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### The Influence of Environments on Energy Transfer

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## Abstract

Energy transfer between atoms/molecules, one of the most basic interactions within atomic and molecular systems, is important in many diverse areas of science. The ability to control these processes is therefore a powerful tool with applications in various fields, and one method to achieve this influence is through the use of macroscopic bodies. Making use of the theoretical framework of macroscopic quantum electrodynamics (QED), the environment of a microscopic system can be introduced into the quantum description, and its influence on intermolecular energy transfer can be characterized. In this work, we explore the ways in which intermolecular interactions can be impacted by a macroscopic environment. We derive a general expression for the rate of resonant energy transfer (RET) between a donor and an acceptor in an arbitrary, reciprocal environment and examine how the medium's properties and the molecular positions affect the interaction rate. Our consideration is then extended to include non-reciprocal media, again calculating a general expression for the energy transfer rate and applying to a simple setup containing non-reciprocal media. In particular, we investigate how the properties of the medium can be altered to promote unidirectional energy propagation. We will also explore an application of this principle, which makes use of inverse design in the creation of an optical isolator. In real-world situations, a donor and acceptor can also be coupled to additional interacting bodies as well as their environment, and these can have an intricate impact on the rate of energy transfer between them. The introduction of a third molecule significantly complicates the calculation of the rate, so in this work we use canonical transformations to reduce this computational complexity and derive a general expression for the rate of three-body RET in a macroscopic background. Applying this to some simple setups demonstrates the distinctive effect the mediating body can have. Finally, we investigate how a macroscopic body can be used to induce a superabsorbing state in a system of dipoles via control of the intermolecular coupling. After a demonstration of this principle for a simple model system, we consider a ring of optical dipoles, inspired by naturally occurring photosynthetic systems. We demonstrate how the placement of a macroscopic

sphere inside the ring can produce superabsorption in the system, making it suitable for use in artificial light harvesting and showing performance superior to previous methods.

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## List of Publications

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# CHAPTER 1

## Introduction

Macroscopic bodies can exert a powerful influence on the way atoms and molecules interact in their presence. An understanding of an environment's impact can allow for the engineering of certain microscopic processes to achieve particular results. For this, we require macroscopic backgrounds to be introduced into the quantum description, which can be achieved using macroscopic quantum electrodynamics [4, 5], in which environments are described by their effective properties, avoiding the atomistic approach [6] which becomes extremely cumbersome when considering macroscopic bodies.

One such microscopic process is the transport of energy between atoms/molecules, which is essential in many areas of science, such as synthetic light harvesting [7], the "spectroscopic ruler" [8] and radiation biology [9]. The most fundamental of the intermolecular energy transfer processes is resonant energy transfer (RET), which facilitates energy transport in plants. It involves the de-excitation of a donor atom/molecule, releasing a virtual photon which is absorbed by an acceptor, causing it to excite. This process, first introduced by Förster in 1946 [10, 11] and later developed into a fully quantum theory by Gomberoff and Power [12], was first derived for a general macroscopic environment in 2002 [13]. Since then, two-body RET has been studied in the presence of various specific backgrounds [14–17].

An area of interest in this field is the influence that the non-reciprocity of a medium can have on intermolecular energy transport. Reciprocity dictates much about how we experience the world, for example how we can be sure that if we can hear someone then they can hear us too. In the context of light, we would assume that information transmitted by a laser would be the same if the positions of the source and observation points were switched. However, non-reciprocal media can break this symmetry (see [18] for a review), making them advantageous in the design of devices which utilise one-way propagation, e.g. optical isolators [19]. There are several paths to achieving non-reciprocity, the most common being the Faraday effect [20], with others including methods based on inherently nonlinear waveguides [21–25], spatiotemporal modulation [26–30] and optomechanical coupling [31]. In this thesis, a general formula for RET in a non-reciprocal environment is calculated and used to explore how an environment can be adapted to promote one-way energy transfer. The results from this section have been published in Ref. [2].

The complexity of the description of RET in a macroscopic background is significantly increased with the addition of a third molecule [32–37]. In this work, we make use of canonical transformations to simplify the effective Hamiltonian of a three-body system, leading to an alternative method for the calculation of a general rate formula. This work has been published in Ref. [1]. Calculations which include a mediating body have previously been carried out for simple homogenous environments [38, 39], but in this work we extend this to arbitrary backgrounds.

Macroscopic environments can also influence dipolar interactions, which are fundamental in many diverse scientific areas, (see e.g. [40–45]). In particular, dipole-dipole interactions can enhance absorption rates in optical systems [46, 47], for example in synthetic light-harvesters [48–55]. Our work, published in Ref. [3], explores the possibility of using a macroscopic body to manipulate dipolar interactions in such a system to induce superabsorption, which could be beneficial in improving solar energy conversion.

The structure of this work is as follows. We begin with an overview of macroscopic quantum electrodynamics (QED) in chapter 2, the crucial theoretical framework employed in this thesis. We review how the electromagnetic field is quantized within this framework while taking into account absorbing and dispersing media. In particular, we focus on the differences in how this must be approached when considering reciprocal vs non-reciprocal media. We also examine the Green's tensor, a critical component of macroscopic QED, and how its properties vary depending on the reciprocity of the media considered. The specific forms of the Green's tensor for various environmental setups will be covered in appendix B.

We next turn our attention to the process of RET. Through perturbation theory, we calculate a general formula for the rate of RET between two bodies, making use of macroscopic QED to account for an external environment. Firstly, chapter 3 will consider reciprocal media only, and to demonstrate some proof-of-principles, we will apply our derived rate expression to some simple systems, exploring how the properties of the environment and the positions of the molecules affect the rate of energy transfer between them.

We then extend our consideration to include non-reciprocal media in chapter 4, again deriving a general rate expression for two-body RET, before examining a simple setup containing non-reciprocal media. We will focus on the conditions that must be met by the system to induce a change in the rate of interaction between two molecules when their positions are swapped, allowing us to see how the medium's properties can be manipulated to maximise energy transfer in one direction over the other. An application of this will then be discussed, presenting results from our paper, Ref. [2] in which inverse design is used to optimize one-way energy transfer in an optical isolator.

In chapter 5, the influence of the addition of a third mediating body on the energy transfer between two molecules will be examined. Canonical transformations will be used to produce a new effective Hamiltonian and thus reduce the order of perturbation theory required to calculate a general formula for the rate of energy transfer in such a system. Again, macroscopic QED will be utilised to account for the effects of an external environment. This work has been published in our paper, Ref. [1]. Some simple systems containing three bodies and a macroscopic environment will then be examined as a proof-of-principle for the use of this formula.

We lastly investigate how the intermolecular coupling in a system can be engineered through the manipulation of macroscopic environments. In particular, we study how this principle could be applied to induce superabsorption in a system of optical dipoles, thus improving its suitability for use in synthetic light harvesting. After an overview of the basics of photosynthesis and superabsorption, we introduce a system of a ring of dipoles for which it has previously been shown in Ref. [46] that a superabsorbing state can be reached and sustained through careful tilting of the dipole moments. We aim to achieve the same effect through the use of a macroscopic environment, thus allowing the dipole moments to remain parallel, enhancing the system's potential for superabsorption. As a proof-of-principle, we initially consider a simple situation in which the properties of a macroscopic environment can be be exploited to control the intermolecular coupling of two bodies, before examining how the same principles can be applied to the ring system. Finally, we present the results from our paper, Ref. [3], which models the system as a quantum heat engine and calculates how its power output scales with the number of dipoles making up the ring.

# CHAPTER 2

## Macroscopic Quantum Electrodynamics

This thesis focuses on how intermolecular energy transfer can be affected by macroscopic environments, so it is crucial to be able to account for macroscopic media when quantizing the electromagnetic field. The theoretical framework used to achieve this is macroscopic quantum electrodynamics (macroscopic QED), and the aim of this chapter is to provide an overview of this theory to lay the groundwork for the thesis at hand.

Macroscopic QED facilitates the quantum description of macroscopic objects [4, 5, 56, 57] by describing their effective properties, such as overall permittivity and permeability. This means that the effects of an environment near the system can be accounted for more readily than the atomistic approach in [6], where there are so many individual particles making up a medium that following the dynamics of all of them becomes incredibly complex, if not impossible. The presence of such an environment, which can include arbitrarily shaped, dispersing, and absorbing material bodies, will be accounted for via the Green's tensor.

In this chapter, we give an overview of the derivation of the fundamentals of macroscopic QED. Beginning with the classical theory and then quantizing the field, we focus on the difference in methods required when dealing with "simple" reciprocal media compared with more general non-reciprocal media (what is meant by "simple" and general will be covered in the next section). We will then study the Green's tensor in more detail, looking at its definition for different types of media and along with some useful properties.

### 2.1 Field Quantizations

We begin by reviewing some basic concepts of classical electrodynamics in the presence of magnetoelectric media. In this work, we will focus on the case of no free charges, so that the only charges present are the bound charges contained within the media. We then quantize the field by connecting phenomenological noise fields to quantized excitations of the combined body-field system. In this section, we concentrate on how our methods must be adjusted depending on the properties of the media we are dealing with. In particular, we look at the "simple" case of local, isotropic, reciprocal, magnetodielectric media with no cross-susceptibilities, compared with more "general" non-local, non-isotropic and nonreciprocal media, where the fluctuations of the electric and magnetic field are both coupled to both the polarization and magnetization.

#### 2.1.1 Quantization of Field in Reciprocal Media

In this section, we consider only "simple" magnetodielectric media, by which we mean that the response of the medium is local, isotropic, reciprocal, and the electric/magnetic field fluctuations are decoupled from the polarization/magnetization, resulting in no cross-susceptibilities. We first give an overview of the description of the classical field in the presence of reciprocal media, then use this to construct a quantum theory for the field.

#### **Classical Field in Reciprocal Media**

In frequency space, a system with no free charges in a reciprocal medium is described by the Maxwell equations [58],

$$\boldsymbol{\nabla} \cdot \boldsymbol{B}(\boldsymbol{r}, \omega) = 0, \qquad (2.1a)$$

$$\boldsymbol{\nabla} \cdot \boldsymbol{D}(\boldsymbol{r}, \omega) = 0, \qquad (2.1b)$$

$$\nabla \times \boldsymbol{E}(\boldsymbol{r},\omega) - i\omega \boldsymbol{B}(\boldsymbol{r},\omega) = 0,$$
 (2.1c)

$$\nabla \times \boldsymbol{H}(\boldsymbol{r},\omega) + i\omega \boldsymbol{D}(\boldsymbol{r},\omega) = 0,$$
 (2.1d)

and the constitutive relations,

$$\boldsymbol{D}(\boldsymbol{r},\omega) = \varepsilon_0 \left[ \boldsymbol{E}(\boldsymbol{r},\omega) + \int d^3 r' \, \boldsymbol{\chi}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \boldsymbol{E}(\boldsymbol{r}',\omega) \right] + \boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r},\omega), \quad (2.2a)$$

$$\boldsymbol{H}(\boldsymbol{r},\omega) = \frac{1}{\mu_0} \left[ \boldsymbol{B}(\boldsymbol{r},\omega) - \int d^3 r' \boldsymbol{\zeta}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \boldsymbol{B}(\boldsymbol{r}',\omega) \right] - \boldsymbol{M}_{\rm N}(\boldsymbol{r},\omega), \qquad (2.2b)$$

where  $\chi$  and  $\zeta$  are the electric and magnetic susceptibility response functions of the medium, respectively, and the medium's fluctuations are described by the noise polarization,  $P_N$ , and noise magnetization,  $M_N$ . The derivations of these constitutive relations can be found in App. A. When considering only "simple" reciprocal media, we can assume that the medium response is local,

$$\boldsymbol{\chi}(\boldsymbol{r},\boldsymbol{r}',\omega) = \boldsymbol{\chi}(\boldsymbol{r},\omega)\delta(\boldsymbol{r}-\boldsymbol{r}'), \qquad (2.3)$$

$$\boldsymbol{\zeta}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \boldsymbol{\zeta}(\boldsymbol{r}, \omega) \delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad (2.4)$$

and isotropic,

$$\boldsymbol{\chi}(\boldsymbol{r},\omega) = \boldsymbol{\chi}(\boldsymbol{r},\omega)\mathbb{I}, \qquad (2.5)$$

$$\boldsymbol{\zeta}(\boldsymbol{r},\omega) = \zeta(\boldsymbol{r},\omega)\mathbb{I},\tag{2.6}$$

simplifying the constitutive relations for reciprocal media to,

$$\boldsymbol{D}(\boldsymbol{r},\omega) = \varepsilon_0 \varepsilon(\boldsymbol{r},\omega) \boldsymbol{E}(\boldsymbol{r},\omega) + \boldsymbol{P}_{\rm N}(\boldsymbol{r},\omega), \qquad (2.7a)$$

$$\boldsymbol{H}(\boldsymbol{r},\omega) = \frac{1}{\mu_0 \mu(\boldsymbol{r},\omega)} \boldsymbol{B}(\boldsymbol{r},\omega) - \boldsymbol{M}_{\rm N}(\boldsymbol{r},\omega), \qquad (2.7b)$$

where we have introduced the electric permittivity,

$$\varepsilon(\mathbf{r},\omega) = 1 + \chi(\mathbf{r},\omega),$$
(2.8)

and the magnetic permeability,

$$\mu(\mathbf{r},\omega) = \frac{1}{1 - \zeta(\mathbf{r},\omega)},\tag{2.9}$$

of the medium.

Substituting the constitutive relations, (2.7a) and (2.7b), into (2.1d) we find,

$$\boldsymbol{\nabla} \times \frac{1}{\mu_0 \mu(\boldsymbol{r},\omega)} \boldsymbol{B}(\boldsymbol{r},\omega) - \boldsymbol{\nabla} \times \boldsymbol{M}_{\mathrm{N}}(\boldsymbol{r},\omega) + i\omega\varepsilon_0\varepsilon(\boldsymbol{r},\omega)\boldsymbol{E}(\boldsymbol{r},\omega) + i\omega\boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r},\omega) = 0. \quad (2.10)$$

Then substituting in the rearranged (2.1c),  $\boldsymbol{B}(\omega) = -\frac{i}{\omega} \boldsymbol{\nabla} \times \boldsymbol{E}(\omega)$ , and making use of the

identity  $\varepsilon_0 \mu_0 = c^{-2}$  we obtain an inhomogeneous Helmholtz equation for the electric field,

$$\frac{i}{\omega} \left[ -\boldsymbol{\nabla} \times \frac{1}{\mu_0 \mu(\boldsymbol{r},\omega)} \boldsymbol{\nabla} \times + \omega^2 \varepsilon_0 \varepsilon(\boldsymbol{r},\omega) \right] \boldsymbol{E}(\boldsymbol{r},\omega) = \boldsymbol{\nabla} \times \boldsymbol{M}_{\mathrm{N}}(\boldsymbol{r},\omega) - i\omega \boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r},\omega)$$
$$\Rightarrow \left[ \boldsymbol{\nabla} \times \frac{1}{\mu(\boldsymbol{r},\omega)} \boldsymbol{\nabla} \times - \frac{\omega^2}{c^2} \varepsilon(\boldsymbol{r},\omega) \right] \boldsymbol{E}(\boldsymbol{r},\omega) = i\mu_0 \omega \boldsymbol{j}_{\mathrm{N}}(\boldsymbol{r},\omega), \qquad (2.11)$$

where the source term is the noise current density,

$$\boldsymbol{j}_{\mathrm{N}}(\boldsymbol{r},\omega) = \boldsymbol{\nabla} \times \boldsymbol{M}_{\mathrm{N}}(\boldsymbol{r},\omega) - i\omega \boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r},\omega). \tag{2.12}$$

In the free space case, the Helmholtz equation is homogeneous, so this source term encapsulates the effect of the medium. To solve (2.11), we introduce the Green's tensor for reciprocal media which satisfies the Helmholtz equation [4, 59],

$$\left[\boldsymbol{\nabla} \times \frac{1}{\mu(\boldsymbol{r},\omega)} \boldsymbol{\nabla} \times -\frac{\omega^2}{c^2} \varepsilon(\boldsymbol{r},\omega)\right] \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}'), \qquad (2.13)$$

with  $\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}') = \text{diag}(1,1,1)\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')$ , and obeys the boundary condition,

$$G(\mathbf{r}, \mathbf{r}', \omega) \to \mathbf{0} \quad \text{for} \quad |\mathbf{r} - \mathbf{r}'| \to \infty.$$
 (2.14)

More information on the defining Helmholtz equations of the Green's tensor will be given in section 2.2. Using the Green's tensor, we find that a formal solution to this Helmholtz equation is given by,

$$\boldsymbol{E}(\boldsymbol{r},\omega) = i\mu_0\omega \int d^3r' \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r'},\omega) \cdot \boldsymbol{j}_{\rm N}(\boldsymbol{r},\omega).$$
(2.15)

A classical effect of the medium compared to the vacuum case is that the electromagnetic field becomes a fluctuating quantity, caused by the source fluctuations. The fluctuationdissipation theorem relates the fluctuations of a physical quantity to the imaginary part of the respective response function [60, 61]. In our case the fluctuations of the medium are described by the noise polarization and magnetization, and the response functions are the electric and magnetic susceptibilities of the medium. Therefore, the fluctuation-dissipation theorem reads [4],

$$\langle \Delta \boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r},\omega) \Delta \boldsymbol{P}_{\mathrm{N}}^{*}(\boldsymbol{r}',\omega') \rangle_{\mathrm{cl}} = \frac{k_{\mathrm{B}}T}{\pi\omega} \varepsilon_{0} \operatorname{Im} \chi(\boldsymbol{r},\omega) \boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}') \delta(\omega-\omega'), \qquad (2.16)$$

$$\langle \Delta \boldsymbol{M}_{\mathrm{N}}(\boldsymbol{r},\omega) \Delta \boldsymbol{M}_{\mathrm{N}}^{*}(\boldsymbol{r}',\omega') \rangle_{\mathrm{cl}} = \frac{k_{\mathrm{B}}T}{\pi\omega} \frac{\mathrm{Im}\,\zeta(\boldsymbol{r},\omega)}{\mu_{0}} \boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\delta(\omega-\omega'), \qquad (2.17)$$

where  $k_{\rm B}$  is the Boltzmann constant, T is the temperature and  $\Delta f = f - \langle f \rangle_{\rm cl}$  denotes the classical fluctuations of a quantity f. If the imaginary parts of the response functions are positive it means that the medium is absorbing, whereas negative means it is amplifying [4]. We can see from the above equations that any absorbing system at a non-zero temperature must have fluctuations. We also note that since these noise terms represent fluctuations, they vanish on their classical average [4],

$$\langle \boldsymbol{P}_{\mathrm{N}} \rangle_{\mathrm{cl}} = \boldsymbol{0}, \quad \langle \boldsymbol{M}_{\mathrm{N}} \rangle_{\mathrm{cl}} = \boldsymbol{0}.$$
 (2.18)

Now that we understand the behaviour of the classical field in reciprocal media, we can transition from classical to quantum theory.

#### Quantization of Field in Reciprocal Media

When dealing with the free field, i.e. when no media is present, we can apply canonical quantization to the electromagnetic field to build a quantum theory. However, in the presence of media, we cannot easily formulate a Hamiltonian from the respective classical theory [4], so instead we aim to construct a quantum theory for the field in the presence of media by ensuring that the behaviour resembles the classical field as closely as possible, while making sure the free-space QED is reproduced in the absence of charges.

To ensure that the quantized field's behaviour replicates that of the classical field, we require that the classical Maxwell equations (2.1) and the constitutive relations (2.7) hold. To this end, the classical fields are replaced with operator-valued quantum observables so that the Maxwell equations for the quantized field are,

$$\boldsymbol{\nabla} \cdot \hat{\boldsymbol{B}}(\omega) = 0, \qquad (2.19a)$$

$$\boldsymbol{\nabla} \cdot \hat{\boldsymbol{D}}(\omega) = 0, \qquad (2.19b)$$

$$\nabla \times \hat{E}(\omega) - i\omega \hat{B}(\omega) = 0,$$
 (2.19c)

$$\boldsymbol{\nabla} \times \hat{\boldsymbol{H}}(\omega) + i\omega\hat{\boldsymbol{D}}(\omega) = 0, \qquad (2.19d)$$

and the constitutive relations are,

$$\hat{\boldsymbol{D}}(\boldsymbol{r},\omega) = \varepsilon_0 \varepsilon(\boldsymbol{r},\omega) \hat{\boldsymbol{E}}(\boldsymbol{r},\omega) + \hat{\boldsymbol{P}}_{N}(\boldsymbol{r},\omega), \qquad (2.20a)$$

$$\hat{\boldsymbol{H}}(\boldsymbol{r},\omega) = \frac{1}{\mu_0 \mu(\boldsymbol{r})} \hat{\boldsymbol{B}}(\boldsymbol{r},\omega) - \hat{\boldsymbol{M}}_{N}(\boldsymbol{r},\omega).$$
(2.20b)

We also must ensure that the quantum fluctuations behave in the same way as the classical ones, meaning that the noise field operators,  $\hat{P}_{\rm N}$  and  $\hat{M}_{\rm N}$ , must vanish on their ground state average, as in the classical case (2.18), and obey the fluctuation-dissipation theorem [60, 61],

$$\left\langle \mathcal{S}\left[\Delta\hat{\boldsymbol{P}}_{\mathrm{N}}(\boldsymbol{r},\omega)\Delta\hat{\boldsymbol{P}}_{\mathrm{N}}^{\dagger}(\boldsymbol{r}',\omega')\right]\right\rangle = \frac{\hbar}{2\pi}\varepsilon_{0}\operatorname{Im}\chi(\boldsymbol{r},\omega)\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\delta(\omega-\omega'),\tag{2.21}$$

$$\left\langle \mathcal{S}\left[\Delta \hat{M}_{\mathrm{N}}(\boldsymbol{r},\omega)\Delta \hat{M}_{\mathrm{N}}^{\dagger}(\boldsymbol{r}',\omega')\right] \right\rangle = \frac{\hbar}{2\pi} \frac{\mathrm{Im}\,\zeta(\boldsymbol{r},\omega)}{\mu_{0}} \boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\delta(\omega-\omega'), \qquad (2.22)$$

where  $S\left[\hat{a}\hat{b}\right] = \frac{1}{2}\left(\hat{a}\hat{b} + \hat{b}\hat{a}\right)$  is the symmetrized operator product. We can see that in making the transition from classical to quantum theory, the average thermal energy  $k_{\rm B}T$  that appears in the classical fluctuation-dissipation theorem, (2.16) and (2.17), has been replaced with the quantum ground-state energy  $\frac{1}{2}\hbar\omega$ .

These requirements can be fulfilled by introducing fundamental creation and annihilation operators,  $\hat{f}^{\dagger}_{\lambda}(\boldsymbol{r},\omega)$  and  $\hat{f}_{\lambda}(\boldsymbol{r},\omega)$ , respectively, which obey the bosonic commutation relations,

$$\left[\hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{r},\omega), \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{r}',\omega')\right] = \left[\hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{r},\omega), \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{r}',\omega')\right] = 0, \qquad (2.23a)$$

$$\left[\hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{r},\omega), \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{r}',\omega')\right] = \delta_{\lambda\lambda'}\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}')\boldsymbol{\delta}(\omega-\omega'), \qquad (2.23b)$$

where  $\delta(\mathbf{r} - \mathbf{r}') = \text{diag}(1, 1, 1)\delta(\mathbf{r} - \mathbf{r}')$  and  $\lambda, \lambda' = e, m$ . The vacuum state of the electromagnetic field is denoted  $|\{0\}\rangle$ , such that,

$$\hat{f}_{\lambda}(\boldsymbol{r},\omega) |\{0\}\rangle = \mathbf{0} \quad \forall \,\lambda, \boldsymbol{r}, \omega \,,$$

$$(2.24)$$

and the excited states of the system are then reached with repeated action of the creation operator,

$$\left|\mathbf{1}_{\lambda}(\boldsymbol{r},\omega)\right\rangle = \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{r},\omega)\left|\{0\}\right\rangle.$$
(2.25)

From the above definition of the ground state (2.24), we can see that both the creation and

annihilation operators vanish on their ground-state average,

$$\left\langle \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{r},\omega) \right\rangle = \left\langle \{0\} \middle| \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{r},\omega) \middle| \{0\} \right\rangle = \boldsymbol{0},$$
 (2.26)

$$\left\langle \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{r},\omega) \right\rangle = \left\langle \{0\} \middle| \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{r},\omega) \middle| \{0\} \right\rangle = \boldsymbol{0}.$$
 (2.27)

To satisfy the fluctuation-dissipation theorem, we can relate  $\hat{P}_N$  and  $\hat{M}_N$  to the creation and annihilation operators via,

$$\hat{\boldsymbol{P}}_{\mathrm{N}}(\boldsymbol{r},\omega) = i\sqrt{\frac{\hbar\varepsilon_{0}}{\pi}}\operatorname{Im}\varepsilon(\boldsymbol{r},\omega)}\hat{\boldsymbol{f}}_{e}(\boldsymbol{r},\omega), \qquad (2.28)$$

$$\hat{\boldsymbol{M}}_{N}(\boldsymbol{r},\omega) = \sqrt{\frac{\hbar}{\pi\mu_{0}}} \frac{\mathrm{Im}\,\mu(\boldsymbol{r},\omega)}{|\mu(\boldsymbol{r},\omega)|^{2}} \hat{\boldsymbol{f}}_{m}(\boldsymbol{r},\omega), \qquad (2.29)$$

so that (2.21) and (2.22) hold as required. We can also see from (2.26) that the noise polarization and magnetization vanish on their ground-state average as required,

$$\left\langle \hat{P}_{\mathrm{N}} \right\rangle = \mathbf{0}, \quad \left\langle \hat{M}_{\mathrm{N}} \right\rangle = \mathbf{0}.$$
 (2.30)

Now we have decided on our forms for the noise polarization and magnetization, we can follow the same method as for the classical field in the previous subsection to create a Helmholtz equation for the electric field in reciprocal media by combining (2.19c), (2.19d), (2.20a) and (2.20b) to obtain,

$$\left[\boldsymbol{\nabla} \times \frac{1}{\mu(\boldsymbol{r},\omega)} \boldsymbol{\nabla} \times -\frac{\omega^2}{c^2} \varepsilon(\boldsymbol{r},\omega)\right] \hat{\boldsymbol{E}}(\boldsymbol{r},\omega) = i\mu_0 \omega \hat{\boldsymbol{j}}_{\mathrm{N}}(\boldsymbol{r},\omega), \qquad (2.31)$$

which, in analogy with the classical case, can be formally solved via,

$$\hat{\boldsymbol{E}}(\boldsymbol{r},\omega) = i\mu_0\omega \int d^3r' \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r'},\omega) \cdot \hat{\boldsymbol{j}}_{\rm N}(\boldsymbol{r'},\omega).$$
(2.32)

If we substitute in our definition for the noise current density,

$$\hat{\boldsymbol{j}}_{\mathrm{N}}(\boldsymbol{r},\omega) = \boldsymbol{\nabla} \times \hat{\boldsymbol{M}}_{\mathrm{N}}(\boldsymbol{r},\omega) - i\omega\hat{\boldsymbol{P}}_{\mathrm{N}}(\boldsymbol{r},\omega), \qquad (2.33)$$

and substitute in our expressions for the noise polarization and magnetization, (2.28) and

(2.29) respectively, we can express the electric field in terms of the fundamental fields,

$$\hat{\boldsymbol{E}}(\boldsymbol{r},\omega) = i\mu_{0}\omega \int d^{3}\boldsymbol{r}' \left[ \sqrt{\frac{\hbar}{\pi\mu_{0}} \frac{\operatorname{Im}\mu(\boldsymbol{r}',\omega)}{|\mu(\boldsymbol{r}',\omega)|^{2}}} \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \boldsymbol{\nabla}' \times \hat{\boldsymbol{f}}_{m}(\boldsymbol{r}',\omega) + \omega \sqrt{\frac{\hbar\varepsilon_{0}}{\pi} \operatorname{Im}\varepsilon(\boldsymbol{r}',\omega)} \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \hat{\boldsymbol{f}}_{e}(\boldsymbol{r}',\omega) \right],$$

$$= i \int d^{3}\boldsymbol{r}' \left[ -\frac{\omega}{c} \sqrt{\frac{\hbar}{\pi\varepsilon_{0}} \frac{\operatorname{Im}\mu(\boldsymbol{r}',\omega)}{|\mu(\boldsymbol{r}',\omega)|^{2}}} \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) \times \overleftarrow{\boldsymbol{\nabla}}' \cdot \widehat{\boldsymbol{f}}_{m}(\boldsymbol{r}',\omega) + \frac{\omega^{2}}{c^{2}} \sqrt{\frac{\hbar}{\pi\varepsilon_{0}} \operatorname{Im}\varepsilon(\boldsymbol{r}',\omega)} \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \widehat{\boldsymbol{f}}_{e}(\boldsymbol{r}',\omega) \right], \quad (2.34)$$

where we have performed partial integration and again made use of the identity  $\varepsilon_0 \mu_0 = c^{-2}$  to obtain the second equality. Here, the operation  $\overleftarrow{\nabla}$  is mathematically defined as  $\left[ \boldsymbol{T} \times \overleftarrow{\nabla} \right]_{ij} (\boldsymbol{r}, \boldsymbol{r'}) = \varepsilon_{jkl} \partial'_l T_{ik}(\boldsymbol{r}, \boldsymbol{r'})$ . Finally, writing in terms of frequency components via,

$$\hat{f} = \int_0^\infty d\omega \hat{f}(\omega) + \text{H.c.}$$
(2.35)

and splitting the electric and magnetic contributions, we obtain,

$$\hat{\boldsymbol{E}}(\boldsymbol{r}) = \int_{0}^{\infty} d\omega \, \hat{\boldsymbol{E}}(\boldsymbol{r},\omega) + \text{H.c.}$$

$$= \sum_{\lambda=e,m} \int_{0}^{\infty} d\omega \int d^{3}\boldsymbol{r}' \, \boldsymbol{G}_{\lambda}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{r}',\omega) + \text{H.c.}$$
(2.36)

where we have defined the G coefficients as,

$$\boldsymbol{G}_{e}(\boldsymbol{r},\boldsymbol{r}',\omega) = i\frac{\omega^{2}}{c^{2}}\sqrt{\frac{\hbar}{\pi\varepsilon_{0}}}\operatorname{Im}\varepsilon(\boldsymbol{r}',\omega)}\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega), \qquad (2.37)$$

$$\boldsymbol{G}_{m}(\boldsymbol{r},\boldsymbol{r}',\omega) = -i\frac{\omega}{c}\sqrt{\frac{\hbar}{\pi\varepsilon_{0}}\frac{\mathrm{Im}\,\mu(\boldsymbol{r}',\omega)}{|\mu(\boldsymbol{r}',\omega)|^{2}}}\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega)\times\overleftarrow{\boldsymbol{\nabla}'}.$$
(2.38)

This definition of the electric field will be utilized extensively in the coming chapters. In the next subsection, we extend our consideration to more "general" non-reciprocal media.

#### 2.1.2 Quantization of Field in Non-reciprocal Media

We now turn our attention to how the electromagnetic field behaves in the presence of general non-local, non-isotropic and non-reciprocal media. The non-local and non-isotropic natures of the material are easy to take into consideration, namely by not making the simplifications given by (2.64) and (2.65), respectively. On the other hand, non-reciprocity is more difficult to account for.

In the context of electromagnetism, non-reciprocity means that a source-generated field at an observation point is not the same when the source and observation points are interchanged [62]. An important feature of non-reciprocal media is that an electric response can be induced via the magnetic field, and vice versa [63, 64]. This means that the polarization and magnetization can no longer be described simply by electric permittivities and magnetic permeabilities (as in (2.20)), but cross-susceptibilities must also be included. Further to this, and crucially, we need to deal with the complication that Lorentz reciprocity,  $\boldsymbol{G}^{\mathrm{T}}(\boldsymbol{r}', \boldsymbol{r}, \omega) = \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)$ , does not hold in non-reciprocal media (as we will see in section 2.2.1). This section follows Ref. [65].

#### Classical Field in Non-reciprocal Media

In this section we will discard the spatial and frequency arguments unless necessary for understanding. Although the Maxwell equations (2.1) are unchanged by the reciprocity of the material, the polarization and magnetization fields respond differently via,

$$\boldsymbol{P} = \varepsilon_0 \left( \boldsymbol{\varepsilon} - \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 - \mathbb{I} \right) \star \boldsymbol{E} + \sqrt{\frac{\varepsilon_0}{\mu_0}} \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \star \boldsymbol{B} + \boldsymbol{P}_{\mathrm{N}}, \qquad (2.39\mathrm{a})$$

$$\boldsymbol{M} = \frac{1}{\mu_0} \left( \mathbb{I} - \boldsymbol{\mu}^{-1} \right) \star \boldsymbol{B} + \sqrt{\frac{\varepsilon_0}{\mu_0}} \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 \star \boldsymbol{E} + \boldsymbol{M}_{\mathrm{N}}, \qquad (2.39\mathrm{b})$$

where the medium is characterized by its permittivity  $\varepsilon(\mathbf{r}, \mathbf{r}', \omega)$ , permeability  $\mu(\mathbf{r}, \mathbf{r}', \omega)$ , and magnetoelectric susceptibilities  $\xi_1(\mathbf{r}, \mathbf{r}', \omega)$  and  $\xi_2(\mathbf{r}, \mathbf{r}', \omega)$ . We have also introduced an abbreviation denoting the spatial convolution of a tensor and vector field or between two tensor fields,

$$[\mathbf{X} \star \mathbf{v}](\mathbf{r}) \equiv \int d^3 \mathbf{s} \mathbf{X}(\mathbf{r}, \mathbf{s}) \cdot \mathbf{v}(\mathbf{s}),$$
$$[\mathbf{X} \star \mathbf{Y}](\mathbf{r}, \mathbf{r}') \equiv \int d^3 \mathbf{s} \mathbf{X}(\mathbf{r}, \mathbf{s}) \cdot \mathbf{Y}(\mathbf{s}, \mathbf{r}').$$
(2.40)

We can use equations (2.39) along with the relations  $D = \varepsilon_0 E + P$  and  $H = \mu_0^{-1} B - M$  to build the relevant constitutive relations for non-reciprocal media,

$$\boldsymbol{D} = \varepsilon_0 \left( \boldsymbol{\varepsilon} - \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 \right) \star \boldsymbol{E} + \sqrt{\frac{\varepsilon_0}{\mu_0}} \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \star \boldsymbol{B} + \boldsymbol{P}_{\mathrm{N}}, \qquad (2.41\mathrm{a})$$

$$\boldsymbol{H} = \frac{1}{\mu_0} \boldsymbol{\mu}^{-1} \star \boldsymbol{B} - \sqrt{\frac{\varepsilon_0}{\mu_0}} \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 \star \boldsymbol{E} - \boldsymbol{M}_{\mathrm{N}}, \qquad (2.41\mathrm{b})$$

which reduce to the reciprocal constitutive relations, (2.7), when the cross-susceptibilities are zero and we assume the medium to be local and isotropic through the replacements  $\varepsilon(\mathbf{r}, \mathbf{r}') = \varepsilon(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')\mathbb{I}$  and  $\mu(\mathbf{r}, \mathbf{r}') = \mu(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')\mathbb{I}$ .

To find a Helmholtz equation for the electric field in a non-reciprocal medium, we substitute these constitutive relations into (2.1d), giving us,

$$-\frac{1}{i\omega\mu_{0}}\boldsymbol{\nabla}\times\boldsymbol{\mu}^{-1}\star\boldsymbol{B}-\sqrt{\frac{\varepsilon_{0}}{\mu_{0}}}\boldsymbol{\nabla}\times\boldsymbol{\mu}^{-1}\star\boldsymbol{\xi}_{2}\star\boldsymbol{E}$$
$$+i\omega\varepsilon_{0}\left(\boldsymbol{\varepsilon}-\boldsymbol{\xi}_{1}\star\boldsymbol{\mu}^{-1}\star\boldsymbol{\xi}_{2}\right)\star\boldsymbol{E}+\sqrt{\frac{\varepsilon_{0}}{\mu_{0}}}\boldsymbol{\xi}_{1}\star\boldsymbol{\mu}^{-1}\star\boldsymbol{B}=\boldsymbol{\nabla}\times\boldsymbol{M}_{\mathrm{N}}-i\omega\boldsymbol{P}_{\mathrm{N}}.$$
 (2.42)

Combining with (2.1c) as we did for the reciprocal case, defining the noise current density by (2.12) and performing integration by parts, we obtain the inhomogeneous Helmholtz equation for the electric field,

$$-\frac{1}{i\omega\mu_{0}}\nabla\times\mu^{-1}\times\overleftarrow{\nabla}\star\boldsymbol{E}-\sqrt{\frac{\varepsilon_{0}}{\mu_{0}}}\left(\nabla\times\mu^{-1}\star\boldsymbol{\xi}_{2}+\boldsymbol{\xi}_{1}\star\mu^{-1}\times\overleftarrow{\nabla}\right)\star\boldsymbol{E}$$
$$+i\omega\varepsilon_{0}\left(\boldsymbol{\varepsilon}-\boldsymbol{\xi}_{1}\star\mu^{-1}\star\boldsymbol{\xi}_{2}\right)\star\boldsymbol{E}=\boldsymbol{j}_{\mathrm{N}}$$
$$\Rightarrow\left[\nabla\times\nabla\times-\frac{\omega^{2}}{c^{2}}\right]\boldsymbol{E}-i\mu_{0}\omega\boldsymbol{Q}\star\boldsymbol{E}=i\mu_{0}\omega\boldsymbol{j}_{\mathrm{N}},\qquad(2.43)$$

where we have introduced the conductivity tensor [65],

$$\boldsymbol{Q} = \frac{1}{i\omega\mu_0} \boldsymbol{\nabla} \times \left(\boldsymbol{\mu}^{-1} - \mathbb{I}\right) \times \overleftarrow{\boldsymbol{\nabla}} + \sqrt{\frac{\varepsilon_0}{\mu_0}} \left(\boldsymbol{\nabla} \times \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 + \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \times \overleftarrow{\boldsymbol{\nabla}}\right) - i\omega\varepsilon_0 \left(\boldsymbol{\varepsilon} - \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 - \mathbb{I}\right), \qquad (2.44)$$

where  $\mathbb{I}$  has been defined such that  $\mathbf{T} \star \mathbb{I} = \mathbf{T}$  for any tensor  $\mathbf{T}$ . This Helmholtz equation (2.43) reduces to (2.11) as required when reciprocal magnetodielectric media is considered, as shown in the next section 2.2.1. As for the reciprocal case, the Helmholtz equation can be solved by means of the non-reciprocal Green's tensor which satisfies the more general

Helmholtz equation [65],

$$\left[\nabla \times \nabla \times -\frac{\omega^2}{c^2}\right] \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}') - i\mu_0 \omega \left[\boldsymbol{Q} \star \boldsymbol{G}\right](\boldsymbol{r}, \boldsymbol{r}') = \boldsymbol{\delta}(\boldsymbol{r} - \boldsymbol{r}'), \qquad (2.45)$$

and the boundary condition (2.14). In analogy with the reciprocal case, the formal solution for the electric field is again found to be,

$$\boldsymbol{E}(\boldsymbol{r},\boldsymbol{r}') = i\mu_0\omega \left[\boldsymbol{G} \star \boldsymbol{j}_N\right](\boldsymbol{r},\boldsymbol{r}'). \tag{2.46}$$

Now, as in the previous section, we can transition from classical to quantum theory.

#### Quantization of Field in Non-reciprocal Media

As in the reciprocal case, we construct a quantum theory for the electromagnetic field by replicating the behaviour of the classical field. Therefore, the quantized Maxwell equations are the same as in the reciprocal case, (2.19), but the quantized constitutive relations take the form of (2.41) with the classical fields replaced with operator-valued quantum observables.

Firstly, it is useful to decompose the conductivity tensor (2.44),

$$\boldsymbol{Q}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{1}{i\omega} \begin{pmatrix} -i\omega, \quad \boldsymbol{\nabla} \times \end{pmatrix} \cdot \begin{bmatrix} \mathcal{M}(\boldsymbol{r},\boldsymbol{r}',\omega) - \begin{pmatrix} \varepsilon_0 & 0\\ 0 & -\mu_0^{-1} \end{pmatrix} \end{bmatrix} \cdot \begin{pmatrix} i\omega\\ -\times \overleftarrow{\boldsymbol{\nabla}} \end{pmatrix}, \quad (2.47)$$

where we have defined the matrix,

$$\mathcal{M} = \begin{pmatrix} \varepsilon_0 \left[ \boldsymbol{\varepsilon} - \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 \right] & \sqrt{\frac{\varepsilon_0}{\mu_0}} \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \\ \sqrt{\frac{\varepsilon_0}{\mu_0}} \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 & -\frac{1}{\mu_0} \boldsymbol{\mu}^{-1} \end{pmatrix}.$$
(2.48)

It can also be shown that,

$$\mathcal{R}\mathbf{e}[\boldsymbol{Q}] = \frac{1}{\omega} \left( -i\omega, \quad \boldsymbol{\nabla} \times \right) \cdot \mathcal{I}\mathbf{m}[\mathcal{M}] \cdot \begin{pmatrix} i\omega \\ -\times \overleftarrow{\boldsymbol{\nabla}} \end{pmatrix}.$$
(2.49)

where due to the violation of Lorentz reciprocity (discussed in the next section), it is conve-

nient to introduce generalized real and imaginary parts of a tensor field according to,

$$\mathcal{R}e[\boldsymbol{T}(\boldsymbol{r},\boldsymbol{r}')] = \frac{1}{2}[\boldsymbol{T}(\boldsymbol{r},\boldsymbol{r}') + \boldsymbol{T}^{\dagger}(\boldsymbol{r}',\boldsymbol{r})], \qquad (2.50)$$

$$\mathcal{I}m[\boldsymbol{T}(\boldsymbol{r},\boldsymbol{r}')] = \frac{1}{2i}[\boldsymbol{T}(\boldsymbol{r},\boldsymbol{r}') - \boldsymbol{T}^{\dagger}(\boldsymbol{r}',\boldsymbol{r})].$$
(2.51)

When considering reciprocal media where Lorentz reciprocity (2.75) holds, these expressions reduce to the ordinary definitions of real and imaginary parts,

$$\operatorname{Re}[\boldsymbol{T}(\boldsymbol{r},\boldsymbol{r}')] = \frac{1}{2}[\boldsymbol{T}(\boldsymbol{r},\boldsymbol{r}') + \boldsymbol{T}^{*}(\boldsymbol{r},\boldsymbol{r}')], \qquad (2.52)$$

$$\operatorname{Im}[\boldsymbol{T}(\boldsymbol{r},\boldsymbol{r}')] = \frac{1}{2i}[\boldsymbol{T}(\boldsymbol{r},\boldsymbol{r}') - \boldsymbol{T}^{*}(\boldsymbol{r},\boldsymbol{r}')]. \qquad (2.53)$$

To satisfy the fluctuation dissipation theorem, we relate the noise polarization and magnetization for non-reciprocal media to the creation and annihilation operators in a similar way to the previous section,

$$\begin{pmatrix} \hat{\boldsymbol{P}}_{\mathrm{N}} \\ \hat{\boldsymbol{M}}_{\mathrm{N}} \end{pmatrix} = \sqrt{\frac{\hbar}{\pi}} \boldsymbol{\mathcal{V}} \star \begin{pmatrix} \hat{\boldsymbol{f}}_{e} \\ \hat{\boldsymbol{f}}_{m} \end{pmatrix}, \qquad (2.54)$$

where  $\hat{f}_{\lambda}^{\dagger}$  and  $\hat{f}_{\lambda}$  are defined in the same way as in the previous section, obeying the bosonic commutation relations (2.23), and we have introduced the matrix  $\mathcal{V}$  such that it satisfies,

$$\mathcal{V} \star \mathcal{V}^{\dagger} = \mathcal{I}\mathrm{m}[\mathcal{M}], \qquad (2.55)$$

where  $\mathcal{M}$  is defined by (2.48). The noise current density for non-reciprocal media is then given by,

$$\hat{\boldsymbol{j}}_N = \sqrt{\frac{\hbar\omega}{\pi}} \boldsymbol{R} \star \boldsymbol{\hat{f}},$$
(2.56)

where  $\boldsymbol{R}$  is a square root of the positive definite tensor field  $\mathcal{R}e[\boldsymbol{Q}]$ ,

$$\boldsymbol{R} \star \boldsymbol{R}^{\dagger} = \mathcal{R}\mathbf{e}[\boldsymbol{Q}]. \tag{2.57}$$

Substituting this into our expression for the electric field, (2.46), we find that we can express the electric field in non-reciprocal media as,

$$\boldsymbol{E}(\boldsymbol{r},\omega) = i\mu_0\omega\sqrt{\frac{\hbar\omega}{\pi}} \left[\boldsymbol{G}\star\boldsymbol{R}\star\boldsymbol{\hat{f}}\right](\boldsymbol{r},\omega).$$
(2.58)

It is useful to rewrite in terms of frequency components as,

$$\boldsymbol{E}(\boldsymbol{r}) = \int_{0}^{\infty} d\omega \, \boldsymbol{E}(\boldsymbol{r},\omega) + H.c.$$
  
=  $i\mu_{0}\sqrt{\frac{\hbar}{\pi}} \int_{0}^{\infty} d\omega \, \omega^{3/2} \left[\boldsymbol{G} \star \boldsymbol{R} \star \boldsymbol{\hat{f}}\right](\boldsymbol{r},\omega) + H.c.$   
=  $\int_{0}^{\infty} d\omega \int d^{3}\boldsymbol{s} \, \boldsymbol{F}(\boldsymbol{r},\boldsymbol{s},\omega) \cdot \boldsymbol{\hat{f}}(\boldsymbol{s},\omega) + H.c.$  (2.59)

where we have defined,

$$\boldsymbol{F}(\boldsymbol{r},\boldsymbol{s},\omega) = i\mu_0 \sqrt{\frac{\hbar}{\pi}} \omega^{3/2} \int d^3 \boldsymbol{r}' \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \boldsymbol{R}(\boldsymbol{r}',\boldsymbol{s},\omega), \qquad (2.60)$$

$$\boldsymbol{F}^{\dagger}(\boldsymbol{r},\boldsymbol{s},\omega) = -i\mu_0 \sqrt{\frac{\hbar}{\pi}} \omega^{3/2} \int d^3 \boldsymbol{r}' \boldsymbol{G}^{\dagger}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \boldsymbol{R}^{\dagger}(\boldsymbol{r}',\boldsymbol{s},\omega).$$
(2.61)

This is the form of the quantized electric field that we will use in chapter 4 when investigating the effects of non-reciprocal environments on intermolecular energy transfer.

Now that we have used the Green's tensor to account for macroscopic environments in our quantization of the electric field, in the next section, we will look at the Green's tensor in more detail to gain a deeper understanding of how it can be used.

### 2.2 Green's Tensor

This section focusses on the Green's tensor, which plays a central role in macroscopic QED. We begin by comparing the defining Helmholtz equations that were presented in the previous section for "simple" reciprocal media and "general" non-reciprocal media, and show how they are connected. We then present and derive some general properties of the Green's tensor, including Lorentz reciprocity and integral relations that will be made use of in subsequent chapters. Specific forms the Green's tensor takes can be found in appendix B.

#### 2.2.1 Definition and Properties

In the previous section 2.1, the Green's tensor was introduced as the solution to two Helmholtz equations, (2.13) for "simple" reciprocal magnetodielectric media in subsection 2.1.1 and (2.45) for "general" non-reciprocal media in subsection 2.1.2, with the boundary condition (2.14). In this section, we show that these Helmholtz equations are equivalent, with (2.45) being the general form, reducing to (2.13) when "simple" reciprocal magnetodielectric media is considered.

#### **Defining Helmholtz Equations**

We begin with the general Helmholtz equation (2.45) that is valid for non-reciprocal media,

$$\left[\boldsymbol{\nabla} \times \boldsymbol{\nabla} \times -\frac{\omega^2}{c^2}\right] \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega) - i\mu_0 \omega \int d^3 \boldsymbol{s} \, \boldsymbol{Q}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \boldsymbol{G}(\boldsymbol{s}, \boldsymbol{r}', \omega) = \boldsymbol{\delta}(\boldsymbol{r} - \boldsymbol{r}'), \quad (2.62)$$

where Q is the conductivity tensor given in (2.44) and again below,

$$\boldsymbol{Q} = \frac{1}{i\omega\mu_0} \boldsymbol{\nabla} \times \left(\boldsymbol{\mu}^{-1} - \mathbb{I}\right) \times \overleftarrow{\boldsymbol{\nabla}} + \sqrt{\frac{\varepsilon_0}{\mu_0}} \left(\boldsymbol{\nabla} \times \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 + \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \times \overleftarrow{\boldsymbol{\nabla}}\right) - i\omega\varepsilon_0 \left(\boldsymbol{\varepsilon} - \boldsymbol{\xi}_1 \star \boldsymbol{\mu}^{-1} \star \boldsymbol{\xi}_2 - \mathbb{I}\right).$$
(2.63)

where  $\boldsymbol{\varepsilon}$  is the electric permittivity,  $\boldsymbol{\mu}$  is the magnetic permeability and  $\boldsymbol{\xi}_1$  and  $\boldsymbol{\xi}_2$  are the medium's magnetoelectric susceptibilities. When considering "simple" reciprocal magnetodielectric media only, we assume that the cross-susceptibilities  $\boldsymbol{\xi}_1$  and  $\boldsymbol{\xi}_2$  are zero, and we consider the response of the medium to be local,

$$\boldsymbol{\varepsilon}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \boldsymbol{\varepsilon}(\boldsymbol{r}, \omega) \delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad (2.64a)$$

$$\boldsymbol{\mu}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \boldsymbol{\mu}(\boldsymbol{r}, \omega) \delta(\boldsymbol{r} - \boldsymbol{r}'), \qquad (2.64b)$$

and isotropic,

$$\boldsymbol{\varepsilon}(\boldsymbol{r},\omega) = \boldsymbol{\varepsilon}(\boldsymbol{r},\omega)\mathbb{I},$$
 (2.65a)

$$\boldsymbol{\mu}(\boldsymbol{r},\omega) = \boldsymbol{\mu}(\boldsymbol{r},\omega)\mathbb{I}.$$
(2.65b)

Applying to the Helmholtz equation (2.62) gives us,

$$\left[\boldsymbol{\nabla} \times \boldsymbol{\nabla} \times -\frac{\omega^2}{c^2} - i\mu_0 \omega Q(\boldsymbol{r}, \omega)\right] \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \boldsymbol{\delta}(\boldsymbol{r} - \boldsymbol{r}'), \qquad (2.66)$$

with

$$\boldsymbol{Q}(\boldsymbol{r},\boldsymbol{r}',\omega) = Q(\boldsymbol{r},\omega)\delta(\boldsymbol{r}-\boldsymbol{r}')\mathbb{I}$$
$$= \left\{\frac{1}{i\omega\mu_0}\boldsymbol{\nabla}\times\left[\frac{1}{\mu(\boldsymbol{r},\omega)}-1\right]\times\overleftarrow{\boldsymbol{\nabla}}-i\omega\varepsilon_0\left[\varepsilon(\boldsymbol{r},\omega)-1\right]\right\}\delta(\boldsymbol{r}-\boldsymbol{r}')\mathbb{I}.$$
(2.67)

Combining these and performing integration by parts leaves us with the well-known Helmholtz equation for reciprocal magnetodielectric media,

$$\left[\boldsymbol{\nabla} \times \frac{1}{\mu(\boldsymbol{r},\omega)} \boldsymbol{\nabla} \times -\frac{\omega^2}{c^2} \varepsilon(\boldsymbol{r},\omega)\right] \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}'), \qquad (2.68)$$

which is (2.13) in the previous section 2.1.1. The other defining feature of the Green's tensor is that is obeys the boundary condition,

$$G(\mathbf{r}, \mathbf{r}', \omega) \to \mathbf{0} \quad \text{for} \quad |\mathbf{r} - \mathbf{r}'| \to \infty,$$
 (2.69)

which is assumed for both reciprocal and non-reciprocal media.

In the next section, we discuss and derive some useful properties of the Green's tensor, including the defining difference between reciprocal and non-reciprocal media.

#### Properties

The permittivity, permeability and magnetoelectric cross-susceptibilities of the medium are causal response functions, and so are also analytic functions of frequency in the upper half of the complex frequency plane. Since these are the functions that appear in both defining equations of the Green's tensor, (2.68) and (2.62), we can deduce that the Green's tensor is also an analytic function in the upper half of the complex  $\omega$  plane [4].

Similarly, since the medium properties obey the Schwarz reflection principle,  $\boldsymbol{\varepsilon}^*(\omega) = \boldsymbol{\varepsilon}(-\omega^*)$ ,  $\boldsymbol{\mu}^*(\omega) = \boldsymbol{\mu}(-\omega^*)$ ,  $\boldsymbol{\xi}^*_{1,2}(\omega) = \boldsymbol{\xi}_{1,2}(-\omega^*)$ , we can infer that the Schwarz reflection principle is also valid for the Green's tensor,

$$\boldsymbol{G}^{*}(\boldsymbol{r},\boldsymbol{r}',\omega) = \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',-\omega^{*}). \tag{2.70}$$

We now derive the crucial Lorentz reciprocity relation that holds for reciprocal media and not for non-reciprocal media. Considering reciprocal media only, the defining equation (2.68) states that the Green's tensor is the right inverse of the Helmholtz operator, so it must also be the left-inverse of the Helmholtz operator,

$$\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega)\left[\times\overleftarrow{\boldsymbol{\nabla}}'\frac{1}{\mu(\boldsymbol{r}',\omega)}\times\overleftarrow{\boldsymbol{\nabla}}'-\frac{\omega^2}{c^2}\varepsilon(\boldsymbol{r}',\omega)\right]=\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}').$$
(2.71)

After exchanging r and r', this expression can be rewritten as,

$$\left[\boldsymbol{\nabla} \times \frac{1}{\mu(\boldsymbol{r},\omega)} \boldsymbol{\nabla} \times -\frac{\omega^2}{c^2} \varepsilon(\boldsymbol{r},\omega)\right] \boldsymbol{G}^{\mathrm{T}}(\boldsymbol{r}',\boldsymbol{r},\omega) = \boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}'), \qquad (2.72)$$

where we have used the relation<sup>1</sup>,

$$\left[\nabla \times \frac{1}{\mu(\boldsymbol{r},\omega)}\nabla \times -\frac{\omega^2}{c^2}\varepsilon(\boldsymbol{r},\omega)\right]_{ij} = \left[\times\overleftarrow{\nabla}\frac{1}{\mu(\boldsymbol{r},\omega)}\times\overleftarrow{\nabla}-\frac{\omega^2}{c^2}\varepsilon(\boldsymbol{r},\omega)\right]_{ji}.$$
 (2.73)

Now comparing (2.72) with the original defining equation for the reciprocal Green's tensor (2.68), we find that, for reciprocal media, Lorentz reciprocity [66, 67] holds,

$$G_{ij}^{\mathrm{T}}(\boldsymbol{r}',\boldsymbol{r},\omega) = G_{ji}(\boldsymbol{r}',\boldsymbol{r},\omega) = G_{ij}(\boldsymbol{r},\boldsymbol{r}',\omega), \qquad (2.74)$$

or equivalently,

$$\boldsymbol{G}^{\mathrm{T}}(\boldsymbol{r}',\boldsymbol{r},\omega) = \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega). \tag{2.75}$$

To better understand this physically, we consider a point source at position  $\mathbf{r}_1$  with orientation  $\mathbf{e}_1$  giving rise to an electric field at observation point at position  $\mathbf{r}_2$  with orientation  $\mathbf{e}_2$ . The component along the direction  $\mathbf{e}_2$  at position  $\mathbf{r}_2$  is given by  $\mathbf{e}_2 \cdot \mathbf{G}(\mathbf{r}_2, \mathbf{r}_1, \omega) \cdot \mathbf{e}_1$ . Lorentz reciprocity tells us that the reverse situation, with exchanged positions and orientations, is also connected by the same Green's tensor,  $\mathbf{e}_2 \cdot \mathbf{G}(\mathbf{r}_2, \mathbf{r}_1, \omega) \cdot \mathbf{e}_1 = \mathbf{e}_1 \cdot \mathbf{G}(\mathbf{r}_1, \mathbf{r}_2, \omega) \cdot \mathbf{e}_2$ .

However, when we extend our consideration to include non-reciprocal media defined by Helmholtz equation (2.62), we are unable to make the same arguments. In analogy with the reciprocal case, the non-reciprocal Green's tensor must be the left-inverse of the Helmholtz operator as well as the right-inverse,

$$\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega)\left[\times\overleftarrow{\boldsymbol{\nabla}}'\times\overleftarrow{\boldsymbol{\nabla}}'-\frac{\omega^2}{c^2}\right]-i\mu_0\omega\int d^3\boldsymbol{s}\,\boldsymbol{G}(\boldsymbol{r},\boldsymbol{s},\omega)\cdot\boldsymbol{Q}(\boldsymbol{s},\boldsymbol{r}',\omega)=\boldsymbol{\delta}(\boldsymbol{r}-\boldsymbol{r}').$$
 (2.76)

By the same reasoning as the reciprocal case, after exchanging r and r' the first term can be rewritten,

$$G_{ij}(\mathbf{r}',\mathbf{r},\omega)\left[\times\overleftarrow{\boldsymbol{\nabla}}\times\overleftarrow{\boldsymbol{\nabla}}-\frac{\omega^2}{c^2}\right]_{jk}=\left[\boldsymbol{\nabla}\times\boldsymbol{\nabla}\times-\frac{\omega^2}{c^2}\right]_{kj}\boldsymbol{G}_{ji}^{\mathrm{T}}(\mathbf{r}',\mathbf{r},\omega).$$
(2.77)

<sup>&</sup>lt;sup>1</sup>The first term of the left hand side can be written using index notation as  $\partial_k \varepsilon_{kli} \mu^{-1} \partial_m \varepsilon_{mjl}$  and the first term of the right side is  $\varepsilon_{jno} \partial_n \mu^{-1} \varepsilon_{opi} \partial_p$ . Making the index replacements  $p \to k$ ,  $o \to l$  and  $n \to m$  in the right hand side and rearranging, these expressions can be shown to be equivalent.



Figure 2.1: Figure adapted from [4]. Distinction between bulk  $G^{(0)}$  and scattering  $G^{(1)}$ Green's tensors for piecewise homogeneous media.

However, we cannot do the same for the second term, since  $Q_{ij}(\mathbf{r}, \mathbf{s}) = Q_{ji}(\mathbf{s}, \mathbf{r})$  does not necessarily hold for non-reciprocal media. Therefore, we deduce that Lorentz reciprocity does not hold for non-reciprocal media,

$$G_{ij}^{\mathrm{T}}(\boldsymbol{r}',\boldsymbol{r},\omega) = G_{ji}(\boldsymbol{r}',\boldsymbol{r},\omega) \neq G_{ij}(\boldsymbol{r},\boldsymbol{r}',\omega).$$
(2.78)

Physically, this means the Green's tensor that connects a source at position  $\mathbf{r}_1$  with orientation  $\mathbf{e}_1$  with the induced field at position  $\mathbf{r}_2$  with orientation  $\mathbf{e}_2$  is not the same Green's tensor that connects the source and field in the reverse situation, with the positions and orientation exchanged,  $\mathbf{e}_2 \cdot \mathbf{G}(\mathbf{r}_2, \mathbf{r}_1, \omega) \cdot \mathbf{e}_1 \neq \mathbf{e}_1 \cdot \mathbf{G}(\mathbf{r}_1, \mathbf{r}_2, \omega) \cdot \mathbf{e}_2$ .

Lorentz reciprocity is the defining difference between non-reciprocal and reciprocal media, and is a property that will be extensively used in later chapters.

#### Piecewise media

In later chapters, we study environments made up of piecewise homogeneous bodies, in which we can assume that  $\varepsilon(\mathbf{r}, \omega)$  and  $\mu(\mathbf{r}, \omega)$  are piecewise constant functions of position. We divide the volume of interest into homogeneous regions  $V_i$ , with corresponding permittivity and permeability functions  $\varepsilon_i(\omega)$  and  $\mu_i(\omega)$ , as in figure 2.1.

If the field point  $\mathbf{r}$  is in the region  $V_i$  but the source point  $\mathbf{r'}$  is not, then  $\delta(\mathbf{r} - \mathbf{r'}) \to 0$ , so the left-hand side of the defining Helmholtz equations, (2.62) and (2.68), are zero. The solution of the homogeneous Helmholtz equations is known as the scattering Green's tensor  $\mathbf{G}^{(1)}(\mathbf{r}, \mathbf{r'}, \omega)$ . If instead both  $\mathbf{r}$  and  $\mathbf{r}'$  are in  $V_i$ , then the Helmholtz equations are inhomogeneous, and a particular solution must be added to  $\mathbf{G}^{(1)}$  to reach the full solution. The particular solution is chosen to be the case when  $V_i$  would extend over all space, and is called the bulk Green's tensor  $\mathbf{G}^{(0)}(\mathbf{r}, \mathbf{r}', \omega)$ . For a piecewise homogeneous system, the full solution can be written as,

$$\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \begin{cases} \boldsymbol{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) + \boldsymbol{G}^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega) & \text{for } \boldsymbol{r} \in V_i \text{ and } \boldsymbol{r}' \in V_i \\ \boldsymbol{G}^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega) & \text{for } \boldsymbol{r} \in V_i \text{ and } \boldsymbol{r}' \notin V_i \end{cases}$$
(2.79)

So,  $\boldsymbol{G}^{(0)}$  describes the field at  $\boldsymbol{r}$  as if it had been induced by a source at  $\boldsymbol{r}'$  if all space was filled with the homogeneous material making up  $V_i$ .  $\boldsymbol{G}^{(1)}$  then gives the field contribution due to reflection at and transmission through regions with different magneto-electric properties. These two contributions are represented in figure 2.1.

In the rest of this work, we will be considering setups consisting of a single homogeneous body in a vacuum where both the source and observation points are in the vacuum. This means that  $G^{(0)}(\mathbf{r}, \mathbf{r}', \omega)$  will be the free-space Green's tensor given in appendix B.1, and  $G^{(1)}(\mathbf{r}, \mathbf{r}', \omega)$  will be determined by the geometry and material properties of the body in question.

#### 2.2.2 Integral relations

In this section, we derive two important integral relations that will be useful in later chapters. The first is one that holds for "simple" reciprocal media only, and the second also holds when more "general" non-reciprocal media are considered.

#### **Reciprocal Media**

Beginning with the defining equation of the Green's tensor for "simple"<sup>2</sup> reciprocal media (2.13) for  $G(s, r', \omega)$ , multiplying by  $G^*(r, s, \omega)$  from the left and integrating over s we obtain,

$$\int d^{3}s \, \boldsymbol{G}^{*}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \left[ \boldsymbol{\nabla}_{s} \times \frac{1}{\mu(\boldsymbol{s}, \omega)} \boldsymbol{\nabla}_{s} \times -\frac{\omega^{2}}{c^{2}} \varepsilon(\boldsymbol{s}, \omega) \right] \boldsymbol{G}(\boldsymbol{s}, \boldsymbol{r}', \omega) = \int d^{3}s \, \boldsymbol{G}^{*}(\boldsymbol{r}, \boldsymbol{s}, \omega) \boldsymbol{\delta}(\boldsymbol{s} - \boldsymbol{r}') d^{3}s \, \boldsymbol{G}^{*}(\boldsymbol{r}, \boldsymbol{s}, \omega) \left[ \times \overleftarrow{\boldsymbol{\nabla}}_{s} \cdot \frac{1}{\mu(\boldsymbol{s}, \omega)} \boldsymbol{\nabla}_{s} \times +\frac{\omega^{2}}{c^{2}} \varepsilon(\boldsymbol{s}, \omega) \right] \boldsymbol{G}(\boldsymbol{s}, \boldsymbol{r}', \omega) = \boldsymbol{G}^{*}(\boldsymbol{r}, \boldsymbol{r}', \omega),$$

$$(2.80)$$

<sup>&</sup>lt;sup>2</sup>As explained at the beginning of section 2.1.1, we have defined "simple" media to be magnetodielectric, local (2.64) and isotropic (2.65) with zero cross-susceptibilities  $\boldsymbol{\xi}_1 = 0 = \boldsymbol{\xi}_2$ .

where we have integrated by parts and made use of the Green's tensor's defining boundary condition (2.14). Taking the complex conjugate of (2.71) for  $G(\mathbf{r}, \mathbf{s}, \omega)$ , multiplying with  $G(\mathbf{s}, \mathbf{r}', \omega)$  from the right and again integrating over  $\mathbf{s}$  we find,

$$-\int d^3 \boldsymbol{s} \, \boldsymbol{G}^*(\boldsymbol{r}, \boldsymbol{s}, \omega) \left[ \times \overleftarrow{\boldsymbol{\nabla}}_s \frac{1}{\mu^*(\boldsymbol{s}, \omega)} \cdot \boldsymbol{\nabla}_s \times + \frac{\omega^2}{c^2} \varepsilon^*(\boldsymbol{s}, \omega) \right] \boldsymbol{G}(\boldsymbol{s}, \boldsymbol{r}', \omega) = \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega), \quad (2.81)$$

where again we have applied partial integration and the boundary condition (2.14). Now subtracting (2.80) from (2.81) we obtain,

$$-\int d^{3}\boldsymbol{s} \left\{ \frac{\operatorname{Im} \boldsymbol{\mu}(\boldsymbol{s},\omega)}{|\boldsymbol{\mu}(\boldsymbol{s},\omega)|^{2}} \left[ \boldsymbol{G}^{*}(\boldsymbol{r},\boldsymbol{s},\omega) \times \overleftarrow{\boldsymbol{\nabla}}_{\boldsymbol{s}} \right] \cdot \left[ \boldsymbol{\nabla}_{\boldsymbol{s}} \times \boldsymbol{G}(\boldsymbol{s},\boldsymbol{r}',\omega) \right] - \frac{\omega^{2}}{c^{2}} \operatorname{Im} \boldsymbol{\varepsilon}(\boldsymbol{s},\omega) \boldsymbol{G}^{*}(\boldsymbol{r},\boldsymbol{s},\omega) \cdot \boldsymbol{G}(\boldsymbol{s},\boldsymbol{r}',\omega) \right\} = \operatorname{Im} \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega)$$
(2.82)

where we have used  $\text{Im } z = (z - z^*)/(2i)$ .

We can use this result to derive an integral relation for the coefficients  $G_e$  and  $G_m$ , defined by (2.37) and (2.38) respectively. We calculate,

$$\boldsymbol{G}_{e}(\boldsymbol{r},\boldsymbol{s},\omega)\cdot\boldsymbol{G}_{e}^{*T}(\boldsymbol{r}',\boldsymbol{s},\omega) = \frac{\omega^{4}}{c^{4}}\frac{\hbar}{\pi\varepsilon_{0}}\operatorname{Im}\varepsilon(\boldsymbol{s},\omega)\boldsymbol{G}(\boldsymbol{r},\boldsymbol{s},\omega)\cdot\boldsymbol{G}^{*T}(\boldsymbol{r}',\boldsymbol{s},\omega), \quad (2.83)$$

where we have made use of Lorentz reciprocity (2.75), and

$$\boldsymbol{G}_{m}(\boldsymbol{r},\boldsymbol{s},\omega)\cdot\boldsymbol{G}_{m}^{*T}(\boldsymbol{r}',\boldsymbol{s},\omega) = -\frac{\omega^{2}}{c^{2}}\frac{\hbar}{\pi\varepsilon_{0}}\frac{\mathrm{Im}\,\mu(\boldsymbol{s},\omega)}{|\mu(\boldsymbol{s},\omega)|^{2}}\left[\boldsymbol{G}(\boldsymbol{r},\boldsymbol{s},\omega)\times\overleftarrow{\boldsymbol{\nabla}}_{s}\right]\cdot\left[\boldsymbol{\nabla}_{s}\times\boldsymbol{G}^{*}(\boldsymbol{s},\boldsymbol{r}',\omega)\right],\qquad(2.84)$$

where we have used  $\left[ \boldsymbol{G}^*(\boldsymbol{r}',\boldsymbol{s},\omega) \times \overleftarrow{\boldsymbol{\nabla}}_s \right]^T = -\boldsymbol{\nabla}_s \times \boldsymbol{G}^*(\boldsymbol{s},\boldsymbol{r}',\omega)$  for reciprocal media<sup>3</sup>. Summing these results and differentiating over s before comparing with the complex conjugate of (2.82), we can see that,

$$\sum_{\lambda=e,m} \int d^3 \boldsymbol{s} \, \boldsymbol{G}_{\lambda}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \boldsymbol{G}_{\lambda}^{*T}(\boldsymbol{r}', \boldsymbol{s}, \omega) = \frac{\hbar \mu_0}{\pi} \omega^2 \operatorname{Im} \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega), \qquad (2.85)$$

where we have again made use of the identity  $\varepsilon_0 \mu_0 = c^{-2}$ . This relation will be made use of later on in Chapters 3 and 5.

<sup>3</sup>This can be verified using index notation:  $\begin{bmatrix} \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}') \times \overleftarrow{\boldsymbol{\nabla}}' \end{bmatrix}^T = \begin{bmatrix} \boldsymbol{G}_{ij}(\boldsymbol{r},\boldsymbol{r}') \boldsymbol{e}_i \boldsymbol{e}_j \times \partial_k \boldsymbol{e}_k \end{bmatrix}^T = \begin{bmatrix} \boldsymbol{G}_{ij}(\boldsymbol{r},\boldsymbol{r}') \boldsymbol{e}_i \boldsymbol{e}_i \boldsymbol{e}_j \times \partial_k \boldsymbol{e}_k \end{bmatrix}^T = \begin{bmatrix} \boldsymbol{G}_{ij}(\boldsymbol{r},\boldsymbol{r}') \partial_k \varepsilon_{jkl} \boldsymbol{e}_i \boldsymbol{e}_l \boldsymbol{e}_l = -\partial_k \varepsilon_{kjl} \boldsymbol{G}_{ji}(\boldsymbol{r}',\boldsymbol{r}) \boldsymbol{e}_l \boldsymbol{e}_i = -\boldsymbol{\nabla}' \times \boldsymbol{G}(\boldsymbol{r}',\boldsymbol{r}) \text{ where we have used } \varepsilon_{jkl} = \varepsilon_{kjl} \text{ and Lorentz reciprocity means that } \boldsymbol{G}_{ij}(\boldsymbol{r},\boldsymbol{r}') = \boldsymbol{G}_{ji}(\boldsymbol{r}',\boldsymbol{r}) \text{ for reciprocal media.} \end{bmatrix}$ 

#### Non-reciprocal media

We now begin with the general Helmholtz equation for the Green's tensor (2.62),

$$\left[\nabla \times \nabla \times -\frac{\omega^2}{c^2}\right] \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega) - i\mu_0 \omega \int d^3 \boldsymbol{s} \boldsymbol{Q}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \boldsymbol{G}(\boldsymbol{s}, \boldsymbol{r}', \omega) = \boldsymbol{\delta}(\boldsymbol{r} - \boldsymbol{r}'). \quad (2.86)$$

where Q is defined in (2.63). It is useful to rewrite this expression as,

$$\hat{\boldsymbol{H}} \cdot \hat{\boldsymbol{G}} = \hat{\boldsymbol{I}},\tag{2.87}$$

where we have defined the Helmholtz operator  $\hat{H}$  and the Green operator  $\hat{G}$ , respectively, as,

$$\langle \boldsymbol{r} | \, \hat{\boldsymbol{H}} \, \big| \boldsymbol{r}' \rangle = \left[ \nabla \times \nabla \times -\frac{\omega^2}{c^2} \right] \boldsymbol{\delta}(\boldsymbol{r} - \boldsymbol{r}') - i\mu_0 \omega \boldsymbol{Q}(\boldsymbol{r}, \boldsymbol{r}', \omega), \qquad (2.88)$$

$$\langle \boldsymbol{r} | \, \hat{\boldsymbol{G}} \, | \boldsymbol{r}' \rangle = \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega),$$
(2.89)

and  $\delta(\mathbf{r} - \mathbf{r}') = \text{diag}(1, 1, 1)\delta(\mathbf{r} - \mathbf{r}')$ . As in the reciprocal case, the fact that the Green's tensor is the right-inverse of the Helmholtz operator means that it is also the left-inverse,

$$\hat{\boldsymbol{G}} \cdot \hat{\boldsymbol{H}} = \hat{\boldsymbol{I}}.\tag{2.90}$$

If we multiply this expression from the right by  $\hat{G}^{\dagger}$  and multiply the hermitian conjugate of this expression from the left by  $\hat{G}$  and subtract those from each other, we find,

$$\hat{\boldsymbol{G}} \cdot \hat{\boldsymbol{H}} \cdot \hat{\boldsymbol{G}}^{\dagger} = \hat{\boldsymbol{G}}^{\dagger}, \quad \hat{\boldsymbol{G}} \cdot \hat{\boldsymbol{H}}^{\dagger} \cdot \hat{\boldsymbol{G}}^{\dagger} = \hat{\boldsymbol{G}},$$
(2.91)

$$\hat{\boldsymbol{G}} \cdot \left(\hat{\boldsymbol{H}} - \hat{\boldsymbol{H}}^{\dagger}\right) \cdot \hat{\boldsymbol{G}}^{\dagger} = \hat{\boldsymbol{G}}^{\dagger} - \hat{\boldsymbol{G}}.$$
(2.92)

We now need to write this expression in coordinate space. Beginning with the right hand side of (2.92),

$$\langle \boldsymbol{r} | \, \hat{\boldsymbol{G}}^{\dagger} - \hat{\boldsymbol{G}} \, \big| \boldsymbol{r}' \rangle = \left( \langle \boldsymbol{r}' | \, \hat{\boldsymbol{G}} \, | \boldsymbol{r} \rangle \right)^{\dagger} - \langle \boldsymbol{r} | \, \hat{\boldsymbol{G}} \, \big| \boldsymbol{r}' \rangle$$
  
=  $\boldsymbol{G}^{\dagger}(\boldsymbol{r}', \boldsymbol{r}, \omega) - \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)$   
=  $-2i \, \mathcal{I} \mathrm{m} \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega),$  (2.93)

where we have made use of the definition of general imaginary part of a tensor field (2.51). We now look at the expanded left hand side of (2.92), split into,

$$\langle \boldsymbol{r} | \, \hat{\boldsymbol{G}} \cdot \hat{\boldsymbol{H}} \cdot \hat{\boldsymbol{G}}^{\dagger} \, | \boldsymbol{r}' \rangle = \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \, \langle \boldsymbol{r} | \, \hat{\boldsymbol{G}} \, | \boldsymbol{s} \rangle \, \langle \boldsymbol{s} | \, \hat{\boldsymbol{H}} \, | \boldsymbol{s}' \rangle \left( \langle \boldsymbol{r}' | \, \hat{\boldsymbol{G}} \, | \boldsymbol{s}' \rangle \right)^{\dagger}$$

$$= \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \left[ \nabla_{\boldsymbol{s}} \times \nabla_{\boldsymbol{s}} \times -\frac{\omega^{2}}{c^{2}} \right] \boldsymbol{I} \cdot \boldsymbol{G}^{\dagger}(\boldsymbol{r}', \boldsymbol{s}', \omega)$$

$$- i\mu_{0}\omega \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \boldsymbol{Q}(\boldsymbol{s}, \boldsymbol{s}', \omega) \cdot \boldsymbol{G}^{\dagger}(\boldsymbol{r}', \boldsymbol{s}', \omega), \quad (2.94)$$

and

$$\langle \boldsymbol{r} | \, \hat{\boldsymbol{G}} \cdot \hat{\boldsymbol{H}}^{\dagger} \cdot \hat{\boldsymbol{G}}^{\dagger} \, | \boldsymbol{r}' \rangle = \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \, \langle \boldsymbol{r} | \, \hat{\boldsymbol{G}} \, | \boldsymbol{s} \rangle \left( \langle \boldsymbol{s}' | \, \hat{\boldsymbol{H}} \, | \boldsymbol{s} \rangle \right)^{\dagger} \left( \langle \boldsymbol{r}' | \, \hat{\boldsymbol{G}} \, | \boldsymbol{s}' \rangle \right)^{\dagger}$$

$$= \int d^{3}\boldsymbol{s} \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \left[ \nabla_{\boldsymbol{s}} \times \nabla_{\boldsymbol{s}} \times -\frac{\omega^{2}}{c^{2}} \right] \boldsymbol{I} \cdot \boldsymbol{G}^{\dagger}(\boldsymbol{r}', \boldsymbol{s}', \omega)$$

$$+ i\mu_{0}\omega \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \boldsymbol{Q}^{\dagger}(\boldsymbol{s}', \boldsymbol{s}, \omega) \cdot \boldsymbol{G}^{\dagger}(\boldsymbol{r}', \boldsymbol{s}', \omega).$$

$$(2.95)$$

Subtracting these from each other we obtain,

$$\langle \boldsymbol{r} | \, \hat{\boldsymbol{G}} \cdot \left( \hat{\boldsymbol{H}} - \hat{\boldsymbol{H}}^{\dagger} \right) \cdot \hat{\boldsymbol{G}}^{\dagger} \, | \boldsymbol{r}' \rangle$$

$$= -i\mu_{0}\omega \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \left[ \boldsymbol{Q}(\boldsymbol{s}, \boldsymbol{s}', \omega) + \boldsymbol{Q}^{\dagger}(\boldsymbol{s}', \boldsymbol{s}, \omega) \right] \cdot \boldsymbol{G}^{\dagger}(\boldsymbol{r}', \boldsymbol{s}', \omega)$$

$$= -2i\mu_{0}\omega \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \mathcal{R}e\left[ \boldsymbol{Q}(\boldsymbol{s}, \boldsymbol{s}', \omega) \right] \cdot \boldsymbol{G}^{\dagger}(\boldsymbol{r}', \boldsymbol{s}', \omega),$$

$$(2.96)$$

where we have made use of the general definition of real and imaginary parts of a tensor (2.50). Now equating (2.93) and (2.96), we reach the integral relation,

$$\int d^3 \boldsymbol{s} \int d^3 \boldsymbol{s}' \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \mathcal{R}e\left[\boldsymbol{Q}(\boldsymbol{s}, \boldsymbol{s}', \omega)\right] \cdot \boldsymbol{G}(\boldsymbol{r}', \boldsymbol{s}', \omega) = \mathcal{I}m\left[\boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)\right], \qquad (2.97)$$

in agreement with [65]. This relation will be made use of in Chapter 4.

### 2.3 Summary and Conclusion

In this chapter, we have provided an overview of the quantization of the electric field in the presence of "simple" reciprocal media, and also covered how the method must be adapted to include more "general" non-reciprocal media. We then established the equivalence of the ways that the Green's tensor are defined for each medium type, before looking at a few of

its properties that we will make use of later. In the next chapter, we investigate a system of two bodies near a reciprocal environment and look at how the environment can affect the rate of energy transfer between them.

# CHAPTER 3

# Two-body RET in a Reciprocal Environment

In this chapter, we look at two-body resonant energy transfer (RET) and how macroscopic environments can affect the rate of this interaction. We focus on how the system is affected by "simple"<sup>1</sup> reciprocal media only in this chapter (see subsection 2.1.1).

In order to determine a formula for the rate of energy transfer, we begin with the calculation of the matrix element, firstly via standard perturbation theory and then the alternative method of canonical perturbation theory, demonstrating that the same result is obtained for each. Macroscopic QED is then applied to the Fermi Golden Rule to reach a formula for the rate of energy transfer between two bodies in an arbitrary macroscopic environment consisting of reciprocal media.

As a demonstration of some proof-of-principles, we then calculate an analytic expression for the rate of energy transfer between two bodies in a vacuum, including the retarded and non-retarded limits. We also provide analytic expressions for rate of energy transfer between two bodies in a colinear arrangement near a semi-infinite half-space in the retarded and non-retarded limits.

<sup>&</sup>lt;sup>1</sup>As explained at the beginning of section 2.1.1, we have defined "simple" media to be magnetodielectric, local (2.64) and isotropic (2.65) with zero cross-susceptibilities  $\boldsymbol{\xi}_1 = 0 = \boldsymbol{\xi}_2$ .



Figure 3.1: System of two two-level atoms/molecules transmitting energy through the electromagnetic field due to resonance energy transfer. The donor begins in an excited energy state and the acceptor in the ground state. Energy is emitted from the donor, transmitted through the field and absorbed by the acceptor which becomes excited.

### 3.1 Calculation of Matrix Element

This section focuses on the calculation of a general expression for the matrix element for the process of resonance energy transfer between two bodies, which will then be used in the Fermi Golden Rule to obtain a formula for the rate of interaction.

We consider the simplest RET system, made up of two two-level atoms/molecules, a donor and an acceptor. Energy from the donor is released via spontaneous decay and transferred to the acceptor via the transmission of a virtual photon, as shown in figure 3.1. Such a system is modelled by the Hamiltonian,

$$H = H_0 + H_{\text{int}}$$
$$= H_0 + H_{\text{int}}^{\text{A}} + H_{\text{int}}^{\text{D}}, \qquad (3.1)$$

where

$$H_0 = H_{\rm rad} + H_{\rm mol}^{\rm A} + H_{\rm mol}^{\rm D}, \qquad (3.2)$$

 $H_{\rm rad}$  is the Hamiltonian of the radiation field,  $H_{\rm mol}^{\xi}$  is the Hamiltonian of the molecule  $\xi$  for which we assume that the eigenstates are known, and,

$$H_{\rm int}^{\xi} = -\hat{\boldsymbol{d}}_{\xi} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\xi}), \qquad (3.3)$$

where  $\hat{d}_{\xi}$  is the transition dipole moment of molecule  $\xi$ , and  $\hat{E}(r_{\xi})$  is the electric field at the position, r, of the molecule  $\xi$ . The initial and final states of the system are chosen as,

$$|i\rangle = |e_{\rm D}, g_{\rm A}; 0\rangle, \qquad |f\rangle = |g_{\rm D}, e_{\rm A}; 0\rangle, \qquad (3.4)$$

where  $g_{\rm D}(g_{\rm A})$  denotes the ground state of the donor (acceptor),  $e_{\rm D}(e_{\rm A})$  the excited state of
the donor (acceptor) and 0 the ground state of the electromagnetic field.

The aim of this section is to calculate an expression for the matrix element for this interaction that can then be applied to the Fermi Golden Rule to obtain the energy transfer rate. We will first use the conventional method in section 3.1.1, which is second-order perturbation theory, and then apply an alternate method in section 3.1.2 which makes use of canonical transformations. We will see that both methods produce the same end result.

#### 3.1.1 Standard Perturbation Theory

Here, we find the matrix element for the resonance energy transfer process between two bodies using standard perturbation theory [68, 69]. A single RET interaction involves two light-matter events, namely the emission of the virtual photon from the first molecule, and the absorption of the photon by the second. Since the interaction Hamiltonian (3.3) is linear in the electric field operator, we must have at least two actions of  $H_{\rm int}$  to link the initial and final states, meaning we require at least second-order perturbation theory. Therefore, the matrix element is [68],

$$M_{fi} = \sum_{I} \frac{\langle f | H_{\text{int}} | I \rangle \langle I | H_{\text{int}} | i \rangle}{E_i - E_I}, \qquad (3.5)$$

summing over a complete set of intermediate states I. Due to the linearity of  $H_{\text{int}}$  in  $\hat{d}$ , only two types of intermediate states contribute,

$$|I_1\rangle = |g_{\rm D}, g_{\rm A}; 1_{\rm F}\rangle, \qquad |I_2\rangle = |e_{\rm D}, e_{\rm A}; 1_{\rm F}\rangle.$$
(3.6)

The first intermediate state type,  $|I_1\rangle$ , corresponds to the resonant interaction depicted in figure 3.2a, where the excitation is transmitted through the field while both molecules are in their ground state. In this instance, the donor emits energy, it is transferred through the field, and then absorbed by the acceptor, and is therefore energy conserving in each step. However, for the second type of intermediate state shown figure 3.2b,  $|I_2\rangle$ , the excitation is transmitted through the field while both molecules are excited, which means an additional excitation is generated in the system during the intermediate step. This process is not energy conserving in all steps, and is therefore known as the off-resonant interaction. However, the violation of energy conservation is rectified at the final step, meaning the overall process is allowed.

We begin by considering only the energy denominators of the matrix element contributions. For the initial and final states, the field is in the ground state and the energy comes from the



Figure 3.2: The two possible time-orderings for two-body resonant energy transfer.

molecular excitations only,

$$E_i = E_{e_{\rm D}} + E_{q_{\rm A}}, \qquad E_f = E_{q_{\rm D}} + E_{e_{\rm A}}.$$
 (3.7)

For the resonant intermediate state, both the molecules are in the ground state, and the field contains a single photon, so the energy is calculated to be,

$$E_{I_1} = E_{g_{\rm D}} + E_{g_{\rm A}} + \hbar ck. \tag{3.8}$$

We therefore find the energy denominators for the resonant and off-resonant time-orderings to respectively be,

$$E_i - E_{I_1} = E_{e_{\rm D}} - E_{g_{\rm D}} - \hbar ck = E_{eg} - \hbar ck, \qquad (3.9)$$

$$E_i - E_{I_2} = E_{g_A} - E_{e_A} - \hbar ck = -(E_{eg} + \hbar ck), \qquad (3.10)$$

where we have defined  $E_{eg} = E_{e_{\xi}} - E_{g_{\xi}}$  as the transition energy between the molecular excited and ground states. We can therefore rewrite the matrix element by splitting the two time-orderings, giving us,

$$M_{fi} = -\sum_{I_1, I_2} \left[ \frac{\langle f | H_{\text{int}} | I_1 \rangle \langle I_1 | H_{\text{int}} | i \rangle}{\hbar ck - E_{eg}} + \frac{\langle f | H_{\text{int}} | I_2 \rangle \langle I_2 | H_{\text{int}} | i \rangle}{\hbar ck + E_{eg}} \right], \quad (3.11)$$

where the sum is over all accessible photon modes for each of the intermediate step type.

Now considering only the first term in the numerator of the resonant time-ordering, we can

substitute in the definition of the interaction Hamiltonian via (3.3) to obtain,

$$\langle f | H_{\text{int}} | I_1 \rangle = \langle g_{\text{D}}, e_{\text{A}}; 0 | - \hat{\boldsymbol{d}}_{\text{D}} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) - \hat{\boldsymbol{d}}_{\text{A}} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) | g_{\text{D}}, g_{\text{A}}; 1_{\text{F}} \rangle$$

$$= - \langle g_{\text{D}} | \hat{\boldsymbol{d}}_{\text{D}} | g_{\text{D}} \rangle \langle e_{\text{A}} | g_{\text{A}} \rangle \cdot \langle 0 | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) | 1_{\text{F}} \rangle - \langle g_{\text{D}} | g_{\text{D}} \rangle \langle e_{\text{A}} | \hat{\boldsymbol{d}}_{\text{A}} | g_{\text{A}} \rangle \cdot \langle 0 | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) | 1_{\text{F}} \rangle$$

$$= - \langle e_{\text{A}} | \hat{\boldsymbol{d}}_{\text{A}} | g_{\text{A}} \rangle \cdot \langle 0 | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) | 1_{\text{F}} \rangle ,$$

$$(3.12)$$

where we have used that  $\langle g_{\xi} | e_{\xi} \rangle = 0$  and  $\langle g_{\xi} | g_{\xi} \rangle = 1$  for orthogonal molecular states  $e_{\xi}$  and  $g_{\xi}$ . We note that the above can be rewritten as,

$$\langle f | H_{\text{int}} | I_1 \rangle = \langle f | - \hat{\boldsymbol{d}}_{\text{A}} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) | I_1 \rangle = \langle f | H_{\text{int}}^{\text{A}} | I_1 \rangle.$$
 (3.13)

Similarly for the second term in the resonant time ordering numerator we find that,

$$\langle I_{1} | H_{\text{int}} | i \rangle = \langle g_{\text{D}}, g_{\text{A}}; 1_{\text{F}} | - \hat{\boldsymbol{d}}_{\text{D}} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) - \hat{\boldsymbol{d}}_{\text{A}} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) | e_{\text{D}}, g_{\text{A}}; 0 \rangle$$

$$= - \langle g_{\text{D}} | \hat{\boldsymbol{d}}_{\text{D}} | e_{\text{D}} \rangle \langle g_{\text{A}} | g_{\text{A}} \rangle \cdot \langle 1_{\text{F}} | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) | 0 \rangle - \langle g_{\text{D}} | e_{\text{D}} \rangle \langle g_{\text{A}} | \hat{\boldsymbol{d}}_{\text{A}} | g_{\text{A}} \rangle \cdot \langle 1_{\text{F}} | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) | 0 \rangle$$

$$= - \langle g_{\text{D}} | \hat{\boldsymbol{d}}_{\text{D}} | e_{\text{D}} \rangle \cdot \langle 1_{\text{F}} | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) | 0 \rangle$$

$$= \langle I_{1} | H_{\text{int}}^{\text{D}} | i \rangle .$$

$$(3.14)$$

Combining (3.13) and (3.14) we find that we can write the resonant component of the matrix element (3.11) as,

$$M_{fi}^{\text{res}} = \sum_{I_1} \frac{\langle f | H_{\text{int}}^{\text{A}} | I_1 \rangle \langle I_1 | H_{\text{int}}^{\text{D}} | i \rangle}{E_{eg} - \hbar ck}.$$
(3.15)

Using the same reasoning for the off-resonant contribution of (3.11) we find that,

$$M_{fi}^{\text{off}} = \sum_{I_2} -\frac{\langle f | H_{\text{int}}^{\text{D}} | I_2 \rangle \langle I_2 | H_{\text{int}}^{\text{A}} | i \rangle}{E_{eg} + \hbar ck}, \qquad (3.16)$$

which combined with (3.15) gives us a formula for the matrix element for two-body resonant energy transfer,

$$M_{fi} = \sum_{I_1, I_2} -\frac{\langle f | H_{\text{int}}^{\text{A}} | I_1 \rangle \langle I_1 | H_{\text{int}}^{\text{D}} | i \rangle}{\hbar ck - E_{eg}} - \frac{\langle f | H_{\text{int}}^{\text{D}} | I_2 \rangle \langle I_2 | H_{\text{int}}^{\text{A}} | i \rangle}{E_{eg} + \hbar ck}$$
(3.17)

This can alternatively be written as,

$$M_{fi} = -\sum_{k} \langle f | \left( \frac{H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}}}{\hbar ck - E_{eg}} + \frac{H_{\text{int}}^{\text{D}} H_{\text{int}}^{\text{A}}}{\hbar ck + E_{eg}} \right) | i \rangle, \qquad (3.18)$$

where we have used  $\sum_{I} |I\rangle \langle I| = 1$ . This is in agreement with [68], and we will make use of this form in section 5.1.

#### 3.1.2 Canonical Perturbation Theory

An alternative method for calculating the matrix element of an interaction involves the use of canonical (unitary) transformations. These are operations that satisfy  $\hat{U}\hat{U}^{\dagger} = 1$  [68, 70]. In this work, we restrict our discussion to transformations of the form  $e^{iS}$  where S is a Hermitian operator, which act on the generalized coordinate q and conjugate momentum p via,

$$q_{\rm new} = e^{iS} q e^{-iS}, \quad p_{\rm new} = e^{iS} p e^{-iS},$$
 (3.19)

and preserve the commutator relation  $[q, p] = i\hbar$ , as can be easily demonstrated,

$$[q_{\text{new}}, p_{\text{new}}] = e^{iS}[q, p]e^{-iS} = i\hbar e^{iS}e^{-iS} = i\hbar.$$
(3.20)

A new Hamiltonian is then obtained in the same way,

$$H_{\rm new} = e^{iS} H e^{-iS}.$$
(3.21)

We are aiming to create a new effective Hamiltonian that encodes the information for the two one-photon interactions into one term, so this new coupling term will be second order in the electric dipole. We express the Hamiltonian as  $H = H_0 + H_{\text{int}}$  where  $H_{\text{int}} = H_{\text{int}}^{\text{A}} + H_{\text{int}}^{\text{D}}$  and perform a unitary transformation via (3.21),

$$H_{\text{new}} = e^{iS} H e^{-iS} = \sum_{n=0}^{\infty} \frac{1}{n!} [iS, [iS, ...H]]$$
  
=  $H_0 + H_{\text{int}} + [iS, H_0] + [iS, H_{\text{int}}] + \frac{1}{2} [iS, [iS, H_0]] + ...,$  (3.22)

where S is assumed to be first order in the electric dipole moment. We seek a Hamiltonian of second order in  $H_{\text{int}}$  (and thereby  $\hat{d}$ ), so we eliminate the first order  $H_{\text{int}}$  term by choosing  $[iS, H_0] = -H_{\text{int}}$ . This leaves, up to second order in the electric dipole,

$$H_{\rm new} = H_0 + \frac{1}{2} [iS, H_{\rm int}].$$
 (3.23)

From our chosen definition of the generator, for initial state  $|M\rangle$  and final state  $|N\rangle$  we have,

$$\langle N | [iS, H_0] | M \rangle = \langle N | iSH_0 | M \rangle - \langle N | H_0 iS | M \rangle = (E_M - E_N) \langle N | iS | M \rangle, \qquad (3.24)$$

where we have used  $H_0 |M\rangle = E_M |M\rangle$  and  $H_0 |N\rangle = E_N |N\rangle$ . We therefore have a definition of the generator S,

$$\langle N | iS | M \rangle = \frac{\langle N | H_{\text{int}} | M \rangle}{E_N - E_M}, \qquad (3.25)$$

that we can use to calculate the expectation value of the new second order interaction term,

$$\frac{1}{2} \langle N | [iS, H_{int}] | M \rangle = \frac{1}{2} \left( \langle N | iSH_{int} | M \rangle - \langle N | H_{int} iS | M \rangle \right) 
= \frac{1}{2} \sum_{I} \left( \langle N | iS | I \rangle \langle I | H_{int} | M \rangle - \langle N | H_{int} | I \rangle \langle I | iS | M \rangle \right) 
= -\frac{1}{2} \sum_{I} \langle N | H_{int} | I \rangle \langle I | H_{int} | M \rangle \left( \frac{1}{E_{I} - E_{N}} + \frac{1}{E_{I} - E_{M}} \right), \quad (3.26)$$

where we have used  $\sum_{I} |I\rangle \langle I| = 1$ .

Now applying to two-body resonant energy transfer using initial and final states (3.4) and intermediate states (3.6) we find,

$$\frac{1}{2} \langle f | [iS, H_{int}] | i \rangle = -\frac{1}{2} \sum_{I_1, I_2} \left[ \langle f | H_{int} | I_1 \rangle \langle I_1 | H_{int} | i \rangle \left( \frac{1}{E_{I_1} - E_f} + \frac{1}{E_{I_1} - E_i} \right) + \langle f | H_{int} | I_2 \rangle \langle I_2 | H_{int} | i \rangle \left( \frac{1}{E_{I_2} - E_f} + \frac{1}{E_{I_2} - E_i} \right) \right] \\
= -\frac{1}{2} \sum_{I_1, I_2} \left[ \langle f | H_{int} | I_1 \rangle \langle I_1 | H_{int} | i \rangle \left( \frac{1}{\hbar ck - E_{eg}} + \frac{1}{\hbar ck - E_{eg}} \right) + \langle f | H_{int} | I_2 \rangle \langle I_2 | H_{int} | i \rangle \left( \frac{1}{\hbar ck + E_{eg}} + \frac{1}{\hbar ck + E_{eg}} \right) \right] \\
= -\sum_{I_1, I_2} \left[ \frac{\langle f | H_{int} | I_1 \rangle \langle I_1 | H_{int} | i \rangle}{\hbar ck - E_{eg}} + \frac{\langle f | H_{int} | I_2 \rangle \langle I_2 | H_{int} | i \rangle}{\hbar ck - E_{eg}} \right].$$
(3.27)

We note that this is in agreement with (3.11), meaning we achieve the same matrix element (3.18) using this method, showing its validity as an alternative to standard perturbation theory. In this situation this method does not offer any advantages over the standard method, but we will see in chapter 5 that this method can be extended for use in three-body resonance energy transfer to significantly reduce the computational complexity of the calculations.

Now we have a general expression for the matrix element for two-body resonance energy transfer, we can focus on including the influence of a macroscopic environment into our description. This can be done via macroscopic QED, a theoretical framework introduced in chapter 2.

# 3.2 Rate of Energy Transfer in Reciprocal Media

In this section, we apply macroscopic QED (see chapter 2) to the general expression for the matrix element calculated in the previous section. This allows us to express the matrix element in terms of the Green's tensor (see section 2.2), incorporating the effects of a macroscopic reciprocal environment. We then apply this to the Fermi Golden Rule to find an expression for the rate of energy transfer between the two bodies.

#### 3.2.1 Applying Macroscopic QED

We begin by considering only the numerator of the resonant (first) term of the matrix element, (3.18), and, combining with the definition of the interaction Hamiltonian (3.3), we rewrite as,

$$\langle f | H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}} | i \rangle = \langle g_{\text{D}}, e_{\text{A}}; 0 | \left( \hat{\boldsymbol{d}}_{\text{A}} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) \right) \left( \hat{\boldsymbol{d}}_{\text{D}} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) \right) | e_{\text{D}}, g_{\text{A}}; 0 \rangle$$

$$= \langle e_{\text{A}} | \hat{\boldsymbol{d}}_{\text{A}} | g_{\text{A}} \rangle \langle 0 | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) | 0 \rangle \langle g_{\text{D}} | \hat{\boldsymbol{d}}_{\text{D}} | e_{\text{D}} \rangle ,$$

$$(3.28)$$

where we have separated the molecular and field terms. We now incorporate the effects of a reciprocal medium by employing macroscopic QED. More specifically, we do this by expressing the quantized electric field via (2.36), which accounts for a reciprocal macroscopic environment. Substituting this into only the field term of the resonant numerator (3.28) we find,

$$\langle 0 | \, \hat{\boldsymbol{E}}(\boldsymbol{r}_{\mathrm{A}}) \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\mathrm{D}}) | 0 \rangle = \sum_{\lambda,\lambda'} \langle 0 | \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \int_{0}^{\infty} d\omega \int_{0}^{\infty} d\omega' \\ \times \left[ \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{s},\omega) + \boldsymbol{G}_{\lambda}^{\dagger}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{s},\omega) \right] \\ \cdot \left[ \boldsymbol{G}_{\lambda'}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}(\boldsymbol{s}',\omega') + \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}^{\dagger}(\boldsymbol{s}',\omega') \right] | 0 \rangle$$

$$= \sum_{\lambda,\lambda'} \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \int_{0}^{\infty} d\omega \int_{0}^{\infty} d\omega' \langle 0 | \left[ \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{s},\omega) \cdot \boldsymbol{G}_{\lambda'}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}(\boldsymbol{s}',\omega') \right. \\ \left. + \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{s},\omega) \cdot \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}(\boldsymbol{s}',\omega') \right. \\ \left. + \boldsymbol{G}_{\lambda}^{\dagger}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{s},\omega) \cdot \boldsymbol{G}_{\lambda'}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}(\boldsymbol{s}',\omega') \right. \\ \left. + \boldsymbol{G}_{\lambda}^{\dagger}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{s},\omega) \cdot \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}(\boldsymbol{s}',\omega') \right. \\ \left. + \boldsymbol{G}_{\lambda}^{\dagger}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}^{\dagger}(\boldsymbol{s},\omega) \cdot \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}^{\dagger}(\boldsymbol{s}',\omega') \right] \left| 0 \right\rangle.$$
 (3.29)

Since the initial and final field states are the same, we know that terms that contain two creation or two annihilation operators will not contribute. Only terms that contain both a creation and annihilation operators will contribute, allowing the elimination of the first and fourth terms of (3.29). We can also use the fact that the annihilation operator acting on the ground state gives zero, shown in equation (2.24), to eliminate the third term of (3.29), leaving us with the second term only,

$$\langle 0 | \, \hat{\boldsymbol{E}}(\boldsymbol{r}_{\mathrm{A}}) \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\mathrm{D}}) | 0 \rangle = \sum_{\lambda,\lambda'} \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \int_{0}^{\infty} d\omega \int_{0}^{\infty} d\omega' \\ \times \langle 0 | \, \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{s},\omega) \cdot \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}^{\dagger}(\boldsymbol{s}',\omega') | 0 \rangle .$$
(3.30)

Substituting this back into (3.28) we find,

$$\langle f | H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}} | i \rangle = \langle e_{\text{A}} | \hat{\boldsymbol{d}}_{\text{A}} | g_{\text{A}} \rangle \langle 0 | \sum_{\lambda,\lambda'} \int d^{3}\boldsymbol{s} \int d^{3}\boldsymbol{s}' \int_{0}^{\infty} d\omega \int_{0}^{\infty} d\omega' \\ \times \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\text{A}}, \boldsymbol{s}, \omega) \cdot \hat{\boldsymbol{f}}_{\lambda}(\boldsymbol{s}, \omega) \cdot \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\text{D}}, \boldsymbol{s}', \omega') \cdot \hat{\boldsymbol{f}}_{\lambda'}^{\dagger}(\boldsymbol{s}', \omega') | 0 \rangle \langle g_{\text{D}} | \hat{\boldsymbol{d}}_{\text{D}} | e_{\text{D}} \rangle.$$
(3.31)

We define,

$$\boldsymbol{d}^{\uparrow} \equiv \langle e | \, \boldsymbol{\hat{d}} \, | g \rangle \,, \quad \boldsymbol{d}^{\downarrow} \equiv \langle g | \, \boldsymbol{\hat{d}} \, | e \rangle \,, \tag{3.32}$$

allowing us to rewrite as,

$$= \sum_{\lambda,\lambda'} \int d^3 \boldsymbol{s} \int d^3 \boldsymbol{s}' \int_0^\infty d\omega \int_0^\infty d\omega' \, \boldsymbol{\hat{d}}_{A}^{\dagger} \cdot \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{A}, \boldsymbol{s}, \omega) \\ \times \langle 0 | \, \boldsymbol{\hat{f}}_{\lambda}(\boldsymbol{s}, \omega) \cdot \boldsymbol{\hat{f}}_{\lambda'}^{\dagger}(\boldsymbol{s}', \omega') \, | 0 \rangle \, \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{D}, \boldsymbol{s}', \omega') \cdot \boldsymbol{\hat{d}}_{D}^{\downarrow}.$$
(3.33)

Using  $\langle 0 | \hat{f}_{\lambda}(\boldsymbol{s},\omega) \cdot \hat{f}_{\lambda'}^{\dagger}(\boldsymbol{s}',\omega') | 0 \rangle = \delta_{\lambda\lambda'} \delta(\boldsymbol{s}-\boldsymbol{s}') \delta(\omega-\omega')$  (see subsection 2.1.1) we obtain,

$$= \sum_{\lambda,\lambda'} \int d^3 \boldsymbol{s} \int d^3 \boldsymbol{s}' \int_0^\infty d\omega \int_0^\infty d\omega' \, \hat{\boldsymbol{d}}_{\mathrm{A}}^{\dagger} \cdot \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \delta(\boldsymbol{s}-\boldsymbol{s}') \delta(\omega-\omega') \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s}',\omega') \cdot \hat{\boldsymbol{d}}_{\mathrm{D}}^{\downarrow}$$
$$= \sum_{\lambda} \int d^3 \boldsymbol{s} \int_0^\infty d\omega \, \boldsymbol{d}_{\mathrm{A}}^{\dagger} \cdot \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{s},\omega) \cdot \boldsymbol{G}_{\lambda}^{\dagger}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{s},\omega) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow}.$$
(3.34)

We now make use of the completeness relation for reciprocal media (2.85),

$$\sum_{\lambda=e,m} \int d^3 \boldsymbol{s} \boldsymbol{G}_{\lambda}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \boldsymbol{G}_{\lambda}^{\dagger}(\boldsymbol{r}', \boldsymbol{s}, \omega) = \frac{\hbar \mu_0}{\pi} \omega^2 \operatorname{Im} \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega), \qquad (3.35)$$

to rewrite our expression as,

$$\langle f | H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}} | i \rangle = \frac{\mu_0 \hbar}{\pi} \int_0^\infty d\omega \, \omega^2 \boldsymbol{d}_{\text{A}}^{\uparrow} \cdot \text{Im} \, \boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, \omega) \cdot \boldsymbol{d}_{\text{D}}^{\downarrow}.$$
(3.36)

So we can now express the resonant contribution to the matrix element as,

$$M_{fi}^{\text{res}} = -\sum_{p} \langle f | \frac{H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}}}{\hbar c p - E_{\text{eg}}} | i \rangle$$
$$= -\frac{\mu_{0}}{\pi} \int_{0}^{\infty} d\omega \, \boldsymbol{d}_{\text{A}}^{\uparrow} \cdot \frac{\omega^{2} \, \text{Im} \, \boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, \omega)}{\omega - \omega_{0}} \cdot \boldsymbol{d}_{\text{D}}^{\downarrow}, \qquad (3.37)$$

where we have made the substitutions  $\hbar c p = \hbar \omega$  and  $E_{\rm eg} = \hbar \omega_0$ .

We can apply a similar method to the off-resonant contribution to the matrix element,  $M_{fi}^{\text{off}}$ , where we again initially consider only the numerator,

$$\langle f | H_{\text{int}}^{\text{D}} H_{\text{int}}^{\text{A}} | i \rangle = \langle e_{\text{D}} | \hat{\boldsymbol{d}}_{\text{D}} | g_{\text{D}} \rangle \langle 0 | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) | 0 \rangle \langle g_{\text{A}} | \hat{\boldsymbol{d}}_{\text{A}} | e_{\text{A}} \rangle ,$$
  
$$= \boldsymbol{d}_{\text{D}}^{\downarrow} \langle 0 | \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{A}}) \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\text{D}}) | 0 \rangle \boldsymbol{d}_{\text{A}}^{\uparrow}.$$
(3.38)

Once we have substituted in the electric field expression (2.36), we can use the same reasoning as before to eliminate terms that do not contain both a creation and annihilation operator, as well as terms containing  $\hat{f} |0\rangle$ . This leaves us with,

$$\langle f | H_{\text{int}}^{\text{D}} H_{\text{int}}^{\text{A}} | i \rangle = \sum_{\lambda,\lambda'} \int d^{3} \boldsymbol{s} \int d^{3} \boldsymbol{s}' \int_{0}^{\infty} d\omega \int_{0}^{\infty} d\omega' \times \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\text{D}}, \boldsymbol{s}, \omega) \langle 0 | \, \boldsymbol{\hat{f}}(\boldsymbol{s}, \omega) \cdot \boldsymbol{\hat{f}}^{\dagger}(\boldsymbol{s}', \omega') | 0 \rangle \, \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\text{A}}, \boldsymbol{s}', \omega') \cdot \boldsymbol{d}_{\text{A}}^{\dagger} = \sum_{\lambda,\lambda'} \int d^{3} \boldsymbol{s} \int_{0}^{\infty} d\omega \, \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\text{D}}, \boldsymbol{s}, \omega) \cdot \boldsymbol{G}_{\lambda'}^{\dagger}(\boldsymbol{r}_{\text{A}}, \boldsymbol{s}', \omega') \cdot \boldsymbol{d}_{\text{A}}^{\dagger} = \frac{\mu_{0} \hbar}{\pi} \int_{0}^{\infty} d\omega \, \omega^{2} \, \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \text{Im} \, \boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, \omega) \cdot \boldsymbol{d}_{\text{A}}^{\dagger},$$
(3.39)

where we have again made use of the completeness relation. We therefore obtain an expression for the off-resonant component of the matrix element,

$$M_{fi}^{\text{off}} = -\sum_{p} \langle f | \frac{H_{\text{int}}^{\text{D}} H_{\text{int}}^{\text{A}}}{\hbar c p + E_{\text{eg}}} | i \rangle$$
$$= -\frac{\mu_{0}}{\pi} \int_{0}^{\infty} d\omega \, \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \frac{\omega^{2} \, \text{Im} \, \boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, \omega)}{\omega + \omega_{0}} \cdot \boldsymbol{d}_{\text{A}}^{\uparrow}, \qquad (3.40)$$

where we have again made the substitutions  $\hbar c p = \hbar \omega$  and  $E_{\rm eg} = \hbar \omega_0$ .

Now we have expressions for both components of the matrix element in terms of the functions  $\int_0^\infty d\omega \, [\omega^2 \, \text{Im} \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r'}, \omega)] / (\omega \pm \omega_0)$ . We can apply complex contour integration techniques to solve integrals of this form, but first we need to rearrange the integrals to a more convenient form. For an integral of the form,

$$\int_0^\infty d\omega \frac{\omega^2 \operatorname{Im} G(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega \pm \omega_0}, \qquad (3.41)$$

we can use the relation for the imaginary part of a function,

$$\operatorname{Im} f(\omega) = \frac{1}{2i} [f(\omega) - f^*(\omega)], \qquad (3.42)$$

so the frequency integral can be written as,

$$\frac{1}{2i} \int_0^\infty d\omega \frac{\omega^2}{\omega \pm \omega_0} \left[ G(\boldsymbol{r}, \boldsymbol{r}', \omega) - G^*(\boldsymbol{r}, \boldsymbol{r}', \omega) \right].$$
(3.43)

This can be re-written by use of the Schwarz reflection principle (2.70) for real  $\omega$ ,  $f^*(\omega) = f(-\omega^*) = f(-\omega)$ , as,

$$\frac{1}{2i} \int_0^\infty d\omega \frac{\omega^2}{\omega \pm \omega_0} \left[ G(\boldsymbol{r}, \boldsymbol{r}', \omega) - G(\boldsymbol{r}, \boldsymbol{r}', -\omega) \right].$$
(3.44)

Finally, we use the identity  $\int_a^b f(-x)dx = -\int_{-a}^{-b} f(x)dx$  to rewrite the integral as:

$$\int_{0}^{\infty} d\omega \frac{\omega^{2} \operatorname{Im} G(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega \pm \omega_{0}} = \frac{1}{2i} \left[ \int_{0}^{\infty} d\omega \frac{\omega^{2} G(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega \pm \omega_{0}} - \int_{0}^{-\infty} d\omega \frac{\omega^{2} G(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega \mp \omega_{0}} \right].$$
(3.45)

Applying this to our expressions for the matrix element components, (3.37) and (3.40), we get,

$$M_{fi}^{\rm res} = -\frac{\mu_0}{2\pi i} \boldsymbol{d}_{\rm A}^{\uparrow} \cdot \left[ \int_0^\infty d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega)}{\omega - \omega_0} - \int_0^{-\infty} d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega)}{\omega + \omega_0} \right] \cdot \boldsymbol{d}_{\rm D}^{\downarrow}, \qquad (3.46)$$

$$M_{fi}^{\text{off}} = -\frac{\mu_0}{2\pi i} \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \left[ \int_0^\infty d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, \omega)}{\omega + \omega_0} - \int_0^{-\infty} d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, \omega)}{\omega - \omega_0} \right] \cdot \boldsymbol{d}_{\text{A}}^{\uparrow}. \tag{3.47}$$

These frequency integrals can be evaluated by means of contour integration, which is done in the next subsection.



Figure 3.3: Contour integration in a single quadrant. (a) shows the pole at  $\omega_0$  on the real axis, and (b) shows the pole after it has been shifted by  $i\epsilon$  so that it is completely inside the closed contour.

#### 3.2.2 Contour Integration

The frequency integrals in (3.46) and (3.47) have poles on the real axis at  $\pm \omega_0$ , which pose a problem when attempting integration around a closed contour along the real axis. To overcome this, we let the eigenenergies of the atom take on a small imaginary part which shifts them into the upper or lower half of the complex plane (see figure 3.3). This means that the poles become  $\pm(\omega_0 + i\epsilon)$  which allows the frequency integrals to be evaluated using complex contour integration [71, 72].

To do this, we begin with the first term of the resonant contribution to the matrix element (3.46),

$$\int_{0}^{\infty} d\omega \frac{\omega^{2} \boldsymbol{G}_{\lambda}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega)}{\omega - (\omega_{0} + i\epsilon)},\tag{3.48}$$

where the pole has been shifted into the upper half of the complex plane. We extend the integration along the  $\omega$  axis by a quarter arc at  $\omega = a$  up to the imaginary axis and then downward to the origin to form a closed contour in the complex plane as in figure 3.3. The integral of the closed loop can then be parameterized as,

$$\oint_C \frac{f(z)}{z - (\omega_0 + i\epsilon)} dz = \int_0^a d\omega \frac{f(\omega)}{\omega - (\omega_0 + i\epsilon)} + \int_a^{ia} d\zeta \frac{f(\zeta)}{\zeta - (\omega_0 + i\epsilon)} + i \int_a^0 d\xi \frac{f(i\xi)}{i\xi - (\omega_0 + i\epsilon)}, \quad (3.49)$$

where we have set  $f(\omega) = \omega^2 \boldsymbol{G}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega)$ . Since the Green's tensor vanishes at infinity [4],

$$\lim_{\omega \to \infty} \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega) = 0 \quad \text{for } \boldsymbol{r} \neq \boldsymbol{r}', \tag{3.50}$$

the quarter arc integral vanishes as  $a \to \infty$ . So,

$$\oint_C \frac{f(z)}{z - (\omega_0 + i\epsilon)} dz = \int_0^\infty d\omega \frac{f(\omega)}{\omega - (\omega_0 + i\epsilon)} + i \int_\infty^0 d\xi \frac{f(i\xi)}{i\xi - (\omega_0 + i\epsilon)}.$$
(3.51)

Since the Green's tensor is an analytic function in the upper half of the complex plane (see section 2.2.1), we can make use of the Residue Theorem, which states that the value of a integral around a closed loop is equal to the sum of the residues of the function at the enclosed poles,

$$\oint_C \frac{F(z)}{z - z_0} dz = 2\pi i \sum_{\text{poles}} \operatorname{Res}\left(\frac{F(z)}{z - z_0}\right) = 2\pi i \sum_{\text{poles}} F(z_0).$$
(3.52)

Therefore, the above closed integral is equal to the residue at the pole  $\omega_0 + i\epsilon$ . As a result,

$$\int_0^\infty d\omega \frac{f(\omega)}{\omega - (\omega_0 + i\epsilon)} + i \int_\infty^0 d\xi \frac{f(i\xi)}{i\xi - (\omega_0 + i\epsilon)} = 2\pi i f(\omega_0 + i\epsilon).$$
(3.53)

We now let the infinitesimal  $\epsilon$  tend to zero and rearrange to obtain an expression for the first integral term in (3.46),

$$\int_0^\infty d\omega \, \frac{\omega^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega)}{\omega - \omega_0} = i \int_0^\infty d\xi \, \frac{(i\xi)^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi)}{i\xi - \omega_0} + 2\pi i \omega_0^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0). \tag{3.54}$$

Similarly for the second integral term of (3.46), we extend the integration by a quarter arc at  $\omega = -a$  up to the imaginary axis and then downward to the origin to form a closed contour. We set  $f(\omega) = \omega^2 \mathbf{G}(\mathbf{r}_{\rm A}, \mathbf{r}_{\rm D}, \omega)$  and parameterise in the same way, noting that the quarter arc integral vanishes as  $a \to \infty$  giving,

$$\oint_C \frac{f(z)}{z + (\omega_0 + i\epsilon)} dz = \int_0^{-\infty} d\omega \frac{f(\omega)}{\omega + (\omega_0 + i\epsilon)} + i \int_\infty^0 d\xi \frac{f(i\xi)}{i\xi + (\omega_0 + i\epsilon)}.$$
 (3.55)

In this case, the pole is at  $(-\omega_0 - i\epsilon)$  so is in the lower half of the complex plane, meaning it is not enclosed by the contour. Therefore, the closed contour contains no poles, so,

$$\int_0^{-\infty} d\omega \frac{f(\omega)}{\omega + (\omega_0 + i\epsilon)} + i \int_\infty^0 d\xi \frac{f(i\xi)}{i\xi + (\omega_0 + i\epsilon)} = 0.$$
(3.56)

Also setting  $\epsilon \to 0$ ,

$$\int_0^{-\infty} d\omega \frac{f(\omega)}{\omega + \omega_0} = i \int_0^{\infty} d\xi \frac{f(i\xi)}{i\xi + \omega_0},$$
(3.57)

we find that the second integral term of (3.46) can be written as,

$$\int_{0}^{-\infty} d\omega \, \frac{\omega^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega)}{\omega + \omega_0} = i \int_{0}^{\infty} d\xi \, \frac{(i\xi)^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi)}{i\xi + \omega_0}.$$
(3.58)

Combining these two integral terms, (3.54) and (3.58), we obtain an expression for the resonant component of the matrix element (3.46),

$$M_{fi}^{\text{res}} = -\frac{\mu_0}{2\pi i} \left( \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot i \int_0^\infty d\xi \, (i\xi)^2 \left[ \frac{\boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi)}{i\xi - \omega_0} - \frac{\boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi)}{i\xi + \omega_0} \right] \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow} + 2\pi i \omega_0^2 \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow} \right) = -\frac{\mu_0}{2\pi} \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \left( \int_0^\infty d\xi \, \xi^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi) \frac{\omega_0}{\omega_0^2 + \xi^2} + 2\pi \omega_0^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0) \right) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow}.$$
(3.59)

We repeat the same steps for the two frequency integrals that make up the off-resonant component of the matrix element, (3.47). For the first integral,

$$\int_0^\infty d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm A}, \omega)}{\omega + \omega_0 + i\epsilon},\tag{3.60}$$

we extend the integration along the  $\omega$  axis by a quarter arc at  $\omega = a$  up to the imaginary axis and then downward to the origin forming a closed contour, and note that the pole at  $(-\omega_0 - i\epsilon)$  is in the lower half of the complex plane, and so not enclosed by the contour. We therefore find,

$$\int_0^\infty d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm A}, \omega)}{\omega + \omega_0 + i\epsilon} = i \int_0^\infty d\xi \, \frac{(i\xi)^2 \boldsymbol{G}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm A}, i\xi)}{i\xi + \omega_0}.$$
(3.61)

For the second integral of (3.47),

$$\int_{0}^{-\infty} d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm A}, \omega)}{\omega - \omega_0},\tag{3.62}$$

we extend the integration by a quarter arc at  $\omega = -a$  up to the imaginary axis and then downward to the origin forming a closed contour, and note that the pole at  $(\omega_0 + i\epsilon)$ , although in the upper half of the complex plane is not enclosed by the contour, since the pole is positive in  $\omega$  and the contour encloses only negative values of  $\omega$ . We can therefore rewrite the integral as,

$$\int_0^{-\infty} d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, \omega)}{\omega - \omega_0} = i \int_0^{\infty} d\xi \, \frac{(i\xi)^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, i\xi)}{i\xi - \omega_0}.$$
(3.63)

These two integral terms, (3.61) and (3.63), can be combined to give an expression for the

off-resonant component of the matrix element (3.46),

$$M_{fi}^{\text{off}} = -\frac{\mu_0}{2\pi i} \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot i \int_0^\infty d\xi \, (i\xi)^2 \left[ \frac{\boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, i\xi)}{i\xi + \omega_0} - \frac{\boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, i\xi)}{i\xi - \omega_0} \right] \cdot \boldsymbol{d}_{\text{A}}^{\uparrow}$$
$$= \frac{\mu_0}{2\pi} \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \int_0^\infty d\xi \, \xi^2 \, \boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, i\xi) \frac{\omega_0}{\omega_0^2 + \xi^2} \cdot \boldsymbol{d}_{\text{A}}^{\uparrow}.$$
(3.64)

We are now able to sum the resonant and the off-resonant components of the matrix element, (3.59) and (3.64), to find the full matrix element,

$$M_{fi} = -\mu_0 \omega_0^2 \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow} -\frac{\mu_0}{2\pi} \int_0^\infty d\xi \, \frac{\omega_0 \xi^2}{\omega_0^2 + \xi^2} \Biggl( \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow} - \boldsymbol{d}_{\mathrm{D}}^{\downarrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, i\xi) \cdot \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \Biggr).$$
(3.65)

Since in this chapter we are focusing on reciprocal media, we can make use of Lorentz reciprocity (2.74),

$$\boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_{0}) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow} = \boldsymbol{d}_{\mathrm{D}}^{\downarrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, \omega_{0}) \cdot \boldsymbol{d}_{\mathrm{A}}^{\uparrow}$$
(3.66)

to see that the second term of (3.65) disappears, and we can rewrite the total matrix element as,

$$M_{fi} = -\mu_0 \omega_0^2 \, \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow}.$$
(3.67)

We now use the matrix element (3.67) in the Fermi Golden Rule [68] to calculate the energy transfer rate,

$$\Gamma_{fi} = \frac{2\pi}{\hbar} |M_{fi}|^2 \delta(E_{\mathrm{I}} - E_f)$$
  
=  $\frac{2\pi \mu_0^2 \omega_0^4}{\hbar} |\boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow}|^2.$  (3.68)

The physical interpretation of this rate formula when read from right to left is that the donor dipole relaxes  $(\boldsymbol{d}_{\mathrm{D}}^{\downarrow})$ , transmits its energy to the acceptor dipole  $(\boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_{0}))$ , which excites  $(\boldsymbol{d}_{\mathrm{A}}^{\uparrow})$ , and then the reverse process happens.

This general formula for two-body RET is in agreement with the literature, e.g. Refs. [13, 73], and can be applied to any arbitrary (reciprocal) macroscopic environment for which the Green's tensor is known. In the next section, we demonstrate how this formula can be applied to simple environments as a proof-of-principle.

### 3.3 Results

The rate formula (3.68) is applicable to any external environment, but in this section we focus on two simple examples, a vacuum and a semi-infinite half-space, to allow us to write down simple Green's tensors in position space (i.e., without using an angular spectrum representation). However, we emphasize that this formula could be used to calculate interactions within far more complex systems using numerically calculated Green's tensors, including proteins and other biological systems [74]. In these types of systems, the dipole moments are often randomly oriented, necessitating the calculation of the rate averaged over all possible dipole alignments. We therefore make the replacement (see, for example, [75]),

$$\boldsymbol{d}_{\mathrm{A/D}}^{\uparrow} \otimes \boldsymbol{d}_{\mathrm{A/D}}^{\downarrow} \to \frac{1}{3} |\boldsymbol{d}_{\mathrm{A/D}}|^2 \mathbb{I},$$
 (3.69)

where  $\otimes$  is the outer product and I is the 3 × 3 identity matrix. Applying this to (3.68), we obtain a formula for the isotropic rate for two bodies in a reciprocal environment,

$$\Gamma^{\rm iso} = \frac{2\pi\mu_0^2\omega_0^4}{9\hbar} |\boldsymbol{d}_{\rm A}|^2 |\boldsymbol{d}_{\rm D}|^2 \operatorname{Tr} \left[ \boldsymbol{G}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega_0) \cdot \boldsymbol{G}^*(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm A}, \omega_0) \right].$$
(3.70)

Now, for environments where the form of the Green's tensor is known, it can substituted into this expression to explore how the positions of the two molecules and the properties of the medium influence the rate of energy transfer.

In this section, we look first at the simplest possible environment, a vacuum. The Green's tensor that describes free space is sufficiently simple that an analytical expression for the rate of interaction between two bodies in a vacuum can be found. We will also examine the intermolecular distance dependence of the rate in the near-field and far-field limits.

We will also look at an environment made up of a semi-infinite half-space in a vacuum. The Green's tensor for this setup is more complicated, and in order to calculate an analytic expression for the rate, we are required to simplify the system by specifying the arrangement of the bodies with respect to each other and the half-space, and also imposing near-field or far-field limits. The behaviour of the rate can be examined outside of these conditions by way of a density plot, allowing us to see how the rate is affected by the positions of the bodies in two dimensions.

#### 3.3.1 Vacuum

We first consider an environment made up of only free space. The Green's tensor that describes this is well-known and is given in appendix section B.1. To simplify things, and

without loss of generality, we can place the two dipoles on the z-axis which will be henceforth be referred to as a "colinear" arrangement. Therefore, the separation vector,  $\boldsymbol{\rho} \equiv \boldsymbol{r} - \boldsymbol{r}'$ , becomes  $\boldsymbol{\rho} = (0, 0, z - z')$  and we can define the intermolecular distance,  $\boldsymbol{\rho} \equiv |\boldsymbol{\rho}|$ , and the separation unit vector,  $\boldsymbol{e}_{\rho} \equiv \boldsymbol{\rho}/\rho$ , respectively as  $\boldsymbol{\rho} = |z - z'|$  and  $\boldsymbol{e}_{\rho} = (0, 0, 1)$ . We will calculate analytical expressions for the rate of energy transfer using the full vacuum Green's tensor, and also with near-field and far-field limits applied.

#### Full Vacuum Rate

We begin with the full vacuum Green's tensor (B.1) applied to two bodies at different points on the z-axis,

$$\boldsymbol{G}^{(0,C)}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{c^2 e^{i\omega\rho/c}}{4\pi\omega^2 \rho^3} \left\{ \left[ 1 - i\frac{\omega\rho}{c} - \left(\frac{\omega\rho}{c}\right)^2 \right] \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{pmatrix} - \left[ 3 - 3i\frac{\omega\rho}{c} - \left(\frac{\omega\rho}{c}\right)^2 \right] \begin{pmatrix} 0 & 0 & 0\\ 0 & 0 & 0\\ 0 & 0 & 1 \end{pmatrix} \right\}, \quad (3.71)$$

where C references the colinear arrangement. Renaming the first square bracket A and the second B, we can rewrite the above in the much simpler form,

$$\boldsymbol{G}^{(0,C)}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{c^2 e^{i\omega\rho/c}}{4\pi\omega^2\rho^3} \begin{pmatrix} A & 0 & 0\\ 0 & A & 0\\ 0 & 0 & A-B \end{pmatrix},$$
(3.72)

where we find  $A - B = 2(i\omega\rho/c - 1)$ . We can then calculate,

$$\boldsymbol{G}^{(0,C)}(\boldsymbol{r}_{A},\boldsymbol{r}_{D},\omega_{0})\cdot\boldsymbol{G}^{(0,C)*}(\boldsymbol{r}_{D},\boldsymbol{r}_{A},\omega_{0}) = \frac{c^{4}}{16\pi^{2}\omega_{0}^{4}\rho^{6}} \begin{pmatrix} AA^{*} & 0 & 0\\ 0 & AA^{*} & 0\\ 0 & 0 & (A-B)(A^{*}-B^{*}) \end{pmatrix},$$
(3.73)

Substituting this into the rate equation (3.70) we get,

$$\Gamma^{\text{iso,C}} = \frac{\mu_0^2 c^4}{36\hbar\pi} |\mathbf{d}_{\text{A}}|^2 |\mathbf{d}_{\text{D}}|^2 [3AA^* + BB^* - (AB^* + BA^*)]$$
$$= \frac{\mu_0^2}{36\hbar\pi} |\mathbf{d}_{\text{A}}|^2 |\mathbf{d}_{\text{D}}|^2 \left(\frac{3c^4}{\rho^6} + \frac{c^2\omega_0^2}{\rho^4} + \frac{\omega_0^4}{\rho^2}\right).$$
(3.74)

We can make the substitution  $q \equiv \rho/\lambda_0 = \rho c/\omega_0$  so that our distances are in units of the transition wavelength,  $\lambda_0$ . This means we can rewrite the rate as,

$$\Gamma^{\rm iso,C} = \eta_0 \left( \frac{3}{q^6} + \frac{1}{q^4} + \frac{1}{q^2} \right), \qquad (3.75)$$

where we have defined,

$$\eta_0 = \frac{\mu_0^2 \omega_0^6}{36\hbar\pi c^2} |\mathbf{d}_{\rm A}|^2 |\mathbf{d}_{\rm D}|^2.$$
(3.76)

This result is in agreement with [76, 77].

#### Non-Retarded Vacuum Rate

Beginning with the non-retarded limit,  $q \ll 1$ , of the vacuum Green's tensor (B.3) for bodies at different positions on the z-axis,

$$\boldsymbol{G}_{\mathrm{NR}}^{(0,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{c^2}{4\pi\omega^2\rho^3} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -2 \end{pmatrix}.$$
 (3.77)

Substituting this into the rate equation (3.70), we can write the non-retarded limit of the vacuum

$$\Gamma_{\rm NR}^{(0,\rm C)} = \frac{c^4 \mu_0^2}{12\hbar\pi\rho^6} |\boldsymbol{d}_{\rm A}|^2 |\boldsymbol{d}_{\rm D}|^2 = 3\eta_0 q^{-6}.$$
(3.78)

This is in agreement with the well-known result for two-body resonance energy transfer in a vacuum [11].

#### **Retarded Vacuum Rate**

Similarly, the retarded limit,  $q \gg 1$ , of the vacuum Green's tensor (B.4) for bodies on the *z*-axis can be written as,

$$\boldsymbol{G}_{\mathrm{R}}^{(0,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{e^{i\omega\rho/c}}{4\pi\rho} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0 \end{pmatrix}.$$
 (3.79)

Substituting this into the rate equation (3.70), we can write the retarded limit of the vacuum as,

$$\Gamma_{\rm R}^{(0,{\rm C})} = \frac{\mu_0^2 \omega_0^4}{36\hbar\pi\rho^2} |\boldsymbol{d}_{\rm A}|^2 |\boldsymbol{d}_{\rm D}|^2 = \eta_0 q^{-2}.$$
(3.80)



Figure 3.4: Influence of intermolecular distance on the rate of energy transfer between a donor and acceptor in a vacuum. Intermolecular distance is in units of the transition wavelength  $q = \rho/\lambda_0$ , and the rate has been normalized to the quantity  $\eta_0$ , defined in equation (3.76) in the main text.

#### Vacuum Plot

Figure 3.4 visually demonstrates the union of the near-field and far-field theories. We can see that in the non-retarded regime where  $\rho/\lambda_0 \ll 1$ , the rate of energy transfer follows a  $r^{-6}$ dependence as predicted by (3.78), whereas in the retarded regime where  $r/\lambda_0 \gg 1$ , the rate follows a  $\rho^{-2}$  dependence, as in (3.80). The figure also makes clear the intermediate stage where  $\rho \sim \lambda_0$ , where the rate follows  $r^{-4}$ , which we can see from (3.75).

We now turn our attention to a environment consisting of a semi-infinite half-space, and investigate the influence it has on the rate of energy transfer between two molecules.

#### 3.3.2 Colinear Half-space System

A step up from the vacuum in terms of simplicity of environment is the semi-infinite halfspace, which we set up to have a boundary at z = 0, so that the medium extends infinitely into z < 0 while z > 0 is made up of a vacuum.

As discussed in section 2.2.1, the Green's tensors for inhomogeneous environments such as this can in general be split into the sum of a translation-invariant "bulk" part  $G^{(0)}$  and a "scattering" part  $G^{(1)}$ . In our system, this means that each Green's tensor in (3.68) is the sum of the vacuum Green's tensor (bulk) and the half-space Green's tensor (scattering), so that the Green's tensor for the entire system can be written as,

$$\boldsymbol{G}^{\mathrm{HS}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \boldsymbol{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) + \boldsymbol{G}^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega).$$
(3.81)

 $G^{(0)}$  is the vacuum Green's tensor given in (B.1) and is sufficiently simple that it can be



Figure 3.5: Colinear arrangement of two bodies, a donor D and an acceptor A, near a semiinfinite half-space at z < 0.

applied to our rate equation and yield analytical results. However,  $G^{(1)}$  is more complex due to the presence of infinite integrals (as can be seen in equation (B.5)).

We can significantly simplify our system by positioning the bodies in a "colinear" arrangement, where we assume that both atoms are placed on the z-axis, as shown in figure 3.5. This assumption simplifies  $G^{(1)}$  significantly (see equation (B.23)), but we are still required to apply near-field and far-field limits to be able to perform the infinite integrals. These simplifications lead to the useable results (B.38) and (B.40) for the near- and far-field limits respectively, which we can apply to our rate equation to produce analytical results.

#### Non-Retarded Half-Space Rate

When considering the situation where the bodies are sufficiently close to the half-space and to each other, we can employ the non-retarded limit on both the vacuum Green's tensor (3.77) and the half-space Green's tensor (B.38). Summing these gives for the effective Green's tensor,

$$\boldsymbol{G}_{\mathrm{NR}}^{\mathrm{HS,C}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{c^2}{4\pi\omega^2} \begin{bmatrix} \frac{1}{Z^3} \begin{pmatrix} -1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2 \end{pmatrix} + \frac{R_{\mathrm{NR}}}{\bar{Z}^3} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 2 \end{pmatrix} \end{bmatrix}, \quad (3.82)$$

where we have defined  $Z \equiv |z - z'|$ ,  $\overline{Z} \equiv |z + z'|$  and  $R_{\text{NR}} = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}$ .

To find the rate for isotropically averaged dipoles, we need to calculate,

$$\boldsymbol{G}_{\mathrm{NR}}^{\mathrm{HS,C}}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}},\omega_{0}) \cdot \boldsymbol{G}_{\mathrm{NR}}^{\mathrm{HS,C^{*}}}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}},\omega_{0}) = \frac{c^{4}}{16\pi^{2}\omega_{0}^{4}} \begin{pmatrix} \left(\frac{R_{\mathrm{NR}}}{Z^{3}} - \frac{1}{Z^{3}}\right)^{2} & 0 & 0\\ 0 & \left(\frac{R_{\mathrm{NR}}}{Z^{3}} - \frac{1}{Z^{3}}\right)^{2} & 0\\ 0 & 0 & 4\left(\frac{R_{\mathrm{NR}}}{Z^{3}} + \frac{1}{Z^{3}}\right)^{2} \end{pmatrix}, \quad (3.83)$$

which we can then substitute into the rate equation for isotropically averaged dipoles (3.70), giving us,

$$\Gamma_{\rm NR}^{\rm HS,C} = \frac{\mu_0^2 c^4}{36\hbar\pi} |\boldsymbol{d}_{\rm A}|^2 |\boldsymbol{d}_{\rm D}|^2 \left(\frac{3}{Z^6} + \frac{3R_{\rm NR}^2}{\bar{Z}^6} + \frac{2R_{\rm NR}}{\bar{Z}^3 Z^3}\right).$$
(3.84)

In this form, we can clearly see that the first term is the contribution from the direct interaction between the donor and acceptor that travels only through the vacuum without involving the half-space, as it has the same  $r^{-6}$  dependence on the direct intermolecular distance,  $|z_{\rm A} - z_{\rm D}|$ , as in (3.78). The second term is the contribution of the interaction that occurs via the half-space, with the characteristic  $r^{-6}$  dependence on the distance from the donor to the acceptor via the surface,  $|z_{\rm A} + z_{\rm D}|$ . The final term is then a blend of these two interaction types.

It can also be useful to normalize this result to the isotropic non-retarded vacuum rate given in (3.78), which yields,

$$\Gamma_{\rm NR}^{\rm HS,C(norm)} = 1 + R_{\rm NR}^2 \tilde{q}^6 + \frac{2R_{\rm NR}\tilde{q}^3}{3}, \qquad (3.85)$$

where we have defined  $\tilde{q} \equiv Z/\bar{Z}$ .

This formula for the two-body isotropically averaged rate near a dielectric interface is a result we presented in Ref. [1]. To the best of our knowledge, it does not appear anywhere else in the literature, the closest known result being that for oriented (non-random) dipoles near a perfect reflector reported in Eq.(20) of [16].

#### **Retarded Half-Space Rate**

Similarly, we can calculate the rate of interaction for two colinear arranged bodies near a reciprocal half-space where the bodies are far enough away from the surface and each other for the retarded limit to be introduced. In this case, we sum the retarded limit of the vacuum

Green's tensor, (3.79), and the retarded limit of the half-space Green's tensor, (B.40), to get,

$$\boldsymbol{G}_{\mathrm{R}}^{\mathrm{HS,C}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{1}{4\pi} \left( \frac{e^{iZ\omega/c}}{Z} + \frac{e^{i\bar{Z}\omega/c}}{\bar{Z}} R_{\mathrm{R}} \right) \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0 \end{pmatrix},$$
(3.86)

where we have again defined  $Z \equiv |z - z'|$  and  $\overline{Z} \equiv |z + z'|$ , as well as  $R_{\rm R} \equiv \frac{\sqrt{\mu(\omega)} - \sqrt{\varepsilon(\omega)}}{\sqrt{\mu(\omega)} + \sqrt{\varepsilon(\omega)}}$ . We now calculate,

$$\boldsymbol{G}_{\mathrm{R}}^{\mathrm{HS,C}}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}},\omega_{0}) \cdot \boldsymbol{G}_{\mathrm{R}}^{\mathrm{HS,C^{*}}}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}},\omega_{0}) \\ = \frac{1}{16\pi^{2}} \left( \frac{e^{iZ\omega_{0}/c}}{Z} + \frac{e^{i\bar{Z}\omega_{0}/c}}{\bar{Z}} R_{\mathrm{R}} \right) \left( \frac{e^{-iZ\omega_{0}/c}}{Z} + \frac{e^{-i\bar{Z}\omega_{0}/c}}{\bar{Z}} R_{\mathrm{R}} \right) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (3.87)$$

allowing us to then easily calculate,

$$\operatorname{Tr} \left[ \boldsymbol{G}_{\mathrm{R}}^{\mathrm{HS,C}}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}},\omega_{0}) \cdot \boldsymbol{G}_{\mathrm{R}}^{\mathrm{HS,C^{*}}}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}},\omega_{0}) \right] \\ = \frac{1}{8\pi^{2}} \left( \frac{e^{iZ\omega_{0}/c}}{Z} + \frac{e^{i\bar{Z}\omega_{0}/c}}{\bar{Z}} R_{\mathrm{R}} \right) \left( \frac{e^{-iZ\omega_{0}/c}}{Z} + \frac{e^{-i\bar{Z}\omega_{0}/c}}{\bar{Z}} R_{\mathrm{R}} \right) \\ = \frac{1}{8\pi^{2}} \left( \frac{1}{Z^{2}} + \frac{R_{\mathrm{R}}^{2}}{\bar{Z}^{2}} + \frac{e^{i(Z-\bar{Z})\omega_{0}/c}}{Z\bar{Z}} + \frac{e^{i(\bar{Z}-Z)\omega_{0}/c}}{Z\bar{Z}} R_{\mathrm{R}} \right) \\ = \frac{1}{8\pi^{2}} \left\{ \frac{1}{Z^{2}} + \frac{R_{\mathrm{R}}^{2}}{\bar{Z}^{2}} + \frac{2R_{\mathrm{R}}\cos\left[\frac{\omega_{0}}{c}(Z-\bar{Z})\right]}{Z\bar{Z}} \right\}.$$
(3.88)

Now substituting this into the rate equation (3.70) gives,

$$\Gamma_{\rm R}^{\rm HS,C} = \frac{\mu_0^2 \omega_0^4}{36\hbar\pi} |\boldsymbol{d}_{\rm A}|^2 |\boldsymbol{d}_{\rm D}|^2 \left\{ \frac{1}{Z^2} + \frac{R_{\rm R}^2}{\bar{Z}^2} + \frac{2R_{\rm R}\cos\left[\frac{\omega_0}{c}(Z-\bar{Z})\right]}{Z\bar{Z}} \right\}.$$
 (3.89)

Similarly to the non-retarded result, in this form we can clearly see the contribution from the direct vacuum interaction (first term), the interaction involving the half-space (second term), and the blend of the two interaction types (third term), all with the characteristic  $r^{-2}$ distance dependence. This final term contains an oscillatory contribution that is not present in the non-retarded limit, which depends on the distance between the surface and the closest of the two molecules. This can be seen by considering that when  $z_A > z_D$ , i.e. the donor is closest to the half-space, then the oscillation depends on  $z_D$ . However, when  $z_A < z_D$ , i.e. the acceptor is closer, then the oscillatory term depends on  $z_A$  instead. We can again normalize to the isotropic retarded vacuum rate (3.80),

$$\Gamma_{\rm R}^{\rm HS(norm)} = 1 + R_{\rm R}^2 \tilde{q}^2 + 2R_{\rm R} \tilde{q} \cos\left[\frac{\omega_0}{c} (Z - \bar{Z})\right], \qquad (3.90)$$

where  $\tilde{q}$  is defined as in section 3.3.2.

#### Hybrid Half-Space Rate

For completeness, we can also calculate an analytical expression for the rate for two bodies that are close enough to each other to employ the non-retarded limit, but far enough away from the surface to employ the retarded limit. In this instance, we sum the non-retarded vacuum Green's tensor and the retarded half-space Green's tensor to find the effective Green's tensor,

$$\boldsymbol{G}_{\text{Mix}}^{\text{HS,C}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \boldsymbol{G}_{\text{NR}}^{(0,\text{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) + \boldsymbol{G}_{\text{R}}^{(1,\text{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) \\ = \frac{1}{4\pi} \left[ \frac{c^2}{\omega^2 Z^3} \begin{pmatrix} -1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2 \end{pmatrix} + \frac{e^{i\bar{Z}\omega/c}}{\bar{Z}} R_{\text{R}} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0 \end{pmatrix} \right].$$
(3.91)

Substituting into the rate equation (3.70), we find,

$$\Gamma_{\rm Mix}^{\rm HS,C} = \frac{\mu_0^2 \omega_0^4}{36\hbar\pi} |\boldsymbol{d}_{\rm A}|^2 |\boldsymbol{d}_{\rm D}|^2 \left[ \frac{3c^4}{\omega_0^4 Z^6} + \frac{R_{\rm R}^2}{\bar{Z}^2} - \frac{2c^2 R_{\rm R}}{\omega_0^2 Z^3 \bar{Z}} \cos\left(\frac{\omega_0 \bar{Z}}{c}\right) \right].$$
(3.92)

As before, we can pick out the contributions that relate to the different interaction types. The first term corresponds to the direct vacuum interaction, which in this setup is in the non-retarded limit since the molecules are very close to each other, meaning it has a  $Z^{-6}$  dependence. The second term relates to the interaction via the half-space, which has a  $\bar{Z}^{-2}$  dependence due to the molecules being very far away from the surface. The final blended term contains elements of both interaction types, with the oscillation this time depending on  $z_{\rm A} + z_{\rm D}$ , rather than being conditional on which of the two molecules is closest to the surface.

When calculating analytical expressions for the interaction rate, we are restricted in the setups we are able to model by the complexity of the Green's tensors that describe the system. This is the reason we have implemented the near- and far-field limits and studied only the colinear arrangement. However, it is possible to expand our investigation to general geometries and without the constraints of near- and far-field limits via the use of numerical plots, which allows more complex Green's tensor forms to be included.



Figure 3.6: Rate of energy transfer for a donor and acceptor near a reciprocal half-space with reflection coefficients  $r_p = 1$  and  $r_s = -1$ . The surface is positioned at z = 0, the donor is fixed at position  $\{x_D, z_D\}/\lambda_0 = \{-1, 1\}$ , while the acceptor is free to move in the *x*-*z* plane. The rate is normalised to the isotropic two-body rate in free space, and the acceptor position is in units of the transition wavelength  $\lambda_0$ .

#### 3.3.3 Plot of general geometries

We can extend our study to general geometries in two dimensions by fixing the donor and plotting how the rate of energy transfer changes when the acceptor is in different positions on the xz-plane. For this, the full form of the half-space Green's tensor can be used (without limits being placed on arrangement or distances), which is given by (B.15).

As an example, figure 3.6 shows the effect of a half-space that has been modelled as a perfect reflector, so with reflection coefficients  $r_p = 1$  and  $r_s = -1$ , where  $r_s$  represents the *s* (perpendicular) polarization and  $r_p$  represents the *p* (parallel) polarization. These quantities are defined in (B.10). We can see that there are arrangements of the two bodies for which the half-space enhances the rate of energy transfer between them as well as positions where the half-space suppresses the interaction rate. This points to the complex influence even a simple macroscopic environment can have on energy transfer rates between bodies.

# 3.4 Summary and Conclusion

In this chapter, we have calculated the matrix element for two-body RET using two different methods, and shown them to produce the same result. This equivalence will be useful in chapter 5. We then applied macroscopic QED to the matrix element to include an arbitrary environment, which was then used in the Fermi Golden Rule to find a general formula for the rate of energy transfer between two bodies. We then applied the formula to some simple setups, firstly by calculating analytical expressions for the rate of interaction of two bodies in vacuum, demonstrating the characteristic  $r^{-6}$  and  $r^{-2}$  dependencies for the near- and far-field limits, respectively. We then looked at two bodies in a colinear arrangement near a semiinfinite half-space, and were able to distinguish contributions stemming from direct vacuum interactions and those involving the half-space. Finally, a plot allowed the investigation of general arrangements of the bodies with respect to the half-space, demonstrating the intricate influence even a simple environment can have on the rate of energy transfer.

# CHAPTER 4

# Two-body RET in a Non-Reciprocal Environment

In this chapter, we investigate the effect on the rate of two-body RET of a non-reciprocal environment (see subsection 2.1.2). We will first extend the method for calculating an expression for the rate of energy transfer is section 3.2 to apply to non-reciprocal media, again making use of macroscopic QED (section 2.1).

We then look at a system of two bodies near a non-reciprocal half-space, and investigate the conditions under which the non-reciprocity of the medium will affect the rate of energy transfer. Finally, we give an application of our calculated rate formula as the starting point in the optimization of one-way energy transfer via inverse design [2].

# 4.1 Rate of Energy Transfer in Non-Reciprocal Media

This section considers the same system as the previous chapter, 3, made up of two two-level bodies interacting via RET. We again calculate a formula for the rate of energy transfer between the bodies, but this time relax the assumption that the environment is made up of reciprocal media.

### 4.1.1 Applying Macroscopic QED

Since we are studying the same system as in the previous chapter, the Hamiltonian is set up in the same way as in section 3.1. The initial and final states, (3.4), are also unchanged, so the matrix element is also calculated via (3.18), given again below,

$$M_{fi} = -\sum_{k} \langle f | \left( \frac{H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}}}{\hbar ck - E_{eg}} + \frac{H_{\text{int}}^{\text{D}} H_{\text{int}}^{\text{A}}}{\hbar ck + E_{eg}} \right) | i \rangle , \qquad (4.1)$$

where the interaction Hamiltonian is again defined by (3.3), given by,

$$H_{\text{int}}^{\xi} = -\hat{\boldsymbol{d}}_{\xi} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\xi}). \tag{4.2}$$

However, the way that the electric field is expressed via macroscopic QED for non-reciprocal media is different than for reciprocal media. In section 2.1.2, we saw that for non-reciprocal media we can express the electric field as (2.59), given again below,

$$\boldsymbol{E}(\boldsymbol{r}) = \int_0^\infty d\omega \int d^3 \boldsymbol{s} \, \boldsymbol{F}(\boldsymbol{r}, \boldsymbol{s}, \omega) \cdot \boldsymbol{\hat{f}}(\boldsymbol{s}, \omega) + H.c.$$
(4.3)

where F and  $F^{\dagger}$  are given by (2.60) and (2.61), respectively.

Substituting this into the first term of the matrix element expression, (4.1), via the interaction Hamiltonian, (4.2), and using the same reasoning as in section 3.2.1 where F is analogous to G, we can express the numerator of the first term of (4.1) as,

$$\langle f | H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}} | i \rangle = \int d^{3} \boldsymbol{s} \int_{0}^{\infty} d\omega \, \boldsymbol{d}_{\text{A}}^{\uparrow} \cdot \boldsymbol{F}(\boldsymbol{r}_{\text{A}}, \boldsymbol{s}, \omega) \cdot \boldsymbol{F}^{\dagger}(\boldsymbol{r}_{\text{D}}, \boldsymbol{s}, \omega) \cdot \boldsymbol{d}_{\text{D}}^{\downarrow}.$$
(4.4)

Now substituting in our expressions for F and  $F^{\dagger}$ , given by (2.60) and (2.61) respectively, we obtain,

$$= \int d^{3}\boldsymbol{s} \int_{0}^{\infty} d\omega \, \boldsymbol{d}_{A}^{\dagger} i\mu_{0} \sqrt{\frac{\hbar}{\pi}} \omega^{3/2} \int d^{3}\boldsymbol{r}' \boldsymbol{G}(\boldsymbol{r}_{A}, \boldsymbol{r}', \omega) \cdot \boldsymbol{R}(\boldsymbol{r}', \boldsymbol{s}, \omega)$$

$$\times -i\mu_{0} \sqrt{\frac{\hbar}{\pi}} \omega^{3/2} \int d^{3}\boldsymbol{r}'' \boldsymbol{G}^{\dagger}(\boldsymbol{r}_{D}, \boldsymbol{r}'', \omega) \cdot \boldsymbol{R}^{\dagger}(\boldsymbol{r}'', \boldsymbol{s}, \omega) \cdot \boldsymbol{d}_{D}^{\downarrow}$$

$$= \frac{\mu_{0}^{2}\hbar}{\pi} \int_{0}^{\infty} d\omega \, \omega^{3} \int d^{3}\boldsymbol{r}' \int d^{3}\boldsymbol{r}'' \int d^{3}\boldsymbol{s}$$

$$\times \boldsymbol{d}_{A}^{\dagger} \cdot \boldsymbol{G}(\boldsymbol{r}_{A}, \boldsymbol{r}', \omega) \cdot \boldsymbol{R}(\boldsymbol{r}', \boldsymbol{s}, \omega) \cdot \boldsymbol{G}^{\dagger}(\boldsymbol{r}_{D}, \boldsymbol{r}'', \omega) \cdot \boldsymbol{R}^{\dagger}(\boldsymbol{r}'', \boldsymbol{s}, \omega) \cdot \boldsymbol{d}_{D}^{\downarrow}.$$
(4.5)

Making use of the definition of the  $\mathbf{R}$  function (2.57), we can rewrite as,

$$=\frac{\mu_0^2\hbar}{\pi}\int_0^\infty d\omega\,\omega^3\int d^3\boldsymbol{r}'\int d^3\boldsymbol{r}''\boldsymbol{d}_{\rm A}^{\uparrow}\cdot\boldsymbol{G}(\boldsymbol{r}_{\rm A},\boldsymbol{r}',\omega)\cdot\mathcal{R}\mathbf{e}\boldsymbol{Q}(\boldsymbol{r}',\boldsymbol{r}'',\omega)\cdot\boldsymbol{G}^{\dagger}(\boldsymbol{r}_{\rm D},\boldsymbol{r}'',\omega)\cdot\boldsymbol{d}_{\rm D}^{\downarrow}, \quad (4.6)$$

where  $\mathcal{R}e$  denotes the general real part of a tensor, defined in (2.50).

We use the integral relation (2.97) applicable to non-reciprocal media to rewrite our expression as,

$$\langle f | H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}} | i \rangle = \frac{\mu_0 \hbar}{\pi} \int_0^\infty d\omega \, \omega^2 \boldsymbol{d}_{\text{A}}^{\uparrow} \cdot \mathcal{I} \text{m} \boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, \omega) \cdot \boldsymbol{d}_{\text{D}}^{\downarrow}, \tag{4.7}$$

where  $\mathcal{I}m$  denotes the general imaginary part of a tensor, defined in (2.51). So, we can now express the resonant contribution to the matrix element as,

$$M_{fi}^{res} = -\sum_{p} \langle f | \frac{H_{\text{int}}^{\text{A}} H_{\text{int}}^{\text{D}}}{\hbar c p - E_{\text{eg}}} | i \rangle$$
$$= -\frac{\mu_{0}}{\pi} \int_{0}^{\infty} d\omega \, \boldsymbol{d}_{\text{A}}^{\uparrow} \cdot \frac{\omega^{2} \, \mathcal{I} \mathbf{m} \boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, \omega)}{\omega - \omega_{0}} \cdot \boldsymbol{d}_{\text{D}}^{\downarrow}, \tag{4.8}$$

where we have made the substitutions  $\hbar cp = \hbar \omega$  and  $E_{eg} = \hbar \omega_0$ . For the off-resonant contribution, we can apply similar methods which leads to,

$$M_{fi}^{\text{off}} = -\sum_{p} \langle f | \frac{H_{\text{int}}^{\text{D}} H_{\text{int}}^{\text{A}}}{\hbar c p + E_{\text{eg}}} | i \rangle$$
$$= -\frac{\mu_{0}}{\pi} \int_{0}^{\infty} d\omega \, \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \frac{\omega^{2} \, \mathcal{I} \mathbf{m} \boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, \omega)}{\omega + \omega_{0}} \cdot \boldsymbol{d}_{\text{A}}^{\uparrow}.$$
(4.9)

Now we want to rearrange these integrals so we can apply complex contour integration techniques to solve them. For an integral of the form,

$$\int_{0}^{\infty} d\omega \frac{\omega^{2} \mathcal{I} \mathbf{m} \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega \pm \omega_{0}}, \qquad (4.10)$$

we can use the relation for the general imaginary part of a tensor (2.51) to write the frequency integral as,

$$\frac{1}{2i} \int_0^\infty d\omega \frac{\omega^2}{\omega \pm \omega_0} \left[ \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega) - \boldsymbol{G}^{\dagger}(\boldsymbol{r}', \boldsymbol{r}, \omega) \right].$$
(4.11)

As we did for the reciprocal case, we can make us of the Schwarz reflection principle (2.70)

and the identity  $\int_{a}^{b} f(-x)dx = -\int_{-a}^{-b} f(x)dx$  to rewrite the integral as,

$$\int_{0}^{\infty} d\omega \frac{\omega^{2} \mathcal{I} \mathbf{m} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega)}{\omega \pm \omega_{0}} = \frac{1}{2i} \left[ \int_{0}^{\infty} d\omega \frac{\omega^{2} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega)}{\omega \pm \omega_{0}} + \int_{0}^{-\infty} d\omega \frac{(-\omega)^{2} \mathbf{G}^{\mathrm{T}}(\mathbf{r}', \mathbf{r}, \omega)}{-\omega \pm \omega_{0}} \right]$$
$$= \frac{1}{2i} \left[ \int_{0}^{\infty} d\omega \frac{\omega^{2} \mathbf{G}(\mathbf{r}, \mathbf{r}', \omega)}{\omega \pm \omega_{0}} - \int_{0}^{-\infty} d\omega \frac{\omega^{2} \mathbf{G}^{\mathrm{T}}(\mathbf{r}', \mathbf{r}, \omega)}{\omega \mp \omega_{0}} \right]. \tag{4.12}$$

Applying this to our expressions for the matrix element components, (4.8) and (4.9), we get,

$$M_{fi}^{\rm res} = -\frac{\mu_0}{2\pi i} \boldsymbol{d}_{\rm A}^{\uparrow} \cdot \left[ \int_0^\infty d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega)}{\omega - \omega_0} - \int_0^{-\infty} d\omega \, \frac{\omega^2 \, \boldsymbol{G}^{\rm T}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm A}, \omega)}{\omega + \omega_0} \right] \cdot \boldsymbol{d}_{\rm D}^{\downarrow}, \qquad (4.13)$$

$$M_{fi}^{\text{off}} = -\frac{\mu_0}{2\pi i} \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \left[ \int_0^\infty d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, \omega)}{\omega + \omega_0} - \int_0^{-\infty} d\omega \, \frac{\omega^2 \, \boldsymbol{G}^{\text{T}}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, \omega)}{\omega - \omega_0} \right] \cdot \boldsymbol{d}_{\text{A}}^{\uparrow}. \tag{4.14}$$

We notice the presence of the transposes as a key difference when comparing to the reciprocal result, (3.46) and (3.47), at this stage. In the case of reciprocal media, Lorentz reciprocity (2.75) means that  $\boldsymbol{G}^{\mathrm{T}}(\boldsymbol{r}_{\mathrm{D}(\mathrm{A})}, \boldsymbol{r}_{\mathrm{A}(\mathrm{D})}, \omega) = \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}(\mathrm{D})}, \boldsymbol{r}_{\mathrm{D}(\mathrm{A})}, \omega)$  and the above expressions reduce to (3.46) and (3.47).

#### 4.1.2 Contour Integration

As for the reciprocal case, the frequency integrals in (4.13) and (4.14) have poles on the real axis at  $\pm \omega_0$ , so we let the eigenenergies of the atom take on a small imaginary part, and use the same complex contour integration techniques as in section 3.2.2. Using the same method as for the reciprocal case, we obtain an expression for the first integral term in (4.13),

$$\int_0^\infty d\omega \, \frac{\omega^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega)}{\omega - \omega_0} = i \int_0^\infty d\xi \, \frac{(i\xi)^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi)}{i\xi - \omega_0} + 2\pi i \omega_0^2 \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0). \tag{4.15}$$

Similarly for the second integral term of (4.13), we rewrite as,

$$\int_{0}^{-\infty} d\omega \, \frac{\omega^2 \boldsymbol{G}^{\mathrm{T}}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, \omega)}{\omega + \omega_0} = i \int_{0}^{\infty} d\xi \, \frac{(i\xi)^2 \boldsymbol{G}^{\mathrm{T}}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, i\xi)}{i\xi + \omega_0}.$$
 (4.16)

Combining these two integral terms, (4.15) and (4.16), we obtain an expression for the resonant component of the matrix element (4.13),

$$M_{fi}^{\text{res}} = -\frac{\mu_0}{2\pi i} \left( \boldsymbol{d}_{\text{A}}^{\uparrow} \cdot i \int_0^\infty d\xi \, (i\xi)^2 \left[ \frac{\boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, i\xi)}{i\xi - \omega_0} - \frac{\boldsymbol{G}^{\text{T}}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, i\xi)}{i\xi + \omega_0} \right] \cdot \boldsymbol{d}_{\text{D}}^{\downarrow} + 2\pi i \omega_0^2 \boldsymbol{d}_{\text{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, \omega_0) \cdot \boldsymbol{d}_{\text{D}}^{\downarrow} \right) = \frac{\mu_0}{2\pi} \boldsymbol{d}_{\text{A}}^{\uparrow} \cdot \left( \int_0^\infty d\xi \, \xi^2 \left[ \frac{\boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, i\xi)}{i\xi - \omega_0} - \frac{\boldsymbol{G}^{\text{T}}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, i\xi)}{i\xi + \omega_0} \right] - 2\pi \omega_0^2 \boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, \omega_0) \right) \cdot \boldsymbol{d}_{\text{D}}^{\downarrow}.$$

$$(4.17)$$

We note here that in the reciprocal case, at this point we made use of the Lorentz reciprocity (2.75) of the Green's tensor to combine the terms in the square brackets into a single term. However, we are unable to do this when considering non-reciprocal media, since Lorentz reciprocity (2.75) does not hold.

We repeat the same steps for the off-resonant component of the matrix element, (4.14),

$$M_{fi}^{\text{off}} = -\frac{\mu_0}{2\pi i} \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot i \int_0^\infty d\xi \, (i\xi)^2 \left[ \frac{\boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, i\xi)}{i\xi + \omega_0} - \frac{\boldsymbol{G}^{\text{T}}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, i\xi)}{i\xi - \omega_0} \right] \cdot \boldsymbol{d}_{\text{A}}^{\uparrow} \\ = \frac{\mu_0}{2\pi} \, \boldsymbol{d}_{\text{D}}^{\downarrow} \cdot \int_0^\infty d\xi \, \xi^2 \left[ \frac{\boldsymbol{G}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{A}}, i\xi)}{i\xi + \omega_0} - \frac{\boldsymbol{G}^{\text{T}}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, i\xi)}{i\xi - \omega_0} \right] \cdot \boldsymbol{d}_{\text{A}}^{\uparrow}.$$
(4.18)

We are now able to sum the resonant and the off-resonant components of the matrix element, (4.17) and (4.18), to find the full matrix element,

$$M_{fi} = -\mu_0 \omega_0^2 \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow} + \frac{\mu_0}{2\pi} \int_0^{\infty} d\xi \, \xi^2 \left( \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \left[ \frac{\boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi)}{i\xi - \omega_0} - \frac{\boldsymbol{G}^{\mathrm{T}}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, i\xi)}{i\xi + \omega_0} \right] \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow} + \boldsymbol{d}_{\mathrm{D}}^{\downarrow} \cdot \left[ \frac{\boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, i\xi)}{i\xi + \omega_0} - \frac{\boldsymbol{G}^{\mathrm{T}}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, i\xi)}{i\xi - \omega_0} \right] \cdot \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \right).$$
(4.19)

We can use the relation  $\boldsymbol{a} \cdot \boldsymbol{B} \cdot \boldsymbol{c} = \boldsymbol{c} \cdot \boldsymbol{B}^{\mathrm{T}} \cdot \boldsymbol{a}$  for vectors  $\boldsymbol{a}$  and  $\boldsymbol{c}$  and matrix  $\boldsymbol{B}$ , to see that all terms under the integral vanish, leaving,

$$M_{fi} = -\mu_0 \omega_0^2 \, \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_0) \cdot \boldsymbol{d}_{\mathrm{D}}^{\downarrow}.$$
(4.20)

We note that this is the same result that is obtained for the reciprocal case by comparing with (3.65). However, the G that goes into the above equation will be that for non-reciprocal media (see, for example, B.3). Physically, it makes sense that the integral terms cancel, since these correspond to the non-resonant, and therefore fully quantum, time ordering. Since non-reciprocity is not a quantum effect, we would expect this result to agree with the classical case.

#### 4.1.3 Calculating the Rate

In analogy with the reciprocal case, we now use the matrix element (4.20) in Fermi's Golden Rule;

$$\Gamma_{fi} = \frac{2\pi}{\hbar} |M_{fi}|^2 \delta(E_{\rm I} - E_f)$$
  
=  $\frac{2\pi \mu_0^2 \omega_0^4}{\hbar} |\boldsymbol{d}_{\rm A}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega_0) \cdot \boldsymbol{d}_{\rm D}^{\downarrow}|^2$  (4.21)

where we have assumed real dipole moments. This formula is valid for both reciprocal and non-reciprocal media, as can be seen by comparison with (3.68).

If we were to multiply out the modulus squared, we find that for non-reciprocal media we can rewrite as,

$$\Gamma_{fi}^{\rm NR} = \frac{2\pi\mu_0^2\omega_0^4}{\hbar} \left( \boldsymbol{d}_{\rm A}^{\uparrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega_0) \cdot \boldsymbol{d}_{\rm D}^{\downarrow} \right) \cdot \left( \boldsymbol{d}_{\rm A}^{\downarrow} \cdot \boldsymbol{G}^*(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega_0) \cdot \boldsymbol{d}_{\rm D}^{\uparrow} \right).$$
(4.22)

However, we recall that for reciprocal media Lorentz reciprocity holds (2.74), so we could rewrite this as,

$$\Gamma_{fi}^{R} = \frac{2\pi\mu_{0}^{2}\omega_{0}^{4}}{\hbar} \left( \boldsymbol{d}_{\mathrm{D}}^{\downarrow} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}, \omega_{0}) \cdot \boldsymbol{d}_{\mathrm{A}}^{\uparrow} \right) \cdot \left( \boldsymbol{d}_{\mathrm{A}}^{\downarrow} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}, \omega_{0}) \cdot \boldsymbol{d}_{\mathrm{D}}^{\uparrow} \right), \qquad (4.23)$$

allowing us to directly compare and notice the difference in the first bracketed term. We also note that the physical interpretation we were able to make for the reciprocal rate at the end of section 3.2.2 cannot be made for the rate in non-reciprocal media. In other words, while the form of the matrix element (3.67) remains unchanged in terms of G, its modulus square appearing in Fermi's Golden Rule (and therefore the rate) cannot be simplified and interpreted in the same way as for reciprocal media.

We now apply our rate formula to a specific example of two-bodies near a non-reciprocal semi-infinite half-space. We will investigate under which conditions a swap in the positions of the donor and acceptor will result in a change in the rate of energy transfer between them.

# 4.2 Non-reciprocal Half-space

In the context of resonant energy transfer, non-reciprocity reveals itself when the positions of the donor and acceptor are swapped. In the presence of reciprocal media, the rate of energy transfer between a donor at point 1 and acceptor at point 2 will be the same as between a donor at point 2 and acceptor at point 1. However, in non-reciprocal media, there are certain circumstances under which a swap of this kind will affect the rate of interaction between the molecules.

In this section, we will look at a simple environment of a semi-infinite half space for different arrangements and dipole orientations, and examine the effects of swapping the position of a donor and acceptor (or equivalently,  $\mathbf{r}$  and  $\mathbf{r'}$  being swapped in  $\mathbf{G}(\mathbf{r}, \mathbf{r'}, \omega)$ ). We make use of the Green's function for a layered topological insulator calculated in Ref. [78] (see section B.3). This Green's function has a complex form, given in (B.46), that requires the evaluation of an infinite integral. For this reason, instead of calculating the rate of interaction for different arrangements as was done in the previous chapter, we will look only at quantities that are directly affected by a position swap, and from that deduce if the rate of interaction is also affected.

To simplify things, will consider two specific arrangements of the bodies with respect to a surface at z < 0, shown in figure 4.1. The first of these is "parallel", where both bodies are equidistant from the surface and at equal distances above and below the z-axis, so that the line connecting the bodies is parallel to the surface. The other is "colinear", where, as in the previous chapter, both bodies are on the z-axis. We will also be considering different orientations of the dipole moments of the two bodies. In the previous chapter, we only calculated the rate of interaction between two bodies with dipole moments that are randomly oriented, whereas in this chapter, we will also consider how the rate is affected when the dipole moments have specific orientations in relation to the half-space and to each other. As we will see, this will be a crucial element for distinguishing cases where a position switch affects the interaction rate.



Figure 4.1: Two possible arrangements of two bodies, a donor D and an acceptor A, near a semi-infinite half-space at z < 0.

# 4.2.1 Oriented dipole moments

We first consider the case where the dipole moments are oriented in either the x, y or z directions. We can write these cases as,

$$\boldsymbol{d}^{(x)} = |\boldsymbol{d}| (1,0,0), \quad \boldsymbol{d}^{(y)} = |\boldsymbol{d}| (0,1,0), \quad \boldsymbol{d}^{(z)} = |\boldsymbol{d}| (0,0,1).$$
(4.24)

We now consider the rate of energy transfer between two dipole moments,  $d^{(m)}$  positioned at r and oriented in the m direction, and  $d'^{(n)}$  at r' and oriented in the n direction, where m and n could be x, y or z. We can calculate the rate, first assuming that  $d^{(m)}$  is the donor and  $d'^{(n)}$  is the acceptor, and then vice versa. Using the rate equation (4.22), we find,

$$\Gamma_{(m),(n)}^{\text{NRec}} = \frac{2\pi\mu_0^2\omega_D^4}{\hbar} \left( \boldsymbol{d}^{(m)} \cdot \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}') \cdot \boldsymbol{d}'^{(n)} \right) \cdot \left( \boldsymbol{d}^{(m)} \cdot \boldsymbol{G}^*(\boldsymbol{r}, \boldsymbol{r}') \cdot \boldsymbol{d}'^{(n)} \right) \\
= \frac{2\pi\mu_0^2\omega_D^4}{\hbar} |\boldsymbol{d}|^2 |\boldsymbol{d}'|^2 G_{mn}(\boldsymbol{r}, \boldsymbol{r}') G_{mn}^*(\boldsymbol{r}, \boldsymbol{r}'), \qquad (4.25a)$$

$$\Gamma_{(n),(m)}^{\text{NRec}} = \frac{2\pi\mu_0^2\omega_D^4}{\hbar} \left( \boldsymbol{d}'^{(n)} \cdot \boldsymbol{G}(\boldsymbol{r}', \boldsymbol{r}) \cdot \boldsymbol{d}^{(m)} \right) \cdot \left( \boldsymbol{d}'^{(n)} \cdot \boldsymbol{G}^*(\boldsymbol{r}', \boldsymbol{r}) \cdot \boldsymbol{d}^{(m)} \right) \\
= \frac{2\pi\mu_0^2\omega_D^4}{\hbar} |\boldsymbol{d}|^2 |\boldsymbol{d}'|^2 G_{nm}(\boldsymbol{r}', \boldsymbol{r}) G_{nm}^*(\boldsymbol{r}', \boldsymbol{r}), \qquad (4.25b)$$

where we have omitted the dependence on  $\omega_0$  for ease of reading. This shows that the orientation of the two dipole moments and where they are positioned determines which component of the Green's tensor matrix contributes to the calculation of the rate. It is therefore clear that a change in the rate of interaction will only occur if,

$$G_{mn}(\boldsymbol{r},\boldsymbol{r}')G_{mn}^{*}(\boldsymbol{r},\boldsymbol{r}') \neq G_{nm}(\boldsymbol{r}',\boldsymbol{r})G_{nm}^{*}(\boldsymbol{r}',\boldsymbol{r}).$$

$$(4.26)$$

where m and n could be x, y or z. So,  $G_{mn}$  denotes a single component of the tensor, determined by the orientation of the dipole moments. This will be how we can determine for which systems switching the donor and acceptor will change the interaction rate.

We note here that Lorentz reciprocity, (2.74), which states that  $G(\mathbf{r}, \mathbf{r}') = \mathbf{G}^T(\mathbf{r}', \mathbf{r})$  for reciprocal media, implies that the above will never be true for reciprocal media. So we can conclude that the rate of energy transfer will be unaffected by a position swap for reciprocal media for oriented dipole moments, as expected.

We will now specifically consider the two arrangements shown in figure 4.1, and explore the effect the different dipole moment orientations have on the rate when the molecule positions are swapped.

#### Parallel Arrangement

We first investigate two bodies in a parallel arrangement with the non-reciprocal half-space, as in figure 4.1a. The expression for the Green's tensor for a half-space made up of nonreciprocal media for a parallel arrangement is given in (B.52) and again below,

$$\boldsymbol{G}^{(1,\mathrm{P})}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{4\pi} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{2ik^{\perp}z} \boldsymbol{R}_{\mathrm{P}}^{ij}, \qquad (4.27)$$

where P references the parallel arrangement. The  $\mathbf{R}_{\rm P}^{ij}$  components are given by (B.53), which depend on  $X \equiv x - x'$  along with the Fresnel coefficients  $r_{s,s}$ ,  $r_{p,p}$ ,  $r_{s,p}$  and  $r_{p,s}$  which are defined by (B.43).  $r_{s,s}$  represents the *s* (perpendicular) polarization,  $r_{p,p}$  represents the *p* (parallel) polarization, and  $r_{s,p}$  and  $r_{p,s}$  denote the mixing of the two polarizations that occurs due to the magnetoelectric coupling present in non-reciprocal media [78].

We note that in this arrangement, switching the donor and acceptor amounts to making the replacement  $X \to -X$ . Therefore, it is the way that the  $X \to -X$  replacement affects the  $\mathbf{R}_{\rm P}^{ij}$  components that will determine if a rate change is observed. This means we can write our condition (4.26) as,

$$R_{\rm P}^{mn}(X)R_{\rm P}^{mn^*}(X) \neq R_{\rm P}^{nm}(-X)R_{\rm P}^{nm^*}(-X).$$
(4.28)

To see if the rate changes for oriented dipole moments, we need to consider the possible dipole orientation combinations and see which satisfy (4.28).

If we firstly consider the cases where both dipole moments are oriented in the same direction,

then the inequality that must be satisfied is,

$$R_{\rm P}^{mm}(X)R_{\rm P}^{mm^*}(X) \neq R_{\rm P}^{mm}(-X)R_{\rm P}^{mm^*}(-X)$$
(4.29)

where m is x, y or z. The diagonal elements of  $\mathbf{R}_{\rm P}$  are,

$$R_{\rm P}^{xx} = \frac{J_1(k^{\parallel}|X|)}{|X|} \left( r_{s,s} + \frac{k_z^2}{k_1^2} r_{p,p} \right) - J_0(k^{\parallel}|X|) \frac{k_z^2}{k_1^2} r_{p,p}, \qquad (4.30a)$$

$$R_{\rm P}^{yy} = -\left[\frac{J_1(k^{\parallel}|X|)}{|X|}\left(r_{s,s} + \frac{k_z^2}{k_1^2}r_{p,p}\right) - J_0(k^{\parallel}|X|)r_{s,s}\right],\tag{4.30b}$$

$$R_{\rm P}^{zz} = -J_0(k^{\parallel}|X|) \frac{k^{\parallel^2}}{k_1^2} r_{p,p}.$$
(4.30c)

We can see that the only explicit position dependence in these components are of the form |X|, so it is clear that none of these would be affected by the replacement  $X \to -X$ . We can therefore deduce that the condition (4.29) cannot be satisfied in this system when the dipole moments have the same orientation.

We now consider the case where the two dipole moments have different orientations, so we must examine the off-diagonal components of  $\mathbf{R}_{\rm P}$  and if they satisfy (4.28). Here we must be more careful, as a switch in the positions of the bodies also means a switch in the positions of the different dipole moment orientations, which correspond to different components of  $\mathbf{R}_{\rm P}$ .

Looking first at the case where one dipole moment is oriented in the x direction and the other in the y direction, the relevant  $\mathbf{R}_{\rm P}$  components are,

$$R_{\rm P}^{xy} = \frac{k_z}{k_1} \left[ \frac{J_1(k^{\parallel}|X|)}{|X|} \left( r_{s,p} + r_{p,s} \right) - J_0(k^{\parallel}|X|) r_{p,s} \right],$$
(4.31a)

$$R_{\rm P}^{yx} = \frac{k_z}{k_1} \left[ \frac{J_1(k^{\parallel}|X|)}{|X|} \left( r_{s,p} + r_{p,s} \right) - J_0(k^{\parallel}|X|) r_{s,p} \right].$$
(4.31b)

We can see that although the only explicit position dependence is |X|, which is unaffected by a position swap, since  $R_{\rm P}^{xy} \neq R_{\rm P}^{yx}$  when  $r_{p,s} \neq r_{s,p}$ , a switch in which molecule has which orientation  $(x \leftrightarrow y)$  can result in a change. Calculating the quantities of interest according to (4.28), we find,

$$R_{\rm P}^{xy}(X)R_{\rm P}^{xy^*}(X) = \frac{k_z^2}{k_1^2} \left[ \frac{J_1(k^{\parallel}|X|)}{|X|} \left( r_{s,p} + r_{p,s} \right) - J_0(k^{\parallel}|X|) r_{p,s} \right]^2$$
$$= \frac{k_z^2}{k_1^2} \left[ \left( \frac{J_1(k^{\parallel}|X|)}{|X|} \right)^2 \left( r_{s,p} + r_{p,s} \right)^2 + J_0(k^{\parallel}|X|)^2 r_{p,s}^2 - \frac{J_1(k^{\parallel}|X|)J_0(k^{\parallel}|X|)}{|X|} \left( r_{s,p} + r_{p,s} \right) r_{p,s} \right], \qquad (4.32a)$$

$$R_{\rm P}^{yx}(-X)R_{\rm P}^{yx^*}(-X) = \frac{k_z^2}{k_1^2} \left[ \left( \frac{J_1(k^{\parallel}|X|)}{|X|} \right)^2 \left( r_{s,p} + r_{p,s} \right)^2 + J_0(k^{\parallel}|X|)^2 r_{s,p}^2 - \frac{J_1(k^{\parallel}|X|)J_0(k^{\parallel}|X|)}{|X|} \left( r_{s,p} + r_{p,s} \right) r_{s,p} \right], \qquad (4.32b)$$

which we can see are different only if  $r_{s,p} \neq \pm r_{p,s}$ .

We can perform the same test for x and z oriented dipole moments, which correspond to the components,

$$R_{\rm P}^{xz} = -R_{\rm P}^{zx} = -i\frac{k^{\parallel}k_z}{k_1^2}J_1(k^{\parallel}X)r_{p,p}.$$
(4.33)

We then calculate the quantities of interest,

$$R_{\rm P}^{xz}(X)R_{\rm P}^{xz^*}(X) = \left(\frac{k^{\parallel}k_z}{k_1^2}J_1(k^{\parallel}X)r_{p,p}\right)^2$$
(4.34)

and

$$R_{\rm P}^{zx}(-X)R_{\rm P}^{zx^*}(-X) = \left(-\frac{k^{\parallel}k_z}{k_1^2}J_1(k^{\parallel}X)r_{p,p}\right)^2$$
(4.35)

where we have used the fact that  $J_1(x)$  (a Bessel function of the first kind) is an odd function, meaning  $J_1(-x) = -J_1(x)$ . We can therefore see that these components are equal, meaning the inequality (4.26) will never hold for these dipole orientations.



Figure 4.2: The combinations of positions and dipole moment orientations for two bodies near a semi-infinite half-space at z < 0 that produce a rate change when the two bodies switch positions. Small arrows indicate the dipole moment orientation, with dots signifying the moment pointing out of the page in the y direction.

Finally, we can test y and z oriented dipole moments, corresponding to components,

$$R_{\rm P}^{yz} = i \frac{k^{\parallel}}{k_1} J_1(k^{\parallel} X) r_{s,p}, \qquad (4.36a)$$

$$R_{\rm P}^{zy} = -i\frac{k^{\parallel}}{k_1}J_1(k^{\parallel}X)r_{p,s}.$$
(4.36b)

So the quantities of interest are,

$$R_{\rm P}^{yz}(X)R_{\rm P}^{yz^*}(X) = \left(\frac{k^{\parallel}}{k_1}J_1(k^{\parallel}X)r_{s,p}\right)^2, \qquad (4.37a)$$

$$R_{\rm P}^{zy}(-X)R_{\rm P}^{zy^*}(-X) = \left(-\frac{k^{\parallel}}{k_1}J_1(k^{\parallel}X)r_{p,s}\right)^2,\tag{4.37b}$$

which are only different when  $r_{s,p} \neq \pm r_{p,s}$ , the same condition we saw for the x, y orientation combination.

We can conclude that when one of the parallel-arranged dipole moments is oriented in the y direction and the other in the x or z direction (see figure 4.2), we see a change in the rate of energy transfer when in the presence of a non-reciprocal half-space with  $r_{s,p} \neq \pm r_{p,s}$ .

#### **Colinear Arrangement**

We now consider the colinear arrangement setup shown in figure 4.1b. The expression for the Green's tensor for a half-space made up of non-reciprocal media for a colinear arrangement is given in (B.55) and again below,

$$\boldsymbol{G}^{(1,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\perp}\bar{Z}} \boldsymbol{R}_{\mathrm{C}}^{ij}, \qquad (4.38)$$

where C references the colinear arrangement, and the  $\mathbf{R}_{C}^{ij}$  components are given by (B.56). We note that the only explicit position dependence is  $\overline{Z} \equiv z + z'$ , which is unaffected by a position swap  $(z \leftrightarrow z')$ .

First looking at the diagonal elements of  $\mathbf{R}_{\rm C}^{ij}$  which correspond to both dipole moments having the same orientation,

$$R_{\rm C}^{xx} = R_{\rm C}^{yy} = r_{s,s} - \frac{k_z^2}{k_1^2} r_{p,p}, \qquad (4.39a)$$

$$R_{\rm C}^{zz} = -\frac{k^{\parallel^2}}{k_1^2} r_{p,p}, \qquad (4.39b)$$

we can see that none of them have explicit position dependence, meaning the condition (4.29) cannot be satisfied. The only non-zero off-diagonal elements are given by,

$$R_{\rm C}^{xy} = -R_{\rm C}^{yx} = \frac{k_z}{k_1} \left( r_{s,p} - r_{p,s} \right).$$
(4.40)

which also do not have an explicit position dependence. By noting that  $R^{xy}R^{xy^*} = R^{yx}R^{yx^*}$ , we can see that the criterion (4.26) is never satisfied. This means that in the collinear arrangement with oriented dipole moments, a position swap will never affect the rate of interaction.

From this section we can conclude that when the two molecules are in a colinear arrangement with a non-reciprocal half-space, none of the dipole moment orientation combinations considered will affect the rate of interaction if the molecule positions are swapped. However, when they are in a parallel arrangement and one of the dipole moments is y oriented and the other is x or z oriented, a change in the rate of interaction can be detected under a position swap as long as  $r_{s,p} \neq \pm r_{p,s}$ . We now move on to the situation where the dipole moments do not have specific orientations, but instead are randomly oriented.

#### 4.2.2 Isotropic Dipole Moments

To consider the case where the dipole moments are isotropically averaged, we make the same replacement as in the previous chapter in eq. (3.69),  $d^{\uparrow}_{A/D} \otimes d^{\downarrow}_{A/D} \rightarrow \frac{1}{3} |d_{A/D}|^2 \mathbb{I}$ , in our rate equation (4.22) to obtain,

$$\Gamma_{\rm iso}^{\rm NRec} = \frac{2\pi\mu_0^2\omega_0^4}{9\hbar} |\boldsymbol{d}_{\rm A}|^2 |\boldsymbol{d}_{\rm D}|^2 \operatorname{Tr} \left[ \boldsymbol{G}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega_0) \cdot \boldsymbol{G}^*(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega_0) \right].$$
(4.41)

We want to see if a swap in the positions of the donor and acceptor would affect the rate of energy transfer between them. For isotropically averaged dipole moments, we would see a
rate change only if,

Tr 
$$\left[\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}')\cdot\boldsymbol{G}^{*}(\boldsymbol{r},\boldsymbol{r}')\right] \neq$$
 Tr  $\left[\boldsymbol{G}(\boldsymbol{r}',\boldsymbol{r})\cdot\boldsymbol{G}^{*}(\boldsymbol{r}',\boldsymbol{r})\right],$  (4.42)

where we have again omitted the dependence on  $\omega_0$ . So, we need to examine the forms of the Green's tensor for the different geometries near a half-space and see if they fit this criterion.

It is useful to explicitly write out the trace in terms of the components of G,

$$\operatorname{Tr}\left[\boldsymbol{G}\cdot\boldsymbol{G}^*\right] = \sum_{m,n} G_{mn} G_{nm}^*,\tag{4.43}$$

making it easy to see that the condition (4.42) can equivalently be written in index notation as,

$$G_{ij}(\boldsymbol{r},\boldsymbol{r}')G_{ji}^*(\boldsymbol{r},\boldsymbol{r}') \neq G_{ij}(\boldsymbol{r}',\boldsymbol{r})G_{ji}^*(\boldsymbol{r}',\boldsymbol{r}).$$

$$(4.44)$$

As an aside, we note that since reciprocal media obeys Lorentz reciprocity (2.74), which states that  $G_{ij}(\mathbf{r}, \mathbf{r}') = G_{ji}(\mathbf{r}', \mathbf{r})$ , we can see that the inequality (4.44) will never be fulfilled for reciprocal media. Therefore, we can conclude that for isotropically averaged dipole moments, a position swap in reciprocal media will not effect the rate of energy transfer, as we would expect.

#### Parallel Arrangement

To test if the isotropic rate will change with a position switch, instead of comparing individual components as in the previous section, we are checking if the trace changes when the positions are swapped. We can again examine the  $\mathbf{R}_{\rm P}^{ij}$  components to check this, noting that in the parallel arrangement, a position swap is equivalent to the replacement  $X \to -X$ . This means that our requirement (4.42) for a parallel arrangement can also be written,

$$\sum_{m,n} R_{\rm P}^{mn}(X) R_{\rm P}^{nm^*}(X) \neq \sum_{m,n} R_{\rm P}^{mn}(-X) R_{\rm P}^{nm^*}(-X).$$
(4.45)

We need to examine the requirement (4.45) for each of the possible index combinations and see if any of them present an inequality.

Firstly, when m = n, i.e. the diagonal components given in (4.30), we can use the same reasoning as the previous section to again see that  $R_{\rm P}^{mm}(X)R_{\rm P}^{mm^*}(X) \neq R_{\rm P}^{mm}(-X)R_{\rm P}^{mm^*}(-X)$  cannot be satisfied.

When  $\{m, n\} = \{x, y\}$ , we note that the relevant components given in (4.31),  $R_{\rm P}^{xy}$  and  $R_{\rm P}^{yx}$ , have explicit position dependence of the form |X| only. As a result,  $R_{\rm P}^{mn}(X) = R_{\rm P}^{mn}(-X)$  and  $R_{\rm P}^{mn^*}(X) = R_{\rm P}^{mn^*}(-X)$ , meaning (4.45) cannot be fulfilled.

For the index pairs  $\{m, n\} = \{x, z\}$  and  $\{m, n\} = \{y, z\}$ , we see an explicit dependence on X in the corresponding components  $R_{\rm P}^{xz}$  and  $R_{\rm P}^{zx}$  given in (4.33), and  $R_{\rm P}^{yz}$  and  $R_{\rm P}^{zy}$  given in (4.36). However, for both index pairs we find  $R_{\rm P}^{mn}(X) = -R_{\rm P}^{mn}(-X)$  and  $R_{\rm P}^{nm^*}(X) = -R_{\rm P}^{nm^*}(-X)$ , so the quantity of interest in (4.45) is again unchanged by the replacement  $X \to -X$ .

Therefore, although we saw in the previous section that it is possible to observe a rate change in this arrangement for certain dipole moment orientations, the same is not true for isotropically averaged dipole moments.

#### **Colinear Arrangement**

For the colinear arrangement, upon inspection of the non-zero  $R_{\rm C}^{mn}$  components given in (4.39) and (4.40), we can see that none of them have an explicit position dependence, and so will be unaffected by a position swap. Therefore, switching the positions of two molecules in a colinear arrangement near a non-reciprocal half-space will not result in a change in the interaction rate if the dipole moments are isotropically averaged.

In this section, we have found that when two molecules near a non-reciprocal surface have randomly oriented dipole moments, a change in the rate of interaction will not be observed under a position swap for either the colinear or the parallel arrangements.

In the next section, we use our findings to focus on setups where a position swap can lead to a rate change. We investigate two situations of interest, and plot how the interaction rate is affected by the molecules' positions for energy transfer between the bodies in one direction compared to the other.

### 4.2.3 Plots and Discussion

Based on the calculations of the previous two sections, we can conclude that following conditions must be met in order to observe a change in the rate of energy transfer when the positions of the donor and acceptor near a half-space are swapped:

- The dipoles must be in a parallel arrangement
- One of the dipole moments must be oriented in the y direction, and the other in either the x or z directions
- The coefficients  $r_{s,p}$  and  $r_{p,s}$  of the half-space must be non-zero and satisfy  $r_{s,p} \neq \pm r_{p,s}$

Physically, it makes sense that the rate of interaction in a colinear arrangement would not



Figure 4.3: Figure showing how energy is transferred between a donor D and an acceptor A near a semi-infinite half-space at z < 0 for two different arrangements.

be affected by the non-reciprocity of the half-space. Since the dipoles are both on the z-axis, a position swap would not affect the way the energy interacts with the half-space, as can be seen in figure 4.3b. On the other hand, a position swap in the parallel arrangement would mean that the radiation propagates in the opposite direction through the medium, as in figure 4.3a, which for non-reciprocal media would result in different properties.

Under the above conditions, we can plot the rate of energy transfer against intermolecular distance and see how switching the positions of the dipoles affects the results.

Figure 4.4a shows how the rate of interaction depends on intermolecular distance for a yoriented donor and an x-oriented acceptor, and how this is altered when these orientations
are switched, so the donor becomes the acceptor and vice versa. We note that both plots
oscillate, which is due to the Bessel functions present in (4.32). We can also see that the
presence of the half-space produces only enhancement of the rate compared to the vacuum,
although there are intermolecular distances for which the half-space provides no enhancement
for the  $y \to x$  direction.

The difference in plot shapes and maximum values for the different directions is determined by the different reflection coefficient values chosen. From (4.32), we can see that although both directions depend on both the reflection coefficients  $r_{s,p}$  and  $r_{p,s}$ , the  $x \to y$  direction has an extra dependence on  $r_{p,s}$  and the opposite direction on  $r_{p,s}$ . We can think of the direction corresponding to the larger reflection coefficient as being the dominant direction. So since we chose  $r_{p,s} > r_{s,p}$  for figure 4.4,  $x \to y$  is the dominant direction, and therefore provides more rate enhancement. So if we wanted to maximise energy transfer in one direction and minimise it in the other, this could be achieved by increasing the reflection coefficient that corresponds to the desirable direction. For example, if we wanted to maximise the  $y \to x$ interaction, we would increase  $r_{p,s}$  and decrease  $r_{s,p}$ .





(a) Rate of energy being transferred from an *x*-oriented dipole moment to a *y*-oriented dipole moment, compared to the other direction.

(b) Rate of energy being transferred from an z-oriented dipole moment to a y-oriented dipole moment, compared to the other direction.

Figure 4.4: Plot of rate of energy transfer against intermolecular distance for two bodies near a non-reciprocal half-space, normalised to the isotropic vacuum rate. The reflection coefficients are set at  $r_{p,p} = 1$ ,  $r_{s,s} = -1$ ,  $r_{p,s} = 0.5$  and  $r_{s,p} = 0.2$ . The intermolecular distance is in units of the transition wavelength  $\lambda_0$ . The surface is positioned at z < 0, and the donor and acceptor are both  $1.05\lambda_0$  from the surface, with their positions varying along the x-axis.

We also note that periodically there are intermolecular distances where the interaction occurs at the same rate for both directions, and then between those distances the dominant direction observes a further rate enhancement, and the other drops to zero. So for some distances, the direction makes no difference to the rate, and for others, one direction is more desirable.

Figure 4.4b is for a y-oriented donor and an z-oriented acceptor, and shows how the rate of interaction changes when the dipoles are swapped. In this case, we can see that the shape of the plot is the same for both directions; the rate increases with intermolecular distance, and once a certain distance is reached (~  $10\lambda_0$ ), the enhancement of the rate of energy transfer remains constant as the distances increases. The difference in the maximum rate reached is determined by the reflection coefficients,  $r_{s,p}$  and  $r_{p,s}$ . From (4.37), we can see that the  $y \to z$  direction is dependent on  $r_{s,p}$  while the opposite direction is determined by  $r_{p,s}$ . The choice made for figure 4.4 of  $r_{p,s} > r_{s,p}$  is reflected by the maximum value of the  $z \to y$  direction being larger. So increasing the relevant reflection coefficient will increase the maximum rate in the corresponding direction;  $r_{s,p}$  for  $y \to z$  and  $r_{p,s}$  for  $z \to y$ .

From this section we can see that in a setup of two molecules in a parallel arrangement near a non-reciprocal half-space, under certain conditions the properties of the medium can be engineered in order to maximise energy transfer between the two molecules in one direction over the other. This demonstrates an example of how non-reciprocity can be a vital tool in the design of components that require one-way propagation, for example the elimination of backreflection in communication technologies (see e.g. Ref. [19]).

In the next section, we look at an application of this principle presented in the publication [2], namely the use of non-reciprocity in the design of an optical isolator. This is a situation which requires the unidirectional propagation of light, and as we saw in this section, there are situations where properties of a non-reciprocal medium can be manipulated to achieve this.

# 4.3 Application in Inverse Design of RET Isolation

In this section, we review the methods and results of C. Cisowski, which are based on our result (4.21) and presented in our publication [2]. In this work, inverse design and threedimensional topology optimization are used to optimize one-way energy transfer through non-reciprocal Faraday media.

We first give a brief overview of the principles of inverse design, specifically how Green's tensors can be made use of to account for non-reciprocity. Next, we look at how these methods can be combined with our result (4.21) to create a device that maximises unidirectional energy transfer between two molecules either side of it. Finally, we review the results produced by C. Cisowski et al. for our publication [2] in which the inverse design of such a device is carried out.

## 4.3.1 Inverse Design

Our calculated formula for the rate of energy transfer in non-reciprocal media (4.21) can be made use of in the design of the non-reciprocal response of a device. The method used by C. Cisowski et al. in our publication [2] is based on inverse design, which uses an efficient, free-form algorithm to find improved structures for a goal specified by the designer with any required constraints considered. This is instead of the traditional method of a designer specifying a structure and testing against a set of desired characteristics (for a review of the use of inverse design in nanophotonics, see [79].)

A prominent technique used in modern inverse design is the adjoint method [80–82], which is used to reduce the number of simulations that must be carried out. This is done by considering the way radiation propagates through the same system in a "forward" direction (source to observer) and "adjoint" direction (observer to source). However, the challenge for a non-reciprocal medium is that these two directions are physically distinct and therefore do not represent the same physical system. This can be resolved by using a Green's tensor-based inverse design approach [83], on which this section will focus.

#### Inverse Design using Green's Tensors

To carry out an optimization, the goal is to increase the value of a merit function F of some functional f of the Green's tensor  $G(\mathbf{r}, \mathbf{r}', \omega)$  [83],

$$F = f[\boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)]. \tag{4.46}$$

To find the maximum of F, we take a functional derivative. In principle, we would have to take functional derivatives with respect to the real and imaginary parts of G separately, but it is in fact more convenient to consider G and its complex conjugate  $G^*$  separately instead (see [83]). Each of the independent components of the Green's tensor must be varied during an optimization, so we can make use of the Frobenius product denoted by  $\odot$ , where  $A \odot B \equiv \sum_{ij} A_{ij} B_{ij}$  for matrices A and B. The required derivative is,

$$\delta F = \frac{\partial f}{\partial \boldsymbol{G}}(\boldsymbol{r}, \boldsymbol{r}', \omega) \odot \delta \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega) + \frac{\partial f}{\partial \boldsymbol{G}^*}(\boldsymbol{r}, \boldsymbol{r}', \omega) \odot \delta \boldsymbol{G}^*(\boldsymbol{r}, \boldsymbol{r}', \omega)$$
$$= 2 \operatorname{Re} \left[ \frac{\partial f}{\partial \boldsymbol{G}}(\boldsymbol{r}, \boldsymbol{r}', \omega) \odot \delta \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega) \right], \qquad (4.47)$$

where  $\delta \boldsymbol{G}$  is an unknown change in the Green's tensor due to an infinitesimal change in the environment. This can be written via a truncated Born series as [84],

$$\delta \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \mu_0 \omega^2 \int_V d^3 \boldsymbol{r}'' n(\boldsymbol{r}'') \alpha(\boldsymbol{r}'') \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}'',\omega) \cdot \boldsymbol{G}(\boldsymbol{r}'',\boldsymbol{r}',\omega), \qquad (4.48)$$

where the volume V contains the region of the environment that has changed,  $n(\mathbf{r})$  is the number density of the atoms within V, and  $\alpha(\mathbf{r})$  are their polarizabilities. We now assume that we are dealing with a homogeneous scattering body, so the number density and polarizabilities are constant over the volume. Using (4.47) and (4.48), we find that the change in merit function due to an additional small piece of dielectric material is given by,

$$\delta F = 2\alpha n \operatorname{Re} \int_{V} d^{3} \boldsymbol{r}'' \left\{ \frac{\partial f}{\partial \boldsymbol{G}}(\boldsymbol{r}, \boldsymbol{r}', \omega) \odot \left[ \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}'', \omega) \cdot \boldsymbol{G}(\boldsymbol{r}'', \boldsymbol{r}', \omega) \right] \right\}.$$
(4.49)

Dropping the positive constants  $2\alpha n$ , since we only require the maximum as a function of the perturbation choice, we arrive at,

$$\delta F = \operatorname{Re} \int_{V} d^{3} \boldsymbol{r}'' \frac{\partial f}{\partial \boldsymbol{G}}(\boldsymbol{r}, \boldsymbol{r}', \omega) \odot \left[ \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}'', \omega) \cdot \boldsymbol{G}(\boldsymbol{r}'', \boldsymbol{r}', \omega) \right],$$
(4.50)

which will be used to carry out the optimization.

#### Level-Set approach

To perform the optimization via (4.50), the level-set approach [85] can be used. In this method, an initial geometry is chosen and its boundaries are gradually changed to optimize the desired effect. The medium is described as a level-set function  $\Phi$ , where  $\Phi < 0$  inside the medium, and  $\Phi > 0$  outside, and its boundary is set as the zero-level contour  $\Phi(t) = 0$ . Here, an artificial "time" parameter is introduced which represents the progress of the iterative process. If the initial boundary shape is set as  $\Phi(\mathbf{r}(t), t)$ , the evolution of the boundary is governed by,

$$\frac{\partial \Phi}{\partial t} + \mathbf{v} \cdot \nabla \Phi = 0. \tag{4.51}$$

By considering the vector normal to the boundary  $\mathbf{n} = \nabla \Phi / |\nabla \Phi|$ , the above can be rewritten as,

$$\frac{\partial \Phi}{\partial t} + v_n \left| \nabla \Phi \right| = 0, \tag{4.52}$$

where  $v_n = \mathbf{v} \cdot \mathbf{n}$  is the scalar velocity field in the direction normal to the boundary. By choosing  $v_n$  appropriately, the boundary will deform in such a way that the merit function Fincreases, which is the goal of the optimization. This is equivalent to ensuring that  $\delta F > 0$ , so we need (4.50) to be positive.

To this end, the integration over r'' can be rewritten as [86],

$$\int_{V} d^{3}\mathbf{r}'' \to \int_{\partial V} dA \delta x(\mathbf{r}'') = \int_{\partial V} dA v_{n} \delta t, \qquad (4.53)$$

where  $\delta x$  represents the size of an infinitesimal deformation normal to the boundary, and integration is now performed over its area A. The deformation has then been replaced with the product of the velocity perpendicular to the boundary,  $v_n$ , and an infinitesimal time step,  $\delta t$ . Substituting (4.53) into (4.50) gives,

$$\delta F = \operatorname{Re} \int_{\partial V} dA \, v_n \delta t \frac{\partial f}{\partial \boldsymbol{G}}(\boldsymbol{r}, \boldsymbol{r}', \omega) \odot \left[ \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}'', \omega) \cdot \boldsymbol{G}(\boldsymbol{r}'', \boldsymbol{r}', \omega) \right].$$
(4.54)

If the velocity field is chosen as,

$$v_n = \operatorname{Re}\left\{\frac{\partial f}{\partial \boldsymbol{G}}(\boldsymbol{r}, \boldsymbol{r}', \omega) \odot \left[\boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}'', \omega) \cdot \boldsymbol{G}(\boldsymbol{r}'', \boldsymbol{r}', \omega)\right]\right\},\tag{4.55}$$

then  $\delta F = \int_{\partial V} dA v_n^2$ , which is always positive, guaranteeing that F is increasing as required.

#### Faraday Media

We face a problem using (4.55) in optimization, as the optimization position r'' appears in the second (source) point in one of the Green's tensors. An optimization must consider each "candidate" position for the perturbation via a separate simulation with different sources. In a large-scale 3D problem there could be far too many of these to consider, so in order to make the scheme numerically feasible, we want the observation positions to appear only in the first (observation) point in the Green's tensors [83].

For reciprocal media, we are able to make use of Lorentz reciprocity (2.74) to say  $\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega) = \boldsymbol{G}^T(\boldsymbol{r}',\boldsymbol{r},\omega)$  to achieve this, but of course this is not possible for non-reciprocal media. However, a particular case of a non-reciprocal medium is a Faraday medium [20], where non-reciprocity arises from the interplay between media response and an applied external magnetic field  $\boldsymbol{B}_0$ . We can make use of a property of the Green's tensor in Faraday media given by [87, 88],

$$\boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',\omega;\boldsymbol{B}_0) = \boldsymbol{G}^T(\boldsymbol{r}',\boldsymbol{r},\omega;-\boldsymbol{B}_0), \qquad (4.56)$$

where  $B_0$  is the external applied field, to rewrite (4.55) as,

$$v_n = \operatorname{Re}\left\{\frac{\partial f}{\partial \boldsymbol{G}}(\boldsymbol{r}, \boldsymbol{r}', \omega) \odot \left[\boldsymbol{G}^T(\boldsymbol{r}'', \boldsymbol{r}, \omega; -\boldsymbol{B}_0) \cdot \boldsymbol{G}(\boldsymbol{r}'', \boldsymbol{r}', \omega; \boldsymbol{B}_0)\right]\right\},\tag{4.57}$$

which has the required property of the optimization position r'' appearing in the first argument of the Green's tensors only. We are now in a position to apply this to a situation of interest, namely the optimization of a non-reciprocal device that will maximise unidirectional energy transfer between two molecules either side of it.

#### 4.3.2 Inverse Design of RET Isolation

We consider a system of a donor and acceptor either side of a finite non-reciprocal medium in a vacuum, and aim to deform the medium boundary to maximise one-way RET from donor to acceptor. We label the desirable forward interaction from  $D \to A$  as  $\Gamma_+$  and the backward direction as  $\Gamma_-$ . By application of our key result (4.21), we can therefore express the isolator strength as [83],

$$I = \frac{\Gamma_{+}}{\Gamma_{-}} = \frac{\left| \boldsymbol{d}_{\mathrm{A}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}) \cdot \boldsymbol{d}_{\mathrm{D}} \right|^{2}}{\left| \boldsymbol{d}_{\mathrm{D}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}) \cdot \boldsymbol{d}_{\mathrm{A}} \right|^{2}}$$
(4.58)

where have dropped the frequency argument for ease of reading. The Green's tensors  $G(\mathbf{r}, \mathbf{r}')$ and  $G(\mathbf{r}', \mathbf{r})$  are, in principle, unrelated for non-reciprocal media. Therefore, the functional we begin with is,

$$F = f[\boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}'), \boldsymbol{G}(\boldsymbol{r}', \boldsymbol{r})].$$
(4.59)

When a functional depends on multiple Green's tensors, the variation is the sum of the variations with respect to the individual Green's tensors [83]. So, (4.55) becomes,

$$v_n^I = \operatorname{Re}\left\{\frac{\partial I}{\partial \boldsymbol{G}}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{D}}) \odot \left[\boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{opt}}) \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{opt}}, \boldsymbol{r}_{\mathrm{D}})\right] + \frac{\partial I}{\partial \boldsymbol{G}}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}) \odot \left[\boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{opt}}) \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{opt}}, \boldsymbol{r}_{\mathrm{A}})\right]\right\}.$$
(4.60)

Beginning with the first partial derivative and substituting in (4.58) we get,

$$\frac{\partial I}{\partial \boldsymbol{G}}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) = \frac{1}{\left|\boldsymbol{d}_{\mathrm{D}}\cdot\boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}})\cdot\boldsymbol{d}_{\mathrm{A}}\right|^{2}} \frac{\partial}{\partial \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}})} \left|\boldsymbol{d}_{\mathrm{A}}\cdot\boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}})\cdot\boldsymbol{d}_{\mathrm{D}}\right|^{2}.$$
 (4.61)

Expanding the modulus squared in the partial differential and utilising index notation,

$$\frac{\partial}{\partial G_{ij}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}})} \left| \boldsymbol{d}_{\mathrm{A}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) \cdot \boldsymbol{d}_{\mathrm{D}} \right|_{ij}^{2} = \frac{\partial}{\partial G_{ij}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}})} \left[ d_{p}^{\mathrm{A}} G_{pq}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) d_{q}^{\mathrm{D}} d_{l}^{\mathrm{A}} G_{lk}^{*}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) d_{k}^{\mathrm{D}} \right] \\
= d_{p}^{\mathrm{A}} \delta_{pi} \delta_{qj} d_{q}^{\mathrm{D}} d_{l}^{\mathrm{A}} G_{lk}^{*}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) d_{k}^{\mathrm{D}} \\
= d_{i}^{\mathrm{A}} d_{j}^{\mathrm{D}} d_{l}^{\mathrm{A}} G_{lk}^{*}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) d_{k}^{\mathrm{D}} \\
= (\boldsymbol{d}_{\mathrm{A}} \otimes \boldsymbol{d}_{\mathrm{D}}) \left( \boldsymbol{d}_{\mathrm{A}} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) \cdot \boldsymbol{d}_{\mathrm{D}} \right), \quad (4.62)$$

where we have treated G and  $G^*$  as independent.

Moving on to the partial derivative in the second line of (4.60),

$$\frac{\partial I}{\partial \boldsymbol{G}}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}}) = \left|\boldsymbol{d}_{\mathrm{A}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) \cdot \boldsymbol{d}_{\mathrm{D}}\right|^{2} \frac{\partial}{\partial \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}})} \left[\frac{1}{\left|\boldsymbol{d}_{\mathrm{D}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}}) \cdot \boldsymbol{d}_{\mathrm{A}}\right|^{2}}\right] \\
= \frac{\left|\boldsymbol{d}_{\mathrm{A}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}}) \cdot \boldsymbol{d}_{\mathrm{D}}\right|^{2}}{\left|\boldsymbol{d}_{\mathrm{D}} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}}) \cdot \boldsymbol{d}_{\mathrm{A}}\right|^{2}} \frac{\partial}{\partial \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}})} \left[\frac{1}{\left|\boldsymbol{d}_{\mathrm{D}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}}) \cdot \boldsymbol{d}_{\mathrm{A}}\right|^{2}}\right]. \quad (4.63)$$

To deal with this derivative we employ the quotient rule from elementary calculus,

$$\left(\frac{1}{v}\right)' = -\frac{v'}{v^2},\tag{4.64}$$

and apply by setting  $v = d_p^{\rm D} G_{pq}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm A}) d_q^{\rm A}$  using index notation, so that,

$$v' = \frac{\partial}{\partial \boldsymbol{G}_{ij}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}})} \left[ d_p^{\mathrm{D}} \boldsymbol{G}_{pq}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{A}}) d_q^{\mathrm{A}} \right]$$
$$= d_p^{\mathrm{D}} \delta_{ip} \delta_{jq} d_q^{\mathrm{A}} = d_i^{\mathrm{D}} d_j^{\mathrm{A}}, \qquad (4.65)$$

which means that,

$$\frac{\partial}{\partial \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}})} \left[ \frac{1}{\boldsymbol{d}_{\mathrm{D}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}}) \cdot \boldsymbol{d}_{\mathrm{A}}} \right] = -\frac{d_{i}^{\mathrm{D}} d_{j}^{\mathrm{A}}}{\left( d_{p}^{\mathrm{D}} G_{pq}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}}) d_{q}^{\mathrm{A}} \right)^{2}} = -\frac{\boldsymbol{d}_{\mathrm{D}} \otimes \boldsymbol{d}_{\mathrm{A}}}{\left( \boldsymbol{d}_{\mathrm{D}} \cdot \boldsymbol{G}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{A}}) \cdot \boldsymbol{d}_{\mathrm{A}} \right)^{2}}.$$
(4.66)

Substituting (4.62) and (4.66) into (4.60) we reach,

$$v_{n}^{I} = \operatorname{Re}\left\{\frac{\left(\boldsymbol{d}_{A} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{A}, \boldsymbol{r}_{D}) \cdot \boldsymbol{d}_{D}\right)}{\left|\boldsymbol{d}_{D} \cdot \boldsymbol{G}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}) \cdot \boldsymbol{d}_{A}\right|^{2}} \left(\boldsymbol{d}_{A} \otimes \boldsymbol{d}_{D}\right) \odot \left[\boldsymbol{G}(\boldsymbol{r}_{A}, \boldsymbol{r}_{opt}) \cdot \boldsymbol{G}(\boldsymbol{r}_{opt}, \boldsymbol{r}_{D})\right] - \frac{\left|\boldsymbol{d}_{A} \cdot \boldsymbol{G}(\boldsymbol{r}_{A}, \boldsymbol{r}_{D}) \cdot \boldsymbol{d}_{D}\right|^{2}}{\left(\boldsymbol{d}_{D} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}) \cdot \boldsymbol{d}_{A}\right) \left(\boldsymbol{d}_{D} \cdot \boldsymbol{G}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}) \cdot \boldsymbol{d}_{A}\right)^{2}} \left(\boldsymbol{d}_{D} \otimes \boldsymbol{d}_{A}\right) \odot \left[\boldsymbol{G}(\boldsymbol{r}_{D}, \boldsymbol{r}_{opt}) \cdot \boldsymbol{G}(\boldsymbol{r}_{opt}, \boldsymbol{r}_{A})\right]\right\}.$$

$$(4.67)$$

The following identity for arbitrary vectors  $\boldsymbol{a}$  and  $\boldsymbol{b}$  and an arbitrary matrix  $\boldsymbol{C}$  can be utilised,

$$(\boldsymbol{a}\otimes\boldsymbol{b})\boldsymbol{C} = \boldsymbol{a}\cdot\boldsymbol{C}\cdot\boldsymbol{b},\tag{4.68}$$

to rewrite the above as,

$$v_{n}^{I} = \operatorname{Re} \left\{ \frac{\left(\boldsymbol{d}_{A} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{A}, \boldsymbol{r}_{D}) \cdot \boldsymbol{d}_{D}\right)}{\left|\boldsymbol{d}_{D} \cdot \boldsymbol{G}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}) \cdot \boldsymbol{d}_{A}\right|^{2}} \left[\boldsymbol{d}_{A} \cdot \boldsymbol{G}(\boldsymbol{r}_{A}, \boldsymbol{r}_{opt}) \cdot \boldsymbol{G}(\boldsymbol{r}_{opt}, \boldsymbol{r}_{D}) \boldsymbol{d}_{D}\right] - \frac{\left|\boldsymbol{d}_{A} \cdot \boldsymbol{G}(\boldsymbol{r}_{A}, \boldsymbol{r}_{D}) \cdot \boldsymbol{d}_{D}\right|^{2}}{\left(\boldsymbol{d}_{D} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}) \cdot \boldsymbol{d}_{A}\right) \left(\boldsymbol{d}_{D} \cdot \boldsymbol{G}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}) \cdot \boldsymbol{d}_{A}\right)^{2}} \left[\boldsymbol{d}_{D} \cdot \boldsymbol{G}(\boldsymbol{r}_{D}, \boldsymbol{r}_{opt}) \cdot \boldsymbol{G}(\boldsymbol{r}_{opt}, \boldsymbol{r}_{A}) \boldsymbol{d}_{A}\right]. \quad (4.69)$$

As mentioned below (4.50), calculating  $G(\mathbf{r}_{\rm D}, \mathbf{r}_{\rm opt})$  is computationally expensive, so we make use of the Faraday relation, (4.56), to rewrite as,

$$v_{n}^{I} = \operatorname{Re}\left\{\frac{\left(\boldsymbol{d}_{A} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{A}, \boldsymbol{r}_{D}; \mathbf{B}_{0}) \cdot \boldsymbol{d}_{D}\right)\left[\boldsymbol{d}_{A} \cdot \boldsymbol{G}^{T}(\boldsymbol{r}_{opt}, \boldsymbol{r}_{A}; -\mathbf{B}_{0}) \cdot \boldsymbol{G}(\boldsymbol{r}_{opt}, \boldsymbol{r}_{D}; \mathbf{B}_{0}) \cdot \boldsymbol{d}_{D}\right]}{\left|\boldsymbol{d}_{D} \cdot \boldsymbol{G}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}; \mathbf{B}_{0}) \cdot \boldsymbol{d}_{A}\right|^{2}} - \frac{\left|\boldsymbol{d}_{A} \cdot \boldsymbol{G}(\boldsymbol{r}_{A}, \boldsymbol{r}_{D}; \mathbf{B}_{0}) \cdot \boldsymbol{d}_{D}\right|^{2}\left[\boldsymbol{d}_{D} \cdot \boldsymbol{G}^{T}(\boldsymbol{r}_{opt}, \boldsymbol{r}_{D}; -\mathbf{B}_{0}) \cdot \boldsymbol{G}(\boldsymbol{r}_{opt}, \boldsymbol{r}_{A}; \mathbf{B}_{0}) \cdot \boldsymbol{d}_{A}\right]}{\left[\boldsymbol{d}_{D} \cdot \boldsymbol{G}^{*}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}; \mathbf{B}_{0}) \cdot \boldsymbol{d}_{A}\right]\left|\boldsymbol{d}_{D} \cdot \boldsymbol{G}(\boldsymbol{r}_{D}, \boldsymbol{r}_{A}; \mathbf{B}_{0}) \cdot \boldsymbol{d}_{A}\right|^{2}}\right\}.$$

$$(4.70)$$

This is the quantity used by C. Cisowski to perform the inverse design of magneto-optical RET isolation in the publication [2]. The next subsection reviews these results, produced by C. Cisowski and presented in our paper [2], which builds on the formula (4.70).



Figure 4.5: Figure reproduced from [2] under the terms of the Creative Commons Attribution 4.0 International license. Slices of the advected geometry at x = 0 showing the evolution of the boundary as the iteration number increases.

## 4.3.3 Results

In this section, we present results produced by C. Cisowski et al. for our publication [2], which make use of the expression (4.70) in a 3D algorithm to optimize a structure for one-way energy transfer.

Since the form of the Green's tensor for any non-trivial geometry is very complex, requiring integration over all possible frequencies [4], it is not feasible to analytically evaluate equation (4.70) for a donor and acceptor either side of a finite non-reciprocal medium in a vacuum. However, the right hand side of (4.70) can be determined for any geometry using the finite-difference time-domain (FDTD) procedure.

To calculate a Green's tensor using FDTD, we note that the ij components of  $G(\mathbf{r}, \mathbf{r}', \omega)$  correspond to the *i*th component of an electric field at  $\mathbf{r}$  stemming from the *j*th component of a point current source at  $\mathbf{r}'$ , meaning we can write [83],

$$G_{ij}(\boldsymbol{r}, \boldsymbol{r}', \omega) = \frac{E_i(\mathbf{r}, \omega)}{i\mu_0 \omega j_j(\mathbf{r}', \omega)},$$
(4.71)

where  $j(\mathbf{r}', \omega)$  is the source current in the frequency domain. In Ref. [2], the Meep FDTD implementation [89] is used to calculate the electric field of a time-domain source  $\mathbf{j}(t)$ , and then the components of the Green's tensor are found by implementing the current as a short Gaussian pulse [83]. For the setup considered here, the quantities that must be calculated are  $\mathbf{G}(\mathbf{r}_{opt}, \mathbf{r}_{D}; \mathbf{B}_{0})$ ,  $\mathbf{G}(\mathbf{r}_{opt}, \mathbf{r}_{A}; \mathbf{B}_{0})$ ,  $\mathbf{G}(\mathbf{r}_{opt}, \mathbf{r}_{D}; -\mathbf{B}_{0})$  and  $\mathbf{G}(\mathbf{r}_{opt}, \mathbf{r}_{A}; -\mathbf{B}_{0})$ . These are substituted into (4.70) to find  $v_{n}^{I}$ , which is then be used to perform the inverse design of magneto-optical RET isolation.



Figure 4.6: Figure reproduced from [2] under the terms of the Creative Commons Attribution 4.0 International license. The isolation strength  $\Gamma$  of the optical isolator, normalized to the initial isolation strength  $\Gamma_0$ , increases during iterative optimization process.



Figure 4.7: Figure reproduced from [2] under the terms of the Creative Commons Attribution 4.0 International license. (a) Initial geometry and (b)-(d) final geometry of the inversedesigned non-reciprocal RET isolator. The donor, D, and acceptor, A, are represented as gold spheres.

In Ref. [2], a custom-made 3D algorithm is used to carry out topology optimization, beginning with a finite sphere of non-reciprocal media with a vacuum background. The velocity on the boundary is calculated via (4.70) and the boundary is then updated using the advection equation (4.52), resulting in a new geometry which is used as the starting point for the next iteration. The way that the initial sphere evolves is shown in figure 4.5.

We can see from figure 4.6 that as the iterations progress, the isolation strength of the magneto-optical RET isolator increases, eventually converging to a factor of approximately 2.3 after around 80 iterations when the structure converges to a final shape. Figure 4.7 shows the initial geometry and multiple perspectives on the final geometry of the topology-optimized Faraday medium.

This work from Ref. [2] demonstrates how the Green's tensor formalism can be used to perform the inverse design of isolation processes, and how these tools can be exploited to perform inverse design of Faraday media, opening up an avenue of research in the pursuit of an integrated photonic isolator.

# 4.4 Summary and Conclusion

To summarize, in this chapter we used macroscopic QED to calculate a general formula for energy transfer between two bodies in a non-reciprocal environment, before applying it to a simple setup of two molecules near a semi-infinite half-space. After considering different arrangements and dipole moment orientations, we found that for a parallel arrangement there are certain dipole moment orientation combinations that produce a change in the rate of interaction when the positions of the molecules are switched. We then plotted how the rate varied with the molecular positions in one direction vs the other.

We then gave an overview of an application presented in Ref. [2] that uses the principles of non-reciprocity in the inverse design of an optical device that promotes one-way energy transfer. We provided an outline of how our result was applied, and finally a summary of the results produced by C. Cisowski that demonstrate the optimization of such a RET isolator using a custom-made algorithm.

# CHAPTER 5

# Three-body RET in a Reciprocal Environment

In this chapter, we look at three-body resonance energy transfer (RET) and how the presence of an external environment affects the rate of energy transfer, as shown in figure 5.1. We will focus on how the system is affected by reciprocal media only, as we did in chapter 3.

We begin by using canonical perturbation theory (introduced in section 3.1.2) to eliminate some of the computational complexity arising from the presence of the third body, and then use macroscopic QED (introduced in chapter 2) to model the effects of an external



Figure 5.1: System of three bodies (donor, mediator and acceptor) in the presence of an arbitrary external environment. Figure reproduced from [1] under the terms of the Creative Commons Attribution 4.0 International license.



Figure 5.2: Figure reproduced from [1] under the terms of the Creative Commons Attribution 4.0 International license. System of three two-level atoms/molecules transmitting energy through the electromagnetic field due to resonance energy transfer. The donor begins in an excited energy state, the acceptor in the ground state and the mediator in its lower state. Energy emitted from the donor is absorbed by the mediator causing it to become temporarily excited. The mediator releases this energy again and it is absorbed by the acceptor which then becomes excited.

reciprocal environment and obtain a general formula for the rate of three-body RET in an arbitrary environment. We note that similar calculations have been carried out for three-body Interatomic Coulombic decay (ICD) in a vacuum by considering the mediator as part of the environment of the two-body system [37], but this method makes it awkward to extend the calculations to complex geometries.

As a proof-of-principle, we apply our formula to a setup in which the donor and and acceptor are very close to each other and the mediator is distant from them. We place this system in some simple environments, namely a vacuum and near a semi-infinite half-space, to calculate analytic expressions for the rate of energy transfer.

# 5.1 Calculation of Matrix Element

In this section, we consider a system of three two-level atoms/molecules, a donor, acceptor and mediator, and calculate the matrix element for energy transfer between the donor and acceptor, considering both the direct interaction and the indirect interaction via the mediator. We will apply canonical transformations to the Hamiltonian in order to reduce the order of perturbation theory required in the calculation.

### 5.1.1 Setup

We consider a system of a donor, acceptor and mediator, as seen in figure 5.1. Energy from the donor is released and transferred to the acceptor, either directly as in figure 3.1 or via the mediator as in figure 5.2. In analogy to the two-body system set up in section 3.1, we can model the system via the Hamiltonian,

$$H = H_0 + H_{\rm int} = H_0 + H_{\rm int}^{\rm A} + H_{\rm int}^{\rm D} + H_{\rm int}^{\rm M},$$
(5.1)

where,

$$H_0 = H_{\rm rad} + H_{\rm mol}^{\rm A} + H_{\rm mol}^{\rm D} + H_{\rm mol}^{\rm M},$$
(5.2)

where  $H_{\rm rad}$  is the Hamiltonian of the radiation field,  $H_{\rm mol}^{\xi}$  is the Hamiltonian of the molecule  $\xi$  which we assume is known, and  $H_{\rm int}^{\xi}$  is defined by,

$$H_{\text{int}}^{\xi} = -\hat{\boldsymbol{d}}_{\xi} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\xi}).$$
(5.3)

The initial and final states of the system are taken to be,

$$|i\rangle = |e_{\rm D}, s_{\rm M}, g_{\rm A}; 0\rangle, \qquad |f\rangle = |g_{\rm D}, s_{\rm M}, e_{\rm A}; 0\rangle, \qquad (5.4)$$

where  $g_{\rm D}(g_{\rm A})$  denotes the ground state of the donor (acceptor),  $e_{\rm D}(e_{\rm A})$  is the excited state of the donor (acceptor),  $s_{\rm M}$  is an arbitrary state of the mediator and 0 is the ground state of the electromagnetic field.

When considering the mediated interaction involving all three molecules, four emission/absorption events take place as shown in 5.3a. This means that fourth order perturbation theory would be required in principle. The complexity of such a calculation means that it is useful to simplify the Hamiltonian as much as possible, which will be done in section 5.1.2. The direct interaction involving only the donor and acceptor also needs to be taken into account, but since it can be treated as a two-body interaction it is covered in section 3.1.

To find the contribution to the matrix element from the indirect interaction involving the mediator, fourth order perturbation theory is generally used,

$$M_{fi} = \sum_{I,II,III} \frac{\langle f | H_{\text{int}} | I \rangle \langle I | H_{\text{int}} | II \rangle \langle II | H_{\text{int}} | III \rangle \langle III | H_{\text{int}} | i \rangle}{(E_i - E_I)(E_i - E_{II})(E_i - E_{III})},$$
(5.5)

where we are required to sum over all possible intermediate states for each of the steps I, II and III (see figure 5.3a). This corresponds to four one-photon vertices and so gives rise to 24 time-ordered diagrams, as shown in figure 5.3b.

We can make use of canonical transformations, introduced in section 3.1.2, to simplify this calculation in two steps. Firstly, by collapsing the two one-photon vertices at the mediator into one two-photon vertex, thus lowering the perturbation theory required to third order, as applied at lower orders in Ref. [90]. Secondly, by using the same principles we can find a





(b) The 24 possible time orderings of mediated energy transfer.

Figure 5.3: Feynman diagrams depicting energy transfer between a donor D and acceptor A via a mediator M. (a) shows one of the possible time orderings, known as the resonant interaction, highlighting the four emission/absorption events and three intermediate states. (b) shows a simplified depiction of the 24 possible time-orderings that must be considered when calculating the matrix element for this process.

new interaction term which is fourth order in the electric dipole moment, thereby reducing the order of perturbation theory required to first.

## 5.1.2 Reducing order of Perturbation Theory

The first step in simplifying our calculation is to consider only the interaction at the mediator. In other words, we temporarily disregard the donor and acceptor, and consider only the subsystem of the mediator absorbing a photon and then emitting a photon, as in figure 5.4a. We aim to create a new coupling term that is second order in the electric dipole moment and can therefore describe both the absorption and emission events at the mediator, as in figure 5.4b, thus effectively eliminating the intermediate state.

To this end, we consider the subsystem described by the Hamiltonian,

$$H^{\rm M} = H_0 + H^{\rm M}_{\rm int},$$
 (5.6)

with initial and final states labelled M and N respectively,

$$|M\rangle = |s_{\rm M}; 1(\boldsymbol{p}, \lambda)\rangle, \qquad |N\rangle = |s_{\rm M}; 1(\boldsymbol{p}', \lambda')\rangle.$$
(5.7)



Figure 5.4: Feynman diagram of the subsystem of the interaction at the mediator only. (a) shows the two possible time orderings where the mediator begins in and ends the interaction in its lower s state, and is excited to its r state in the intermediate state. (b) shows how the interaction is considered after the unitary transformations have been applied, condensing the two absorption and emission events into a single photon event.

We perform a unitary transformation on the Hamiltonian as we did in subsection 3.1.2,

$$H_{\text{new}}^{\text{M}} = e^{iS} H^{\text{M}} e^{-iS} = \sum_{n=0}^{\infty} \frac{1}{n!} \left[ iS, \left[ iS, \dots H^{\text{M}} \right] \right]$$
$$= H_0 + H_{\text{int}}^{\text{M}} + [iS, H_0] + \left[ iS, H_{\text{int}}^{\text{M}} \right] + \frac{1}{2} \left[ iS, [iS, H_0] \right] + \dots, \qquad (5.8)$$

where again S is an as-yet undetermined generator that is assumed to be first order in the electric dipole moment. We require a second order interaction term, so we eliminate the first order  $H_{\text{int}}^{\text{M}}$  term by choosing  $[iS, H_0] = -H_{\text{int}}^{\text{M}}$ , leaving up to second order in the electric dipole,

$$H_{\rm new}^{\rm M} = H_0 + \frac{1}{2} \Big[ iS, H_{\rm int}^{\rm M} \Big],$$
 (5.9)

with expectation value,

$$\frac{1}{2} \langle N | \left[ iS, H_{\text{int}}^{\text{M}} \right] | M \rangle = -\frac{1}{2} \sum_{I} \langle N | H_{\text{int}}^{\text{M}} | I \rangle \langle I | H_{\text{int}}^{\text{M}} | M \rangle \left[ \frac{1}{E_{I} - E_{N}} + \frac{1}{E_{I} - E_{M}} \right].$$
(5.10)

Making use of the diagrams depicted in figure 5.4a, we can see that there are two types of intermediate states. In the resonant interaction, the  $(\mathbf{p}, \lambda)$  photon is absorbed before the  $(\mathbf{p}', \lambda')$  photon is emitted, and in the second off-resonant time ordering, the emission takes place before the absorption. Therefore, the two types of intermediate states have different energies. Labelling the resonant intermediate state type as  $I_1$  and the off-resonant as  $I_2$  we

find the energies to be,

$$E_M = E_s + \hbar c p,$$
  $E_{I_1} = E_r,$   
 $E_N = E_s + \hbar c p',$   $E_{I_2} = E_r + \hbar c p + \hbar c p'.$  (5.11)

Making use of these and taking into account both the time orderings, (5.10) becomes,

$$\Rightarrow \frac{1}{2} \langle N | \left[ iS, H_{\text{int}}^{\text{M}} \right] | M \rangle$$
  
=  $-\frac{1}{2} \sum_{r} \langle N | H_{\text{int}}^{\text{M}} H_{\text{int}}^{\text{M}} | M \rangle \left[ \frac{1}{E_{rs} + \hbar cp} + \frac{1}{E_{rs} - \hbar cp} + \frac{1}{E_{rs} + \hbar cp'} + \frac{1}{E_{rs} - \hbar cp'} \right], \quad (5.12)$ 

where  $E_{rs}$  is the transition energy of the mediator going from the excited r state to its lower s state. Since in three-body RET, the mediator responds at the frequency of the donor decay transition [36], we can replace  $\hbar cp \to E_{eg}$  and  $\hbar cp' \to -E_{eg}$ , giving,

$$\Rightarrow \frac{1}{2} \langle N | \left[ iS, H_{\text{int}}^{\text{M}} \right] | M \rangle = -\sum_{r} \langle N | H_{\text{int}}^{\text{M}} H_{\text{int}}^{\text{M}} | M \rangle \left[ \frac{1}{E_{rs} + E_{eg}} + \frac{1}{E_{rs} - E_{eg}} \right].$$
(5.13)

Now substituting in the definition for the interaction Hamiltonian given in (5.3) and using index notation, we obtain,

$$= -\sum_{\boldsymbol{r},\boldsymbol{p},\boldsymbol{p}'} \langle N | \left( \hat{d}_{\mathrm{M}_{i}} \hat{E}_{i}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{p}) \right) \left( \hat{d}_{\mathrm{M}_{j}} \hat{E}_{j}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{p}') \right) | M \rangle \left[ \frac{1}{E_{rs} + E_{eg}} + \frac{1}{E_{rs} - E_{eg}} \right]$$
(5.14)

$$= -\sum_{p,p'} \langle N | \alpha_{ij}^{\mathrm{M}} \hat{E}_i(\boldsymbol{r}_{\mathrm{M}}, p) \hat{E}_j(\boldsymbol{r}_{\mathrm{M}}, p') | M \rangle , \qquad (5.15)$$

where,

$$\alpha_{ij}^{\mathrm{M}} = \sum_{r} \left[ \frac{\langle s | \hat{d}_{M_i} | r \rangle \langle r | \hat{d}_{M_j} | s \rangle}{E_{rs} + E_{eg}} + \frac{\langle s | \hat{d}_{M_j} | r \rangle \langle r | \hat{d}_{M_i} | s \rangle}{E_{rs} - E_{eg}} \right]$$
$$= \frac{1}{3} \sum_{r} |d_{\mathrm{M}}^{sr}|_{ij}^2 \left[ \frac{1}{E_{rs} + E_{eg}} + \frac{1}{E_{rs} - E_{eg}} \right], \qquad (5.16)$$

is identified as the dynamic polarizability of the mediator [68], where we have taken the rotational average of the molecular orientation via  $d^{\uparrow} \otimes d^{\downarrow} = \frac{1}{3} |d|^2 \mathbb{I}$  (also given in (3.69)). We can therefore define a new coupling term as given below,

$$H_{2} = \frac{1}{2} \Big[ iS, H_{\text{int}}^{\text{M}} \Big] = -\sum_{p,p'} \alpha_{ij}^{\text{M}} \hat{E}_{i}(\boldsymbol{r}_{\text{M}}, p) \hat{E}_{j}(\boldsymbol{r}_{\text{M}}, p'), \qquad (5.17)$$



Figure 5.5: The three-body resonant interaction diagrams (a) before and (b) after the reduction of the order of perturbation theory. Figure reproduced from [1] under the terms of the Creative Commons Attribution 4.0 International license.

and can write the new Hamiltonian as,

$$H_{\rm new} = H_0 + H_{\rm int}^A + H_{\rm int}^D + H_2, \tag{5.18}$$

where we have effectively collapsed the two one-photon vertices at the mediator into one two-photon vertex, as seen in figure 5.5. This means that when considering three-body RET, instead of fourth order perturbation theory being required, now only third order is needed. This reduces the usual 24 time-ordered diagrams 5.3b required for this calculation to just six, as shown in figure 5.6. This is equivalent to using a polarizability-based Hamiltonian, as in Ref. [91] for example.

We now go one step further and use the same techniques to create an effective fourth order term that describes the entire interaction including all three bodies. We now consider the full system made up of all of the molecules, and need to calculate both the direct interaction between the donor and acceptor, which is second order in the dipole operator, and also the mediated interaction, which is fourth order. The four one-photon vertices of the mediated interaction have now been collapsed into two one-photon vertices and one two-photon vertex at the mediator. We can simplify this further by way of additional unitary transformations.

Beginning with the new Hamiltonian,

$$H_{\rm new} = H_0 + H_1 + H_2, \tag{5.19}$$

where  $H_2$  is defined by (5.17) and the acceptor and donor interaction terms have been combined into a single term which is linear in the electric dipole,  $H_1 = H_{\text{int}}^{\text{A}} + H_{\text{int}}^{\text{D}}$ , for simplicity. For convenience, we introduce the dimensionless constant  $\lambda$  which is proportional to the



Figure 5.6: The six time ordered diagrams for three-body RET once the two one-photon vertices have been collapsed into one two-photon vertex. Figure reproduced from [1] under the terms of the Creative Commons Attribution 4.0 International license.

electric dipole moment, giving us,

$$H_{\rm new} = H_0 + \lambda H_1 + \lambda^2 H_2.$$
 (5.20)

Performing a unitary transformation where the generator  $S_1$  is linear in the electric dipole, and taking terms up to fourth order, we obtain,

$$\begin{aligned} H_{\text{new}}^{(1)} &= e^{i\lambda S_1} H_{\text{new}} e^{-i\lambda S_1} = \sum_{n=0}^{\infty} \frac{1}{n!} \left[ i\lambda S_1, [i\lambda S_1, \dots, H_{\text{new}}] \right] \\ &= H_0 + \lambda H_1 + \lambda^2 H_2 + \lambda [iS_1, H_0] + \lambda^2 [iS_1, H_1] + \lambda^3 [iS_1, H_2] + \frac{\lambda^2}{2} \left[ iS_1, [iS_1, H_0] \right] \\ &+ \frac{\lambda^3}{2} \left[ iS_1, [iS_1, H_1] \right] + \frac{\lambda^4}{2} \left[ iS_1, [iS_1, H_2] \right] + \frac{\lambda^3}{6} \left[ iS_1, [iS_1, [iS_1, H_0] \right] \right] \\ &+ \frac{\lambda^4}{6} \left[ iS_1, [iS_1, [iS_1, H_1] \right] + \frac{\lambda^4}{24} \left[ iS_1, [iS_1, [iS_1, H_0] \right] \right]. \end{aligned}$$
(5.21)

To eliminate the terms that are first order in the electric dipole, we choose  $[iS_1, H_0] = -H_1$ , which simplifies the Hamiltonian to,

$$H_{\text{new}}^{(1)} = H_0 + \lambda^2 H_2 + \frac{\lambda^2}{2} [iS_1, H_1] + \lambda^3 [iS_1, H_2] + \frac{\lambda^3}{3} [iS_1, [iS_1, H_1]] + \frac{\lambda^4}{2} [iS_1, [iS_1, H_2]] + \frac{\lambda^4}{8} [iS_1, [iS_1, [iS_1, H_1]]].$$
(5.22)

We now perform a second unitary transformation, this time where the generator  $S_2$  is second order in the electric dipole,

$$H_{\text{new}}^{(2)} = e^{i\lambda^2 S_2} H_{\text{new}}^{(1)} e^{-i\lambda^2 S_2} = \sum_{n=0}^{\infty} \frac{1}{n!} \left[ i\lambda^2 S_2, \left[ i\lambda^2 S_2, \dots, H_{\text{new}}^{(1)} \right] \right]$$
  
=  $H_0 + \lambda^2 H_2 + \frac{\lambda^2}{2} [iS_1, H_1] + \lambda^3 [iS_1, H_2] + \frac{\lambda^3}{3} [iS_1, [iS_1, H_1]]$   
+  $\frac{\lambda^4}{2} [iS_1, [iS_1, H_2]] + \frac{\lambda^4}{8} [iS_1, [iS_1, [iS_1, H_1]]] + \lambda^2 [iS_2, H_0]$   
+  $\lambda^4 [iS_2, H_2] + \frac{\lambda^4}{2} [iS_2, [iS_1, H_1]] + \frac{\lambda^4}{2} [iS_2, [iS_2, H_0]].$  (5.23)

We want to eliminate the second order terms except for  $\frac{1}{2}[iS_1, H_1]$ , as this is the direct interaction of the donor and acceptor. So we choose  $[iS_2, H_0] = -H_2$ , leaving,

$$\begin{aligned} H_{\text{new}}^{(2)} = &H_0 + \frac{1}{2} [iS_1, H_1] + \lambda^3 [iS_1, H_2] + \frac{\lambda^3}{3} [iS_1, [iS_1, H_1]] + \frac{\lambda^4}{2} [iS_1, [iS_1, H_2]] \\ &+ \frac{\lambda^4}{8} \Big[ iS_1, [iS_1, [iS_1, H_1]] \Big] + \lambda^4 [iS_2, H_2] + \frac{\lambda^4}{2} [iS_2, [iS_1, H_1]] - \frac{\lambda^4}{2} [iS_2, H_2] \\ = &H_0 + \frac{1}{2} [iS_1, H_1] + \lambda^3 [iS_1, H_2] + \frac{\lambda^3}{3} [iS_1, [iS_1, H_1]] + \frac{\lambda^4}{2} [iS_1, [iS_1, H_2]] \\ &+ \frac{\lambda^4}{8} \Big[ iS_1, [iS_1, [iS_1, H_1]] \Big] + \frac{\lambda^4}{2} [iS_2, H_2] + \frac{\lambda^4}{2} [iS_2, [iS_1, H_1]]. \end{aligned}$$
(5.24)

We finally perform a third unitary transformation with a generator which is third order in  $\lambda$ , and taking terms only up to fourth order we obtain,

$$H_{\text{new}}^{(3)} = e^{i\lambda^3 S_3} H_{\text{new}}^{(2)} e^{-i\lambda^3 S_3} = \sum_{n=0}^{\infty} \frac{1}{n!} \left[ i\lambda^3 S_3, \left[ i\lambda^3 S_3, \dots H_{\text{new}}^{(2)} \right] \right]$$
$$= H_{\text{new}}^{(2)} + \lambda^3 [iS_3, H_0].$$
(5.25)

To eliminate the third order terms, we choose  $[iS_3, H_0] = -[iS_1, H_2] - [iS_1, [iS_1, H_1]]$ , leaving,

$$H_{\text{new}}^{(3)} = H_0 + \frac{1}{2} [iS_1, H_1] + \frac{\lambda^4}{2} [iS_1, [iS_1, H_2]] + \frac{\lambda^4}{8} [iS_1, [iS_1, [iS_1, H_1]]] + \frac{\lambda^4}{2} [iS_2, H_2] + \frac{\lambda^4}{2} [iS_2, [iS_1, H_1]].$$
(5.26)

We know that the  $[iS_1, [iS_1, [iS_1, H_1]]]$  term cannot contribute to the mediator-assisted rate, since it is fourth order in the electric dipole, but contains no mediator term. Also, the  $[iS_2, H_2]$ term cannot contribute, since it does not contain donor or acceptor terms. This leaves us with our new interaction Hamiltonian, the mediator-dependent parts of which are fourth order in the electric dipole moment as required,

$$H_{\text{int}} = H_{\text{int}}^{\text{dir}} + H_{\text{int}}^{\text{indir}} = \frac{1}{2} \left( [iS_1, H_1] + [iS_1, [iS_1, H_2]] + [iS_2, [iS_1, H_1]] \right),$$
(5.27)

where we have decomposed into the direct second-order contribution and indirect fourth-order (mediator-dependent) contribution by defining,

$$H_{\rm int}^{\rm dir} = \frac{1}{2} [iS_1, H_1], \tag{5.28a}$$

$$H_{\rm int}^{\rm indir} = \frac{1}{2} \left( \left[ iS_1, \left[ iS_1, H_2 \right] \right] + \left[ iS_2, \left[ iS_1, H_1 \right] \right] \right).$$
(5.28b)

 $H_{\rm int}$  will form the basis of our perturbative treatment in the next subsection.

## 5.1.3 Perturbation Theory

We now apply this Hamiltonian (5.27) to our system and perform perturbation theory to find the matrix element for three-body RET. In the previous section, we chose the generators  $S_1$ and  $S_2$  such that they satisfy  $[iS_1, H_0] = -H_1$  and  $[iS_2, H_0] = -H_2$  respectively. Thus, we can say that,

$$\langle N | iS_1 | M \rangle = \frac{\langle N | H_1 | M \rangle}{E_N - E_M}, \qquad \langle N | iS_2 | M \rangle = \frac{\langle N | H_2 | M \rangle}{E_N - E_M}, \tag{5.29}$$

where  $|M\rangle$  and  $|N\rangle$  are arbitrary initial and final states.

We now look at the interaction states in the new interaction Hamiltonian (5.27), noting that the first term corresponds to the direct interaction and was calculated in section 3.1.2 to be (3.26). The second term of (5.27) is fourth order in the dipole operator, so corresponds to the mediated interaction,

$$\langle N | \frac{1}{2} [iS_{1}, [iS_{1}, H_{2}]] | M \rangle =$$

$$= \frac{1}{2} \sum_{I,II} \left[ \frac{\langle N | H_{1} | II \rangle \langle II | H_{1} | I \rangle \langle I | H_{2} | M \rangle}{(E_{N} - E_{II})(E_{II} - E_{I})} + \frac{\langle N | H_{2} | II \rangle \langle II | H_{1} | I \rangle \langle I | H_{1} | M \rangle}{(E_{II} - E_{I})(E_{I} - E_{M})} - \frac{2 \langle N | H_{1} | II \rangle \langle II | H_{2} | I \rangle \langle I | H_{1} | M \rangle}{(E_{N} - E_{II})(E_{I} - E_{M})} \right].$$
(5.30)

For the final term of (5.27) we obtain,

$$\langle N | \frac{1}{2} [iS_{2}, [iS_{1}, H_{1}]] | M \rangle$$

$$= -\frac{1}{2} \sum_{I,II} \left[ \frac{\langle N | H_{1} | II \rangle \langle II | H_{1} | I \rangle \langle I | H_{2} | M \rangle}{E_{I} - E_{M}} \left( \frac{1}{E_{N} - E_{II}} - \frac{1}{E_{II} - E_{I}} \right) \right.$$

$$+ \frac{\langle N | H_{2} | II \rangle \langle II | H_{1} | I \rangle \langle I | H_{1} | M \rangle}{E_{N} - E_{II}} \left( \frac{1}{E_{II} - E_{I}} - \frac{1}{E_{I} - E_{M}} \right) \right]. \quad (5.31)$$

Combining the two contributions for the mediated interaction, we arrive at,

$$\langle N | H_{int}^{indir} | M \rangle = \sum_{I,II} \left[ \frac{1}{2} \left( \langle N | H_1 | II \rangle \langle II | H_1 | I \rangle \langle I | H_2 | M \rangle + \langle N | H_2 | II \rangle \langle II | H_1 | I \rangle \langle I | H_1 | M \rangle \right) \left( \frac{1}{(E_N - E_{II})(E_{II} - E_I)} - \frac{1}{(E_I - E_M)(E_N - E_{II})} + \frac{1}{(E_I - E_M)(E_{II} - E_I)} \right) - \frac{\langle N | H_1 | II \rangle \langle II | H_2 | I \rangle \langle I | H_1 | M \rangle}{(E_N - E_{II})(E_I - E_M)} \right].$$
(5.32)

As before, each of the terms gives rise to two different time orderings depending on the order of  $H_D$  and  $H_A$ , resulting in six time orderings all together. In both the first and second time orderings, (a) and (b) in figure 5.6, both the donor and acceptor absorb photons and the mediator emits two photons, meaning those terms can be grouped. Likewise, in the third and fourth orderings, (d) and (e), both the donor and acceptor emit photons and the mediator absorbs them, so the terms can be grouped. So now combining all six time orderings we have four terms,

$$M_{fi}^{\text{indir}} = \sum_{p,p'} \langle f | \left[ -\frac{H_D H_A H_2}{(E_{eg} + \hbar cp)(E_{eg} - \hbar cp')} - \frac{H_2 H_D H_A}{(E_{eg} - \hbar cp)(E_{eg} + \hbar cp')} + \frac{H_D H_2 H_A}{(E_{eg} + \hbar cp)(E_{eg} + \hbar cp')} + \frac{H_A H_2 H_D}{(E_{eg} - \hbar cp)(E_{eg} - \hbar cp)(E_{eg} - \hbar cp')} \right] |i\rangle .$$
(5.33)

To obtain our total matrix element, we need to sum the results from the direct interaction,

given in (3.18), and indirect interactions, calculated above. So we have,

$$M_{fi} = M_{fi}^{\text{dir}} + M_{fi}^{\text{indir}}$$

$$= \sum_{p,p'} \langle f | \left[ -\frac{H_{\text{A}}H_{\text{D}}}{\hbar cp - E_{\text{eg}}} - \frac{H_{\text{D}}H_{\text{A}}}{\hbar cp + E_{\text{eg}}} + \frac{H_{\text{D}}H_{\text{A}}H_{2}}{(\hbar cp + E_{\text{eg}})(\hbar cp' - E_{\text{eg}})} + \frac{H_{2}H_{\text{D}}H_{\text{A}}}{(\hbar cp - E_{\text{eg}})(\hbar cp' + E_{\text{eg}})} + \frac{H_{\text{D}}H_{2}H_{\text{A}}}{(\hbar cp - E_{\text{eg}})(\hbar cp' + E_{\text{eg}})} + \frac{H_{\text{D}}H_{2}H_{\text{A}}}{(\hbar cp - E_{\text{eg}})(\hbar cp' - E_{\text{eg}})} \right] |i\rangle,$$

$$(5.34)$$

where,

$$H_{\rm D} = -\hat{\boldsymbol{d}}_{\rm D} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\rm D}),$$
  

$$H_{\rm A} = -\hat{\boldsymbol{d}}_{\rm A} \cdot \hat{\boldsymbol{E}}(\boldsymbol{r}_{\rm A}),$$
  

$$H_{2} = -\alpha_{ij}^{\rm M}(k)\hat{E}_{i}(\boldsymbol{r}_{\rm M}, p)\hat{E}_{j}(\boldsymbol{r}_{\rm M}, p').$$
(5.35)

This matrix element (5.34) contains the information from all of the different time orderings, meaning we no longer have any explicit intermediate states. As a result, the order of perturbation theory required has been further reduced to first order. The first two terms of (5.34) are the direct (two-body) interaction terms, the first corresponding to the resonant time ordering and the second the off-resonant. The other terms describe different time orderings of the mediated interaction. The third and fourth terms are the half-resonant contributions, where the third term corresponds to (d) and (e) in figure 5.6 and the fourth term to (a) and (b). The fifth term describes the completely off-resonant interaction, shown in (c), and the sixth is the completely resonant interaction, (f).

We can now use this matrix element in the Fermi Golden Rule to calculate the rate of interaction.

## 5.2 Rate of Energy Transfer in Reciprocal Media

In this section, we combine our general expression for the matrix element of three-body RET (5.34) with macroscopic QED (introduced in chapter 2), which allows for the description of external environments via the Green's tensor (see section 2.2). This will then be used in the Fermi Golden Rule to calculate a general formula for three-body RET in an arbitrary environment.

## 5.2.1 Applying Macroscopic QED

We now employ macroscopic QED by expressing the electric field in terms of the Green's tensor via (2.36). The first two terms of (5.34) were calculated in section 3.2 and were been found to be (3.46) and (3.47), so we now need to apply the same methods to the other four terms.

The numerator of the third term in the matrix element (5.34) combined with the interaction Hamiltonian (3.3) can be written as,

$$\langle f | H_{\rm D} H_{\rm A} H_2 | i \rangle = - \langle g_{\rm D}, s_{\rm M}, e_{\rm A}; 0 | \hat{\boldsymbol{d}}_{D_i} \hat{E}_i(\boldsymbol{r}_{\rm D}) \hat{\boldsymbol{d}}_{A_j} \hat{E}_j(\boldsymbol{r}_{\rm A}) \times \hat{E}_k(\boldsymbol{r}_{\rm M}, p) \alpha_{kl}^{\rm M}(k) \hat{E}_l(\boldsymbol{r}_{\rm M}, p') | e_{\rm D}, s_{\rm M}, g_{\rm A}; 0 \rangle = - d_{D_i}^{\downarrow} d_{A_j}^{\uparrow} \alpha_{kl}^{\rm M}(k) \langle 0 | \hat{E}_i(\boldsymbol{r}_{\rm D}) \hat{E}_j(\boldsymbol{r}_{\rm A}) \hat{E}_k(\boldsymbol{r}_{\rm M}, p) \hat{E}_l(\boldsymbol{r}_{\rm M}, p') | 0 \rangle ,$$
 (5.36)

where we have redefined the dipole moments using (3.32). To begin with, we substitute our expression for the electric field in reciprocal media (2.36) to the mediator terms,  $\hat{E}(\mathbf{r}_{\rm M}, p)$  and  $\hat{E}(\mathbf{r}_{\rm M}, p')$ , only. Using the fact that the annihilation operator acting on the ground state gives zero (2.24), we know that the only surviving term will be,

$$\langle f | H_{\rm D} H_{\rm A} H_2 | i \rangle = -\sum_{\lambda} \int_0^\infty d\omega \int d^3 \boldsymbol{r} \sum_{\lambda'} \int_0^\infty d\omega' \int d^3 \boldsymbol{r}' d^{\downarrow}_{D_i} d^{\uparrow}_{A_j} \alpha^{\rm M}_{kl}(k) \times \langle 0 | \hat{E}_i(\boldsymbol{r}_{\rm D}) \hat{E}_j(\boldsymbol{r}_{\rm A}) G^{\dagger}_{\lambda_{km}}(\boldsymbol{r}_{\rm M}, \boldsymbol{r}, \omega) \hat{\boldsymbol{f}}^{\dagger}_{\lambda_m}(\boldsymbol{r}, \omega) G^{\dagger}_{\lambda_{ln}}(\boldsymbol{r}_{\rm M}, \boldsymbol{r}', \omega') \hat{\boldsymbol{f}}^{\dagger}_{\lambda'_n}(\boldsymbol{r}', \omega') | 0 \rangle = -\sum_{\lambda} \int_0^\infty d\omega \int d^3 \boldsymbol{r} \sum_{\lambda'} \int_0^\infty d\omega' \int d^3 \boldsymbol{r}' d^{\downarrow}_{D_i} d^{\uparrow}_{A_j} \alpha^{\rm M}_{kl}(k) \times \langle 0 | \hat{E}_i(\boldsymbol{r}_{\rm D}) \hat{E}_j(\boldsymbol{r}_{\rm A}) G^{\dagger}_{\lambda_{km}}(\boldsymbol{r}_{\rm M}, \boldsymbol{r}, \omega) G^{\dagger}_{\lambda_{ln}}(\boldsymbol{r}_{\rm M}, \boldsymbol{r}', \omega') \left| 1_{\lambda'_m}(\boldsymbol{r}', \omega'), 1_{\lambda_n}(\boldsymbol{r}, \omega) \right\rangle,$$
(5.37)

where we have used  $\hat{f}_{\lambda}^{\dagger}(\boldsymbol{r},\omega)|0\rangle = |1_{\lambda}(\boldsymbol{r},\omega)\rangle$ . Now, as in section 3.2.1, we know that only terms containing both creation and annihilation operators for each mode will contribute, meaning we get,

$$\langle f | H_{\rm D} H_{\rm A} H_2 | i \rangle = -\sum_{\lambda} \int_0^\infty d\omega \int d^3 \boldsymbol{r} \sum_{\lambda'} \int_0^\infty d\omega' \int d^3 \boldsymbol{r}' \, d_{D_i}^{\downarrow} d_{A_j}^{\uparrow} \alpha_{kl}^{\rm M}(k) \times \langle 0 | G_{\lambda_{im}}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}, \omega) G_{\lambda_{jn}}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}', \omega') G_{\lambda_{km}}^{\dagger}(\boldsymbol{r}_{\rm M}, \boldsymbol{r}, \omega) G_{\lambda_{ln}}^{\dagger}(\boldsymbol{r}_{\rm M}, \boldsymbol{r}', \omega') | 0 \rangle ,$$
 (5.38)

where we have used  $\hat{f}^{\dagger}_{\lambda''}(\mathbf{r}'',\omega'') \left| 1_{\lambda}(\mathbf{r},\omega) \right\rangle = \delta_{\lambda''\lambda} \delta(\mathbf{r}''-\mathbf{r}) \delta(\omega''-\omega)$ . Now using the com-

pleteness relation defined in (2.85), we can rewrite as,

$$\langle f | H_{\rm D} H_{\rm A} H_2 | i \rangle = -\frac{\hbar^2 \mu_0^2}{\pi^2} d_{D_i}^{\downarrow} d_{A_j}^{\uparrow} \alpha_{kl}^{\rm M}(k) \times \int_0^{\infty} d\omega \int_0^{\infty} d\omega' \, {\rm Im} G_{ik}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm M}, \omega) \, {\rm Im} G_{jl}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm M}, \omega').$$
(5.39)

So now we have an expression for the third term of the matrix element (5.34),

$$\langle f | \frac{H_{\rm D}H_{\rm A}H_2}{(\hbar cp + E_{\rm eg})(\hbar cp' - E_{\rm eg})} | i \rangle = -\frac{\mu_0^2}{\pi^2} d_{D_i}^{\downarrow} d_{A_j}^{\uparrow} \alpha_{kl}^{\rm M}(k) \int_0^{\infty} d\omega \int_0^{\infty} d\omega' \times \frac{\omega^2 \operatorname{Im} G_{ik}(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm M}, \omega)}{\omega - \omega_0} \frac{\omega'^2 \operatorname{Im} G_{jl}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm M}, \omega)}{\omega + \omega_0'}, \quad (5.40)$$

where we have made the substitutions  $\hbar cp = \hbar \omega$ ,  $\hbar cp' = \hbar \omega'$  and  $E_{eg} = \hbar \omega_0$ . We can apply the same method to the remaining three terms of (5.34) so that the indirect matrix element (the final four terms of (5.34)) is calculated to be,

$$M_{fi}^{\text{indir}} = -\frac{\mu_0^2}{\pi^2} \int_0^\infty d\omega \int_0^\infty d\omega' \omega^2 \omega'^2 \left[ d_{D_i}^{\downarrow} d_{A_j}^{\uparrow} \alpha_{kl}^{\mathrm{M}}(k) \frac{\mathrm{Im}G_{ik}(\mathbf{r}_{\mathrm{D}}, \mathbf{r}_{\mathrm{M}}, \omega)}{\omega + \omega_0} \frac{\mathrm{Im}G_{jl}(\mathbf{r}_{\mathrm{A}}, \mathbf{r}_{\mathrm{M}}, \omega')}{\omega' - \omega_0} \right] + \alpha_{ij}^{\mathrm{M}}(k) d_{D_k}^{\downarrow} d_{A_l}^{\uparrow} \frac{\mathrm{Im}G_{ik}(\mathbf{r}_{\mathrm{M}}, \mathbf{r}_{\mathrm{D}}, \omega)}{\omega - \omega_0} \frac{\mathrm{Im}G_{jl}(\mathbf{r}_{\mathrm{M}}, \mathbf{r}_{\mathrm{A}}, \omega')}{\omega' + \omega_0} \\+ d_{D_i}^{\downarrow} \alpha_{jk}^{\mathrm{M}}(k) d_{A_l}^{\uparrow} \frac{\mathrm{Im}G_{ik}(\mathbf{r}_{\mathrm{D}}, \mathbf{r}_{\mathrm{M}}, \omega)}{\omega + \omega_0} \frac{\mathrm{Im}G_{jl}(\mathbf{r}_{\mathrm{M}}, \mathbf{r}_{\mathrm{A}}, \omega')}{\omega' + \omega_0} \\+ d_{A_i}^{\uparrow} \alpha_{jk}^{\mathrm{M}}(k) d_{D_l}^{\downarrow} \frac{\mathrm{Im}G_{jl}(\mathbf{r}_{\mathrm{M}}, \mathbf{r}_{\mathrm{D}}, \omega)}{\omega - \omega_0} \frac{\mathrm{Im}G_{ik}(\mathbf{r}_{\mathrm{A}}, \mathbf{r}_{\mathrm{M}}, \omega')}{\omega' - \omega_0} \right].$$
(5.41)

The next step is to apply contour integration techniques to evaluate these frequency integrals.

## 5.2.2 Contour Integration

We can rearrange these as in section 3.2.1 using the result (3.45). We can also apply the results found in section 3.2.2, which have been generalized and summarized below,

$$\int_0^\infty d\omega \, \frac{\omega^2 \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega - \omega_0} = -i \int_0^\infty d\xi \, \frac{\xi^2 \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', i\xi)}{i\xi - \omega_0} + 2\pi i \omega_0^2 \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega_0), \tag{5.42}$$

$$\int_{0}^{-\infty} d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega - \omega_0} = -i \int_{0}^{\infty} d\xi \, \frac{\xi^2 \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', i\xi)}{i\xi - \omega_0},\tag{5.43}$$

$$\int_0^\infty d\omega \, \frac{\omega^2 \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega + \omega_0} = \int_0^{-\infty} d\omega \, \frac{\omega^2 \, \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega + \omega_0} = -i \int_0^\infty d\xi \, \frac{\xi^2 \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', i\xi)}{i\xi + \omega_0}, \qquad (5.44)$$

to make the substitutions,

$$\int_{0}^{\infty} d\omega \frac{\omega^{2} \operatorname{Im} \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega + \omega_{0}} = \boldsymbol{F}(\boldsymbol{r}, \boldsymbol{r}'), \qquad (5.45a)$$

$$\int_0^\infty d\omega \frac{\omega^2 \operatorname{Im} \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega)}{\omega - \omega_0} = -\boldsymbol{F}(\boldsymbol{r}, \boldsymbol{r}') + \pi \omega_0^2 \boldsymbol{G}(\boldsymbol{r}, \boldsymbol{r}', \omega_0), \qquad (5.45b)$$

where we have defined the function,

$$\boldsymbol{F}(\boldsymbol{r},\boldsymbol{r}') \equiv \frac{1}{2} \int_0^\infty d\xi \xi^2 \boldsymbol{G}(\boldsymbol{r},\boldsymbol{r}',i\xi) \left(\frac{1}{\omega-\omega_0} - \frac{1}{\omega+\omega_0}\right),\tag{5.46}$$

noting that in the case of reciprocal media, Lorentz reciprocity (2.74) holds for the Green's tensor and therefore also for this function. Applying (5.45) to the indirect matrix element (5.41) we obtain,

$$M_{fi}^{\text{indir}} = -\frac{\mu_0^2}{\pi^2} \left\{ \boldsymbol{d}_{D_i}^{\downarrow} \boldsymbol{d}_{A_j}^{\uparrow} \alpha_{kl}^{\text{M}}(k) F_{ik}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{M}}) \left[ -F_{jl}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{M}}) + \pi \omega_0^2 G_{jl}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{M}}, \omega_0) \right] \right. \\ \left. + \alpha_{ij}^{\text{M}}(k) \boldsymbol{d}_{D_k}^{\downarrow} \boldsymbol{d}_{A_l}^{\uparrow} \left[ -F_{ik}(\boldsymbol{r}_{\text{M}}, \boldsymbol{r}_{\text{D}}) + \pi \omega_0^2 G_{ik}(\boldsymbol{r}_{\text{M}}, \boldsymbol{r}_{\text{D}}, \omega_0) \right] F_{jl}(\boldsymbol{r}_{\text{M}}, \boldsymbol{r}_{\text{A}}) \right. \\ \left. + \boldsymbol{d}_{D_i}^{\downarrow} \alpha_{jk}^{\text{M}}(k) \boldsymbol{d}_{A_l}^{\uparrow} F_{ik}(\boldsymbol{r}_{\text{D}}, \boldsymbol{r}_{\text{M}}) F_{jl}(\boldsymbol{r}_{\text{M}}, \boldsymbol{r}_{\text{A}}) \right. \\ \left. + \boldsymbol{d}_{A_i}^{\uparrow} \alpha_{jk}^{\text{M}}(k) \boldsymbol{d}_{D_l}^{\downarrow} \left[ -F_{jl}(\boldsymbol{r}_{\text{M}}, \boldsymbol{r}_{\text{D}}) + \pi \omega_0^2 G_{jl}(\boldsymbol{r}_{\text{M}}, \boldsymbol{r}_{\text{D}}, \omega_0) \right] \right] \\ \left. \times \left[ -F_{ik}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{M}}) + \pi \omega_0^2 G_{ik}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{M}}, \omega_0) \right] \right\}.$$
(5.47)

We now make use of the Lorentz reciprocity of of our function, so  $F_{ij}(\mathbf{r}, \mathbf{r}') = F_{ji}(\mathbf{r}', \mathbf{r})$ , and also that the dynamic polarizability is symmetric in its indices,  $\alpha_{ij}^{\mathrm{M}}(k) = \alpha_{ji}^{\mathrm{M}}(k)$ . For the terms with no poles, we find,

$$\boldsymbol{d}_{D_{i}}^{\downarrow}\boldsymbol{d}_{A_{j}}^{\uparrow}\alpha_{kl}^{\mathrm{M}}(k)F_{ik}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{M}})F_{jl}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}}) = \boldsymbol{d}_{A_{j}}^{\uparrow}F_{jl}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{kl}^{\mathrm{M}}(k)F_{ik}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{M}})\boldsymbol{d}_{D_{i}}^{\downarrow} = \boldsymbol{d}_{A_{j}}^{\uparrow}F_{jl}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{kl}^{\mathrm{M}}(k)F_{ki}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{i}}^{\downarrow}, \alpha_{ij}^{\mathrm{M}}(k)\boldsymbol{d}_{D_{k}}^{\downarrow}\boldsymbol{d}_{A_{l}}^{\uparrow}F_{ik}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})F_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{A}}) = \boldsymbol{d}_{A_{l}}^{\uparrow}F_{lj}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{ji}^{\mathrm{M}}(k)F_{ik}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{k}}^{\downarrow}, \boldsymbol{d}_{D_{i}}^{\downarrow}\alpha_{jk}^{\mathrm{M}}(k)\boldsymbol{d}_{A_{l}}^{\uparrow}F_{ik}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{M}})F_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{A}}) = \boldsymbol{d}_{A_{l}}^{\uparrow}F_{lj}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{jk}^{\mathrm{M}}(k)F_{ki}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{i}}^{\downarrow}, \boldsymbol{d}_{A_{i}}^{\uparrow}\alpha_{jk}^{\mathrm{M}}(k)\boldsymbol{d}_{D_{l}}^{\downarrow}F_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})F_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}}) = \boldsymbol{d}_{A_{i}}^{\uparrow}F_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{kj}^{\mathrm{M}}(k)F_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{l}}^{\downarrow},$$
(5.48)

all of which can be written as  $\boldsymbol{d}_{A}^{\uparrow} \cdot \boldsymbol{F}(\boldsymbol{r}_{A}, \boldsymbol{r}_{M}) \cdot \alpha^{M}(k) \cdot \boldsymbol{F}(\boldsymbol{r}_{M}, \boldsymbol{r}_{D}) \cdot \boldsymbol{d}_{D}^{\downarrow}$ , so we see that all four terms without poles cancel each other. Similarly for the terms with one pole,

$$\begin{aligned} \boldsymbol{d}_{D_{i}}^{\downarrow}\boldsymbol{d}_{A_{j}}^{\uparrow}\alpha_{kl}^{\mathrm{M}}(k)\boldsymbol{F}_{ik}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{M}})\pi\omega_{0}^{2}\boldsymbol{G}_{jl}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}}) &= \pi\omega_{0}^{2}\boldsymbol{d}_{A_{j}}^{\uparrow}\boldsymbol{G}_{jl}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{ik}^{\mathrm{M}}(k)\boldsymbol{F}_{ki}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{i}}^{\downarrow},\\ \alpha_{ij}^{\mathrm{M}}(k)\boldsymbol{d}_{D_{k}}^{\downarrow}\boldsymbol{d}_{A_{l}}^{\uparrow}\pi\omega_{0}^{2}\boldsymbol{G}_{ik}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{F}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{A}}) &= \pi\omega_{0}^{2}\boldsymbol{d}_{A_{l}}^{\uparrow}\boldsymbol{F}_{lj}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{ji}^{\mathrm{M}}(k)\boldsymbol{G}_{ik}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{k}}^{\downarrow},\\ \boldsymbol{d}_{A_{i}}^{\uparrow}\alpha_{jk}^{\mathrm{M}}(k)\boldsymbol{d}_{D_{l}}^{\downarrow}\boldsymbol{F}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\pi\omega_{0}^{2}\boldsymbol{G}_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}}) &= \pi\omega_{0}^{2}\boldsymbol{d}_{A_{i}}^{\uparrow}\boldsymbol{G}_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{kj}^{\mathrm{M}}(k)\boldsymbol{F}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{l}}^{\downarrow},\\ \boldsymbol{d}_{A_{i}}^{\uparrow}\alpha_{jk}^{\mathrm{M}}(k)\boldsymbol{d}_{D_{l}}^{\downarrow}\pi\omega_{0}^{2}\boldsymbol{G}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{F}_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}}) &= \pi\omega_{0}^{2}\boldsymbol{d}_{A_{i}}^{\uparrow}\boldsymbol{F}_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{kj}^{\mathrm{M}}(k)\boldsymbol{G}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{l}}^{\downarrow},\\ \boldsymbol{d}_{A_{i}}^{\uparrow}\alpha_{jk}^{\mathrm{M}}(k)\boldsymbol{d}_{D_{l}}^{\downarrow}\pi\omega_{0}^{2}\boldsymbol{G}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{F}_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}}) &= \pi\omega_{0}^{2}\boldsymbol{d}_{A_{i}}^{\uparrow}\boldsymbol{F}_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{kj}^{\mathrm{M}}(k)\boldsymbol{G}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{l}}^{\downarrow},\\ \boldsymbol{d}_{A_{i}}^{\uparrow}\alpha_{jk}^{\mathrm{M}}(k)\boldsymbol{d}_{D_{l}}^{\downarrow}\pi\omega_{0}^{2}\boldsymbol{G}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{F}_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}}) &= \pi\omega_{0}^{2}\boldsymbol{d}_{A_{i}}^{\uparrow}\boldsymbol{F}_{ik}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}})\alpha_{kj}^{\mathrm{M}}(k)\boldsymbol{G}_{jl}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\boldsymbol{d}_{D_{l}}^{\downarrow},\\ \boldsymbol{d}_{A_{i}}^{\downarrow}\alpha_{jk}^{\mathrm{M}}(k)\boldsymbol{d}_{D_{l}}^{\downarrow}\boldsymbol{K}^{\mathrm{M}}(\boldsymbol{k})\boldsymbol{K}_{jl}(\boldsymbol{k})\boldsymbol{K$$

we see that the first and third are equal, and the second and fourth are equal, meaning that all of the one-pole terms cancel. This just leaves the two-pole term, meaning our expression for the indirect matrix element becomes,

$$M_{fi}^{\text{indir}} = -\mu_0^2 \pi^2 \omega_0^4 \boldsymbol{d}_{A_i}^{\uparrow} \boldsymbol{G}_{ik}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{M}}, \omega_0) \alpha_{kj}^{\text{M}}(k) \boldsymbol{G}_{jl}(\boldsymbol{r}_{\text{M}}, \boldsymbol{r}_{\text{D}}, \omega_0) \boldsymbol{d}_{D_l}^{\downarrow}.$$
(5.50)

Now, combining the direct and indirect contributions we obtain,

$$M_{fi} = M_{fi}^{\text{dir}} + M_{fi}^{\text{indir}}$$
  
=  $-\mu_0 \omega_0^2 \boldsymbol{d}_{A_i}^{\uparrow} \cdot \left[ \boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{D}}, \omega_0) + \mu_0 \omega_0^2 \boldsymbol{G}(\boldsymbol{r}_{\text{A}}, \boldsymbol{r}_{\text{M}}, \omega_0) \cdot \alpha^{\text{M}}(k) \cdot \boldsymbol{G}(\boldsymbol{r}_{\text{M}}, \boldsymbol{r}_{\text{D}}, \omega_0) \right] \cdot \boldsymbol{d}_{\text{D}}^{\downarrow}.$  (5.51)

We can now substitute this expression into Fermi's Golden rule [68], calculating the rate to be,

$$\Gamma_{fi} = \frac{2\pi}{\hbar} |M_{fi}|^2 \delta(E_{\mathrm{I}} - E_f)$$
  
=  $\frac{2\pi \mu_0^2 \omega_0^4}{\hbar} |\mathbf{d}_{\mathrm{A}}^{\uparrow} \cdot [\mathbf{G}(\mathbf{r}_{\mathrm{A}}, \mathbf{r}_{\mathrm{D}}, \omega_0)$   
+  $\mu_0 \omega_0^2 \mathbf{G}(\mathbf{r}_{\mathrm{A}}, \mathbf{r}_{\mathrm{M}}, \omega_0) \cdot \alpha_{\mathrm{M}}(k) \cdot \mathbf{G}(\mathbf{r}_{\mathrm{M}}, \mathbf{r}_{\mathrm{D}}, \omega_0)] \cdot \mathbf{d}_{\mathrm{D}}^{\downarrow}|^2.$  (5.52)

The first term of (5.52) describes the direct interaction between the donor and acceptor, where the field propagates from the donor at position  $r_{\rm D}$  and is observed at the acceptor at  $r_{\rm A}$ , therefore corresponding to the resonant interaction. The second term describes the mediated interaction, where the field propagates from the donor to the mediator, and then from the mediator to the acceptor. We can see therefore that the fully resonant interaction is the only time ordering that ends up contributing to the overall rate of energy transfer.

This result reduces to the three-body ICD formula given in [37] if the acceptor's transition dipole moment is expressed in terms of a photoionization cross section and the vacuum



Figure 5.7: Two possible arrangements of three bodies (donor, acceptor and mediator) in a vacuum.

Green's tensor (B.1) is used. As a proof-of-principle, in the next section we apply this formula to some simple environments.

## 5.3 Results

This formula (5.52) allows the calculation of the rate of energy transfer of three-bodies in an arbitrary external environment. As a proof-of-concept, we demonstrate the use of the formula for two simple environments, namely a vacuum and a semi-infinite half-space. However, we emphasize that the formula is applicable to any external environment, and could be used to calculate interactions within far more complex systems, such as proteins and other biological systems using a numerically calculated Green's tensor.

There are two geometries we are particularly interested in. The "colinear" arrangement, where all three molecules are on the z-axis as in figure 5.7a, and the "T-shape" arrangement, where the donor and acceptor are at an equal distance above and below the z-axis respectively, and the mediator is again on the z-axis, as shown in figure 5.7b.

The main challenge is how complex the forms of the Green's tensor can be (see App. B), making it difficult to derive analytic expressions for the rate, even for these simple geometries. To simplify our calculations, we can either impose simplifying limits on the Green's tensor in order to calculate the rate analytically, or numerically calculate the rate of interaction for different arrangements. This would involve fixing the donor and acceptor's positions, and calculating how the rate changes for different mediator positions along the z-axis. We will take both of these routes in this section.

The simplifying limits we impose to allow the calculation of analytic expressions are that the donor and acceptor are close enough to each other that the direct interaction between them is in the non-retarded limit. This is equivalent to assuming that the intermolecular distance between the donor and acceptor is significantly less that the characteristic wavelength. The

other limit we impose is that the mediator is far enough away from the donor and acceptor that the retarded limit can be used. This corresponds to a system of experimental interest consisting of a dimer trapped near a surface controlled by a distant mediating agent (e.g. Ref. [92]). Therefore, we need to use the non-retarded limit of the Green's tensor when describing the direct interaction between the donor and acceptor, and the retarded approximation to describe the mediated interaction. So when we are making this approximations, our rate formula (5.52) becomes,

$$\Gamma_{\rm lim} = \frac{2\pi\mu_0^2\omega_0^4}{\hbar} |\boldsymbol{d}_{\rm A}^{\uparrow} \cdot \left[ \boldsymbol{G}_{\rm NR}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm D}, \omega_0) + \mu_0\omega_0^2 \boldsymbol{G}_{\rm R}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm M}, \omega_0) \cdot \alpha^{\rm M}(k) \cdot \boldsymbol{G}_{\rm R}(\boldsymbol{r}_{\rm M}, \boldsymbol{r}_{\rm D}, \omega_0) \right] \cdot \boldsymbol{d}_{\rm D}^{\downarrow} |^2,$$
(5.53)

where  $G_{\text{NR}}$  is the non-retarded limit of the Green's tensor, and  $G_{\text{R}}$  is the retarded limit. We will use this form of the rate equation when performing subsequent calculations for a system in a vacuum and a system in the presence of a half-space.

As in section 3.3, we use the isotropic average when calculating the rate, so making the substitution given in (3.69), (5.53) becomes,

$$\Gamma_{\rm lim}^{\rm iso} = \frac{2\pi\mu_0^2\omega_0^4}{9\hbar} |\boldsymbol{d}_{\rm A}|^2 |\boldsymbol{d}_{\rm D}|^2 \operatorname{Tr} \left[ \boldsymbol{K}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm M}, \boldsymbol{r}_{\rm D}) \cdot \boldsymbol{K}^*(\boldsymbol{r}_{\rm D}, \boldsymbol{r}_{\rm M}, \boldsymbol{r}_{\rm A}) \right],$$
(5.54)

where we have defined,

$$\boldsymbol{K}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}}) \equiv \boldsymbol{G}_{\mathrm{NR}}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}},\omega_{0}) + \mu_{0}\omega_{0}^{2}\boldsymbol{G}_{\mathrm{R}}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}},\omega_{0}) \cdot \alpha^{\mathrm{M}}(k) \cdot \boldsymbol{G}_{\mathrm{R}}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}},\omega_{0}).$$
(5.55)

We now apply our rate equation (5.54) to two simple environments, namely a vacuum and a semi-infinite half-space.

### 5.3.1 Vacuum

In the vacuum case, the form of the Green's tensor (B.1) is sufficiently simple that we are able to analytically calculate the rate of energy transfer for both geometries of interest in figure 5.7, the colinear arrangement and the T-shape arrangement. We use the approximate forms of the Green's tensor for a vacuum for the near- and far-field limits in our limiting rate equation (5.54) and apply this to the geometries of interest.

#### **Colinear Analytic Expression**

For the colinear arrangement shown in figure 5.7a, we note that  $z_{\rm M} > z_{\rm A} > z_{\rm D}$ , allowing the substitutions,

$$|z_{A} - z_{D}| = |z_{D} - z_{A}| = z_{A} - z_{D} \equiv z_{AD},$$
  

$$|z_{A} - z_{M}| = |z_{M} - z_{A}| = z_{M} - z_{A} \equiv z_{MA},$$
  

$$|z_{D} - z_{M}| = |z_{M} - z_{D}| = z_{M} - z_{D} \equiv z_{MD}.$$
(5.56)

We can use the expressions for the non-retarded and retarded limits of the vacuum Green's tensor, (3.77) and (3.79) respectively, to calculate the trace of the functions from (5.55),

$$\operatorname{Tr} \begin{bmatrix} \boldsymbol{K}_{\mathrm{C}}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{M}}, \boldsymbol{r}_{\mathrm{D}}) \cdot \boldsymbol{K}_{\mathrm{C}}^{*}(\boldsymbol{r}_{\mathrm{D}}, \boldsymbol{r}_{\mathrm{M}}, \boldsymbol{r}_{\mathrm{A}}) \end{bmatrix}$$

$$= \operatorname{Tr} \begin{bmatrix} \begin{pmatrix} B_{\mathrm{C}} - A_{\mathrm{C}} & 0 & 0 \\ 0 & B_{\mathrm{C}} - A_{\mathrm{C}} & 0 \\ 0 & 0 & 2A_{\mathrm{C}} \end{pmatrix} \cdot \begin{pmatrix} B_{\mathrm{C}}^{*} - A_{\mathrm{C}} & 0 & 0 \\ 0 & B_{\mathrm{C}}^{*} - A_{\mathrm{C}} & 0 \\ 0 & 0 & 2A_{\mathrm{C}} \end{pmatrix} \end{bmatrix}$$

$$= 6A_{\mathrm{C}}^{2} + 2B_{\mathrm{C}}B_{\mathrm{C}}^{*} - 2A_{\mathrm{C}}(B_{\mathrm{C}} + B_{\mathrm{C}}^{*}), \qquad (5.57)$$

where we have defined,

$$A_{\rm C} \equiv \frac{c^2}{4\pi\omega_0^2 z_{\rm AD}^3}, \quad B_{\rm C} \equiv \frac{\mu_0 \omega_0^2 \alpha_{\rm M} e^{i\omega_0 (z_{\rm MA} + z_{\rm MD})/c}}{16\pi^2 z_{\rm MA} z_{\rm MD}}.$$
 (5.58)

Substituting (5.57) into the isotropic rate equation (5.54) we find,

$$\Gamma_{\rm C}^{\rm iso} = \frac{2\pi\mu_0^2\omega_0^4}{9\hbar} |d_{\rm A}|^2 |d_{\rm D}|^2 \left\{ 6 \left( \frac{c^2}{4\pi\omega_0^2 z_{\rm AD}^3} \right)^2 + 2 \left( \frac{\mu_0\omega_0^2\alpha_{\rm M}}{16\pi^2 z_{\rm MA} z_{\rm MD}} \right)^2 - 2 \frac{c^2}{4\pi\omega_0^2 z_{\rm AD}^3} \times \frac{\mu_0\omega_0^2\alpha_{\rm M}\cos[\frac{\omega_0}{c}(z_{\rm MA} + z_{\rm MD})]}{16\pi^2 z_{\rm MA} z_{\rm MD}} \right\}$$
$$= \frac{\mu_0^2\omega_0^4}{9\hbar} |d_{\rm A}|^2 |d_{\rm D}|^2 \left\{ \frac{3c^2}{4\pi\omega_0^4 z_{\rm AD}^6} + \frac{\mu_0^2\omega_0^4\alpha_{\rm M}^2}{64\pi^3 z_{\rm MA}^2 z_{\rm MD}^2} - \frac{c^2\mu_0\alpha_{\rm M}\cos[\frac{\omega_0}{c}(z_{\rm MA} + z_{\rm MD})]}{16\pi^2 z_{\rm AD}^3 z_{\rm MA} z_{\rm MD}} \right\}.$$
(5.59)

In this first term, we can recognize the characteristic  $r^{-6}$  dependence that arises from direct two-body energy transfer between the donor and acceptor without the influence of the mediator in the non-retarded limit. The other two terms correspond to the mediated interaction, and we see this oscillating contribution which only appears with the addition of the third body.

#### **T-shape Analytic Expression**

For the T-shape arrangement, we label the distance between the donor and acceptor as L, so that the donor is at a position L/2 above the z-axis, and the acceptor is L/2 below the z-axis, as shown in figure 5.7b. In this geometry, we find,

$$\left( \boldsymbol{e}_{\rho} \otimes \boldsymbol{e}_{\rho} \right)_{\text{AD/DA}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$
 (5.60)

$$\left(\boldsymbol{e}_{\rho}\otimes\boldsymbol{e}_{\rho}\right)_{\mathrm{DM/MD}} = \frac{1}{R_{+}^{2}} \begin{pmatrix} L^{2} & 0 & -2LZ \\ 0 & 0 & 0 \\ -2LZ & 0 & 4Z^{2} \end{pmatrix},$$
(5.61)

$$\left(\boldsymbol{e}_{\rho} \otimes \boldsymbol{e}_{\rho}\right)_{\text{AM/MA}} = \frac{1}{R_{+}^{2}} \begin{pmatrix} L^{2} & 0 & 2LZ \\ 0 & 0 & 0 \\ 2LZ & 0 & 4Z^{2} \end{pmatrix}, \qquad (5.62)$$

where we have defined  $R_{+}^{2} \equiv 4Z^{2} + L^{2}$ . We can use these to obtain expressions for the non-retarded and retarded limits of the vacuum Green's tensor in this geometry,

$$\boldsymbol{G}_{\mathrm{NR}}^{(0,\mathrm{T})}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{D}},\omega_{0}) = -\frac{c^{2}}{4\pi\omega_{0}^{2}L^{3}} \begin{pmatrix} -2 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{pmatrix},$$
(5.63)

$$\boldsymbol{G}_{\mathrm{R}}^{(0,\mathrm{T})}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}},\omega_{0}) = -\frac{e^{i\omega_{0}R_{+}/2c}}{2\pi R_{+}^{3}} \begin{pmatrix} 4Z^{2} & 0 & 2LZ \\ 0 & R_{+}^{2} & 0 \\ 2LZ & 0 & L^{2} \end{pmatrix}, \qquad (5.64)$$

$$\boldsymbol{G}_{\mathrm{R}}^{(0,\mathrm{T})}(\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}},\omega_{0}) = -\frac{e^{i\omega_{0}R_{+}/2c}}{2\pi R_{+}^{3}} \begin{pmatrix} 4Z^{2} & 0 & -2LZ \\ 0 & R_{+}^{2} & 0 \\ -2LZ & 0 & L^{2} \end{pmatrix}.$$
 (5.65)

So, we can calculate the function (5.55),

$$\boldsymbol{K}_{\mathrm{T}}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{M}}, \boldsymbol{r}_{\mathrm{D}}) = -A_{\mathrm{T}} \begin{pmatrix} -2 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1 \end{pmatrix} + B_{\mathrm{T}} \begin{pmatrix} 4Z^{2}R_{-}^{2} & 0 & 2LZR_{-}^{2}\\ 0 & R_{+}^{4} & 0\\ 2LZR_{-}^{2} & 0 & -L^{2}R_{-}^{2} \end{pmatrix},$$
(5.66)

where we have defined,

$$R_{-}^{2} \equiv 4Z^{2} - L^{2}, \quad A_{\rm T} \equiv \frac{c^{2}}{4\pi\omega_{0}^{2}L^{3}}, \quad B_{\rm T} \equiv \frac{\mu_{0}\omega_{0}^{2}\alpha_{\rm M}e^{i\omega_{0}R_{+}/c}}{4\pi^{2}R_{+}^{6}}.$$
 (5.67)

We can therefore can calculate,

$$Tr \left[ \mathbf{K}_{T}(\mathbf{r}_{A}, \mathbf{r}_{M}, \mathbf{r}_{D}) \cdot \mathbf{K}_{T}^{*}(\mathbf{r}_{D}, \mathbf{r}_{M}, \mathbf{r}_{A}) \right]$$
  
=(2A<sub>T</sub> + 4B<sub>T</sub>Z<sup>2</sup>R<sup>2</sup><sub>-</sub>)(2A<sub>T</sub> + 4B<sub>T</sub><sup>\*</sup>Z<sup>2</sup>R<sup>2</sup><sub>-</sub>) - 4B<sub>T</sub>B<sub>T</sub><sup>\*</sup>L<sup>2</sup>Z<sup>2</sup>R<sup>4</sup><sub>-</sub> + (B<sub>T</sub>R<sup>4</sup><sub>+</sub> - A<sub>T</sub>)(B<sub>T</sub><sup>\*</sup>R<sup>4</sup><sub>+</sub> - A<sub>T</sub>)  
- 4B<sub>T</sub>B<sub>T</sub><sup>\*</sup>L<sup>2</sup>Z<sup>2</sup>R<sup>4</sup><sub>-</sub> + (A<sub>T</sub> + B<sub>T</sub>L<sup>2</sup>R<sup>2</sup><sub>-</sub>)(A<sub>T</sub> + B<sub>T</sub><sup>\*</sup>L<sup>2</sup>R<sup>2</sup><sub>-</sub>)  
=6A<sub>T</sub><sup>2</sup> + B<sub>T</sub>B<sub>T</sub><sup>\*</sup>(R<sup>8</sup><sub>-</sub> + R<sup>8</sup><sub>+</sub>) + A<sub>T</sub>(B<sub>T</sub> + B<sub>T</sub><sup>\*</sup>)R<sup>2</sup><sub>+</sub>(R<sup>2</sup><sub>-</sub> + R<sup>2</sup><sub>+</sub>), (5.68)

and substitute into the expression for the isotropic rate (5.54),

$$\Gamma_{\rm T}^{\rm iso} = \frac{2\pi\mu_0^2\omega_0^4}{9\hbar} |d_{\rm A}|^2 |d_{\rm D}|^2 \left\{ 6 \left( \frac{c^2}{4\pi\omega_0^2 L^3} \right)^2 + \frac{\mu_0^2\omega_0^4\alpha_{\rm M}^2(R_-^8 + R_+^8)}{16\pi^4 R_+^{12}} + R_+^2(R_-^2 + R_+^2) \frac{c^2}{4\pi\omega_0^2 L^3} \frac{\mu_0\omega_0^2\alpha_{\rm M}\cos[\frac{\omega_0}{c}R_+]}{4\pi^2 R_+^6} \right\} \\
= \frac{\mu_0^2\omega_0^4}{9\hbar} |d_{\rm A}|^2 |d_{\rm D}|^2 \left\{ \frac{3c^4}{4\pi\omega_0^4 L^6} + \frac{\mu_0^2\omega_0^4\alpha_{\rm M}^2}{8\pi^3} \left( \frac{R_-^8}{R_+^{12}} + \frac{1}{R_+^8} \right) + \frac{c^2\mu_0\omega_0^2\alpha_{\rm M}\cos[\frac{\omega_0}{c}R_+]}{4\pi^2\omega_0^2 L^3} \left( \frac{R_-^2}{R_+^4} - \frac{1}{R_+^2} \right) \right\}.$$
(5.69)

We can identify similarities between this and the colinear expression (5.59). The first term describes the direct interaction, displaying the characteristic  $r^{-6}$  dependence, and the mediated interaction again contains an oscillating contribution.

#### **Comparison Plots**

We can plot the rate's dependence on the mediator position by fixing the positions of the donor and acceptor and allowing the position of the mediator to vary along the z-axis. Due to the approximations we have applied, the calculated rate is only applicable when the mediator is sufficiently far enough away from the donor and acceptor, since the retarded limit has been applied. The rates for both the geometries are plotted in figure 5.8. We can see that both geometries display oscillatory behaviour, meaning the mediator can suppress or enhance the rate of energy transfer between the donor and acceptor depending on its position.

To study more general geometries, we can extend this to allow the mediator to vary its



Figure 5.8: Plot of rate of energy transfer against mediator position for two arrangements of a three-body system in a vacuum, normalised to the isotropic two-body vacuum rate. The approximate analytic expressions, (5.59) and (5.69), are compared with the exact results. The mediator position is in units of the transition wavelength  $\lambda_0$  and the polarizability volume  $\alpha_M/4\pi\epsilon_0$  of the mediator is chosen as  $0.1\lambda_0^3$ . For the colinear configuration, the donor is at  $\{x_D, z_D\}/\lambda_0 = \{0, 0.04\}$  and the acceptor is at  $\{x_A, z_A\}/\lambda_0 = \{0, 0.08\}$  as indicated by the blue and red vertical lines and dictated by the imposition of the non-retarded limit in that section of the system. For the T-shape setup, the donor is at  $\{x_D, z_D\}/\lambda_0 = \{0.02, 0.08\}$  and the acceptor is at  $\{x_A, z_A\}/\lambda_0 = \{-0.02, 0.08\}$ . In order for the retarded approximation to hold in its section of the system, the mediator should not be brought nearer than approximately a wavelength away from the donor, acceptor or boundary. This is indicated by the dashed vertical grey line.



Figure 5.9: Rate of energy transfer for a donor and acceptor in a vacuum. The donor is fixed at position  $\{x_{\rm D}, z_{\rm D}\}/\lambda_0 = \{-1, 1\}$ , the acceptor at position  $\{x_{\rm A}, z_{\rm A}\}/\lambda_0 = \{1, 2\}$ , while the mediator is free to move in the *xz*-plane. The other parameters and normalisation are the same as in Fig. 5.8. The grey regions around the donor and acceptor indicate where the rate enhancement goes off the colour scale, the limits of which have been chosen to demonstrate the oscillations the mediator induces.

position over the *xz*-plane and investigate how this affects the rate (see figure 5.9). This gives us a clear visual representation of how the geometry of the molecules affects the energy transfer rate, even when just in a vacuum environment. The grey regions around the donor and acceptor in figure 5.9 represent values that are too large (ranging from  $\sim 10^3$  and  $\sim 10^5$ ) to show on the colour scale while preserving the visibility of the oscillatory behaviour.

## 5.3.2 Half-space

We now move on to studying a system of three bodies in a colinear arrangement near a semiinfinite half-space. We will again apply the near- and far-field limits, which corresponds to a setup of a dimer trapped near a surface controlled by a distant mediating agent, a situation of experimental interest (e.g. Ref. [92]).

#### **Colinear Analytic Expression**

The form of the Green's tensor when a dielectric half space is introduced is significantly more complicated than that of just a vacuum, even when only considering simple reciprocal media (see Appendix B.2). To make things simpler, we will just consider the colinear case where all three molecules are positioned along the z-axis, as shown in figure 5.10.


Figure 5.10: Colinear system made up of three bodies and a semi-infinite dielectric half-space. The donor and acceptor are assumed close enough together and to the surface to apply the non-retarded (NR) limit to their direct interaction, and the mediator is assumed far enough away from both that the retarded (R) limit can be applied. Figure reproduced from [1] under the terms of the Creative Commons Attribution 4.0 International license.

We are interested in the case where the donor and acceptor are positioned very close to each other and to the half-space, and the mediator is far away from them. This means that we can again apply the non-retarded limit to the direct interaction between the donor and acceptor, and the retarded limit to the mediated interaction (see figure 5.10), so we use (5.54) to calculate the rate. As discussed in subsection 2.2.1, the effective Green's tensor we require is the sum of the vacuum Green's tensor and the half-space Green's tensor. Substituting these effective Green's tensors for the non-retarded and retarded regimes, (B.38) and (B.40) respectively, into our function defined in (5.55), we find,

$$\boldsymbol{K}_{\mathrm{C}}^{\mathrm{HS}}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{M}}, \boldsymbol{r}_{\mathrm{D}}) = \frac{c^{2}}{4\pi\omega_{0}^{2}} \begin{bmatrix} \frac{1}{z_{\mathrm{AD}}^{3}} \begin{pmatrix} -1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2 \end{pmatrix} \\ + \frac{R_{\mathrm{NR}}}{\bar{z}_{\mathrm{AD}}^{3}} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 2 \end{pmatrix} \end{bmatrix} + \frac{\mu_{0}\omega_{0}^{2}\alpha_{\mathrm{M}}}{16\pi^{2}} C \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0 \end{pmatrix}, \quad (5.70)$$

where we have again made use of the substitutions (5.56) for our three-body collinear arrangement and we have defined,

$$C \equiv \left[\frac{e^{iz_{\rm MA}\omega_0/c}}{z_{\rm MA}} + \frac{e^{i\bar{z}_{\rm MA}\omega_0/c}}{\bar{z}_{\rm MA}}R_{\rm R}\right] \left[\frac{e^{iz_{\rm MD}\omega_0/c}}{z_{\rm MD}} + \frac{e^{i\bar{z}_{\rm MD}\omega_0/c}}{\bar{z}_{\rm MD}}R_{\rm R}\right].$$
(5.71)

So we can now calculate,

$$\operatorname{Tr}\left[\boldsymbol{K}_{\mathrm{C}}^{\mathrm{HS}}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{D}})\cdot\boldsymbol{K}_{\mathrm{C}}^{\mathrm{HS}^{*}}(\boldsymbol{r}_{\mathrm{D}},\boldsymbol{r}_{\mathrm{M}},\boldsymbol{r}_{\mathrm{A}})\right] = \left[\frac{c^{2}}{2\pi\omega_{0}^{2}}\left(\frac{1}{z_{\mathrm{AD}}^{3}}+\frac{R_{\mathrm{NR}}}{\bar{z}_{\mathrm{AD}}^{3}}\right)\right]^{2} + 2\left[\frac{c^{2}}{4\pi\omega_{0}^{2}}\left(\frac{R_{\mathrm{NR}}}{\bar{z}_{\mathrm{AD}}^{3}}-\frac{1}{z_{\mathrm{AD}}^{3}}\right)+\frac{\mu_{0}\omega_{0}^{2}\alpha_{\mathrm{M}}}{16\pi^{2}}C\right]\left[\frac{c^{2}}{4\pi\omega_{0}^{2}}\left(\frac{R_{\mathrm{NR}}}{\bar{z}_{\mathrm{AD}}^{3}}-\frac{1}{z_{\mathrm{AD}}^{3}}\right)+\frac{\mu_{0}\omega_{0}^{2}\alpha_{\mathrm{M}}}{16\pi^{2}}C^{*}\right]\right] = \frac{c^{4}}{4\pi^{2}\omega_{0}^{4}}\left(\frac{1}{z_{\mathrm{AD}}^{3}}+\frac{R_{\mathrm{NR}}}{\bar{z}_{\mathrm{AD}}^{3}}\right)^{2}+\frac{c^{4}}{8\pi^{2}\omega_{0}^{4}}\left(\frac{R_{\mathrm{NR}}}{\bar{z}_{\mathrm{AD}}^{3}}-\frac{1}{z_{\mathrm{AD}}^{3}}\right)^{2}+\frac{\mu_{0}^{2}\omega_{0}^{4}\alpha_{\mathrm{M}}^{2}}{128\pi^{4}}CC^{*} + \frac{c^{2}\mu_{0}\alpha_{\mathrm{M}}}{32\pi^{3}}\left(\frac{R_{\mathrm{NR}}}{\bar{z}_{\mathrm{AD}}^{3}}-\frac{1}{z_{\mathrm{AD}}^{3}}\right)(C+C^{*}),$$
(5.72)

and substitute this into the rate equation (5.54) to find,

$$\Gamma_{\rm C}^{\rm HS} = \frac{\mu_0^2 \omega_0^4}{18\pi\hbar} |d_{\rm A}|^2 |d_{\rm D}|^2 \left\{ \frac{c^4}{2\omega_0^4} \left[ \frac{3}{Z^6} + \frac{3R_{\rm NR}^2}{\bar{Z}^6} + \frac{2R_{\rm NR}}{\bar{Z}^3 Z^3} \right] + \frac{\mu_0 \alpha_{\rm M}}{8\pi} \left[ \frac{\mu_0 \omega_0^4 \alpha_{\rm M}}{4\pi} CC^* + c^2 \left( \frac{R_{\rm NR}}{\bar{z}_{\rm AD}^3} - \frac{1}{z_{\rm AD}^3} \right) (C+C^*) \right] \right\}.$$
(5.73)

As we have done for previous results, we are able to identify the origin of some of the contributions in this expression. For example, upon comparison with the two-body non-retarded half-space rate in (3.84), it is clear that the first square bracket of (5.73) describes the direct interaction between the donor and acceptor, including the effect of the half-space. We can similarly identify the contributions that correspond to the three-body vacuum interaction by considering the form of the function C defined in (5.71). Picking out only the vacuum terms in this function by setting  $R_{\rm R} \rightarrow 0$ , we find  $C \rightarrow \exp[i(z_{\rm MA} + z_{\rm MD})\omega_0/c]/z_{\rm MA}z_{\rm MD}$ . By comparing with (5.59), can then see that the first term in the second square bracket of (5.73) contains the contribution from the solely mediated vacuum interaction (second term of (5.59)) and the second term in the second square bracket of (5.73) contains the oscillating term arising from the interference of the direct and indirect vacuum interactions (final term of (5.59)).

#### **Comparison Plots**

Based on Ref. [92], we are particularly interested in how changing the position of the mediator affects the rate of energy transfer between the donor and acceptor. Figure 5.11 shows how the rate of energy transfer changes as the position of the mediator is varied along the z-axis, both



Figure 5.11: Plot of rate of energy transfer against mediator position for a colinear threebody system near a half-space (shaded region) modelled as a perfect reflector (corresponding to  $\varepsilon \to \infty$  so that  $r_{\rm NR} = 1 = -r_{\rm R}$ ). The surface is positioned at z = 0, and the donor and acceptor are in the same positions as in the colinear setup of figure 5.8. The other parameters and normalization are the same as in 5.8.

using the approximate formula (5.73) and for an exact numerical calculation using the full formula (5.52) and the full form of the half-space Green's tensor for the collinear arrangement given in (B.15).

We can see from figure 5.11 that the presence of the mediator creates an oscillating effect, as with the vacuum case, and that there are certain positions for which the mediator enhances or suppresses the rate of energy transfer at the few percentage level. It is clear from figure 5.11 that the approximations we applied to write down (5.54) work where they are expected to (mediator significantly more than one wavelength away from donor, acceptor and surface), but fail outside of that. It is interesting to note that for this particular situation the effect of the mediator is actually diminished by the presence of the half-space. In other words, when the environment contains this half-space, adding a controllable third body will have a less of effect on the energy transfer rate between the donor and acceptor than if no half-space were present.

This points towards a highly non-trivial dependence of the donor-acceptor transfer rate when accompanied by a mediator and a nearby surface. To investigate this (and to go beyond the colinear case) we use the full form of the Green's tensor for an environment containing a half-space (B.5). A density plot showing the rate for different positions of the mediator in the xz-plane is shown in figure 5.12. The plot demonstrates the intricate dependence of the mediator's position on the rate of energy transfer between the donor and acceptor even in the presence of a relatively simple environment, producing both enhancement and suppression in different regions. As for the vacuum case, the values represented by the grey regions around



Figure 5.12: Rate of energy transfer for a donor and acceptor near a half-space with reflection coefficient  $r_p = 1$ . The bodies are positioned in the same way as in figure 5.9. The other parameters and normalisation are the same as in Fig. 5.11. The grey regions around donor and acceptor indicate where the rate enhancement goes off the colour scale, the limits of which have been chosen to demonstrate the oscillations the mediator induces.

the donor and acceptor go off the colour scale, which has been chosen so that we are able to see the oscillatory behaviour produced by the presence of the mediator.

### 5.4 Summary and Conclusion

In this chapter, we have used canonical transformations to calculate a general formula (5.52) which can be used to find the rate of energy transfer between three bodies in any arbitrary reciprocal environment. We could have obtained this using standard perturbation theory, but the use of canonical perturbation theory beyond second order reduced the number of time orderings we were required to consider, decreasing the complexity of the calculation. We then applied this formula to simple situations for which the Green's tensor is analytically known, namely three bodies in free space and near an external semi-infinite reciprocal half-space. However, the key point is that the formula could be applied to any environment for which the Green's tensor is known either analytically or numerically.

The work presented in this chapter presents possible applications in several areas. For example, our calculated formula for the rate of energy transfer between three bodies (5.52) can be thought of as a minimal model of a RET in a more complex environment, and as such could be used as a starting point for investigations of this sort. More specifically, the

mediated RET discussed in this chapter may play a part in long-range energy transfer within photosynthetic complexes, so this work could be useful in exploring this area further.

Furthermore, our work could indicate a potential way to observe retardation in RET. Ordinarily the energy transfer rate at retarded distances is extremely small compared to the corresponding (observable) rates at smaller distances [93], but adding a distant mediator to a non-retarded, surface enhanced reaction could be a way of increasing the rate of interaction, overcoming the complication of low rates and allowing the observation of the role of retardation in RET.

It is also interesting to note that the form of the rate equation found, (5.52), is exactly as one would anticipate from intuition about transition dipole moments and the Green's tensor. As indicated in Casimir and Polder's 1948 paper on interatomic potentials [94], this could likewise point towards a simpler way to obtain fully quantum formulae of this nature. This would be the start of a powerful method to carry out more complex many-body calculations.

# CHAPTER 6

## **Controlling Intermolecular Coupling**

In this chapter, we explore how a macroscopic environment can be used to manipulate intermolecular coupling in a system. In particular, we investigate how this can be applied to enhance the superabsorbing properties of a nanostructured synthetic light-harvesting system. We begin with an overview of the fundamental concepts utilized in such a system, before turning our attention to a specific setup consisting of a ring of optical dipoles. In such a setup, inspired by photosynthetic systems, a superabsorbing state can be reached and sustained by effective structure of energy levels which induces the required interplay between optical and vibrational environments.

We define a "guide-slide" superabsorber to be a collection of optical dipoles with: 1) a ladder of excitation manifolds that each has rapid relaxation to a well-defined lowest-energy state, 2) collectively enhanced optical rates coupling the lowest-energy states of adjacent manifolds. In previous work [46], it has been found that a ring of dipoles can meet the above conditions if the sign of the coupling relative to free space is changed. This can be achieved by a suitable skewing of the dipole moment orientations, at the cost of reduced collective dipole moment (hindering superabsorption), as well as the need for ad-hoc re-initialization and placement of the structure in a photonic band gap. In this chapter, we explore how the so-called guideslide effect can also be achieved by careful engineering of dipole-dipole coupling within the ring through the addition of a macroscopic dielectric environment.

To firstly illustrate the manipulation of dipolar interactions, we present a simple demonstra-

tion of coupling control in a system that we can describe analytically, namely two bodies near a dielectric half-space. As a proof-of-principle, we show how the characteristics of the half-space and the dipole positions can be chosen to change the sign of the coupling. Next, we apply these principles to the ring system by demonstrating how the placement of a dielectric sphere inside the dipole ring can induce the "guide-slide" effect. The characteristics required of the sphere to produce the necessary effect are then explored. Finally, we give an overview of the methods and results of A. Burgess et al. in our publication [3], in which an open quantum systems approach is used to model our presented ring system as a quantum heat engine.

### 6.1 Superabsorption in Light Harvesting

We begin this section with an overview of the process of photosynthesis and how its concepts can be harnessed in the creation of artificial light harvesting systems. The fundamentals of superabsorption are then given, before exploring how this phenomenon can be applied to improve photon capture in photosynthetic nanostructures. Finally, we take inspiration from naturally occurring light-harvesting structures to present a simple nanosystem made up of a ring of dipoles, on which the rest of the chapter will focus.

#### 6.1.1 Photosynthesis and Light Harvesters

In humanity's quest to more effectively utilise solar energy to fit our growing demand, an obvious area of study is the way that nature is able to efficiently capture the sun's energy during photosynthesis [52, 95]. Understanding the mechanisms involved in photosynthesis could be key to improving synthetic light-harvesting for use in the production of solar energy [96, 97].

The photosynthesis process begins with energy from sunlight being captured by light-harvesting complexes made up of chromophores<sup>1</sup>. The energy is stored in the electronic excited states of the chromophores, before being transferred within and among the light-harvesting networks until it reaches a reaction centre [96]. The energy transfer process that makes this possible is RET (resonant energy transfer), which has been the main focus of this thesis. It has been found that the energy is directed by means of an energy gradient, whereby the excitation moves towards the acceptor chromophore whose absorbance has the most overlap with the donor's fluorescence [96]. This results in a small energy loss with each downhill energy transfer that takes place.

 $<sup>^1\</sup>mathrm{Choromophores}$  are molecules or sections of larger compounds that absorb a particular wavelength of light.

Two possible routes to enhancing the efficiency of artificial photosynthesis are to improve the effective capture of photons, or to improve the transfer of the excitation energy. In this chapter, we focus on the former.

A fundamental limit on the efficiency of solar cells was found to be due to electron-hole pairs being prematurely lost due to radiative recombination [98]. Consequentially, significant research has been done into preventing this recombination as a means to improving light-harvesting efficiency [55, 99–101]. However, an alternative method for improving the efficiency is to create and sustain what is known as a superabsorbing state within the lightharvesting system [47]. The next two subsections discuss the fundamentals of superabsorption and how this phenomenon could be utilized in light-harvesting systems.

#### 6.1.2 Fundamentals of Superabsorption

Superabsorption can be considered as the time-reversal of superradiance, a process first introduced by Dicke in 1954 [102]. In superradiance, an ensemble of N atoms are correlated in such a way that the power of the field spontaneously radiated by them is proportional to  $N^2$ , rather than being linearly proportional to N as it would be for an ensemble of uncorrelated atoms. These correlations arise when individual atoms align their dipoles in a given direction, creating a collective dipole [103].

To investigate this, we assume that the atoms are confined to a volume that is small in comparison to the transition wavelength  $\lambda$ , and that they are therefore coupled to the same electric field. In other words, the emission or absorption of a photon with wavelength  $\lambda$  cannot be attributed to a single specific atom in the system, and therefore the system coherently radiates. An ensemble of atoms modelled as two-level systems which can be in the ground state,  $|g\rangle$ , or an excited state,  $|e\rangle$ , can be described by the Dicke Model [102]. In this model, each atom is mapped to a spin 1/2 particle, where the  $|g\rangle$  and  $|e\rangle$  states are the spin down and up states, respectively. We can therefore describe the system using the language of angular momentum.

The atoms transition between their ground and excited states via raising and lowering operators that are analogous to the Pauli spin matrices [103],

$$\hat{\sigma}_i^+ = |e_i\rangle \langle g_i| , \qquad (6.1a)$$

$$\hat{\sigma}_i^- = |g_i\rangle \langle e_i| , \qquad (6.1b)$$

$$\hat{\sigma}_{i}^{z} = \frac{1}{2} \left( \left| e_{i} \right\rangle \left\langle e_{i} \right| - \left| g_{i} \right\rangle \left\langle g_{i} \right| \right).$$
(6.1c)

The electric dipole operator of the *i*th atom can then be defined by use of these operators

as,

$$\hat{\boldsymbol{d}}_i = \boldsymbol{d}_i \left( \hat{\sigma}_i^+ + \hat{\sigma}_i^- \right).$$
(6.2)

The states of a collective system are described by N + 1 "Dicke states",  $|J; M\rangle$ , which are defined by two quantum numbers; J = N/2 and  $M \in \{-J, -J + 1, ..., J - 1, J\}$ . In this representation, J + M is the number of excited atoms and J - M is the number of ground state atoms. We introduce the collective raising and lowering operators,

$$\hat{J}_{\pm} = \sum_{i=1}^{N} \hat{\sigma}_{i}^{\pm},$$
 (6.3)

which can be used to retrieve the number of atoms in the excited and ground states via,

$$\langle J; M | \hat{J}_{+} \hat{J}_{-} | J; M \rangle = J + M,$$
 (6.4)

$$\langle J; M | \hat{J}_{-} \hat{J}_{+} | J; M \rangle = J - M.$$
 (6.5)

An arbitrary Dicke state can be reached by repeated application of the lowering operator  $\hat{J}_{-}$ on the fully excited state,

$$|J;M\rangle = \sqrt{\frac{(J+M)!}{N!(J-M)!}} \cdot \hat{J}_{-}^{J-M} |e,e,...,e\rangle.$$
(6.6)

We can also define the collective operators,

$$\hat{J}_{z} = \sum_{i=1}^{N} \hat{\sigma}_{i}^{3}, \tag{6.7}$$

$$\hat{J}^2 = \frac{1}{2} \left( \hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+ \right) + \hat{J}_3^2, \tag{6.8}$$

of which  $|J, M\rangle$  are eigenstates with eigenvalues M and J(J+1),

$$\hat{J}_z |J, M\rangle = M |J, M\rangle, \qquad (6.9)$$

$$\hat{J}^2 |J, M\rangle = J(J+1) |J, M\rangle.$$
 (6.10)

Using this formalism, a collection of N non-interacting atoms can be treated as a single system with N + 1 equidistant levels, rather than N individual two-level systems. The atomic evolution is then a cascade of decays down a ladder of N + 1 equidistant levels, as shown in figure 6.1.

Since the emission of a photon cannot be attributed to a specific atom in the system, the



Figure 6.1: Figure inspired by Ref. [103] showing the ladder of N+1 symmetrical states. During superradiance, the system cascades from the fully excited state  $|J, M = J\rangle \equiv |e, e, e, ...e\rangle$  down to the ground state  $|J, M = -J\rangle \equiv |g, g, g, ...g\rangle$ .

transition from the fully excited state to the one immediately below in the ladder can be due to the de-excitation of any atom in the ensemble. However, in subsequent decay steps, the number of pathways increases since there are more combinations of possible relaxations leading to the same state, resulting in a maximum transition enhancement at the centre of the ladder at M = 0. In following decays from there the transition enhancement decreases, since there are fewer excited atoms and therefore fewer possible decay pathways. This results in the short radiation burst at the ladder midpoint characteristic of a superradiant system.

Up to this point, we have only considered symmetrical superradiant states, where the ensemble of atoms are non-interacting and the Dicke ladder states are equidistant. The presence of interatomic interactions results in a "chirped" ladder states profile, breaking the degeneracy and meaning that each transition has a unique frequency [47]. The levels with the same number of excitations (i.e. the same quantum number M) are said to be in the same manifold. Optical processes allow transitions between the manifolds, and the ladder states are the levels linked by collectively enhanced optical transitions. As we will see in the next subsection, the positions of the ladder states within the manifolds has important consequences for the suitability of the system for superabsorption.

#### 6.1.3 Superabsorption in Nanostructures

Our aim is to investigate the feasibility of creating and sustaining a superabsorbing (rather than superradiant) state in a condensed-matter nanostructured synthetic light-harvesting system.

Due to the time-reversal symmetry of quantum mechanics, we would expect superradiating systems to also have enhanced absorption rates. However, superabsorption is generally not present in natural systems, since emission tends to dominate over absorption for a given transition, even in an intense light field [47]. Furthermore, natural superradiant systems do not remain in a state near the middle of the Dicke ladder long enough for superabsorption to take place, instead moving down the states ladder to the bottom-most rung [47].

One method for artificially achieving superasborption is using the phase between the atoms and photon field to time-reverse the superradiance process [104]. Another, and the one upon which we will be focussed, is by manipulating the interatomic interactions of a system to suppress the emission process and extend the time that the system is in a superabsorbing state [46, 47, 105]. As we saw in the previous subsection, the introduction of interatomic interactions in an ensemble system results in each transition having a unique frequency. This allows the system to be trapped in an effective two-level system around the M = 0 transition, as the middle of the Dicke ladder is where transitions are most strongly collectively enhanced.

To investigate the way superabsorption could be made use of in an artificial light-harvesting system, it is useful to model a simplified natural light-harvesting complex. There are two common types of light-harvesting complexes, named LH-I (or B875) and LH-II (or B800-850) [106]. The LH-I complexes surround the reaction centre, and the LH-I are in turn surrounded by the LH-II complexes [107]. Augmenting the reaction centre with light-harvesting antenna in this way increases the cross-section for light absorption [96], with the number of LH-II complexes present depending on the growth conditions of the plant (e.g. light intensity, temperature) [108].

A common element shared by different LH complexes in nature is a ring-shaped functional group made up of heterodimers<sup>2</sup> [109]. A generic model that is very similar to LH-I consists of a central "acceptor", representing the reaction centre, surrounded by a ring of coupled "donors", which represent the chromophores [110]. These donors can be modelled as two-level systems, since many naturally occurring light-harvesting complexes contain no more that one excitation at any one time [111]. Therefore, a suitable toy model to represent a simple light-harvesting system is an ensemble of two-level dipoles arranged in a ring. In natural photosynthetic systems, the dipole moments in the ring are tangentially aligned [112], but collective effects can be enhanced if the dipole moments are instead aligned in parallel [46].

In the rest of this chapter, we will be considering the possibility of creating and sustaining a superabsorbing state in condensed-matter ring-shaped nanostructures. Since we are looking at a molecular system, vibrational relaxation should be considered [113] due to additional vibrational degrees of freedom not present for atoms. This involves phonons creating

<sup>&</sup>lt;sup>2</sup>A heterodimer is a protein complex composed of two different subunits.

transitions within the energy manifolds in the downward direction [46].

When the collectively enhanced states (discussed in the previous subsection) are at the top of their respective manifolds, this vibrational relaxation results in a pull away from the ladder states, ruining the system's suitability for superabsorption. On the other hand, if the ladder states are at the bottom of the manifolds, the relaxation works to stabilize the superabsorbing states. Therefore, we ideally want the ladder states to be at the bottom of their respective excitation manifolds, as this way the vibrational relaxation will guide the system towards the ladder states rather than pull away from them [46]. This is the reasoning behind the defining conditions of a "guide-slide" superabsorber given at the beginning of this chapter.

## 6.2 Ring System

In this section, we model the system of an arbitrary number of dipoles arranged in a ring, and work out the connections between ring eigenstates by optical processes. The ladder states are identified as the strongest optical transitions between adjacent manifolds. As discussed in the previous section, phonon processes will guide the system to the eigenstates at the bottom of the manifolds, so having the ladder states at the bottom of their respective manifolds will aid in achieving superabsorption. We show in this section how tilting the dipoles in the ring is one way to achieve this, following Ref. [46].

#### 6.2.1 Setup of Ring System

A system of N dipoles positioned in a ring can be modelled via the following Hamiltonian,

$$\hat{H}_{\text{ring}} = \omega_0 \sum_{i=0}^{N} \hat{\sigma}_i^z + \sum_{i,j=1}^{N} J_{i,j} (\hat{\sigma}_i^+ \hat{\sigma}_j^- + \hat{\sigma}_i^- \hat{\sigma}_j^+), \qquad (6.11)$$

where the usual definition of site-defined Pauli operators given in (6.1) have been used. The first term describes the self-interactions of the dipoles and the second term describes the interactions between the dipoles.

The eigenstates of the ring system are defined by  $\hat{H}_{\text{ring}} |\psi_{k,\text{ring}}\rangle = E_{k,\text{ring}} |\psi_{k,\text{ring}}\rangle$ , where k = 1, 2, ..., N. This, combined with the degeneracies, reveals the  $N^2$  energy levels of the system, with energies defined by  $E_{k,\text{ring}}$ . These energy levels are evenly spaced if there are no intermolecular interactions, but coupling perturbs the energy levels and lifts the degeneracy of the ladder rung spacings, as shown in figure 6.2. These energy levels are organised in manifolds corresponding to the number of excitations in the system. There are  $2^N$  manifolds in a system made up of N dipoles. For an uncoupled system, all of the levels in a manifold



Figure 6.2: Plot of the energy eigenstates of a four-dipole ring system against the nearest neighbour coupling strength, showing the perturbation of the energy levels due to the introduction of intermolecular coupling. For this plot, the energy states are normalized to the transition frequency,  $\omega_0$ , and the coupling of the dipoles across the ring is set to one third of the nearest neighbour coupling. The colours represent the groupings of the five energy manifolds.

will have the same energy.

The inter-dipole coupling is introduced via the interaction matrix  $J_{i,j}$  between two dipoles  $d_i$ and  $d_j$  of transition frequency  $\omega_0$  and at positions  $r_i$  and  $r_j$ . Due to the rotational symmetry of the system, it is sufficient to calculate the interactions between a single dipole and each of the others, and then re-use this for the other dipoles in the ring. In macroscopic QED (introduced in chapter 2), the strength of coupling between dipoles at sites *i* and *j* is given by [114, 115],

$$J_{i,j} = -\mu_0 \omega_0^2 \, \boldsymbol{d}_i^{\uparrow} \cdot \operatorname{Re}\left[\boldsymbol{G}(\boldsymbol{r}_i, \boldsymbol{r}_j, \omega_0)\right] \cdot \boldsymbol{d}_j^{\downarrow},\tag{6.12}$$

where  $\omega_0$  is the transition frequency of the dipole. We note that by splitting up the real and imaginary parts of the Green's tensor, the matrix element we calculated previously (3.67) can be decomposed into the interaction strength, (6.12), and the associated decay rate,  $\gamma_{i,j} = -\mu_0 \omega_0^2 \boldsymbol{d}_i^{\uparrow} \cdot \text{Im} \left[ \boldsymbol{G}(\boldsymbol{r}_i, \boldsymbol{r}_j, \omega_0) \right] \cdot \boldsymbol{d}_j^{\downarrow}.$ 

The Hamiltonian that governs how the eigenstates of the ring system are connected by optical processes is [47],

$$\hat{H}_{I,\text{opt}} = \sum_{i=0}^{N} \boldsymbol{d}_{i} \hat{\sigma}_{i}^{x} \otimes \sum_{k} f_{k} (\hat{a}_{k} + \hat{a}_{k}^{\dagger}), \qquad (6.13)$$

where  $\hat{a}_k^{(\dagger)}$  is the annihilation (creation) operator for optical mode k, and  $f_k$  is the coupling strength of this photon mode to the dipole  $d_i$ . We can transform the optical Hamiltonian into the eigenbasis of the ring Hamiltonian by first identifying the matrix R that diagonalizes



Figure 6.3: (a) Diagram of four dipoles in a ring with radius  $R_{\text{ring}}$  in the *xy*-plane. (b) Representation of the angles used to defined the dipole moment orientations, namely the equatorial angle  $\theta_{eq}$  and the zenith angle  $\theta_{zen}$ . Adapted from [46] under the terms of the Creative Commons Attribution 4.0 International license.

 $\hat{H}_{\text{ring}}$  via  $R^{-1}\hat{H}_{\text{ring}}R$ , and then performing the same transformation on  $\hat{H}_{I,\text{opt}}$ . We can write this as,

$$R^{-1}\hat{H}_{I,\text{opt}}R \equiv \hat{\tilde{H}}_{I,\text{opt}},\tag{6.14}$$

where we have defined the transformed optical Hamiltonian as  $\hat{H}_{I,\text{opt}}$ .

By considering  $\langle \psi_{l,\text{ring}} | \tilde{H}_{I,\text{opt}} | \psi_{k,\text{ring}} \rangle$ , we can reveal the allowed optical interactions between the *k*th and *l*th ring eigenstates and how likely the transitions are to take place, with a higher transition weight corresponding to a higher transition probability. The ladder states are identified as the most probable transitions between each adjacent manifold, and these are the states that are linked by collectively enhanced optical transitions. As discussed in the previous subsection, we require the ladder states to lie at the bottom at their respective manifolds to aid the superabsorption process.

In the next subsection, we demonstrate that for a ring of dipoles, the dipole moments all being oriented perpendicular to the plane of the ring ("parallel" setup) does not induce the required level scheme. However, tilting the dipoles as in Ref. [46] ("tilted" setup) achieves the desired effect.

#### 6.2.2 Parallel and Tilted Setup Comparison

We place N dipoles in a ring in the xy-plane centred at the origin with radius  $R_{\text{ring}}$ , so that the *i*th dipole has position  $\mathbf{r}_i$  and dipole moment  $\mathbf{d}_i$ . The first dipole is placed on the y axis, with Cartesian coordinates  $\mathbf{r}_0 = (0, R_{\text{ring}}, 0)$ , and the remaining N - 1 dipoles are placed in





Figure 6.4: Energy eigenstates of a ring of four dipoles, normalised to the transition frequency  $\omega_0$ , comparing the (a) parallel setup to (b) tilted setup presented in Ref. [46]. The nearest neighbour intermolecular distance is set to  $r_{NN} = 2.5$ nm and the ring radius is found from equation (6.16). The red levels identify the ladder states, and the vertical dashed lines separate the different excitation manifolds.

a ring around the origin on the xy-plane with the origin at the centre. If we label the angle anti-clockwise from the y-axis in the xy-plane as  $\varphi$ , then the positions of the dipoles can be expressed as  $\mathbf{r}_i = (R_{\text{ring}} \sin \varphi_i, R_{\text{ring}} \cos \varphi_i, 0)$  where  $\varphi_i = 2\pi i/N$  with i = 1, 2, ..., N - 1. The case of N = 4 is shown in figure 6.3a.

The orientations of the dipole moments are defined according to figure 6.3b, so that the dipole moment at site i is given as,

$$\boldsymbol{d}_{i} = |\boldsymbol{d}|(\sin(\varphi_{i} + \theta_{\text{eq}})\cos\theta_{\text{zen}}, \cos(\varphi_{i} + \theta_{\text{eq}})\cos\theta_{\text{zen}}, \sin\theta_{\text{zen}}), \quad (6.15)$$

where  $|\boldsymbol{d}|$  is the dipole strength. For the parallel setup, the equatorial angle  $\theta_{eq}$ , and zenith angle  $\theta_{zen}$ , are both chosen to be  $\pi/2$ . This results in the dipole moments all being aligned in the z direction, so the dipole moment at site i is  $\boldsymbol{d}_i = |\boldsymbol{d}|(0,0,1)$ . In Ref. [46] however, the tilted setup is achieved by choosing  $\theta_{eq} = \pi/2$  and  $\theta_{zen} = \pi/4$ .

The resulting level schemes for an example system of a ring of four dipoles are given in figure 6.4. We can see that for the parallel setup, the ladder states are positioned at the top of each manifold, but the tilted setup results in the ladder states being at the bottom of the manifolds instead. As discussed in section 6.1, having the ladder states at the bottom of their respective manifolds allows superabsorption to be achieved.

If we are to replicate this level scheme using a different method, we need to know what characteristic of the system creates this effect. We know that the dipole moments determine the intermolecular coupling via equation (6.12), so we next examine how the different dipole moment orientation schemes discussed in this section impact the intermolecular couplings in



(a) Parallel setup with  $\theta_{eq} = \theta_{zen} = \pi/2$ . (b) Tilted setup with  $\theta_{eq} = \pi/2$  and  $\theta_{zen} = \pi/4$ .

Figure 6.5: Coupling strengths between an arbitrary anchor dipole and another dipole at positions around the ring for different numbers of dipoles, N. The nearest neighbour intermolecular distance is set to  $r_{NN} = 2.5$ nm and the ring radius increases with N according to equation (6.16). The points on the plots highlight the positions of the N dipoles in the different rings.

the ring. To this end, we investigate how the intermolecular coupling between two dipoles is affected by their respective positions in the ring.

We are not only interested in the case of four dipoles making up the ring, and also need to consider how the system is affected when the ring is made up of different numbers of bodies. For our investigations, we will fix the intermolecular distance,  $r_{NN}$ , and allow the radius of the ring to increase with the number of dipoles according to,

$$R_{\rm ring} = \frac{r_{NN}}{2\sin\left(\pi/N\right)}.\tag{6.16}$$

Considering the two dipole moment orientation setups separately, figure 6.5 shows how the value of the intermolecular coupling,  $J_{ij}$ , would change between one dipole at a fixed position and a second dipole at different positions around the ring, with comparisons for different values of N. The clear distinction between the different dipole moment orientations setup is that when the moments are all parallel, the intermolecular couplings are positive, but skewing the dipoles in this way generates negative intermolecular couplings instead. This is a good indication that in order to ensure the required level scheme, we should aim to create a negative intermolecular coupling in our system.

In the next section, we demonstrate how a macroscopic body can be used to generate a negative intermolecular coupling between two dipoles. We consider a simple system that can be described analytically as a proof-of-principle, namely two bodies near a semi-infinite half-space, and investigate how the properties of the system can be chosen to manipulate the

intermolecular coupling in the required way.

### 6.3 Demonstration of Coupling Control

In the previous section we saw that tilting the dipoles moments in the ring in the correct way results in the ladder scheme we are looking for. However, this method means that the dipole structure is no longer perfectly aligned, which decreases the superabsorption effects of the system. We aim to create the same ladder scheme while allowing the dipole moments to remain perfectly aligned with the use of a macroscopic dielectric body.

In order to demonstrate how a macroscopic environment can, in theory, be manipulated to achieve a desired intermolecular coupling, we consider a system made up of two bodies near a semi-infinite half-space (the same system studied in sections 3.3.2 and 4.2). To ensure an analytic description, we concentrate on two simple dipole arrangements, "colinear" and "parallel" shown in figure 4.1, and we will be concentrating on the non-retarded regime, where the dipoles are close enough to each other and the half-space to ignore relativistic effects. As a proof-of-principle, we will demonstrate how the characteristics of the half-space can be chosen to achieve a negative intermolecular coupling.

In particular, we note that the nearest neighbour inter-dipole interactions in a system of a sphere surrounded by a ring of dipoles could be approximated as two dipoles in parallel placement with a semi-infinite half-space. Therefore, demonstrating the ability to ensure a negative coupling in this toy system is a good indication that the same is possible in the more complex system of a ring of N dipoles surrounding a sphere.

From the expression for the coupling strength given by (6.12), we can see that achieving a negative coupling is equivalent to choosing a Green's tensor that results in,

$$\operatorname{Re}\left[\boldsymbol{G}_{\operatorname{NR}_{mn}}^{\operatorname{HS}}(\boldsymbol{r},\boldsymbol{r}',\omega)\right] > 0, \qquad (6.17)$$

for the relevant component, where the component is dependent on the orientation of the dipole moments. The characteristics of the system that we can control are; (1) the positions of the dipoles in relation to the half-space and each other, (2) the orientations of the dipole moments, and (3) the material that the half-space is made up of. For each orientation combination, we can determine the constraints on the material's permittivity in terms of the dipoles' positions that must be met to achieve a negative coupling.

#### 6.3.1 Colinear Arrangement

For completeness, we first consider two dipoles positioned in a colinear arrangement with a semi-infinite half-space (see figure 4.1b). The non-retarded Green's tensor for a half-space in a vacuum for colinearly placed dipoles is given by (B.39) and again below,

$$\boldsymbol{G}_{\mathrm{NR}}^{\mathrm{HS,C}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{c^2}{4\pi\omega^2} \begin{bmatrix} 1 & -1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2 \end{bmatrix} + \frac{r_p^{\mathrm{NR}}}{\bar{Z}^3} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 2 \end{bmatrix} \end{bmatrix}, \quad (6.18)$$

where  $Z \equiv z - z'$  and  $r_p^{\text{NR}} \equiv \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1}$ . By setting the condition that  $\text{Re}\left[\boldsymbol{G}_{\text{NR}_{mn}}^{\text{HS,C}}(\boldsymbol{r}, \boldsymbol{r}', \omega)\right] > 0$  for dipole moment orientations  $\{m, n\}$ , we find that we get a negative coupling if the permittivity obeys,

$$\{z, z\}: \quad \epsilon > \frac{1 - (\bar{z}/z)^3}{1 + (\bar{z}/z)^3} \qquad \qquad = \frac{(b+1)^3 + (b-1)^3}{(b+1)^3 - (b-1)^3} \tag{6.19b}$$

where we have defined  $z'/z \equiv b$ .

Figure 6.6a shows the permittivity and position combinations that result in a positive Green's tensor component for the different dipole moment orientations. We note that not every permittivity-position combination considered will achieve the desired effect. There is a small region when the dipoles are very close together and the permittivity is between 0 and -1 where the effect cannot be achieved, no matter which dipole moment orientations are chosen.

#### 6.3.2 Parallel Arrangement

The parallel arrangement shown in figure 4.1a is of particular interest as it can be considered as a simplified toy model of the nearest neighbour interactions of a ring of dipoles around a sphere. In this arrangement, the non-retarded effective Green's tensor, which includes both the vacuum background and the half-space, is given in (B.33) and again below,

$$\boldsymbol{G}_{\mathrm{NR}}^{\mathrm{HS,P}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{c^2}{4\pi\omega^2} \begin{bmatrix} \frac{1}{X^3} \begin{pmatrix} 2 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1 \end{pmatrix} + \frac{r_p^{\mathrm{NR}}}{R_+^5} \begin{pmatrix} R_+^2 - 3X^2 & 0 & 6zX\\ 0 & R_+^2 & 0\\ -6zX & 0 & 2R_+^2 - 3X^2 \end{pmatrix} \end{bmatrix},$$
(6.20)



Figure 6.6: Plot of the positions of two dipoles against the permittivity of a semi-infinite half-space positioned at z < 0. Shaded regions indicate combinations of parameters that result in Re  $[\mathbf{G}_{\text{NR}_{mn}}^{\text{HS}}(\mathbf{r}, \mathbf{r}', \omega)] > 0$  for the selected dipole moment orientations  $\{m, n\}$ , which are indicated by colour. We have limited our investigation to the non-retarded regime, which is only valid for the position range plotted here.

where  $X \equiv x - x'$ ,  $R_{+}^{2} \equiv 4Z^{2} + X^{2}$  and  $r_{p}^{\text{NR}} \equiv \frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}$ . By setting the condition that  $\operatorname{Re}\left[\boldsymbol{G}_{\operatorname{NR}_{mn}}^{\operatorname{HS},\operatorname{P}}(\boldsymbol{r},\boldsymbol{r}',\omega)\right] > 0$  for dipole moment orientations  $\{m,n\}$ , we find that we get a negative coupling if the permittivity obeys,

$$\{x,x\}: \quad \epsilon > \frac{(R_+^2 - 3X^2)X^3 - 2R_+^5}{(R_+^2 - 3X^2)X^3 + 2R_+^5} \qquad \qquad = \frac{2a^2 - 1 - (4a^2 + 1)^{5/2}}{2a^2 - 1 + (4a^2 + 1)^{5/2}}, \tag{6.21a}$$

$$\{y, y\}: \quad \epsilon > \frac{X^3 + R_+^3}{X^3 - R_+^3} \qquad \qquad = \frac{1 + (4a^2 + 1)^{3/2}}{1 - (4a^2 + 1)^{3/2}}, \tag{6.21b}$$

$$\{z, z\}: \quad \epsilon > \frac{(2R_+^2 - 3X^2)X^3 + 2R_+^5}{(2R_+^2 - 3X^2)X^3 - 2R_+^5} \qquad \qquad = \frac{8a^2 - 1 + 2(4a^2 + 1)^{5/2}}{8a^2 - 1 - 2(4a^2 + 1)^{5/2}}, \tag{6.21c}$$

$$\{x, z\}: |\epsilon| > 1, \qquad \{z, x\}: |\epsilon| < 1, \qquad (6.21d)$$

where we have defined  $X/Z \equiv a$ .

Figure 6.6b shows the position and permittivity combinations that achieve the desired effect for the different orientation combinations. We can see that if suitable dipole moment orientations are chosen, any of the permittivity and position combinations considered could be used to achieve a negative coupling. It is interesting to note from (6.21d) that if one of the dipole moments is aligned in the x direction and the other in the z direction, a suitable permittivity can be chosen without needing to consider the positions of the dipoles. In particular, we note that the case where the dipole moments are oriented perpendicular to the plane on which they are positioned corresponds to the ring of parallel oriented dipole moments discussed in the previous section. For the setup considered here where the dipoles are positioned in the xz-plane, this corresponds to both dipole moments being oriented in the y direction. From figure 6.6b we can see that for the half-space to produce the desired effect, its permittivity must be lower than -1. Furthermore, we see that a smaller intermolecular distance compared to distance to the surface is preferred. This is a good indication that by manipulating the system of a sphere in a ring of dipoles in a similar way, we can also achieve a negative coupling. This is explored in the next section.

### 6.4 Parallel Spherical System

In this section, we investigate achieving the desired ladder state configuration in a ring of parallel dipole moments by placing a dielectric spherical body in the centre (see figure 6.7a). Keeping the dipole moments perfectly aligned in this way maximizes the potential for superabsorbing effects in the system.

We can see from the previous section that it is possible in principle to create a negative coupling between two dipoles by controlling the positions of the dipoles and the properties of its environment. This was demonstrated using the simple environment of a semi-infinite half-space. In this section, we apply the same principles to a spherical dielectric environment inside a ring of dipoles, which is too complicated to describe analytically.

#### 6.4.1 Setup of Sphere inside Ring

We set up a system of N dipoles in a ring arrangement in the xz-plane around a sphere of radius R with its centre coinciding with the origin of the coordinate system. A schematic of this system is shown in 6.7a and a diagram of the N = 4 case is given in figure 6.7c. The dipole moments will all be oriented in the y direction.

It is useful to consider the system in spherical coordinates  $(r, \theta, \phi)$  (see figure 6.7b), in which the positions of the dipole at site *i* can be written as,

$$\boldsymbol{r}_{i} = (r_{i}, \theta_{i}, \phi_{i}) = \begin{cases} \left(R, \frac{2\pi i}{N}, 0\right) & \text{for } x \ge 0, \\ \left(R, 2\pi - \frac{2\pi i}{N}, \pi\right) & \text{for } x \le 0. \end{cases}$$
(6.22)

We note here that when x = 0, the value of  $\phi$  can be chosen to be 0 or  $\pi$ .

The coupling matrix is calculated via (6.12). We can pick one dipole and consider its inter-



Figure 6.7: (a) is taken from [3] under the terms of the Creative Commons Attribution 4.0 International license. (b) shows the spherical coordinate system used in this work. (c) is the setup of four dipoles in a ring of radius  $R_{\rm ring}$  in the *xz*-plane positioned around a sphere of radius  $R_{\rm sph}$  (shaded green portion).

action with each of the other N-1 dipoles around the ring to calculate the first row of  $J_{i,j}$ , and then exploit the rotational symmetry of the system to build the rest of the matrix. The effective Green's tensor for a sphere in a vacuum is found by summing the bulk (vacuum) Green's tensor in spherical coordinates given by (B.68), and the scattering Green's tensor for a sphere (B.109).

We also need to express the orientations of the dipole moments in spherical coordinates. As in section 6.2.1, the dipole moments are all oriented in the y direction. To convert this to spherical coordinates, we use the standard unit vector conversions,

$$e_{r} = \sin \theta \cos \phi e_{x} + \sin \theta \sin \phi e_{y} + \cos \theta e_{z},$$

$$e_{\theta} = \cos \theta \cos \phi e_{x} + \cos \theta \sin \phi e_{y} - \sin \theta e_{z},$$

$$e_{\phi} = -\sin \phi e_{x} + \cos \phi e_{y}.$$
(6.23)

For a y orientation,  $\boldsymbol{e}_x = 0 = \boldsymbol{e}_z$  and  $\boldsymbol{e}_y = 1$ , so,

$$\begin{aligned} \boldsymbol{e}_r &= \sin \theta \sin \phi = 0, \\ \boldsymbol{e}_\theta &= \cos \theta \sin \phi = 0, \\ \boldsymbol{e}_\phi &= \begin{cases} 1 & \text{for } x \ge 0, \\ -1 & \text{for } x \le 0, \end{cases} \end{aligned}$$
(6.24)

where we have used  $\sin 0 = \sin \pi = 0$ ,  $\cos 0 = 1$  and  $\cos \pi = -1$ . So we can write the dipole moments in spherical coordinates as  $\mathbf{d}_i = (d_i, \theta_i, \phi_i) = \pm |\mathbf{d}| (0, 0, 1)$ , with the sign depending on the sign of x. As discussed above, due to the rotational symmetry of the system, we only need to calculate the interactions between a single dipole and each of the others. If we choose the interacting dipole to be on the z-axis, then  $\phi$  can be chosen to be 0 or  $\pi$  so that it is always different from the dipole it is interacting with. So in our coordinate system, we can say that for all dipole combinations, the dipole moments used in the calculation of the coupling matrix are  $\mathbf{d}_i = |\mathbf{d}|(0,0,1)$  and  $\mathbf{d}_j = |\mathbf{d}|(0,0,-1)$ .

This means that the coupling matrix for our system is calculated via,

$$J_{i,j}^{\text{ring}} = -\frac{\omega^2 |\boldsymbol{d}|^2}{\epsilon_0 c^2} (0, 0, 1) \cdot \text{Re} \left[ \boldsymbol{G}^{(0)}(\boldsymbol{r}_i, \boldsymbol{r}_j, \omega) + \boldsymbol{G}^{(1)}(\boldsymbol{r}_i, \boldsymbol{r}_j, \omega) \right] \cdot (0, 0, 1),$$
(6.25)

where  $G^{(0)}$  is given by (B.68) and  $G^{(1)}$  by (B.109). Our aim is to find constraints on the sphere parameters (the radius and the permittivity) that will achieve the "guide-slide" effect, as defined at the beginning of this chapter.

#### 6.4.2 Results

A plot showing the combinations of sphere size and permittivity that achieve the required level scheme for a ring of four dipoles is shown in figure 6.8. Interestingly, we can see that the effect can only be achieved by a sphere with a negative permittivity.

As a demonstration of the effectiveness of such a sphere, we consider an example system made up of a ring of dipoles and a sphere with permittivity  $\epsilon = -2.37$ , which is similar to the permittivity of chromium at 1.8eV [3]. As in section 6.2.2, the ring size is allowed to increase with the number of dipoles via (6.16), and the radius of the sphere  $R_{\rm sph}$  is chosen to be one nanometre smaller than the radius of the ring. The resulting intermolecular coupling around such a ring for different number of dipoles is shown in figure 6.9a. We can see that this size and permittivity combination results in a negative intermolecular coupling for all of the dipole numbers considered (3-6). Using the four dipole case as an example, figure



Figure 6.8: Plot of permitivity and radius (normalised to the ring radius) of a sphere inside a ring of four dipoles set up in the same way as in figure 6.4a. Combinations of parameters that result in the required level scheme for the guide-slide effect are indicated by red points.

6.9b shows that the ladder states are indeed at the bottom of their respective manifolds as required, demonstrating the sphere's effectiveness as a method of aiding in superabsorption in such a ring system.

We now turn our attention to the work carried out by A. Burgess et al. presented in Ref. [3], which uses an open quantum systems approach to model the system presented in this section as an effective quantum heat engine. This allows for the comparison of the power outputs of our presented parallel spherical setup with the tilted setup introduced in [46] (see section 6.2.2).

### 6.5 Application to Solar Cell

In this section, we explain the methods and results of A. Burgess presented in our publication [3]. This work characterizes the superabsorbing parallel spherical system presented in the previous section by calculating its power output and how it scales with the number of dipoles in the ring. In this work, an open quantum systems approach is used to model the system as an effective quantum heat engine, demonstrating the system's suitability for use as a solar cell.



(a) Coupling strengths between an arbitrary anchor dipole and another dipole at positions around the ring for N dipoles.

(b) Energy eigenstates of a ring of four dipoles, normalised to the transition frequency  $\omega_0$ . Red levels indicate ladder states.

Figure 6.9: (a) Coupling plot for varying N and (b) level scheme for N = 4 for a ring of dipoles with parallel oriented moments surrounding a sphere with radius  $R_{\rm sph} = (R_{\rm ring} - 1)$ nm and permittivity  $\epsilon = -2.37$ . The other parameters are the same as for figures 6.5 and 6.4, respectively.

#### 6.5.1 Calculating the Power Output

To model the vibrational relaxation present in typical nano-structures, N vibrational baths are introduced that are coupled to each of the dipoles via the Hamiltonian term,

$$H_{I,\text{vib}} = \sum_{i=1}^{N} \sigma_z^{(i)} \sum_{v} g_{i,v} (b_{i,v} + b_{i,v}^{\dagger}), \qquad (6.26)$$

where  $g_{i,v}$  and  $b_{i,v}^{(\dagger)}$  are the coupling strength and the annihilation (creation) operator of the phonon mode v of the *i*th dipole's vibrational bath, respectively.

The open quantum dynamics of the system are modelled using a weak-coupling Born-Markov approximation, allowing the calculation of the Bloch-Redfield equations [116]. This model assumes second-order perturbation theory is used for the bath-system coupling and that vibrational relaxation happens on a timescale so much faster than the other system dynamics that the bath correlations can be modelled as delta functions. The Bloch-Redfield equations then lead to a master equation of the form [3],

$$\frac{d}{dt}\rho_{\rm ring} = -i \left[ H_{\rm ring}, \rho_{\rm ring} \right] + \left( \mathcal{D}_{\rm opt} + \mathcal{D}_{\rm vib} + \mathcal{D}_X + \mathcal{D}_t \right) \rho_{\rm ring}, \tag{6.27}$$

where the terms in the brackets are the system dissipators.  $\mathcal{D}_{opt}$  is the optical dissipator, which determines the optical transitions between the excitation number manifolds, and  $\mathcal{D}_{vib}$ is the vibrational dissipator, dictating the vibrational transitions within these manifolds. The final two dissipator terms are added in order to model the extraction of excitons from the ring system, which would then be converted into useful energy, allowing the calculation of the efficiency of the system. This extraction is achieved by means of an extra dipole placed below the centre of the ring, coupled incoherently to the system, which acts as a trap. This is characterised by the extraction dissipator term,

$$\mathcal{D}_X \rho_{\rm ring} = \gamma_X \left( X \rho_{\rm ring} X^{\dagger} - \frac{1}{2} \left\{ X^{\dagger} X, \rho_{\rm ring} \right\} \right), \tag{6.28}$$

where  $\gamma_X$  represents the extraction rate from the ring system to the trap, and the Lindblad operator, X, determines the incoherent transport and is given by,

$$X = \sum_{i=1}^{N} \sigma_{-}^{(i)} \otimes \sigma_{+}^{(t)}.$$
 (6.29)

The final dissipator term describes the decay within the trap, in the form of incoherent transitions from the trap's excited state to its ground state. This decay dissipator term is given by,

$$\mathcal{D}_t \rho_{\rm ring} = \Gamma_t \left( \sigma_-^{(t)} \rho_{\rm ring} \sigma_+^{(t)} - \frac{1}{2} \left\{ \sigma_+^{(t)} \sigma_-^{(t)}, \rho_{\rm ring} \right\} \right), \tag{6.30}$$

where  $\Gamma_t$  is the trap decay rate. Since the temperature of the solar photons is high and the phonons and trap are room temperature, the system can be modelled as an effective quantum heat engine (QHE), from which the power output at the steady state can be calculated, where the steady states are found from (6.27). The power output at the steady state is calculated via,

$$P = IV, (6.31)$$

where the I is the current of the QHE, given by,

$$I = e\Gamma_t \langle \rho_{t,e} \rangle, \tag{6.32}$$

where  $\langle \rho_{t,e} \rangle$  represents the expectation value of the steady state population of the trap's excited state, and V is the potential difference which can be found using,

$$eV = \hbar\omega_t + k_B T_{\rm vib} \ln\left[\frac{\langle \rho_{t,e} \rangle}{\langle \rho_{t,g} \rangle}\right],\tag{6.33}$$

where  $k_B$  is Boltzmann's constant,  $T_{\text{vib}}$  is the temperature of the vibrational baths and  $\langle \rho_{t,g} \rangle$  is the expectation value of the steady state population of the trap's ground state. The power

output P can then be maximised for each ring configuration by choosing  $\Gamma_t$  such that,

$$P_{\max} = \max_{\Gamma_t} \left\{ I\left(\Gamma_t\right) V\left(\Gamma_t\right) \right\}.$$
(6.34)

This method for the calculation of the power output is used by A. Burgess in Ref. [3], the results of which are reviewed in the next section.

#### 6.5.2 Results and Discussion

In this section, the results of A. Burgess from Ref. [3] are presented, which compare the power output of the previously developed tilted ring system [46] with the spherical parallel ring system explored in section 6.4. From these we will see that the spherical system is a more advantageous configuration for a superabsorber than the tilted system.

Figure 6.10 shows the results of numerical simulations carried out by A. Burgess and presented in our paper [3], showing the power output for different numbers of dipoles making up the ring. It is immediately apparent from figure 6.10a that the spherical setup has an enhanced scaling of power with N when compared with the tilted setup. This is quantified in figure 6.10b with a log-log plot showing the exponent, m, for each configuration's power output of the form  $P = \alpha N^m$ . The growth exponent is calculated to be m = 1.55 for the spherical setup compared to m = 1.08 for the tilted setup. The theoretical maximum Dicke scaling of  $N^2$  is also included as well as linear scaling for reference, and it is clear that the scaling of the spherical setup is noticeably enhanced when compared to the tilted. This is because tilting the dipole moments causes destructive interference between the molecules, which limits the superabsorbing effects (see section 6.1.2).

From figure 6.10c it can be seen that for small values of N, the power output per dipole is greater for the tilted setup, and that the spherical system only begins to dominate for N > 4. This because we have set the system up so that the distance between the dipoles and the central sphere is constant, and so the addition of more dipoles changes the size ratio of the sphere in comparison to the ring. Therefore, for small N the relative size of the spherical body is small compared to the size of the ring, which limits the ability to engineer the intermolecular couplings.

Further advantages of the spherical setup arise from the lack of some of the additional processes that were required in the previously presented tilted setup [46] to sustain the superabsorbing state. These include a reinitialisation process and confining the system within a photonic band gap. These are in addition to the dipole moments needing to be symmetrically tilted about the ring to engineer the required dipole-dipole coupling. In contrast, the



Figure 6.10: Figure reproduced from [3] under the terms of the Creative Commons Attribution 4.0 International license. Scaling of power output of the solar cell with number of dipoles for both the parallel spherical setup and the previously developed tilted setup. (a) Power output, (b) log-log plot of power output and (c) power output per dipole for increasing Nare given. Super-linear scaling for both configurations were calculated via  $P = \alpha N^m$  and are plotted in (b). It was found that m = 1.55 for the parallel setup (red solid) and m = 1.05for the tilted setup (blue solid).  $N^2$  (green dashed) and linear scaling (black dashed) are plotted for comparison in (b). Parameters are the same as in figure 6.9, with  $T_{\rm vib} = 300$ K,  $T_{\rm opt} = 5800$ K,  $\gamma_{\rm opt} = \gamma_{\rm X} = 1\mu$ eV and  $\gamma_{\rm vib} = 10^3 \gamma_{\rm opt}$ .

system presented here requires the inclusion of a metallic nanoparticle in the centre of a ring of dipoles. Encouragingly, recent experimental studies that use DNA origami to combine nanoparticle systems with molecular rings provide a promising path to this realisation [117–119].

Furthermore, because of the super-extensive power generation of the presented model, it is predicted that increasing the ring size would result in power outputs greater than the sum of its parts [3]. We note that our method of modelling the inter-dipolar coupling via macroscopic QED is preserved in the limit of large N, and that in fact the approximation that the dipoles are effectively next to a semi-infinite dielectric plane becomes more accurate in this limit.

## 6.6 Summary and Conclusion

In summary, beginning with an overview of photosynthesis, this chapter presented superabsorption as one of the routes to improved synthetic light harvesting, and introduced the idea of a "guide-slide" superabsorber as a set of criteria that can be met by a system of optical dipoles to achieve and sustain superabsorption. A system consisting of a ring of dipoles was then presented, and we demonstrated how tilting the dipole moments as in Ref. [46] can affect the sign of the intermolecular coupling such that the system acts as a "guide-slide" superabsorber.

By considering a simple toy model of two dipoles near a semi-infinite half-space, it was then demonstrated that it is possible to change the sign of the inter-dipole coupling by manipulating the properties of the environment. Applying this principle to the ring system, we showed that a sphere placed inside the ring has the potential to alter the inter-dipole coupling in such a way that the system behaves as a "guide-slide" superabsorber without requiring any tilting of the dipole moments. Finally, we presented work by A. Burgess in our publication [3] in which the way the power output of such a parallel spherical system scales with the number of dipoles was calculated, and found to be preferable to the tilted setup introduced in Ref. [46].

# CHAPTER 7

## Conclusion

The broad goal of this thesis was to study the way that macroscopic environments can influence intermolecular interactions. We first used macroscopic QED to derive a general formula for the rate of two-body RET that can be applied to an arbitrary reciprocal macroscopic background. This was achieved using second order perturbation theory, but we also demonstrated that the use of canonical transformations to reduce the order of perturbation theory required leads to the same result. As a proof-of-principle, we then applied the formula to two bodies in a vacuum by way of the Green's tensor, calculating analytic expressions for the rate of energy transfer between the bodies for the near- and far-field regimes, demonstrating the characteristic  $r^{-6}$  and  $r^{-2}$  distance dependencies, respectively. We then considered the two bodies to be near a semi-infinite half-space, and by employing the colinear arrangement and the near- and far-field limits, calculated analytic formulae for the interaction rate. We found that when the far-field regime is considered, an oscillatory dependence on the intermolecular distance is observed, and a plot in two dimensions demonstrated the non-trivial influence on the rate of even simple environments.

We next extended our consideration to non-reciprocal media, again applying macroscopic QED to reach a general formula for the rate of energy transfer in an arbitrary environment. We then considered two bodies near a non-reciprocal half-space in a parallel or collinear arrangement, and examined under which conditions switching the positions of the donor and acceptor would induce a change in the rate of energy transfer between them. We found that if the dipole moments are randomly oriented, a position swap will not cause a rate change in

either setup, but that if the bodies are in a parallel arrangement, then there are certain dipole moment orientations that will result in a change in the rate of interaction under a position swap. By plotting the dependence of the rate on the molecular positions, we note that the reflective properties of the half-space can be chose to favour energy transfer in one direction over the other. An application of this principle presented in our paper [2] is then discussed, where an optical isolator that maximises unidirectional propagation is created using inverse design. The work presented could be built upon to move towards the creation of an integrated optical isolator, or be used in the improvement of bulk isolators.

We then looked at three-body RET, applying canonical transformations to simplify the calculation and reduce the perturbation theory order required from fourth order to first, before reaching a general rate formula using macroscopic QED. We found that of all the 24 timeorderings considered, only the resonant interaction ended up contributing to the overall rate of energy transfer. The formula was then applied to a situation of experimental interest, where the donor and acceptor are in the near-field regime and the mediator is in the far-field limit. Considering colinear and T-shape arrangements, analytic expressions for the rate of interaction were calculated for three bodies in a vacuum for both arrangements, and for the colinear arrangement near a semi-infinite half-space. A density plot demonstrated the intricate dependence of the rate on the molecular positions in the presence of a simple half-space. This work could be relevant in the study of long-range energy transport in photosynthesis, and could possibly be used to observe retardation in RET.

We finally investigated how a macroscopic environment could engineer the intermolecular coupling in a ring of optical dipoles to induce and sustain a superabsorbing state. We first demonstrated how tilting the dipole moments as in Ref. [46] could produce the desired effect, and found that this was equivalent to changing the sign of the inter-dipolar coupling. A toy system of two bodies near a semi-infinite half-space was then considered to illustrate how in principle the properties of the environment and the positions of the bodies can be used to change the sign of the intermolecular coupling. We then applied this idea to the ring system, by placing a macroscopic sphere inside the ring and exploring the properties that sphere must have to induce the required intermolecular coupling. We noticed that a negative permittivity is necessary (but not sufficient) to produce the desired effect. We then presented the results of A. Burgess et al. in Ref [3], which calculated the power output of our spherical setup and how it scales as the number of dipoles in the ring is increased. When compared with the tilted setup, we found that the scaling of the spherical system is noticeably enhanced, due to the fact that keeping the dipole moments parallel eliminates destructive interference, which reduces the system's superabsorbing potential. We also noted that the spherical setup offers further advantages over the tilted setup, such as not requiring a reinitialisation process or the singular coupling of a trap to a particular state. This highlights this work as an ideal candidate for use in the design of light-harvesting superabsorbers. More generally, the methods of engineering inter-dipolar coupling through design of macroscopic environments could be useful in the design of quantum-enhanced devices.

# APPENDIX A

# Classical Electromagnetism in Fourier Space

In this Appendix, we transform the well-known classical Maxwell equations and constitution relations in a reciprocal medium from the time domain to the frequency domain. The classical Maxwell equations for a electromagnetic field in a reciprocal medium are [58, 68],

$$\boldsymbol{\nabla} \cdot \boldsymbol{B}(t) = 0, \tag{A.1}$$

$$\boldsymbol{\nabla} \cdot \boldsymbol{D}(t) = \boldsymbol{\rho},\tag{A.2}$$

$$\nabla \times \boldsymbol{E}(t) + \frac{\partial \boldsymbol{B}(t)}{\partial t} = 0,$$
 (A.3)

$$\nabla \times \boldsymbol{H}(t) - \frac{\partial \boldsymbol{D}(t)}{\partial t} = \boldsymbol{J},$$
 (A.4)

where E and B represent the electric and magnetic fields, and D and H are the corresponding derived fields, related to E and B via the constitutive relations,

$$\boldsymbol{D}(t) = \epsilon_0 \boldsymbol{E}(t) + \boldsymbol{P}(t), \tag{A.5}$$

$$\boldsymbol{H}(t) = \frac{1}{\mu_0} \boldsymbol{B}(t) - \boldsymbol{M}(t), \qquad (A.6)$$

where P and M are the polarization and magnetization of the medium, respectively. We will only be considering the case where there are no free charges, meaning we can set both the free charge density  $\rho$  and the free current density J to zero. It is useful for us to move from the time domain into the frequency domain. The Fourier transform of an arbitrary function f is defined as,

$$\mathcal{F}\left[f(t)\right] \equiv \tilde{f}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, f(t) e^{i\omega t}.$$
(A.7)

When applied to Maxwell's equations for no free charges, we find (A.1) and (A.2) simply become,

$$\boldsymbol{\nabla} \cdot \boldsymbol{\hat{B}}(\omega) = 0, \tag{A.8}$$

$$\boldsymbol{\nabla} \cdot \tilde{\boldsymbol{D}}(\omega) = 0, \tag{A.9}$$

while (A.3) transforms as,

$$\mathcal{F}\left[\boldsymbol{\nabla} \times \boldsymbol{E}(t) + \frac{\partial \boldsymbol{B}(t)}{\partial t}\right] = \boldsymbol{\nabla} \times \mathcal{F}\left[\boldsymbol{E}(t)\right] + \mathcal{F}\left[\frac{\partial \boldsymbol{B}(t)}{\partial t}\right]$$
$$= \boldsymbol{\nabla} \times \tilde{\boldsymbol{E}}(\omega) + \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, \frac{\partial \boldsymbol{B}(t)}{\partial t} e^{i\omega t} = \boldsymbol{\nabla} \times \tilde{\boldsymbol{E}}(\omega) - \frac{i\omega}{2\pi} \int_{-\infty}^{\infty} dt \, \boldsymbol{B}(t) e^{i\omega t}$$
$$= \boldsymbol{\nabla} \times \tilde{\boldsymbol{E}}(\omega) - i\omega \tilde{\boldsymbol{B}}(\omega) = 0, \qquad (A.10)$$

where in the second line we have integrated by parts. In a similar way, (A.4) becomes,

$$\boldsymbol{\nabla} \times \tilde{\boldsymbol{H}}(\omega) + i\omega \tilde{\boldsymbol{D}}(\omega) = 0. \tag{A.11}$$

The constitutive relations also need to be transformed into the frequency domain, so we need to know how P and M transform. We apply the simplifying assumption that we can describe the bound charges by some equilibrium arrangement which is weakly perturbed by the electromagnetic field, and further assume that the response of these charges are linear and causal. The constitutive relations for reciprocal media in the time domain can be written as [4],

$$\boldsymbol{P}(\boldsymbol{r},t) = \epsilon_0 \int_{-\infty}^{\infty} d\tau \int d^3 r' \, \boldsymbol{\chi}(\boldsymbol{r},\boldsymbol{r}',\tau) \cdot \boldsymbol{E}(\boldsymbol{r}',t-\tau) + \boldsymbol{P}_{\rm N}(\boldsymbol{r},t), \qquad (A.12)$$

$$\boldsymbol{M}(\boldsymbol{r},t) = \frac{1}{\mu_0} \int_{-\infty}^{\infty} d\tau \int d^3 r' \boldsymbol{\zeta}(\boldsymbol{r},\boldsymbol{r}',\tau) \cdot \boldsymbol{B}(\boldsymbol{r}',t-\tau) + \boldsymbol{M}_{\rm N}(\boldsymbol{r},t). \tag{A.13}$$

These expressions can be interpreted as being made up of a reactive part and a random part. The reactive part describes the linear response of the medium to the electromagnetic field, where  $\boldsymbol{\chi}$  and  $\boldsymbol{\zeta}$  are the electric and magnetic susceptibility response functions of the medium, respectively. Since we assumed that the response of the bound charges is causal, we require that  $\boldsymbol{\chi}(\boldsymbol{r}, \boldsymbol{r}', \tau) = 0$  and  $\boldsymbol{\zeta}(\boldsymbol{r}, \boldsymbol{r}', \tau) = 0$  for  $|\boldsymbol{r} - \boldsymbol{r}'| > c\tau$ , so that the reactive part of the polarisation and magnetisation only depends on previous influences at a given instant. The random part accounts of the medium's fluctuations, and is described by the noise polarisation,  $P_{\rm N}$ , and noise magnetisation,  $M_{\rm N}$ . These relate to the noise charge density,  $\rho_{\rm N}$ , and the noise current density,  $j_{\rm N}$ , via,

$$\rho_{\rm N} = -\boldsymbol{\nabla} \cdot \boldsymbol{P}_{\rm N},\tag{A.14}$$

$$\boldsymbol{j}_{\mathrm{N}} = \boldsymbol{P}_{\mathrm{N}} + \boldsymbol{\nabla} \times \boldsymbol{M}_{\mathrm{N}}, \qquad (A.15)$$

which obey the continuity equation,

$$\dot{\rho}_{\rm N} + \boldsymbol{\nabla} \cdot \boldsymbol{j}_{\rm N} = 0. \tag{A.16}$$

To transform into the frequency domain, we make use of the convolution theorem. The convolution of two functions f and g is defined as,

$$(f * g)(t) := \int_{-\infty}^{\infty} d\tau f(\tau)g(t-\tau), \qquad (A.17)$$

and the convolution theorem tells us,

$$\mathcal{F}[f * g] = \mathcal{F}[f] \mathcal{F}[g].$$
(A.18)

We can apply this to our expressions by writing,

$$\boldsymbol{P}(\boldsymbol{r},t) = \epsilon_0 \int d^3 r' \left[ \boldsymbol{\chi}(\boldsymbol{r},\boldsymbol{r}') * \boldsymbol{E}(\boldsymbol{r}') \right](t) + \boldsymbol{P}_{\mathrm{N}}(\boldsymbol{r},t), \qquad (A.19)$$

$$\boldsymbol{M}(\boldsymbol{r},t) = \frac{1}{\mu_0} \int d^3 \boldsymbol{r}' \left[ \boldsymbol{\zeta}(\boldsymbol{r},\boldsymbol{r}') * \boldsymbol{B}(\boldsymbol{r}) \right](t) + \boldsymbol{M}_{\rm N}(\boldsymbol{r},t), \qquad (A.20)$$

so that,

$$\tilde{\boldsymbol{P}}(\boldsymbol{r},\omega) = \epsilon_0 \int d^3 r' \, \tilde{\boldsymbol{\chi}}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \tilde{\boldsymbol{E}}(\boldsymbol{r}',\omega) + \tilde{\boldsymbol{P}}_{\rm N}(\boldsymbol{r},\omega), \qquad (A.21)$$

$$\tilde{\boldsymbol{M}}(\boldsymbol{r},\omega) = \frac{1}{\mu_0} \int d^3 r' \, \tilde{\boldsymbol{\zeta}}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \tilde{\boldsymbol{B}}(\boldsymbol{r}',\omega) + \tilde{\boldsymbol{M}}_{\rm N}(\boldsymbol{r},\omega). \tag{A.22}$$

We can now apply these to the constitutive relations (A.5) and (A.6) to find,

$$\tilde{\boldsymbol{D}}(\boldsymbol{r},\omega) = \epsilon_0 \left[ \tilde{\boldsymbol{E}}(\boldsymbol{r},\omega) + \int d^3 r' \, \tilde{\boldsymbol{\chi}}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \tilde{\boldsymbol{E}}(\boldsymbol{r}',\omega) \right] + \tilde{\boldsymbol{P}}_{\rm N}(\boldsymbol{r},\omega), \tag{A.23}$$

$$\tilde{\boldsymbol{H}}(\boldsymbol{r},\omega) = \frac{1}{\mu_0} \left[ \tilde{\boldsymbol{B}}(\boldsymbol{r},\omega) - \int d^3 r' \, \tilde{\boldsymbol{\zeta}}(\boldsymbol{r},\boldsymbol{r}',\omega) \cdot \tilde{\boldsymbol{B}}(\boldsymbol{r}',\omega) \right] - \tilde{\boldsymbol{M}}_{\rm N}(\boldsymbol{r},\omega). \tag{A.24}$$

So now we have the Maxwell equations given by (A.8), (A.9), (A.10) and (A.11), and the constitutive relations given by (A.23) and (A.24), in Fourier space ready to use. In the main text, we will omit the tildes for ease of reading.

# APPENDIX B

## Green's Tensor Expressions

In this appendix, forms of the Green's tensor are presented and/or derived for the specific environments relevant to this work.

## B.1 Vacuum

In the case of an environment consisting entirely of a vacuum, the form of the Green's tensor is given by (see, for example, [4, 59]),

$$\boldsymbol{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{c^2}{3\omega^2}\boldsymbol{\delta}(\boldsymbol{\rho}) - \frac{c^2 e^{i\omega\rho/c}}{4\pi\omega^2\rho^3} \left\{ \left[ 1 - i\frac{\omega\rho}{c} - \left(\frac{\omega\rho}{c}\right)^2 \right] \mathbb{I} - \left[ 3 - 3i\frac{\omega\rho}{c} - \left(\frac{\omega\rho}{c}\right)^2 \right] \boldsymbol{e}_{\rho}\boldsymbol{e}_{\rho} \right\}, \quad (B.1)$$

where  $\rho = r - r'$ ,  $\rho = |\rho|$  and  $e_{\rho} = \rho/\rho$ . For the systems considered in this work, the source and observation points will always be at different positions, so  $\rho$  will never be 0, meaning the first term of the above equation will not contribute and can be omitted. We can equivalently rewrite in the condensed form,

$$\boldsymbol{G}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{c^2 e^{i\omega\rho/c}}{4\pi\omega^2\rho^3} \left[ a\left(-i\rho\omega/c\right) \mathbb{I} - b\left(-i\rho\omega/c\right) \boldsymbol{e}_{\rho} \boldsymbol{e}_{\rho} \right], \tag{B.2}$$
where we have defined  $a(x) \equiv 1 + x + x^2$  and  $b(x) \equiv 3 + 3x + x^2$ .

It can be useful to simplify by applying the non-retarded limit, which corresponds to short distances where  $\omega \rho/c \ll 1$ , which gives us the following form,

$$\boldsymbol{G}_{NR}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{c^2}{4\pi\omega^2\rho^3} (\mathbb{I} - 3\boldsymbol{e}_{\rho}\boldsymbol{e}_{\rho}), \qquad (B.3)$$

where we have omitted the  $\delta(\rho)$  term.

We can similarly apply the retarded limit, corresponding to long distances  $\omega \rho/c \gg 1$ , where relativistic effects become significant. This results in,

$$\boldsymbol{G}_{R}^{(0)}(\boldsymbol{r},\boldsymbol{r}',\omega) = -\frac{e^{i\omega\rho/c}}{4\pi\rho}(\mathbb{I} - \boldsymbol{e}_{\rho}\boldsymbol{e}_{\rho}). \tag{B.4}$$

## **B.2** Reciprocal Half Space

In this section, we present the Green's tensor for a semi-infinite half-space made up of reciprocal media (introduced in 2.1.1). We will then apply to two simple configurations and apply the near- and far-field limits to simplify the Green's tensor expressions.

The scattering Green's tensor for a planar multilayer system with n homogeneous layers (see e.g. [4]) can be adapted to apply to a semi-infinite half-space with permittivity  $\epsilon(\omega)$  and permeability  $\mu(\omega)$  where both source and field points are in the vacuum,

$$\boldsymbol{G}^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi^2} \int \frac{d^2k^{\parallel}}{k^{\perp}} e^{i\boldsymbol{k}^{\parallel}\cdot(\boldsymbol{r}-\boldsymbol{r}')+ik^{\perp}(z+z')} \sum_{\sigma=s,p} r_{\sigma}\boldsymbol{e}_{\sigma+}\boldsymbol{e}_{\sigma-}, \qquad (B.5)$$

where  $\boldsymbol{k}^{\parallel} \perp \boldsymbol{e}_{z}$  and,

$$\mathbf{k}^{\parallel} = (k_x, k_y, 0), \quad k^{\parallel} = \sqrt{k_x^2 + k_y^2},$$
 (B.6)

$$k^{\perp} = \sqrt{\frac{\omega^2}{c^2} - k^{\parallel 2}}, \quad \text{Im} \, k^{\perp} > 0,$$
 (B.7)

are the parallel and perpendicular components of the wave vector with respect to the interfaces. The polarisation unit vectors for s- and p-polarised waves (perpendicular and parallel to the plane of incidence, respectively) in layer 1 are,

$$\boldsymbol{e}_{s\pm} = \boldsymbol{e}_{s\pm}(\boldsymbol{k}^{\parallel}, \omega) = \boldsymbol{e}_{k\parallel} \times \boldsymbol{e}_{z}$$
  
=  $\frac{1}{k^{\parallel}}(k_{x}, k_{y}, 0) \times (0, 0, 1) = \frac{1}{k^{\parallel}}(k_{y}, -k_{x}, 0),$  (B.8)

$$\boldsymbol{e}_{p\pm} = \boldsymbol{e}_{p\pm}(\boldsymbol{k}^{\parallel}, \omega) = \frac{1}{k_1} (k^{\parallel} \boldsymbol{e}_z \mp k_1^{\perp} \boldsymbol{e}_{k^{\parallel}}) \\ = \frac{1}{k_1} \left[ k^{\parallel}(0, 0, 1) - \frac{k_1^{\perp}}{k^{\parallel}} (k_x, k_y, 0) \right] = \frac{1}{k_1} \left( \mp \frac{k_1^{\perp} k_x}{k^{\parallel}}, \mp \frac{k_1^{\perp} k_y}{k^{\parallel}}, k^{\parallel} \right).$$
(B.9)

For a two-layer system, the Fresnel coefficients can be written as,

$$r_s = r_s(k^{\parallel}, \omega) = \frac{\mu(\omega)k^{\perp} - k_1^{\perp}}{\mu(\omega)k^{\perp} + k_1^{\perp}},$$
(B.10a)

$$r_p = r_p(k^{\parallel}, \omega) = \frac{\epsilon(\omega)k^{\perp} - k_1^{\perp}}{\epsilon(\omega)k^{\perp} + k_1^{\perp}},$$
(B.10b)

where,

$$k_1^{\perp} = \sqrt{\epsilon(\omega)\mu(\omega)\frac{\omega^2}{c^2} - k^{\parallel 2}}, \quad \text{Im} \, k^{\perp} > 0.$$
(B.11)

Using (B.8) and (B.9), we can calculate the components,

$$\begin{aligned} \boldsymbol{e}_{s+} \boldsymbol{e}_{s-} &= (\boldsymbol{e}_{k\parallel} \times \boldsymbol{e}_{z})(\boldsymbol{e}_{k\parallel} \times \boldsymbol{e}_{z}) \\ &= \frac{1}{k^{\parallel 2}}(k_{y}, -k_{x}, 0) \otimes (k_{y}, -k_{x}, 0) = \frac{1}{k^{\parallel 2}} \begin{pmatrix} k_{y}^{2} & -k_{y}k_{x} & 0 \\ -k_{x}k_{y} & k_{x}^{2} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \end{aligned}$$
(B.12)  
$$\boldsymbol{e}_{p+} \boldsymbol{e}_{p-} &= \frac{1}{k_{1}^{2}}(k^{\parallel}\boldsymbol{e}_{z} - k_{1}^{\perp}\boldsymbol{e}_{k\parallel})(k^{\parallel}\boldsymbol{e}_{z} + k_{1}^{\perp}\boldsymbol{e}_{k\parallel}) \\ &= \frac{1}{k_{1}^{2}} \begin{pmatrix} -\frac{k_{1}^{\perp}k_{x}}{k^{\parallel}}, -\frac{k_{1}^{\perp}k_{y}}{k^{\parallel}}, k^{\parallel} \end{pmatrix} \otimes \begin{pmatrix} \frac{k_{1}^{\perp}k_{x}}{k^{\parallel}}, \frac{k_{1}^{\perp}k_{y}}{k^{\parallel}}, k^{\parallel} \end{pmatrix} \\ &= \frac{1}{k_{1}^{2}} \begin{pmatrix} -\frac{k_{1}^{\perp 2}k_{x}^{2}}{k^{\parallel 2}} & -\frac{k_{1}^{\perp 2}k_{y}k_{x}}{k^{\parallel 2}} & -k_{1}^{\perp}k_{x} \\ \frac{-\frac{k_{1}^{\perp 2}k_{x}k_{y}}{k^{\parallel 2}} & -\frac{k_{1}^{\perp 2}k_{y}k_{x}}{k^{\parallel 2}} & -k_{1}^{\perp}k_{y} \\ k_{1}^{\perp}k_{x} & k_{1}^{\perp}k_{y} & k^{\parallel 2} \end{pmatrix}. \end{aligned}$$
(B.13)

Now we transform into polar coordinates via the transformations,

$$\int d^2 k^{\parallel} \to \int dk^{\parallel} k^{\parallel} \int_0^{2\pi} d\phi,$$
  
$$k_x \to k^{\parallel} \cos \phi, \quad k_y \to k^{\parallel} \sin \phi,$$
 (B.14)



Figure B.1: Two arrangements of two bodies, a donor D and an acceptor A, near a semiinfinite half-space at z < 0.

resulting in,

$$\boldsymbol{G}^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi^2} \int dk^{\parallel} \int_0^{2\pi} d\phi \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\parallel}(\cos\phi,\sin\phi,0)\cdot(\boldsymbol{r}-\boldsymbol{r}')+ik^{\perp}(z+z')} \times \left(r_s \boldsymbol{e}_{s+} \boldsymbol{e}_{s-} + r_p \boldsymbol{e}_{p+} \boldsymbol{e}_{p-}\right), \quad (B.15)$$

where,

$$\boldsymbol{e}_{s+}\boldsymbol{e}_{s-} = \begin{pmatrix} \sin^2 \phi & -\cos \phi \sin \phi & 0\\ -\cos \phi \sin \phi & \cos^2 \phi & 0\\ 0 & 0 & 0 \end{pmatrix},$$
(B.16)  
$$\boldsymbol{e}_{p+}\boldsymbol{e}_{p-} = \frac{1}{k_1^2} \begin{pmatrix} -k_1^{\perp 2} \cos^2 \phi & -k_1^{\perp 2} \cos \phi \sin \phi & -k_1^{\perp} k^{\parallel} \cos \phi\\ -k_1^{\perp 2} \cos \phi \sin \phi & -k_1^{\perp 2} \sin^2 \phi & -k_1^{\perp} k^{\parallel} \sin \phi\\ k_1^{\perp} k^{\parallel} \cos \phi & k_1^{\perp} k^{\parallel} \sin \phi & k^{\parallel 2} \end{pmatrix}.$$
(B.17)

We now consider two specific arrangements of the source and observation points in relation to the half-space in an effort to simplify the above Green's tensor expression. These configurations are the "parallel" and "colinear" arrangements, and are shown in figure B.1.

## B.2.1 Parallel arrangement

We can arrange the bodies so that they are in the xz-plane and equidistant from the surface, as in figure B.1a, i.e.  $\mathbf{r} = (x, 0, z)$  and  $\mathbf{r}' = (x', 0, z)$ . Defining  $x - x' \equiv X$ , we therefore have  $\mathbf{k}^{\parallel} \cdot (\mathbf{r} - \mathbf{r}') = (k_x, k_y, 0) \cdot (X, 0, 0) = k_x X = k^{\parallel} X \cos \phi$ , where we have transformed into polar coordinates via (B.14). So the Green's tensor (B.15) becomes,

$$\boldsymbol{G}^{(1,P)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i}{8\pi^2} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{2ik^{\perp}z} \int_0^{2\pi} d\phi e^{ik^{\parallel}X\cos\phi} \left( r_s \boldsymbol{e}_{s+} \boldsymbol{e}_{s-} + r_p \boldsymbol{e}_{p+} \boldsymbol{e}_{p-} \right), \quad (B.18)$$

where  $e_{s+}e_{s-}$  and  $e_{p+}e_{p-}$  are defined by (B.16) and (B.17) respectively, and P references the parallel arrangement. We can now perform the angular integration using the results [120],

$$\int_{0}^{2\pi} e^{ik^{\parallel} X \cos \phi} d\phi = 2\pi J_0(k^{\parallel} X), \tag{B.19a}$$

$$\int_{0}^{2\pi} \cos \phi e^{ik^{\parallel} X \cos \phi} d\phi = 2\pi i J_1(k^{\parallel} X), \tag{B.19b}$$

$$\int_0^{2\pi} \sin \phi e^{ik^{\parallel} X \cos \phi} d\phi = \int_0^{2\pi} \sin \phi \cos \phi e^{ik^{\parallel} X \cos \phi} d\phi = 0, \qquad (B.19c)$$

$$\int_{0}^{2\pi} \sin^2 \phi e^{ik^{\parallel} X \cos \phi} d\phi = \pi \left[ J_0(k^{\parallel} X) + J_2(k^{\parallel} X) \right],$$
(B.19d)

$$\int_{0}^{2\pi} \cos^{2} \phi e^{ik^{\parallel} X \cos \phi} d\phi = \pi \left[ J_{0}(k^{\parallel} X) - J_{2}(k^{\parallel} X) \right],$$
(B.19e)

where the  $J_{\alpha}$  terms are Bessel functions of the first kind, arriving at the result,

$$\begin{aligned} \boldsymbol{G}^{(1,P)}(\boldsymbol{r},\boldsymbol{r}',\omega) &= \frac{i}{8\pi} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{2ik^{\perp}z} \begin{bmatrix} r_s \begin{pmatrix} J_0(k^{\parallel}X) + J_2(k^{\parallel}X) & 0 & 0 \\ 0 & J_0(k^{\parallel}X) - J_2(k^{\parallel}X) & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ &+ \frac{c^2}{\omega^2} r_p \begin{pmatrix} -k_1^{\perp^2} \begin{bmatrix} J_0(k^{\parallel}X) - J_2(k^{\parallel}X) \end{bmatrix} & 0 & -2ik_1^{\perp}k^{\parallel}J_1(k^{\parallel}X) \\ 0 & -k_1^{\perp^2} \begin{bmatrix} J_0(k^{\parallel}X) + J_2(k^{\parallel}X) \end{bmatrix} & 0 \\ 2ik_1^{\perp}k^{\parallel}J_1(k^{\parallel}X) & 0 & 2k^{\parallel^2}J_0(k^{\parallel}X) \end{pmatrix} \end{bmatrix}, \end{aligned}$$

$$(B.20)$$

where we have made the replacement  $k_1 = \omega/c$ .

As an aside, we can check that this expression obeys Lorentz Reciprocity (2.75) by taking the transpose and making the replacement  $X \to -X$ . Looking at the only non-diagonal elements, and noting that  $J_1(x)$  is an odd function and so  $J_1\left(k^{\parallel}\left(-X\right)\right) = -J_1\left(k^{\parallel}X\right)$ , we can see that  $\mathbf{G}_{xz}^{(1,P)}(\mathbf{r}',\mathbf{r}) \propto -\frac{k^{\parallel}}{k_1^{\perp}}iJ_1\left(k^{\parallel}(-X)\right) = \frac{k^{\parallel}}{k_1^{\perp}}iJ_1\left(k^{\parallel}X\right) \propto \mathbf{G}_{zx}^{(1,P)}(\mathbf{r},\mathbf{r}')$ . We thus know that  $\mathbf{G}^{(1,P)^T}(\mathbf{r},\mathbf{r}') = \mathbf{G}^{(1,P)}(\mathbf{r}',\mathbf{r})$ , meaning Lorentz Reciprocity holds as required.

#### B.2.2 Colinear arrangement

It simplifies things significantly to consider the situation where all bodies are positioned along the z-axis (as in figure B.1b), which we term the colinear arrangement. In this case,  $\mathbf{k}^{\parallel} \cdot (\mathbf{r} - \mathbf{r}') = (k_x, k_y, 0) \cdot (x - x', y - y', z - z') = 0$ , so we can write the colinear half-space Green's tensor as,

$$\boldsymbol{G}^{(1,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i}{8\pi^2} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\perp}\bar{z}} \int_0^{2\pi} d\phi \left( r_s \boldsymbol{e}_{s+} \boldsymbol{e}_{s-} + r_p \boldsymbol{e}_{p+} \boldsymbol{e}_{p-} \right), \qquad (B.21)$$

where we have made the substitution  $(z + z') \equiv \overline{Z}$ ,  $e_{s+}e_{s-}$  and  $e_{p+}e_{p-}$  are defined by (B.16) and (B.17) respectively, and C references the collinear arrangement. Now, since there is no  $\phi$  dependence in the exponential argument of (B.21), it is simple to perform the angular integral using,

$$\int_{0}^{2\pi} \cos \phi d\phi = \int_{0}^{2\pi} \sin \phi d\phi = \int_{0}^{2\pi} \sin \phi \cos \phi d\phi = 0,$$
 (B.22a)

$$\int_{0}^{2\pi} \sin^2 \phi d\phi = \int_{0}^{2\pi} \cos^2 \phi d\phi = \pi.$$
 (B.22b)

We note that this result only holds for the colinear arrangement, since otherwise a  $k^{\parallel}$  remains in the exponential, which would need to be included in the angular integral, leading to more complicated results. We therefore arrive at,

$$\begin{aligned} \boldsymbol{G}^{(1,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) &= \frac{i}{8\pi^2} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\perp}\bar{Z}} \\ &\times \left[ r_s \begin{pmatrix} \pi & 0 & 0 \\ 0 & \pi & 0 \\ 0 & 0 & 0 \end{pmatrix} + \frac{c^2}{\omega^2} r_p \begin{pmatrix} -k^{\perp 2}\pi & 0 & 0 \\ 0 & -k^{\perp 2}\pi & 0 \\ 0 & 0 & 2k^{\parallel 2}\pi \end{pmatrix} \right] \\ &= \frac{i}{8\pi} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\perp}\bar{Z}} \left[ r_s \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} + \frac{c^2}{\omega^2} r_p \begin{pmatrix} -k^{\perp 2} & 0 & 0 \\ 0 & -k^{\perp 2} & 0 \\ 0 & 0 & 2k^{\parallel 2} \end{pmatrix} \right], \end{aligned}$$
(B.23)

where we have made the replacement  $k_1 = \omega/c$ . It is clear to see here that Lorentz reciprocity (2.74) is obeyed by this expression, since the only explicit coordinate dependence is  $\bar{Z} \equiv z+z'$ , which is unchanged when swapping the positions of the molecules, and the expression is diagonal, meaning  $\boldsymbol{G}^{(1,C)^T}(\boldsymbol{r},\boldsymbol{r}') = \boldsymbol{G}^{(1,C)}(\boldsymbol{r}',\boldsymbol{r})$ .

Although the full Green's tensor expression (B.5) has been significantly simplified with the

application of these two arrangements, both results (B.20) and (B.23) still contain an infinite integral that cannot be easily performed due to the fact that the reflection coefficients (B.10a) and (B.10b) are also dependent on  $k^{\parallel}$ . By implementing the non-retarded and retarded limits, we can simplify the reflection coefficients enough to perform the integral analytically, further simplifying our expression.

#### B.2.3 Limits

In this section, we consider the non-retarded regime by imposing the limit  $\omega \rho/c \ll 1$  and the retarded regime where  $\omega \rho/c \ll 1$ . The Green's tensors for the parallel and collinear arrangements will be considered separately.

In the non-retarded limit, the intermolecular distances are small enough that relativistic effects become negligible. In this case, the main contribution to the integral in (B.23) is due to regions of large  $k^{\parallel}$ . Therefore  $k^{\parallel}$  dominates the  $\omega/c$  term, so we can make the approximation  $k^{\perp} \simeq \sqrt{-k^{\parallel 2}} = ik^{\parallel} \simeq k_1^{\perp}$ . We can make this substitution in the reflection coefficients (B.10a) and (B.10b) and define new reflection coefficients that no longer depend on  $k^{\parallel}$ ,

$$r_s = \frac{\mu(\omega)ik^{\parallel} - ik^{\parallel}}{\mu(\omega)ik^{\parallel} + ik^{\parallel}} = \frac{\mu(\omega) - 1}{\mu(\omega) + 1} \equiv r_s^{\rm NR},\tag{B.24}$$

$$r_p = \frac{\epsilon(\omega)ik^{\parallel} - ik^{\parallel}}{\epsilon(\omega)ik^{\parallel} + ik^{\parallel}} = \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 1} \equiv r_p^{\text{NR}}.$$
(B.25)

In the retarded regime, we assume all of the bodies are far enough away from each other and the half-space for relativistic effects to become significant. Large z means that the integral in (B.23) oscillates quickly, due to the complex exponential. The dominant wavenumbers are given by the stationary-phase point  $dk^{\perp}/dk^{\parallel} = 0$  so we see that,

$$\frac{d}{dk^{\parallel}}\sqrt{\frac{\omega^2}{c^2} - k^{\parallel 2}} = \frac{-k^{\parallel}}{\sqrt{\frac{\omega^2}{c^2} - k^{\parallel 2}}} = 0,$$
 (B.26)

meaning that  $k^{\parallel} = 0$  dominates. This means that we can make the substitutions  $k^{\perp} \simeq \omega/c$ and  $k_1^{\perp} \simeq \sqrt{\epsilon(\omega)\mu(\omega)}\omega/c$ , allowing the definitions of reflection coefficients that don't depend on  $k^{\parallel}$ ,

$$r_s = \frac{\mu(\omega) - \sqrt{\epsilon(\omega)\mu(\omega)}}{\mu(\omega) + \sqrt{\epsilon(\omega)\mu(\omega)}} = \frac{\sqrt{\mu(\omega)} - \sqrt{\epsilon(\omega)}}{\sqrt{\mu(\omega)} + \sqrt{\epsilon(\omega)}} \equiv r_s^{\rm R}, \tag{B.27}$$

$$r_p = \frac{\epsilon(\omega) - \sqrt{\epsilon(\omega)\mu(\omega)}}{\epsilon(\omega) + \sqrt{\epsilon(\omega)\mu(\omega)}} = \frac{\sqrt{\epsilon(\omega)} - \sqrt{\mu(\omega)}}{\sqrt{\epsilon(\omega)} + \sqrt{\mu(\omega)}} \equiv -r_s^{\rm R}.$$
 (B.28)

Now we can apply these simplified the reflection coefficients for each of the considered regimes to the Green's tensor expressions for the two arrangements.

#### Parallel Arrangement

Applying the non-retarded limit to the expression for the parallel arrangement, (B.20), we can make the substitutions  $k^{\perp} \simeq \sqrt{-k^{\parallel 2}} = ik^{\parallel} \simeq k_1^{\perp}$  to obtain,

$$\begin{aligned} \boldsymbol{G}_{\mathrm{NR}}^{(1,P)}(\boldsymbol{r},\boldsymbol{r}',\omega) &= \frac{1}{8\pi} \int dk^{\parallel} e^{-2k^{\parallel} z} \begin{bmatrix} r_{\mathrm{s}}^{\mathrm{lim}} \begin{pmatrix} J_{0}(k^{\parallel}X) + J_{2}(k^{\parallel}X) & 0 & 0 \\ 0 & J_{0}(k^{\parallel}X) - J_{2}(k^{\parallel}X) & 0 \\ 0 & 0 & 0 \end{pmatrix} \\ &+ \frac{c^{2}}{\omega^{2}} r_{p}^{\mathrm{lim}} k^{\parallel^{2}} \begin{pmatrix} J_{0}(k^{\parallel}X) - J_{2}(k^{\parallel}X) & 0 & 2J_{1}(k^{\parallel}X) \\ 0 & J_{0}(k^{\parallel}X) + J_{2}(k^{\parallel}X) & 0 \\ -2J_{1}(k^{\parallel}X) & 0 & 2J_{0}(k^{\parallel}X) \end{pmatrix} \end{bmatrix}. \end{aligned}$$
(B.29)

Using the integral results [120],

$$\int_{0}^{\infty} dx e^{-ax} J_0(bx) = \frac{1}{\sqrt{a^2 + b^2}},$$
(B.30a)

$$\int_0^\infty dx e^{-ax} J_2(bx) = \frac{\left(\sqrt{a^2 + b^2} - a\right)^2}{b^2 \sqrt{a^2 + b^2}},$$
 (B.30b)

$$\int_0^\infty dx e^{-ax} J_0(bx) x^2 = \frac{2a^2 - b^2}{\sqrt{a^2 + b^2}},$$
(B.30c)

$$\int_0^\infty dx e^{-ax} J_1(bx) x^2 = \frac{3ab}{\sqrt{a^2 + b^2}},$$
(B.30d)

$$\int_0^\infty dx e^{-ax} J_2(bx) x^2 = \frac{3b^2}{\sqrt{a^2 + b^2}},$$
(B.30e)

we reach,

$$\begin{aligned} \boldsymbol{G}_{\mathrm{NR}}^{(1,P)}(\boldsymbol{r},\boldsymbol{r}',\omega) = & \frac{1}{8\pi} \left[ \frac{r_s^{\mathrm{lim}}}{X^2 R_+} \begin{pmatrix} X^2 + (R_+ - 2z)^2 & 0 & 0\\ 0 & X^2 - (R_+ - 2z)^2 & 0\\ 0 & 0 & 0 \end{pmatrix} \right. \\ & \left. + \frac{c^2}{\omega^2} \frac{r_p^{\mathrm{lim}}}{R_+^5} \begin{pmatrix} 8z^2 - 4X^2 & 0 & 12zX\\ 0 & 8z^2 + 2X^2 & 0\\ -12zX & 0 & 2(8z^2 - X^2) \end{pmatrix} \right] \\ & \left. = \frac{1}{4\pi} \left[ \frac{r_s^{\mathrm{lim}}}{X^2 R_+} \begin{pmatrix} R_+^2 - 2zR_+ & 0 & 0\\ 0 & 2zR_+ - 4z^2 & 0\\ 0 & 0 & 0 \end{pmatrix} \right. \\ & \left. + \frac{c^2}{\omega^2} \frac{r_p^{\mathrm{lim}}}{R_+^5} \begin{pmatrix} R_+^2 - 3X^2 & 0 & 6zX\\ 0 & R_+^2 & 0\\ -6zX & 0 & 2R_+^2 - 3X^2 \end{pmatrix} \right], \end{aligned}$$
(B.31)

where we have made the defined  $\sqrt{4z^2 + X^2} \equiv R_+$ . In the non-retarded limit, intermolecular distance is small, so  $\{R_+, z, X\} \ll 1$ , so  $R_+^{-5}$  terms will dominate. We can therefore approximate the expression as,

$$\boldsymbol{G}_{\mathrm{NR}}^{(1,P)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{c^2 r_p^{\mathrm{NR}}}{4\pi\omega^2 R_+^5} \begin{pmatrix} R_+^2 - 3X^2 & 0 & 6zX\\ 0 & R_+^2 & 0\\ -6zX & 0 & 2R_+^2 - 3X^2 \end{pmatrix},$$
(B.32)

where from (B.25) we know that  $r_p^{\text{NR}} \equiv \frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}$ . Summing with the non-retarded limit of the vacuum Green's tensor, (B.3), we obtain the effective Green's tensor,

$$\boldsymbol{G}_{\mathrm{NR}}^{(1,P)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{c^2}{4\pi\omega^2} \begin{bmatrix} \frac{1}{X^3} \begin{pmatrix} 2 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & -1 \end{pmatrix} + \frac{r_p^{\mathrm{NR}}}{R_+^5} \begin{pmatrix} R_+^2 - 3X^2 & 0 & 6zX\\ 0 & R_+^2 & 0\\ -6zX & 0 & 2R_+^2 - 3X^2 \end{pmatrix} \end{bmatrix}.$$
(B.33)

## **Colinear Arrangement**

With the simplified reflection coefficients, we can perform the integral in (B.23) using the following integral results,

$$\int_{0}^{\infty} dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\perp}\bar{Z}} = \left[ \frac{ie^{i\bar{Z}\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\parallel}^{2}}}}{\bar{Z}} \right]_{0}^{\infty} = \frac{i}{\bar{Z}} \left( \lim_{k^{\parallel} \to \infty} e^{i\bar{Z}\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\parallel}^{2}}} - \lim_{k^{\parallel} \to 0} e^{i\bar{Z}\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\parallel}^{2}}} \right) \\ = 0 - \frac{ie^{i\bar{Z}\frac{\omega}{c}}}{\bar{Z}} = -\frac{ie^{i\bar{Z}\frac{\omega}{c}}}{\bar{Z}}, \tag{B.34}$$

$$\begin{split} \int_{0}^{\infty} dk^{\|} \frac{k^{\|3}}{k^{\perp}} e^{ik^{\perp}\bar{Z}} &= \left[ e^{i\bar{Z}\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\|2}}} \left( \frac{2\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\|2}}}{\bar{Z}^{2}} + \frac{ik^{\|2}}{\bar{Z}} + \frac{2i}{\bar{Z}^{3}} \right) \right]_{0}^{\infty} \\ &= -\frac{2}{\bar{Z}^{2}} \lim_{k^{\|\to\infty}} e^{i\bar{Z}\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\|2}}} \sqrt{\frac{\omega^{2}}{c^{2}} - k^{\|2}} - \frac{2}{\bar{Z}} \lim_{k^{\|\to\infty}} e^{i\bar{Z}\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\|2}}} k^{\|2} \\ &- \frac{2i}{\bar{Z}^{3}} \lim_{k^{\|\to\infty}} e^{i\bar{Z}\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\|2}}} - \left(\frac{2\omega}{c\bar{Z}^{2}} e^{i\bar{Z}\frac{\omega}{c}} + 0 + e^{i\bar{Z}\frac{\omega}{c}}\frac{2i}{\bar{Z}^{3}}\right) \\ &= -0 - 0 - 0 - \frac{2\omega}{c\bar{Z}} e^{i\bar{Z}\frac{\omega}{c}} - e^{i\bar{Z}\frac{\omega}{c}}\frac{2i}{\bar{Z}^{3}} \\ &= -e^{i\bar{Z}\frac{\omega}{c}} \left(\frac{2\omega}{c\bar{Z}^{2}} + \frac{2i}{\bar{Z}^{3}}\right), \end{split}$$
(B.35)

$$\int_{0}^{\infty} dk^{\parallel} k^{\perp} e^{ik^{\perp}\bar{Z}} = \left[ -e^{i\bar{Z}\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\parallel 2}}} \left( \frac{2\sqrt{\frac{\omega^{2}}{c^{2}} - k^{\parallel 2}}}{\bar{Z}^{2}} + \frac{ik^{\parallel 2}}{\bar{Z}} - \frac{i\omega^{2}}{c^{2}\bar{Z}} + \frac{2i}{\bar{Z}^{3}} \right) \right]_{0}^{\infty} = e^{i\bar{Z}\frac{\omega}{c}} \left( \frac{2\omega}{c\bar{Z}^{2}} - \frac{i\omega^{2}}{c^{2}\bar{Z}} + \frac{2i}{\bar{Z}^{3}} \right),$$
(B.36)

obtaining,

$$\begin{aligned} \boldsymbol{G}^{(1,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) &= \frac{i}{8\pi} e^{i\bar{Z}\frac{\omega}{c}} \begin{bmatrix} -\frac{i}{\bar{Z}} r_s^{\lim} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0 \end{pmatrix} \\ &+ \frac{c^2}{\omega^2} r_p^{\lim} \begin{pmatrix} -\left(\frac{2\omega}{c\bar{Z}^2} - \frac{i\omega^2}{c^2\bar{Z}} + \frac{2i}{\bar{Z}^3}\right) & 0 & 0\\ 0 & -\left(\frac{2\omega}{c\bar{Z}^2} - \frac{i\omega^2}{c^2\bar{Z}} + \frac{2i}{\bar{Z}^3}\right) & 0\\ 0 & 0 & -2\left(\frac{2\omega}{c\bar{Z}^2} + \frac{2i}{\bar{Z}^3}\right) \end{pmatrix} \end{bmatrix} \\ &= \frac{e^{i\bar{Z}\frac{\omega}{c}}}{8\pi} \begin{bmatrix} \frac{r_s^{\lim} - r_p^{\lim}}{\bar{Z}} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0 \end{pmatrix} + \frac{2cr_p^{\lim}}{\omega} \left(\frac{c}{\omega\bar{Z}^3} - \frac{i}{\bar{Z}^2}\right) \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 2 \end{pmatrix} \end{bmatrix}. \end{aligned}$$
(B.37)

Now we can find expressions for the limits of the colinear Green's tensor by picking out the dominant terms in each limit. For the non-retarded limit,  $z \ll c/\omega$  so  $z^{-3}$  terms dominate and  $e^{i\bar{Z}\frac{\omega}{c}} \rightarrow 1$ , resulting in,

$$\boldsymbol{G}_{\mathrm{NR}}^{(1,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{c^2 r_p^{\mathrm{NR}}}{4\pi\omega^2 \bar{Z}^3} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 2 \end{pmatrix},$$
(B.38)

where  $r_p^{\text{NR}} \equiv \frac{\epsilon(\omega)-1}{\epsilon(\omega)+1}$ . Summing with the non-retarded vacuum Green's tensor, (B.3) to get,

$$\boldsymbol{G}_{\mathrm{NR}}^{\mathrm{HS,C}}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{c^2}{4\pi\omega^2} \begin{bmatrix} 1\\ \frac{1}{\bar{Z}^3} \begin{pmatrix} -1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 2 \end{pmatrix} + \frac{r_p^{\mathrm{NR}}}{\bar{Z}^3} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 2 \end{pmatrix} \end{bmatrix}.$$
 (B.39)

In the retarded limit  $z \gg c/\omega$ , so  $z^{-1}$  terms dominate, so we find the Green's tensor to be,

$$\boldsymbol{G}_{\mathrm{R}}^{(1,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{e^{i\bar{Z}\omega/c}r_{s}^{\mathrm{R}}}{4\pi\bar{Z}} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0 \end{pmatrix},$$
(B.40)

where  $r_s^{\rm R} = \frac{\sqrt{\mu(\omega)} - \sqrt{\epsilon(\omega)}}{\sqrt{\mu(\omega)} + \sqrt{\epsilon(\omega)}}$  and we recall from (B.28) that  $r_s^{\rm R} = -r_p^{\rm R}$ . Similarly, we can sum

with the retarded limit of the vacuum Green's tensor to find the effective Green's tensor for the system,

$$\boldsymbol{G}_{\mathrm{R}}^{(1,\mathrm{C})}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{e^{i\bar{Z}\omega/c}}{4\pi} \begin{bmatrix} \frac{1}{z} \begin{pmatrix} -1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 0 \end{pmatrix} + \frac{r_s^{\mathrm{R}}}{\bar{Z}} \begin{pmatrix} 1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 0 \end{pmatrix} \end{bmatrix}.$$
 (B.41)

# **B.3** Non-reciprocal Half-Space

In this section, we briefly outline the derivation of the Green's tensor given in Ref. [78] for a layered time-reversal-symmetry-broken topological insulator (TSB-TI), and apply to some simple geometric arrangements.

The origin of the non-reciprocity in topological insulators is the ability to mix electric E and magnetic induction B fields [63, 64]. Therefore, when calculating the Green's tensor, the cross components of the unit vectors of the s, p polarizations must also be considered. So, we can write the Green's tensor as [78],

$$\boldsymbol{G}^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi^2} \int \frac{d^2k^{\parallel}}{k^{\perp}} e^{i\boldsymbol{k}^{\parallel}\cdot(\boldsymbol{r}-\boldsymbol{r}')+ik^{\perp}(z+z')} \sum_{\sigma=s,p} \sum_{\tau=s,p} r_{\sigma,\tau}\boldsymbol{e}_{\sigma+}\boldsymbol{e}_{\tau-}, \quad (B.42)$$

where we have newly defined Fresnel coefficients for a TSB-TI [78],

$$r_{s,s} = \frac{\left(\mu(\omega)k^{\perp} - k_1^{\perp}\right)\Omega_{\epsilon} - k^{\perp}k_1^{\perp}\Delta^2}{\left(\mu(\omega)k^{\perp} - k_1^{\perp}\right)\Omega_{\epsilon} + k^{\perp}k_1^{\perp}\Delta^2},\tag{B.43a}$$

$$r_{p,p} = \frac{\left(\epsilon(\omega)k^{\perp} + k_1^{\perp}\right)\Omega_{\mu} - k^{\perp}k_1^{\perp}\Delta^2}{\left(\epsilon(\omega)k^{\perp} - k_1^{\perp}\right)\Omega_{\mu} + k^{\perp}k_1^{\perp}\Delta^2},\tag{B.43b}$$

$$r_{s,p} = \frac{-2\mu(\omega)k^{\perp}k_1^{\perp}\Delta}{\left(\epsilon(\omega)k^{\perp} - k_1^{\perp}\right)\Omega_{\mu} + k^{\perp}k_1^{\perp}\Delta^2},\tag{B.43c}$$

$$r_{p,s} = \frac{-2\mu(\omega)k^{\perp}k_1^{\perp}\Delta}{\left(\mu(\omega)k^{\perp} - k_1^{\perp}\right)\Omega_{\epsilon} + k^{\perp}k_1^{\perp}\Delta^2},\tag{B.43d}$$

where  $\Delta = \alpha \mu(\omega)(\Theta_1 - \Theta)/\pi$ ,  $\Omega_{\epsilon} = \mu(\omega)(k^{\perp}\epsilon(\omega) + k_1^{\perp})$ ,  $\Omega_{\mu} = \mu(\omega)(k^{\perp}\mu(\omega) + k_1^{\perp})$  and  $\alpha$  is the fine structure constant.

 $\Theta(\mathbf{r}, \omega)$  is termed the axion coupling in particle physics, which in electromagnetism merely acts as a space and frequency dependent coupling parameter [121]. It takes even multiples of  $\pi$  in a conventional magnetodielectric and odd multiples of  $\pi$  in TSB-TI, with the magnitude and sign of the multiple determined by the strength and direction of the time-symmetrybreaking perturbation [122].

For layered homogeneous media,  $\Theta(\mathbf{r}, \omega) = \Theta(\omega)$  and the effects of axion coupling are only felt at interfaces where the properties of the medium change [78]. When  $\Theta_1 - \Theta \rightarrow 0$ , this means that there is no change in the axion coupling over the interface, which corresponds to an interface between reciprocal media and a vacuum. In this case, we note that the coefficients  $r_{s,p}, r_{p,s} \rightarrow 0$  and  $r_{s,s}$  and  $r_{p,p}$  reduce to the usual Fresnel coefficients for reciprocal media,  $r_s$ (B.10a) and  $r_p$  (B.10b) respectively.

The cross terms are found to be,

$$\boldsymbol{e}_{s+}\boldsymbol{e}_{p-} = (\boldsymbol{e}_{k^{\parallel}} \times \boldsymbol{e}_{z})(k^{\parallel}\boldsymbol{e}_{z} + k_{1}^{\perp}\boldsymbol{e}_{k^{\parallel}}) = \frac{1}{k^{\parallel}}(k_{y}, -k_{x}, 0) \otimes \frac{1}{k^{\parallel}k_{1}} \left(k_{1}^{\perp}k_{x}, k_{1}^{\perp}k_{y}, k^{\parallel^{2}}\right)$$
$$= \frac{1}{k_{1}k^{\parallel^{2}}} \begin{pmatrix} k_{y}k_{x}k_{1}^{\perp} & k_{y}^{2}k_{1}^{\perp} & k_{y}k^{\parallel^{2}}\\ -k_{1}^{\perp}k_{x}^{2} & -k_{1}^{\perp}k_{x}k_{y} & k_{x}k^{\parallel^{2}}\\ 0 & 0 & 0 \end{pmatrix}, \qquad (B.44)$$

$$\boldsymbol{e}_{p+}\boldsymbol{e}_{s-} = (k^{\parallel}\boldsymbol{e}_{z} - k_{1}^{\perp}\boldsymbol{e}_{k\parallel})(\boldsymbol{e}_{k\parallel} \times \boldsymbol{e}_{z}) = \frac{1}{k^{\parallel}k_{1}} \left(-k_{1}^{\perp}k_{x}, -k_{1}^{\perp}k_{y}, k^{\parallel^{2}}\right) \otimes \frac{1}{k^{\parallel}}(k_{y}, -k_{x}, 0)$$
$$= \frac{1}{k_{1}k^{\parallel^{2}}} \begin{pmatrix} -k_{y}k_{x}k_{1}^{\perp} & k_{x}^{2}k_{1}^{\perp} & 0\\ -k_{1}^{\perp}k_{y}^{2} & k_{1}^{\perp}k_{x}k_{y} & 0\\ k_{y}k^{\parallel^{2}} & k_{x}k^{\parallel^{2}} & 0 \end{pmatrix}.$$
(B.45)

Transformed to polar coordinates via (B.14) we get,

$$\boldsymbol{G}^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi^2} \int dk^{\parallel} \int_0^{2\pi} d\phi \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\parallel}(\cos\phi,\sin\phi,0)\cdot(\boldsymbol{r}-\boldsymbol{r}')+ik^{\perp}(z+z')} \times \left(r_{s,s}\boldsymbol{e}_{s+}\boldsymbol{e}_{s-}+r_{p,p}\boldsymbol{e}_{p+}\boldsymbol{e}_{p-}+r_{s,p}\boldsymbol{e}_{s+}\boldsymbol{e}_{p-}+r_{p,s}\boldsymbol{e}_{p+}\boldsymbol{e}_{s-}\right), \quad (B.46)$$

where

$$\boldsymbol{e}_{s+}\boldsymbol{e}_{p-} = \frac{1}{k_1} \begin{pmatrix} k_1^{\perp} \sin\phi\cos\phi & k_1^{\perp} \sin^2\phi & k^{\parallel} \sin\phi \\ -k_1^{\perp} \cos^2\phi & -k_1^{\perp} \sin\phi\cos\phi & k^{\parallel} \cos\phi \\ 0 & 0 & 0 \end{pmatrix}, \quad (B.47)$$
$$\boldsymbol{e}_{p+}\boldsymbol{e}_{s-} = \frac{1}{k_1} \begin{pmatrix} -k_1^{\perp} \sin\phi\cos\phi & k_1^{\perp} \cos^2\phi & 0 \\ -k_1^{\perp} \sin^2\phi & k_1^{\perp} \sin\phi\cos\phi & 0 \\ k^{\parallel} \sin\phi & k^{\parallel} \cos\phi & 0 \end{pmatrix}, \quad (B.48)$$

and  $e_{s+}e_{s-}$  and  $e_{p+}e_{p-}$  are defined by (B.16) and (B.17) respectively.

The Green's tensor can equivalently be written in the form,

$$\boldsymbol{G}^{(1)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi^2} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\perp}(z+z')} \int_0^{2\pi} d\phi \, e^{ik^{\parallel}(\cos\phi,\sin\phi,0)\cdot(\boldsymbol{r}-\boldsymbol{r}')} \boldsymbol{R}^{ij}, \qquad (B.49)$$

where the definitions from section B.2 apply and  $\mathbf{R}^{ij}(\mathbf{k}^{\parallel}, k_z)$  is a reflectivity tensor with components,

$$R^{xx} = \sin^2 \phi \, r_{s,s} - \cos^2 \phi \, \frac{k_z^2}{k_1^2} \, r_{p,p} + \sin \phi \cos \phi \, \frac{k_z}{k_1} \left( r_{s,p} - r_{p,s} \right), \tag{B.50a}$$

$$R^{yy} = \cos^2 \phi \, r_{s,s} - \sin^2 \phi \, \frac{k_z^2}{k_1^2} \, r_{p,p} - \sin \phi \cos \phi \, \frac{k_z}{k_1} \left( r_{s,p} - r_{p,s} \right), \tag{B.50b}$$

$$R^{xy} = -\sin\phi\cos\phi\left(r_{s,s} + \frac{k_z^2}{k_1^2}r_{p,p}\right) + \frac{k_z}{k_1}\left(\sin^2\phi\,r_{s,p} - \cos^2\phi\,r_{p,s}\right),\tag{B.50c}$$

$$R^{yx} = -\sin\phi\cos\phi\left(r_{s,s} + \frac{k_z^2}{k_1^2}r_{p,p}\right) - \frac{k_z}{k_1}\left(\cos^2\phi\,r_{s,p} - \sin^2\phi\,r_{p,s}\right),\tag{B.50d}$$

$$R^{xz} = \frac{k^{\parallel}}{k_1} \left( -\cos\phi \, \frac{k_z}{k_1} r_{p,p} + \sin\phi \, r_{s,p} \right), \tag{B.50e}$$

$$R^{zx} = \frac{k^{\parallel}}{k_1} \left( \cos \phi \, \frac{k_z}{k_1} r_{p,p} + \sin \phi \, r_{p,s} \right), \tag{B.50f}$$

$$R^{yz} = \frac{k^{\parallel}}{k_1} \left( \sin \phi \, \frac{k_z}{k_1} r_{p,p} - \cos \phi \, r_{s,p} \right), \tag{B.50g}$$

$$R^{zy} = \frac{k^{\parallel}}{k_1} \left( \sin \phi \, \frac{k_z}{k_1} r_{p,p} - \cos \phi \, r_{p,s} \right), \tag{B.50h}$$

$$R^{zz} = -\frac{k^{\parallel^2}}{k_1^2} r_{p,p}, \tag{B.50i}$$

which is in agreement with Ref. [78]. We will now apply this result to two simple configurations shown in figure B.1.

## **B.3.1** Parallel Arrangement

As in section B.2.1 and shown in figure B.1a, we can place the bodies in the xz-plane and equidistant from the surface and define  $x - x' \equiv X$  to express our Green's tensor (B.49) as,

$$\boldsymbol{G}^{(1,\mathrm{P})}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi^2} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{2ik^{\perp}z} \int_0^{2\pi} d\phi \, e^{ik^{\parallel}X\cos\phi} \boldsymbol{R}^{ij}, \qquad (B.51)$$

where  $\mathbf{R}^{ij}$  is defined via (B.50). We can now perform the angular integral using the results (B.19) and obtain,

$$\boldsymbol{G}^{(1,\mathrm{P})}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{4\pi} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{2ik^{\perp}z} \boldsymbol{R}_P^{ij}, \qquad (B.52)$$

with

$$R_P^{xx} = \frac{J_1(k^{\parallel}|X|)}{|X|} \left( r_{s,s} + \frac{k_z^2}{k_1^2} r_{p,p} \right) - J_0(k^{\parallel}|X|) \frac{k_z^2}{k_1^2} r_{p,p},$$
(B.53a)

$$R_P^{yy} = -\left[\frac{J_1(k^{\parallel}|X|)}{|X|}\left(r_{s,s} + \frac{k_z^2}{k_1^2}r_{p,p}\right) - J_0(k^{\parallel}|X|)r_{s,s}\right],\tag{B.53b}$$

$$R_P^{xy} = \frac{k_z}{k_1} \left[ \frac{J_1(k^{\parallel}|X|)}{|X|} \left( r_{s,p} + r_{p,s} \right) - J_0(k^{\parallel}|X|) r_{p,s} \right],$$
(B.53c)

$$R_P^{yx} = \frac{k_z}{k_1} \left[ \frac{J_1(k^{\parallel}|X|)}{|X|} \left( r_{s,p} + r_{p,s} \right) - J_0(k^{\parallel}|X|) r_{s,p} \right],$$
(B.53d)

$$R_P^{xz} = -R_P^{zx} = -i\frac{k^{\parallel}k_z}{k_1^2}J_1(k^{\parallel}X)r_{p,p},$$
(B.53e)

$$R_P^{yz} = i \frac{k^{\parallel}}{k_1} J_1(k^{\parallel} X) r_{s,p}, \tag{B.53f}$$

$$R_P^{zy} = -i\frac{k^{\parallel}}{k_1}J_1(k^{\parallel}X)r_{p,s}, \qquad (B.53g)$$

$$R_P^{zz} = -J_0(k^{\parallel}|X|) \frac{k^{\parallel^2}}{k_1^2} r_{p,p}.$$
 (B.53h)

By examining the off-diagonal components, we can see that the Green's tensor does not satisfy Lorentz Reciprocity (2.75) as expected. This is demonstrated explicitly below,

$$R_P^{xy}(\mathbf{r}', \mathbf{r}) \neq R_P^{yx}(\mathbf{r}, \mathbf{r}') \quad \text{unless } r_{s,p} = r_{p,s}, \tag{B.54a}$$

$$R_P^{xz}(\boldsymbol{r}',\boldsymbol{r}) = R_P^{zx}(\boldsymbol{r},\boldsymbol{r}'),\tag{B.54b}$$

$$R_P^{yz}(\boldsymbol{r}',\boldsymbol{r}) \neq R_P^{zy}(\boldsymbol{r},\boldsymbol{r}') \quad \text{unless } r_{s,p} = r_{p,s}.$$
(B.54c)

It is interesting to note here that if  $r_{s,p} = r_{p,s}$ , then  $\boldsymbol{G}^{(1,P)}(\boldsymbol{r},\boldsymbol{r}') = \boldsymbol{G}^{(1,P)^{\mathrm{T}}}(\boldsymbol{r}',\boldsymbol{r})$  and reciprocal behaviour will be exhibited.

#### B.3.2 Colinear Arrangement

As in section B.2.2, we can position the bodies along the z-axis and use the integral results (B.22) to arrive at,

$$\boldsymbol{G}^{(1,C)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\perp}\bar{Z}} \boldsymbol{R}_C^{ij}, \qquad (B.55)$$

where  $\bar{Z} \equiv z + z'$  and the components of  $\mathbf{R}_{C}^{ij}$  are,

$$R^{xx} = R^{yy} = r_{s,s} - \frac{k_z^2}{k_1^2} r_{p,p},$$
(B.56a)

$$R^{xy} = -R^{yx} = \frac{k_z}{k_1} \left( r_{s,p} - r_{p,s} \right),$$
(B.56b)

$$R^{xz} = R^{zx} = R^{zy} = R^{yz} = 0, (B.56c)$$

$$R^{zz} = -\frac{k^{\parallel^2}}{k_1^2} r_{p,p},\tag{B.56d}$$

which we can rewrite as,

$$\boldsymbol{G}^{(1,C)}(\boldsymbol{r},\boldsymbol{r}',\omega) = \frac{i\mu_1(\omega)}{8\pi} \int dk^{\parallel} \frac{k^{\parallel}}{k^{\perp}} e^{ik^{\perp}\bar{Z}} \begin{pmatrix} r_{s,s} - \frac{k_z^2}{k_1^2} r_{p,p} & \frac{k_z}{k_1} \left( r_{s,p} - r_{p,s} \right) & 0\\ -\frac{k_z}{k_1} \left( r_{s,p} - r_{p,s} \right) & r_{s,s} - \frac{k_z^2}{k_1^2} r_{p,p} & 0\\ 0 & 0 & -\frac{k^{\parallel^2}}{k_1^2} r_{p,p} \end{pmatrix}.$$
(B.57)

By examining the off-diagonal elements, we can again see that Lorentz reciprocity (2.74) does not hold as we would expect, since  $G_{xy}^{(1)}(\boldsymbol{r},\boldsymbol{r}') = -G_{yx}^{(1)}(\boldsymbol{r}',\boldsymbol{r})$ , so  $G^{(1)}(\boldsymbol{r},\boldsymbol{r}') \neq -G^{(1)^{T}}(\boldsymbol{r}',\boldsymbol{r})$ . However, as for the parallel case, we note that if  $r_{s,p} = r_{p,s}$  then reciprocal behaviour will be exhibited. This can be seen by the fact that for this arrangement,  $r_{s,p} = r_{p,s}$  means that  $G_{xy}^{(1)}(\boldsymbol{r},\boldsymbol{r}') = 0 = G_{yx}^{(1)}(\boldsymbol{r}',\boldsymbol{r})$ , and so the Green's tensor becomes diagonal, so clearly  $G^{(1)^{T}}(\boldsymbol{r},\boldsymbol{r}') = G^{(1)^{T}}(\boldsymbol{r}',\boldsymbol{r})$ .

## **B.4** Spherical Green's tensor

To describe a system with rotational symmetry, it is convenient to use spherical coordinates. We set  $\mathbf{r} = (r, \theta, \phi)$ , where r is the radial distance,  $\theta$  is the polar angle, and  $\phi$  is the azimuthal angle as shown in figure B.2. Without loss of generality, we can place the two bodies in the xz-plane and assume that the bodies are on opposite sides of the z-axis, such that one body has  $\phi_{\rm A} = 0$  and the other has  $\phi_{\rm B} = \pi$ . So we can set up two bodies at positions  $\mathbf{r}_{\rm A}$  and  $\mathbf{r}_{\rm B}$ 



Figure B.2: Spherical coordinate system used in this work.

defined in spherical coordinates as,

$$\boldsymbol{r}_{\mathrm{A}} = (r_{\mathrm{A}}, \theta_{\mathrm{A}}, 0), \quad \boldsymbol{r}_{\mathrm{B}} = (r_{\mathrm{B}}, \theta_{\mathrm{B}}, \pi).$$
 (B.58)

In this section, we consider an environment of a spherical body in a vacuum. The Green's tensor for this system can be split into a bulk and scattering part, as explained in 2.2.1. To find the bulk part, we transform the vacuum Green's tensor given in (B.1) into spherical coordinates.

#### B.4.1 Bulk Green's tensor

Our chosen coordinates of  $r_{\rm A}$  and  $r_{\rm B}$  (B.58) can be equivalently given in Cartesian coordinates using the conversion,

$$\begin{aligned} x &= r \sin \theta \cos \phi, \\ y &= r \sin \theta \sin \phi, \\ z &= r \cos \theta, \end{aligned} \tag{B.59}$$

giving us,

$$\boldsymbol{r}_{\mathrm{A}} = (r_{\mathrm{A}}\sin\theta_{\mathrm{A}}, 0, r_{\mathrm{A}}\cos\theta_{\mathrm{A}}), \tag{B.60a}$$

$$\boldsymbol{r}_{\rm B} = (-r_{\rm B}\sin\theta_{\rm B}, 0, r_{\rm B}\cos\theta_{\rm B}). \tag{B.60b}$$

The vacuum Green's tensor (B.1) in our chosen coordinates is given by,

$$\boldsymbol{G}^{(0)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = -\frac{c^{2}e^{i\omega\rho_{\mathrm{AB}}/c}}{4\pi\omega^{2}\rho_{\mathrm{AB}}^{3}} \left[ a\left(-i\rho_{\mathrm{AB}}\omega/c\right)\mathbb{I} - b\left(-i\rho_{\mathrm{AB}}\omega/c\right)\boldsymbol{e}_{\mathrm{AB}}\boldsymbol{e}_{\mathrm{AB}} \right], \qquad (B.61)$$

where  $a(x) \equiv 1 + x + x^2$ ,  $b(x) \equiv 3 + 3x + x^2$ ,  $\boldsymbol{e}_{AB} = \boldsymbol{\rho}_{AB}/\rho_{AB}$  and we can calculate,

$$\boldsymbol{\rho}_{AB} = \boldsymbol{r}_{A} - \boldsymbol{r}_{B} = (r_{A}\sin\theta_{A} + r_{B}\sin\theta_{B}, 0, r_{A}\cos\theta_{A} - r_{B}\cos\theta_{B}), \qquad (B.62a)$$

$$\rho_{AB} = |\boldsymbol{\rho}_{AB}| = \sqrt{(r_{A}\sin\theta_{A} + r_{B}\sin\theta_{B})^{2} + (r_{A}\cos\theta_{A} - r_{B}\cos\theta_{B})^{2}}$$

$$= \sqrt{r_{A}^{2}(\sin^{2}\theta_{A} + \cos^{2}\theta_{A}) + r_{B}^{2}(\sin^{2}\theta_{B} + \cos^{2}\theta_{B}) + 2r_{A}r_{B}(\sin\theta_{A}\sin\theta_{B} - \cos\theta_{A}\cos\theta_{B})}$$

$$= \sqrt{r_{A}^{2} + r_{B}^{2} - 2r_{A}r_{B}\cos\Theta}, \qquad (B.62b)$$

$$\boldsymbol{e}_{AB} = \boldsymbol{\rho}_{AB} / \rho_{AB} = (r_A \sin \theta_A + r_B \sin \theta_B, 0, r_A \cos \theta_A - r_B \cos \theta_B) / \rho_{AB}, \tag{B.62c}$$

where we have defined  $\Theta = \theta_{\rm A} + \theta_{\rm B}$  and used the geometric identities  $\sin^2 x + \cos^2 = 1$  and  $\cos x \cos y - \sin x \sin y = \cos(x + y)$ .

The standard unit vector conversions are,

$$e_r = (\sin \theta \cos \phi, \sin \theta \sin \phi, + \cos \theta),$$
  

$$e_\theta = (\cos \theta \cos \phi, \cos \theta \sin \phi, - \sin \theta),$$
  

$$e_\phi = (-\sin \phi, \cos \phi, 0).$$
 (B.63)

Applying to our coordinates produces the spherical unit vectors at  $\boldsymbol{r}_{\mathrm{A}}$  and  $\boldsymbol{r}_{\mathrm{B}},$ 

$$\boldsymbol{e}_{r_{\mathrm{A}}} = (\sin \theta_{\mathrm{A}}, 0, \cos \theta_{\mathrm{A}}), \qquad \boldsymbol{e}_{r_{\mathrm{B}}} = (-\sin \theta_{\mathrm{B}}, 0, \cos \theta_{\mathrm{B}}), \qquad (\mathrm{B.64a})$$

$$\boldsymbol{e}_{\theta_{\mathrm{A}}} = (\cos \theta_{\mathrm{A}}, 0, -\sin \theta_{\mathrm{A}}), \qquad \boldsymbol{e}_{\theta_{\mathrm{B}}} = (-\cos \theta_{\mathrm{B}}, 0, -\sin \theta_{\mathrm{B}}), \qquad (\mathrm{B.64b})$$

$$e_{\phi_{\rm A}} = (0, 1, 0),$$
  $e_{\phi_{\rm B}} = (0, -1, 0).$  (B.64c)

We want to express the vacuum Green's tensor in terms of these spherical unit vectors. The rr component, for example, of the Green's tensor in our coordinates is given by,

$$\boldsymbol{G}_{rr}^{(0)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = \boldsymbol{e}_{r_{\mathrm{A}}} \cdot \boldsymbol{G}^{(0)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) \cdot \boldsymbol{e}_{r_{\mathrm{B}}}$$
$$= -\frac{c^{2}e^{i\omega\rho_{\mathrm{AB}}/c}}{4\pi\omega^{2}\rho_{\mathrm{AB}}^{3}} \left[ a \left( -i\rho_{\mathrm{AB}}\omega/c \right) \boldsymbol{e}_{r_{\mathrm{A}}} \cdot \boldsymbol{e}_{r_{\mathrm{B}}} - b \left( -i\rho_{\mathrm{AB}}\omega/c \right) \left( \boldsymbol{e}_{r_{\mathrm{A}}} \cdot \boldsymbol{e}_{\mathrm{AB}} \right) \left( \boldsymbol{e}_{r_{\mathrm{B}}} \cdot \boldsymbol{e}_{\mathrm{AB}} \right) \right]. \quad (B.65)$$

We can use (B.64a) and (B.62c) to calculate,

$$\begin{aligned} \boldsymbol{e}_{r_{\mathrm{A}}} \cdot \boldsymbol{e}_{r_{\mathrm{B}}} &= (\sin \theta_{\mathrm{A}}, 0, \cos \theta_{\mathrm{A}}) \cdot (-\sin \theta_{\mathrm{B}}, 0, \cos \theta_{\mathrm{B}}) = \cos \Theta, \end{aligned} \tag{B.66a} \\ \boldsymbol{e}_{r_{\mathrm{A}}} \cdot \boldsymbol{e}_{\mathrm{AB}} &= (\sin \theta_{\mathrm{A}}, 0, \cos \theta_{\mathrm{A}}) \cdot (r_{\mathrm{A}} \sin \theta_{\mathrm{A}} + r_{\mathrm{B}} \sin \theta_{\mathrm{B}}, 0, r_{\mathrm{A}} \cos \theta_{\mathrm{A}} - r_{\mathrm{B}} \cos \theta_{\mathrm{B}}) / \rho_{\mathrm{AB}} \\ &= \left( r_{\mathrm{A}} \sin^{2} \theta_{\mathrm{A}} + r_{\mathrm{B}} \sin \theta_{\mathrm{A}} \sin \theta_{\mathrm{B}} + r_{\mathrm{A}} \cos^{2} \theta_{\mathrm{A}} - r_{\mathrm{B}} \cos \theta_{\mathrm{A}} \cos \theta_{\mathrm{B}} \right) / \rho_{\mathrm{AB}} \\ &= \left( r_{\mathrm{A}} - r_{\mathrm{B}} \cos \Theta \right) / \rho_{\mathrm{AB}}, \end{aligned} \tag{B.66b} \\ \boldsymbol{e}_{r_{\mathrm{B}}} \cdot \boldsymbol{e}_{\mathrm{AB}} = \left( -\sin \theta_{\mathrm{B}}, 0, \cos \theta_{\mathrm{B}} \right) \cdot \left( r_{\mathrm{A}} \sin \theta_{\mathrm{A}} + r_{\mathrm{B}} \sin \theta_{\mathrm{B}}, 0, r_{\mathrm{A}} \cos \theta_{\mathrm{A}} - r_{\mathrm{B}} \cos \theta_{\mathrm{B}} \right) / \rho_{\mathrm{AB}} \\ &= \left( r_{\mathrm{A}} \cos \Theta - r_{\mathrm{B}} \right) / \rho_{\mathrm{AB}}, \end{aligned} \tag{B.66c}$$

and substitute these in to (B.65) to give the rr component of the vacuum Green's tensor. Similarly, we can calculate the other components of the Green's tensor using,

$$\boldsymbol{e}_{r_{\mathrm{A}}} \cdot \boldsymbol{e}_{\theta_{\mathrm{B}}} = \boldsymbol{e}_{\theta_{\mathrm{A}}} \cdot \boldsymbol{e}_{r_{\mathrm{B}}} = -\sin\Theta, \ \boldsymbol{e}_{\theta_{\mathrm{A}}} \cdot \boldsymbol{e}_{\theta_{\mathrm{B}}} = -\cos\Theta, \ \boldsymbol{e}_{\phi_{\mathrm{A}}} \cdot \boldsymbol{e}_{\phi_{\mathrm{B}}} = -1, \tag{B.67a}$$

$$\boldsymbol{e}_{r_{\mathrm{A}}} \cdot \boldsymbol{e}_{\phi_{\mathrm{B}}} = \boldsymbol{e}_{\theta_{\mathrm{A}}} \cdot \boldsymbol{e}_{\phi_{\mathrm{B}}} = \boldsymbol{e}_{\phi_{\mathrm{A}}} \cdot \boldsymbol{e}_{r_{\mathrm{B}}} = \boldsymbol{e}_{\phi_{\mathrm{A}}} \cdot \boldsymbol{e}_{\theta_{\mathrm{B}}} = 0, \qquad (\mathrm{B.67b})$$

$$\boldsymbol{e}_{\theta_{\mathrm{A}}} \cdot \boldsymbol{e}_{\mathrm{AB}} = \frac{r_{\mathrm{B}} \sin \Theta}{\rho_{\mathrm{AB}}}, \ \boldsymbol{e}_{\theta_{\mathrm{B}}} \cdot \boldsymbol{e}_{\mathrm{AB}} = -\frac{r_{\mathrm{A}} \sin \Theta}{\rho_{\mathrm{AB}}}, \ \boldsymbol{e}_{\phi_{\mathrm{A}}} \cdot \boldsymbol{e}_{\mathrm{AB}} = \boldsymbol{e}_{\phi_{\mathrm{B}}} \cdot \boldsymbol{e}_{\mathrm{AB}} = 0.$$
(B.67c)

Substituting these in to (B.61), we find the non-zero components of the Green's tensor to be,

$$\boldsymbol{G}_{rr}^{(0)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = -\frac{c^{2}e^{-\xi}}{4\pi\omega^{2}\rho_{\mathrm{AB}}^{3}} \left[ a\left(\xi\right)\cos\Theta - b\left(\xi\right)\frac{\left(r_{\mathrm{A}}-r_{\mathrm{B}}\cos\Theta\right)\left(r_{\mathrm{A}}\cos\Theta - r_{\mathrm{B}}\right)}{\rho_{\mathrm{AB}}^{2}} \right], \quad (\mathrm{B.68a})$$

$$\boldsymbol{G}_{r\theta}^{(0)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = \frac{c^{2}e^{-\xi}}{4\pi\omega^{2}\rho_{\mathrm{AB}}^{3}} \left[ a\left(\xi\right)\sin\Theta - b\left(\xi\right)\frac{\left(r_{\mathrm{A}} - r_{\mathrm{B}}\cos\Theta\right)r_{\mathrm{A}}\sin\Theta}{\rho_{\mathrm{AB}}^{2}} \right],\tag{B.68b}$$

$$\boldsymbol{G}_{\theta r}^{(0)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = \frac{c^{2}e^{-\xi}}{4\pi\omega^{2}\rho_{\mathrm{AB}}^{3}} \left[ a\left(\xi\right)\sin\Theta + b\left(\xi\right)\frac{\left(r_{\mathrm{A}}\cos\Theta - r_{\mathrm{B}}\right)r_{\mathrm{B}}\sin\Theta}{\rho_{\mathrm{AB}}^{2}} \right],\tag{B.68c}$$

$$\boldsymbol{G}_{\theta\theta}^{(0)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = \frac{c^{2}e^{-\xi}}{4\pi\omega^{2}\rho_{\mathrm{AB}}^{3}} \left[ a\left(\xi\right)\cos\Theta - b\left(\xi\right)\frac{r_{\mathrm{A}}r_{\mathrm{B}}\sin^{2}\Theta}{\rho_{\mathrm{AB}}^{2}} \right],\tag{B.68d}$$

$$\boldsymbol{G}_{\phi\phi}^{(0)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = \frac{c^2 e^{-\xi}}{4\pi\omega^2 \rho_{\mathrm{AB}}^3} a\left(\xi\right),\tag{B.68e}$$

where we have defined  $\xi \equiv -i\omega\rho_{AB}/c$ . This result is in agreement with [4, 123].

## B.4.2 Scattering Green's tensor

We now calculate the Green's tensor for a spherical macroscopic body. We choose the centre of the spherical body to align with the origin of the coordinate system, as in figure B.3. The scattering Green's tensor for two bodies near a dielectric sphere with radius R can be written



Figure B.3: Two bodies A and B near a sphere of radius R. Adapted from [123].

in this coordinate system as [4, 123],

$$\boldsymbol{G}^{(1)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = \frac{i\omega}{4\pi c} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \sum_{m=0}^{n} \frac{(n-m)!}{(n+m)!} (2-\delta_{0m})$$

$$\times \sum_{p=\pm 1} \left[ B_{n}^{M} \boldsymbol{M}_{nm,p}(\boldsymbol{r}_{\mathrm{A}},\omega/c) \boldsymbol{M}_{nm,p}(\boldsymbol{r}_{\mathrm{B}},\omega/c) + B_{n}^{N} \boldsymbol{N}_{nm,p}(\boldsymbol{r}_{\mathrm{A}},\omega/c) \boldsymbol{N}_{nm,p}(\boldsymbol{r}_{\mathrm{B}},\omega/c) \right], \quad (B.69)$$

where  $M_{nm,p}(\mathbf{r},q)$  and  $N_{nm,p}(\mathbf{r},q)$  are even (p = +1) and odd (p = -1) spherical wave vector functions, given below,

$$\boldsymbol{M}_{nm,-1}(\boldsymbol{r},q) = \frac{m}{\sin\theta} h_n^{(1)}(qr) P_n^m(\cos\theta) \cos(m\phi) \boldsymbol{e}_{\theta} - h_n^{(1)}(qr) \frac{dP_n^m(\cos\theta)}{d\theta} \sin(m\phi) \boldsymbol{e}_{\phi}, \quad (B.70a)$$
$$\boldsymbol{M}_{nm,+1}(\boldsymbol{r},q) = -\frac{m}{\sin\theta} h_n^{(1)}(qr) P_n^m(\cos\theta) \sin(m\phi) \boldsymbol{e}_{\theta} - h_n^{(1)}(qr) \frac{dP_n^m(\cos\theta)}{d\theta} \cos(m\phi) \boldsymbol{e}_{\phi}, \quad (B.70b)$$

$$\boldsymbol{N}_{nm,-1}(\boldsymbol{r},q) = \frac{n(n+1)}{qr} h_n^{(1)}(qr) P_n^m(\cos\theta) \sin(m\phi) \boldsymbol{e}_r + \frac{1}{qr} \frac{d\left[qrh_n^{(1)}(qr)\right]}{dr} \left(\frac{dP_n^m(\cos\theta)}{d\theta} \sin(m\phi) \boldsymbol{e}_\theta + \frac{m}{\sin\theta} P_n^m(\cos\theta) \cos(m\phi) \boldsymbol{e}_\phi\right), \quad (B.70c)$$

$$\boldsymbol{N}_{nm,+1}(\boldsymbol{r},q) = \frac{n(n+1)}{qr} h_n^{(1)}(qr) P_n^m(\cos\theta) \cos(m\phi) \boldsymbol{e}_r + \frac{1}{qr} \frac{d\left[qrh_n^{(1)}(qr)\right]}{dr} \left(\frac{dP_n^m(\cos\theta)}{d\theta} \cos(m\phi) \boldsymbol{e}_\theta - \frac{m}{\sin\theta} P_n^m(\cos\theta) \sin(m\phi) \boldsymbol{e}_\phi\right), \quad (B.70d)$$

where  $h_n^{(1)}(x)$  is the spherical Hankel function of the first kind and  $P_n^m(x)$  is the Legendre function. The coefficients  $B_n^M$  and  $B_n^N$  are the Mie reflection coefficients [124] given by,

$$B_n^M(\omega) = \frac{\mu(\omega) \left[ zJ_n(z) \right]' J_n(z_1) - J_n(z) \left[ z_1 J_n(z_1) \right]'}{\mu(\omega) \left[ zH_n(z) \right]' J_n(z_1) - H_n(z) \left[ z_1 J_n(z_1) \right]'},$$
(B.71a)

$$B_{n}^{N}(\omega) = -\frac{\epsilon(\omega) \left[zJ_{n}(z)\right]' J_{n}(z_{1}) - J_{n}(z) \left[z_{1}J_{n}(z_{1})\right]'}{\epsilon(\omega) \left[zH_{n}(z)\right]' J_{n}(z_{1}) - H_{n}(z) \left[z_{1}J_{n}(z_{1})\right]'},$$
(B.71b)

where  $J_n(z)$  is the spherical Bessel function of the first kind,  $z = \omega R/c$ ,  $z_1 = \sqrt{\epsilon(\omega)\mu(\omega)}z_0$ and the prime denotes differentiation with respect to the respective argument.

It is useful to split the sum into its four constituent terms,

$$\boldsymbol{G}^{(1)}(\boldsymbol{r}_{\mathrm{A}}, \boldsymbol{r}_{\mathrm{B}}, \omega) = \frac{i\omega}{4\pi c} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left[ \Sigma_m^{(1)} + \Sigma_m^{(2)} + \Sigma_m^{(3)} + \Sigma_m^{(4)} \right], \quad (B.72)$$

where we have defined,

$$\Sigma_m^{(1)} = \sum_{m=0}^n C_{nm} B_n^M \boldsymbol{M}_{nm,-1}(\boldsymbol{r}_{\mathrm{A}}, \omega/c) \boldsymbol{M}_{nm,-1}(\boldsymbol{r}_{\mathrm{B}}, \omega/c), \qquad (B.73a)$$

$$\Sigma_m^{(2)} = \sum_{m=0}^n C_{nm} B_n^M \boldsymbol{M}_{nm,+1}(\boldsymbol{r}_{\mathrm{A}}, \omega/c) \boldsymbol{M}_{nm,+1}(\boldsymbol{r}_{\mathrm{B}}, \omega/c), \qquad (B.73b)$$

$$\Sigma_m^{(3)} = \sum_{\substack{m=0\\n}}^n C_{nm} B_n^N \boldsymbol{N}_{nm,-1}(\boldsymbol{r}_{\mathrm{A}}, \omega/c) \boldsymbol{N}_{nm,-1}(\boldsymbol{r}_{\mathrm{B}}, \omega/c), \qquad (B.73c)$$

$$\Sigma_m^{(4)} = \sum_{m=0}^n C_{nm} B_n^N \boldsymbol{N}_{nm,+1}(\boldsymbol{r}_{\mathrm{A}}, \omega/c) \boldsymbol{N}_{nm,+1}(\boldsymbol{r}_{\mathrm{B}}, \omega/c), \qquad (\mathrm{B.73d})$$

where we have defined,

$$C_{nm} \equiv \frac{(n-m)!}{(n+m)!} (2 - \delta_{0m}).$$
(B.74)

Beginning with the  $\Sigma_m^{(1)}$  term and considering  $\mathbf{r}_A$  and  $\mathbf{r}_B$  separately, we can calculate from (B.70a),

$$\boldsymbol{M}_{nm,-1}(\boldsymbol{r}_{\mathrm{A}},q) = \frac{m}{\sin\theta_{\mathrm{A}}} h_{n}^{(1)}(qr_{\mathrm{A}}) P_{n}^{m}(\cos\theta_{\mathrm{A}}) \boldsymbol{e}_{\theta_{\mathrm{A}}}, \tag{B.75a}$$

$$\boldsymbol{M}_{nm,-1}(\boldsymbol{r}_{\mathrm{B}},q) = \frac{m}{\sin\theta_{\mathrm{B}}} h_{n}^{(1)}(qr_{\mathrm{B}}) P_{n}^{m}(\cos\theta_{\mathrm{B}}) \cos(m\pi)\boldsymbol{e}_{\theta_{\mathrm{B}}}, \qquad (B.75b)$$

where we have used,

$$\cos(m\phi_{\rm A}) = \cos(0) = 1, \, \sin(m\phi_{\rm A}) = \sin(0) = 0, \tag{B.76}$$

$$\cos(m\phi_{\rm B}) = \cos(m\pi), \, \sin(m\phi_{\rm B}) = \sin(m\pi) = 0. \tag{B.77}$$

Substituting these into (B.73a) we find,

$$\Sigma_m^{(1)} = B_n^M \frac{Q_n^{(1)} \boldsymbol{e}_{\theta_{\mathrm{A}}} \boldsymbol{e}_{\theta_{\mathrm{B}}}}{\sin \theta_{\mathrm{A}} \sin \theta_{\mathrm{B}}} \sum_{m=0}^n m^2 C_{nm} P_n^m (\cos \theta_{\mathrm{A}}) P_n^m (\cos \theta_{\mathrm{B}}) \cos(m\pi), \qquad (B.78)$$

where we have defined,

$$Q_n^{(1)} = h_n^{(1)}(r_{\rm A}\omega/c)h_n^{(1)}(r_{\rm B}\omega/c).$$
(B.79)

Likewise, we can rewrite the other three terms that make up (B.72) in a similar way, giving us,

$$\Sigma_m^{(2)} = B_n^M Q_n^{(1)} \boldsymbol{e}_{\phi_{\mathrm{A}}} \boldsymbol{e}_{\phi_{\mathrm{B}}} \sum_{m=0}^n C_{nm} \frac{dP_n^m(\cos\theta_{\mathrm{A}})}{d\theta_{\mathrm{A}}} \frac{dP_n^m(\cos\theta_{\mathrm{B}})}{d\theta_{\mathrm{B}}} \cos(m\pi), \tag{B.80}$$

$$\Sigma_m^{(3)} = B_n^N Q_n^{(4)} \frac{c^2}{r_{\rm A} r_{\rm A} \omega^2} \frac{\boldsymbol{e}_{\phi_{\rm A}} \boldsymbol{e}_{\phi_{\rm B}}}{\sin \theta_{\rm A} \sin \theta_{\rm B}} \sum_{m=0}^n m^2 C_{nm} P_n^m (\cos \theta_{\rm A}) P_n^m (\cos \theta_{\rm B}), \tag{B.81}$$

$$\Sigma_{m}^{(4)} = \frac{c^{2}}{r_{\mathrm{A}}r_{\mathrm{B}}\omega^{2}}B_{n}^{N} \left[ Q_{n}^{(1)}n^{2}(n+1)^{2}\boldsymbol{e}_{r_{\mathrm{A}}}\boldsymbol{e}_{r_{\mathrm{B}}}\sum_{m=0}^{n}C_{nm}P_{n}^{m}(\cos\theta_{\mathrm{A}})P_{n}^{m}(\cos\theta_{\mathrm{B}})\cos(m\pi) + Q_{n}^{(4)}\boldsymbol{e}_{\theta_{\mathrm{A}}}\boldsymbol{e}_{\theta_{\mathrm{B}}}\sum_{m=0}^{n}C_{nm}\frac{dP_{n}^{m}(\cos\theta_{\mathrm{A}})}{d\theta_{\mathrm{A}}}\frac{dP_{n}^{m}(\cos\theta_{\mathrm{B}})}{d\theta_{\mathrm{B}}}\cos(m\pi) + n(n+1)Q_{n}^{(2)}\boldsymbol{e}_{r_{\mathrm{A}}}\boldsymbol{e}_{\theta_{\mathrm{B}}}\sum_{m=0}^{n}C_{nm}P_{n}^{m}(\cos\theta_{\mathrm{A}})\frac{dP_{n}^{m}(\cos\theta_{\mathrm{B}})}{d\theta_{\mathrm{B}}}\cos(m\pi) + n(n+1)Q_{n}^{(3)}\boldsymbol{e}_{\theta_{\mathrm{A}}}\boldsymbol{e}_{r_{\mathrm{B}}}\sum_{m=0}^{n}C_{nm}\frac{dP_{n}^{m}(\cos\theta_{\mathrm{A}})}{d\theta_{\mathrm{A}}}P_{n}^{m}(\cos\theta_{\mathrm{B}})\cos(m\pi) \right],$$
(B.82)

where we have defined,

$$Q_n^{(2)} = h_n^{(1)}(r_{\rm A}\omega/c) \left[zh_n^{(1)}(z)\right]'_{z=r_{\rm B}\omega/c},\tag{B.83a}$$

$$Q_n^{(3)} = h_n^{(1)}(r_{\rm B}\omega/c) \left[ y h_n^{(1)}(y) \right]'_{y=r_{\rm A}\omega/c},$$
(B.83b)

$$Q_n^{(4)} = \left[ y h_n^{(1)}(y) \right]'_{y = r_{\rm A}\omega/c} \left[ z h_n^{(1)}(z) \right]'_{z = r_{\rm B}\omega/c}.$$
 (B.83c)

To perform the summations over m in (B.72), we can make use of the addition theorem for

spherical harmonics [58],

$$\sum_{m=0}^{n} C_{nm} P_n^m(\cos\theta) P_n^m(\cos\theta') \cos(m\phi) = P_n(\psi), \qquad (B.84)$$

where,

$$\psi = \cos\theta\cos\theta' + \sin\theta\sin\theta'\cos\phi. \tag{B.85}$$

To tackle the sums in  $\Sigma_m^{(1)}$  and  $\Sigma_m^{(3)}$ , we differentiate (B.84) twice with respect to  $\phi$ . For the left hand side we get,

$$\frac{d^2}{d\phi^2} \sum_{m=0}^n C_{nm} P_n^m(\cos\theta) P_n^m(\cos\theta') \cos(m\phi) = \sum_{m=0}^n C_{nm} P_n^m(\cos\theta) P_n^m(\cos\theta') \frac{d^2}{d\phi^2} \cos(m\phi)$$
$$= -\sum_{m=0}^n m^2 C_{nm} P_n^m(\cos\theta) P_n^m(\cos\theta') \cos(m\phi), \tag{B.86}$$

and the right hand side gives,

$$\frac{d^2}{d\phi^2} P_n(\psi) = \frac{d}{d\phi} \left( \frac{d}{d\phi} P_n(\psi) \right) = \frac{d}{d\phi} \left( \frac{d}{d\phi} P_n(\psi) \frac{d\psi}{d\psi} \right) = \frac{d}{d\phi} \left( \frac{d\psi}{d\phi} \frac{dP_n(\psi)}{d\psi} \right)$$

$$= \frac{d}{d\phi} \left( \frac{d\psi}{d\phi} \right) \frac{dP_n(\psi)}{d\psi} + \frac{d\psi}{d\phi} \frac{d}{d\phi} \left( \frac{dP_n(\psi)}{d\psi} \right)$$

$$= \frac{d^2\psi}{d\phi^2} \frac{dP_n(\psi)}{d\psi} + \frac{d\psi}{d\phi} \frac{d}{d\phi} \left( \frac{dP_n(\psi)}{d\psi} \right) \frac{d\psi}{d\psi}$$

$$= \frac{d^2\psi}{d\phi^2} \frac{dP_n(\psi)}{d\psi} + \left( \frac{d\psi}{d\phi} \right)^2 \frac{d^2P_n(\psi)}{d\psi^2}.$$
(B.87)

Combining the left and right hand sides, we can write,

$$\sum_{m=0}^{n} m^2 C_{nm} P_n^m(\cos\theta) P_n^m(\cos\theta') \cos(m\phi) = -\frac{d^2\psi}{d\phi^2} \frac{dP_n(\psi)}{d\psi} - \left(\frac{d\psi}{d\phi}\right)^2 \frac{d^2 P_n(\psi)}{d\psi^2}$$
$$= \sin\theta \sin\theta' \left(\cos\phi \frac{dP_n(\psi)}{d\psi} + \sin\phi \frac{d^2 P_n(\psi)}{d\psi^2}\right), \tag{B.88}$$

where we have used the definition of  $\psi$  given in (B.85) to calculate and substitute in,

$$\frac{d\psi}{d\phi} = -\sin\theta\sin\theta'\sin\phi, \ \frac{d^2\psi}{d\phi^2} = -\sin\theta\sin\theta'\cos\phi.$$
(B.89)

To apply this to (B.78), we make the substitutions  $\theta \to \theta_A$ ,  $\theta' \to \theta_B$  and  $\phi \to \pi$ . Applying

this to (B.85) results in,

$$\psi \to \cos \theta_{\rm A} \cos \theta_{\rm B} + \sin \theta_{\rm A} \sin \theta_{\rm B} \cos \pi$$
$$= \cos \theta_{\rm A} \cos \theta_{\rm B} - \sin \theta_{\rm A} \sin \theta_{\rm B} = \cos \Theta = \gamma, \qquad (B.90)$$

where we have defined  $\Theta \equiv \theta_A + \theta_B$  and  $\gamma \equiv \cos \Theta$ . Applying this to (B.88) gives,

$$\sum_{m=0}^{n} m^{2} C_{nm} P_{n}^{m} (\cos \theta_{\rm A}) P_{n}^{m} (\cos \theta_{\rm B}) = \sin \theta_{\rm A} \sin \theta_{\rm B} \cos \pi \frac{d P_{n}(\gamma)}{d \gamma}$$
$$= -\sin \theta_{\rm A} \sin \theta_{\rm B} P_{n}'(\gamma). \tag{B.91}$$

We can use this to rewrite (B.78) and (B.81) as,

$$\Sigma_m^{(1)} = -B_n^M Q_n^{(1)} P_n'(\gamma) \boldsymbol{e}_{\theta_{\mathrm{A}}} \boldsymbol{e}_{\theta_{\mathrm{B}}},\tag{B.92}$$

$$\Sigma_m^{(3)} = -\frac{c^2}{r_{\rm A} r_{\rm A} \omega^2} B_n^N Q_n^{(4)} P_n'(\gamma) \boldsymbol{e}_{\phi_{\rm A}} \boldsymbol{e}_{\phi_{\rm B}}.$$
(B.93)

To perform the sum in  $\Sigma_m^{(2)}$ , we again make use of the addition theorem for spherical harmonics (B.84), but this time we differentiate with respect to  $\theta$  and  $\theta'$ . Applying to the right side of (B.84) results in,

$$\frac{d}{d\theta'}\frac{d}{d\theta}P_n(\psi) = \frac{d}{d\theta'}\left(\frac{dP_n(\psi)}{d\theta}\frac{d\psi}{d\psi}\right) = \frac{d}{d\theta'}\left(\frac{dP_n(\psi)}{d\psi}\frac{d\psi}{d\theta}\right)$$

$$= \frac{d}{d\theta'}\left(\frac{dP_n(\psi)}{d\psi}\right)\frac{d\psi}{d\theta} + \frac{dP_n(\psi)}{d\psi}\frac{d}{d\theta'}\left(\frac{d\psi}{d\theta}\right)$$

$$= \frac{d\psi}{d\theta'}\frac{d^2P_n(\psi)}{d\psi^2}\frac{d\psi}{d\theta} + \frac{dP_n(\psi)}{d\psi}\frac{d^2\psi}{d\theta'd\theta}.$$
(B.94)

From the definition of  $\psi$  from (B.85) we can calculate,

$$\frac{d\psi}{d\theta} = -\sin\theta\cos\theta' + \cos\theta\sin\theta'\cos\phi, \qquad (B.95a)$$

$$\frac{d\psi}{d\theta'} = -\cos\theta\sin\theta' + \sin\theta\cos\theta'\cos\phi, \qquad (B.95b)$$

$$\frac{d^2\psi}{d\theta'd\theta} = \sin\theta\sin\theta' + \cos\theta\cos\theta'\cos\phi. \tag{B.95c}$$

Again making the substitutions  $\theta \to \theta_A$ ,  $\theta' \to \theta_B$  and  $\phi \to \pi$  which we know from (B.90)

results in  $\psi \to \cos \Theta \equiv \gamma$ , where  $\Theta \equiv \theta_{\rm A} + \theta_{\rm B}$ , we find,

$$\frac{d\gamma}{d\theta_{\rm A}} = -\sin\theta_{\rm A}\cos\theta_{\rm B} - \cos\theta_{\rm A}\sin\theta_{\rm B} = -\sin(\theta_{\rm A} + \theta_{\rm B}) = -\sin\Theta, \qquad (B.96a)$$

$$\frac{d\gamma}{d\theta_{\rm B}} = -\cos\theta_{\rm A}\sin\theta_{\rm B} - \sin\theta\cos\theta' = -\sin\Theta, \tag{B.96b}$$

$$\frac{d^2\gamma}{d\theta_{\rm B}d\theta_{\rm A}} = \sin\theta_{\rm A}\sin\theta_{\rm B} - \cos\theta_{\rm A}\cos\theta_{\rm B} = -\cos\Theta. \tag{B.96c}$$

Making these substitutions in (B.94) we arrive at,

$$\frac{d^2 P_n(\gamma)}{d\theta_A d\theta_B} = \sin^2 \Theta \frac{d^2 P_n(\gamma)}{d\gamma^2} - \frac{dP_n(\gamma)}{d\gamma} \cos \Theta$$
$$= (1 - \cos^2 \Theta) P_n''(\gamma) - P_n'(\gamma) \cos \Theta$$
$$= (1 - \gamma^2) P_n''(\gamma) - \gamma P_n'(\gamma). \tag{B.97}$$

We can use the Legendre Equation (see e.g. Ref. [58]) to rewrite this expression. The Legendre Equation is given as,

$$\frac{d}{dx}\left[(1-x^2)\frac{dP}{dx}\right] + n(n+1)P = 0.$$
(B.98)

By use of the chain rule this can be written as,

$$\frac{d}{dx} \left[ (1-x^2) \right] \frac{dP}{dx} + (1-x^2) \frac{d^2P}{dx^2} + n(n+1)P$$

$$= -2x \frac{dP}{dx} + (1-x^2) \frac{d^2P}{dx^2} + n(n+1)P = 0$$

$$(1-x^2) \frac{d^2P}{dx^2} - x \frac{dP}{dx} = x \frac{dP}{dx} - n(n+1)P.$$
(B.99)

We can use this to rewrite (B.97) as,

$$\frac{d^2 P_n(\gamma)}{d\theta_{\rm A} d\theta_{\rm B}} = \gamma P'_n(\gamma) - n(n+1)P_n(\gamma) = -F_n(\gamma), \qquad (B.100)$$

where we have defined

$$F_n(x) = n(n+1)P_n(x) - xP'_n(x).$$
 (B.101)

Bringing this back to the addition theorem (B.84), we have,

$$\sum_{m=0}^{n} C_{nm} \frac{dP_n^m(\cos\theta_{\rm A})}{d\theta_{\rm A}} \frac{dP_n^m(\cos\theta_{\rm B})}{d\theta_{\rm B}} \cos(m\pi) = -F_n(\gamma), \tag{B.102}$$

which can directly be substituted into the expression for  $\Sigma_m^{(2)}$ , (B.80), giving,

$$\Sigma_m^{(2)} = -B_n^M Q^{(1)} F_n(\gamma) \boldsymbol{e}_{\phi_{\rm A}} \boldsymbol{e}_{\phi_{\rm B}}.$$
(B.103)

Finally, for  $\Sigma_m^{(4)}$  we can differentiate the addition theorem (B.84) by  $\theta$  and and  $\theta'$  separately. From (B.96a) and (B.96b) we have,

$$\frac{d\gamma}{d\theta_{\rm A}} = -\sin\Theta = \frac{d\gamma}{d\theta_{\rm B}},\tag{B.104}$$

which means that,

$$\frac{d}{d\theta_{\rm A}}P_n(\gamma) = \frac{dP_n(\gamma)}{d\gamma}\frac{d\gamma}{d\theta_{\rm A}} = -\sin\Theta\frac{dP_n(\gamma)}{d\gamma} = \frac{d}{d\theta_{\rm B}}P_n(\gamma) = \frac{dP_n(\gamma)}{d\gamma}\frac{d\gamma}{d\theta_{\rm B}}.$$
(B.105)

Applying this to the addition theorem (B.84) gives,

$$\sum_{m=0}^{n} C_{nm} P_n^m(\cos\theta_{\rm A}) \frac{dP_n^m(\cos\theta_{\rm B})}{d\theta_{\rm B}} \cos(m\pi) = -\sin\Theta P_n'(\gamma)$$
$$= \sum_{m=0}^{n} C_{nm} \frac{dP_n^m(\cos\theta_{\rm A})}{d\theta_{\rm A}} P_n^m(\cos\theta_{\rm B}) \cos(m\pi). \tag{B.106}$$

Substituting this into (B.82), along with (B.84) and (B.102), gives,

$$\Sigma_{m}^{(4)} = \frac{c^{2}}{r_{\rm A}r_{\rm B}\omega^{2}}B_{n}^{N} \left[Q_{n}^{(1)}n^{2}(n+1)^{2}\boldsymbol{e}_{r_{\rm A}}\boldsymbol{e}_{r_{\rm B}}P_{n}(\gamma) - Q_{n}^{(4)}\boldsymbol{e}_{\theta_{\rm A}}\boldsymbol{e}_{\theta_{\rm B}}F_{n}(\gamma) - n(n+1)\sin\Theta P_{n}'(\gamma) \left(Q_{n}^{(2)}\boldsymbol{e}_{r_{\rm A}}\boldsymbol{e}_{\theta_{\rm B}} + Q_{n}^{(3)}\boldsymbol{e}_{\theta_{\rm A}}\boldsymbol{e}_{r_{\rm B}}\right)\right].$$
(B.107)

Now we can substitute our results, (B.92), (B.103), (B.93) and (B.107), into (B.72) to generate an expression for the spherical Green's tensor,

$$\boldsymbol{G}^{(1)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = \sum_{i,j=r,\theta,\phi} \boldsymbol{G}^{(1)}_{ij}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega)\boldsymbol{e}_{i_{\mathrm{A}}}\boldsymbol{e}_{j_{\mathrm{B}}}, \qquad (B.108)$$

with the non-zero components given by,

$$G_{rr}^{(1)}(\mathbf{r}_{\rm A}, \mathbf{r}_{\rm B}, \omega) = \frac{ic}{4\pi\omega r_{\rm A}r_{\rm B}} \sum_{n=1}^{\infty} n(n+1)(2n+1)B_n^N(\omega)P_n(\gamma)Q_n^{(1)},$$
(B.109a)

$$G_{r\theta}^{(1)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = -\frac{ic\sin\Theta}{4\pi\omega r_{\mathrm{A}}r_{\mathrm{B}}}\sum_{n=1}^{\infty} (2n+1)B_{n}^{N}(\omega)P_{n}'(\gamma)Q_{n}^{(2)},\tag{B.109b}$$

$$G_{\theta r}^{(1)}(\boldsymbol{r}_{\mathrm{A}},\boldsymbol{r}_{\mathrm{B}},\omega) = -\frac{ic\sin\Theta}{4\pi\omega r_{\mathrm{A}}r_{\mathrm{B}}}\sum_{n=1}^{\infty} (2n+1)B_{n}^{N}(\omega)P_{n}'(\gamma)Q_{n}^{(3)},\tag{B.109c}$$

$$G_{\theta\theta}^{(1)}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm B}, \omega) = -\frac{i\omega}{4\pi c} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left[ B_n^M(\omega) P_n'(\gamma) Q_n^{(1)} + \frac{c^2 B_n^N(\omega)}{\omega^2 r_{\rm A} r_{\rm B}} F_n(\gamma) Q_n^{(4)} \right], \quad (B.109d)$$

$$G_{\phi\phi}^{(1)}(\boldsymbol{r}_{\rm A}, \boldsymbol{r}_{\rm B}, \omega) = -\frac{i\omega}{4\pi c} \sum_{n=1}^{\infty} \frac{2n+1}{n(n+1)} \left[ B_n^M(\omega) F_n(\gamma) Q_n^{(1)} + \frac{c^2 B_n^N(\omega)}{\omega^2 r_{\rm A} r_{\rm B}} P_n'(\gamma) Q_n^{(4)} \right].$$
(B.109e)

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