$
(2.66)
The total time-averaged energy of the beam is

$$\overline{W} = \omega^2 \frac{\varepsilon_0}{2} \int_V \mathrm{d}^3 r \, |u|^2, \qquad (2.67)$$

and thus the ratio of AM in the z-direction to energy is [8, 10]

$$\frac{\overline{J_z}}{\overline{W}} = \frac{m+\sigma}{\omega}.$$
(2.68)

Using the same reasoning as above, this suggests the quite general result that a cylindricallysymmetric paraxial beam, with polarization σ and topological charge m, carries a total AM which is equivalent to $(m + \sigma)\hbar$ per photon. The spin contribution $(\sigma\hbar)$ is essentially the same as we discovered for the plane wave. The orbital contribution $(m\hbar)$ is now very similar, but whilst σ is constrained between ± 1 , the mode index m can be indefinitely large, implying that the OAM can take any integer value. We again see a striking similarity between optical AM and QM: an electron in a hydrogen atom, say, can only have the spin projection values $\pm 1/2$, whilst the orbital projection value m_{ℓ} can take any value belonging to $\{-\ell, \ldots, \ell\}$, where ℓ is unbounded.

By analogy with Beth's work, Allen et al. [8] envisaged that the existence of optical OAM could be experimentally verified by measuring the torque about the beam axis that should be applied to an optical element (such as a cylindrical lens) which converts a beam with zero OAM into one with non-zero OAM. As far as I am aware, this experiment has still not been realized, due to great technical difficulty. However, it was not long after the original paper [8] that He et al. [87] experimentally confirmed the existence of optical OAM by observing its effects on trapped micro-particles—more detail on the experimental aspects of optical OAM can be found in [11, 56, 88].

This concludes my overview of the OAM in paraxial beams. In the next Section I discuss some more interesting (spin) AM structures, outside of the paraxial approximation.

2.3 Optical Spin Structures

In §2.1.3 I discussed the AM of a plane wave and showed that the SAM in the direction of propagation can be non-zero, whilst the OAM in this direction is identically zero. Then in §2.2 we have seen that paraxial beams of light can possess both SAM and OAM in the direction of propagation, the SAM being related to the polarization structure (σ) and the OAM to the mode structure (m) of the beam. It is well-known that, outside of the paraxial approximation, this relationship breaks down [89]. For instance, in a tightly-focussed rather than collimated vortex beam, L can depend on m and σ [15]. What this discussion is intended to highlight is that, as we add more structure to an optical field, the AM can exhibit more interesting and unexpected properties. To put this another way, we can rarely infer the behaviour of the optical AM in more complex fields from knowledge of its behaviour in less complex fields.

In this Section I touch on the exploration of optical AM in more exotic structured light fields. In particular, I shall be interested in the nature of the *local* optical spin in so-called non-interfering superpositions. It is generally the local angular momenta (i.e., AM densities) which interact with small (subwavelength) particles [15, 37, 90], such that novel spin density structures can open the door to novel light-matter interactions, a topic which has received much attention in recent years [15, 16, 91–101]. Perhaps the greatest interest has been in the behaviour of the local SAM in '3D' optical fields, i.e., fields for which the full threedimensional polarization is taken into account [16, 93–96]. In the simplest case, this can just mean taking into account the z-components of the electric and magnetic fields of a paraxial beam, and even this can show interesting features which one might not expect from the discussion in §2.2 [16]. More interesting, however, are the spin structures which arise when one considers inherently non-paraxial optical fields, such as a tightly-focussed beam [94, 96] or two plane waves propagating at an arbitrary angle to one another [93]. The work I present in this Section fits within this theme, but before I can elaborate on this, we need to discuss an alternative expression for the spin.

The SAM has thus far been written in the form

$$oldsymbol{S} = arepsilon_0 \int_V \mathrm{d}^3 r \, oldsymbol{E}_\perp imes oldsymbol{A}_\perp$$

The transverse electric field which appears in this expression can be written in terms of a so-called electric or 'second' vector potential [102],

$$\boldsymbol{E}_{\perp} = -c^2 \nabla \times \boldsymbol{C}, \qquad (2.69)$$

the prefactor being chosen for later convenience. Using (2.69) and integration by parts one can show, provided the fields vanish at the boundary of the integration volume, that S may

be written in the alternative form (see derivation in Appendix D.1.3) [69]

$$\boldsymbol{S} = \varepsilon_0 c^2 \int_V \mathrm{d}^3 r \, \boldsymbol{B} \times \boldsymbol{C}_\perp. \tag{2.70}$$

We can obviously also write \boldsymbol{S} in the 'dual' form,

$$\boldsymbol{S} = \frac{\varepsilon_0}{2} \int_V \mathrm{d}^3 r \left[\boldsymbol{E}_{\perp} \times \boldsymbol{A}_{\perp} + c^2 \boldsymbol{B} \times \boldsymbol{C}_{\perp} \right].$$
(2.71)

The equality of the different expressions for S relies on the fact that, in (2.25b), it was defined in terms of the gauge-invariant transverse vector potential A_{\perp} [69] (and in (2.70) is defined in terms of the gauge-invariant transverse part of C). Whenever I refer to S or to the optical spin, I will always mean this gauge-invariant quantity. If one defined S in terms of A or C (instead of A_{\perp} or C_{\perp}), then it would not be gauge invariant, but the change produced by a gauge transformation would be exactly cancelled by the corresponding change in L (if that too were defined in a non-gauge invariant way). The gauge-invariant forms are thus the physically relevant ones. Note the two forms of S are equivalent in the presence of charges as well as in vacuum, because the SAM is inherently linked to the *transverse* electric field, which always satisfies (2.69). Henceforth, I shall refer to

$$\boldsymbol{s}_e \equiv \varepsilon_0 \boldsymbol{E}_\perp \times \boldsymbol{A}_\perp, \qquad (2.72a)$$

$$\boldsymbol{s}_m \equiv \varepsilon_0 c^2 \boldsymbol{B} \times \boldsymbol{C}_\perp \tag{2.72b}$$

as the *electric* and *magnetic* spin densities, respectively, and

$$\boldsymbol{s} \equiv \frac{1}{2} (\boldsymbol{s}_e + \boldsymbol{s}_m) = \frac{\varepsilon_0}{2} \left[\boldsymbol{E}_{\perp} \times \boldsymbol{A}_{\perp} + c^2 \boldsymbol{B} \times \boldsymbol{C}_{\perp} \right]$$
(2.73)

as 'the' spin density, or sometimes the dual-symmetric spin density (for reasons which are discussed in §4.2). In the remainder of this Section, the discussion is specialized to freely-propagating monochromatic optical fields.

In the absence of charges Maxwell's equations exhibit a great degree of electric-magnetic symmetry. A manifestation of this is the fact that, in vacuum, both \boldsymbol{E} and \boldsymbol{B} can be written in terms of either the traditional vector potential (\boldsymbol{A}) or the second vector potential

(C). These relationships are [38, 52, 69, 102]:

$$\boldsymbol{E} = -\dot{\boldsymbol{A}}_{\perp} = -c^2 \nabla \times \boldsymbol{C}, \qquad (2.74a)$$

$$\boldsymbol{B} = -\dot{\boldsymbol{C}}_{\perp} = \nabla \times \boldsymbol{A}.$$
 (2.74b)

As in §2.2, I will write the monochromatic fields and potentials as the real part of a complex vector: $\tilde{F} = \text{Re}\{Fe^{-i\omega t}\}$. Note that, subsequently, E denotes the time-independent complex electric field, whilst \tilde{E} is the real electric field, and so on. From (2.74) we have the relationships

$$\boldsymbol{E} = i\omega \boldsymbol{A}_{\perp}, \quad \boldsymbol{B} = i\omega \boldsymbol{C}_{\perp}. \tag{2.75}$$

For a monochromatic field (2.72a) and (2.72b) become

$$\boldsymbol{s}_{e} = \frac{\varepsilon_{0}}{2\omega} \operatorname{Im} \{ \boldsymbol{E}^{*} \times \boldsymbol{E} \} = \frac{\varepsilon_{0}}{2i\omega} \boldsymbol{E}^{*} \times \boldsymbol{E}, \qquad (2.76a)$$

$$\boldsymbol{s}_m = \frac{\varepsilon_0 c^2}{2\omega} \operatorname{Im} \{ \boldsymbol{B}^* \times \boldsymbol{B} \} = \frac{\varepsilon_0 c^2}{2i\omega} \boldsymbol{B}^* \times \boldsymbol{B}.$$
(2.76b)

Because matter generally interacts differently with electric and magnetic fields (it is dual *asymmetric*), the electric and magnetic spin densities are separately observable quantities [16, 37, 90, 103]. One can show that, in a plane wave, $\mathbf{s}_e = \mathbf{s}_m$. The same is true if we consider only the 2D polarization of a paraxial beam, as in Eqs. (2.51). In both cases, the equality of \mathbf{s}_e with \mathbf{s}_m stems from the relationship $c\mathbf{B} = \hat{\mathbf{z}} \times \mathbf{E}$. However, in the paraxial beam this is only an approximate relationship, and when the full 3D polarization is taken into account we generally have $\mathbf{s}_e \neq \mathbf{s}_m$ [15, 16]. Differences between the electric and magnetic spins are of interest because of their separate physical influences. In the next Section I will explore the behaviours of the local spins in paraxial and non-paraxial superpositions of non-interfering plane waves. These optical fields exhibit remarkably rich spin structures and are also of particular interest in light-matter interactions, as I shall discuss.

2.3.1 Non-Interfering Superpositions

The time-averaged electric energy density of a monochromatic optical field is

$$\overline{w_e} = \overline{\varepsilon_0 \tilde{E}^2} = \frac{\varepsilon_0}{2} E \cdot E^*.$$
(2.77)

When we superpose various monochromatic waves, such that $\mathbf{E}e^{-i\omega t} = e^{-i\omega t}\sum_{j} \mathbf{E}_{j}$, the resulting 'intensity' is

$$\boldsymbol{E} \cdot \boldsymbol{E}^* = \sum_j |\boldsymbol{E}_j|^2 + \sum_j \sum_{k \neq j} \boldsymbol{E}_j \cdot \boldsymbol{E}_k^*.$$
(2.78)

The second term shows one of the defining features of any wave system, namely, interference. In this Section I am interested in superpositions which do not interfere, i.e., for which the overall intensity is simply given by

$$\boldsymbol{E} \cdot \boldsymbol{E}^* = \sum_j |\boldsymbol{E}_j|^2. \tag{2.79}$$

The easiest way to form such non-interfering superpositions is to choose each E_j to be a plane wave, and for their polarizations to be mutually orthogonal. This can easily be done for up to three linearly polarized waves and this is what I shall focus on here.

Let's start by considering the spins in the simplest possible example, a superposition of two orthogonally polarized plane waves, chosen to propagate in the yz-plane, separated by an angle of 2θ (see Figure 2.3). The specific wave and polarization vectors I consider are:

$$\boldsymbol{k}_1 = k_0 \hat{\boldsymbol{z}}, \quad \hat{\boldsymbol{\epsilon}}_1 = \hat{\boldsymbol{y}}, \tag{2.80a}$$

$$\boldsymbol{k}_2 = k_0 (\cos 2\theta \hat{\boldsymbol{z}} - \sin 2\theta \hat{\boldsymbol{y}}), \quad \hat{\boldsymbol{\epsilon}}_2 = \hat{\boldsymbol{x}}, \quad (2.80b)$$

where $k_0 = \omega/c$ is the wave number of both waves. The complex electric field is

$$\boldsymbol{E} = a_1 \hat{\boldsymbol{\epsilon}}_1 e^{i\boldsymbol{k}_1 \cdot \boldsymbol{r}} + a_2 \hat{\boldsymbol{\epsilon}}_2 e^{i\boldsymbol{k}_2 \cdot \boldsymbol{r}}.$$
(2.81)

For simplicity I will take $a_1 = a = a_2$. The associated magnetic field is

$$\boldsymbol{B} = \frac{a}{c}\hat{\boldsymbol{\beta}}_1 e^{i\boldsymbol{k}_1\cdot\boldsymbol{r}} + \frac{a}{c}\hat{\boldsymbol{\beta}}_2 e^{i\boldsymbol{k}_2\cdot\boldsymbol{r}},\tag{2.82}$$

where $\hat{\beta}_i$ are the magnetic polarization unit vectors, which follow from Maxwell's equation (2.42d):

$$\hat{\boldsymbol{\beta}}_i = \frac{\boldsymbol{k}_i \times \hat{\boldsymbol{\epsilon}}_i}{|\boldsymbol{k}_i|}.$$
(2.83)

In this particular case

$$\hat{\boldsymbol{\beta}}_1 = -\hat{\mathbf{x}}, \qquad \hat{\boldsymbol{\beta}}_2 = \cos 2\theta \hat{\mathbf{y}} + \sin 2\theta \hat{\mathbf{z}}.$$
 (2.84)



Figure 2.3: Configuration leading to a two-wave non-interfering superposition: the longer (grey) arrows are the wave vectors and the shorter (green) arrows indicate the electric polarization vectors.

Using (2.76) we find the following spin densities:

$$\boldsymbol{s}_e = s_0 \hat{\boldsymbol{z}},\tag{2.85a}$$

$$\mathbf{s}_m = s_0(\cos 2\theta \hat{\mathbf{z}} - \sin 2\theta \hat{\mathbf{y}}), \qquad (2.85b)$$

where

$$s_0 = \frac{\varepsilon_0 |a|^2}{\omega} \sin\left[(1 - \cos 2\theta) k_0 z + \sin 2\theta k_0 y \right].$$
(2.86)

This is an illustrative toy model because we can observe different behaviours for different separation angles. An interesting feature is that s_e always points in the direction of $\mathbf{k}_1 = k_0 \hat{\mathbf{z}}$, whilst s_m always points in the direction of \mathbf{k}_2 , which depends on θ . When $\theta = 0$ identically, we unsurprisingly find that both spin densities are identically zero. When $2\theta \ll 1$, but non-zero, we can make the paraxial approximation ($\cos 2\theta \approx 1$, $\sin 2\theta \approx 2\theta$), so

$$\boldsymbol{s}_m \approx s_0 \hat{\mathbf{z}} - 2\theta s_0 \hat{\mathbf{y}} \tag{2.87}$$

and

$$s_0 \approx \frac{\varepsilon_0 |a|^2}{\omega} \sin(2\theta k_0 y), \qquad (2.88)$$

and thus for two paraxial waves, the local electric and magnetic spins are approximately



Figure 2.4: Spin densities in the two-wave non-interfering superposition defined by Eqs. (2.80), for $2\theta = \pi/2$. We see that the electric and magnetic spin vectors are perpendicular everywhere. The lengths of the arrows and the background density plot indicate the magnitude of the spin vectors, with black corresponding to zero magnitude and white to the maximum (which is scaled to equal one).

equal, as expected from the above discussion.

More interesting results arise outside of the paraxial approximation. To take two extreme examples, consider the cases when the waves propagate at right angles or in opposite directions. When $2\theta = \pi/2$, the spin densities are everywhere orthogonal (see Figure 2.4),

$$\boldsymbol{s}_{e} = \frac{\varepsilon_{0}|a|^{2}}{\omega}\sin(k_{0}z + k_{0}y)\hat{\boldsymbol{z}}, \qquad \boldsymbol{s}_{m} = -\frac{\varepsilon_{0}|a|^{2}}{\omega}\sin(k_{0}z + k_{0}y)\hat{\boldsymbol{y}}, \qquad (2.89)$$

whilst for $2\theta = \pi$, the spin densities point in opposite directions along the z-axis,

$$\boldsymbol{s}_e = \frac{\varepsilon_0 |\boldsymbol{a}|^2}{\omega} \sin(2k_0 z) \hat{\boldsymbol{z}} = -\boldsymbol{s}_m.$$
(2.90)

This simple model highlights the degree to which non-paraxiality can influence local spin structures.

As a slight aside, let's mention that some constraints do exist between electric and magnetic spin structures. In particular, one can show that $\nabla \cdot \mathbf{s}_e = -\nabla \cdot \mathbf{s}_m$ in any monochromatic field (see Chapter 4), and thus from the divergence (Gauss') theorem [64], the fluxes of \mathbf{s}_e



Figure 2.5: Spin densities in the three-wave non-interfering superposition defined by Eqs. (2.92). The colour scheme is the same as in Figure 2.4.

and \boldsymbol{s}_m through any closed surface are the exact opposite of one another,

$$\oint_{S} \boldsymbol{s}_{e} \cdot d\boldsymbol{a} = -\oint_{S} \boldsymbol{s}_{m} \cdot d\boldsymbol{a}.$$
(2.91)

Next, let's consider a more complex three-wave non-interfering superposition, defined by the wave vectors, polarizations, and amplitudes:

$$\mathbf{k}_1 = k_0 \hat{\mathbf{x}}, \quad \hat{\boldsymbol{\epsilon}}_1 = \hat{\mathbf{y}}, \quad a_1 = a,$$
 (2.92a)

$$\boldsymbol{k}_2 = \frac{k_0}{\sqrt{2}} (\hat{\mathbf{x}} + \hat{\mathbf{y}}), \quad \hat{\boldsymbol{\epsilon}}_2 = \hat{\mathbf{z}}, \quad a_2 = \sqrt{2}a, \qquad (2.92b)$$

$$\mathbf{k}_3 = k_0 \hat{\mathbf{y}}, \quad \hat{\boldsymbol{\epsilon}}_3 = \hat{\mathbf{x}}, \quad a_3 = a,$$
 (2.92c)

which has previously been considered in a different context in [17]. Using (2.83) the magnetic polarization vectors are

$$\hat{\boldsymbol{\beta}}_1 = \hat{\mathbf{z}} = -\hat{\boldsymbol{\beta}}_3, \quad \hat{\boldsymbol{\beta}}_2 = \frac{1}{\sqrt{2}}(\hat{\mathbf{x}} - \hat{\mathbf{y}}).$$
 (2.93)

After a lengthy but simple calculation the x- and y-components of the local magnetic spin

can be shown to equal

$$s_m^x = s_m^y = \frac{\varepsilon_0 |a|^2}{\omega} \left\{ \sin\left[\left(\frac{1}{\sqrt{2}} - 1 \right) k_0 x + \frac{1}{\sqrt{2}} k_0 y \right] - \sin\left[\frac{1}{\sqrt{2}} k_0 x + \left(\frac{1}{\sqrt{2}} - 1 \right) k_0 y \right] \right\},\tag{2.94}$$

whilst the z-component is identically zero everywhere, $s_m^z = 0$. The components of the local electric spin are

$$s_e^x = +\sqrt{2} \frac{\varepsilon_0 |a|^2}{\omega} \sin\left[\left(\frac{1}{\sqrt{2}} - 1\right) k_0 x + \frac{1}{\sqrt{2}} k_0 y\right],$$
 (2.95a)

$$s_e^y = -\sqrt{2} \frac{\varepsilon_0 |a|^2}{\omega} \sin\left[\frac{1}{\sqrt{2}}k_0 x + \left(\frac{1}{\sqrt{2}} - 1\right)k_0 y\right],$$
 (2.95b)

$$s_e^z = \frac{\varepsilon_0 |a|^2}{\omega} \sin\left[k_0 x - k_0 y\right]. \tag{2.95c}$$

We see that, despite the three plane waves propagating in the xy-plane, the electric spin density has a non-zero z-component, a feature which has previously been studied in two-wave superpositions [93].

The spin densities for the three-wave configuration are plotted in Figure 2.5. The differences between the electric and magnetic spin densities are much greater in this case, as compared to the spins in the two-wave superposition (Figure 2.4). In the two-wave case, the spins have the same magnitude everywhere, only differing in their directions. In the three-wave case this is not true; we can see from Figure 2.5a that the magnetic spin density has much more pronounced regions of zero magnitude (the darkest regions) as compared to the electric spin density.

It is also interesting to compare the spin densities to the *local optical helicity*, h, which I discuss in detail in Chapter 4. For a single plane wave of amplitude A_0 the local helicity is

$$h = \frac{\varepsilon_0}{2} \omega \sigma |A_0|^2,$$

which, comparing to Eq. (2.30), is equal to the magnitude of the spin density (electric or magnetic) of the wave. This similarity between the helicity and spin in simple fields has led to some confusion between the two, and whilst deep connections do exist (as discussed in §4.3), they are distinct physical quantities. In Figure 2.6 I show the local helicity of the three-wave superposition discussed above. This highlights well the potential pitfalls of



Figure 2.6: The local optical helicity for the three-wave non-interfering superposition defined by Eqs. (2.92). Note the helicity is scaled with respect to \overline{w}_e/ω , where \overline{w}_e is given by (2.77). The dashed grey lines indicate regions where h = 0.

naively assuming that helicity and spin are synonymous: whilst we can see that the regions of zero helicity correspond exactly to the darkest regions of the magnetic spin plot (Figure 2.5a), the bright and dark regions of the electric spin plot (Figure 2.5b) are far less correlated to the helicity. In fact, there are several regions in which both the local helicity and local magnetic spin are identically zero, but the local electric spin has its greatest magnitude. It is very important, therefore, to properly distinguish between all three quantities in theoretical and experimental analyses.

Another difference which we may observe from Figure 2.5 is that the magnetic spin vectors always point in the $\pm(\hat{\mathbf{x}} + \hat{\mathbf{y}})$ direction, whilst the electric spin vectors appear to circulate about certain points. As the curl of a vector field encapsulates its local circulation [64], it seems natural to expect $\nabla \times \mathbf{s}_e$ and $\nabla \times \mathbf{s}_m$ to differ in this example. This is indeed the case, as a direct calculation shows: the curl of the electric spin density has components

$$(\nabla \times \boldsymbol{s}_e) \cdot \hat{\mathbf{x}} = -\frac{\varepsilon_0 |a|^2}{c} \cos(k_0 x - k_0 y) = (\nabla \times \boldsymbol{s}_e) \cdot \hat{\mathbf{y}}, \qquad (2.96a)$$

$$(\nabla \times \boldsymbol{s}_e) \cdot \hat{\boldsymbol{z}} = -\frac{\varepsilon_0 |\boldsymbol{a}|^2}{c} \left\{ \cos\left[\left(\frac{1}{\sqrt{2}} - 1 \right) k_0 x + \frac{1}{\sqrt{2}} k_0 y \right] + \cos\left[\frac{1}{\sqrt{2}} k_0 x + \left(\frac{1}{\sqrt{2}} - 1 \right) k_0 y \right] \right\},$$
(2.96b)

and the curl of \boldsymbol{s}_m has components

$$(\nabla \times \boldsymbol{s}_m) \cdot \hat{\mathbf{x}} = 0 = (\nabla \times \boldsymbol{s}_m) \cdot \hat{\mathbf{y}},$$
 (2.97a)

$$(\nabla \times \boldsymbol{s}_m) \cdot \hat{\mathbf{z}} = (\nabla \times \boldsymbol{s}_e) \cdot \hat{\mathbf{z}}.$$
 (2.97b)

The curls of the (monochromatic) spin densities are of some physical significance. To discuss this, first we note the following identities:

$$\nabla \times \left(\frac{\varepsilon_0}{2i\omega} \boldsymbol{E}^* \times \boldsymbol{E}\right) \equiv \varepsilon_0 \operatorname{Re}\{\boldsymbol{E} \times \boldsymbol{B}^*\} - \frac{\varepsilon_0}{2i\omega} (E_j^* \nabla E_j - E_j \nabla E_j^*), \quad (2.98a)$$

$$\nabla \times \left(\frac{\varepsilon_0 c^2}{2i\omega} \boldsymbol{B}^* \times \boldsymbol{B}\right) \equiv \varepsilon_0 \operatorname{Re} \{\boldsymbol{E} \times \boldsymbol{B}^*\} - \frac{\varepsilon_0 c^2}{2i\omega} (B_j^* \nabla B_j - B_j \nabla B_j^*), \quad (2.98b)$$

where repeated indices are summed over. The term $\varepsilon_0 \operatorname{Re} \{ \boldsymbol{E} \times \boldsymbol{B}^* \}$ is almost the time-average of the Poynting vector (2.10),

$$\boldsymbol{\mathcal{S}} \equiv \frac{\varepsilon_0 c^2}{2} \operatorname{Re} \{ \boldsymbol{E} \times \boldsymbol{B}^* \}.$$
(2.99)

The other terms which appear on the right of (2.98) are very similar in form to the probability current from quantum mechanics [104],

$$\boldsymbol{j}_{\psi} = \frac{\hbar}{2im} (\psi^* \nabla \psi - \psi \nabla \psi^*). \qquad (2.100)$$

This similarity, together with their appearance alongside the Poynting vector, suggests that these terms may be interpreted as representing the energy 'currents' associated with each component of the electric and magnetic field. As it turns out this is a known result [15, 59, 61], although it is usually phrased in terms of the momentum rather than energy flow of the field.

Recall that the energy flux and linear momentum density only differ by a factor of c^2 , and

the time-averaged linear momentum density is thus

$$\overline{\mathbf{g}} = \frac{1}{c^2} \mathbf{\mathcal{S}} = \frac{\varepsilon_0}{2} \operatorname{Re} \{ \mathbf{E} \times \mathbf{B}^* \}.$$
(2.101)

Rearranging the Equations in (2.98) we have

$$\overline{\mathbf{g}} = \frac{1}{2} \nabla \times \boldsymbol{s}_e + \boldsymbol{\varPi}_e = \frac{1}{2} \nabla \times \boldsymbol{s}_m + \boldsymbol{\varPi}_m, \qquad (2.102)$$

where

$$\boldsymbol{\Pi}_{e} \equiv \frac{\varepsilon_{0}}{2\omega} \operatorname{Im} \{ \boldsymbol{E}^{*} \cdot (\nabla) \boldsymbol{E} \}, \qquad (2.103a)$$

$$\boldsymbol{\Pi}_{m} \equiv \frac{\varepsilon_{0}c^{2}}{2\omega} \operatorname{Im} \{ \boldsymbol{B}^{*} \cdot (\nabla) \boldsymbol{B} \}, \qquad (2.103b)$$

with the notation $\mathbf{F}^* \cdot (\nabla) \mathbf{F} = \sum_j F_j^* \nabla F_j$ now being used. $\mathbf{\Pi}_e$ and $\mathbf{\Pi}_m$ are the electric and magnetic *canonical* (also called orbital) linear momentum densities [15, 60, 61]. Often, the dual-symmetric (electric-magnetic) relationship is preferred,

$$\overline{\mathbf{g}} = \frac{1}{2} \nabla \times \boldsymbol{s} + \boldsymbol{\varPi}, \qquad (2.104)$$

where

$$\boldsymbol{\Pi} \equiv \frac{1}{2} (\boldsymbol{\Pi}_e + \boldsymbol{\Pi}_m) = \frac{\varepsilon_0}{2\omega} \operatorname{Im} \{ \boldsymbol{E}^* \cdot (\nabla) \boldsymbol{E} + c^2 \boldsymbol{B}^* \cdot (\nabla) \boldsymbol{B} \}$$
(2.105)

is 'the' canonical momentum density and s is the dual-symmetric spin density (2.73). The canonical momentum has been widely studied over the last decade or so [15, 59–61, 91, 93, 105], stemming in part from the fact that the traditional 'Poynting form', $\overline{\mathbf{g}}$, is in many ways deficient as a measure of local optical momentum and energy flow in monochromatic fields (see articles [59] and [61] for in-depth discussions). The interpretation of $c^2 \boldsymbol{\Pi}_{(e/m)}$ as energy currents is bolstered by noting that it is only the divergence of the Poynting vector which appears in Poynting's theorem (2.8), meaning that any vector which differs from the Poynting vector by the addition of a curl term would also satisfy the theorem, and this is exactly the relationship between the canonical and Poynting momenta. Equivalently, from the divergence theorem, the fluxes of the Poynting and canonical energies through a closed surface are identical,

$$\oint_{S} \boldsymbol{\mathcal{S}} \cdot \mathrm{d}\boldsymbol{a} = \oint_{S} c^{2} \boldsymbol{\Pi} \cdot \mathrm{d}\boldsymbol{a}.$$
(2.106)

From these results we see some immediate physical consequences of the spin structures

discussed above. Firstly, from (2.104) and Stokes' theorem [64], we find

$$\int_{S} \boldsymbol{\mathcal{S}} \cdot d\boldsymbol{a} = \int_{S} c^{2} \boldsymbol{\Pi} \cdot d\boldsymbol{a} + \frac{c^{2}}{2} \Gamma_{\boldsymbol{s}}, \qquad (2.107)$$

where

$$\Gamma_{\boldsymbol{s}} \equiv \oint_{C} \boldsymbol{s} \cdot \mathrm{d}\boldsymbol{\ell}.$$
 (2.108)

In words, the fluxes of $c^2 \Pi$ and S are only the same through an arbitrary *open* surface if the circulation of the dual-symmetric spin density about the curve which bounds that surface is zero. Secondly, from (2.102), we have that

$$\boldsymbol{\Pi}_{m} = \boldsymbol{\Pi}_{e} + \frac{1}{2} \nabla \times (\boldsymbol{s}_{e} - \boldsymbol{s}_{m}), \qquad (2.109)$$

i.e., the electric and magnetic canonical energy currents in an optical field are only equal when the local circulations of s_e and s_m are the same. The three-wave superposition discussed above is an example of a field for which this is not the case, and we find that

$$\boldsymbol{\Pi}_{e} = \frac{\varepsilon_{0}|a|^{2}}{2c}(1+\sqrt{2})(\hat{\mathbf{x}}+\hat{\mathbf{y}}), \qquad (2.110a)$$

$$\boldsymbol{\Pi}_{m} = \frac{\varepsilon_{0}|a|^{2}}{2c} (1 + \sqrt{2} - \cos(k_{0}x - k_{0}y))(\hat{\mathbf{x}} + \hat{\mathbf{y}}).$$
(2.110b)

This is in contrast to the two-wave superposition, which as one might expect from Figure (2.4), has $\nabla \times \mathbf{s}_e = \nabla \times \mathbf{s}_m$ and thus $\mathbf{\Pi}_e = \mathbf{\Pi}_m$ for all values of θ . Note however that the curls do not vanish, they are simply equal, and thus $\mathbf{\overline{g}} \neq \mathbf{\Pi}$. We also have $\mathbf{\overline{g}} \neq \mathbf{\Pi}$ in the three-wave superposition of course. In both cases $\mathbf{\overline{g}}$ has a component which is transverse to the plane of propagation of the waves, whilst the canonical momentum lies entirely in the plane containing the wave vectors, which is in-keeping with the well-known connections between $\mathbf{\Pi}$ and the local wave vector [59, 61, 78, 97].

The reason why the three-wave superposition exhibits different electric and magnetic spin structures (energy currents), whilst the two-wave superposition does not, is likely due to the fact that the two-wave field contains no electric *or* magnetic field interference terms, i.e., both the electric and magnetic energy densities are homogeneous, whilst the three-wave field does contain magnetic field interferences. A simple calculation shows that the magnetic intensity is

$$\boldsymbol{B} \cdot \boldsymbol{B}^* = 2|a|^2 (2 - \cos(k_0 x - k_0 y)), \qquad (2.111)$$

which has clear connections with (2.110b).

To conclude this Section, and to emphasise the physical significance of some of the above observations, I should point out that the spin densities also appear very naturally in lightmatter interactions. Consider, for instance, the time-averaged optical force exerted by a monochromatic field on a molecule within the electric-dipole approximation. The well-known result is (see derivation in Appendix D.2) [15, 37, 90, 93, 105, 106]

$$\overline{\boldsymbol{F}_{\text{ED}}} = \frac{1}{2\varepsilon_0} \operatorname{Re}\{\tilde{\alpha}\} \nabla \overline{w_e} + \frac{\omega}{\varepsilon_0} \operatorname{Im}\{\tilde{\alpha}\} \left[\overline{\mathbf{g}} - \frac{1}{2} \nabla \times \boldsymbol{s}_e\right], \qquad (2.112)$$

where $\tilde{\alpha}$ is the complex electric polarizability, related to the complex electric field and dipole moment via $\tilde{\mu} = \tilde{\alpha} E$ [24]. The first term in (2.112) is the electric gradient (also called dipole) force [107, 108], which is responsible for the dynamical Stark shift and is useful in optical trapping, whilst the second term is the radiation-pressure or scattering force [37, 106]. In a field for which $\nabla \times s_e$ is zero (or approximately so), the radiation-pressure force may be interpreted as arising from the Poynting momentum, but comparing Eqs. (2.112) and (2.102), we see that it is actually Π_e which is the relevant momentum density here. An equivalent magnetic-dipole force exists as well, which is also formed from a gradient term ($\propto \nabla \overline{w_m}$) and a radiation-pressure term ($\propto \Pi_m$) [37, 90, 109]. Furthermore, the torque exerted on an electric (magnetic) dipole is directly proportional to s_e (s_m) [37, 91, 93, 105].

In a non-interfering superposition the time-averaged electric energy density (2.77) is, by definition, spatially homogeneous, and thus the electric gradient force vanishes in such a field. This allows the radiation-pressure force, or contributions from higher-order multipole moments [38], to come to the fore. This fact coupled with the richness of the spin structures which arise in non-interfering superpositions means that they are an ideal setting for exploring exotic light-matter interactions. One potential application could be in characterizing the interactions of synthetic nanoparticles with electric and magnetic fields. Whilst most molecules have greater electric than magnetic polarizabilities [93, 103], it is possible to engineer metamaterials which have a dominant magnetic response [16, 110, 111], which could be tested by placing such particles in non-interfering superpositions.

2.4 Summary

In this Chapter I have considered various aspects of optical AM.

In §2.1 I have derived from Maxwell's theory the spin and orbital contributions to the optical angular momentum. After examining their properties in a single plane wave, I turned to the

quantum theory, discussing how the operator forms of the optical SAM and OAM do not obey the 'correct' angular momentum commutation relations. I argued, somewhat against the prevailing view, that because of the inherently relativistic nature of photons, these results should not necessarily preclude us from considering S and L as 'true' angular momenta of light.

In §2.2 I discussed the theory of paraxial laser beams, deriving from the vector potential the general expressions for the electric and magnetic fields within the paraxial approximation, and discussing the characteristics of the Laguerre-Gaussian modes. I then examined what properties a beam must possess in order for it to have non-zero OAM in its direction of propagation, showing that LG modes possess this property.

In §2.3 I showed that an alternative expression for the SAM exists, which leads to the identification of distinct electric and magnetic spin densities. I then studied these local optical spins in non-interfering superpositions of plane waves, studying two specific examples which showcase the diverse spin dynamics which can be exhibited outside of the paraxial approximation. Finally, I highlighted the influence that these highly non-trivial spin structures could have on light-matter interactions.

CHAPTER 3

Molecular Quantum Electrodynamics with an Application to the Faraday Effect

In this Chapter I start by reviewing the theory of molecular QED, drawing heavily from the textbooks by Cohen-Tannoudji, Dupont-Roc and Grynberg [20], Healy [19], and Craig and Thirunamachandran [18]. I then put the molecular QED formalism to use in §3.2, presenting a new derivation of the Faraday effect, which is based on earlier work by Power and Thirunamachandran on natural optical rotation [112].

3.1 Overview of Molecular QED

QED is our most fundamental theory for the interaction of charged particles with electromagnetic fields [7, 113]. It is a fully-fledged quantum field theory, in the sense that the EM fields and charges are both treated as *quantized fields*. Molecular QED is a low-energy approximation to this more fundamental theory, which holds when the particles travel at speeds much less than the speed of light, and the likelihood of creating or annihilating matter particles is negligible [19]. The starting point for developing the theory is the Lagrangian formulation of (microscopic) classical electrodynamics, as I outline below.

3.1.1 Lagrangian and Hamiltonian Formalisms

The classical equations of motion for a system of N particles may be found from Hamilton's principle, which states that the true trajectories of the particles are those which minimize the integral

$$S = \int_{t_1}^{t^2} \mathrm{d}t \ L(q, \dot{q}, t), \tag{3.1}$$

where $L(q, \dot{q}, t)$ is the Lagrangian, which is a function of the generalized coordinates (q_1, \ldots, q_{3N}) , the generalized velocities $(\dot{q}_1, \ldots, \dot{q}_{3N})$, and, potentially, of time [114]. The equations of motion are then determined explicitly from the Euler-Lagrange equations,

$$\frac{\mathrm{d}}{\mathrm{d}t} \left(\frac{\partial L}{\partial \dot{q}_n} \right) - \frac{\partial L}{\partial q_n} = 0, \qquad (3.2)$$

for n = 1, ..., 3N. This variational (Lagrangian) approach to mechanics is transformed to the so-called canonical (Hamiltonian) formalism by means of the Legendre transformation. This essentially entails moving away from a description in terms of generalized coordinates and velocities to one in terms of the coordinates and their canonically conjugate momenta. The momentum p_n which is conjugate to q_n is

$$p_n \equiv \frac{\partial L}{\partial \dot{q}_n}.\tag{3.3}$$

The Legendre transformation defines the Hamiltonian function [19, 114]:

$$H(q, p, t) \equiv \left[\sum_{n} p_n \dot{q}_n - L(q, \dot{q}, t)\right]_{(q, p)},$$
(3.4)

where the notation $[\cdot]_{(q,p)}$ is to emphasise that the generalized velocities should be written in terms of q and p. In most cases of practical interest, H corresponds to the energy of the mechanical system. The equations of motion are given by Hamilton's equations,

$$\dot{q}_n = \frac{\partial H}{\partial p_n}, \qquad \dot{p}_n = -\frac{\partial H}{\partial q_n}.$$
(3.5)

These can also be written as

$$\dot{q}_n = \{q_n, H\}, \qquad \dot{p}_n = \{p_n, H\},$$
(3.6)

where

$$\{A, B\} = \sum_{n} \left(\frac{\partial A}{\partial q_n} \frac{\partial B}{\partial p_n} - \frac{\partial A}{\partial p_n} \frac{\partial B}{\partial q_n} \right)$$
(3.7)

is the *Poisson bracket* of two functions A(q, p) and B(q, p). The time derivative of an arbitrary function of q and p is given by

$$\dot{A} = \{A, H\} + \frac{\partial A}{\partial t}.$$
(3.8)

The Lagrangian and Hamiltonian formalisms may be extended to the study of fields. To specify the state or configuration of a field at a particular time we must know its value at all points, so the generalized coordinates are no longer indexed by the discrete label n but by the continuous label \mathbf{r} , $Q = Q(\mathbf{r})$ [19, 20]. It might be the case, as in electrodynamics, that the system actually depends on multiple generalized coordinate fields, $Q_m(\mathbf{r})$, $m = 1, \ldots, M$. The Lagrangian is written as

$$L = \int \mathrm{d}^3 r \ \mathcal{L},\tag{3.9}$$

where $\mathcal{L} = \mathcal{L}(Q, \dot{Q}, \nabla Q, t)$ is the Lagrangian density (note it may also be a function of the spatial derivatives of $Q_m(\mathbf{r})$). The Euler-Lagrange equations in this case are [18]

$$\frac{\partial}{\partial t} \left(\frac{\partial \mathcal{L}}{\partial \dot{Q}_m(\boldsymbol{r})} \right) + \frac{\partial}{\partial x_j} \left(\frac{\partial \mathcal{L}}{\partial (\partial_j Q_m(\boldsymbol{r}))} \right) - \frac{\partial \mathcal{L}}{\partial Q_m(\boldsymbol{r})} = 0, \qquad (3.10)$$

for m = 1, ..., M, and the repeated j index implies summation. The canonical momenta are defined in a similar way to (3.3),

$$\Pi_m(\mathbf{r}) \equiv \frac{\partial \mathcal{L}}{\partial \dot{Q}_m(\mathbf{r})}.$$
(3.11)

The Hamiltonian can be expressed as

$$H = \int \mathrm{d}^3 r \ \mathcal{H},\tag{3.12}$$

where $\mathcal{H} = \mathcal{H}(Q, \Pi, \nabla Q, t)$ is the Hamiltonian density, which is defined via

$$\mathcal{H}(Q,\Pi,\nabla Q,t) = \sum_{m} \Pi_{m} \dot{Q}_{m} - \mathcal{L}.$$
(3.13)

In electrodynamics we have a system which is partially discrete (the charges) and partially continuous (the EM field). For the particles the generalized coordinates and velocities are simply the Cartesian components of each particle's position and velocity vectors, $\{\boldsymbol{q}_{\alpha}, \boldsymbol{v}_{\alpha} \mid \alpha = 1, \ldots, N\}$. It turns out that the most appropriate generalized coordinates and velocities for the EM field are the potentials and their time derivatives, $\{A_i(\boldsymbol{r}), \dot{A}_i(\boldsymbol{r}), \phi(\boldsymbol{r}), \dot{\phi}(\boldsymbol{r}) \mid i = x, y, z\}$.

An appropriate Lagrangian for the combined system of particles + field—which following [20] I call the 'standard' Lagrangian—is

$$L_S = L_{\text{par}}^S + \int d^3r \left[\mathcal{L}_{\text{rad}}^S + \mathcal{L}_{\text{int}}^S \right], \qquad (3.14)$$

where¹

$$L_{\rm par}^S = \sum_{\alpha} \frac{1}{2} m_{\alpha} \boldsymbol{v}_{\alpha}^2, \qquad (3.15a)$$

$$\mathcal{L}_{\rm rad}^{S} = \frac{\varepsilon_0}{2} \left[\boldsymbol{E}^2(\boldsymbol{r}) - c^2 \boldsymbol{B}^2(\boldsymbol{r}) \right], \qquad (3.15b)$$

$$\mathcal{L}_{int}^{S} = \boldsymbol{j}(\boldsymbol{r}) \cdot \boldsymbol{A}(\boldsymbol{r}) - \rho(\boldsymbol{r})\phi(\boldsymbol{r}), \qquad (3.15c)$$

are the particle, radiation, and interaction parts of the Lagrangian, respectively. Although \mathcal{L}_{rad}^{S} is written in terms of the EM *fields*, they should be understood as functions of the generalized coordinates and velocities, through Eqs. (B.14),

$$oldsymbol{B} =
abla imes oldsymbol{A},$$
 $oldsymbol{E} = -\dot{oldsymbol{A}} -
abla \phi.$

I say that L_S is 'an' appropriate Lagrangian for the system because any two Lagrangians

¹In Appendix B.1 the microscopic EM fields are denoted using lowercase letters and the macroscopic fields using uppercase letters. All of the fields considered in this Chapter are, naturally, of the microscopic variety, but I shall now denote these by uppercase letters as no confusion should arise.

related by

$$L' = L + \frac{\mathrm{d}}{\mathrm{d}t}F,\tag{3.16}$$

for some arbitrary function F(q, Q, t), are entirely equivalent, in the sense that they lead to the same equations of motion [20].

Whilst the standard Lagrangian reproduces the Maxwell and Lorentz equations, it is actually not particularly useful for my purposes. The most important point in this regard is that L_S does not contain the generalized velocity $\dot{\phi}$, which means the canonical momentum Π_{ϕ} is zero. This presents a major problem when we try to move to the quantum theory via canonical quantization (covered in the next Section), which requires a commutator between ϕ and Π_{ϕ} which is not identically zero. For further discussion see [20, Ch. II].

To avoid this issue, I follow the usual approach of non-relativistic QED and work in the Coulomb gauge (B.21),

 $\nabla \cdot \boldsymbol{A} = 0,$

so the vector potential is entirely transverse, $A = A_{\perp}$. In this gauge we have the relationships

$$\boldsymbol{B} = \nabla \times \boldsymbol{A}_{\perp}, \tag{3.17a}$$

$$\boldsymbol{E}_{\perp} = -\dot{\boldsymbol{A}}_{\perp}, \qquad (3.17b)$$

$$\boldsymbol{E}_{\parallel} = -\nabla\phi. \tag{3.17c}$$

The last of these is equivalent (recall Eq. (B.8a)) to Poisson's equation from electrostatics,

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon_0},\tag{3.18}$$

which demonstrates that ϕ is not an actual dynamical variable of the EM field but a prescribed function of the particles' position vectors. Thus, the components of the transverse field (A_i^{\perp}) and its time derivative (\dot{A}_i^{\perp}) act alone as the generalized coordinates and velocities of the field. Therefore instead of L_S I shall take as my Lagrangian [18–20]

$$L = L_{\text{par}} + \int d^3 r \bigg[\mathcal{L}_{\text{rad}} + \mathcal{L}_{\text{int}} \bigg], \qquad (3.19)$$

where

$$L_{\text{par}} = \sum_{\alpha} \frac{1}{2} m_{\alpha} \boldsymbol{v}_{\alpha}^2 - V_{\text{Coul}}, \qquad (3.20a)$$

$$\mathcal{L}_{\rm rad} = \frac{\varepsilon_0}{2} \left[\dot{\boldsymbol{A}}_{\perp}^2(\boldsymbol{r}) - c^2 (\nabla \times \boldsymbol{A}_{\perp}(\boldsymbol{r}))^2 \right], \qquad (3.20b)$$

$$\mathcal{L}_{\text{int}} = \boldsymbol{j}(\boldsymbol{r}) \cdot \boldsymbol{A}_{\perp}(\boldsymbol{r}), \qquad (3.20c)$$

are again the particle, radiation, and interaction contributions. V_{Coul} is the Coulomb energy of the charges (associated with $\phi = \phi_C$, the Coulomb potential).

We can transition to the Hamiltonian via the method outlined above. The canonical momentum of particle α is found to be

$$\boldsymbol{p}_{\alpha} = m_{\alpha} \boldsymbol{v}_{\alpha} + e_{\alpha} \boldsymbol{A}_{\perp}(\boldsymbol{q}_{\alpha}), \qquad (3.21)$$

which clearly differs from the mechanical momentum $m_{\alpha} \boldsymbol{v}_{\alpha}$. The two are equal in the absence of fields, and the substitution

$$m_{lpha} \boldsymbol{v}_{lpha}
ightarrow m_{lpha} \boldsymbol{v}_{lpha} + e_{lpha} \boldsymbol{A}_{\perp}(\boldsymbol{q}_{lpha})$$

when fields are present is known as 'minimal coupling'. For the momentum conjugate to A_{\perp} we find

$$\boldsymbol{\Pi}(\boldsymbol{r}) = \varepsilon_0 \dot{\boldsymbol{A}}_{\perp}(\boldsymbol{r}) = -\varepsilon_0 \boldsymbol{E}_{\perp}(\boldsymbol{r}). \tag{3.22}$$

Note that the *canonical* AM of the field is $\mathbf{A}_{\perp} \times \mathbf{\Pi} = \varepsilon_0 \mathbf{A}_{\perp} \times \dot{\mathbf{A}}_{\perp} = \varepsilon_0 \mathbf{E}_{\perp} \times \mathbf{A}_{\perp}$, which is the spin AM density discussed in the previous Chapter.

The Hamiltonian is

$$H = \sum_{\alpha} \frac{1}{2m_{\alpha}} \left[\boldsymbol{p}_{\alpha} - e_{\alpha} \boldsymbol{A}_{\perp}(\boldsymbol{q}_{\alpha}) \right]^{2} + V_{\text{Coul}} + \frac{1}{2} \int \mathrm{d}^{3}r \left[\varepsilon_{0}^{-1} \boldsymbol{\Pi}^{2}(\boldsymbol{r}) + \mu_{0}^{-1} (\nabla \times \boldsymbol{A}_{\perp}(\boldsymbol{r}))^{2} \right].$$
(3.23)

Rewriting the integral in terms of the fields allows us to recognize this as the classical energy of the combined system.

3.1.2 Canonical Quantization

The theory of electrodynamics may be 'quantized', as was first done by Dirac [115], by replacing the generalized coordinates and their conjugate momenta by operators and imposing upon them the so-called canonical commutation relations. This procedure is known as 'canonical quantization'². The canonical commutation relations in our case are [18–20]

$$[\hat{q}_{\alpha i}, \hat{p}_{\beta j}] = i\hbar \delta_{\alpha\beta} \delta_{ij}, \qquad (3.24a)$$

$$[\hat{A}_i^{\perp}(\boldsymbol{r}), \hat{\Pi}_j(\boldsymbol{r}')] = i\hbar \delta_{ij}^{\perp}(\boldsymbol{r} - \boldsymbol{r}'), \qquad (3.24b)$$

with all other commutators between these operators being identically zero. The fact that it is the transverse delta function $\delta_{ij}^{\perp}(\mathbf{r})$ (see Appendix A.1) which appears on the right-hand side of (3.24b) is due to our working in the Coulomb gauge [19, 20] (see in particular p. 120 of [20]). Note that the operators in (3.24) are in the Schrödinger picture (see Appendix C.2), but the relations also hold for operators in the Heisenberg picture at equal times.

The Hamiltonian *operator* is just (3.23) with the coordinates and momenta promoted to operators,

$$\hat{H} = \sum_{\alpha} \frac{1}{2m_{\alpha}} \left[\hat{\boldsymbol{p}}_{\alpha} - e_{\alpha} \hat{\boldsymbol{A}}_{\perp}(\hat{\boldsymbol{q}}_{\alpha}) \right]^{2} + \hat{V}_{\text{Coul}} + \frac{1}{2} \int \mathrm{d}^{3}r \left[\varepsilon_{0}^{-1} \hat{\boldsymbol{\Pi}}^{2}(\boldsymbol{r}) + \mu_{0}^{-1} (\nabla \times \hat{\boldsymbol{A}}_{\perp}(\boldsymbol{r}))^{2} \right]. \quad (3.25)$$

(Note \hat{V}_{Coul} is an operator only through its dependence on the \hat{q}_{α} .)

Because the nuclei are much more massive than the electrons, it is often reasonable to work within the fixed-nuclei approximation [18, 19] (a zeroth-order Born-Oppenheimer approximation [24]), in which we ignore nuclear dynamics. It is also convenient to explicitly take account of the grouping of particles into atoms or molecules. Under these assumptions, we write \hat{H} in the form [18]

$$\hat{H} = \hat{H}_{\rm mol} + \hat{H}_{\rm rad} + \hat{H}_{\rm int}^{\rm min}, \qquad (3.26)$$

²Alternative quantization procedures exist, e.g., the path integral approach [74, 116]. However, the canonical approach is the most common, especially in the non-relativistic theory.

where

$$\hat{H}_{\rm mol} = \sum_{\zeta} \hat{H}_{\rm mol}(\zeta); \qquad \hat{H}_{\rm mol}(\zeta) = \sum_{\alpha} \frac{1}{2m_e} \hat{\boldsymbol{p}}_{\alpha}^2(\zeta) + \hat{V}(\zeta), \qquad (3.27a)$$

$$\hat{H}_{\rm rad} = \frac{1}{2} \int \mathrm{d}^3 r \left[\varepsilon_0^{-1} \hat{\boldsymbol{\Pi}}^2(\boldsymbol{r}) + \mu_0^{-1} (\nabla \times \hat{\boldsymbol{A}}_{\perp}(\boldsymbol{r}))^2 \right] = \frac{\varepsilon_0}{2} \int \mathrm{d}^3 r \left[\hat{\boldsymbol{E}}_{\perp}^2(\boldsymbol{r}) + c^2 \hat{\boldsymbol{B}}^2(\boldsymbol{r}) \right], \quad (3.27b)$$

$$\hat{H}_{\text{int}}^{\min} = -\frac{e_e}{m_e} \sum_{\zeta,\alpha} \hat{\boldsymbol{p}}_{\alpha}(\zeta) \cdot \hat{\boldsymbol{A}}_{\perp}(\hat{\boldsymbol{q}}_{\alpha}(\zeta)) + \frac{e_e^2}{2m_e} \sum_{\zeta,\alpha} \hat{\boldsymbol{A}}_{\perp}^2(\hat{\boldsymbol{q}}_{\alpha}(\zeta)) + \hat{V}_{\text{inter}}.$$
(3.27c)

The sums over ζ extend over the molecules, the sums over α are now restricted to the electrons, and m_e and e_e are the mass and charge of an electron. $\hat{H}_{\text{mol}}(\zeta)$ is the Hamiltonian of the ζ^{th} molecule, which includes the momenta of ζ 's electrons, and $\hat{V}(\zeta)$ is the Coulomb interaction between the nuclei and electrons of ζ . \hat{H}_{rad} is the Hamiltonian of the transverse radiation field, which in the absence of charges coincides with the total energy operator of the field. $\hat{H}_{\text{int}}^{\min}$ is the interaction Hamiltonian—it contains all the terms which explicitly couple the charges and fields. The superscript 'm.c.' indicates that this is the 'minimal coupling' form of the interaction. \hat{V}_{inter} is the Coulomb interaction between different molecules. When it comes to performing calculations, particularly in perturbation theory, we usually write the Hamiltonian in the form $\hat{H} = \hat{H}_0 + \hat{H}_{\text{int}}^{\min}$, where

$$\hat{H}_0 = \hat{H}_{\rm mol} + \hat{H}_{\rm rad} \tag{3.28}$$

is treated as the 'unperturbed' Hamiltonian, whose eigenspectrum is assumed to be know.

It is practical to Fourier transform the field operators and to write them as sums (or integrals) over transverse field modes, defined by the wave vectors \mathbf{k} and their orthogonal polarization vectors $\hat{\mathbf{\epsilon}}_{\mathbf{k}\lambda}$ ($\lambda = 1, 2$) [18–20, 23]. The derivation is simple and I shall just state the results. The transverse vector potential operator (in the Schrödinger picture) has the expansion [18, 23]

$$\hat{\boldsymbol{A}}_{\perp}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\lambda} \mathcal{N}(k) \omega_{k}^{-1} \left[\hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda} + \hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda}^{*} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda}^{\dagger} \right], \qquad (3.29)$$

where $\omega_k = ck = c|\mathbf{k}|$. A particular choice of polarization basis is assumed here, the most common choices being the linear or circular bases, and the mode operators $\hat{a}_{\mathbf{k}\lambda}^{(\dagger)}$ are defined relative to this basis. The normalization coefficient is

$$\mathcal{N}(k) = \sqrt{\frac{\hbar c k}{2\varepsilon_0 V}},\tag{3.30}$$

where V is the 'quantization volume' within which the field is confined. The expansion of

the canonical field momentum is

$$\hat{\boldsymbol{\Pi}}(\boldsymbol{r}) = -i\varepsilon_0 \sum_{\boldsymbol{k},\lambda} \mathcal{N}(k) \left[\hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda} - \hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda}^* e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda}^\dagger \right].$$
(3.31)

The mode expansions for the Schrödinger-picture transverse electric field and magnetic field operators are easily found from those for \hat{A}_{\perp} and $\hat{\Pi}$ [18, 23]:

$$\hat{\boldsymbol{E}}_{\perp}(\boldsymbol{r}) = i \sum_{\boldsymbol{k},\lambda} \mathcal{N}(k) \bigg[\hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda} - \hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda}^* e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda}^{\dagger} \bigg], \qquad (3.32a)$$

$$\hat{\boldsymbol{B}}(\boldsymbol{r}) = \frac{i}{c} \sum_{\boldsymbol{k},\lambda} \mathcal{N}(k) \left[\hat{\boldsymbol{\beta}}_{\boldsymbol{k}\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda} - \hat{\boldsymbol{\beta}}_{\boldsymbol{k}\lambda}^* e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}_{\boldsymbol{k}\lambda}^\dagger \right],$$
(3.32b)

where

$$\hat{\boldsymbol{\beta}}_{\boldsymbol{k}\lambda} \equiv \frac{\boldsymbol{k} \times \hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda}}{k}.$$
(3.33)

For brevity I will often replace the double sum over \boldsymbol{k} and λ with a single sum over the label s, with the understanding that a single value of s specifies a particular mode $(\boldsymbol{k}, \lambda)$.

The mode operators \hat{a}_s and \hat{a}_s^{\dagger} acquire a physical meaning by noting the mode expansion of \hat{H}_{rad} , Eq. (3.27b), which is

$$\hat{H}_{\rm rad} = \sum_{s} \hbar \omega_s \left(\hat{a}_s^{\dagger} \hat{a}_s + \frac{1}{2} \right). \tag{3.34}$$

This is formally identical to an infinite set of (non-interacting) harmonic oscillators [18, 23]. The eigenstates of each mode are known as the number states, denoted $|n(\mathbf{k}, \lambda)\rangle$ or $|n_s\rangle$. The eigenspectrum of each mode (oscillator) is a discrete 'ladder' of states, each separated by the same energy difference $\hbar\omega_s$. This gives the physical intuition behind the name 'number state'—a state which is N steps up the ladder can be thought of as a state which contains N quanta, or photons, of the radiation field. The operator \hat{a}_s^{\dagger} creates an excitation of mode s (i.e., moves one rung up the ladder), whilst \hat{a}_s destroys an excitation of mode s (moves one rung down the ladder), and for this reason they are known as the creation and annihilation operators, respectively. More precisely:

$$\hat{a}_{\boldsymbol{k}\lambda} |n(\boldsymbol{k},\lambda)\rangle = \sqrt{n} |n-1(\boldsymbol{k},\lambda)\rangle,$$
 (3.35a)

$$\hat{a}_{\boldsymbol{k}\lambda}^{\dagger} | n(\boldsymbol{k},\lambda) \rangle = \sqrt{n+1} | n+1(\boldsymbol{k},\lambda) \rangle.$$
(3.35b)

The creation and annihilation operators obey the commutation relations

$$[\hat{a}_{\boldsymbol{k}\lambda}, \hat{a}^{\dagger}_{\boldsymbol{k}'\lambda'}] = \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{\lambda\lambda'}, \qquad (3.36a)$$

$$[\hat{a}_{\boldsymbol{k}\lambda}, \hat{a}_{\boldsymbol{k}'\lambda'}] = 0, \qquad (3.36b)$$

$$[\hat{a}_{\boldsymbol{k}\lambda}^{\dagger}, \hat{a}_{\boldsymbol{k}'\lambda'}^{\dagger}] = 0. \tag{3.36c}$$

Note that these are the commutation relations for the mode operators with respect to a particular choice of polarization basis. The operators relative to two different bases can have commutation relations which differ from the above, which can be deduced by writing the operators relative to one basis in terms of the operators relative to the other [19, p. 76]. The operator $\hat{n}_s \equiv \hat{a}_s^{\dagger} \hat{a}_s$ which appears in (3.34) is the *number operator* of mode *s*, and simply counts the number of excitations present in that mode:

$$\hat{n}_{\boldsymbol{k}\lambda} |n(\boldsymbol{k},\lambda)\rangle = n |n(\boldsymbol{k},\lambda)\rangle.$$
 (3.37)

The total photon number operator, $\hat{N} \equiv \sum_{s} \hat{n}_{s}$, gives the number of excitations present in all modes.

Each mode contains a special state known as the ground or vacuum state, $|0(\mathbf{k}, \lambda)\rangle$, which is defined via [18, 23]

$$\hat{a}_{\boldsymbol{k}\lambda} \left| 0(\boldsymbol{k}, \lambda) \right\rangle = 0. \tag{3.38}$$

The unique state

$$|\operatorname{vac}\rangle \equiv |0(\boldsymbol{k}_1, \lambda_1); 0(\boldsymbol{k}_2, \lambda_2); \dots; 0(\boldsymbol{k}_i, \lambda_i); \dots; 0(\boldsymbol{k}_j, \lambda_j); \dots\rangle$$
(3.39)

i.e., the state which contains no photons in any mode, is known as 'the' vacuum state. Obviously

$$\hat{N} |\mathrm{vac}\rangle = 0,$$
 (3.40)

or equivalently, $\hat{a}_{\boldsymbol{k}\lambda} |\text{vac}\rangle = 0$ for all $(\boldsymbol{k}, \lambda)$.

It is often physically intuitive and useful to partition the field operators into two terms,

$$\hat{oldsymbol{F}}(oldsymbol{r})=\hat{oldsymbol{F}}^+(oldsymbol{r})+\hat{oldsymbol{F}}^-(oldsymbol{r}),$$

where \hat{F}^+ is responsible for absorption (photon annihilation) and \hat{F}^- for emission (photon creation). These are known as the 'positive' and 'negative' frequency contributions, respectively [23, 113]. We have the following positive-frequency contributions to \hat{A}_{\perp} , \hat{E}_{\perp} and \hat{B}

from mode $s = (\mathbf{k}_s, \lambda_s)$:

$$\hat{A}_{s}^{+} = \frac{\mathscr{N}(k_{s})}{\omega_{s}} \hat{\boldsymbol{\epsilon}}_{s} e^{i\boldsymbol{k}_{s}\cdot\boldsymbol{r}} \hat{a}_{s}, \qquad (3.41a)$$

$$\hat{\boldsymbol{E}}_{s}^{+} = i \mathcal{N}(k_{s}) \hat{\boldsymbol{\epsilon}}_{s} e^{i\boldsymbol{k}_{s} \cdot \boldsymbol{r}} \hat{a}_{s}, \qquad (3.41b)$$

$$\hat{\boldsymbol{B}}_{s}^{+} = i \frac{\mathcal{N}(k_{s})}{c} \hat{\boldsymbol{\beta}}_{s} e^{i\boldsymbol{k}_{s}\cdot\boldsymbol{r}} \hat{a}_{s}.$$
(3.41c)

3.1.3 Multipolar Hamiltonian

Molecular dimensions are often small compared to optical wavelengths, which means the value of the vector potential varies by only a small amount across the molecule. We can therefore replace the operators $\hat{A}_{\perp}(q_{\alpha}(\zeta))$ in (3.27c) with Taylor expansions about some point R_{ζ} , usually chosen as the position of the molecular centre-of-mass, and usually taken as a *c*-number (i.e., $R_{\zeta} = \langle \hat{R}_{\zeta} \rangle$, not \hat{R}_{ζ}). This is the long-wavelength approximation (LWA). To zeroth-order the interaction Hamiltonian (3.27c) becomes

$$\hat{H}_{\text{int}}^{\min} = -\frac{e_e}{m_e} \sum_{\zeta,\alpha} \hat{\boldsymbol{p}}_{\alpha}(\zeta) \cdot \hat{\boldsymbol{A}}_{\perp}(\boldsymbol{R}_{\zeta}) + \frac{e_e^2}{2m_e} \sum_{\zeta} \hat{\boldsymbol{A}}_{\perp}^2(\boldsymbol{R}_{\zeta}) + \hat{V}_{\text{inter}}.$$
(3.42)

So far, I have been considering the *minimal coupling* form of the interaction Hamiltonian. I shall now discuss an alternative form for the interaction, known as the *multipolar* form, which is particularly useful when working within the LWA, and involves writing the interaction in terms of the molecular multipole moments (see Appendix B.3).

We can go from the minimal coupling to the multipolar form of Hamiltonian in a variety of ways. One is to transform the Coulomb-gauge Lagrangian (3.19) into an equivalent one, via a transformation of the form (3.16), which is essentially equivalent to a change of gauge [18, 20, 117]. Canonical quantization then proceeds relative to this new Lagrangian, producing different canonical momentum and Hamiltonian operators. Alternatively, we can use the Coulomb-gauge Lagrangian to reach the quantum theory, as above, and then perform a unitary transformation, known as the Power-Zienau-Woolley (PZW) transformation [118, 119], to reach an equivalent quantum description of the system [19, 20, 120–122]. This is the approach I take. The basic idea is to find the transformed coordinates and momenta,

$$\hat{\boldsymbol{q}}'_{\alpha} = U_{\text{PZW}} \hat{\boldsymbol{q}}_{\alpha} U_{\text{PZW}}^{\dagger}, \qquad \hat{\boldsymbol{A}}'_{\perp} = U_{\text{PZW}} \hat{\boldsymbol{A}}_{\perp} U_{\text{PZW}}^{\dagger},$$
$$\hat{\boldsymbol{p}}'_{\alpha} = U_{\text{PZW}} \hat{\boldsymbol{p}}_{\alpha} U_{\text{PZW}}^{\dagger}, \qquad \hat{\boldsymbol{\Pi}}' = U_{\text{PZW}} \hat{\boldsymbol{\Pi}} U_{\text{PZW}}^{\dagger},$$

and to then rewrite the Hamiltonian (3.25) in terms of these. The unitary operator which effects the transformation is [18–20, 23, 122]

$$U_{\rm PZW} = \exp\left\{\frac{i}{\hbar}W\right\}, \qquad W = \int d^3r \; \hat{\boldsymbol{P}}(\boldsymbol{r}) \cdot \hat{\boldsymbol{A}}_{\perp}(\boldsymbol{r}), \qquad (3.43)$$

where $\hat{P}(r)$ is the microscopic polarization field operator (see Eq. (B.37)) [18, 20, 23]. A very useful identity in the derivation is [18–20]

$$e^{X}Ae^{-X} = A + [X, A] + \frac{1}{2!}[X, [X, A]] + \dots$$
 (3.44)

W is a function of \hat{A}_{\perp} and $\{\hat{q}_{\alpha}\}$ (through \hat{P}), but not of the canonical momenta, and thus W clearly commutes with the generalized coordinates, so that

$$\hat{oldsymbol{q}}_lpha'=\hat{oldsymbol{q}}_lpha,\qquad \hat{oldsymbol{A}}_\perp'=\hat{oldsymbol{A}}_\perp.$$

To find the new field momentum we need to evaluate the following commutator,

$$[W, \hat{\Pi}_{i}(\boldsymbol{r})] = \int \mathrm{d}^{3}r' \, \hat{P}_{j}(\boldsymbol{r}')[\hat{A}_{j}^{\perp}(\boldsymbol{r}'), \, \hat{\Pi}_{i}(\boldsymbol{r})]$$

$$= \int \mathrm{d}^{3}r' \, \hat{P}_{j}(\boldsymbol{r}')i\hbar\delta_{ji}^{\perp}(\boldsymbol{r}'-\boldsymbol{r})$$

$$= i\hbar\hat{P}_{i}^{\perp},$$
(3.45)

where we have used the canonical commutation relation (3.24), and \hat{P}_i^{\perp} is the *i*th component of the transverse polarization field, \hat{P}_{\perp} . This leads to

$$\hat{\boldsymbol{\Pi}}' = \hat{\boldsymbol{\Pi}} - \hat{\boldsymbol{P}}_{\perp}, \qquad (3.46)$$

which, using Eqs. (3.22) and (B.6a), may be written as

$$\hat{\boldsymbol{\Pi}}' = -(\varepsilon_0 \hat{\boldsymbol{E}}_{\perp} + \hat{\boldsymbol{P}}_{\perp}) = -\hat{\boldsymbol{D}}_{\perp}.$$
(3.47)

Thus the transformed field momentum is no longer physically associated with the electric field operator, but with the transverse component of the *electric displacement* field operator [120].

From (3.44) we can show that the transformed particle momenta may be written as [19]

$$\hat{p}_{\alpha i}' = \hat{p}_{\alpha i} - \frac{\partial}{\partial \hat{q}_{\alpha i}} W.$$
(3.48)

The multipolar Hamiltonian can be written in an entirely general form, but it is not of much interest here, as I will only be interested in the Hamiltonian up to the magnetic dipole and electric quadrupole contributions (for the full multipolar Hamiltonian see, e.g., [18, §10.10]). The Hamiltonian to the desired order is derived by expanding the polarization field that appears in (3.48) and (3.47), using (B.39), to include the necessary terms (i.e., electric dipole, electric quadrupole, and so on). After some work, the multipolar form of the Hamiltonian, up to magnetic dipole and electric quadrupole terms, can be written as

$$\hat{H} = \hat{H}_0' + \hat{H}_{\text{int}}^{\text{mult}}, \qquad (3.49)$$

where $\hat{H}'_0 = U_{\text{PZW}} \hat{H}_0 U^{\dagger}_{\text{PZW}}$ (recall Eqs. (3.28) and (3.27a)–(3.27b)) and [18]

$$\hat{H}_{\text{int}}^{\text{mult}} = -\sum_{\zeta} \left[\hat{\boldsymbol{\mu}}(\zeta) \cdot \varepsilon_0^{-1} \hat{\boldsymbol{D}}_{\perp}(\boldsymbol{R}_{\zeta}) + \hat{Q}_{ij}(\zeta) \partial_i \varepsilon_0^{-1} \hat{D}_j^{\perp}(\boldsymbol{R}_{\zeta}) + \hat{\boldsymbol{m}}(\zeta) \cdot \hat{\boldsymbol{B}}(\boldsymbol{R}_{\zeta}) \right] \\ + \frac{e_e^2}{8m_e} \sum_{\zeta,\alpha} \left[(\hat{\boldsymbol{q}}_{\alpha} - \boldsymbol{R}_{\zeta}) \times \hat{\boldsymbol{B}}(\boldsymbol{R}_{\zeta}) \right]^2 + \frac{1}{2\varepsilon_0} \sum_{\zeta} \int d^3r \, \hat{\boldsymbol{P}}_{\zeta\perp}^2(\boldsymbol{r}). \quad (3.50)$$

The first line contains the electric dipole (E1), electric quadrupole (E2), and magnetic dipole (M1) interactions. The first term of the second line is quadratic in the magnetic field operator and can therefore almost always be neglected. The reasons for this are twofold: firstly, because this term is quadratic in the magnetic field, it is also quadratic in the creation and annihilation operators. It can therefore only take part in interactions involving an even number of photon emissions and/or absorptions. Secondly, the strength of the magnetic interaction is inherently weaker than the electric interaction, and thus those interactions involving an even number of photon creations or annihilations are more likely to occur via two E1 interactions or an E1 interaction and an M1 interaction. The final term depends only on the molecular degrees of freedom, so cannot take part in radiative processes, and essentially represents a correction to the molecular self-energies [18, 20]. In applications, I will only ever consider the first line of this expression.

The multipolar Hamiltonian (3.49) corresponds to the minimal coupling Hamiltonian (3.26) expanded to 'first-order' in the LWA, i.e., first derivatives are retained in the Taylor expansion of the vector potentials. The multipolar Hamiltonian which corresponds to the zeroth-order minimal coupling Hamiltonian, Eq. (3.42), is

$$\hat{H} = \hat{H}'_0 + \hat{H}^{\rm ED}_{\rm int},$$
(3.51)

where

$$\hat{H}_{\text{int}}^{\text{ED}} = -\sum_{\zeta} \hat{\boldsymbol{\mu}}(\zeta) \cdot \varepsilon_0^{-1} \hat{\boldsymbol{D}}_{\perp}(\boldsymbol{R}_{\zeta}) + \frac{1}{2\varepsilon_0} \sum_{\zeta} \int \mathrm{d}^3 r \, \hat{\boldsymbol{P}}_{\zeta\perp}^2(\boldsymbol{r}).$$
(3.52)

This is known as the electric dipole (ED) Hamiltonian. Because of the close connection between this and the (zeroth-order) LWA, the term *electric-dipole approximation* is often used synonymously.

The field operators can be expanded in terms of the transformed creation and annihilation operators, $\hat{a}'_s = U_{\text{PZW}} \hat{a}_s U^{\dagger}_{\text{PZW}}$ and $\hat{a}'^{\dagger}_s = U_{\text{PZW}} \hat{a}^{\dagger}_s U^{\dagger}_{\text{PZW}}$. The new vector potential and field momentum have the mode expansions

$$\hat{A}'_{\perp}(\boldsymbol{r}) = \sum_{s} \frac{\mathscr{N}(k_{s})}{\omega_{s}} \left[\hat{\boldsymbol{\epsilon}}_{s} e^{i\boldsymbol{k}_{s}\cdot\boldsymbol{r}} \hat{a}'_{s} + \hat{\boldsymbol{\epsilon}}^{*}_{s} e^{-i\boldsymbol{k}_{s}\cdot\boldsymbol{r}} \hat{a}'_{s}^{\dagger} \right],$$
$$\hat{\boldsymbol{\Pi}}'(\boldsymbol{r}) = -i\varepsilon_{0} \sum_{s} \mathscr{N}(k_{s}) \left[\hat{\boldsymbol{\epsilon}}_{s} e^{i\boldsymbol{k}_{s}\cdot\boldsymbol{r}} \hat{a}'_{s} - \hat{\boldsymbol{\epsilon}}^{*}_{s} e^{-i\boldsymbol{k}_{s}\cdot\boldsymbol{r}} \hat{a}'_{s}^{\dagger} \right].$$

Because $\hat{A}'_{\perp} = \hat{A}_{\perp}$, the vector potential has the special feature that it can be written identically in terms of either set of mode operators. Whilst the same is not true of the momentum, it is the case that the operator \hat{E}_{\perp} expanded in terms of the original operators, $\hat{a}_{s}^{(\dagger)}$, has the *exact same form* as the operator $\varepsilon_{0}^{-1}\hat{D}_{\perp}$ expanded in terms of the transformed operators, $\hat{a}_{s}^{\prime(\dagger)}$:

$$\varepsilon_0^{-1} \hat{\boldsymbol{D}}_{\perp}(\boldsymbol{r}) = i \sum_{\boldsymbol{k},\lambda} \mathcal{N}(k) \bigg[\hat{\boldsymbol{\epsilon}}_{\boldsymbol{k}\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}'_{\boldsymbol{k}\lambda} - \hat{\boldsymbol{\epsilon}}^*_{\boldsymbol{k}\lambda} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \hat{a}'_{\boldsymbol{k}\lambda} \bigg].$$
(3.53)

As with the other field operators, we can write \hat{D}_{\perp} as the sum of a positive-frequency and a negative-frequency contribution, with the positive-frequency contribution from mode s being

$$\varepsilon_0^{-1} \hat{\boldsymbol{D}}_s^+ = i \mathcal{N}(k_s) \hat{\boldsymbol{\epsilon}}_s e^{i \boldsymbol{k}_s \cdot \boldsymbol{r}} \hat{a}'_s.$$
(3.54)

In the next Section, I show how to apply the molecular QED formalism outlined above, in

a new derivation of the Faraday effect.

3.2 Faraday Effect as a Two-State Quantum Process

3.2.1 Optical Rotation Overview

Optical rotation (OR) refers to the rotation of the plane of polarization of linearly polarized (LP) light as it passes through a medium [24, 25]. Its discovery came in the early 19th Century through the experiments of Arago and Biot on quartz crystals, and was soon also found to occur in certain fluids, such as aqueous sugar solution—see the first chapters of Barron [24] and Mason [25] for further historical details and references.

It was not until Fresnel's development of the transverse-wave theory of light and discovery of circular polarization over a decade later that OR found an explanation as being due to the *circular birefringence* of certain media, i.e., a difference in the refractive indices for LCP and RCP light. Fresnel's equation links this difference to the rotation angle [25]:

$$\theta = \frac{\pi L}{\lambda} (n_L - n_R), \qquad (3.55)$$

where $n_{L/R}$ are the refractive indices for L/RCP light, λ is the optical wavelength, and L is the length of the optically active system.

Optical rotation can be induced by a *chiral* sample, so-called natural OR, or by the presence of an external, static magnetic field applied in the direction of the light. This is known as magnetic optical rotation or the Faraday effect, as it was discovered by Faraday in 1846 [123]. Both natural and magnetic OR can be explained by circular birefringence, with Fresnel's equation (3.55) holding true, but in the latter it is common to write the rotation angle in the form

$$\theta = VBL\cos\phi,\tag{3.56}$$

where ϕ is the angle the magnetic field **B** makes with the light beam, and V is the so-called Verdet constant [24, 124], which depends on both the medium and the optical frequency. In this Section, I derive an expression for the Verdet constants of atomic and molecular gases.

3.2.2 Two-State Model of Power and Thirunamachandran

My approach to the Faraday effect is an extension of the work by Power and Thirunamachandran on natural OR [112]. The basic idea is to consider OR as a forward Rayleigh scattering process between two orthogonally-polarized field modes. The refractive indices do not play a role in this derivation.

The physical situation in an OR experiment is as follows. A light beam is incident on a fluid sample of molecules; the (classical) electric field of the light is initially in, say, an $\hat{\mathbf{x}}$ -polarized mode, which I refer to as mode 1,

$$\boldsymbol{E} = \mathcal{E}_0 \hat{\mathbf{x}} e^{ikz}.$$
(3.57)

After interacting with the fluid sample, the scattered field is of the form

$$\boldsymbol{E} = \mathcal{E}_0(\alpha \hat{\mathbf{x}} + \beta \hat{\mathbf{y}}) e^{ikz}, \qquad (3.58)$$

where $\alpha = \cos \theta$ and $\beta = \sin \theta$, θ being the angle the new polarization vector makes with $\hat{\mathbf{x}}$. The initial intensity of the light beam is $I_0 = \mathbf{E} \cdot \mathbf{E}^* = |\mathcal{E}_0|^2$, whilst the intensity of radiation scattered into the $\hat{\mathbf{y}}$ -polarized mode, henceforth known as mode 2, is, from (3.58), equal to $I_2 = \beta^2 |\mathcal{E}_0|^2$. Thus, in terms of directly measurable physical quantities, the angle of rotation is

$$\sin^2 \theta = \frac{I_2}{I_0}.$$
 (3.59)

Note that I have assumed the intensity of the scattered field is exactly equal to the intensity of the initial field $(|\mathcal{E}_0|^2)$. In other words, there is no absorption. This analysis can therefore only be used if the light is far from any molecular resonances.

To develop a quantum theory of OR, in which both light and matter are quantized, we replace (3.59) with the following equivalent expression,

$$\sin^2 \theta(t) = \frac{\langle \hat{n}_2(t) \rangle}{\langle \hat{N} \rangle_0},\tag{3.60}$$

where $\langle \hat{n}_2(t) \rangle$ is the expectation value of the number operator for mode 2 at time t and $\langle \hat{N} \rangle_0$ is the initial expectation value of the number operator for all modes. In terms of the initial and final states, $|\Psi(0)\rangle$ and $|\Psi(t)\rangle$, these quantities are

$$\langle \hat{n}_2(t) \rangle = \langle \Psi(t) | \hat{n}_2 | \Psi(t) \rangle \tag{3.61}$$

and

$$\langle \hat{N} \rangle_0 = \langle \Psi(0) | \hat{N} | \Psi(0) \rangle, \qquad (3.62)$$

where $\hat{N} = \sum_{s} \hat{n}_{s}$, as discussed in §3.1.2. Let us suppose the initial number of photons present is $\langle \hat{N} \rangle_{0} = n$. Then the expression involving the angle of rotation becomes

$$\sin^2 \theta(t) = \frac{1}{n} \left\langle \Psi(t) | \hat{n}_2 | \Psi(t) \right\rangle, \qquad (3.63)$$

and thus to find θ we must find the expectation value of \hat{n}_2 .

To begin with, we consider scattering by a single molecule. We take the initial state of the system to be

$$|\Psi(0)\rangle = |a\rangle = |E_g; n(1)\rangle, \qquad (3.64)$$

where $|E_g\rangle$ is the ground state of the molecule and $|n(1)\rangle$ is a number state of mode $1 = (\mathbf{k}, \hat{\mathbf{\epsilon}}_1)$ containing n photons. As above we say this mode has linear polarization $\hat{\mathbf{\epsilon}}_1 = \hat{\mathbf{x}}$, and we are interested in scattering to the mode with the same wave vector but orthogonal polarization $\hat{\mathbf{\epsilon}}_2 = \hat{\mathbf{y}}$, i.e., forward Rayleigh scattering [18] from mode 1 to mode $2 = (\mathbf{k}, \hat{\mathbf{\epsilon}}_2)$. After interaction with the molecule there is a non-zero probability of mode 2 containing any number of photons between zero and n, however, the most likely occupation numbers are zero or one. As in all Rayleigh scattering the molecular state is unchanged. Non-forward scattering is also possible, but is less likely than its forward counterpart, and besides this it would not lead to optical rotation in the sense we have defined above. Given these considerations, I follow Power and Thirunamachandran in treating the system as an effective two-state model [112], with the only states of interest being the initial state $|a\rangle$ and the final state

$$|b\rangle = |E_g; (n-1)(1); 1(2)\rangle.$$
 (3.65)

 $|1(2)\rangle$ is simplified notation for the state $|1(\mathbf{k}, \hat{\epsilon}_2)\rangle$. We are in particular interested in transitions $|a\rangle \rightarrow |b\rangle$ and the likelihood of finding the system in state $|b\rangle$ at time t. The usefulness of the two-state assumption is that the dynamics of the system now become very simple. A general state of the system at time t is given by

$$|\Psi(t)\rangle = C_a(t) |a\rangle + C_b(t) |b\rangle, \qquad (3.66)$$

and the Schrödinger equation becomes

$$i\hbar\frac{\partial}{\partial t}\left|\Psi(t)\right\rangle = H_{\rm eff}\left|\Psi(t)\right\rangle,\tag{3.67}$$

where H_{eff} is the effective two-state Hamiltonian

$$H_{\text{eff}} = \begin{pmatrix} E_0 & M^* \\ M & E_0 \end{pmatrix}. \tag{3.68}$$

 $E_0 = E_g + n\hbar ck$ is the energy of states $|a\rangle$ and $|b\rangle$, i.e., $E_0 = \langle a|H_0|a\rangle = \langle b|H_0|b\rangle$, and M is the amplitude for the transition $|a\rangle \rightarrow |b\rangle$.

Using the time-evolved state we can write the expectation value of \hat{n}_2 as

$$\langle \Psi(t)|\hat{n}_2(t)|\Psi(t)\rangle = |C_b(t)|^2,$$
(3.69)

which gives for the angle of rotation

$$\sin^2 \theta(t) = \frac{1}{n} |C_b(t)|^2.$$
(3.70)

We can solve the Schrödinger equation (3.67) analytically to find $C_b(t)$. After a simple calculation we find [18]

$$C_b(t) = e^{i(\varphi - \pi/2)} e^{-iE_0 t/\hbar} \sin\left(\frac{|M|t}{\hbar}\right), \qquad (3.71)$$

where $M = |M|e^{i\varphi}$. Therefore

$$\sin^2 \theta(t) = \frac{1}{n} \sin^2 \left(\frac{|M|t}{\hbar} \right).$$
(3.72)

Making the assumption that the angle of OR is small, we have

$$\theta \approx \frac{|M|t}{\hbar\sqrt{n}}.\tag{3.73}$$

This result is for a single molecule, and M is the single-molecule transition amplitude. If instead we assume that the light interacts with a dilute gas of N atoms or molecules, then the total angle of rotation is

$$\theta \approx \frac{N |\langle M \rangle | L}{\hbar c \sqrt{n}},\tag{3.74}$$

where we have used c = L/t, L being the length of the gas sample. Here $\langle \cdot \rangle$ denotes rotational averaging over the possible molecular orientations [18, 24], which must be done for particles in an isotropic fluid. The result for a gas is simply N times the single-molecule result because in *forward* Rayleigh scattering $\langle M_{\rm N \, molecules} \rangle = N \langle M \rangle$ [18]. The expression (3.74) for the angle of rotation is Power and Thirunamachandran's central result [112]. It directly relates OR to the calculation of a quantum transition amplitude for a scattering process. They go on to apply (3.74) to the case of natural OR. It is instructive to review how they proceed, so that the differences between natural OR and the Faraday effect are clear.

As we have just demonstrated, the key to finding an OR angle in this approach is the calculation of the matrix element M, the form of which depends on the choice of interaction Hamiltonian, H_{int} . I will work here, following [112], with the multipolar interaction Hamiltonian. As with other chiroptical effects, the electric dipole (ED) interaction alone is not sufficient to induce natural OR, which requires the mixing of ED and higher order multipole moments [24]. Therefore I shall use (the relevant terms from) the Hamiltonian (3.50) [18, 112]:

$$H_{\rm int} = -\hat{\boldsymbol{\mu}} \cdot \varepsilon_0^{-1} \hat{\boldsymbol{D}}_{\perp}(\boldsymbol{R}) - \hat{\boldsymbol{m}} \cdot \hat{\boldsymbol{B}}(\boldsymbol{R}), \qquad (3.75)$$

where $\varepsilon_0^{-1} \hat{D}_{\perp}(\mathbf{R})$ and $\hat{\mathbf{B}}(\mathbf{R})$ are the operators defined in the previous Section (see Eqs. (3.53) and (3.32b)). Note I have not included the electric quadrupole term from (3.50), because its contribution vanishes upon rotational averaging [112].

The first-order transition amplitude $M^{(1)} = \langle b | H_{int} | a \rangle = 0$ for this Hamiltonian, as can be appreciated by noting that the initial and final states differ by two photons, whilst (3.75) is linear in the creation and annihilation operators, so to first order can only cause transitions between states which differ by one EM field excitation. The lowest order that is non-zero is thus second, for which [18]

$$M^{(2)} = \sum_{I} \frac{\langle b|H_{\rm int}|I\rangle \langle I|H_{\rm int}|a\rangle}{E_a - E_I}.$$
(3.76)

In this expression $|I\rangle$ is an eigenstate of the combined Hamiltonian $H_0 = H_{\rm mol} + H_{\rm rad}$, with energy E_I , and the sum is over all such states. The vast majority of states do not contribute to $M^{(2)}$, on account of the fact that $|I\rangle$ must differ from $|a/b\rangle$ by one photon, as discussed. There are two possible routes by which the intermediate or 'virtual' states $|I\rangle$ can connect $|a\rangle$ and $|b\rangle$ (to second order). The first is when $|I\rangle$ contains one photon fewer than $|a\rangle$ does (absorption occurs before emission); the second is when $|I\rangle$ contains one more photon than $|a\rangle$ does (emission followed by absorption). The two possible types of intermediate state are thus

$$|I_1\rangle = |E_r; n - 1(1)\rangle,$$
 (3.77a)

$$|I_2\rangle = |E_r; n(1); 1(2)\rangle,$$
 (3.77b)

where $|E_r\rangle$ is an eigenstate of $H_{\rm mol}$. The total matrix element is

$$M^{(2)} = M^{(2)}(I_1) + M^{(2)}(I_2), (3.78)$$

where

$$M^{(2)}(I_i) = \sum_{I_i} \frac{\langle b | H_{\text{int}} | I_i \rangle \langle I_i | H_{\text{int}} | a \rangle}{E_a - E_{I_i}}.$$
(3.79)

The OR angle follows directly from calculating these matrix elements but is not of interest to me. Let us now apply the results of this Section to the Faraday effect.

3.2.3 Application to the Faraday Effect

The general theory outlined above still holds, so we can use the expression (3.74) for the rotation angle. The matrix element, however, differs from the natural OR case, because the interaction Hamiltonian is no longer (3.75) but

$$H_{\rm int} = -\hat{\boldsymbol{\mu}} \cdot \varepsilon_0^{-1} \hat{\boldsymbol{D}}_{\perp}(\boldsymbol{R}) - \hat{\boldsymbol{m}} \cdot \boldsymbol{B}.$$
(3.80)

The differences between this and (3.75) are subtle but important. The first term of each Hamiltonian is the same, it is the ED interaction between the molecule and the radiation field, but the second term of (3.80) now contains the vector \boldsymbol{B} , which represents an external, static magnetic field. Being an external field, \boldsymbol{B} is not associated with the radiation field, and it assumed to be unaltered by the light-matter interaction. For this reason, \boldsymbol{B} (unlike $\hat{\boldsymbol{B}}(\boldsymbol{R})$ from (3.75)) is *not* a field operator, but a simple c-number.

It is tempting to just plug the new Hamiltonian straight into (3.76) for $M^{(2)}$, as is done with (3.75), but this approach does not work for the Faraday effect. The problem is that the second term of (3.80) cannot create or destroy photons (as it is not an operator of the EM field). This means that the only way to connect states $|a\rangle$ and $|b\rangle$ at second order is via the ED coupling. However, as discussed, the ED coupling is insufficient for generating OR. The lowest order in this case which can connect the initial and final states, through a mixture of electric and magnetic interactions, is third order, for which the matrix element is [18, p.

235]

$$M^{(3)} = \sum_{I,J} \frac{\langle b|H_{\rm int}|J\rangle \langle J|H_{\rm int}|I\rangle \langle I|H_{\rm int}|a\rangle}{(E_a - E_I)(E_a - E_J)}.$$
(3.81)

This matrix element contains three 'actions' of the interaction Hamiltonian (3.80) and two intermediate states $|I\rangle$, $|J\rangle$, with the same physical interpretation as was given for the single intermediate state in $M^{(2)}$.

Unfortunately the third-order matrix element presents another difficulty. One of the three interactions between $|a\rangle$ and $|b\rangle$ will be $-\hat{\mathbf{m}} \cdot \mathbf{B}$, which means that $|I\rangle$ or $|J\rangle$ must contain the same number of photons as $|a/b\rangle$. This state will have energy $E_{I/J} = E_r + n\hbar\omega$, so $E_a - E_{I/J} = E_g - E_r$, where E_r is an eigenenergy of the molecule. Thus if the molecular eigenspectrum contains degeneracy we are in trouble³, because the denominator in $M^{(3)}$ will become zero, leading to a singularity, and this expression becomes useless. This has led me to develop an alternative approach for handling the external \mathbf{B} field, as I outline below.

I begin by disregarding the radiation field altogether, so we are left with the molecule and its interaction with the static magnetic field. The Hamiltonian is then

$$H'_{\rm mol} = H_{\rm mol} - \hat{\boldsymbol{m}} \cdot \boldsymbol{B}. \tag{3.82}$$

The eigenspectrum of $H_{\rm mol}$ is, as always, assumed to be known, i.e., we can solve the Schrödinger equation

$$H_{\rm mol} |n^{(0)}\rangle = E_n^{(0)} |n^{(0)}\rangle.$$
(3.83)

Assuming that the usual conditions are met such that we can apply time-independent perturbation theory, we write the solutions of the full eigenvalue problem,

$$(H_{\rm mol} - \lambda \hat{\boldsymbol{m}} \cdot \boldsymbol{B}) |n\rangle = E_n |n\rangle, \qquad (3.84)$$

as a power series in the order parameter λ (which is introduced for bookkeeping purposes and will be set equal to one at the end of the calculation). To first order, we have the

³The same problem does not occur using $M^{(2)}$ for natural OR because one of our stated assumptions is that $\hbar\omega$ is not resonant with *any* of the molecular energy transitions and thus when $|I\rangle$ contains a different number of photons from $|a\rangle$ we are safe to use these expressions. The intermediate state will always differ from the initial state in number of photons if every term in $H_{\rm int}$ is capable of creating/destroying photons.
well-known results [74, 125]

$$|n\rangle = |n^{(0)}\rangle + \lambda |n^{(1)}\rangle, \qquad (3.85a)$$

$$E_n = E_n^{(0)} + \lambda \Delta_n^{(1)}.$$
 (3.85b)

The exact forms of $|n^{(1)}\rangle$ and $\Delta_n^{(1)}$ depend on whether the state $|n^{(0)}\rangle$ is degenerate with any of the other initial states $|m^{(0)}\rangle$, i.e., whether or not $E_n^{(0)} = E_m^{(0)}$ for some $m \neq n$. We shall assume that any initial degeneracy is lifted by the first-order correction given above.

Reintroducing the radiation field, the Hamiltonian of the combined system is

$$H = H_0' + H_{\rm int},$$
 (3.86)

where $H'_0 = H'_{mol} + H_{rad}$. The initial and final states of interest are still

$$|a\rangle = |g;n(1)\rangle, \qquad (3.87a)$$

$$|b\rangle = |g; n - 1(1); 1(2)\rangle,$$
 (3.87b)

but now $|g\rangle$ is the approximate ground state of $H'_{\rm mol}$ given by (3.85a) (note I am now using a slightly simpler notation for the molecular eigenstates, so as to not clutter the notation too much). The interaction Hamiltonian is no longer (3.80) because the second term has been 'absorbed' into the molecular Hamiltonian and thus we are just left with the ED term. Now to find the transition amplitude M we use the second-order expression (3.76), once more free from the problem of singularities, which leads to

$$M = \sum_{I_1} \frac{\langle b | V_{E1} | I_1 \rangle \langle I_1 | V_{E1} | a \rangle}{E_a - E_{I_1}} + \sum_{I_2} \frac{\langle b | V_{E1} | I_2 \rangle \langle I_2 | V_{E1} | a \rangle}{E_a - E_{I_2}},$$
(3.88)

with $V_{E1} = -\hat{\boldsymbol{\mu}} \cdot \varepsilon_0^{-1} \hat{\boldsymbol{D}}_{\perp}$ and the possible intermediate states again given by (3.77).

The transitions from $|a\rangle$ to $|b\rangle$ via the intermediate states can be visualized by using Feynman diagrams (also called time-ordered graphs), which can be a very useful aid to calculations. The diagrams for this particular calculation are shown in Figure 3.1.

Defining the atomic transition frequencies,

$$\omega_{mn} \equiv \frac{E_{mn}}{\hbar} \equiv \frac{E_m - E_n}{\hbar},\tag{3.89}$$



(a) Absorption then emission. (b) Emission then absorption.

Figure 3.1: Feynman diagrams for the Faraday effect. In these diagrams the arrow of time points vertically upwards. The curly lines indicate photons and the solid straight line indicates the molecule. The black circles show the interactions between the light and the molecule via, in this case, the E1 coupling. In both diagrams the molecule starts in the ground state $|g\rangle$, is excited to the intermediate molecular state $|r\rangle$, and then returns to the ground state. In both cases there are two photon-molecule interactions, an absorption and an emission. In (a) the absorption occurs before the emission but in (b) the other time-ordering occurs. These correspond to the intermediate states $|I_1\rangle$ and $|I_2\rangle$, respectively.

and the electric dipole transition moments,

$$\boldsymbol{\mu}^{mn} \equiv \langle m | \hat{\boldsymbol{\mu}} | n \rangle , \qquad (3.90)$$

the matrix element becomes

$$M = -\frac{1}{\hbar} \sum_{r} \frac{\boldsymbol{\mu}^{gr} \cdot \langle 1(2); n - 1(1) | \varepsilon_{0}^{-1} \hat{\boldsymbol{D}}_{\perp} | n - 1(1) \rangle \, \boldsymbol{\mu}^{rg} \cdot \langle n - 1(1) | \varepsilon_{0}^{-1} \hat{\boldsymbol{D}}_{\perp} | n(1) \rangle}{\omega_{rg} - \omega} \\ - \frac{1}{\hbar} \sum_{r} \frac{\boldsymbol{\mu}^{gr} \cdot \langle 1(2); n - 1(1) | \varepsilon_{0}^{-1} \hat{\boldsymbol{D}}_{\perp} | n(1); 1(2) \rangle \, \boldsymbol{\mu}^{rg} \cdot \langle 1(2); n(1) | \varepsilon_{0}^{-1} \hat{\boldsymbol{D}}_{\perp} | n(1) \rangle}{\omega_{rg} + \omega}.$$
(3.91)

The transitions between the field modes are easily calculated using (3.54):

$$\langle n-1(1)|\varepsilon_0^{-1}\hat{\boldsymbol{D}}_{\perp}|n(1)\rangle = \langle n-1(1)|\varepsilon_0^{-1}\hat{\boldsymbol{D}}_{\boldsymbol{k}_1\lambda_1}^+|n(1)\rangle$$

$$= i\mathcal{N}(k)\hat{\boldsymbol{\epsilon}}_1 e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \langle n-1(1)|\hat{a}_{\boldsymbol{k}_1\lambda_1}|n(1)\rangle = i\sqrt{n}\mathcal{N}(k)\hat{\boldsymbol{\epsilon}}_1 e^{i\boldsymbol{k}\cdot\boldsymbol{R}}, \quad (3.92)$$

and

$$\langle 1(2)|\varepsilon_0^{-1}\hat{\boldsymbol{D}}_{\perp}|0(2)\rangle = \langle 1(2)|\varepsilon_0^{-1}\hat{\boldsymbol{D}}_{\boldsymbol{k}_2\lambda_2}^{-}|0(2)\rangle$$

$$= -i\mathcal{N}(k)\hat{\boldsymbol{\epsilon}}_2^* e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} \langle 1(2)|\hat{a}_{\boldsymbol{k}_2\lambda_2}^{\dagger}|0(2)\rangle = -i\mathcal{N}(k)\hat{\boldsymbol{\epsilon}}_2^* e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}, \quad (3.93)$$

where $\mathcal{N}(k)$ is the normalization constant defined in (3.30). Inputting these into the expression for M, after some manipulation we can write

$$M = -\frac{\mu_0 c^2 \sqrt{n\omega}}{V} \hat{\epsilon}_{1i} \hat{\epsilon}_{2j}^* \sum_r \left(\frac{\omega_{rg}}{\omega_{rg}^2 - \omega^2} \right) \operatorname{Re}\{\langle g | \hat{\mu}_i | r \rangle \langle r | \hat{\mu}_j | g \rangle\} + i \, \frac{\mu_0 c^2 \sqrt{n\omega}}{V} \hat{\epsilon}_{1i} \hat{\epsilon}_{2j}^* \sum_r \left(\frac{\omega}{\omega_{rg}^2 - \omega^2} \right) \operatorname{Im}\{\langle g | \hat{\mu}_i | r \rangle \langle r | \hat{\mu}_j | g \rangle\}, \quad (3.94)$$

where the repeated indices i, j are to be summed over and $\operatorname{Re}\{z\}$ and $\operatorname{Im}\{z\}$ indicate the real and imaginary parts of z, respectively.

To write this result in a more concise form, we now introduce the dynamic polarizability tensor $\tilde{\alpha}(\omega)$ [18, 24]. This is essentially the microscopic analogue of the susceptibility χ_e . Recall that the (macroscopic) polarization field \boldsymbol{P} is related to the incident field \boldsymbol{E} which induces it via (B.7),

$$\tilde{\boldsymbol{P}} = \varepsilon_0 \tilde{\chi}_e \tilde{\boldsymbol{E}},$$

now using tildes to indicate that these quantities are in general complex. Similarly, when an oscillating electric field interacts with a molecule, a temporary electric dipole moment is induced, the form of which is given by [24, 126]

$$\tilde{\boldsymbol{\mu}} = \tilde{\alpha} \, \tilde{\boldsymbol{E}}.\tag{3.95}$$

The complex polarizability tensor can be written as

$$\tilde{\alpha} = \alpha - i\alpha',\tag{3.96}$$

where the real tensors $\alpha(\omega)$ and $\alpha'(\omega)$ are defined in the quantum theory via [24, p. 91]:

$$\alpha_{ij}(\omega) = \frac{2}{\hbar} \sum_{r} \frac{\omega_{rg}}{\omega_{rg}^2 - \omega^2} \operatorname{Re}\{\langle g | \hat{\mu}_i | r \rangle \langle r | \hat{\mu}_j | g \rangle\}, \qquad (3.97a)$$

$$\alpha_{ij}'(\omega) = -\frac{2}{\hbar} \sum_{r} \frac{\omega}{\omega_{rg}^2 - \omega^2} \operatorname{Im}\{\langle g | \hat{\mu}_i | r \rangle \langle r | \hat{\mu}_j | g \rangle\}.$$
(3.97b)

I shall call α the symmetric polarizability and α' the anti-symmetric polarizability, on account of the properties

$$\alpha_{ji} = \alpha_{ij}, \quad \alpha'_{ji} = -\alpha'_{ij}, \tag{3.98}$$

which follow from the properties of $\operatorname{Re}\{z\}$ and $\operatorname{Im}\{z\}$. With these results the angle of rotation (3.74) can be written in the concise form

$$\theta = \frac{1}{2} \mu_0 c \omega \eta \left| \hat{\epsilon}_{1i} \hat{\epsilon}^*_{2j} \left\langle \alpha_{ij}(\omega; \mathbf{B}) + i \alpha'_{ij}(\omega; \mathbf{B}) \right\rangle \right| L, \qquad (3.99)$$

where η is the number of molecules per unit volume present in the gas, and $\alpha_{ij}^{(\prime)}(\omega; B)$ indicates that these are the perturbed polarizabilities.

To proceed we need to choose a form for the first-order perturbation expansions (3.85), which we then substitute into the formulae (3.97). I shall assume that states of the unperturbed molecule are non-degenerate, so the correct expressions are [74, 125]

$$|n\rangle = |n^{(0)}\rangle + \lambda \frac{B_k}{\hbar} \sum_{s \neq n} \frac{m_k^{sn(0)}}{\omega_{sn}^{(0)}} |s^{(0)}\rangle, \qquad (3.100a)$$

$$\omega_n = \omega_n^{(0)} - \lambda \frac{B_k}{\hbar} m_k^{n(0)}. \qquad (3.100b)$$

Here I have introduced some new notation:

$$\begin{split} \omega_n^{(0)} &\equiv E_n^{(0)}/\hbar, \\ m_k^{sn(0)} &\equiv \langle s^{(0)} | \hat{m}_k | n^{(0)} \rangle , \\ m_k^{n(0)} &\equiv \langle n^{(0)} | \hat{m}_k | n^{(0)} \rangle , \end{split}$$

where $E_s^{(0)}$ and $|s^{(0)}\rangle$ are the energies and eigenstates of the unperturbed molecular Hamiltonian. If the unperturbed molecule does contain degeneracy then these expressions can still be used so long as the degenerate eigenstates are chosen such that $m_k^{sn(0)} = 0$ whenever $\omega_{sn}^{(0)} = 0$ (i.e., the perturbation is diagonal in the degenerate subspace(s)). I will assume this to be the case, to facilitate direct comparison with Barron [24], but note that it is entirely possible to use proper degenerate perturbation theory to find correct expressions to any order when the perturbation is not diagonal in the degenerate subspace.

Using (3.100) we find, up to $\mathcal{O}(\lambda)$,

$$\frac{1}{\omega_{rg}^2 - \omega^2} = \frac{1}{\omega_{rg}^{(0)2} - \omega^2} \left[1 + \lambda \frac{2B_k}{\hbar} \frac{\omega_{rg}^{(0)}}{\omega_{rg}^{(0)2} - \omega^2} (m_k^{r(0)} - m_k^{g(0)}) \right]$$
(3.101)

and

$$\mu_i^{gr} \mu_j^{rg} = \mathcal{M}_{ij}^{(0)} + \lambda \mathcal{M}_{ij}^{(1)}, \qquad (3.102)$$

where

$$\mathcal{M}_{ij}^{(0)} = \mu_i^{gr(0)} \mu_j^{rg(0)} = \langle g^{(0)} | \hat{\mu}_i | r^{(0)} \rangle \langle r^{(0)} | \hat{\mu}_j | g^{(0)} \rangle$$
(3.103)

and

$$\mathcal{M}_{ij}^{(1)} = \frac{B_k}{\hbar} \left[\sum_{s \neq g} \frac{1}{\omega_{sg}^{(0)}} \left(\mu_i^{gr(0)} \mu_j^{rs(0)} m_k^{sg(0)} + m_k^{gs(0)} \mu_i^{sr(0)} \mu_j^{rg(0)} \right) + \sum_{s \neq r} \frac{1}{\omega_{sr}^{(0)}} \left(\mu_i^{gr(0)} m_k^{rs(0)} \mu_j^{sg(0)} + \mu_i^{gs(0)} m_k^{sr(0)} \mu_j^{rg(0)} \right) \right]. \quad (3.104)$$

Inputting these into (3.97) we find that the perturbed polarizabilities can be written in the forms

$$\alpha_{ij}(\omega; \boldsymbol{B}) = \alpha_{ij}^{(0)}(\omega) + B_k \alpha_{ij,k}^{(m)}(\omega), \qquad (3.105a)$$

$$\alpha_{ij}'(\omega; \boldsymbol{B}) = \alpha_{ij}'^{(0)}(\omega) + B_k \alpha_{ij,k}'^{(m)}(\omega), \qquad (3.105b)$$

again only retaining terms up to order λ , which I now set equal to one. In the notation $\alpha_{ij,k}^{(m)}(\omega)$, the superscript indicates the molecular operator which is present in the interaction (in this case the magnetic dipole moment operator $\hat{\boldsymbol{m}}$) and the ', k' in the subscript indicates that k is the index attached to the perturbing term. The next term in the expansion, to order $|\boldsymbol{B}|^2$, would be written as $B_k B_l \alpha_{ij,kl}^{(mm)}(\omega)$, and so on [24, p. 104].

The zeroth-order polarizabilities are

$$\alpha_{ij}^{(0)}(\omega) = \frac{2}{\hbar} \sum_{r} \frac{\omega_{rg}^{(0)}}{\omega_{rg}^{(0)2} - \omega^2} \operatorname{Re}\{\langle g^{(0)} | \hat{\mu}_i | r^{(0)} \rangle \langle r^{(0)} | \hat{\mu}_j | g^{(0)} \rangle\},$$
(3.106a)

$$\alpha_{ij}^{\prime(0)}(\omega) = -\frac{2}{\hbar} \sum_{r} \frac{\omega}{\omega_{rg}^{(0)2} - \omega^2} \operatorname{Im}\{\langle g^{(0)} | \hat{\mu}_i | r^{(0)} \rangle \langle r^{(0)} | \hat{\mu}_j | g^{(0)} \rangle\},\tag{3.106b}$$

and the first-order terms are

$$\begin{aligned} \alpha_{ij,k}^{(m)}(\omega) &= \frac{2}{\hbar^2} \sum_{r} \left[\frac{\omega_{rg}^{(0)2} + \omega^2}{(\omega_{rg}^{(0)2} - \omega^2)^2} (m_k^{r(0)} - m_k^{g(0)}) \operatorname{Re} \{\mu_i^{gr(0)} \mu_j^{rg(0)} \} \\ &+ \sum_{s \neq g} \frac{\omega_{rg}^{(0)}}{\omega_{sg}^{(0)} (\omega_{rg}^{(0)2} - \omega^2)} \operatorname{Re} \{m_k^{sg(0)} (\mu_i^{gr(0)} \mu_j^{rs(0)} + \mu_j^{gr(0)} \mu_i^{rs(0)})\} \\ &+ \sum_{s \neq r} \frac{\omega_{rg}^{(0)}}{\omega_{sr}^{(0)} (\omega_{rg}^{(0)2} - \omega^2)} \operatorname{Re} \{m_k^{rs(0)} (\mu_i^{gr(0)} \mu_j^{sg(0)} + \mu_j^{gr(0)} \mu_i^{sg(0)})\} \end{aligned}$$
(3.107)

and

$$\begin{aligned} \alpha_{ij,k}^{\prime(m)}(\omega) &= -\frac{2}{\hbar^2} \sum_{r} \left[\frac{2\omega \omega_{rg}^{(0)}}{(\omega_{rg}^{(0)2} - \omega^2)^2} (m_k^{r(0)} - m_k^{g(0)}) \operatorname{Im} \{\mu_i^{gr(0)} \mu_j^{rg(0)} \} \right. \\ &+ \sum_{s \neq g} \frac{\omega}{\omega_{sg}^{(0)} (\omega_{rg}^{(0)2} - \omega^2)} \operatorname{Im} \{m_k^{sg(0)} (\mu_i^{gr(0)} \mu_j^{rs(0)} - \mu_j^{gr(0)} \mu_i^{rs(0)})\} \\ &+ \sum_{s \neq r} \frac{\omega}{\omega_{sr}^{(0)} (\omega_{rg}^{(0)2} - \omega^2)} \operatorname{Im} \{m_k^{rs(0)} (\mu_i^{gr(0)} \mu_j^{sg(0)} - \mu_j^{gr(0)} \mu_i^{sg(0)})\} \right]. \quad (3.108)$$

We now need to perform the rotational averaging. If $T_{ijk...}$ represents the components of a molecular property tensor (such as the polarizability) with respect to a set of space-fixed (laboratory) axes, then the rotational average, denoted by $\langle \cdot \rangle$, is given by [18, 24]

$$\langle T_{ijk\dots} \rangle = \langle \ell_{i\alpha} \ell_{j\beta} \ell_{k\gamma} \dots \rangle T_{\alpha\beta\gamma\dots}, \qquad (3.109)$$

where $T_{\alpha\beta\gamma...}$ is the same tensor but with respect to a set of molecule-fixed axes, and $\{\ell_{m\lambda}\}$ are the direction cosines between the space- and molecule-fixed frames (see Appendix A.3 and Eq. (A.14) in particular). The average of the direction cosines depends on the rank of the tensor. I am only interested in rank-2 and rank-3 tensors, for which we have (see Barron [24, p. 183] or Craig and Thirunamachandran [18, p. 189])

$$\langle \ell_{i\alpha}\ell_{j\beta}\rangle = \frac{1}{3}\delta_{ij}\delta_{\alpha\beta} \tag{3.110}$$

and

$$\langle \ell_{i\alpha}\ell_{j\beta}\ell_{k\gamma}\rangle = \frac{1}{6}\epsilon_{ijk}\epsilon_{\alpha\beta\gamma},\tag{3.111}$$

respectively, where δ_{ij} is the Kronecker delta [64] and ϵ_{ijk} is the Levi-Civita symbol (2.13).

Considering first of all the rank-2 terms, that is, the terms which depend on the zeroth-order polarizabilities, such as $\hat{\epsilon}_{1i}\hat{\epsilon}_{2j}^* \langle \alpha_{ij}^{(0)}(\omega) \rangle$, it is easy to see that these terms *do not* contribute to the OR. This is somewhat obvious, for if it were not the case then all achiral gases would exhibit OR without the need for a magnetic field⁴. This result follows from a simple application of (3.110) to the relevant parts of (3.99):

$$\hat{\epsilon}_{1i}\hat{\epsilon}_{2j}^* \langle \alpha_{ij}^{(0)}(\omega) \rangle = \frac{1}{3}\hat{\epsilon}_{1i}\hat{\epsilon}_{2j}^* \delta_{ij}\delta_{\alpha\beta}\alpha_{\alpha\beta}^{(0)}(\omega) = \frac{1}{3}\hat{\epsilon}_1 \cdot \hat{\epsilon}_2^* \alpha_{\alpha\alpha}^{(0)}(\omega) = 0, \qquad (3.112)$$

which equals zero because $\hat{\boldsymbol{\epsilon}}_1 \equiv \hat{\mathbf{x}}$ and $\hat{\boldsymbol{\epsilon}}_2 \equiv \hat{\mathbf{y}}$ and thus $\hat{\boldsymbol{\epsilon}}_1 \cdot \hat{\boldsymbol{\epsilon}}_2^* = 0$. The average of the term which depends on the zeroth-order anti-symmetric polarizability vanishes for the same reason.

Let us next look at the contribution from the first-order symmetric polarizability. Applying (3.111) to the relevant term we find

$$\hat{\epsilon}_{1i}\hat{\epsilon}_{2j}^*B_k \left\langle \alpha_{ij,k}^{(m)} \right\rangle = \frac{1}{6} \epsilon_{ijk}\hat{\epsilon}_{1i}\hat{\epsilon}_{2j}^*B_k\epsilon_{\alpha\beta\gamma}\alpha_{\alpha\beta\gamma}^{(m)}.$$
(3.113)

The *i*th component of the cross product of two vectors can be written as $[\boldsymbol{U} \times \boldsymbol{V}]_i = \epsilon_{ijk} U_j V_k$. With this and $\hat{\boldsymbol{\epsilon}}_1 \times \hat{\boldsymbol{\epsilon}}_2^* \equiv \hat{\boldsymbol{k}} = \hat{\boldsymbol{z}}$ we have $\epsilon_{ijk} \hat{\epsilon}_{1i} \hat{\epsilon}_{2j}^* B_k = \boldsymbol{B} \cdot \hat{\boldsymbol{z}}$. To evaluate $\epsilon_{\alpha\beta\gamma} \alpha_{\alpha\beta,\gamma}^{(m)}$, consider

$$\epsilon_{\alpha\beta\gamma}m_{\gamma}^{n}(\mu_{\alpha}^{p}\mu_{\beta}^{q}+\mu_{\alpha}^{q}\mu_{\beta}^{p}) = \boldsymbol{m}^{n}\cdot(\boldsymbol{\mu}^{p}\times\boldsymbol{\mu}^{q}+\boldsymbol{\mu}^{q}\times\boldsymbol{\mu}^{p})$$
$$= \boldsymbol{m}^{n}\cdot(\boldsymbol{\mu}^{p}\times\boldsymbol{\mu}^{q}-\boldsymbol{\mu}^{p}\times\boldsymbol{\mu}^{q})$$
$$= 0,$$
(3.114)

using the anti-commutativity of the cross product. Each line of (3.107) contains a term of this form and thus the rotational average of the symmetric polarizability is identically zero—it does not contribute to magnetic optical rotation in an isotropic sample.

⁴Atomic and achiral molecular gases actually do produce a very small natural OR, due to the effects of the parity-violating weak force [24], but these effects are beyond the scope of this model.

The only term which does not vanish upon averaging is the contribution from the first-order anti-symmetric polarizability, which leaves the final result as

$$\theta = \frac{1}{12} \mu_0 c \omega \eta \epsilon_{\alpha\beta\gamma} \alpha_{\alpha\beta\gamma}^{\prime(m)}(\omega) (\boldsymbol{B} \cdot \hat{\boldsymbol{k}}) L.$$
(3.115)

This can be expanded to give the explicit formula:

$$\theta = -\frac{1}{3\hbar^2} \mu_0 c\omega \eta (\boldsymbol{B} \cdot \hat{\boldsymbol{k}}) L \sum_r \left[\frac{\omega \omega_{rg}^{(0)}}{(\omega_{rg}^{(0)2} - \omega^2)^2} (\boldsymbol{m}^{r(0)} - \boldsymbol{m}^{g(0)}) \cdot \operatorname{Im} \{ \boldsymbol{\mu}^{gr(0)} \times \boldsymbol{\mu}^{rg(0)} \} \right. \\ \left. + \sum_{s \neq g} \frac{\omega}{\omega_{sg}^{(0)} (\omega_{rg}^{(0)2} - \omega^2)} \operatorname{Im} \{ \boldsymbol{m}^{sg(0)} \cdot (\boldsymbol{\mu}^{gr(0)} \times \boldsymbol{\mu}^{rs(0)}) \} \right. \\ \left. + \sum_{s \neq r} \frac{\omega}{\omega_{sr}^{(0)} (\omega_{rg}^{(0)2} - \omega^2)} \operatorname{Im} \{ \boldsymbol{m}^{rs(0)} \cdot (\boldsymbol{\mu}^{gr(0)} \times \boldsymbol{\mu}^{sg(0)}) \} \right]. \quad (3.116)$$

This may be compared with (3.56), the Verdet constant being easily identifiable.

The first line of my result corresponds to the so-called 'Faraday A-term' and the second and third lines to the 'Faraday B-term' which are found in the literature [24, 127, 128]. One other term which usually appears in the literature, the 'Faraday C-term', is missing from my expression. This is because one must use a Boltzmann average, rather than a simple isotropic average, to arrive at this term. In an isotropic rotational average all directions are treated equally, but in the presence of an external perturbation (such as a magnetic field) this is not realistic, as the molecule will tend to align with whichever directions are energetically favourable. Thus in a Boltzmann average we weight the orientations, denoted Ω , by the appropriate Boltzmann factor [24, 129],

$$\langle T_{ijk\dots} \rangle_{\text{Boltz}} = \frac{\int d\Omega \ T_{ijk\dots}(\Omega) e^{-V(\Omega)/k_B T}}{\int d\Omega \ e^{-V(\Omega)/k_B T}},$$
(3.117)

where $V(\Omega)$ is the potential energy of the molecule (in the ground state) in the external field for orientation Ω , k_B is the Boltzmann constant, and T is the temperature of the gas. In room temperature samples it is usually appropriate to assume that $V(\Omega) \ll k_B T$, which allows us to Taylor expand the exponential factors and get the approximate form [24]

$$\langle T_{ijk\dots} \rangle_{\text{Boltz}} \approx \langle T_{ijk\dots} \rangle - \frac{1}{k_B T} \bigg[\langle V T_{ijk\dots} \rangle - \langle V \rangle \langle T_{ijk\dots} \rangle \bigg],$$
 (3.118)

where $\langle \cdot \rangle$ denotes the regular rotational average as above.

In the case of the Faraday effect we have $V = -m_k^{g(0)}B_k$, using the previously defined notation, and we wish to perform the Boltzmann average of $\tilde{\alpha}_{ij}^*(\omega; \mathbf{B})$. The first term in (3.118) just leads to the Faraday A- and B-terms, as found above. The terms in the square brackets lead to the Faraday C-term. The second term in the brackets does not contribute anything to first-order in the magnetic field, so we are just left with the $\langle V T_{ijk...} \rangle$ term, which to lowest-order contributes

$$-\langle V T_{ijk\dots} \rangle = B_k \langle \alpha_{ij}^{(0)}(\omega) m_k^{g(0)} \rangle + i B_k \langle \alpha_{ij}^{\prime(0)}(\omega) m_k^{g(0)} \rangle + \mathcal{O}(|B|^2).$$
(3.119)

The term which depends on the zeroth-order symmetric polarizability vanishes upon rotational averaging, so we are left with only the anti-symmetric term. Performing the isotropic average using (3.111), we find the Boltzmann-averaged expression for the rotation angle may be written as [24]

$$\theta = \frac{1}{12}\mu_0 c\omega\eta\epsilon_{\alpha\beta\gamma} \left(\alpha_{\alpha\beta,\gamma}^{\prime(m)}(\omega) + \frac{1}{k_B T} m_{\gamma}^{g(0)} \alpha_{\alpha\beta}^{\prime(0)}(\omega) \right) (\boldsymbol{B} \cdot \hat{\boldsymbol{k}}) L = \theta_{\rm A} + \theta_{\rm B} + \theta_{\rm C}, \qquad (3.120)$$

where the Faraday A- and B-terms are given explicitly in (3.116) and the C-term is, explicitly,

$$\theta_{\rm C} = \frac{1}{12k_BT} \mu_0 c\omega \eta \epsilon_{\alpha\beta\gamma} m_{\gamma}^{g(0)} \alpha_{\alpha\beta}^{\prime(0)}(\omega) (\boldsymbol{B} \cdot \hat{\boldsymbol{k}}) L$$

$$= -\frac{1}{3\hbar k_BT} \mu_0 c\omega \eta (\boldsymbol{B} \cdot \hat{\boldsymbol{k}}) L \sum_r \frac{\omega}{\omega_{rg}^{(0)2} - \omega^2} \boldsymbol{m}^{g(0)} \cdot \left(\boldsymbol{\mu}^{gr(0)} \times \boldsymbol{\mu}^{rg(0)}\right).$$
(3.121)

This concludes my derivation of the Faraday effect by means of a fully quantum-mechanical two-state approach. Although the Faraday effect is not a new result, the approach I have taken here is valuable from a pedagogical standpoint as it demonstrates how a phenomenon which is usually thought of as classical can be explained using quantum theory. The methodology I have developed to derive this result also has wider applications, because it provides a framework for handling external perturbations even in the presence of degeneracies, something which is often overlooked in other treatments [18]. In the next Subsection, I briefly discuss how the model developed above could be applied to another source of optical rotation.

3.2.4 Mechanical Faraday Effect

Another source of OR which exists, which is somewhat less well-known, is a *rotating medium*. The resulting effect is known as 'rotary aether drag' or the *mechanical Faraday effect* (MFE). Although more recent in discovery than the traditional Faraday effect and natural OR, the MFE does have a fairly long history, dating back to an article by Fermi in 1923 [130]. The effect was demonstrated experimentally by Jones in 1976 [131] and this sparked renewed interest in its theoretical underpinnings [124, 132–134]. Interestingly, a rotating medium also causes *image rotation*, i.e., the rotation of a light beam's intensity pattern [135, 136]. This was confirmed in an experiment by Franke-Arnold et al. in 2011 [137]. It appears that a magnetic field is not capable of producing image rotation.

In 2021 Milner et al. experimentally achieved the MFE in a gaseous medium for the first time [138] (see also the theoretical papers [134, 139, 140]). It would be interesting to try and extend the two-state model developed in the previous Subsection to the MFE in a gas. At a glance, this seems like it should not be too difficult, because the situation is very similar to the traditional Faraday effect: instead of the magnetic perturbation term $-\hat{\mathbf{m}} \cdot \mathbf{B}$, we would have something along the lines of $\hat{J} \cdot \Omega$, where \hat{J} is the angular momentum operator of the molecule and Ω is its angular velocity vector [134]. The vectors \mathbf{B} and Ω would play identical roles here as external perturbations, and the AM and magnetic dipole operators are very closely related [24]. However, a difficulty which needs to be overcome is the fact that the rotating atom does not experience the same field as a stationary atom [136], and it is not immediately obvious how to incorporate this into the quantum theory. This is a line of research I am actively pursuing.

3.3 Summary

In this Chapter, I have provided an overview of the basic aspects of molecular QED, starting from the Lagrangian for classical electrodynamics and proceeding to the quantum theory via the usual canonical quantization procedure. I discussed the mode expansions of the field operators in terms of creation and annihilation operators and their physical interpretation. I also discussed the transition from the minimal coupling form of interaction to the multipolar form, and the related long-wavelength approximation.

In the next Section I applied this theory to the Faraday effect in an atomic or molecular gas, which I did by extending an existing model due to Power and Thirunamachandran [112] to take into account external perturbations. The form of this external perturbation is not restricted to the particular case considered here, which could lead to future applications. I am currently working on applying this model to the mechanical Faraday effect.

CHAPTER 4

Optical Helicity and Chirality

This Chapter is dedicated to a discussion of the electromagnetic or optical helicity [52, 53, 141, 142], a measure of the chirality of light which also has deep connections with optical angular momentum.

The term *helicity* is perhaps most familiar from the theory of elementary particles, in which it is defined as the projection of a particle's spin angular momentum onto its direction of motion [75, 76],

$$\mathcal{H}_{\rm PP} = \frac{\boldsymbol{S} \cdot \boldsymbol{P}}{|\boldsymbol{P}|}.\tag{4.1}$$

A more general concept of helicity is found in various other research areas, notably fluid mechanics [143, 144] and plasma physics [145, 146]. Here the term refers to integrals of the form

$$\mathcal{H}_V = \int \mathrm{d}^3 r \, \boldsymbol{V} \cdot (\nabla \times \boldsymbol{V}), \qquad (4.2)$$

which quantifies the helical nature or 'curliness' of the arbitrary vector field V(r,t) [147]. As I shall discuss in detail in §4.3, the optical helicity is of the form (4.2), and possesses the necessary properties to make it a 'chirality observable' for the optical field. Before I can discuss this, I need to go over some prerequisite material in Sections 4.1 and 4.2.

The optical helicity has also been shown to be connected to chiral light-matter interactions [31, 37, 38]. In particular, Cameron et al. [38] showed that a chiral molecule will experience

a force which is directly proportional to the *local* optical helicity. In the other main Section of this Chapter, §4.4, I present a new derivation of their result using the molecular QED formalism of Chapter 3.

Some terminology used in this Chapter, e.g. 'time-even pseudoscalar', is defined in Appendix A.3.

4.1 True and False Chirality

As discussed in the Introduction, Kelvin defined chirality as that property belonging to any object which is non-superposable with its mirror image. It is more customary these days to define chirality with respect to the space inversion operation, rather than mirror reflection. The two notions are equivalent, because space inversion is equivalent to reflection in a plane followed by rotation about the axis perpendicular to that plane by π [24]. Kelvin's definition makes no mention of the time reversal operation (see Appendix A.3), which can lead to ambiguities when considering the chirality of moving objects. This was noticed by Barron in the 1980s, which led him to propose a slight modification to Kelvin's definition [24, 54, 148–150].

To illustrate Barron's idea, consider a cone which rotates about its axis of symmetry, but is otherwise stationary. This exists in two distinct forms which are interconverted by space inversion, but not by rotations and translations. By Kelvin's definition, it would be appropriate to say that the cone exhibits chirality. However, the two forms are also interconvertible via the time reversal operation followed by a rotation (see Figure 4.1, which is modelled after a diagram in [54]).

If we now suppose that the cone rotates as before, but *also* translates in the direction of the rotation axis (see Figure 4.2), then once again the system exists in two forms which are interconverted by space inversion, but this time they are *only* converted by space inversion, not by any combination of time reversal, translations, and rotations. Barron suggested that these two different kinds of enantiomorphism should be distinguished. The spinning cone is an archetype of what he called 'false' chirality, and had previously been called 'time-asymmetric enantiomorphism' by Zocher and Török [151]. In summary, a falsely chiral system exists in two distinct forms which are interconverted by space inversion *and* also by time reversal combined with proper rotations. In contrast, the spinning and translating cone is an archetype of 'true' chirality: a truly chiral system exists in two distinct forms which are



Figure 4.1: The effects of the space inversion (P) and time reversal (T) operations on the spinning cone as described in the main text. It is seen that the action of P is equivalent to T followed by a rotation R_{π} .

only interconverted by space inversion [24, 54, 149, 150]. Note that for systems which are at rest the distinction between true and false chirality vanishes. As we can always transform to a rest frame when dealing with massive particles, the distinction is only Lorentz invariant for massless particles.

The definition of a truly chiral system as one which is invariant under time reversal and rotations but not under space inversion naturally leads to the conclusion that 'the hallmark of a [truly] chiral system is that it can support time-even pseudoscalar observables' [24, p. 39]. In contrast, a falsely chiral system must support time-odd pseudoscalar observables [150]. What we usually consider to be chiral phenomena, such as optical rotation due to chiral molecules, can be shown to be associated with time-even pseudoscalars, and thus Barron's modification is in-keeping with the original meaning of the term.

4.2 Dual Symmetry

I will be interested in the chirality of light in vacuum, so Maxwell's equations are given by (2.42). These equations possess an interesting symmetry which is closely connected with the optical helicity.



Figure 4.2: The effects of P and T on the spinning plus translating cone. The arrows within the cones depict the directions of translational motion. Clearly the results of P and T are not related by any combination of translations and rotations.

Let us introduce the *Riemann-Silberstein vector* [152],

$$\boldsymbol{F} = \boldsymbol{E} + ic\boldsymbol{B}.\tag{4.3}$$

This allows us to reduce the four free-space Maxwell equations (2.42) to the following two:

$$\nabla \cdot \boldsymbol{F} = 0, \tag{4.4a}$$

$$c\nabla \times \boldsymbol{F} = i\boldsymbol{F}.\tag{4.4b}$$

Clearly, these equations are satisfied just as well by any field of the form $\mathbf{F}' = e^{-i\theta}\mathbf{F}$, where θ is a real constant. In other words, Maxwell's equations are invariant to a change of the the global phase of the Riemann-Silberstein vector. It is simple to show that the same is true of the electromagnetic energy, momentum, and angular momentum. I shall call the transformation

$$\boldsymbol{F} \to \boldsymbol{F}' = e^{-i\theta} \boldsymbol{F} \tag{4.5}$$

a *duality rotation* and the associated invariance the *dual symmetry* of electromagnetism in vacuum. In terms of the electric and magnetic fields, the duality transformation corresponds

to a 'rotation' of the form [52, 69, 153, 154]

$$E \to E' = \cos \theta E + \sin \theta c B,$$
 (4.6a)

$$c\mathbf{B} \to c\mathbf{B}' = -\sin\theta \mathbf{E} + \cos\theta c\mathbf{B}.$$
 (4.6b)

Note that for E' and B' to have the required symmetry characteristics, θ must be a time-odd pseudoscalar quantity.

To gain some further physical insight into the nature of duality rotations, let's consider the effect on an optical plane wave, characterized by the fields $\boldsymbol{E} = \hat{\boldsymbol{\epsilon}} E_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}$, $c\boldsymbol{B} = \hat{\boldsymbol{\beta}} E_0 e^{i(\boldsymbol{k}\cdot\boldsymbol{r}-\omega t)}$. Performing the general duality transformation (4.6), and using the fact that the electric and magnetic polarization vectors ($\hat{\boldsymbol{\epsilon}}$ and $\hat{\boldsymbol{\beta}}$) form a right-handed triad with the propagation vector $\hat{\boldsymbol{k}} = \boldsymbol{k}/|\boldsymbol{k}|$, we find that the transformed fields are of the exact same form as before, but with the new polarizations

$$\hat{\boldsymbol{\epsilon}}' = \cos\theta\hat{\boldsymbol{\epsilon}} + \sin\theta\hat{\boldsymbol{k}} \times \hat{\boldsymbol{\epsilon}}, \qquad (4.7a)$$

$$\hat{\boldsymbol{\beta}}' = \cos\theta \hat{\boldsymbol{\beta}} + \sin\theta \hat{\boldsymbol{k}} \times \hat{\boldsymbol{\beta}}.$$
(4.7b)

We recognize these as the results of rotating $\hat{\boldsymbol{\epsilon}}$ and $\hat{\boldsymbol{\beta}}$ about $\hat{\boldsymbol{k}}$ through the angle θ [155]. Thus, for a plane wave, the effect of a duality rotation is an actual physical rotation of the electric and magnetic field vectors about the axis of propagation [53]. In an optical field formed from the sum of many plane waves, the duality transformation will rotate each individual wave about its own wave vector.

The discussion thus far has only mentioned the electromagnetic fields, so it is not clear how a quantity such as the local optical spin, say, which depends on both the electric field and the vector potential, will transform under a duality transformation. To address this we introduce the second vector potential C [102], which was already discussed in Chapter 2 and defined by the relations (2.74). It follows directly from these relations that the *transverse components* of A and C obey the equations [53, 60]:

$$\nabla \cdot \boldsymbol{A}_{\perp} = 0, \tag{4.8a}$$

$$c^2 \nabla \times \boldsymbol{C}_{\perp} = \boldsymbol{A}_{\perp},$$
 (4.8b)

$$\nabla \cdot \boldsymbol{C}_{\perp} = 0, \tag{4.8c}$$

$$\nabla \times \boldsymbol{A}_{\perp} = -\dot{\boldsymbol{C}}_{\perp}.$$
(4.8d)

These are *identical* in form to the Maxwell equations (2.42), and thus possess the same symmetries. In particular, they are also invariant under a duality transformation [52, 60, 69, 102]

$$A_{\perp} \to A'_{\perp} = \cos \theta A_{\perp} + \sin \theta c C_{\perp},$$
 (4.9a)

$$cC_{\perp} \to cC'_{\perp} = -\sin\theta A_{\perp} + \cos\theta cC_{\perp}.$$
 (4.9b)

Under a duality rotation, the (electric) optical spin density (2.29) therefore transforms as $s_e \rightarrow s'_e = \varepsilon_0 E' \times A'_{\perp}$, with E' and A'_{\perp} given by (4.6) and (4.9).

Given the invariance of Maxwell's equations, the electromagnetic energy, and other important quantities with respect to duality rotations, it seems reasonable to expect other derived electromagnetic quantities to possess this symmetry as well (in vacuum) [69]. On this basis, in the coming Sections I will consider a measure of, e.g., the chirality of light, to be a 'good' measure if it is dual-symmetric.

4.3 Fundamental Aspects of Optical Helicity

A quantity of the form $\mathbf{V} \cdot (\nabla \times \mathbf{V})$ is a time-even pseudoscalar, whether \mathbf{V} is time even or time odd, a polar vector or an axial vector, and thus the helicity (4.2) is a possible 'chirality observable' for any system with an associated vector field \mathbf{V} . Because light has several vector fields associated with it (\mathbf{E} , \mathbf{B} , \mathbf{A} , \mathbf{C}), we can define several different 'helicities', and thus several different measures of light's true chirality. I start this Section by reviewing two common choices which have arisen in the literature, one of which is the optical helicity, for characterizing the chirality of monochromatic optical fields.

Tang and Cohen recognized that 'chiral interactions require a time-even pseudoscalar, and no such density is in use' [31]. To fill this void they introduced the *optical chirality*, χ , defined as [13, 31]

$$\chi = \frac{\varepsilon_0}{2} \bigg[\boldsymbol{E} \cdot (\nabla \times \boldsymbol{E}) + c^2 \boldsymbol{B} \cdot (\nabla \times \boldsymbol{B}) \bigg].$$
(4.10)

This quantity was actually discovered a long time ago by Lipkin [156], in connection with a novel electromagnetic conservation law. Note that I am following the terminology of Tang and Cohen in calling χ the optical chirality; it is also common to call this the *chirality density*

or local optical chirality, and to call

$$X = \int \mathrm{d}^3 r \ \chi \tag{4.11}$$

the optical chirality [13, 34, 35]. I will call X the total or global optical chirality.

Using the terminology and notation outlined above, X is the sum of two 'helicities': $X = \varepsilon_0(\mathcal{H}_E + c^2\mathcal{H}_B)/2$. The reasons for preferring χ over just $\mathbf{E} \cdot (\nabla \times \mathbf{E})$, say, as a measure of the chirality of light are twofold. Firstly, X and χ are inherently dual symmetric, which is not the case for the individual helicities \mathcal{H}_E and \mathcal{H}_B . Dual symmetry of χ is easily established by noting its form in terms of the Riemann-Silberstein vector (4.3),

$$\chi = \frac{\varepsilon_0}{2} \operatorname{Re} \{ \boldsymbol{F} \cdot (\nabla \times \boldsymbol{F}^*) \}, \qquad (4.12)$$

which is clearly invariant under a duality rotation (4.5). Secondly, χ , but not $\boldsymbol{E} \cdot (\nabla \times \boldsymbol{E})$ or $\boldsymbol{B} \cdot (\nabla \times \boldsymbol{B})$, is a locally and globally conserved quantity in the absence of charges and currents, satisfying the continuity equation [31, 34, 156]

$$\frac{\partial \chi}{\partial t} + \nabla \cdot \boldsymbol{\varphi} = 0, \qquad (4.13)$$

where

$$\boldsymbol{\varphi} \equiv \frac{\varepsilon_0 c^2}{2} \left[\boldsymbol{E} \times (\nabla \times \boldsymbol{B}) - \boldsymbol{B} \times (\nabla \times \boldsymbol{E}) \right]$$
(4.14)

is the *optical chirality flux*. This is a desirable feature for a measure of the chirality of light, because it means that the total chirality of the field will remain the same, unless it is altered in light-matter interactions, as we would expect.

Let us now turn our attention to the optical helicity. The 'magnetic helicity' [147],

$$\mathcal{H}_m = \int \mathrm{d}^3 r \; \boldsymbol{A} \cdot (\nabla \times \boldsymbol{A}), \tag{4.15}$$

is a time-even pseudoscalar which has been studied in various contexts since the 1950s [145–147], and could reasonably be an optical chirality observable. However, this quantity lacks the two most advantageous features of χ , namely, dual symmetry and conservation in the absence of charges. To remedy this, we define the dual-symmetric *optical helicity*, first studied by Candlin [157], as the sum of the magnetic helicity and an equivalent 'electric

helicity' [13, 38, 52, 53, 141, 142],

$$\mathcal{H} \equiv \int \mathrm{d}^3 r \ h, \quad h \equiv \frac{\varepsilon_0 c}{2} \bigg[\mathbf{A}_{\perp} \cdot \mathbf{B} - \mathbf{C}_{\perp} \cdot \mathbf{E} \bigg], \qquad (4.16)$$

the constant prefactor $\varepsilon_0 c$ being chosen for dimensional reasons. The dual-symmetric integrand h shall be called 'the' helicity density or the local optical helicity. The optical helicity is, as desired, also a conserved quantity in vacuum. I will elaborate on this point shortly.

Note that because I have defined h in terms of the gauge-invariant transverse components of the vector potentials, which is not always done in the literature [141, 142], it is itself gauge invariant. If we had defined the helicity density in terms of the full vector potentials, \boldsymbol{A} and \boldsymbol{C} , then this would not be the case. However, the total optical helicity, \mathcal{H} , is always gauge invariant, because the volume integral of the dot product between a transverse and longitudinal vector field is zero [20, 52, 154]. Thus, it seems natural to define the local optical helicity as *the* gauge-invariant quantity which integrates to give the gauge-invariant total helicity.

The optical helicity relates to the helical nature of the potentials A_{\perp} and C_{\perp} , whilst the optical chirality tells us about the helicity of the fields E and B. In a monochromatic field, the complex potential and field vectors are directly proportional, recall Eqs. (2.75), so we might expect a proportionality between h and χ as well. This is indeed the case, and for a monochromatic field of frequency $\omega = ck$, the optical helicity density is [15, 94]

$$h_{\text{m.c.}} = \frac{\varepsilon_0 c}{2\omega} \text{Im}\{\tilde{\boldsymbol{E}} \cdot \tilde{\boldsymbol{B}}^*\},\tag{4.17}$$

whilst the optical chirality is given by $\chi_{\text{m.c.}} = h_{\text{m.c.}} \times (\omega^2/c)$. It should be stressed that this relationship only holds in monochromatic fields; in polychromatic fields the two observables can exhibit surprisingly different behaviours, as shown explicitly by Mackinnon [158]. This does raise interesting questions about whether h or χ , or some other quantity, is the most appropriate chirality measure in a general optical field, but I will not touch on this here. In all of the applications of the optical helicity or the optical chirality of which I am aware, it is (quasi-)monochromatic fields which are considered, so one could consider h or χ as the chirality observable, but I am more interested in the optical helicity because of some of its other fundamental properties.

As mentioned above, the dual-symmetric optical helicity is a conserved quantity. It can

easily be shown that it obeys the continuity equation [52]

$$\frac{\partial h}{\partial t} + \nabla \cdot \boldsymbol{v} = 0, \qquad (4.18)$$

where \boldsymbol{v} is the optical helicity flux,

$$\boldsymbol{v} = \frac{\varepsilon_0 c}{2} \bigg[\boldsymbol{E} \times \boldsymbol{A}_\perp + c^2 \boldsymbol{B} \times \boldsymbol{C}_\perp \bigg].$$
(4.19)

We see immediately that v = cs, s being the dual-symmetric optical spin density (2.73), which is very reminiscent of the relationship between the energy flux (Poynting vector) and the linear optical momentum density ($S = c^2 g$). This is the first hint at a deep connection which exists between optical helicity and optical spin. Before I discuss that connection in more detail, let us note that, from Noether's theorem [159], the existence of a conservation law such as (4.18) is indicative of a symmetry or invariance of the underlying system. We can ask, therefore, which (continuous) symmetry is associated with the conservation of optical helicity? The answer is the dual symmetry discussed in §4.2! Equivalently, one can show that the optical helicity is the 'generator' of duality rotations [52, 53, 60, 154].

Note that, because h is time-independent in a monochromatic field, it follows from (4.18) that $\nabla \cdot \mathbf{s} = 0$ and thus $\nabla \cdot \mathbf{s}_e = -\nabla \cdot \mathbf{s}_m$ in any such field, as was mentioned in §2.3.

Next, to flesh out the relationship between optical helicity and spin some more, let's consider the helicity in a zeroth-order paraxial beam (with electric and magnetic fields given by (2.51)). Using (4.17) we find

$$\mathcal{H} = \frac{\varepsilon_0}{2} \omega \sigma \int_V \mathrm{d}^3 r \ |u|^2. \tag{4.20}$$

If we now compute the optical spin (the integral of Eq. (2.65b)),

$$\mathbf{S} = \frac{\varepsilon_0}{2} \omega \sigma \int_V \mathrm{d}^3 r \ |u|^2 \hat{\mathbf{z}},\tag{4.21}$$

and the linear momentum of the beam (using (2.101) and (2.6)),

$$\overline{\boldsymbol{P}} = \frac{\varepsilon_0}{2} \omega k \int_V \mathrm{d}^3 r \ |u|^2 \hat{\mathbf{z}},\tag{4.22}$$

then we see that $\overline{\boldsymbol{P}}/|\overline{\boldsymbol{P}}| = \hat{\mathbf{z}}$, and therefore

$$\boldsymbol{S} \cdot \frac{\overline{\boldsymbol{P}}}{|\overline{\boldsymbol{P}}|} = \frac{\varepsilon_0}{2} \omega \sigma \int_V \mathrm{d}^3 r \ |u|^2 = \mathcal{H}.$$
(4.23)

Thus, for the 2D paraxial beam, the optical helicity is nothing but the projection of the spin angular momentum onto the direction of propagation, which is exactly the definition of helicity in particle physics (Eq. (4.1)). We may also compare the ratio of the optical helicity to the time-averaged total energy of the beam (2.67), for which we find

$$\frac{\mathcal{H}}{\overline{W}} = \frac{\sigma}{\omega}.\tag{4.24}$$

Making the same argument as in Chapter 2, we infer from this that each photon in the beam possesses an energy of $\hbar\omega$ and a helicity, i.e., angular momentum in the direction of propagation, of $\sigma\hbar$, which for a circularly polarized photon is $\pm\hbar$.

These connections are even more firmly established by considering the quantum theory. One can show that the optical helicity *operator* takes the form [52, 53, 141]

$$\hat{\mathcal{H}} = \sum_{\boldsymbol{k}} \hbar \left(\hat{n}_{\boldsymbol{k}L} - \hat{n}_{\boldsymbol{k}R} \right), \tag{4.25}$$

where $\hat{n}_{\boldsymbol{k}L/R}$ are the number operators for modes $(\boldsymbol{k}, L/R)$. Thus the total optical helicity is essentially a measure of the number of left-CP photons minus the number of right-CP photons, and is thus inherently linked to polarization. A linearly polarized beam can be thought of as containing equal numbers of CP photons of opposite handedness, and thus it has zero helicity. It should be noted that we are talking here about the *total* optical helicity. The local optical helicity is not inherently linked to the CP content of an optical field; for instance, Forbes [13, 94] has shown that a non-zero h is possible in linearly polarized optical vortex beams (even though $\mathcal{H} = 0$), when the full 3D polarization is taken into account. This is similar to the discussion in §2.3, in which we saw that the association of the local optical spin with polarization structure is largely confined to the paraxial approximation.

4.4 Helicity-Dependent Optical Force

Having discussed some of the fundamentals, in this Section I turn to a more practical aspect of the optical helicity.

Cameron et al. [38] (see also [37]) have shown that a chiral molecule in a monochromatic optical field experiences, in addition to the usual electric and magnetic forces, the time-

averaged, rotationally-averaged force

$$\overline{\langle \boldsymbol{F}_h \rangle} = -\frac{\omega}{\varepsilon_0 c} G' \nabla h_{\text{m.c.}}, \qquad (4.26)$$

where G' is a measure of the molecular chirality, in the sense that G' > 0 for one enantiomer and G' < 0 for the other, whilst for an achiral molecule or atom G' = 0 [24]. The existence of the helicity force has been experimentally verified by Kravets et al. [160].

In a general monochromatic field the helicity force will be several orders of magnitude smaller than the electric gradient force from (2.112), and will thus have a negligible effect on the molecular dynamics. However, Cameron and co-workers [17, 38, 51, 161] recognized that in a non-interfering superposition (as discussed in §2.3.1), the electric force vanishes and thus the helicity force can dominate, leading to potential applications for the sensing and separation of chiral molecules.

In [38] they derive the helicity-dependent force classically using the Lorentz force law, but note that it 'can also be justified by an appropriate calculation in the quantum domain'. However, I am not aware of an explicit calculation showing this in the literature, so in this Section I will derive the force using the molecular QED formalism discussed in Chapter 3, such that the electromagnetic fields as well as the molecules are quantized. I will, in particular, derive the force for a two-wave superposition.

The force (4.26) is conservative and may be written as $-\nabla U_h$, where

$$U_h \equiv \frac{\omega G' h_{\text{m.c.}}}{\varepsilon_0 c} \tag{4.27}$$

may be interpreted as an interaction energy between the light and the molecule. Although the notion of force is inherently classical, we can derive the interaction energy via quantum theory and infer the associated force from this [18, 162]. The energy of the molecule plus EM field when they are in the combined state $|1\rangle$ and are not interacting (i.e., when they are well separated from one another) is

$$E_0 = \langle 1|H_0|1\rangle, \qquad (4.28)$$

where H_0 is the Hamiltonian of the free field plus molecule. When the field and molecule are brought together, the Hamiltonian is modified by the addition of the perturbation term V, and the new energy is

$$E = \langle 1|H_0 + V|1\rangle, \qquad (4.29)$$

i.e., the energy shift is $\Delta E^{(1)} = \langle 1|V|1 \rangle$. If the perturbation does not directly connect $|1\rangle$ to itself then $\Delta E^{(1)} = 0$, and we must consider higher-order corrections to the energy.

The necessary perturbation for chiral light-matter interactions is $V = V_{E1} + V_{M1}$, where $V_{E1} = -\boldsymbol{\mu} \cdot \varepsilon_0^{-1} \hat{\boldsymbol{D}}_{\perp}$ and $V_{M1} = -\boldsymbol{m} \cdot \hat{\boldsymbol{B}}$ are the electric and magnetic dipole interactions¹, and the leading energy shift is of second order [18, 108],

$$\Delta E^{(2)} = \sum_{I} \frac{\langle 1|V|I\rangle \langle I|V|1\rangle}{E_1 - E_I}.$$
(4.30)

For our particular perturbation it is convenient to write this as (now dropping the superscript 2)

$$\Delta E = \Delta E_{E1-E1} + \Delta E_{E1-M1} \tag{4.31}$$

in which

$$\Delta E_{E1-E1} = \sum_{I} \frac{\langle 1|V_{E1}|I\rangle \langle I|V_{E1}|1\rangle}{E_1 - E_I}$$
(4.32)

and

$$\Delta E_{E1-M1} = \Delta \tilde{E}_{E1-M1} + \Delta \tilde{E}^*_{E1-M1}, \qquad (4.33)$$

where

$$\Delta \tilde{E}_{E1-M1} = \sum_{I} \frac{\langle 1|V_{E1}|I\rangle \langle I|V_{M1}|1\rangle}{E_1 - E_I}.$$
(4.34)

The intermediate states $|I\rangle$ are the combined molecular and field eigenstates. In ΔE we have neglected the term that arises from two magnetic interactions, as it is smaller than the other two and not chirally sensitive. The aim is to show that $\langle \Delta E_{E1-M1} \rangle = U_h$.

The specific state $|1\rangle$ which I shall consider is

$$|1\rangle = |E_g; \alpha_1(\mathbf{k}_1, \lambda_1); \alpha_2(\mathbf{k}_2, \lambda_2)\rangle, \qquad (4.35)$$

where $|E_g\rangle$ is the molecular ground state and $|\alpha_1\rangle$ and $|\alpha_2\rangle$ are coherent states of modes $(\mathbf{k}_1, \lambda_1)$ and $(\mathbf{k}_2, \lambda_2)$, which have polarization vectors $\hat{\boldsymbol{\epsilon}}^{(1)}$ and $\hat{\boldsymbol{\epsilon}}^{(2)}$. The two modes will be taken to be monochromatic, so that $|\mathbf{k}_1| = |\mathbf{k}_2| = k = \omega/c$, but $\mathbf{k}_1 \neq \mathbf{k}_2$ in general. We can

¹Strictly we should include the electric quadrupole at this order, but its leading contribution vanishes upon rotational averaging [18, 38].

write the coherent states in the forms

$$|\alpha_1\rangle = \sum_{n_1} c_{n_1} |n_1\rangle, \qquad (4.36)$$

$$|\alpha_2\rangle = \sum_{n_2} d_{n_2} |n_2\rangle, \qquad (4.37)$$

where $|n_i\rangle = |n(\mathbf{k}_i, \lambda_i)\rangle$ are number states of the respective modes. Coherent states are a natural choice because they are the 'most classical' quantum states, and their expectation values resemble plane waves. This is unlike the number states, which are highly non-classical in nature [18, 23]. In fact, one can show that the results of this Section cannot be derived if the initial state is a number state. To see this, suppose the field is in a number state, so $|1\rangle = |E_g; n_1; n_2\rangle$. As we shall see in the below derivation, the helicity-dependent energy shift contains a phase term, $\exp\{\pm i(\mathbf{k}_1 - \mathbf{k}_2) \cdot \mathbf{R}\}$, where \mathbf{R} is the molecular centre-of-mass, which can only arise from non-forward Rayleigh scattering, i.e., scattering from one mode to another. Say the first interaction in (4.30) annihilates a photon of mode 1, then the resulting intermediate state will be of the form $|E_r; n_1 - 1; n_2\rangle$. To achieve the necessary phase term, we require a photon of mode 2 to be created. However, this would result in a state of the radiation field which is proportional to $|n_1 - 1; n_2 + 1\rangle$, which is orthogonal to the state $|1\rangle$, and thus the overlap is zero. Therefore, the helicity-dependent term cannot arise if the field is in a number state.

The energy shift can be evaluated with the aid of Feynman diagrams. The number of possible intermediate states (and thus the number of Feynman diagrams) is quite large. However, I reduce this number by only considering those contributions which are *strictly energy conserving* (which contain one photon absorption and one emission). This is equivalent to the time-averaging that Cameron et al. [38] perform in their classical derivation. This leaves a total of 24 digrams, eight of which contribute to ΔE_{E1-E1} and 16 which contribute to ΔE_{E1-M1} . The total energy shift is the sum of the contributions from each graph. We do not actually have to work out 24 terms though, because of similarities between the different graphs. Of the 16 graphs which contribute to ΔE_{E1-M1} , eight contribute to $\Delta \tilde{E}_{E1-M1}$ and the other eight contribute to $\Delta \tilde{E}_{E1-M1}$. The graphs which contribute to $\Delta \tilde{E}_{E1-M1}$ are those in which the M1 interaction occurs before the E1 interaction. We can find $\Delta \tilde{E}_{E1-M1}$ and get $\Delta \tilde{E}_{E1-M1}$ by taking the complex conjugate. Also, the types of graph which contribute to $\Delta \tilde{E}_{E1-M1}$ and get $\Delta \tilde{E}_{E1-M1}$ and get $\Delta \tilde{E}_{E1-M1}$ if or free' by just replacing the terms involving magnetic quantities with electric quantities.



Figure 4.3: Feynman diagrams involving absorption and emission of a photon from the same mode ('class 1 diagrams').

Just focussing on $\Delta \tilde{E}_{E1-M1}$, and deriving the other terms from this, the eight Feynman diagrams fall into two classes:

- Class 1 (forward Rayleigh scattering): A photon of mode i is created and destroyed (i = 1 or 2). Considering all of the possible time orderings, this class includes four diagrams, see Figures 4.3.
- Class 2 (non-forward Rayleigh scattering): A photon of mode i is destroyed and a photon of mode $j \neq i$ is created. Again, considering all possible time orderings, we have four such diagrams, see Figures 4.4. Note that often only forward Rayleigh scattering is considered in the calculation of energy shifts [18], but this is because the field is usually assumed to be in a number state. As discussed above, the helicity-dependent term which we are seeking only arises if the field is not in a number state, via non-forward scattering.

The evaluation of the total energy shift is quite long and tedious, so I will just explicitly demonstrate the calculation for the graph shown in Figure 4.3a, which I denote $\Delta \tilde{E}(1a)$. Expanding $|1\rangle$ in the number state basis we may write

$$\Delta \tilde{E}(1a) = \sum_{r} \sum_{n_{1}',n_{2}'} \frac{\langle \alpha_{2}; \alpha_{1}; E_{g} | V_{E1} | E_{r}; n_{1}'; n_{2}' \rangle \langle n_{2}'; n_{1}'; E_{r} | V_{M1} | E_{g}; \alpha_{1}; \alpha_{2} \rangle}{E_{gr} + \hbar \omega}$$

$$= \sum_{r} \sum_{n_{1}',n_{2}'} \sum_{n_{1},n_{2}} \sum_{m_{1},m_{2}} \sum_{m_{1},m_{2}} c_{n_{1}} c_{m_{1}}^{*} d_{n_{2}} d_{m_{2}}^{*} \frac{\langle m_{2}; m_{1}; E_{g} | V_{E1} | E_{r}; n_{1}'; n_{2}' \rangle \langle n_{2}'; n_{1}'; E_{r} | V_{M1} | E_{g}; n_{1}; n_{2} \rangle}{E_{gr} + \hbar \omega}.$$

$$(4.38)$$



Figure 4.4: Feynman diagrams involving absorption and emission of photons from different modes ('class 2 diagrams').

The denominator in this case is $E_{gr} + \hbar\omega = E_g - (E_r - \hbar\omega)$, where E_r is the energy of the intermediate molecular eigenstate $|E_r\rangle$. The energy of the intermediate state is $E_r - \hbar\omega$ because, as we can see from Figure 4.3a, one photon is removed from mode $(\mathbf{k}_1, \lambda_1)$, i.e., $n'_1 = n_1 - 1$. The relations between the other summation indices are $m_1 = n_1$, $m_2 = n_2$, and $n'_2 = n_2$. Therefore we are just left with a sum over r, n_1 , and n_2 :

$$\Delta \tilde{E}(1a) = \sum_{r} \sum_{n_1, n_2} |c_{n_1}|^2 |d_{n_2}|^2 \frac{\langle n_2; n_1; E_g | V_{E1} | E_r; n_1 - 1; n_2 \rangle \langle n_2; n_1 - 1; E_r | V_{M1} | E_g; n_1; n_2 \rangle}{E_{gr} + \hbar \omega}$$
(4.39)

Only the positive-frequency (i.e., annihilation) part of the \hat{B} field contributes to the matrix element involving V_{M1} , and only the negative-frequency (creation) part of the \hat{D}_{\perp} field contributes to the matrix element involving V_{E1} . We have

$$\langle n_2; n_1 - 1; E_r | V_{M1} | E_g; n_1; n_2 \rangle = -\boldsymbol{m}^{rg} \cdot \langle n_1 - 1 | \hat{\boldsymbol{B}}^+ | n_1 \rangle, \qquad (4.40)$$

and, using (3.41c),

$$\langle n_1 - 1 | \hat{\boldsymbol{B}}^+ | n_1 \rangle = \frac{i}{c} \mathcal{N}(k) e^{i\boldsymbol{k}_1 \cdot \boldsymbol{R}} \sqrt{n_1} \hat{\boldsymbol{\beta}}^{(1)}, \qquad (4.41)$$

where $\hat{\boldsymbol{\beta}}^{(1)}$ is the magnetic polarization vector of mode 1, $\mathcal{N}(k)$ is the normalization coefficient (3.30), and $\boldsymbol{m}^{rg} \equiv \langle E_r | \boldsymbol{m} | E_g \rangle$ is the magnetic dipole transition moment from state g to r. Putting everything back together:

$$\langle n_2; n_1 - 1; E_r | V_{M1} | E_g; n_1; n_2 \rangle = -\frac{i}{c} \sqrt{n_1} \mathcal{N}(k) e^{i\boldsymbol{k}_1 \cdot \boldsymbol{R}} \boldsymbol{m}^{rg} \cdot \hat{\boldsymbol{\beta}}^{(1)}.$$
(4.42)

A similar calculation for the E1 interaction gives

$$\langle n_2; n_1; E_g | V_{E1} | E_r; n_1 - 1; n_2 \rangle = +i\sqrt{n_1} \mathcal{N}(k) e^{-i\mathbf{k}_1 \cdot \mathbf{R}} \hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \boldsymbol{\mu}^{gr}.$$
 (4.43)

Combining these we find

$$\Delta \tilde{E}(1a) = \frac{\mathscr{N}^2(k)}{c} \left(\sum_{n_2} |d_{n_2}|^2\right) \left(\sum_{n_1} |c_{n_1}|^2 n_1\right) \sum_r \left[\frac{(\hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \boldsymbol{\mu}^{gr})(\hat{\boldsymbol{\beta}}^{(1)} \cdot \boldsymbol{m}^{rg})}{E_{gr} + \hbar\omega}\right].$$
(4.44)

Now the first summation is just $\sum_{n_2} |d_{n_2}|^2 = \langle \alpha_2 | \alpha_2 \rangle = 1$. The second sum, $\sum_{n_1} |c_{n_1}|^2 n_1$, is nothing but the average number of photons in mode 1 for the coherent state α_1 , which is equal to $\bar{n}_1 = |\alpha_1|^2$ [18, 23]. Thus we can write $\Delta \tilde{E}(1a)$ as

$$\Delta \tilde{E}(1a) = -\frac{\bar{n}_1 \hbar \omega}{2c\varepsilon_0 V} \sum_r \left[\frac{(\hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \boldsymbol{\mu}^{gr})(\hat{\boldsymbol{\beta}}^{(1)} \cdot \boldsymbol{m}^{rg})}{E_{rg} - \hbar \omega} \right], \qquad (4.45)$$

where I have now written the denominator in terms of $E_{rg} = -E_{gr}$. As mentioned above, we can derive the equivalent contribution ($\Delta E_{E1}(1a)$) involving two E1 interactions, rather than an M1 and an E1 interaction, by just replacing the magnetic quantities above with the appropriate electric ones:

$$\Delta E_{E1}(1a) = -\frac{\bar{n}_1 \hbar \omega}{2\varepsilon_0 V} \sum_r \left[\frac{(\hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \boldsymbol{\mu}^{gr})(\hat{\boldsymbol{\epsilon}}^{(1)} \cdot \boldsymbol{\mu}^{rg})}{E_{rg} - \hbar \omega} \right].$$
(4.46)

We see from these two contributions a general feature, which is that the 'class 1' diagrams, Figures 4.3, are spatially independent. On the other hand the class 2 diagrams, Figures 4.4, have spatial dependences of $e^{\pm i(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{R}}$.

After summing the contributions from each Feynman diagram, we find that the energy shifts are:

$$\Delta E_{E1-E1} = -\frac{\hbar\omega}{2\varepsilon_0 V} \left\{ \bar{n}_1 \hat{\boldsymbol{\epsilon}}_i^{(1)*} \hat{\boldsymbol{\epsilon}}_j^{(1)} + \bar{n}_2 \hat{\boldsymbol{\epsilon}}_i^{(2)*} \hat{\boldsymbol{\epsilon}}_j^{(2)} \right\} \tilde{\alpha}_{ij}^{gg}(\omega) - \frac{\hbar\omega}{2\varepsilon_0 V} \left\{ \alpha_1^* \alpha_2 e^{i(\boldsymbol{k}_2 - \boldsymbol{k}_1) \cdot \boldsymbol{R}} \hat{\boldsymbol{\epsilon}}_i^{(1)*} \hat{\boldsymbol{\epsilon}}_j^{(2)} + \alpha_1 \alpha_2^* e^{i(\boldsymbol{k}_1 - \boldsymbol{k}_2) \cdot \boldsymbol{R}} \hat{\boldsymbol{\epsilon}}_i^{(2)*} \hat{\boldsymbol{\epsilon}}_j^{(1)*} \hat{\boldsymbol{\epsilon}}_j^{gg}(\omega), \quad (4.47) \right\}$$

and

$$\Delta E_{E1-M1} = -\frac{\hbar\omega}{2c\varepsilon_0 V} \left\{ \bar{n}_1 \left(\hat{\boldsymbol{\epsilon}}_i^{(1)*} \hat{\boldsymbol{\beta}}_j^{(1)} \tilde{G}_{ij}^{gg}(\omega) + \text{c.c.} \right) + \bar{n}_2 \left(\hat{\boldsymbol{\epsilon}}_i^{(2)*} \hat{\boldsymbol{\beta}}_j^{(2)} \tilde{G}_{ij}^{gg}(\omega) + \text{c.c.} \right) \right\} - \frac{\hbar\omega}{2c\varepsilon_0 V} \left\{ \left(\alpha_1^* \alpha_2 e^{i(\boldsymbol{k}_2 - \boldsymbol{k}_1) \cdot \boldsymbol{R}} \hat{\boldsymbol{\epsilon}}_i^{(1)*} \hat{\boldsymbol{\beta}}_j^{(2)} \tilde{G}_{ij}^{gg}(\omega) + \text{c.c.} \right) \right. \\\left. + \left(\alpha_1 \alpha_2^* e^{i(\boldsymbol{k}_1 - \boldsymbol{k}_2) \cdot \boldsymbol{R}} \hat{\boldsymbol{\epsilon}}_i^{(2)*} \hat{\boldsymbol{\beta}}_j^{(1)} \tilde{G}_{ij}^{gg}(\omega) + \text{c.c.} \right) \right\}, \quad (4.48)$$

where

$$\tilde{\alpha}_{ij}^{ba}(\omega) = \sum_{r} \left\{ \frac{\mu_i^{br} \mu_j^{ra}}{E_{rg} - \hbar\omega} + \frac{\mu_j^{br} \mu_i^{ra}}{E_{rg} + \hbar\omega} \right\},\tag{4.49a}$$

$$\tilde{G}_{ij}^{ba}(\omega) = \sum_{r} \left\{ \frac{\mu_i^{br} m_j^{ra}}{E_{rg} - \hbar\omega} + \frac{m_j^{br} \mu_i^{ra}}{E_{rg} + \hbar\omega} \right\},\tag{4.49b}$$

are the complex electric-electric and electric-magnetic dipole polarizability tensors [18].

To get a form comparable to U_h from [38], we need to take the rotational average of the above result. For a rank-2 tensor we have the general result [18, 24]

$$\langle O_{ij} \rangle = \frac{1}{3} \delta_{ij} \delta_{\alpha\beta} O_{\alpha\beta} = \frac{1}{3} \delta_{ij} O_{\beta\beta}, \qquad (4.50)$$

where $O_{\alpha\beta}$ are the components of the molecular property tensor O with respect to the molecule-fixed coordinate axes. We shall denote the isotropic averages of the polarizability tensors as

$$\tilde{\alpha}^{gg}_{\beta\beta}(\omega) \equiv 3\alpha(\omega), \qquad \tilde{G}^{gg}_{\beta\beta}(\omega) \equiv 3\tilde{G}(\omega).$$
(4.51)

Note that, although the tensor $\alpha_{\alpha\beta}^{gg}$ is complex, its isotropic average is a real quantity². To further aid comparison to [38], we shall assume that the molecule has real wave functions, which means that $\operatorname{Re}\{\tilde{G}\} \equiv 0$, and thus $\tilde{G} = -iG'$, where $G'(\omega)$ is a real scalar quantity [24].

Working under the above assumptions, we find that the rotationally-averaged interaction

²One might therefore wonder how the *imaginary part* of the *scalar* polarizability appears in connection with the (classically-derived) optical force (2.112). This term arises when the radiation is close to an atomic/molecular resonance, because of a modification which we must make to the polarizability tensor in order to ensure that it does not diverge [24, p. 96]. In particular, the symmetric part of the polarizability tensor, which is the part which does not vanish upon rotational averaging, acquires an imaginary contribution. I assume the molecular eigenenergies are far-detuned from the optical frequency, as is usual in optical lattices [108], such that absorption is negligible and α is real.

energies are:

$$\langle \Delta E_{E1-E1} \rangle = -\frac{\hbar\omega}{2\varepsilon_0 V} \alpha(\omega) \left\{ |\alpha_1|^2 |\hat{\boldsymbol{\epsilon}}^{(1)}|^2 + |\alpha_2|^2 |\hat{\boldsymbol{\epsilon}}^{(2)}|^2 \alpha_1^* \alpha_2 e^{i(\boldsymbol{k}_2 - \boldsymbol{k}_1) \cdot \boldsymbol{R}} \hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \hat{\boldsymbol{\epsilon}}^{(2)} + \alpha_1 \alpha_2^* e^{i(\boldsymbol{k}_1 - \boldsymbol{k}_2) \cdot \boldsymbol{R}} \hat{\boldsymbol{\epsilon}}^{(1)} \cdot \hat{\boldsymbol{\epsilon}}^{(2)*} \right\}$$
(4.52)

and

$$\langle \Delta E_{E1-M1} \rangle = i \frac{\hbar \omega}{2\varepsilon_0 cV} G'(\omega) \bigg\{ |\alpha_1|^2 (\hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \hat{\boldsymbol{\beta}}^{(1)} - \hat{\boldsymbol{\epsilon}}^{(1)} \cdot \hat{\boldsymbol{\beta}}^{(1)*}) + |\alpha_2|^2 (\hat{\boldsymbol{\epsilon}}^{(2)*} \cdot \hat{\boldsymbol{\beta}}^{(2)} - \hat{\boldsymbol{\epsilon}}^{(2)} \cdot \hat{\boldsymbol{\beta}}^{(2)*}) + \alpha_1^* \alpha_2 e^{i(\boldsymbol{k}_2 - \boldsymbol{k}_1) \cdot \boldsymbol{R}} (\hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \hat{\boldsymbol{\beta}}^{(2)} - \hat{\boldsymbol{\epsilon}}^{(2)} \cdot \hat{\boldsymbol{\beta}}^{(1*)}) + \alpha_1 \alpha_2^* e^{i(\boldsymbol{k}_1 - \boldsymbol{k}_2) \cdot \boldsymbol{R}} (\hat{\boldsymbol{\epsilon}}^{(2)*} \cdot \hat{\boldsymbol{\beta}}^{(1)} - \hat{\boldsymbol{\epsilon}}^{(1)} \cdot \hat{\boldsymbol{\beta}}^{(2)*}) \bigg\}.$$
(4.53)

To show that (4.53) is indeed U_h , we must introduce the optical helicity into this expression somehow. We could approach this in several ways. Most rigorously, perhaps, we could find the expectation value $\langle \alpha_2; \alpha_1 | \hat{h} | \alpha_1; \alpha_2 \rangle$, where \hat{h} is the operator form of the *local* optical helicity, Eq. (4.16). However, the same result can be achieved in a simpler way, and this is how I shall proceed.

We make the assumption that the classical electric field \boldsymbol{E} is equal to the expectation value $\langle \hat{\boldsymbol{E}} \rangle$ (this assumption corresponds to the classical/large $|\alpha_{1/2}|$ limit [23]). The expected value of the electric field operator for coherent states such as $|\alpha_1; \alpha_2\rangle$ takes a well-known form [18], and we may write

$$\boldsymbol{E} = \langle \hat{\boldsymbol{E}} \rangle = \operatorname{Re}\{\tilde{\boldsymbol{E}}e^{-i\omega t}\},\tag{4.54}$$

where I have used the fact that the two modes are monochromatic of frequency ω . The complex (classical) electric field is given by [18]

$$\tilde{\boldsymbol{E}} = 2i\sqrt{\frac{\hbar\omega}{2\varepsilon_0 V}} \left(\alpha_1 \hat{\boldsymbol{\epsilon}}^{(1)} e^{i\boldsymbol{k}_1 \cdot \boldsymbol{R}} + \alpha_2 \hat{\boldsymbol{\epsilon}}^{(2)} e^{i\boldsymbol{k}_2 \cdot \boldsymbol{R}}\right).$$
(4.55)

We similarly take the magnetic field to be $\boldsymbol{B} = \langle \hat{\boldsymbol{B}} \rangle = \operatorname{Re}\{\tilde{\boldsymbol{B}}e^{-i\omega t}\},$ where

$$\tilde{\boldsymbol{B}} = \frac{2i}{c} \sqrt{\frac{\hbar\omega}{2\varepsilon_0 V}} \left(\alpha_1 \hat{\boldsymbol{\beta}}^{(1)} e^{i\boldsymbol{k}_1 \cdot \boldsymbol{R}} + \alpha_2 \hat{\boldsymbol{\beta}}^{(2)} e^{i\boldsymbol{k}_2 \cdot \boldsymbol{R}} \right).$$
(4.56)

We can now evaluate the local optical helicity of the (average) field using (4.17), and we find

$$h_{\text{m.c.}} = i \frac{\hbar}{2V} \bigg\{ |\alpha_1|^2 (\hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \hat{\boldsymbol{\beta}}^{(1)} - \hat{\boldsymbol{\epsilon}}^{(1)} \cdot \hat{\boldsymbol{\beta}}^{(1)*}) + |\alpha_2|^2 (\hat{\boldsymbol{\epsilon}}^{(2)*} \cdot \hat{\boldsymbol{\beta}}^{(2)} - \hat{\boldsymbol{\epsilon}}^{(2)} \cdot \hat{\boldsymbol{\beta}}^{(2)*}) + \alpha_1^* \alpha_2 e^{i(\boldsymbol{k}_2 - \boldsymbol{k}_1) \cdot \boldsymbol{R}} (\hat{\boldsymbol{\epsilon}}^{(1)*} \cdot \hat{\boldsymbol{\beta}}^{(2)} - \hat{\boldsymbol{\epsilon}}^{(2)} \cdot \hat{\boldsymbol{\beta}}^{(1*)}) + \alpha_1 \alpha_2^* e^{i(\boldsymbol{k}_1 - \boldsymbol{k}_2) \cdot \boldsymbol{R}} (\hat{\boldsymbol{\epsilon}}^{(2)*} \cdot \hat{\boldsymbol{\beta}}^{(1)} - \hat{\boldsymbol{\epsilon}}^{(1)} \cdot \hat{\boldsymbol{\beta}}^{(2)*}) \bigg\}. \quad (4.57)$$

Comparing with (4.53), we see that the rotationally-averaged electric-magnetic energy shift can be written as

$$\left\langle \Delta E_{E1-M1} \right\rangle = \frac{\omega G' h_{\text{m.c.}}}{\varepsilon_0 c} \tag{4.58}$$

which is exactly the classical result (4.27) derived by Cameron et al. [38], as required.

Although I have derived this result for a field consisting of only two modes, the same procedure can be applied to any number of field modes.

4.5 Summary

In the first Section of this Chapter I discussed the notions of true and false chirality, as introduced by Barron, which leads to the identification of time-even pseudoscalars as the correct observables for chiral systems. In the next Section I discussed the duality rotations and dual symmetry of electromagnetism in vacuum, and argued in favour of all electromagnetic quantities being written in explicitly dual-symmetric forms in the absence of charges. As I discussed later, this symmetry has close connections with the optical helicity, which was discussed in depth in §4.3. In this Section I compared the optical helicity and the optical chirality and discussed how both possess the necessary properties to be chirality measures of the free optical field. The very close connections between these observables in monochromatic fields was mentioned, although it was stressed that this relationship does not hold for polychromatic fields. I also considered the deep connections between the optical helicity and the optical spin angular momentum, showing that the spin can also be interpreted as the optical helicity flux. Finally, in §4.4 I have used the molecular QED formalism to derive the energy splitting of a chiral molecule in a two-wave superposition, showing that the helicitydependent chiroptical force which was previously derived classically by Cameron et al. [38] has its origin at a deeper level of theory.

CHAPTER 5

Optical Helicity Transfer to a Single Atom

In the previous Chapter, we have seen that the optical helicity plays an important role in chiral light-matter interactions. In this Chapter, I investigate the nature of helicity transfer between light and matter from a more fundamental point of view. In particular, I try to answer the question: can an atom act as a faithful detector of local optical helicity? I consider the light-atom interaction semi-classically, and consider both the internal (electronic) and external (centre-of-mass) states of the atom, and the correlations which arise between the two due to the external perturbation. This is a connection which is often ignored but is crucial for a comprehensive understanding of light-matter interactions [163–168].

We begin in the next Section by defining the exact situation under consideration.

5.1 Hamiltonian and State of the System

We shall suppose that the atom interacts with a monochromatic optical field, with associated electric field

$$\boldsymbol{E}(\boldsymbol{r},t) = \operatorname{Re}\{\tilde{\boldsymbol{E}}(\boldsymbol{r})e^{-i\omega t}\}.$$
(5.1)

The arbitrary complex field \tilde{E} can be written in the Cartesian basis as

$$\tilde{\boldsymbol{E}}(\boldsymbol{r}) = \mathcal{E}_x(\boldsymbol{r})\hat{\mathbf{x}} + \mathcal{E}_y(\boldsymbol{r})\hat{\mathbf{y}} + \mathcal{E}_z(\boldsymbol{r})\hat{\mathbf{z}}, \qquad (5.2)$$

or in the 'circular basis' as

$$\tilde{\boldsymbol{E}}(\boldsymbol{r}) = \mathcal{E}_R(\boldsymbol{r})\hat{\boldsymbol{\epsilon}}_R + \mathcal{E}_L(\boldsymbol{r})\hat{\boldsymbol{\epsilon}}_L + \mathcal{E}_z(\boldsymbol{r})\hat{\mathbf{z}}.$$
(5.3)

The components in this basis may be found by noting the relations

$$\hat{\mathbf{x}} = \frac{1}{\sqrt{2}} (\hat{\boldsymbol{\epsilon}}_R + \hat{\boldsymbol{\epsilon}}_L), \qquad (5.4a)$$

$$\hat{\mathbf{y}} = \frac{i}{\sqrt{2}} (\hat{\boldsymbol{\epsilon}}_R - \hat{\boldsymbol{\epsilon}}_L), \qquad (5.4b)$$

which leads to

$$\mathcal{E}_R = \frac{1}{\sqrt{2}} (\mathcal{E}_x + i\mathcal{E}_y), \tag{5.5a}$$

$$\mathcal{E}_L = \frac{1}{\sqrt{2}} (\mathcal{E}_x - i\mathcal{E}_y). \tag{5.5b}$$

We work in the electric-dipole (ED) approximation, so the interaction between the atom and the field is given by $-\mu \cdot \boldsymbol{E}(\boldsymbol{r},t)$, where $\boldsymbol{\mu}$ is the atom's electric dipole moment and \boldsymbol{r} is the centre-of-mass (COM) position of the atom.

For times t < 0, we assume that the atom is trapped by some potential and is quasi-localized within a small volume, with an associated COM wave packet $\psi_0(\mathbf{r}) \equiv \langle \mathbf{r} | \psi_0 \rangle$. At t = 0, the trap is switched off and the optical field (5.1) simultaneously switched on. Strictly speaking the external wave packet will begin to spread once the trap is removed, however, I shall be concerned with such small time scales that we neglect these variations. Therefore, at t = 0the total state of the atom is assumed to be a product state,

$$|\Psi(t=0)\rangle \equiv |\Psi_0\rangle = |g\rangle |\psi_0\rangle, \qquad (5.6)$$

where $|g\rangle$ is the electronic state. We can alternatively write this directly in terms of the

¹Recall that in §3.1.3, the ED Hamiltonian contained the interaction term $-\hat{\mu} \cdot \hat{D}_{\perp}$, where \hat{D}_{\perp} is the electric displacement field operator. However, in the semi-classical theory, it is actually the electric field, not the displacement field, which couples to the electric dipole moment [20].

wave packet ψ_0 ,

$$|\Psi_0\rangle = \int d^3r \, |g\rangle \, |\mathbf{r}\rangle \, \psi_0(\mathbf{r}).$$
(5.7)

We shall assume that $|g\rangle$ is a zero-angular momentum (j = 0) electronic ground state. We treat the light-atom interaction using first-order time-dependent perturbation theory (TDPT), which corresponds to absorption of a single photon. Considering the well-known selection rules for ED interactions [104, 169], the accessible excited states are

$$|a\rangle \equiv |j=1,m=-1\rangle, \qquad (5.8a)$$

$$b\rangle \equiv |j=1,m=0\rangle,$$
 (5.8b)

$$|c\rangle \equiv |j=1,m=+1\rangle.$$
(5.8c)

In quantum optics it is common to restrict oneself to a two-dimensional state space [163, 170], but as we wish to consider optical fields with non-trivial polarization characteristics it is necessary to consider the possibility of transitions to each of these excited states. Therefore we make a 'four-state approximation', instead of the usual two-state one. The identity operator within this state space is

$$\mathbb{1} = |g\rangle \langle g| + |a\rangle \langle a| + |b\rangle \langle b| + |c\rangle \langle c|.$$
(5.9)

The Hamiltonian of our system from t = 0 onwards is [163, 168]

$$H = \frac{\boldsymbol{P}^2}{2M} + H_{\text{elec}} - \hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(\hat{\boldsymbol{r}}, t).$$
(5.10)

The first term represents the translational kinetic energy of the atom's COM, the second the electronic (internal) energy, and the third term is the previously mentioned ED interaction, now with the electric dipole moment and COM positions promoted to operators². I shall neglect the COM term in my analysis, under the reasonable assumption that the atom's translational energy is very small in the short time period we consider after the trapping potential is removed. The electronic Hamiltonian can be written as $\sum_n \hbar \omega_n |n\rangle \langle n|$, where $|n\rangle$ and $\hbar \omega_n$ are the electronic eigenstates and energies. We choose, for convenience, $\omega_g = 0$. Thus

$$H_{\text{elec}} = \hbar\omega_a \left| a \right\rangle \left\langle a \right| + \hbar\omega_b \left| b \right\rangle \left\langle b \right| + \hbar\omega_c \left| c \right\rangle \left\langle c \right|.$$
(5.11)

²In this Chapter I only use a 'hat' for those operators which might be confused with their classical counterparts, i.e., \hat{r} is the COM position operator, r is the classical COM position.

The interaction term takes a little more consideration to write in the energy basis. The dipole operator can be expanded as

$$\hat{\boldsymbol{\mu}} = \mathbb{1}\hat{\boldsymbol{\mu}}\mathbb{1}$$

$$= (|g\rangle \langle g| + |a\rangle \langle a| + |b\rangle \langle b| + |c\rangle \langle c|)\hat{\boldsymbol{\mu}}(|g\rangle \langle g| + |a\rangle \langle a| + |b\rangle \langle b| + |c\rangle \langle c|) \qquad (5.12)$$

$$= \hat{\sigma}_{a}^{+} \boldsymbol{\mu}^{ag} + \hat{\sigma}_{a}^{-} \boldsymbol{\mu}^{ga} + \hat{\sigma}_{b}^{+} \boldsymbol{\mu}^{bg} + \hat{\sigma}_{b}^{-} \boldsymbol{\mu}^{gb} + \hat{\sigma}_{c}^{+} \boldsymbol{\mu}^{cg} + \hat{\sigma}_{c}^{-} \boldsymbol{\mu}^{gc},$$

where

$$\boldsymbol{\mu}^{ij} = \langle i | \hat{\boldsymbol{\mu}} | j \rangle \,, \tag{5.13}$$

and

$$\hat{\sigma}_m^+ = |m\rangle \langle g|, \quad \hat{\sigma}_m^- = |g\rangle \langle m|$$
(5.14)

are the atomic raising and lowering operators for each excited state. The other terms that might arise from the second line of (5.12) vanish, because the electric dipole can only connect states of opposite parity (the parities are solely determined by the value of j). Using (5.12) we have

$$\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(\hat{\boldsymbol{r}}, t) = \frac{1}{2} \left(\hat{\sigma}_{a}^{+} \boldsymbol{\mu}^{ag} + \hat{\sigma}_{a}^{-} \boldsymbol{\mu}^{ga} \right) \cdot \left(\tilde{\boldsymbol{E}}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \tilde{\boldsymbol{E}}^{*}(\hat{\boldsymbol{r}}) e^{+i\omega t} \right) + \frac{1}{2} \left(\hat{\sigma}_{b}^{+} \boldsymbol{\mu}^{bg} + \hat{\sigma}_{b}^{-} \boldsymbol{\mu}^{gb} \right) \cdot \left(\tilde{\boldsymbol{E}}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \tilde{\boldsymbol{E}}^{*}(\hat{\boldsymbol{r}}) e^{+i\omega t} \right) + \frac{1}{2} \left(\hat{\sigma}_{c}^{+} \boldsymbol{\mu}^{cg} + \hat{\sigma}_{c}^{-} \boldsymbol{\mu}^{gc} \right) \cdot \left(\tilde{\boldsymbol{E}}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \tilde{\boldsymbol{E}}^{*}(\hat{\boldsymbol{r}}) e^{+i\omega t} \right).$$
(5.15)

This can be simplified by considering the selection rules on the magnetic quantum number $(\Delta m = 0 \text{ or } \pm 1)$ [169]. The transition $|g\rangle \rightarrow |c\rangle$, for example, corresponds to $\Delta m = +1$, and therefore to absorption of a photon with positive helicity, i.e., a left-circularly polarized photon. Therefore only the $\mathcal{E}_L \hat{\boldsymbol{\epsilon}}_L$ component of the field takes part in this transition. Following through this line of reasoning leads to

$$\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(\hat{\boldsymbol{r}}, t) = \frac{1}{2} \left[\hat{\sigma}_{a}^{+} \mu_{a} \left(\mathcal{E}_{a}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \mathcal{E}_{c}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} \right) + \hat{\sigma}_{a}^{-} \mu_{a}^{*} \left(\mathcal{E}_{a}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} + \mathcal{E}_{c}(\hat{\boldsymbol{r}}) e^{-i\omega t} \right) \right. \\ \left. + \left(\hat{\sigma}_{b}^{+} \mu_{b} + \hat{\sigma}_{b}^{-} \mu_{b}^{*} \right) \left(\mathcal{E}_{b}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \mathcal{E}_{b}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} \right) \right.$$

$$\left. + \hat{\sigma}_{c}^{+} \mu_{c} \left(\mathcal{E}_{c}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \mathcal{E}_{a}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} \right) + \hat{\sigma}_{c}^{-} \mu_{c}^{*} \left(\mathcal{E}_{c}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} + \mathcal{E}_{a}(\hat{\boldsymbol{r}}) e^{-i\omega t} \right) \right],$$

$$\left. (5.16) \right]$$

where I have introduced

$$\mu_a \equiv \langle a | \hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{\epsilon}}_R | g \rangle, \qquad (5.17a)$$

$$\mu_b \equiv \langle b | \hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{\epsilon}}_z | g \rangle , \qquad (5.17b)$$

$$\mu_c \equiv \langle c | \hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{\epsilon}}_L | g \rangle , \qquad (5.17c)$$

and made the substitutions $\mathcal{E}_R = \mathcal{E}_a$, $\mathcal{E}_z = \mathcal{E}_b$, and $\mathcal{E}_L = \mathcal{E}_c$, for notational convenience.

Next we apply a unitary transformation to remove the dynamics due to H_{elec} and move to an interaction picture (see Appendix C.2). The appropriate unitary operator is

$$U = e^{iH_{\text{elec}}t/\hbar}.$$
(5.18)

A function of a Hermitian operator may be written in terms of its eigenbasis [71, 171],

$$f(A) = \sum_{j} f(a_j) |a_j\rangle \langle a_j|, \qquad (5.19)$$

so we can write U as

$$U = |g\rangle \langle g| + e^{i\omega_a t} |a\rangle \langle a| + e^{i\omega_b t} |b\rangle \langle b| + e^{i\omega_c t} |c\rangle \langle c|.$$
(5.20)

The dynamics of the transformed state $|\Psi_I\rangle = U |\Psi\rangle$ are governed by the Hamiltonian (see Eq. (C.28))

$$H_I = i\hbar \dot{U}U^{\dagger} + UHU^{\dagger}, \tag{5.21}$$

where H is the (Schrödinger-picture) Hamiltonian given in (5.10). By design,

$$i\hbar \dot{U}U^{\dagger} = -H_{\text{elec}}.$$
(5.22)

The other part of the Hamiltonian consists of two terms (recalling that we assumed the translational energy term is negligible):

$$UHU^{\dagger} = UH_{\text{elec}}U^{\dagger} - U\left(\hat{\boldsymbol{\mu}} \cdot \boldsymbol{E}(\hat{\boldsymbol{r}}, t)\right)U^{\dagger}.$$
(5.23)

The electronic Hamiltonian commutes with U, so $UH_{\text{elec}}U^{\dagger} = H_{\text{elec}}$. However, the second term is altered by the unitary operator because of the presence of the atomic raising and

lowering operators. A little bit of algebra shows that they transform as

$$U\hat{\sigma}_m^+ U^\dagger = \hat{\sigma}_m^+ e^{i\omega_m t},\tag{5.24a}$$

$$U\hat{\sigma}_m^- U^\dagger = \hat{\sigma}_m^- e^{-i\omega_m t}.$$
 (5.24b)

Putting everything together, the interaction-picture Hamiltonian is:

$$H_{I} = -\frac{1}{2} \left[\hat{\sigma}_{a}^{+} e^{i\omega_{a}t} \mu_{a} \left(\mathcal{E}_{a}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \mathcal{E}_{c}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} \right) + \hat{\sigma}_{a}^{-} e^{-i\omega_{a}t} \mu_{a}^{*} \left(\mathcal{E}_{a}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} + \mathcal{E}_{c}(\hat{\boldsymbol{r}}) e^{-i\omega t} \right) \right. \\ \left. + \left(\hat{\sigma}_{b}^{+} e^{i\omega_{b}t} \mu_{b} + \hat{\sigma}_{b}^{-} e^{-i\omega_{b}t} \mu_{b}^{*} \right) \left(\mathcal{E}_{b}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \mathcal{E}_{b}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} \right) \right. \\ \left. + \hat{\sigma}_{c}^{+} e^{i\omega_{c}t} \mu_{c} \left(\mathcal{E}_{c}(\hat{\boldsymbol{r}}) e^{-i\omega t} + \mathcal{E}_{a}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} \right) + \hat{\sigma}_{c}^{-} e^{-i\omega_{c}t} \mu_{c}^{*} \left(\mathcal{E}_{c}^{*}(\hat{\boldsymbol{r}}) e^{i\omega t} + \mathcal{E}_{a}(\hat{\boldsymbol{r}}) e^{-i\omega t} \right) \right].$$
(5.25)

I shall make the following simplifying assumptions: firstly, that the excited states are degenerate ($\omega_a = \omega_b = \omega_c$); secondly, that the optical field is resonant with the atomic transition frequencies ($\omega = \omega_m$). Therefore H_I becomes

$$H_{I} = -\frac{1}{2} \left[\hat{\sigma}_{a}^{+} \mu_{a} \left(\mathcal{E}_{a}(\hat{\boldsymbol{r}}) + \mathcal{E}_{c}^{*}(\hat{\boldsymbol{r}})e^{2i\omega t} \right) + \hat{\sigma}_{a}^{-} \mu_{a}^{*} \left(\mathcal{E}_{a}^{*}(\hat{\boldsymbol{r}}) + \mathcal{E}_{c}(\hat{\boldsymbol{r}})e^{-2i\omega t} \right) \right. \\ \left. + \hat{\sigma}_{b}^{+} \mu_{b} \left(\mathcal{E}_{b}(\hat{\boldsymbol{r}}) + \mathcal{E}_{b}^{*}(\hat{\boldsymbol{r}})e^{2i\omega t} \right) + \hat{\sigma}_{b}^{-} \mu_{b}^{*} \left(\mathcal{E}_{b}(\hat{\boldsymbol{r}})e^{-2i\omega t} + \mathcal{E}_{b}^{*}(\hat{\boldsymbol{r}}) \right) \right. \\ \left. + \hat{\sigma}_{c}^{+} \mu_{c} \left(\mathcal{E}_{c}(\hat{\boldsymbol{r}}) + \mathcal{E}_{a}^{*}(\hat{\boldsymbol{r}})e^{2i\omega t} \right) + \hat{\sigma}_{c}^{-} \mu_{c}^{*} \left(\mathcal{E}_{c}^{*}(\hat{\boldsymbol{r}}) + \mathcal{E}_{a}(\hat{\boldsymbol{r}})e^{-2i\omega t} \right) \right]. \quad (5.26)$$

Half of the terms in this Hamiltonian are stationary whilst the other half oscillate with frequency $\pm 2\omega$; we make the *rotating wave approximation* [170, 171] in which we neglect the rapidly oscillating terms on the basis that, for time scales greater than $\sim \omega^{-1}$, these terms average to zero (for optical frequencies this means considering time scales greater than around a femtosecond). We thus arrive at the rotating-wave interaction-picture Hamiltonian,

$$H_I^{\text{RWA}} = -\hbar \sum_m \left[V_m(\hat{\boldsymbol{r}}) \hat{\sigma}_m^+ + V_m^*(\hat{\boldsymbol{r}}) \hat{\sigma}_m^- \right], \qquad (5.27)$$

where I have defined the *Rabi frequencies* [170, 171]

$$V_m(\hat{\boldsymbol{r}}) = \frac{\mu_m \mathcal{E}_m(\hat{\boldsymbol{r}})}{2\hbar},\tag{5.28}$$

for $m \in \{a, b, c\}$ (note that the repeated m index does not imply summation).

We can now find the time-evolved state $|\Psi(t)\rangle$ (henceforth I will only deal with the state in the interaction picture, so the subscript I is no longer necessary). I treat the dynamics perturbatively, using a Dyson series expansion up to first-order in t [18, §4.2]. The perturbed state can be written as $|\Psi(t)\rangle = \hat{\mathscr{U}}_I(t,0) |\Psi(0)\rangle$, where $\hat{\mathscr{U}}_I(t,0)$ is the interaction-picture time-evolution operator (see Appendix C.2 and Eq. (C.23) in particular). The Dyson series is an expansion of the form $\hat{\mathscr{U}}_I(t,0) = \sum_n \hat{\mathscr{U}}_I^{(n)}(t,0)$, where the *n*th term of the expansion is of order *n* in both *t* and H_I^{RWA} . By neglecting all but the zeroth- and first-order terms we are necessarily limiting ourselves to a study of the dynamics for small *t*. To first order we have [18]

$$\hat{\mathscr{U}}_{I}(t,0) \approx \hat{\mathscr{U}}_{I}^{(0)}(t,0) + \hat{\mathscr{U}}_{I}^{(1)}(t,0) = 1 + \frac{1}{i\hbar} \int_{0}^{t} \mathrm{d}t_{1} H_{I}^{\mathrm{RWA}}(t_{1}).$$
(5.29)

The rotating-wave Hamiltonian is time independent so the integral just gives $H_I^{\text{RWA}}t$. The perturbed state may thus be written as

$$|\Psi(t)\rangle = |\Psi_0\rangle + |\Psi_1\rangle t, \qquad (5.30)$$

where $|\Psi_0\rangle$ is the initial state (5.6) and

$$\begin{split} |\Psi_{1}\rangle &= \frac{1}{i\hbar} H_{I}^{\text{RWA}} |\Psi_{0}\rangle \\ &= i |a\rangle V_{a}(\hat{\boldsymbol{r}}) |\psi_{0}\rangle + i |b\rangle V_{b}(\hat{\boldsymbol{r}}) |\psi_{0}\rangle + i |c\rangle V_{c}(\hat{\boldsymbol{r}}) |\psi_{0}\rangle \\ &= \frac{1}{2\hbar} \int d^{3}r |\boldsymbol{r}\rangle \left(\mu_{a} |a\rangle \psi_{a}(\boldsymbol{r}) + \mu_{b} |b\rangle \psi_{b}(\boldsymbol{r}) + \mu_{c} |c\rangle \psi_{c}(\boldsymbol{r}) \right), \end{split}$$
(5.31)

where I have introduced the excited motional wave functions,

$$\psi_m(\mathbf{r}) \equiv i \mathcal{E}_m(\mathbf{r}) \psi_0(\mathbf{r}). \tag{5.32}$$

We see that $|\Psi(t)\rangle$, unlike $|\Psi(0)\rangle$, cannot be written as a simple product state and thus we have *entanglement* between the electronic and motional degrees of freedom. In particular, the motional state of the atom at time t is intrinsically correlated to which transition the electronic state makes: the state associated with the electronic transition $|g\rangle \rightarrow |m\rangle$ is $\psi_m(\mathbf{r})$, thus showing how the polarization structure of the optical field is imprinted onto the state of the atom.
Now that we are in possession of the perturbed state of the system, we turn our attention to the fundamental question of this Chapter: what is the nature of helicity transfer between the optical field and the atom? To answer this, we need to define a suitable measure of the *atomic* helicity.

5.2 Defining a Measure of Atomic Helicity

5.2.1 Basic Idea

In particle physics, the helicity of an elementary particle is [76]

$$\mathcal{H}_{\mathrm{PP}} = rac{oldsymbol{J} \cdot oldsymbol{P}}{|oldsymbol{P}|},$$

where J and P are the angular and linear momenta of the particle (in Eq. (4.1) I defined \mathcal{H}_{PP} in terms of the spin of the particle, but the two are equivalent for an elementary particle). Taking this as a good starting point, we propose the expectation value

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$$
 (5.33)

as a measure of the atomic helicity, where J is the internal (electronic) angular momentum operator and P is the motional (COM) linear momentum operator of the atom. In the coordinate representation, P takes the form

$$\boldsymbol{P} = \frac{\hbar}{i} \nabla, \tag{5.34}$$

 ∇ being the gradient operator with respect to the COM coordinates r.

It will be noted that the helicity (in particle physics and in optics) has the dimensions of angular momentum, but this is not the case for $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$, which is essentially an 'unnormalized' projection of the angular momentum onto the momentum. The reason I do not take the expectation value of $\boldsymbol{J} \cdot \boldsymbol{P}/|\boldsymbol{P}|$ instead is because the linear momentum operator, having a continuous eigenspectrum, would be rather difficult to incorporate in this manner. Thus we have opted for a measure which is as simple as possible, whilst still capturing the essential *physical* (if not dimensional) features of atomic helicity. Ways in which we could define a measure with the correct dimensions will be discussed later; for now I will call $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$ the atomic helicity. Because $J \cdot P$ is a Hermitian operator, its expectation value is real, and it represents, in principle, an observable quantity. Hermiticity can be verified by writing the operator in the expanded form

$$\boldsymbol{J} \cdot \boldsymbol{P} = J_x P_x + J_y P_y + J_z P_z, \tag{5.35}$$

and taking the Hermitian adjoint of each term,

$$(J_i P_i)^{\dagger} = P_i^{\dagger} J_i^{\dagger}$$

= $P_i J_i$
= $J_i P_i$. (5.36)

The second line follows from the Hermiticity of each operator separately, and the third line from the fact that J_i and P_i commute as they act on separate state spaces.

To evaluate the expectation value, we must remember that $|\Psi(t)\rangle$ is in the interaction picture, and therefore we must also transform the operator to obtain a meaningful quantity (which is independent of the dynamical picture used). The necessary transformation is (see Eq. (C.25))

$$(\boldsymbol{J}\cdot\boldsymbol{P})_I = U(\boldsymbol{J}\cdot\boldsymbol{P})U^{\dagger},\tag{5.37}$$

with U given by (5.18), and the expectation value is therefore

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle = \langle \Psi(t) | U(\boldsymbol{J} \cdot \boldsymbol{P}) U^{\dagger} | \Psi(t) \rangle.$$
(5.38)

Strictly speaking this should be divided by $\langle \Psi(t)|\Psi(t)\rangle$, because $|\Psi(t)\rangle$ is not generally normalized. However, $\langle \Psi(t)|\Psi(t)\rangle = 1 + \langle \Psi_1|\Psi_1\rangle t^2 \approx 1$, for $t \ll 1$, which is our assumption.

We have

$$\begin{split} \langle \Psi(t) | U(\boldsymbol{J} \cdot \boldsymbol{P}) U^{\dagger} | \Psi(t) \rangle &= (t \langle \Psi_{1} | + \langle \Psi_{0} |) U(\boldsymbol{J} \cdot \boldsymbol{P}) U^{\dagger} (| \Psi_{0} \rangle + | \Psi_{1} \rangle t) \\ &= \langle \Psi_{0} | U(\boldsymbol{J} \cdot \boldsymbol{P}) U^{\dagger} | \Psi_{0} \rangle + \langle \Psi_{0} | U(\boldsymbol{J} \cdot \boldsymbol{P}) U^{\dagger} | \Psi_{1} \rangle t \\ &+ \langle \Psi_{1} | U(\boldsymbol{J} \cdot \boldsymbol{P}) U^{\dagger} | \Psi_{0} \rangle t + \langle \Psi_{1} | U(\boldsymbol{J} \cdot \boldsymbol{P}) U^{\dagger} | \Psi_{1} \rangle t^{2} \quad (5.39) \\ &= \langle \Psi_{0} | \boldsymbol{J} \cdot \boldsymbol{P} | \Psi_{0} \rangle + \langle \Psi_{0} | \boldsymbol{J} \cdot \boldsymbol{P} | \Psi_{1} \rangle t e^{-i\omega t} \\ &+ \langle \Psi_{1} | \boldsymbol{J} \cdot \boldsymbol{P} | \Psi_{0} \rangle t e^{i\omega t} + \langle \Psi_{1} | \boldsymbol{J} \cdot \boldsymbol{P} | \Psi_{1} \rangle t^{2}, \end{split}$$

where I have used $U^{\dagger} |\Psi_0\rangle = |\Psi_0\rangle$ and $U^{\dagger} |\Psi_1\rangle = e^{-i\omega t} |\Psi_1\rangle$ and their complex conjugates, which are easily verifiable.

To evaluate the above, we need to write $J \cdot P$ in a more computationally convenient form. The ground and excited electronic states are, by assumption, eigenstates of J^2 and J_z ,

$$J^{2}|j,m\rangle = \hbar^{2}j(j+1)|j,m\rangle, \qquad (5.40a)$$

$$J_z |j, m\rangle = \hbar m |j, m\rangle, \qquad (5.40b)$$

but not of J_x and J_y . This means the expansion given above in Eq. (5.35),

$$\boldsymbol{J} \cdot \boldsymbol{P} = J_x P_x + J_y P_y + J_z P_z$$

is not particularly useful. To find a better form, we introduce the *ladder operators*,

$$J_{\pm} = J_x \pm i J_y. \tag{5.41}$$

Consider the effect of J_+ on the states $|j,m\rangle$. It is easy to show that $[J^2, J_{\pm}] = 0$, and therefore $J^2(J_+|j,m\rangle) = \hbar^2 j(j+1)(J_+|j,m\rangle)$, i.e., $J_+|j,m\rangle$ is also an eigenstate of J^2 with the same eigenvalue as $|j,m\rangle$. Similarly, we have $[J_z, J_{\pm}] = \pm \hbar J_{\pm}$, which we can use to show that $J_z(J_+|j,m\rangle) = \hbar(m+1)(J_+|j,m\rangle)$. These results lead us to conclude that $J_+|j,m\rangle \propto |j,m+1\rangle$. Similarly we find $J_-|j,m\rangle \propto |j,m-1\rangle$. Thus we write

$$J_{\pm} |j,m\rangle = \hbar \beta_{jm}^{\pm} |j,m\pm 1\rangle, \qquad (5.42)$$

with the constants of proportionality being found to be [172]

$$\beta_{jm}^{\pm} = \sqrt{j(j+1) - m(m\pm 1)}.$$
(5.43)

Noting that $\beta_{j,j}^+ = 0 = \beta_{j,-j}^-$, and recalling $m_{\max} = j$, $m_{\min} = -j$, we have the particularly useful relations

$$J_{+}|j,m_{\max}\rangle = 0 = J_{-}|j,m_{\min}\rangle.$$
 (5.44)

So, knowing how J_{\pm} act on the states $|j,m\rangle$, a useful form for $\boldsymbol{J}\cdot\boldsymbol{P}$ is

$$\boldsymbol{J} \cdot \boldsymbol{P} = J_{+}P_{-} + J_{-}P_{+} + J_{z}P_{z}, \qquad (5.45)$$

where I have defined

$$P_{\pm} = \frac{1}{2} (P_x \pm i P_y). \tag{5.46}$$

The desired matrix elements are:

$$\langle \Psi_0 | (J_+P_- + J_-P_+ + J_z P_z) | \Psi_0 \rangle$$
, (5.47a)

$$\langle \Psi_1 | (J_+ P_- + J_- P_+ + J_z P_z) | \Psi_0 \rangle$$
, (5.47b)

$$\langle \Psi_1 | (J_+P_- + J_-P_+ + J_zP_z) | \Psi_1 \rangle$$
. (5.47c)

 $(\langle \Psi_0 | \boldsymbol{J} \cdot \boldsymbol{P} | \Psi_1 \rangle$ is simply the complex conjugate of the second term.) The initial state is $|\Psi_0 \rangle = |g\rangle |\psi_0 \rangle$, with $|g\rangle = |0, 0\rangle$, and thus we have $J_z |g\rangle = 0$, $J_{\pm} |g\rangle = 0$, the latter following from (5.44). Therefore the first and second terms above vanish, and we are left with

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle = \langle \Psi_1 | \boldsymbol{J} \cdot \boldsymbol{P} | \Psi_1 \rangle t^2.$$
(5.48)

As we are considering transitions from a spherically-symmetric ground state, we expect the magnitudes of the transition dipole moments, $|\mu_m|$, to be equal. Considering for definiteness a hydrogen-like atom, it can be shown that: $\mu_a = \mu_b = -\mu_c = \mu \in \mathbb{R}$. With these values and some simple rearrangement we find that the expectation value may be written as

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle = \frac{t^2 \mu^2}{4\hbar} \left[\langle \psi_c | P_z | \psi_c \rangle - \langle \psi_a | P_z | \psi_a \rangle + \sqrt{2} \left(\operatorname{Re} \{ \langle \psi_b | P_x | \psi_a \rangle - \langle \psi_c | P_x | \psi_b \rangle \} + \operatorname{Im} \{ \langle \psi_b | P_y | \psi_a \rangle - \langle \psi_c | P_y | \psi_b \rangle \} \right) \right], \quad (5.49)$$

where

$$\langle \psi_m | P_j | \psi_n \rangle = \frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}^3 r \ \mathcal{E}_m^*(\boldsymbol{r}) \mathcal{E}_n(\boldsymbol{r}) \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial x_j} \psi_0(\boldsymbol{r}) + \frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}^3 r \ |\psi_0(\boldsymbol{r})|^2 \mathcal{E}_m^*(\boldsymbol{r}) \frac{\partial}{\partial x_j} \mathcal{E}_n(\boldsymbol{r}), \quad (5.50)$$

the indices $m, n \in \{a, b, c\}$ and $j \in \{x, y, z\}$.

5.2.2 Examples

Now we wish to check whether our expression for the atomic helicity gives physically reasonable results, for some elementary optical fields. To proceed, we need to consider a specific form for $\psi_0(\mathbf{r})$. I shall choose a Gaussian wave packet of width σ centred on the position R_0 [163],

$$\psi_0(\boldsymbol{r}) = N \exp\left(-\frac{|\boldsymbol{r} - \boldsymbol{R}_0|^2}{2\sigma^2}\right),\tag{5.51}$$

which corresponds to the motional ground state of a harmonic potential, and can be closely approximated by atom [107] and ion [173] traps.

Single plane wave. The optical helicity density for a monochromatic field of frequency $\omega = ck_0$ is (4.17),

$$h_{\text{m.c.}} = \frac{\varepsilon_0}{2k_0} \text{Im}\{\tilde{\boldsymbol{E}} \cdot \tilde{\boldsymbol{B}}^*\}.$$

Let's consider a single CP plane wave propagating in the z-direction with amplitude a,

$$\tilde{\boldsymbol{E}} = \frac{a}{\sqrt{2}} (\hat{\mathbf{x}} \pm i\hat{\mathbf{y}}) e^{ik_0 z}, \qquad (5.52)$$

with +(-) corresponding to left (right) CP light. It is easily shown that

$$h_{\rm LCP} = \frac{\varepsilon_0}{2ck_0}|a|^2 = -h_{\rm RCP}.$$
 (5.53)

For a LCP wave, $\mathcal{E}_a = 0 = \mathcal{E}_b$ and $\mathcal{E}_c = ae^{ik_0z}$, so the only non-zero integral in the calculation of the atomic helicity is $\langle \psi_c | P_z | \psi_c \rangle$, whilst for a RCP wave, only $\langle \psi_a | P_z | \psi_a \rangle$ does not vanish. In either case, we have the integrals

$$\frac{\hbar}{i}|a|^2 \int_{-\infty}^{\infty} \mathrm{d}^3 r \ \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial z} \psi_0(\boldsymbol{r}) \tag{5.54}$$

and

$$\frac{\hbar}{i}|a|^2 \int_{-\infty}^{\infty} \mathrm{d}^3 r \ |\psi_0(\boldsymbol{r})|^2 e^{-ik_0 z} \frac{\partial}{\partial z} e^{ik_0 z}.$$
(5.55)

The integral in (5.54) vanishes, which can be appreciated by noting that the initial wave packet (5.51) has zero average momentum. The integral in (5.55) can be easily evaluated and we find

$$\langle \psi_c | P_z | \psi_c \rangle = \hbar k_0 |a|^2 = \langle \psi_a | P_z | \psi_a \rangle , \qquad (5.56)$$

which demonstrates the exchange of momentum from the optical plane wave to the atomic COM in an absorption event, i.e., the recoil effect [168, 174]. The associated atomic helicity is

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle_{\text{LCP}} = \frac{k_0 \mu^2}{4} |a|^2 t^2 = - \langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle_{\text{RCP}}.$$
 (5.57)



Figure 5.1: The local optical helicity (5.60) arising from the two-wave superposition discussed in the main text, for $\theta = \pi/12$. Note that the helicity is scaled with respect to \overline{w}_e/ω , and is plotted with respect to the rotated axes (y', z').

We see that the signs of the atomic and optical helicities are the same, as we would hope. They also both depend on $|a|^2$, so that a more intense optical field will have a higher optical helicity and will transfer, per second, more helicity to the atom. The time dependence of the atomic helicity is to be expected, even though $h_{\text{m.c.}}$ is time independent, because $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$ is the *expected value* of the helicity at a particular time, which naturally increases with the interaction time between light and atom. Of course, by my use of first-order TDPT, we are necessarily considering small times.

For future reference, let's define the 'base values' of the local optical and atomic helicities, which correspond to their magnitudes for a single CP plane wave of unit amplitude:

$$h_0 \equiv \frac{\varepsilon_0}{2ck_0},\tag{5.58}$$

$$\left\langle \boldsymbol{J} \cdot \boldsymbol{P} \right\rangle_0 \equiv \frac{k_0 \mu^2}{4} t^2. \tag{5.59}$$

Helicity grating. Next, to gain more insight into the connection between the optical and atomic helicities, let's consider a helicity grating, i.e., a two-wave non-interfering superpo-

sition with a spatially-varying optical helicity density. The specific setup I shall consider is the one discussed in Chapter 2, recall Figure 2.3 and Eqs. (2.80),

$$oldsymbol{k}_1 = k_0 \hat{f z}, \quad \hat{f \epsilon}_1 = \hat{f y},$$

 $oldsymbol{k}_2 = -k_0 \sin 2\theta \hat{f y} + k_0 \cos 2\theta \hat{f z}, \quad \hat{f \epsilon}_2 = \hat{f x}.$

As in Chapter 2 we suppose that the two waves have equal amplitudes, a. The resulting local optical helicity is found to be

$$h_{\text{grating}} = 2h_0 |a|^2 \cos^2 \theta \sin \left(2k_0 \sin \theta y'\right), \qquad (5.60)$$

where $y' = \cos \theta y + \sin \theta z$. This optical helicity density is plotted in Figure 5.1.

The derivation of the atomic helicity is quite simple but rather lengthy, and it is thus relegated to the Appendix D.3. The result is

$$\left\langle \boldsymbol{J} \cdot \boldsymbol{P} \right\rangle_{\text{grating}} = 2 \left\langle \boldsymbol{J} \cdot \boldsymbol{P} \right\rangle_0 |a|^2 \cos^2 \theta \sin \left(2k_0 \sin \theta Y_0' \right) \times e^{-k_0^2 \sigma^2 \sin^2 \theta}, \quad (5.61)$$

where $Y'_0 = \cos \theta Y_0 + \sin \theta Z_0$. This looks remarkably similar to the local optical helicity (5.60); in particular, it has the exact same spatial variation, but note that the atomic helicity is a function of \mathbf{R}_0 , i.e., the position of the centre of the atomic wave packet.

An important feature of this result is the appearance of the final term in (5.61), which shows that $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$ is dependent on the width of the atomic wave packet, σ . This dependence is due to the inherently quantum-nature of the atomic motion, and the fact that the atom cannot be localized with absolute certainty. This feature was not evident for the single plane wave, because in that case the local optical helicity is spatially independent. This result tells us that the atom is not a *perfect* detector of *local* optical helicity, and that it will always in fact detect a spread of values, rather than just the optical helicity at the point \boldsymbol{R}_0 .

If we consider the so-called Lamb-Dicke regime [173, 175, 176], then the atom is localized to a scale much smaller than wavelength, $k_0\sigma \ll 1$, and the effect of the term $\exp\left(-k_0^2\sigma^2\sin^2\theta\right)$ becomes negligible. Typical values of σ , for relatively small trapped ions, are on the order of 10 nm [173, 177], so for optical wavelengths (~ 500 nm) the Lamb-Dicke regime is easily achievable. Note that being in the Lamb-Dicke regime is not necessarily a requirement for using the ED approximation, because the former is related to the size of the *motional* wave function with respect to the optical wavelength, whilst the latter is related to the size of the electronic wave function. In Figure 5.2 I plot the atomic helicity for two different values of



Figure 5.2: Plots of the atomic helicity (5.61), divided by $|a|^2 \langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle_0$. These plots show the helicity detected by the atom when placed at points (Y'_0, Z'_0) in the 'helicity grating' (5.60), for $\theta = \pi/12$. In (a) we see the atomic helicity which would be detected at each point when $\sigma = 0.01\lambda$, which is well within the Lamb-Dicke regime $(k_0\sigma \ll 1)$, whilst in (b) we see the atomic helicity detected when $\sigma = 0.2\lambda$. We observe, as expected, that the helicity pattern in (b) is 'washed out' as compared to (a). The dashed red contours show the lines on which the (scaled) atomic helicity equals the randomly chosen value of ± 0.83 . In (b) the values of ± 0.83 are close to the maxima and minima of the detected atomic helicity, whereas in (a) they are much further removed from the brightest and darkest regions, clearly demonstrating how the size of the atomic wave packet influences the atom's ability to detect local optical helicity.

the ratio σ/λ ($\lambda = 2\pi/k_0$ being the optical wavelength).

The correlations between the local optical and atomic helicities found above led us to believe that the connection between the two must be a deep one. In the next Subsection I demonstrate that this is the case, by showing that the general expression for the atomic helicity can be written directly in terms of the local optical helicity.

5.2.3 General Expression

Using (5.5) to write the circular components \mathcal{E}_m back in terms of their Cartesian counterparts allows us, after some simplification, to write the atomic helicity (5.49) as

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle = i \frac{t^2 \mu^2}{4\hbar} \left[\langle \psi_z | P_x | \psi_y \rangle - \langle \psi_y | P_x | \psi_z \rangle + \langle \psi_x | P_y | \psi_z \rangle - \langle \psi_z | P_y | \psi_x \rangle + \langle \psi_y | P_z | \psi_x \rangle - \langle \psi_x | P_z | \psi_y \rangle \right].$$
(5.62)

The terms in the square brackets can be combined into a single integral,

$$I = \frac{\hbar}{i} \int_{-\infty}^{\infty} d^3 r \ \psi_0^*(\boldsymbol{r}) \left[\mathcal{E}_z^*(\boldsymbol{r}) \frac{\partial}{\partial x} (\mathcal{E}_y(\boldsymbol{r}) \psi_0(\boldsymbol{r})) - \mathcal{E}_y^*(\boldsymbol{r}) \frac{\partial}{\partial x} (\mathcal{E}_z(\boldsymbol{r}) \psi_0(\boldsymbol{r})) + \mathcal{E}_x^*(\boldsymbol{r}) \frac{\partial}{\partial y} (\mathcal{E}_z(\boldsymbol{r}) \psi_0(\boldsymbol{r})) - \mathcal{E}_z^*(\boldsymbol{r}) \frac{\partial}{\partial y} (\mathcal{E}_x(\boldsymbol{r}) \psi_0(\boldsymbol{r})) + \mathcal{E}_y^*(\boldsymbol{r}) \frac{\partial}{\partial z} (\mathcal{E}_x(\boldsymbol{r}) \psi_0(\boldsymbol{r})) - \mathcal{E}_x^*(\boldsymbol{r}) \frac{\partial}{\partial z} (\mathcal{E}_y(\boldsymbol{r}) \psi_0(\boldsymbol{r})) \right]. \quad (5.63)$$

Applying the product rule to the derivatives we can write this as $I = I_1 + I_2$, where

$$I_{1} = -\frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}^{3}r \ \psi_{0}^{*}(\boldsymbol{r}) \left[(\mathcal{E}_{y}^{*}(\boldsymbol{r})\mathcal{E}_{z}(\boldsymbol{r}) - \mathcal{E}_{y}(\boldsymbol{r})\mathcal{E}_{z}^{*}(\boldsymbol{r})) \frac{\partial}{\partial x} + (\mathcal{E}_{x}(\boldsymbol{r})\mathcal{E}_{z}^{*}(\boldsymbol{r}) - \mathcal{E}_{x}^{*}(\boldsymbol{r})\mathcal{E}_{z}(\boldsymbol{r})) \frac{\partial}{\partial y} + (\mathcal{E}_{x}^{*}(\boldsymbol{r})\mathcal{E}_{y}(\boldsymbol{r}) - \mathcal{E}_{x}(\boldsymbol{r})\mathcal{E}_{y}^{*}(\boldsymbol{r})) \frac{\partial}{\partial z} \right] \psi_{0}(\boldsymbol{r}) \quad (5.64)$$

and

$$I_{2} = \frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}^{3}r |\psi_{0}(\boldsymbol{r})|^{2} \left[\mathcal{E}_{z}^{*}(\boldsymbol{r}) \frac{\partial}{\partial x} \mathcal{E}_{y}(\boldsymbol{r}) - \mathcal{E}_{y}^{*}(\boldsymbol{r}) \frac{\partial}{\partial x} \mathcal{E}_{z}(\boldsymbol{r}) \\ \mathcal{E}_{x}^{*}(\boldsymbol{r}) \frac{\partial}{\partial y} \mathcal{E}_{z}(\boldsymbol{r}) - \mathcal{E}_{z}^{*}(\boldsymbol{r}) \frac{\partial}{\partial y} \mathcal{E}_{x}(\boldsymbol{r}) \\ + \mathcal{E}_{y}^{*}(\boldsymbol{r}) \frac{\partial}{\partial z} \mathcal{E}_{x}(\boldsymbol{r}) - \mathcal{E}_{x}^{*}(\boldsymbol{r}) \frac{\partial}{\partial z} \mathcal{E}_{y}(\boldsymbol{r}) \right]. \quad (5.65)$$

This is looking more complicated than what we had before, but as I shall show, both of these terms can be significantly simplified.

First, notice that the integrand of I_2 contains the term $\tilde{E}^* \cdot (\nabla \times \tilde{E})$. Then using Maxwell's

equation (B.1d), which for a monochromatic field reduces to

$$\nabla \times \tilde{\boldsymbol{E}} = i\omega \tilde{\boldsymbol{B}},\tag{5.66}$$

we have

$$I_{2} = \hbar \omega \int_{-\infty}^{\infty} \mathrm{d}^{3} r \ \psi_{0}^{*}(\boldsymbol{r}) \left(\tilde{\boldsymbol{E}}^{*}(\boldsymbol{r}) \cdot \tilde{\boldsymbol{B}}(\boldsymbol{r}) \right) \psi_{0}(\boldsymbol{r}).$$
(5.67)

Next, it is instructive to recall the form of the (electric) spin density for a monochromatic field (2.76),

$$\boldsymbol{s}_e = \frac{\varepsilon_0}{2i\omega} \tilde{\boldsymbol{E}}^* \times \tilde{\boldsymbol{E}},$$

the components of which are:

$$s_e^x = \frac{\varepsilon_0}{2i\omega} (\mathcal{E}_y^* \mathcal{E}_z - \mathcal{E}_y \mathcal{E}_z^*), \qquad (5.68a)$$

$$s_e^y = \frac{\varepsilon_0}{2i\omega} (\mathcal{E}_x \mathcal{E}_z^* - \mathcal{E}_x^* \mathcal{E}_z), \qquad (5.68b)$$

$$s_e^z = \frac{\varepsilon_0}{2i\omega} (\mathcal{E}_x^* \mathcal{E}_y - \mathcal{E}_x \mathcal{E}_y^*).$$
(5.68c)

Thus analysing the integrand of I_1 , Eq. (5.64), we see that it contains the term $(2i\omega/\varepsilon_0)\mathbf{s}_e\cdot\nabla$. Putting everything back together, we can write the atomic helicity as

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle = i \frac{t^2 \mu^2 \omega}{4} \int_{-\infty}^{\infty} \mathrm{d}^3 \boldsymbol{r} \left[\psi_0^*(\boldsymbol{r}) \left(\tilde{\boldsymbol{E}}^*(\boldsymbol{r}) \cdot \tilde{\boldsymbol{B}}(\boldsymbol{r}) \right) \psi_0(\boldsymbol{r}) - \frac{2}{\varepsilon_0} \boldsymbol{s}_e(\boldsymbol{r}) \cdot \psi_0^*(\boldsymbol{r}) \nabla \psi_0(\boldsymbol{r}) \right].$$
(5.69)

A useful 'trick' is to note that $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$ is real (recalling that $\boldsymbol{J} \cdot \boldsymbol{P}$ is Hermitian), so

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle = \frac{1}{2} \left[\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle + \langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle^* \right].$$
 (5.70)

Therefore $\langle \boldsymbol{J}\cdot\boldsymbol{P}\rangle$ can be written in the final, general form

$$\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle = \frac{t^2 \mu^2 c k_0}{2\varepsilon_0} \int_{-\infty}^{\infty} \mathrm{d}^3 r \bigg[k_0 \psi_0^*(\boldsymbol{r}) h_{\mathrm{m.c.}}(\boldsymbol{r}) \psi_0(\boldsymbol{r}) + \boldsymbol{s}_e(\boldsymbol{r}) \cdot \boldsymbol{j}_0(\boldsymbol{r}) \bigg].$$
(5.71)

The first term in the integrand contains the the local optical helicity (4.17), thus confirming the explicit connection between the atomic and optical helicities in light-matter interactions. In the second term, we see a dependence on the local electric spin, s_e , which couples to

$$\boldsymbol{j}_0 \equiv \frac{1}{2i} \left(\psi_0^* \nabla \psi_0 - \psi_0 \nabla \psi_0^* \right), \qquad (5.72)$$

which is highly reminiscent of the probability current from quantum mechanics (2.100) [104]. In the examples considered above, we did not observe this coupling, because $j_0 = 0$ for the Gaussian wave packet (5.51). The relevance of this term to an atomic helicity measurement can be made clearer if we consider a wave packet of the form

$$\phi_0 = \psi_0 e^{i \boldsymbol{q} \cdot \boldsymbol{r}},\tag{5.73}$$

with ψ_0 the Gaussian wave packet (5.51). We then find

$$\int_{-\infty}^{\infty} \mathrm{d}^3 r \ \boldsymbol{s}_e(\boldsymbol{r}) \cdot \boldsymbol{j}_0(\boldsymbol{r}) = \int_{-\infty}^{\infty} \mathrm{d}^3 r \ \boldsymbol{q} \cdot \boldsymbol{s}_e(\boldsymbol{r}) |\phi_0(\boldsymbol{r})|^2.$$
(5.74)

This is the expectation value of the projection of the local spin AM onto the momentum (divided by \hbar) of the atom in the motional state $|\phi_0\rangle$, making the connection with the atomic helicity $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$ more natural than it might appear at first glance.

5.2.4 Atomic Helicity Measures with the Correct Dimensions

As I mentioned earlier, the 'atomic helicity' I have defined above does not have the dimensions which are usually associated with a helicity. We have seen, nonetheless, that $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$ is closely connected to the optical helicity in light-matter interactions, somewhat justifying this simple choice. It would still be preferable, however, if we could define a measure of the atomic helicity which does have the correct dimensions, i.e., the dimensions of angular momentum.

Some very simple approaches to achieving this include dividing $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$ by the linear momentum of the optical field per photon, $\hbar k_0$, or dividing by the magnitude, $|\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle|$, and multiplying by \hbar . Whilst these are satisfactory from a dimensional point of view, both seem a bit artificial. Two different possibilities, which come closer to the helicity as defined in particle theory, are

$$\mathcal{H}_A = \frac{\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle}{\sqrt{\langle \boldsymbol{P} \rangle \cdot \langle \boldsymbol{P} \rangle}},\tag{5.75}$$

and

$$\mathcal{H}_B = \frac{\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle}{\sqrt{\langle \boldsymbol{P} \cdot \boldsymbol{P} \rangle}},\tag{5.76}$$

which I shall call 'type A' and 'type B', respectively. Once again $\langle \cdot \rangle$ denotes an expectation value with respect to $|\Psi(t)\rangle$. A simple calculation shows that $\mathcal{H}_A = \pm \hbar$ for a single CP plane wave, which is a very appealing result. However, we may wish to discount type A

as a contender because it is not suitable for all monochromatic fields. In particular, one can easily show that in certain optical fields, e.g., a counterpropagating superposition of two waves with equal amplitudes, $\langle \boldsymbol{P} \rangle = 0$, and thus \mathcal{H}_A is singular. It might be that the momentum has a zero expectation value when considered over all space, but that some physically relevant regions possess non-zero momentum. One way to avoid the singularity issue, whilst retaining the intuitive results which type A gives for a plane wave, might be to consider the *density* of the momentum instead. This is something I shall consider in more detail in future work.

Type B does not lead to such a pleasingly simple result for a single plane wave, and I am yet to derive a 'nice' expression for it in terms of physically intuitive quantities. Crucially however, \mathcal{H}_B does not suffer from the same flaw as \mathcal{H}_A , that is, it should never be singular. This follows from noting the relationship between the denominator and the standard deviation,

$$\langle \boldsymbol{P} \cdot \boldsymbol{P} \rangle = (\Delta \boldsymbol{P})^2 + \langle \boldsymbol{P} \rangle^2.$$
 (5.77)

As we are interested in the dynamics of a recently trapped atom, that is, a highly localized atom, it will necessarily have a non-zero standard deviation in its momentum, and thus even if $\langle \mathbf{P} \rangle^2 = 0$, $\langle \mathbf{P} \cdot \mathbf{P} \rangle$ will be non-zero. In future work, I will consider the features of this type of atomic helicity measure in more detail.

In the next Section, I summarize the results obtained in this Chapter, and discuss possible avenues for future research.

5.3 Summary

In the preceding Sections, I have defined a measure of the atomic helicity, $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$, and examined its dependence on the local optical helicity in light-atom interactions. After showing the connections between the atomic and optical helicities in some simple examples, I have derived a general expression for $\langle \boldsymbol{J} \cdot \boldsymbol{P} \rangle$, Eq. (5.71), which shows explicitly that, in the interaction between a monochromatic optical field and an atom, the helicity *is* transferred from field to atom. However, as was clearly shown in the second example above, the helicity which is 'detected' by the atom is not exactly the *local* optical helicity, but instead, due to the finite width of the atomic wave packet, a spread of values. In the case of the helicity grating with an atom in a Gaussian motional state, this led to the modulation of the detected helicity by an exponential factor which depends on $k_0\sigma$. In the experimentally-realizable Lamb-Dicke

regime $(k_0 \sigma \ll 1)$, the effects of this exponential scaling will be minimal, and the atom will, essentially, act as a detector of the local optical helicity. All of this information is contained in the first term of (5.71), which is an integral over the optical helicity density and the probability density of the motional wave function,

$$\int_{-\infty}^\infty \mathrm{d}^3 r \, \, h_{\mathrm{m.c.}}(oldsymbol{r}) \, |\psi_0(oldsymbol{r})|^2,$$

which may be interpreted as the expectation value of $h_{\text{m.c.}}(\hat{r})$ for the initial state $|\psi_0\rangle$. We also found that the general expression for $\langle J \cdot P \rangle$ contains a second term, which depends on the electric spin density of the optical field and the 'probability current' (5.72). The presence of this term was something of a surprise, because in the examples I considered explicitly $j_0 = 0$, and thus only the optical helicity density was detected. I have shown that for an atom in an initial motional state with non-zero (average) momentum, this additional term can be cast in a form which makes its association with a measure of the atomic helicity more natural. One interesting thing to note is that, usually, the optical helicity appears in connection with *chiral* light-matter interactions, which necessarily require a consideration of the electric dipole and higher-order multipole moments (specifically, the magnetic dipole or electric quadrupole terms). In my analysis, I have shown that the optical helicity can play a role in light-matter interactions even within the electric-dipole approximation, which may be due to the consideration of both the internal and external degrees of freedom.

My chosen measure of the atomic helicity does not have the dimensions of angular momentum, and I have discussed how it could be modified to create a measure with the correct dimensions. I considered two possibilities, (5.75) and (5.76), which seem reasonable, but found that the first, 'type A', can lead to a singular and thus unsatisfactory result for some optical fields. On the other hand, 'type B' is never singular and is thus preferable. Future work will involve a more detailed analysis of this particular atomic helicity measure.

It would also be interesting going forward to try and experimentally verify the results of this Chapter. We note again that, because $J \cdot P$ is a Hermitian operator, it is in principle an observable. Whilst it is not easy to see how we could make a *direct* measurement of this quantity, it may be able to be reconstructed from indirect measurements, and experiments on the influence of structured light on the COM motion of single ions have recently been performed [177]. Although I have considered here a hydrogen-like atom, it is more likely that an actual experiment would use a singly-ionized alkaline earth metal, such as Be⁺ or Ca⁺, which are routinely prepared in single-ion traps [173, 177]. The present analysis should not require too much modification for such ions, as they only have a single valence electron.

This work could also be extended in a number of interesting ways, one possibility being to include in the analysis different types of atomic helicity. It is well-known, for instance, that the *orbital* AM of a paraxial beam couples to the external (COM), rather than the internal, atomic degrees of freedom in the dipole approximation [10, 178, 179]. We might therefore be able to define a measure of atomic helicity which takes into account the COM angular momentum (whereas I have considered the internal, electronic AM of the atom). By taking into account both of these mechanisms, a truly comprehensive understanding of helicity exchange between light and atoms would be possible.

CHAPTER 6

Conclusion

In this Thesis I have considered various aspects of two pillars of structured light research: optical angular momentum and optical chirality, focussing in particular on the theoretical foundations of optical spin and optical helicity. I have also presented several original results, which I summarize below.

Firstly, I have presented derivations of two existing results which have previously been considered from the classical or semi-classical perspectives, using an alternative approach based on the molecular QED formalism. Specifically, in Section 3.2 I showed that the Faraday effect may be treated as a two-state quantum process, resulting from forward Rayleigh scattering between orthogonal modes of the quantized field. The essential features of the approach I have developed here are applicable to all molecular QED problems involving external perturbations, even when the molecules are degenerate, a feature which was missing from previous treatments of similar problems. In the future I will extend my derivation to the mechanical Faraday effect. In Section 4.4, I derived the enantioselective energy splitting of a chiral molecule in a monochromatic field consisting of two plane waves, showing that the helicity-dependent optical force experienced by a chiral molecule has its origins in fundamental photonic interactions.

In Section 2.3, I discussed local optical spin structures in non-interfering superpositions of plane waves. By examining two specific examples, I showed that the physically-distinct

CHAPTER 6. CONCLUSION

electric and magnetic spin densities, which possess identical behaviour in a plane wave or paraxial beam, can exhibit highly interesting and diverging behaviours in more structured fields. The complexity of these spin structures appears to increase with the number of plane waves and their non-paraxiality. I also discussed the connections between the spin densities and the optical forces and torques experienced by subwavelength particles. These connections suggest that non-interfering superpositions, with their non-trivial spin structures, could provide an important platform for exploring novel light-matter interactions. This is reinforced by the realization that the homogeneous intensity profile of these optical fields means that the often dominant electric gradient force vanishes, meaning other more interesting optical forces can come to the fore.

In Chapter 5, I presented my work on the transfer of optical helicity to a single hydrogenlike atom. While it is well established that the helicity influences optical interactions with chiral molecules, the primary motivation behind this work was to increase our fundamental understanding of how optical helicity interacts with matter at the atomic level. A practical application of studying the helicity transfer to *atoms* could be the development of alternative approaches for experimentally probing the local helicity of an optical field. In my analysis, I worked within the semi-classical framework of light-matter interactions, and the key to my findings is the full consideration of both the internal and external degrees of freedom of the atom. After defining a suitable *atomic helicity* measure, by analogy with the helicity from particle physics, I examined the connections between this and the optical helicity in some simple examples, which suggested a correlation between the two. This connection was then explicitly demonstrated by considering the interaction with an arbitrary monochromatic field. The result showed that the optical helicity is indeed transferred to an atom in lightmatter interactions, but imperfectly, in the sense that the inherently quantum nature of the (external) atomic motion means that the atom does not perfectly detect the *local* optical helicity, but a spread of values, which is directly related to the spread of the atomic wave packet. We also found the somewhat surprising result that if an atom with a non-zero probability current is considered, then the atomic helicity depends not just on the optical helicity density, but also on the local electric spin. In future work, it would be interesting to extend this analysis to include AM transfer from the optical field to the external motion of the atom, as can be achieved with a Laguerre-Gaussian beam.

Appendices

APPENDIX A

Mathematics

A.1 Delta Functions

The one-dimensional Dirac delta 'function' is defined via the relation [18, 64]

$$\int_{-\infty}^{\infty} \mathrm{d}x \ f(x)\delta(x-x') = f(x'). \tag{A.1}$$

Similarly, for the three-dimensional delta function $\delta(\mathbf{r} - \mathbf{r}') \equiv \delta(x - x')\delta(y - y')\delta(z - z')$, we have

$$\int_{-\infty}^{\infty} \mathrm{d}^3 r \ f(\boldsymbol{r}) \delta(\boldsymbol{r} - \boldsymbol{r}') = f(\boldsymbol{r}'). \tag{A.2}$$

The derivative of the Dirac delta function is defined by applying integration by parts [18, 64],

$$\int_{-\infty}^{\infty} \mathrm{d}^3 r \ f(\boldsymbol{r}) \partial_j \delta(\boldsymbol{r} - \boldsymbol{r}') = -\int_{-\infty}^{\infty} \mathrm{d}^3 r \ \delta(\boldsymbol{r} - \boldsymbol{r}') \partial_j f(\boldsymbol{r}) = -\partial_j f(\boldsymbol{r}'), \tag{A.3}$$

where $\partial_j = \frac{\partial}{\partial x_j}$. It is important to always keep in mind that the delta function and its derivative are only meaningful quantities when they appear in an integrand.

The Helmholtz theorem tells us that an arbitrary vector field V(r) (assuming its divergence

and curl vanish at infinity [64, p. 97]) may be written as the sum

$$\boldsymbol{V}(\boldsymbol{r}) = \boldsymbol{V}_{\perp}(\boldsymbol{r}) + \boldsymbol{V}_{\parallel}(\boldsymbol{r}), \tag{A.4}$$

where $V_{\parallel}(\mathbf{r})$ is a longitudinal (curl-free) vector field and $V_{\perp}(\mathbf{r})$ is a transverse (divergence-free) vector field:

$$\nabla \cdot \boldsymbol{V}_{\perp}(\boldsymbol{r}) = 0, \qquad \nabla \times \boldsymbol{V}_{\parallel}(\boldsymbol{r}) = 0.$$
 (A.5)

In electrodynamics we are often physically interested in the splitting of a vector field (e.g., the electric field) into its transverse and longitudinal components. For these purposes it is useful to define the *transverse* and *longitudinal* delta functions [18, 20], which 'pick out' the transverse and longitudinal parts of a vector field:

$$\int_{-\infty}^{\infty} \mathrm{d}^3 r \ V_j(\boldsymbol{r}) \delta_{ij}^{\perp}(\boldsymbol{r} - \boldsymbol{r}') = V_i^{\perp}(\boldsymbol{r}'), \tag{A.6a}$$

$$\int_{-\infty}^{\infty} \mathrm{d}^3 r \ V_j(\boldsymbol{r}) \delta_{ij}^{\parallel}(\boldsymbol{r}-\boldsymbol{r}') = V_i^{\parallel}(\boldsymbol{r}'). \tag{A.6b}$$

Note that $\delta_{ij}^{\perp}(\mathbf{r}) + \delta_{ij}^{\parallel}(\mathbf{r}) = \delta_{ij}\delta(\mathbf{r})$, where δ_{ij} is the Kronecker delta. Explicit representations of the transverse and longitudinal delta functions, in real and Fourier space, can be found in [18, §3.1].

A.2 Cylindrical Coordinates

Following Arfken and Weber [64, §2.4], the cylindrical coordinates are (ρ, φ, z) and take the values

$$0 \le \rho < \infty, \quad 0 \le \varphi < 2\pi, \quad -\infty < z < \infty.$$

The Cartesian coordinates (x, y, z) are related to (ρ, φ, z) by

$$x = \rho \cos \varphi, \quad y = \rho \sin \varphi, \quad z = z.$$
 (A.7)

The Cylindrical unit vectors $(\hat{\rho}, \hat{\varphi}, \hat{z})$ are related to the Cartesian unit vectors $(\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{z})$ via

$$\hat{\boldsymbol{\rho}} = \cos\varphi \hat{\mathbf{x}} + \sin\varphi \hat{\mathbf{y}}, \qquad (A.8a)$$

$$\hat{\boldsymbol{\varphi}} = -\sin\varphi \hat{\mathbf{x}} + \cos\varphi \hat{\mathbf{y}},\tag{A.8b}$$

$$\hat{\mathbf{z}} = \hat{\mathbf{z}}.$$
 (A.8c)

The unit vectors are mutually orthogonal. We have the cross products

$$\hat{\mathbf{z}} \times \hat{\boldsymbol{\rho}} = \hat{\boldsymbol{\varphi}}, \quad \hat{\boldsymbol{\varphi}} \times \hat{\mathbf{z}} = \hat{\boldsymbol{\rho}}, \quad \hat{\boldsymbol{\rho}} \times \hat{\boldsymbol{\varphi}} = \hat{\mathbf{z}}.$$
 (A.9)

A generic vector \boldsymbol{V} can be written as $\boldsymbol{V} = V_{\rho}\hat{\boldsymbol{\rho}} + V_{\varphi}\hat{\boldsymbol{\varphi}} + V_{z}\hat{\mathbf{z}}$. Position vectors on the other hand are given by

$$\boldsymbol{r} = \rho \hat{\boldsymbol{\rho}} + z \hat{\mathbf{z}}.\tag{A.10}$$

In cylindrical coordinates the gradient operator takes the form

$$\nabla = \hat{\rho} \frac{\partial}{\partial \rho} + \hat{\varphi} \frac{1}{\rho} \frac{\partial}{\partial \varphi} + \hat{z} \frac{\partial}{\partial z}.$$
 (A.11)

The volume element $dV \equiv d^3r$ in cylindrical coordinates is

$$\mathrm{d}V = \rho \mathrm{d}\rho \mathrm{d}\varphi \mathrm{d}z. \tag{A.12}$$

A.3 Cartesian Tensors

A scalar is a physical quantity defined by a single number, its magnitude, which is independent of our chosen coordinate system. A vector is a physical quantity defined by both a magnitude and a direction, thus requiring three numbers in three-dimensional space. Mathematically, scalars and vectors are rank-0 and rank-1 *Cartesian tensors*, respectively. A Cartesian tensor of rank m is a mathematical object, T, which in N-dimensional space is specified by N^m numbers, called its components. The components depend explicitly on our choice of coordinate system, which I will always choose to be a set of Cartesian axes $\{x, y, z\}$. In index notation the tensor T may be written as $T_{i_1i_2...i_m}$, where each index may take the value x, y, or z (equivalently 1, 2, or 3).

The defining feature of Cartesian tensors is how their components transform under rotations [24, 57, 64]. In particular, we are interested in arbitrary rotational transformations between the Cartesian coordinate systems $\{x, y, z\}$ and $\{x', y', z'\}$, which have a common origin O = O'. Here I have implicitly assumed the *passive approach*, in which the physical quantity under consideration, e.g., the position of a particle, is left unchanged, whilst the frame of reference which this quantity is referred to is transformed. Alternatively we could take the *active approach* [57, p. 268], in which the physical quantity is transformed and the coordinate system left the same (see Figure A.1). Under a passive rotational transformation



Figure A.1: 'Passive' vs 'active' approach to transformations. A vector OP is shown on the left with respect to coordinate axes $\{x, y, z\}$, with corresponding unit vectors $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$. In this coordinate system the vector is described by $(x_P, y_P, 0)$. On the top right is the same vector described in a new coordinate system $\{x', y', z'\}$, which is related to the original system by a clockwise rotation about the Oz-axis by an angle θ . In the new coordinate system, OP is described by $(x'_P, y'_P, 0)$. On the bottom right the vector OP is rotated anti-clockwise about the Oz-axis by an angle θ , resulting in the transformed vector $OP' \neq OP$. In the original coordinate system, $\{x, y, z\}$, the new vector is described by $(x_{P'}, y_{P'}, 0)$. These two transformations are equivalent, in the sense that $x'_P = x_{P'}, y'_P = y_{P'}$.

of the aforementioned type, the components of a vector V transform as [24, Ch. 4]

$$V_{i'} = \ell_{i'k} V_k, \tag{A.13}$$

where V_k is the component of V relative to the k^{th} axis (original reference frame), $V_{i'}$ is the component relative to the i'^{th} axis (rotated reference frame), and $\ell_{i'k}$ is the *direction cosine* between the two axes, defined in terms of the unit vectors $\hat{\mathbf{e}}_{i'}$ and $\hat{\mathbf{e}}_k$:

$$\ell_{i'k} \equiv \hat{\mathbf{e}}_{i'} \cdot \hat{\mathbf{e}}_k. \tag{A.14}$$

In (A.13), and all similar equations, I employ the summation convention in which all repeated indices are summed over. The inverse transformation is

$$V_k = \ell_{ki'} V_{i'}.\tag{A.15}$$

These equations highlight the importance of distinguishing between a vector V and its components: the former is a frame-independent physical quantity, whilst the latter are explicitly tied *both* to the physical quantity and the coordinate system. The rotational transformation laws for higher-rank tensors follow simply from the rank-1 case.

What I have discussed so far are the so-called 'proper' rotations. Tensors can also be classified according to their behaviour under 'improper' rotations. Improper rotations combine proper rotations with spatial reflections and inversions [64, §2.9]. The space inversion operation corresponds to a transformation to new coordinate axes defined by the unit vectors $\hat{\mathbf{x}}' = -\hat{\mathbf{x}}$, $\hat{\mathbf{y}}' = -\hat{\mathbf{y}}$, $\hat{\mathbf{z}}' = -\hat{\mathbf{z}}$. Taking the position vector \mathbf{r} as a prototypical example, it is easily seen that under spatial inversion its components transform as

$$x_{i'} = -\delta_{i'k} x_k = -x_i. \tag{A.16}$$

Again, because we are considering passive transformations, the vector \mathbf{r} is unchanged. Any rank-1 tensor whose *components reverse sign* when we transform to the space inverted coordinate system is called a *polar vector*, or simply a vector [24, 57]. Not all rank-1 tensors which transform under proper rotations according to (A.13) are polar vectors. This can be seen by considering the cross product $\mathbf{U} = \mathbf{V} \times \mathbf{W}$, where \mathbf{V} and \mathbf{W} are polar vectors. The components of \mathbf{U} transform under space inversion according to

$$U_{i'} = +\delta_{i'k}U_k = U_i. \tag{A.17}$$

Any rank-1 tensor whose *components are the same* in the original and the space inverted coordinate systems is called an *axial vector*, or a pseudovector [24, 57]. For an axial vector, the transformation law (A.13) requires modification to take into account improper rotations [24],

$$U_{i'} = \det(\Lambda) \,\ell_{i'k} U_k,\tag{A.18}$$

where $\det(\Lambda)$ is the determinant of the matrix Λ with entries $\ell_{m'n}$. For a proper rotation, $\det(\Lambda) = +1$, whilst for an improper rotation $\det(\Lambda) = -1$ [57].

Two types of rank-0 tensor can also be distinguished when improper rotations are involved. Firstly we have the true scalars, which may be formed from the dot product of two polar vectors or two axial vectors, and which *do not change sign* under space inversion. On the other hand, a rank-0 tensor formed from the dot product of a polar vector with an axial vector *does change sign* under space inversion, and these are referred to as *pseudoscalars* [24]. Polar vectors and pseudoscalars are said to have *odd parity*, whilst axial vectors and scalars have even parity [57, 64].

The final spacetime transformation which is useful to consider is the time reversal operation, which corresponds to the replacement $t \to t' = -t$ [19, 24, 57]. The effect on the components of a coordinate vector is $x_i(t) \to x'_i(t') = +x_i(t)$, whilst velocity components transform as $v_i(t) \to v'_i(t') = -v_i(t)$ [24]. All known classical equations of motion are form-invariant under time reversal. A tensor which transforms in the same way as x_i under time reversal, i.e., $W \to W' = +W$, is said to be a *time-even* quantity, whilst a quantity which transforms as $W \to W' = -W$, like a velocity, is said to be *time-odd*.

APPENDIX B

Classical Electrodynamics

B.1 Maxwell's Equations

B.1.1 Macroscopic Equations

Maxwell unified, and extended, the pre-existing 'laws' of electromagnetism, providing a single theoretical framework for electricity, magnetism, and optics [180]. His equations predate the modern consensus on the atomic nature of matter and are thus naturally expressible in a macroscopic form. They can be grouped into four differential equations describing the vector fields $\boldsymbol{E} \equiv \boldsymbol{E}(\boldsymbol{r},t), \ \boldsymbol{B} \equiv \boldsymbol{B}(\boldsymbol{r},t), \ \boldsymbol{D} \equiv \boldsymbol{D}(\boldsymbol{r},t), \ \boldsymbol{H} \equiv \boldsymbol{H}(\boldsymbol{r},t), \ \boldsymbol{J} \equiv \boldsymbol{J}(\boldsymbol{r},t)$, and the scalar field $\eta \equiv \eta(\boldsymbol{r},t)$. Using this notation the Maxwell equations are expressible in the differential form [57, 62]

$$\nabla \cdot \boldsymbol{D} = \eta, \tag{B.1a}$$

$$\nabla \times \boldsymbol{H} - \boldsymbol{\dot{D}} = \boldsymbol{J},\tag{B.1b}$$

$$\nabla \cdot \boldsymbol{B} = 0, \tag{B.1c}$$

$$\nabla \times \boldsymbol{E} + \boldsymbol{B} = 0. \tag{B.1d}$$

An overdot is used to indicate partial differentiation with respect to time, and the dependences on r and t have been suppressed for notational clarity.

The fields J and η are the macroscopic densities of free current and charge, respectively. Their forms are set by the physical situation under consideration and once set they act as boundary conditions for the determination of the other four vector fields. The charge and current densities themselves are linked through a 'charge continuity equation'

$$\dot{\eta} + \nabla \cdot \boldsymbol{J} = 0, \tag{B.2}$$

which expresses the local conservation of the total charge in a system. It should be noted however that this equation is not actually independent from the Maxwell equations [62].

Examining the homogeneous Maxwell equations (B.1c) and (B.1d) it is evident that they can be solved formally by the introduction of appropriate functions \boldsymbol{A} and $\boldsymbol{\Phi}$, known as the vector and scalar potentials respectively (to be discussed further in §B.2). Furthermore it is clear that these two equations permit non-trivial solutions for \boldsymbol{E} and \boldsymbol{B} even in free space, i.e., in the strict absence of charge. We can choose to associate these two vector fields with the electromagnetic forces exerted on charges and currents, a choice which is compatible with Maxwell's equations and experiment [62]. Given these considerations we call \boldsymbol{E} the electric field and \boldsymbol{B} the magnetic field. On the other hand the inhomogeneous Maxwell equations (B.1a) and (B.1b) are not solvable without imposing some conditions on the vector fields \boldsymbol{D} and \boldsymbol{H} , as (B.1a) and (B.1b) actually represent four equations for six unknowns. To proceed we introduce the so-called constitutive relations between these fields and the electric and magnetic fields \boldsymbol{E} and \boldsymbol{B} :

$$\boldsymbol{D} = \boldsymbol{D}[\boldsymbol{E}, \boldsymbol{B}], \qquad \boldsymbol{H} = \boldsymbol{H}[\boldsymbol{E}, \boldsymbol{B}]. \tag{B.3}$$

The particular form of these relations depends on the medium that the fields are being considered in.

In free space the constitutive relations are very simple

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E}, \qquad \boldsymbol{H} = \mu_0^{-1} \boldsymbol{B}, \tag{B.4}$$

where ε_0 is the electric permittivity and μ_0 the magnetic permeability of free space. In SI

units these are related to the speed of light in vacuum, c, via

$$c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}.\tag{B.5}$$

If a material is linear, isotropic, and homogeneous then constitutive relations identical in form to the free space ones exist for that material, but with ε_0 and μ_0 replaced by the permittivity of the material, ε , and its permeability, μ . The majority of materials can be accounted for by relaxing the isotropic and homogeneous constraints but retaining linearity. In these cases ε and μ are tensors which might be functions of \boldsymbol{r} (amongst other things [181]).

An alternative way to link the fields is by using additive relations of the form:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P},\tag{B.6a}$$

$$\boldsymbol{H} = \boldsymbol{\mu}_0^{-1} \boldsymbol{B} - \boldsymbol{M}, \tag{B.6b}$$

where P is the (electric) polarization field and M is the magnetic polarization or magnetization field, which by definition account for the material's response to the electric and magnetic fields. For a linear, isotropic medium we must have [182]

$$\boldsymbol{P} = \varepsilon_0 \chi_e \boldsymbol{E},\tag{B.7}$$

with $\chi_e = \varepsilon_r - 1$ the electric susceptibility and $\varepsilon_r = \varepsilon/\varepsilon_0$ the relative permittivity of the material. As with the permittivity the susceptibility can be generalised to a tensor for anisotropic media. Similar arguments follow for the magnetization.

B.1.2 Microscopic Equations

As mentioned above, the Maxwell equations were formulated before the definite existence of atomic and subatomic particles was established and as such the electromagnetic theory outlined thus far is intrinsically macroscopic. However, as nature is composed of elementary charged particles and the atoms and molecules formed by them, an intrinsically *microscopic* form of Maxwell's equations also exists which is capable of reproducing the macroscopic theory defined by (B.1a)–(B.1d). The microscopic equations are [18, 20, 57]

$$\varepsilon_0 \nabla \cdot \boldsymbol{e} = \rho,$$
 (B.8a)

$$\mu_0^{-1} \nabla \times \boldsymbol{b} - \varepsilon_0 \dot{\boldsymbol{e}} = \boldsymbol{j}, \tag{B.8b}$$

$$\nabla \cdot \boldsymbol{b} = 0, \tag{B.8c}$$

$$\nabla \times \boldsymbol{e} + \boldsymbol{b} = 0, \tag{B.8d}$$

where \boldsymbol{e} , \boldsymbol{b} , ρ , and \boldsymbol{j} are the *microscopic* electric field, magnetic field, charge density, and current density, respectively. Note that the microscopic equations are *not* just the macroscopic equations in the absence of polarization and magnetization fields, because $\boldsymbol{e} \neq \boldsymbol{E}$. Rather $\boldsymbol{E} = \langle \boldsymbol{e} \rangle$ and $\boldsymbol{B} = \langle \boldsymbol{b} \rangle$, where $\langle \cdot \rangle$ denotes a statistical averaging. Detailed discussions of how to go from \boldsymbol{e} to \boldsymbol{E} etc., can be found in [57, 182].

The microscopic charge and current densities are not continuous functions of space (as is required of η and J) because, by assumption, we are considering a collection of point charges. Therefore the densities will be zero everywhere except at the positions of the particles, where they are infinite. They are therefore defined via [18, 20, 57]

$$\rho(\boldsymbol{r},t) = \sum_{\alpha} e_{\alpha} \delta(\boldsymbol{r} - \boldsymbol{q}_{\alpha}(t))$$
(B.9)

and

$$\boldsymbol{j}(\boldsymbol{r},t) = \sum_{\alpha} e_{\alpha} \boldsymbol{v}_{\alpha}(t) \delta(\boldsymbol{r} - \boldsymbol{q}_{\alpha}(t)), \qquad (B.10)$$

where $\delta(\mathbf{r})$ is the three-dimensional Dirac delta function (see Appendix A.1) and e_{α} , \mathbf{q}_{α} , and $\mathbf{v}_{\alpha} \equiv \dot{\mathbf{q}}_{\alpha}$ are the charge, position and velocity of particle α . The total charge is given by

$$\int d^3 r \ \rho(\mathbf{r}, t) = \sum_{\alpha} e_{\alpha} \equiv q. \tag{B.11}$$

The Maxwell equations describe the dynamics of the fields but not the charges. For particle speeds much less than the speed of light $(|\boldsymbol{v}_{\alpha}| \ll c)$, the equation of motion for a charged point particle in the presence of EM fields is given by the Lorentz force law [20, 57]

$$m_{\alpha} \dot{\boldsymbol{v}}_{\alpha} = e_{\alpha} (\boldsymbol{e}(\boldsymbol{q}_{\alpha}) + \boldsymbol{v}_{\alpha} \times \boldsymbol{b}(\boldsymbol{q}_{\alpha})). \tag{B.12}$$

The Lorentz force for an arbitrary charge and current distribution (microscopic or macro-

scopic) may be written as [62]

$$\boldsymbol{F} = \int_{V} \mathrm{d}^{3} r \left[\eta \boldsymbol{E} + \boldsymbol{J} \times \boldsymbol{B} \right].$$
(B.13)

The classical microscopic formulation outlined here is the starting point for my discussion of molecular *quantum* electrodynamics in Chapter 3.

B.2 Gauge Invariance

It was mentioned in the previous section that the homogeneous Maxwell equations (B.1c) and (B.1d) can be formally solved by the introduction of a (magnetic) vector potential, $\boldsymbol{A}(\boldsymbol{r},t)$, and an (electric) scalar potential, $\boldsymbol{\Phi}(\boldsymbol{r},t)$. These are defined in relation to the electric and magnetic fields via

$$\boldsymbol{B} = \nabla \times \boldsymbol{A},\tag{B.14a}$$

$$\boldsymbol{E} = -\boldsymbol{A} - \nabla \Phi, \tag{B.14b}$$

which make use of the vector calculus identities $\nabla \cdot (\nabla \times \mathbf{A}) \equiv 0$ and $\nabla \times \nabla \Phi \equiv 0$ for any \mathbf{A} and Φ . Similarly the homogeneous microscopic Maxwell equations can be solved by introducing the corresponding microscopic potentials, denoted by \mathbf{a} and ϕ .

The potentials are not uniquely defined, because the same \boldsymbol{E} and \boldsymbol{B} are produced by the potentials $\{\boldsymbol{A}', \Phi'\}$ as are produced by $\{\boldsymbol{A}, \Phi\}$, so long as $\boldsymbol{A}' = \boldsymbol{A} + \nabla \chi$ and $\Phi' = \Phi - \dot{\chi}$, for any $\chi(\boldsymbol{r}, t)$. The transformations

$$A \to A' = A + \nabla \chi,$$
 (B.15a)

$$\Phi \to \Phi' = \Phi - \dot{\chi},\tag{B.15b}$$

are called *gauge transformations* and the Maxwell equations, and thus electromagnetism, exhibit *gauge invariance*. We are therefore free to choose the gauge we work with, and the usefulness of working with the potentials in place of the fields is precisely due to this freedom.

The Helmholtz theorem (as discussed in Appendix A.1) tells us that the vector potential can be written in the form

$$A = A_{\perp} + A_{\parallel},$$

where A_{\perp} is a divergence-free (solenoidal) vector field,

$$\nabla \cdot \boldsymbol{A}_{\perp} = 0, \tag{B.16}$$

and A_{\parallel} is a curl-free (irrotational) field,

$$\nabla \times \boldsymbol{A}_{\parallel} = 0. \tag{B.17}$$

I call A_{\perp} the transverse component and A_{\parallel} the longitudinal component of the vector potential. Clearly the curl of any vector field is transverse and the divergence of any scalar field is longitudinal (this reasoning was already used in defining the potentials) and indeed we can define functions V and w such that [64, §1.16]

$$oldsymbol{A}_{\perp} =
abla imes oldsymbol{V},$$

 $oldsymbol{A}_{\parallel} =
abla w.$

The point of this mathematical digression is to note that the magnetic field, being transverse, is independent of the longitudinal part of the vector potential, i.e.,

$$\boldsymbol{B} \equiv \boldsymbol{B}_{\perp} = \nabla \times \boldsymbol{A}_{\perp}, \tag{B.18}$$

whilst the electric field can be decomposed into transverse and longitudinal components, written in terms of the potentials as

$$\boldsymbol{E}_{\perp} = -\dot{\boldsymbol{A}}_{\perp}, \tag{B.19a}$$

$$\boldsymbol{E}_{\parallel} = -\boldsymbol{A}_{\parallel} - \nabla \Phi. \tag{B.19b}$$

Re-examining the gauge transformation (B.15) we see that the vector potential is altered by the addition of $\nabla \chi$, which as we have just discussed is itself a longitudinal vector field. Therefore in changing from one gauge to another we alter the forms of Φ and A_{\parallel} , but not A_{\perp} , which is uniquely defined by (B.19a) and (B.18). Therefore the *transverse* component of the vector potential is gauge independent.

Given the gauge-invariance of A_{\perp} , the statement of a gauge is often just a statement of the

value of $\nabla \cdot \mathbf{A} \equiv \nabla \cdot \mathbf{A}_{\parallel}$. One common choice is the Lorenz gauge¹ [20, 57]

$$\nabla \cdot \boldsymbol{A} = -\frac{1}{c^2} \dot{\Phi}.$$
 (B.20)

This choice is particularly useful in relativistic electrodynamics because it is inherently Lorentz covariant [20, 184]. Another choice is the Coulomb gauge, which I will make much use of in Chapter 3, and is defined by [18, 57]

$$\nabla \cdot \boldsymbol{A} = 0. \tag{B.21}$$

B.3 Multipole Moments

At the length scales commonly encountered in our everyday lives, molecules can reasonably be thought of as point particles. However, a neutral molecule would be a very boring thing if it were truly a point particle; the fact that molecules are *not* point particles is the entire basis for light-molecule interactions. These interactions arise through couplings between the EM fields and the molecular *multipole moments*. The multipole expansion is therefore a crucial tool in developing a (microscopic) picture of light-molecule interactions. The multipole series can be formulated in terms of spherical harmonics [57, 62] or in terms of Cartesian tensors [24]. Here I give an overview of the Cartesian approach, as is common in theories of lightmolecule interactions [18, 24, 185]. I closely follow Barron [24, §2.4], and formally consider collections of point charges, such that the charge and current densities are given by (B.9) and (B.10).

First, let's discuss the electric multipole moments. The *zeroth-order moment* of a collection of point charges is simply the total charge, as in (B.11). I will usually consider neutral systems (q = 0) so the zeroth moment does not contribute to the light-matter coupling. The first-order moment of an atom or molecule is the *electric dipole moment*,

$$\boldsymbol{\mu} \equiv \sum_{\alpha} e_{\alpha} \boldsymbol{q}_{\alpha}, \tag{B.22}$$

where, as above, e_{α} and q_{α} are the charge and position vectors of the individual charges. In a globally neutral system, the electric dipole moment is invariant to a change of origin. The second-order multipole moment is the *electric quadrupole moment*, which is a rank-2 tensor

¹Commonly this is incorrectly called the *Lorentz* gauge, but it was in fact introduced by Lorenz [183].

with components

$$Q_{ij} \equiv \frac{1}{2} \sum_{\alpha} e_{\alpha} q_{\alpha i} q_{\alpha j}. \tag{B.23}$$

The electric quadrupole moment is clearly symmetric: $Q_{ij} = Q_{ji}$. This is the highest-order electric multipole moment I shall consider.

The zeroth-order magnetic multipole moment (the net 'magnetic charge') does not exist, so the lowest-order magnetic multipole is the first-order *magnetic dipole moment*,

$$\boldsymbol{m} \equiv \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} \boldsymbol{q}_{\alpha} \times \boldsymbol{p}_{\alpha}, \tag{B.24}$$

where m_{α} and p_{α} are the mass and momentum of particle α . We can alternatively write this in terms of the angular momenta of the particles, $l_{\alpha} = q_{\alpha} \times p_{\alpha}$. If the particles have spin angular momenta in addition to orbital, these will produce additional contributions to the magnetic dipole moment, leading to the more general definition [24]

$$\boldsymbol{m} = \sum_{\alpha} \frac{e_{\alpha}}{2m_{\alpha}} (\boldsymbol{l}_{\alpha} + g_{\alpha} \boldsymbol{s}_{\alpha}), \qquad (B.25)$$

where g_{α} is the 'g-value' of the α^{th} particle. I will not consider higher-order magnetic dipole moments.

To see how the multipole moments naturally arise in light-matter interactions, let's consider the charge density of a single molecule ζ :

$$\rho_{\zeta}(\boldsymbol{r}) = \sum_{\alpha} e_{\alpha} \delta(\boldsymbol{r} - \boldsymbol{q}_{\alpha}). \tag{B.26}$$

Let \mathbf{R}_{ζ} be a point within the molecule, perhaps its centre-of-mass. Then define \mathbf{r}_{α} as the position of the α^{th} particle of the molecule relative to \mathbf{R}_{ζ} , i.e.,

$$\boldsymbol{q}_{\alpha} = \boldsymbol{R}_{\zeta} + \boldsymbol{r}_{\alpha}, \tag{B.27}$$

and the delta function in (B.26) may be written as

$$\delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta} - \boldsymbol{r}_{\alpha}). \tag{B.28}$$

Assuming $|\boldsymbol{r} - \boldsymbol{R}_{\zeta}| \gg |\boldsymbol{r}_{\alpha}|$, we may Taylor expand the Delta function about $\boldsymbol{r} - \boldsymbol{R}_{\zeta}$, which

leads to the following expression for the charge density [18]:

$$\rho_{\zeta}(\boldsymbol{r}) = q\delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta}) - \mu_i \partial_i \delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta}) + Q_{ij} \partial_i \partial_j \delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta}) + \dots, \qquad (B.29)$$

where q is the net charge of the molecule and μ_i and Q_{ij} are the components of the dipole and quadrupole moments (B.22) and (B.23), but now defined relative to the point \mathbf{R}_{ζ} (i.e., it is \mathbf{r}_{α} rather than \mathbf{q}_{α} which appear in the formulae). This expression can be used, for instance, in calculating the Coulomb potential due to the molecule at point \mathbf{r}' ,

$$\phi_C(\mathbf{r}') = \frac{1}{4\pi\varepsilon_0} \int d^3r \ \frac{\rho_{\zeta}(\mathbf{r})}{|\mathbf{r}' - \mathbf{r}|}.$$
(B.30)

If we have multiple molecules, the total microscopic charge density is

$$\rho = \sum_{\zeta} \rho_{\zeta} \tag{B.31}$$

$$=\sum_{\zeta}q(\zeta)\delta(\boldsymbol{r}-\boldsymbol{R}_{\zeta})+\sum_{\zeta}\bigg[-\mu_{i}(\zeta)\partial_{i}\delta(\boldsymbol{r}-\boldsymbol{R}_{\zeta})+Q_{ij}(\zeta)\partial_{i}\partial_{j}\delta(\boldsymbol{r}-\boldsymbol{R}_{\zeta})+\dots\bigg],\quad(B.32)$$

where $q(\zeta)$ is the charge of the ζ^{th} molecule, etc. From a comparison of the microscopic and macroscopic Maxwell equations, we have

$$\langle \rho \rangle = \eta - \nabla \cdot \boldsymbol{P},\tag{B.33}$$

where η is the macroscopic density of free charges and P is the macroscopic polarization field, associated with the bound charges. It is therefore natural to partition ρ into 'free' and 'bound' terms as well,

$$\rho = \rho_{\text{free}} + \rho_{\text{bound}}.\tag{B.34}$$

From (B.31), the free charge contribution is given by

$$\rho_{\text{free}} = \sum_{\zeta} q(\zeta) \delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta}), \qquad (B.35)$$

whilst the bound contribution is

$$\rho_{\text{bound}} = \sum_{\zeta} \left[-\mu_i(\zeta) \partial_i \delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta}) + Q_{ij}(\zeta) \partial_i \partial_j \delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta}) + \dots \right].$$
(B.36)

We may introduce the microscopic polarization field, p, via

$$\rho_{\text{bound}} = -\nabla \cdot \boldsymbol{p} = -\nabla \cdot \sum_{\zeta} \boldsymbol{p}_{\zeta}, \qquad (B.37)$$

where p_{ζ} is the polarization field due to molecule ζ . Comparing with (B.36), we find that [18]

$$\boldsymbol{p}_{\zeta}(\boldsymbol{r}) = \sum_{\alpha} e_{\alpha} \boldsymbol{r}_{\alpha} \bigg[1 - \frac{1}{2} (\boldsymbol{r}_{\alpha} \cdot \nabla) + \frac{1}{6} (\boldsymbol{r}_{\alpha} \cdot \nabla)^2 - \dots \bigg] \delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta}), \quad (B.38)$$

which may be written in the closed form [18, 20]

$$\boldsymbol{p}_{\zeta}(\boldsymbol{r}) = \sum_{\alpha} e_{\alpha} \boldsymbol{r}_{\alpha} \int_{0}^{1} \mathrm{d}u \ \delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta} - u\boldsymbol{r}_{\alpha}). \tag{B.39}$$

Similar results hold for the partitioning of the microscopic current density into free and bound terms: $\boldsymbol{j} = \boldsymbol{j}_{\text{free}} + \boldsymbol{j}_{\text{bound}}$. If centre-of-mass/nuclear motions are neglected, the bound current may be written as

$$\boldsymbol{j}_{\text{bound}} = \boldsymbol{\dot{p}} + \nabla \times \boldsymbol{\mathcal{M}},$$
 (B.40)

where $\mathcal{M} = \sum_{\zeta} \mathcal{M}_{\zeta}$ is the microscopic magnetization field. The magnetization field of molecule ζ has the closed form [18]

$$\mathcal{M}_{\zeta}(\boldsymbol{r}) = \sum_{\alpha} e_{\alpha} \boldsymbol{r}_{\alpha} \times \dot{\boldsymbol{r}}_{\alpha} \int_{0}^{1} \mathrm{d}u \ u \,\delta(\boldsymbol{r} - \boldsymbol{R}_{\zeta} - u\boldsymbol{r}_{\alpha}). \tag{B.41}$$

APPENDIX C

Elements of Quantum Mechanics

In this Appendix I review some important results from non-relativistic quantum mechanics (QM) which I make reference to in the main body of my Thesis. This is standard material found in most if not all QM textbooks. I have found [70, 74, 104, 125, 172] to be useful.

C.1 Mathematical Preliminaries

Definitions are taken almost verbatim from the books by Jordan [71], Ballentine [125], or Renteln [186].

A (linear) vector space V consists of two sets of objects: firstly the set $\{\psi, \phi, \chi, \dots\}$, the elements of which are called vectors, secondly the set $\{a, b, c, \dots\}$ (defined over a field \mathscr{F}), the elements of which are called scalars. For any two vectors ψ and ϕ the operation of addition defines a new object $\psi + \phi$, and for any vector ψ and any scalar *a* the operation of scalar multiplication defines a new object $a\psi$, with the condition that

$$a\psi + b\phi \in V \quad \forall \ \psi, \phi \in V, \ a, b \in \mathscr{F}.$$
 (C.1)

Furthermore there exists a unique vector $\mathbf{0}$, called the zero vector, such that $\psi + \mathbf{0} = \psi$. The full list of axioms defining a vector space can be found in, e.g., the first chapter of [71].

A set of vectors $\{\psi_i\}$ is linearly independent if none of the elements of the set can be written as a linear combination of the others, or equivalently, if $\sum_i a_i \psi_i = 0$ implies $a_i = 0 \forall i$. A set of vectors $\{\phi_i\}$ is said to span the vector space V if any vector ψ can be written as a linear combination of the vectors ϕ_i , i.e., $\psi = \sum_i b_i \phi_i$, $\forall \psi \in V$. A set of vectors which spans V and is linearly independent is called a basis of V. If a basis set of V contains N vectors, the vector space is N-dimensional.

For any two vectors ψ , $\phi \in V$ we denote by $(\psi, \phi) \in \mathscr{F}$ the inner product of the vectors. An inner product satisfies:

- (i) $(\psi, a\phi) = a(\psi, \phi),$
- (ii) $(\psi, \phi + \chi) = (\psi, \phi) + (\psi, \chi),$
- (iii) $(\psi, \phi)^* = (\phi, \psi),$
- (iv) $(\psi, \psi) = 0$ if and only if $\psi = 0$; otherwise $(\psi, \psi) > 0$.

If $(\psi, \phi) = 0$ then ψ and ϕ are orthogonal. We call $\|\psi\| = \sqrt{(\psi, \psi)}$ the norm of the vector ψ .

A linear operator A is a mapping $A: V \to V$ which satisfies

$$A(a\psi + b\phi) = aA\psi + bA\phi, \tag{C.2}$$

for all $\psi, \phi \in V$ and all $a, b \in \mathscr{F}$.

A linear functional f is a linear mapping from V to the field \mathscr{F} , $f: V \to \mathscr{F}$. The set of all linear functionals (for some V and \mathscr{F}) is itself a vector space which we call the dual space of V, denoted by V^* . For any vector $\psi \in V$ a linear functional $f_{\psi} \in V^*$ is defined via $f_{\psi}(\phi) = (\psi, \phi)$, for all $\phi \in V$. I will call f_{ψ} the dual (vector) of ψ . From the properties of the inner product we have $f_{\psi+\chi}(\cdot) = f_{\psi}(\cdot) + f_{\chi}(\cdot)$ and $f_{a\psi}(\cdot) = a^* f_{\psi}(\cdot)$. It can be shown that a one-to-one correspondence exists between vectors and linear functionals defined in this way [71, §4], i.e., there is a unique vector $\psi_f \in V$ associated with every linear functional $f \in V^*$.

In Dirac's notation we denote vectors $\psi \in V$ by the notation $|\psi\rangle$ (sometimes called ket vectors). The vectors (linear functionals) $f_{\psi} \in V^*$ are denoted by $\langle \psi |$ (sometimes called bra vectors). The bra $\langle \psi |$ is the dual of the ket $|\psi\rangle$ (remembering the one-to-one correspondence). The action of the linear functional $\langle \psi |$ on the vector $|\phi\rangle$ (i.e., $f_{\psi}(\phi)$) is denoted by $\langle \psi | \phi \rangle$.

The exact same notation is used for the inner product of two vectors $|\psi\rangle$, $|\phi\rangle$:

$$(\psi, \phi) = (|\psi\rangle, |\phi\rangle) = \langle \psi | \phi \rangle.$$
(C.3)

The Hermitian adjoint of the linear operator A is the operator A^{\dagger} defined by

$$(\phi, A^{\dagger}\psi) = (A\phi, \psi), \quad \forall \psi, \phi.$$
 (C.4)

From the third property of the inner product an equivalent condition is

$$(\phi, A^{\dagger}\psi) = (\psi, A\phi)^*.$$
(C.5)

A Hermitian operator is a linear operator for which $A = A^{\dagger}$, therefore

$$(\phi, A\psi) = (\phi, A^{\dagger}\psi) = (\psi, A\phi)^*, \quad \forall \psi, \phi.$$
(C.6)

In Dirac's notation the definition of the Hermitian adjoint is written as

$$\langle \phi | A^{\dagger} | \psi
angle = \langle \psi | A | \phi
angle^{*}, \quad \forall \; | \psi
angle, | \phi
angle,$$

and a Hermitian operator satisfies

$$\langle \phi | A | \psi \rangle = \langle \phi | A^{\dagger} | \psi \rangle = \langle \psi | A | \phi \rangle^* \quad \forall | \psi \rangle, | \phi \rangle.$$
(C.7)

The simplicity of Dirac's notation makes it extremely useful in calculations but it can also be somewhat ambiguous. This is especially true if we assume, as is often done, that an operator in an expression such as $\langle \phi | A | \psi \rangle$ can 'act to the left' (on $\langle \phi |$) or 'to the right' (on $|\psi \rangle$). Strictly speaking A is an operator on V (not V^{*}) so can only act on kets and not bras. A useful relation is

$$\begin{aligned} \langle \psi | B | \phi \rangle^* &= (|\psi\rangle, B | \phi \rangle)^* \\ &= (B | \phi \rangle, |\psi\rangle) \\ &= (|\phi\rangle, B^{\dagger} | \psi \rangle) = \langle \phi | B^{\dagger} | \psi \rangle. \end{aligned}$$

As this holds for all $|\phi\rangle$, we write $\langle\psi|B = (B^{\dagger}|\psi\rangle)^*$. Thus if $B^{\dagger}|\psi\rangle = b|\chi\rangle$ then $\langle\psi|B = b^*\langle\chi|$. Whenever we 'act to the left' with an operator it will be consistent with this result.
A linear operator U is unitary if and only if it satisfies [71]

$$UU^{\dagger} = \mathbb{1} = U^{\dagger}U, \tag{C.8}$$

1 being the identity operator. An alternative definition is $(U\psi, U\phi) = (\psi, \phi)$ for all ψ, ϕ .

An operator $A: V \to V$ is said to be anti-linear if

$$A(a\psi + b\phi) = a^*A\psi + b^*A\phi, \tag{C.9}$$

for all $\psi, \phi \in V$ and all $a, b \in \mathscr{F}$. An anti-linear operator T is called anti-unitary if it satisfies

$$(T\psi, T\phi) = (\psi, \phi)^* = (\phi, \psi),$$
 (C.10)

for all ψ, ϕ .

C.2 Quantum Dynamics

In this Section I shall discuss the general theory of time-evolution in QM. First though, let's recall the basic postulates regarding states and dynamical variables.

The state vector $|\Psi(t)\rangle$, which is of unit norm, contains all of the information which can be known about the state of a (pure, closed) quantum system. Any attribute of a physical system which we could *in principle* measure will be called an observable. In QM there is associated to any observable A a Hermitian *operator* \hat{A} . If \hat{A} possesses an eigenspectrum $\{a_i\}$, with associated eigenstates $\{|a_i\rangle\}$, then the possible results of measuring A are nothing but the eigenvalues, which are real, and they occur with probabilities

$$P_i(t) = |\langle a_i | \Psi(t) \rangle|^2. \tag{C.11}$$

After the measurement the system is no longer in state $|\Psi(t)\rangle$ but in the eigenstate corresponding to the measured eigenvalue. Equation (C.11) leads to the result that when a measurement is made of a system to deduce the value of an observable A, and it is known that at the moment of measurement the system is in state $|\Psi(t)\rangle$, the expected value of the measurement is given by

$$\langle A \rangle (t) = \langle \Psi(t) | \hat{A} | \Psi(t) \rangle.$$
 (C.12)

As \hat{A} is Hermitian expectation values are real valued.

The time evolution of a state in non-relativistic QM is governed, by postulate, by the Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H}(t) |\Psi(t)\rangle,$$
 (C.13)

with $\hat{H}(t)$ the Hamiltonian operator. Alternatively we can describe the dynamics in terms of a (unitary) time-evolution operator $\hat{\mathscr{U}}(t, t_0)$ which evolves the state of the system from $|\Psi(t_0)\rangle$ at $t = t_0$ to the state $|\Psi(t)\rangle$ at time $t > t_0$,

$$|\Psi(t)\rangle = \hat{\mathscr{U}}(t, t_0) |\Psi(t_0)\rangle, \qquad (C.14)$$

and obeys an operator form of the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\hat{\mathscr{U}}(t,t_0) = \hat{H}(t)\hat{\mathscr{U}}(t,t_0).$$
(C.15)

Evidently $\hat{\mathscr{U}}(t_0, t_0) = 1$ and therefore an exact integral representation of the time-evolution operator is

$$\hat{\mathscr{U}}(t,t_0) = 1 + \frac{1}{i\hbar} \int_{t_0}^t \mathrm{d}t' \ \hat{H}(t') \hat{\mathscr{U}}(t',t_0).$$
(C.16)

Above I assumed that it was the state vectors which evolve in time whilst the operators representing observables remain fixed. This is one of several equivalent 'dynamical pictures' which one can adopt in QM, and is known as the Schrödinger picture. The opposite approach, so to speak, is the Heisenberg picture, in which all of the time dependence is associated with the operators. It is easy to see the equivalence between these two descriptions. The expectation value of the observable A is (C.12)

$$\langle A \rangle (t) = \langle \Psi(t) | A | \Psi(t) \rangle = \langle \Psi(t_0) | \hat{\mathscr{U}}^{\dagger}(t, t_0) A \hat{\mathscr{U}}(t, t_0) | \Psi(t_0) \rangle,$$

which suggests we define the Heisenberg-picture operators and states via

$$A_H(t) \equiv \hat{\mathscr{U}}^{\dagger}(t, t_0) A_S \hat{\mathscr{U}}(t, t_0), \quad |\Psi_H\rangle \equiv |\Psi_S(t_0)\rangle, \qquad (C.17)$$

where a subscript H(S) denotes an object in the Heisenberg (Schrödinger) picture. (From now on I will drop the 'hats' from operators for the most part, unless extra clarity is required.) This is equivalent to applying a unitary transformation (see Eq. (C.26)) $\hat{U} = \hat{\mathscr{U}}^{\dagger}(t, t_0)$. The equation of motion is no longer the Schrödinger equation (C.13) but the Heisenberg equation

$$\frac{\mathrm{d}}{\mathrm{d}t}A_H(t) = \frac{i}{\hbar}[H_H(t), A_H(t)] + \hat{\mathscr{U}}^{\dagger} \frac{\partial A_S}{\partial t} \hat{\mathscr{U}}.$$
(C.18)

 $H_H(t) \equiv \hat{\mathscr{U}}^{\dagger}(t, t_0) H_S \hat{\mathscr{U}}(t, t_0)$ is the Heisenberg-picture Hamiltonian, which only differs from H_S when it depends explicitly on time, and the final term is only present if the Schrödingerpicture operator A_S contains an explicit time dependence.

I do not use the Heisenberg picture in this Thesis but I do use another alternative to the Schrödinger picture, called the Dirac or interaction picture. Suppose we have a Hamiltonian (in the Schrödinger picture) of the form

$$H_S(t) = H_0 + V(t),$$
 (C.19)

where V(t) is some interaction term of interest to us which may depend explicitly on time. If we want to focus solely on the dynamics due to V, rather than the full Hamiltonian, we can achieve this via a unitary transformation, $|\Psi_I(t)\rangle = U |\Psi_S(t)\rangle$, where a subscript I indicates an object in the interaction picture. The resulting dynamics are then 'in the interaction picture'. The correct unitary transformation is found to be $U = \hat{\mathscr{U}}_0^{\dagger}(t, t_0)$ where $\hat{\mathscr{U}}_0$ is the time-evolution operator associated with 'free evolution' under the Hamiltonian H_0 (see Eq. (C.15)),

$$i\hbar \frac{\partial}{\partial t} \hat{\mathscr{U}}_0(t, t_0) = H_0(t) \hat{\mathscr{U}}_0(t, t_0).$$
(C.20)

I will always assume H_0 is time-independent so we have [171]

$$\hat{\mathscr{U}}_{0}(t,t_{0}) = e^{-iH_{0}t/\hbar} \tag{C.21}$$

and thus

$$U = \hat{\mathscr{U}}_{0}^{\dagger}(t, t_{0}) = e^{+iH_{0}t/\hbar}.$$
 (C.22)

We may choose the interaction and Schrödinger pictures to have the same initial state, $|\Psi_S(t_0)\rangle = |\Psi_I(t_0)\rangle = |\Psi(t_0)\rangle$, so we can write

$$|\Psi_I(t)\rangle \equiv \hat{\mathscr{U}}_I(t,t_0) |\Psi(t_0)\rangle, \quad |\Psi_S(t)\rangle \equiv \hat{\mathscr{U}}_S(t,t_0) |\Psi(t_0)\rangle,$$

and by definition

$$\hat{\mathscr{U}}_{I}(t,t_{0}) \equiv U\hat{\mathscr{U}}_{S}(t,t_{0}) \equiv \hat{\mathscr{U}}_{0}^{\dagger}(t,t_{0})\hat{\mathscr{U}}_{S}(t,t_{0})$$
(C.23)

is the interaction-picture time-evolution operator. It is then easily shown by differentiation of $\hat{\mathscr{U}}_{I}$ (see also Eq. (C.28)) that the dynamics of the state $|\Psi_{I}\rangle$ are governed by the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\Psi_I(t)\rangle = V_I(t) |\Psi_I(t)\rangle, \qquad (C.24)$$

where $V_I(t) \equiv \hat{\mathscr{U}}_0^{\dagger}(t, t_0) V(t) \hat{\mathscr{U}}_0(t, t_0)$ is the interaction term V in the interaction picture. Generally if A_S is the operator representing an observable in the Schrödinger picture then the equivalent operator in the interaction picture is, from (C.29),

$$A_{I}(t) = UA_{S}U^{\dagger} = \hat{\mathscr{U}}_{0}^{\dagger}(t, t_{0})A_{S}\hat{\mathscr{U}}_{0}(t, t_{0}), \qquad (C.25)$$

The separation of the Hamiltonian into the form $H_0 + V$ is not unique and it is possible to transform to different 'interaction pictures' depending on how we partition H.

C.3 Spacetime Symmetries

In this Section I discuss how spacetime transformations and symmetries are incorporated into quantum mechanics (QM). I follow Messiah [70, Ch. XV], Jordan [71, Ch. 7], and Gibson and Pollard [76, Ch. 2].

A theorem due to Wigner [71, 187] tells us that the only transformations of states and operators which leave observable quantities in QM unchanged are of the form

$$|\psi\rangle \to |\psi'\rangle = \hat{U} |\psi\rangle,$$
 (C.26a)

$$\hat{A} \to \hat{A}' = \hat{U}\hat{A}\hat{U}^{\dagger},$$
 (C.26b)

where \hat{U} must be either unitary or anti-unitary (see definitions (C.8) and (C.10)). Time reversal is a well-known transformation with an associated anti-unitary operator but most other physical transformations are associated with unitary operators and I will only consider these.

Whilst the transformations (C.26) always leave expectation values unchanged the Schrödinger equation is not form-invariant to such transformations, in general. Taking the time derivative of $|\Psi'(t)\rangle = \hat{U} |\Psi(t)\rangle$, \hat{U} unitary, we have

$$i\hbar\frac{\partial}{\partial t}\left|\Psi'(t)\right\rangle = \left(i\hbar\hat{U}\hat{U}^{\dagger} + \hat{U}\hat{H}\hat{U}^{\dagger}\right)\left|\Psi'(t)\right\rangle,\tag{C.27}$$

i.e., the dynamics of the transformed state are not governed by the Hamiltonian $\hat{U}\hat{H}\hat{U}^{\dagger}$ but by the Hamiltonian

$$\hat{H}' = i\hbar\hat{U}\hat{U}^{\dagger} + \hat{U}\hat{H}\hat{U}^{\dagger}.$$
(C.28)

Clearly if \hat{U} is time independent then we do have $\hat{H}' = \hat{U}\hat{H}\hat{U}^{\dagger}$; I will assume this to be the

case for the remainder of this Section.

These results concern transformations in Hilbert space; I am interested in physical transformations of a system. If $|\psi\rangle$ is the state of a system, let us denote by $|\psi'\rangle \equiv \mathcal{T}[\psi]$ the state which results from some physical transformation \mathcal{T} of the system. Similarly, for an operator \hat{A} denote by $\hat{A}' \equiv \mathcal{T}[\hat{A}]$ the equivalent operator of the transformed system. Wigner's theorem tells us that $\mathcal{T}[\cdot]$ must take the form given in Eq. (C.26), or else norms will not be preserved. Thus we write

$$|\psi'\rangle = \hat{U}_{\mathcal{T}} |\psi\rangle, \quad \hat{A}' = \hat{U}_{\mathcal{T}} \hat{A} \hat{U}_{\mathcal{T}}^{\dagger}, \tag{C.29}$$

where $\hat{U}_{\mathcal{T}}$ is the unitary transformation corresponding to the physical transformation \mathcal{T} . It is a mathematical fact, just discussed, that this transformation will leave the measurable attributes of the system unchanged. To paraphrase Messiah [70], transforming both the states and operators of the system in this way is equivalent to making the same physical transformation to both the apparatus used to prepare the system and the apparatus used to measure the system. This kind of invariance is universal and physically does not tell us anything particularly interesting about a system. More interesting is the following situation: suppose that instead of transforming the states and operators of a system, we only transform the states (or vice versa). This corresponds to physically transforming the preparation but not the measurement apparatus (or vice versa). Then the expectation value of a measurement of the observable A, with the transformed states, is

$$\langle \psi' | \hat{A} | \psi' \rangle = \langle \psi | \hat{U}_{\mathcal{T}}^{\dagger} \hat{A} \hat{U}_{\mathcal{T}} | \psi \rangle.$$

Clearly this only equals $\langle \psi | \hat{A} | \psi \rangle$ if

$$\hat{U}_{\mathcal{T}}^{\dagger}\hat{A}\hat{U}_{\mathcal{T}}=\hat{A}.$$

Introducing the commutator,

$$[A,B] = AB - BA, (C.30)$$

the above condition is equivalent to the statement that \hat{A} and $\hat{U}_{\mathcal{T}}$ commute, i.e.,

$$[\hat{A}, \hat{U}_{\mathcal{T}}] = 0. \tag{C.31}$$

Physically this is a very important result. It tells us that when the operator representing the observable A commutes with the operator representing the physical transformation \mathcal{T} , the observable is invariant under that transformation. As always the Hamiltonian represents a special case. If

$$[\hat{H}, \hat{U}_{\mathcal{T}}] = 0 \tag{C.32}$$

we call \mathcal{T} (or $\hat{U}_{\mathcal{T}}$) a symmetry transformation of the system [76]. This also implies [70]

$$[\hat{\mathscr{U}}, \hat{U}_{\mathcal{T}}] = 0, \tag{C.33}$$

where $\hat{\mathscr{U}}$ is the time-evolution operator of the system (see the discussion in appendix C.2). It follows from these conditions that under a symmetry transformation \mathcal{T} the energy spectrum and dynamics of the system are unchanged.

An important class of symmetry transformations are the spacetime (or geometric) transformations. These include spatial and temporal translations, rotations, etc. As an example consider a stationary hydrogen atom, well isolated from any external fields, and translate it through space by some amount \boldsymbol{a} . All else being the same we expect the energy of the system to be unchanged, i.e., we expect this to be a symmetry transformation. Under this change the centre-of-mass and relative position vectors transform as $\boldsymbol{R} \to \boldsymbol{R} + \boldsymbol{a}$ and $\boldsymbol{r} \to \boldsymbol{r}$, respectively. The energy of a stationary hydrogen atom in the absence of external fields does not depend on \boldsymbol{R} , so this transformation does leave the energy unchanged. What is the unitary operator, $\hat{T}(\boldsymbol{a})$ say, related to this physical transformation? We have (suppressing the relative position, as it is unchanged)

$$\psi'(\mathbf{R}) = \hat{T}(\mathbf{a})\psi(\mathbf{R}) = \psi(\mathbf{R} - \mathbf{a}).$$
(C.34)

Noticing that the right-hand-side has the same Taylor series as $e^{-a \cdot \nabla}$ leads to the correct operator [71, 76]

$$\hat{T}(\boldsymbol{a}) = e^{-i\boldsymbol{a}\cdot\hat{\boldsymbol{P}}/\hbar},\tag{C.35}$$

where $\hat{\boldsymbol{P}} = (\hbar/i)\nabla$ is the momentum operator of the atomic centre-of-mass. It can be shown that all unitary transformations which depend on a continuous real parameter s are of the form [71, §15]

$$\hat{U}(s) = e^{is\hat{A}},\tag{C.36}$$

where \hat{A} is a unique Hermitian operator. If $[\hat{H}, \hat{U}(s)] = 0$, \hat{A} is called the *generator* of the symmetry transformation $\hat{U}(s)$. Therefore, from (C.35), linear momentum is the generator of spatial translations. Also, if $[\hat{H}, \hat{U}(s)] = 0$ it follows that $[\hat{H}, \hat{A}] = 0 = [\hat{\mathscr{U}}, \hat{A}]$ (from the definitions of $\hat{U}(s)$ and $\hat{\mathscr{U}}$), which implies

$$\langle \Psi(t)|\hat{A}|\Psi(t)\rangle = \langle \Psi(0)|\hat{\mathscr{U}}^{\dagger}(t,0)\hat{A}\hat{\mathscr{U}}(t,0)|\Psi(0)\rangle = \langle \Psi(0)|\hat{A}|\Psi(0)\rangle.$$
(C.37)

Thus if the operator \hat{A} is the generator of a symmetry transformation its expectation value does not change in time and we call A a constant of motion. This is the well-known connec-

tion between symmetries and conservation laws in quantum mechanics.

In the above discussion I have chosen the *active* interpretation of transformations, in which we really imagine transforming the physical system in some way. Alternatively, one could adopt the *passive* viewpoint [70, 76], in which it is not the physical system which is transformed, but our chosen frame of reference.

APPENDIX D

Derivations

D.1 Optical Angular Momentum Derivations

D.1.1 Derivation of Eq. (2.17)

We start from the exact expression (2.16),

$$\boldsymbol{J} = \varepsilon_0 \int_V \mathrm{d}^3 r \left[E_i (\boldsymbol{r} \times \nabla) A_i^{\perp} + \boldsymbol{E} \times \boldsymbol{A}_{\perp} - (\boldsymbol{E} \cdot \nabla) (\boldsymbol{r} \times \boldsymbol{A}_{\perp}) \right].$$
(D.1)

We simplify the third term. Say $\boldsymbol{r} \times \boldsymbol{A}_{\perp} = f_x \hat{\mathbf{x}} + f_y \hat{\mathbf{y}} + f_z \hat{\mathbf{z}}$, then

$$\int d^3 r \, (\boldsymbol{E} \cdot \nabla) (\boldsymbol{r} \times \boldsymbol{A}_{\perp}) = \sum_i \hat{\mathbf{x}}_i \int d^3 r \, E_j \partial_j f_i. \tag{D.2}$$

Using integration by parts we have

$$\int_{a}^{b} E_{j} \partial_{j} f_{i} \,\mathrm{d}x_{j} = \left[E_{j} f_{i}\right]_{a}^{b} - \int_{a}^{b} f_{i} \partial_{j} E_{j} \,\mathrm{d}x_{j}.$$
 (D.3)

Assuming the fields vanish at the boundaries of the volume, this leads to

$$\int d^3 r \, \boldsymbol{E} \cdot \nabla f_i = -\int d^3 r \, f_i (\nabla \cdot \boldsymbol{E}). \tag{D.4}$$

Hence

$$\int d^3 r \left(\boldsymbol{E} \cdot \nabla \right) \left(\boldsymbol{r} \times \boldsymbol{A}_{\perp} \right) = -\int d^3 r \left(\boldsymbol{r} \times \boldsymbol{A}_{\perp} \right) \left(\nabla \cdot \boldsymbol{E} \right), \tag{D.5}$$

and the angular momentum becomes

$$\boldsymbol{J} = \varepsilon_0 \int_V \mathrm{d}^3 r \bigg[E_i (\boldsymbol{r} \times \nabla) A_i^{\perp} + \boldsymbol{E} \times \boldsymbol{A}_{\perp} + (\boldsymbol{r} \times \boldsymbol{A}_{\perp}) (\nabla \cdot \boldsymbol{E}) \bigg], \qquad (\mathrm{D.6})$$

which is (2.17), as desired.

D.1.2 Derivation of Eq. (2.21)

We start from (2.20b),

$$\boldsymbol{J}_{\text{long}} = \varepsilon_0 \int_V \mathrm{d}^3 r \left[E_i^{\parallel}(\boldsymbol{r} \times \nabla) A_i^{\perp} + \boldsymbol{E}_{\parallel} \times \boldsymbol{A}_{\perp} + (\boldsymbol{r} \times \boldsymbol{A}_{\perp}) (\nabla \cdot \boldsymbol{E}_{\parallel}) \right].$$

The longitudinal electric field satisfies $\nabla \cdot \mathbf{E}_{\parallel} = \eta/\varepsilon_0$, and can be written as $\mathbf{E}_{\parallel} = -\nabla \phi_C$, where ϕ_C is the Coulomb potential (note that this does not require us to be using the Coulomb gauge) [20]. In terms of ϕ_C and η we can write

$$\boldsymbol{J}_{\text{long}} = -\varepsilon_0 \int_V \mathrm{d}^3 r \, \left[(\partial_i \phi_C) (\boldsymbol{r} \times \nabla) A_i^{\perp} + (\nabla \phi_C) \times \boldsymbol{A}_{\perp} \right] + \int_V \mathrm{d}^3 r \, \eta (\boldsymbol{r} \times \boldsymbol{A}_{\perp}). \tag{D.7}$$

Using integration by parts, in a similar manner to the previous derivation above, we find (under the usual assumptions)

$$\int_{V} \mathrm{d}^{3} r \, (\partial_{i} \phi_{C})(\boldsymbol{r} \times \nabla) A_{i}^{\perp} = -\int_{V} \mathrm{d}^{3} r \, \phi_{C} \partial_{i}(\boldsymbol{r} \times \nabla) A_{i}^{\perp} \tag{D.8}$$

and

$$\int_{V} \mathrm{d}^{3} r \, (\nabla \phi_{C}) \times \boldsymbol{A}_{\perp} = - \int_{V} \mathrm{d}^{3} r \, \phi_{C} (\nabla \times \boldsymbol{A}_{\perp}). \tag{D.9}$$

It is easily shown, by writing everything in index notation, that

$$\phi_C \partial_i (\boldsymbol{r} \times \nabla) A_i^{\perp} = \phi_C (\boldsymbol{r} \times \nabla) (\nabla \cdot \boldsymbol{A}_{\perp}) - \phi_C (\nabla \times \boldsymbol{A}_{\perp}).$$
(D.10)

We have $\nabla \cdot \mathbf{A}_{\perp} \equiv 0$, and thus the first integral in (D.7) is identically zero, which leaves

$$\boldsymbol{J}_{\text{long}} = \int_{V} \mathrm{d}^{3} r \ \eta(\boldsymbol{r} \times \boldsymbol{A}_{\perp}). \tag{D.11}$$

This is (2.21), as required.

D.1.3 Derivation of Eq. (2.70)

Starting from the usual form for the SAM,

$$\boldsymbol{S} = \varepsilon_0 \int_V \mathrm{d}^3 r \, \boldsymbol{E}_\perp imes \boldsymbol{A}_\perp,$$

we want to write this in the from (2.70) [69],

$$\boldsymbol{S} = \varepsilon_0 c^2 \int_V \mathrm{d}^3 r \, \boldsymbol{B} \times \boldsymbol{C}_\perp.$$

Using $\boldsymbol{E}_{\perp} = -c^2 \nabla \times \boldsymbol{C}_{\perp}$, we can write

$$\boldsymbol{S} = \varepsilon_0 c^2 \int_V \mathrm{d}^3 r \, \boldsymbol{A}_\perp \times (\nabla \times \boldsymbol{C}_\perp). \tag{D.12}$$

This can be written, using index notation for the cross product, as

$$\boldsymbol{S} = \varepsilon_0 c^2 \int_V \mathrm{d}^3 r \left[A_j^{\perp} \nabla C_j^{\perp} - (\boldsymbol{A}_{\perp} \cdot \nabla) \boldsymbol{C}_{\perp} \right].$$
(D.13)

Using integration by parts we have (under the usual assumptions, as above)

$$-\int_{V} \mathrm{d}^{3} r \left(\boldsymbol{A}_{\perp} \cdot \nabla\right) \boldsymbol{C}_{\perp} = \int_{V} \mathrm{d}^{3} r \, \boldsymbol{C}_{\perp} (\nabla \cdot \boldsymbol{A}_{\perp}), \qquad (\mathrm{D.14})$$

and

$$\int_{V} \mathrm{d}^{3}r \, A_{j}^{\perp} \nabla C_{j}^{\perp} = -\int_{V} \mathrm{d}^{3}r \, C_{j}^{\perp} \nabla A_{j}^{\perp}. \tag{D.15}$$

As $\nabla \cdot \boldsymbol{A}_{\perp} = 0$, we have

$$\boldsymbol{S} = -\varepsilon_0 c^2 \int_V \mathrm{d}^3 r \, C_j^{\perp} \nabla A_j^{\perp}. \tag{D.16}$$

We can show, again making use of index notation, that

$$-C_{j}^{\perp}\nabla A_{j}^{\perp} = (\nabla \times \boldsymbol{A}_{\perp}) \times \boldsymbol{C}_{\perp} - (\boldsymbol{C}_{\perp} \cdot \nabla)\boldsymbol{A}_{\perp}.$$
 (D.17)

But $\boldsymbol{B} \equiv \nabla \times \boldsymbol{A}_{\perp}$, so we have

$$\boldsymbol{S} = \varepsilon_0 c^2 \int_V \mathrm{d}^3 r \left[\boldsymbol{B} \times \boldsymbol{C}_\perp - (\boldsymbol{C}_\perp \cdot \nabla) \boldsymbol{A}_\perp \right]. \tag{D.18}$$

Again using integration by parts on the second term in the integrand we have

$$-\int_{V} \mathrm{d}^{3} r \left(\boldsymbol{C}_{\perp} \cdot \nabla \right) \boldsymbol{A}_{\perp} = \int_{V} \mathrm{d}^{3} r \, \boldsymbol{A}_{\perp} (\nabla \cdot \boldsymbol{C}_{\perp}). \tag{D.19}$$

With $\nabla \cdot \boldsymbol{C}_{\perp} = 0$, we finally have

$$\boldsymbol{S} = \varepsilon_0 c^2 \int_V \mathrm{d}^3 r \, \boldsymbol{B} \times \boldsymbol{C}_\perp,\tag{D.20}$$

as required.

D.2 Classical Electric-Dipole Force on an Atom

Here I derive Eq. (2.112) for the time-averaged classical force due to a monochromatic field on an atom/molecule in the electric-dipole (ED) approximation [15, 90, 93, 105, 106],

$$\overline{\boldsymbol{F}_{\text{ED}}} = \frac{1}{2\varepsilon_0} \operatorname{Re}\{\tilde{\alpha}\} \nabla \overline{w_e} + \frac{\omega}{\varepsilon_0} \operatorname{Im}\{\tilde{\alpha}\} \left[\overline{\mathbf{g}} - \frac{1}{2} \nabla \times \boldsymbol{s}_e \right].$$

We start from the Lorentz force law (B.13),

$$\boldsymbol{F} = \int \mathrm{d}^3 r \left[\rho \boldsymbol{E} + \boldsymbol{j} \times \boldsymbol{B} \right], \qquad (D.21)$$

now with microscopic charge and current densities, which are given by (B.9) and (B.10). We can write this as the sum of two terms: $\mathbf{F}^{(E)} + \mathbf{F}^{(B)}$, which are the contributions from the electric and magnetic fields respectively. In the ED approximation, and assuming a neutral atom/molecule, the charge density becomes (see Eq. (B.29)),

$$\rho \approx -\mu_i \partial_i \delta(\boldsymbol{r} - \boldsymbol{R}),$$
(D.22)

where μ_i is the *i*th component of the electric dipole moment (B.22) of the molecule, and **R** is its centre-of-mass. Using the derivative of the delta function property (A.3), we find

$$\boldsymbol{F}^{(E)} = \int \mathrm{d}^3 r \ \rho \boldsymbol{E} = (\boldsymbol{\mu} \cdot \nabla) \boldsymbol{E}(\boldsymbol{R}). \tag{D.23}$$

(Now formally integrating over all space.)

In the ED approximation $\mathbf{j} = \mathbf{\dot{p}}$, where \mathbf{p} is the microscopic polarization field of the molecule (see Eqs. (B.37) and (B.40)). From (B.38) we have $\mathbf{p} \approx \mu \delta(\mathbf{r} - \mathbf{R})$, so

$$\boldsymbol{j} \approx \boldsymbol{\mu} \delta(\boldsymbol{r} - \boldsymbol{R}).$$
 (D.24)

(I am neglecting centre-of-mass motions, i.e., the Röntgen term [18].) The magnetic force is thus

$$\boldsymbol{F}^{(B)} = \int \mathrm{d}^3 r \; \boldsymbol{j} \times \boldsymbol{B} = \dot{\boldsymbol{\mu}} \times \boldsymbol{B}(\boldsymbol{R}). \tag{D.25}$$

Now we assume a monochromatic optical field, and write the electric and magnetic fields in the form $\mathbf{F} = \text{Re}\{\tilde{\mathbf{F}}e^{-i\omega t}\}$. The electric dipole moment is induced by the oscillating fields and thus we also write $\boldsymbol{\mu} = \text{Re}\{\tilde{\boldsymbol{\mu}}e^{-i\omega t}\}$ [24]. The time-averaged electric force is therefore

$$\overline{\boldsymbol{F}^{(E)}} = \frac{1}{4} \bigg[(\tilde{\boldsymbol{\mu}} \cdot \nabla) \tilde{\boldsymbol{E}}^* + \text{c.c.} \bigg], \qquad (D.26)$$

c.c. meaning complex conjugate. Similarly we find the time-averaged magnetic force

$$\overline{\boldsymbol{F}^{(B)}} = \frac{i\omega}{4} \bigg[\tilde{\boldsymbol{\mu}}^* \times \tilde{\boldsymbol{B}} - \text{c.c.} \bigg].$$
(D.27)

We shall assume an isotropic molecular response to the optical field, with the induced electric dipole given by $\tilde{\mu} = \tilde{\alpha} \tilde{E}$, $\tilde{\alpha}$ being the complex scalar electric polarizability. Some simple manipulation and use of Maxwell's equations then leads to

$$\overline{\boldsymbol{F}_{ED}} = \overline{\boldsymbol{F}^{(E)}} + \overline{\boldsymbol{F}^{(B)}} = \frac{1}{4} \operatorname{Re}\{\tilde{\alpha}\} \nabla |\tilde{\boldsymbol{E}}|^2 + \frac{\omega}{2} \operatorname{Im}\{\tilde{\alpha}\} \left[\operatorname{Re}\{\tilde{\boldsymbol{E}} \times \tilde{\boldsymbol{B}}^*\} - \frac{1}{2\omega} \nabla \times \operatorname{Im}\{\tilde{\boldsymbol{E}}^* \times \tilde{\boldsymbol{E}}\} \right], \quad (D.28)$$

which is easily written in terms of the desired optical properties to give (2.112). Higher-order forces are easily derived by considering other molecular responses (i.e., different to $\tilde{\mu} = \tilde{\alpha} \tilde{E}$) and higher-order multipole moments in ρ and j.

D.3 Atomic Helicity Derivation

Here I present the detailed derivation of the atomic helicity in the two-wave grating, Eq. (5.61).

The optical field is defined by (2.80). The components of the electric field in the CP basis are

$$\mathcal{E}_a = \mathcal{E}_R = \frac{a}{\sqrt{2}} (e^{if_2} + ie^{if_1}), \qquad (D.29a)$$

$$\mathcal{E}_b = \mathcal{E}_z = 0, \tag{D.29b}$$

$$\mathcal{E}_c = \mathcal{E}_L = \frac{a}{\sqrt{2}} (e^{if_2} - ie^{if_1}), \qquad (D.29c)$$

where I've defined

$$f_1 \equiv \boldsymbol{k}_1 \cdot \boldsymbol{r} = k_0 z, \tag{D.30a}$$

$$f_2 \equiv \mathbf{k}_2 \cdot \mathbf{r} = k_0 \cos 2\theta z - k_0 \sin 2\theta y. \tag{D.30b}$$

Clearly any spatial dependence is going to depend upon the phase difference $f_1 - f_2$. This is equal to

$$f_1 - f_2 = 2k_0 \sin \theta y', \tag{D.31}$$

where $y' = \cos \theta y + \sin \theta z$. For later calculations it is convenient to write $f_1 - f_2 = \beta_1 y + \beta_2 z$, where $\beta_1 \equiv 2k_0 \sin \theta \cos \theta$, $\beta_2 \equiv 2k_0 \sin^2 \theta$.

We wish to calculate the atomic helicity using (5.49), which involves six integrals of the form $\langle \psi_m | P_j | \psi_n \rangle$ (recall (5.50)). These can be further broken down into two integrals each. I shall define $\langle \psi_m | P_j | \psi_n \rangle = f_j^{mn} + g_j^{mn}$, where

$$f_j^{mn} = \frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}^3 r \ \mathcal{E}_m^*(\boldsymbol{r}) \mathcal{E}_n(\boldsymbol{r}) \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial x_j} \psi_0(\boldsymbol{r}), \tag{D.32a}$$

$$g_j^{mn} = \frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}^3 r \ |\psi_0(\boldsymbol{r})|^2 \mathcal{E}_m^*(\boldsymbol{r}) \frac{\partial}{\partial x_j} \mathcal{E}_n(\boldsymbol{r}).$$
(D.32b)

We could have as many as 12 integrals to evaluate then. However, as $\mathcal{E}_b = 0$, this reduces to 4. The ones we are left with are f_z^{cc} , f_z^{aa} , g_z^{cc} , g_z^{aa} .

Let's note that the f_z functions, which depend on $|\mathcal{E}_{a/c}(\mathbf{r})|^2$, are either pure imaginary (due

to the factor of 1/i at the front and everything in the integrand being real) or identically zero. Now $\langle \psi_m | P_z | \psi_m \rangle$ must be real, because it is the expectation value of a Hermitian operator. Therefore, unless f_z^{mm} is identically zero, it must be exactly cancelled by an imaginary part from g_z^{mm} . Therefore it makes more sense to work out the g terms first, and if they contain an imaginary term we know this will be cancelled by the f terms.

Let's consider g_z^{cc} first. This is defined as

$$\frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ |\psi_0(\boldsymbol{r})|^2 \mathcal{E}_c^*(\boldsymbol{r}) \frac{\partial}{\partial z} \mathcal{E}_c(\boldsymbol{r}). \tag{D.33}$$

We have

$$\frac{\partial}{\partial z} \mathcal{E}_c(\mathbf{r}) = \frac{ak_0}{\sqrt{2}} (i\cos 2\theta e^{if_2} + e^{if_1}), \qquad (D.34)$$

and therefore

$$\mathcal{E}_{c}^{*}(\boldsymbol{r})\frac{\partial}{\partial z}\mathcal{E}_{c}(\boldsymbol{r}) = i\frac{|a|^{2}k_{0}}{2}(\cos 2\theta + 1) + \frac{|a|^{2}k_{0}}{2}(e^{i(f_{1} - f_{2})} - \cos 2\theta e^{-i(f_{1} - f_{2})}).$$
(D.35)

Therefore

$$g_{z}^{cc} = \frac{|a|^{2}\hbar k_{0}}{2} \left[(\cos 2\theta + 1) \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ |\psi_{0}(\boldsymbol{r})|^{2} + \frac{1}{i} \left(\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ |\psi_{0}(\boldsymbol{r})|^{2} e^{i(f_{1} - f_{2})} - \cos 2\theta \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ |\psi_{0}(\boldsymbol{r})|^{2} e^{-i(f_{1} - f_{2})} \right) \right]. \quad (D.36)$$

Recalling that ψ_0 is normalised the first term is very simple, and the only integral we need to consider is

$$I_a = \int_{-\infty}^{\infty} \mathrm{d}oldsymbol{r} \; |\psi_0(oldsymbol{r})|^2 e^{i(f_1 - f_2)}$$

because

$$\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \, |\psi_0(\boldsymbol{r})|^2 e^{-i(f_1 - f_2)} = \left(\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \, |\psi_0(\boldsymbol{r})|^2 e^{i(f_1 - f_2)}\right)^*. \tag{D.37}$$

Written in terms of $\mathbf{u} \equiv \boldsymbol{r} - \boldsymbol{R}_0$ the integral is

$$I_a = N^2 e^{i(\beta_1 Y_0 + \beta_2 Z_0)} \int_{-\infty}^{\infty} \mathrm{d}u_x \ e^{-u_x^2/\sigma^2} \int_{-\infty}^{\infty} \mathrm{d}u_y \ e^{i\beta_1 u_y} e^{-u_y^2/\sigma^2} \int_{-\infty}^{\infty} \mathrm{d}u_z \ e^{i\beta_2 u_z} e^{-u_z^2/\sigma^2}.$$
 (D.38)

(N is the normalization prefactor for ψ_0 , as in (5.51).)

These are simple standard integrals [64]. Firstly,

$$\int_{-\infty}^{\infty} \mathrm{d}u \ e^{-au^2} = \pi^{1/2} a^{-1/2},\tag{D.39}$$

so for $a = 1/\sigma^2$ we have

$$\int_{-\infty}^{\infty} du_x \ e^{-u_x^2/\sigma^2} = \pi^{1/2} \sigma.$$
 (D.40)

Secondly,

$$\int_{-\infty}^{\infty} \mathrm{d}u \ e^{-au^2 - bu} = \pi^{1/2} a^{-1/2} e^{b^2/4a}.$$
 (D.41)

Again $a = 1/\sigma^2$ and $-b = i\beta_1$ or $i\beta_2$. So

$$\int_{-\infty}^{\infty} \mathrm{d}u_y \ e^{i\beta_1 u_y} e^{-u_y^2/\sigma^2} = \pi^{1/2} \sigma e^{-\beta_1^2 \sigma^2/4}, \tag{D.42}$$

and

$$\int_{-\infty}^{\infty} \mathrm{d}u_z \ e^{i\beta_2 u_z} e^{-u_z^2/\sigma^2} = \pi^{1/2} \sigma e^{-\beta_2^2 \sigma^2/4}.$$
 (D.43)

Combining everything we find

$$I_a = e^{i(\beta_1 Y_0 + \beta_2 Z_0)} e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4}$$
(D.44)

where I have used $N^2 \pi^{3/2} \sigma^3 = 1$ (definition of N). Therefore

$$I_a^* = e^{-i(\beta_1 Y_0 + \beta_2 Z_0)} e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4}.$$
 (D.45)

We have

$$I_a - \cos 2\theta I_a^* = e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4} \left((1 - \cos 2\theta) \cos(\beta_1 Y_0 + \beta_2 Z_0) + i(1 + \cos 2\theta) \sin(\beta_1 Y_0 + \beta_2 Z_0) \right).$$
(D.46)

Bringing everything together we have

$$g_z^{cc} = \frac{|a|^2 \hbar k_0}{2} (\cos 2\theta + 1) \left(1 + e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4} \sin(\beta_1 Y_0 + \beta_2 Z_0) \right) \\ + \frac{1}{i} \frac{|a|^2 \hbar k_0}{2} (1 - \cos 2\theta) e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4} \cos(\beta_1 Y_0 + \beta_2 Z_0). \quad (D.47)$$

From the discussion above, it must be the case that f_z^{cc} will exactly cancel the imaginary

term in g_z^{cc} , so we would have

$$\langle \psi_c | P_z | \psi_c \rangle = f_z^{cc} + g_z^{cc} = \frac{|a|^2 \hbar k_0}{2} (\cos 2\theta + 1) \left(1 + e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4} \sin(\beta_1 Y_0 + \beta_2 Z_0) \right). \quad (D.48)$$

Let's verify that f_z^{cc} does indeed cancel the imaginary term. This is defined as

$$f_z^{cc} = \frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ |\mathcal{E}_c(\boldsymbol{r})|^2 \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial z} \psi_0(\boldsymbol{r}). \tag{D.49}$$

 $|\mathcal{E}_c|^2 = |a|^2 (1 + \sin(\beta_1 y + \beta_2 z))$, so

$$f_z^{cc} = \frac{\hbar}{i} |a|^2 \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial z} \psi_0(\boldsymbol{r}) + \frac{\hbar}{i} |a|^2 \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ \sin(\beta_1 y + \beta_2 z) \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial z} \psi_0(\boldsymbol{r}).$$
(D.50)

The first integral is identically zero:

$$\int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial z} \psi_0(\boldsymbol{r})$$
$$= N^2 \int_{-\infty}^{\infty} \mathrm{d}u_x \ e^{-u_x^2/\sigma^2} \int_{-\infty}^{\infty} \mathrm{d}u_y \ e^{-u_y^2/\sigma^2} \int_{-\infty}^{\infty} \mathrm{d}u_z \ e^{-u_z^2/2\sigma^2} \frac{\partial}{\partial u_z} e^{-u_z^2/2\sigma^2},$$

using the change of variables defined above and $\partial/\partial u_z = \partial/\partial z$. Now

$$\int_{-\infty}^{\infty} \mathrm{d}u_z \ e^{-u_z^2/2\sigma^2} \frac{\partial}{\partial u_z} e^{-u_z^2/2\sigma^2} = \frac{-1}{\sigma^2} \int_{-\infty}^{\infty} \mathrm{d}u_z \ u_z e^{-u_z^2/\sigma^2}$$

which equals zero because the integrand is an *odd* function of u_z and the integral is over an even interval. So

$$f_z^{cc} = \frac{\hbar}{i} |a|^2 \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \, \sin(\beta_1 y + \beta_2 z) \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial z} \psi_0(\boldsymbol{r}). \tag{D.51}$$

Let's evaluate this integral, call it I, say. Start by using the trigonometric identity [64]

$$\sin(x+y) = \sin(x)\cos(y) + \cos(x)\sin(y). \tag{D.52}$$

Then $I = I_1 + I_2$ where

$$I_1 = \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \, \sin(\beta_1 y) \cos(\beta_2 z) \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial z} \psi_0(\boldsymbol{r}) \tag{D.53}$$

and

$$I_2 = \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \, \cos(\beta_1 y) \sin(\beta_2 z) \psi_0^*(\boldsymbol{r}) \frac{\partial}{\partial z} \psi_0(\boldsymbol{r}). \tag{D.54}$$

Work out I_1 first. We can write it as

$$I_{1} = \frac{-N^{2}}{\sigma^{2}} \int_{-\infty}^{\infty} du_{x} \ e^{-u_{x}^{2}/\sigma^{2}} \int_{-\infty}^{\infty} du_{y} \ \sin(\beta_{1}u_{y} + \beta_{1}Y_{0})e^{-u_{y}^{2}/\sigma^{2}} \\ \times \int_{-\infty}^{\infty} du_{z} \ \cos(\beta_{2}u_{z} + \beta_{2}Z_{0})u_{z}e^{-u_{z}^{2}/\sigma^{2}}.$$
(D.55)

Again let's use the angle addition formulae, the one for cosine is

$$\cos(x+y) = \cos(x)\cos(y) - \sin(x)\sin(y).$$
(D.56)

So I_1 contains the integrals

$$I_{1}^{a} = \int_{-\infty}^{\infty} du_{y} \sin(\beta_{1}u_{y} + \beta_{1}Y_{0})e^{-u_{y}^{2}/\sigma^{2}}$$

$$= \cos(\beta_{1}Y_{0}) \int_{-\infty}^{\infty} du_{y} \sin(\beta_{1}u_{y})e^{-u_{y}^{2}/\sigma^{2}} + \sin(\beta_{1}Y_{0}) \int_{-\infty}^{\infty} du_{y} \cos(\beta_{1}u_{y})e^{-u_{y}^{2}/\sigma^{2}}$$
(D.57)

and

$$I_{1}^{b} = \int_{-\infty}^{\infty} \mathrm{d}u_{z} \, \cos(\beta_{2}u_{z} + \beta_{2}Z_{0})u_{z}e^{-u_{z}^{2}/\sigma^{2}}$$

$$= \cos(\beta_{2}Z_{0})\int_{-\infty}^{\infty} \mathrm{d}u_{z} \, \cos(\beta_{2}u_{z})u_{z}e^{-u_{z}^{2}/\sigma^{2}} - \sin(\beta_{2}Z_{0})\int_{-\infty}^{\infty} \mathrm{d}u_{z} \, \sin(\beta_{2}u_{z})u_{z}e^{-u_{z}^{2}/\sigma^{2}}$$

(D.58)

All the integrals with odd integrands (i.e., depending on $u \cos u$ or $\sin u$) are zero, so these reduce to

$$I_1^a = \sin(\beta_1 Y_0) \int_{-\infty}^{\infty} du_y \, \cos(\beta_1 u_y) e^{-u_y^2/\sigma^2}$$
(D.59)

and

$$I_1^b = -\sin(\beta_2 Z_0) \int_{-\infty}^{\infty} du_z \, \sin(\beta_2 u_z) u_z e^{-u_z^2/\sigma^2}.$$
 (D.60)

To evaluate I_1^b recall that we can write $\sin u = \text{Im}\{e^{iu}\}$, so we just need to evaluate

$$\int_{-\infty}^{\infty} \mathrm{d}u_z \ u_z e^{i\beta_2 u_z} e^{-u_z^2/\sigma^2},\tag{D.61}$$

which just has the form of a standard integral:

$$\int_{-\infty}^{\infty} du \ u e^{-au^2 - bu} = -\frac{\pi^{1/2}}{2} \frac{b}{a^{3/2}} e^{b^2/4a}.$$
 (D.62)

We have $-b = i\beta_2$, $a = 1/\sigma^2$, so

$$\int_{-\infty}^{\infty} \mathrm{d}u_z \ u_z e^{i\beta_2 u_z} e^{-u_z^2/\sigma^2} = \frac{i}{2} \pi^{1/2} \sigma^3 \beta_2 e^{-\beta_2^2 \sigma^2/4}.$$
 (D.63)

Therefore

$$I_1^b = -\frac{1}{2}\pi^{1/2}\sigma^3\beta_2 e^{-\beta_2^2\sigma^2/4}\sin(\beta_2 Z_0).$$
 (D.64)

Onto I_1^a . Similarly notice $\cos u = \operatorname{Re}\{u\}$, so the integral we need is

$$\int_{-\infty}^{\infty} \mathrm{d}u_y \ e^{i\beta_1 u_y} e^{-u_y^2/\sigma^2},\tag{D.65}$$

which is just a standard integral discussed earlier (D.41). Therefore

$$\int_{-\infty}^{\infty} \mathrm{d}u_y \ e^{i\beta_1 u_y} e^{-u_y^2/\sigma^2} = \pi^{1/2} \sigma e^{-\beta_1^2 \sigma^2/4}.$$
 (D.66)

Therefore

$$I_1^a = \pi^{1/2} \sigma e^{-\beta_1^2 \sigma^2/4} \sin(\beta_1 Y_0).$$
 (D.67)

Combining everything for I_1 we have

$$I_{1} = \frac{-N^{2}}{\sigma^{2}} \int_{-\infty}^{\infty} \mathrm{d}u_{x} \ e^{-u_{x}^{2}/\sigma^{2}} \times \left(\pi^{1/2} \sigma e^{-\beta_{1}^{2} \sigma^{2}/4} \sin(\beta_{1} Y_{0})\right) \\ \times \left(-\frac{1}{2} \pi^{1/2} \sigma^{3} \beta_{2} e^{-\beta_{2}^{2} \sigma^{2}/4} \sin(\beta_{2} Z_{0})\right) \quad (\mathrm{D.68})$$

which upon some tidying up gives

$$I_1 = \frac{1}{2}\beta_2 \sin(\beta_1 Y_0) \sin(\beta_2 Z_0) e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4}.$$
 (D.69)

 ${\cal I}_2$ can be evaluated in much the same way. We find

$$I_2 = -\frac{1}{2}\beta_2 \cos(\beta_1 Y_0) \cos(\beta_2 Z_0) e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4}.$$
 (D.70)

Then with $f_z^{cc} = (\hbar |a|^2/i)(I_1 + I_2)$ we find

$$f_z^{cc} = -\frac{1}{i} \frac{|a|^2 \hbar}{2} \beta_2 e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4} \cos(\beta_1 Y_0 + \beta_2 Z_0).$$
(D.71)

Recalling $\beta_2 = 2k_0 \sin^2 \theta = k_0(1 - \cos 2\theta)$ this becomes

$$f_z^{cc} = -\frac{1}{i} \frac{|a|^2 \hbar k_0}{2} (1 - \cos 2\theta) e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4} \cos(\beta_1 Y_0 + \beta_2 Z_0),$$
(D.72)

which exactly cancels the imaginary part of g_z^{cc} (D.47) as required.

We still need to find the other contributions from g_z^{aa} and f_z^{aa} . Again, we can find the g function and know that the final result will just be the real part of this.

By definition

$$g_z^{aa} = \frac{\hbar}{i} \int_{-\infty}^{\infty} \mathrm{d}\boldsymbol{r} \ |\psi_0|^2 \mathcal{E}_a^* \frac{\partial}{\partial z} \mathcal{E}_a. \tag{D.73}$$

We have

$$\frac{\partial}{\partial z} \mathcal{E}_a = \frac{ak_0}{\sqrt{2}} (i\cos 2\theta e^{if_2} - e^{if_1}), \tag{D.74}$$

 \mathbf{SO}

$$\mathcal{E}_{a}^{*}\frac{\partial}{\partial z}\mathcal{E}_{a} = i\frac{|a|^{2}k_{0}}{2}(\cos 2\theta + 1) + \frac{|a|^{2}k_{0}}{2}(\cos 2\theta e^{-i(f_{1} - f_{2})} - e^{i(f_{1} - f_{2})}).$$
(D.75)

Therefore

$$g_z^{aa} = \hbar k_0 |a|^2 \cos^2 \theta + \frac{1}{i} \frac{|a|^2 \hbar k_0}{2} \bigg(\cos 2\theta \int_{-\infty}^{\infty} |\psi_0|^2 e^{-i(f_1 - f_2)} - \int_{-\infty}^{\infty} |\psi_0|^2 e^{i(f_1 - f_2)} \bigg). \quad (D.76)$$

As in the previous calculation for g_z^{cc} we just have a single integral to evaluate, I_a ,

$$g_z^{aa} = \hbar k_0 |a|^2 \cos^2 \theta - \frac{1}{i} \frac{|a|^2 \hbar k_0}{2} (I_a - \cos 2\theta I_a^*).$$
(D.77)

We worked out $I_a - \cos 2\theta I_a^*$ earlier:

$$I_a - \cos 2\theta I_a^* = e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4} \left((1 - \cos 2\theta) \cos(\beta_1 Y_0 + \beta_2 Z_0) + i(1 + \cos 2\theta) \sin(\beta_1 Y_0 + \beta_2 Z_0) \right).$$
(D.78)

I won't bother showing it explicitly but as expected f_z^{aa} cancels the imaginary part of this. So we have

$$f_z^{aa} + g_z^{aa} = \hbar k_0 |a|^2 \cos^2 \theta - \frac{|a|^2 \hbar k_0}{2} (1 + \cos 2\theta) e^{-(\beta_1^2 + \beta_2^2)\sigma^2/4} \sin(\beta_1 Y_0 + \beta_2 Z_0).$$
(D.79)

Putting everything together according to (5.49) we can finally write down the atomic helicity formula for the atom placed in the helicity grating. The spatially-independent parts cancel and we get, using $\beta_1^2 + \beta_2^2 = 4k_0^2 \sin^2 \theta$,

$$\mathcal{H}_{\text{grating}}^{A} = \frac{t^{2} \mu^{2} |a|^{2} k_{0}}{2} \cos^{2} \theta \sin(2k_{0} \sin \theta Y_{0}') e^{-k_{0}^{2} \sigma^{2} \sin^{2} \theta}, \qquad (D.80)$$

which is (5.61) as required.

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